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Short term clay mineral release and re-capture of potassium in a *Zea mays* field experiment

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ABSTRACT

Potassium (K) is a major element for proper plant nutrition in addition to nitrogen and phosphorus. Soil 2:1 clay minerals serve as a K reservoir for plants because they can fix anhydrous K^+ ions in their interlayer sites (formation of "illite-like" layers) and such "fixed" ions can nonetheless be taken up by plants. The objective of the study was to determine if modifications of the illite structure can be observed within one season of maize growth and if these changes are impacted by fertilization and Arbuscular Mycorrhizal Fungi (AMF) inoculation. To do so, clay fractions recovered from (1) soil adhering to maize roots ("rhizosphere" soil), (2) soil sampled in the vicinity of maize roots but not adhering to the roots ("non rhizosphere" soil) and (3) soil sampled in adjacent un-planted fallow soil ("fallow" soil) were investigated using X-ray diffraction.

The results indicated that extraction of K occurs during growth of the plants (40 days after sowing) and modifies the illite structure differently in the rhizosphere compared to the soil not adhering to the roots. At the end of the growth period (130 days) more K was present in the clay minerals than after 40 days growth except in the rhizosphere of AMF-inoculated roots, showing that mycorrhiza activity tended to affect a slightly greater loss of K compared to non-mycorrhiza clays in the rhizosphere. No influence of K fertilization on soil clay illite structure was observed suggesting that added K has been either already been taken up by maize plants after 40 days, either leached or adsorbed elsewhere than in the 2:1 clay mineral interlayer sites (organic matter or external sites).

The results showed that clay modifications can be observed at the scale of a growing season and suggest that K^+ ions can be extracted by the plants from the illitic layers (in illite minerals and illite layers of mixed layered smectite/illite minerals) and re-stored (being lost from plants and returning to the soil) within one growing season.

1. Introduction

Potassium (K) is an important element for plant growth. Potassium availability often limits plant productivity in agriculture. Hence, K fertilizers are broadly used all over the world. Soil 2:1 clay minerals are key regulators of soil K dynamics. In classical estimations of exchangeable ions on soils, K usually represents only 10–15% of the potentially exchangeable cations. However, it has been established that K held as anhydrous ions in "illite-like" layers (2:1 layer collapsed to 1 nm) in soil is to a large extent plant available. Plant uptake of these K^+ ions and the subsequent increase of 2:1 d-spacing lead to mineral modifications that can be assessed using X-ray diffraction analysis (e.g. Mortland et al., 1956; Hinsinger et al., 1992; Velde and Peck, 2002; Barré et al., 2007a; Khormali et al., 2015). Moreover, 2:1 clay minerals can fix K^+ forming "illite-like" clay layers that collapsed to 1 nm. Such K^+ ions cannot be extracted by water dilution of soil solution concentrations and are consequently not prone to lixiviation and can assure a supply of potassium for plant growth in the following growing seasons. The reversibility of K fixation and release suggests that soil 2:1 clay minerals can be seen as K reservoir for plants (Barré et al., 2008). A better knowledge of the dynamics of the K reservoir is important to obtain an understanding of the long term resources engendered by plant growth and agricultural use of soils.

The difference in mineralogy induced by plant K uptake can be observed very rapidly (a few days in laboratory condition (e.g. Hinsinger et al., 1992; Norouzi and Khademi, 2010) and a few weeks in field conditions (Calvaruso et al., 2009)). The mineralogical modifications can also be detected between rhizosphere and bulk soil mineralogy (Calvaruso et al., 2009; Bourbia et al., 2013; Khormali et al., 2015). The presence of Arbuscular Mycorrhizal Fungi (AMF) increases plant nutrient uptake including alkali metals (Gyuricza et al., 2010). AMF can therefore be expected to increase clay mineral modifications induced by K uptake in the vicinity of roots. This has seldom been studied in laboratory conditions (Arocena et al., 2012) and has not

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been discussed in field conditions at the scale of a growing season thus far. It has also been observed that long-term K fertilization promotes “illite-like” clay layer content (Tributh et al., 1987; Pernes-Debuyser et al., 2003; Barré et al., 2008). However, this effect has seldom been discussed in field conditions at the scale of a growing season.

The objective of the present study was to identify the effects of plant growth under different field experimental conditions on the illite content of the clay assemblage and thus on the potassium content of the clays within one growing season. The study determined the effects of fertilizer and mycorrhizal inoculation on soil clay minerals. Clay minerals recovered from soil adhering to maize roots (“rhizosphere” soil) and soil sampled in the vicinity of maize roots but not adhering to the roots (“non rhizosphere” soil) of fertilized and un-fertilized plots planted with mycorrhiza inoculated or non-inoculated *Zea mays* were studied. Soil sampled in an adjacent un-planted fallow plot (“fallow” soil) was also included in the study. Plots were sampled in the middle of the growing season (40 days after sowing) and at the end of the growing season (130 days). The following hypotheses were tested: (i) due to plant K extraction, illite content would be lower in rhizosphere; (ii) illite content would be lower in rhizosphere of AMF-inoculated plants; (iii) that illite content difference between rhizosphere and non rhizosphere soils would be larger at the end of the growing season.

The presence of the volcanic mineral nepheline ($Na_3KAl_4Si_4O_{16}$) in the studied soils (soil formation in the studied area is influenced by the presence of pyroclastic materials from the activity of the Phlegrean Fields volcanic complex) excludes the use of chemical assessment of available and non-exchangeable K that would occur in clay fractions because K ions can be released from the nepheline mineral structure and will not represent the available potassium in the soil clays.

2. Material and methods

2.1. Experimental design

Maize (cv. Abgaro) was grown in an open field on a Vertic Xerofluvent representative of the lowlands of the Volturno river basin (Campania Region, south Italy) during the period 2008–2010. The experimental design consisted of factorial combinations of two levels of AMF (AMF inoculum) inoculation (−M and +M) in absence of fertilization ($N_0P_0K_0$), and with nitrogen supplied as ammonium nitrate (N, 200 kg ha^{-1}) and potassium as potassium sulphate (K_2O, 160 kg ha^{-1}) in the presence ($N_{200}P_{150}K_{160}$) and absence of phosphorous ($N_{200}P_0K_{160}$). The treatments were applied in a completely randomized design with four replications. The full description of the experimental design is given in Cozzolino et al. (2013). Control fertilized and non-fertilized plots without plants from an adjacent field were also included in the study.

AM commercial fungal inoculum (100 AMF infective propagules g^{-1} of product, information provided by the supplier) consisted of a mixture of calcined clay containing spores, hyphae and root fragments colonized by *Glomus intraradices* (AEGIS® produced by Italpollina, Rivoli Veronese, Italy, for agricultural purposes). The inoculum (25 kg ha^{-1}) was placed at maize sowing with a microgranulator of seed-drill. The experimental plots were water-irrigated every 10 days with 25 m^3 ha^{-1}.

2.2. Soil and plant material

The sampling of the root-soil blocks was performed using shovels by digging around the selected maize plants. The dimension of each block was approximately 30 × 30 × 30 cm. Blocks were collected 40 and 130 days after sowing (das) from fertilized ($N_{200}P_0K_{160}$), unfertilized ($N_0P_0K_0$) and fallow un-planted plots. Maize roots were gently shaken. The soil adhering to the root segments after a gentle shake was called “rhizosphere” soil and was collected by brushing from the roots. Typically, “rhizosphere” soils represented soils being about 2–4 mm from the roots. The soil falling from the roots called “non-rhizosphere” soil. Soils sampled in the fallow un-planted plots were thereafter called “fallow” soil. Fallow, rhizosphere and non-rhizosphere soils were then sieved to 2 mm, kept and processed in a moist state. Due to plant seeding density and sampling protocol, “non rhizosphere” soils have likely been influenced by maize growth. Fallow, non-rhizosphere and rhizosphere soils should therefore be viewed as continuum from no plant influence to maximum plant influence. As fallow un-planted plots were not part of the same experimental design, most of the following results are based on a comparison between “rhizosphere” and “non rhizosphere” soils.

Plants were harvested at 40 and 130 days after sowing (das) and leaves (40 das) and grains (130) were sampled separately. Biomass was determined (fresh and dry weight) from each treatment. The K content of dried leaves or grains was determined by digestion in nitric–fluoridric acid and hydrogen peroxide (6:0.5:2, v/v/v) and measured by atomic absorption spectrometry (PerkinElmer Aanalyst 700).

2.3. X-ray diffraction determinations

2.3.1. Sample preparation

Soil samples were dispersed in deionized water by ultrasonic waves and allowed to settle to extract the <2 μm size fraction. The suspended material was treated with several drops of 1 N SrCl solution which flocculated the clays and exchanged the natural exchangeable ions with Sr ions. This treatment allows the observation of the fully smectitic layers (identified by the interlayer spacing of double hydrated Sr ions) and comparison to the illite layers (one layer of anhydrous potassium ions).

2.3.2. X-ray pattern acquisition and numerical treatment

Oriented preparations were made by pouring several drops of clay suspensions onto glass slides which were allowed to evaporate. Air-dried and glycol treated clay mounts were analyzed using a PANalytical Xpert Pro diffractometer. The machine was set in the θ/θ Bragg–Brentano configuration, with an optical system defined as follows: anti-scatter and diffusion slits respectively 1/4 and 1/2 2θ, Soller slits of 0.04 rad, Ni filter for Cu radiation, and Xcelerator detector counting simultaneously on an angular range of °2θ were the experimental parameters used.

The X-ray patterns were then decomposed (after background subtraction and a four point smoothing routine) into their principal components using the Decomp program (see, Lanson, 1997). Peak areas were determined as the product of peak height and width at half height. 2:1 clay minerals are considered in the following groups: illite with a well (WCI) and a poorly crystallized component (PCI), illite–rich mixed layered smectite illite (I/S), smectite-rich mixed

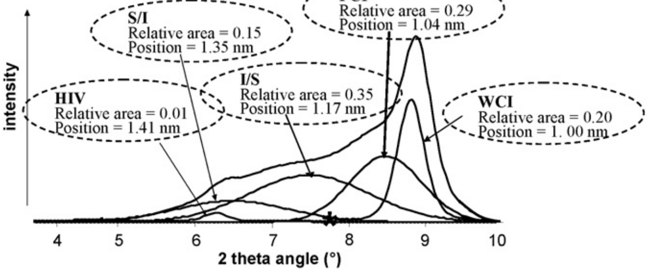

Fig. 1. Example of decomposition of typical X-ray pattern of clay assemblages recovered from rhizosphere and bulk soils. HIV, S/I, I/S, PCI and WCI refer to hydroxy-interlayered vermiculite, interstratified smectite/illite, interstratified illite/smectite, poorly crystallized illite and well crystallized illite respectively. * corresponds to the centre of gravity (cg) position. It is calculated as follow: $cg = 0.01 * 1.41 + 0.15 * 1.35 + 0.35 * 1.17 + 0.29 * 1.04 + 0.20 * 1.00 = 1.13$ nm.