Geoderma 159 (2010) 296–303

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Organic matter induced mineralogical changes in clay-sized phlogopite and muscovite in alfalfa rhizosphere

Z. Naderizadeh [a], H. Khademi [a,*], J.M. Arocena [b]

[a] Department of Soil Science, College of Agriculture, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Canada Research Chair in Soil and Environmental Sciences, University of Northern British Columbia, 3333 University Way, Prince George, BC, Canada V2N 4Z9

ARTICLE INFO

Article history:
Received 28 January 2010
Received in revised form 31 July 2010
Accepted 8 August 2010
Available online 9 September 2010

Keywords:
Potassium release
Organic matter
Phlogopite
Muscovite
Vermiculite
Smectite

ABSTRACT

Weathering of micaceous minerals is the major source of potassium in soils. Many studies have shown the beneficial effects of organic matter (OM) on soil physical, chemical, biological, and nutritional properties. However, there is no information on the effect of OM on the breakdown of K-rich micaceous minerals. The objective of this study was to investigate the transformation of muscovite and phlogopite as influenced by added OM in the rhizosphere zone of alfalfa. Growth medium was a mixture of quartz sand, micaceous mineral (muscovite or phlogopite) and OM (0, 0.5 and 1% cocopeat on a weight basis). During 120 days of alfalfa cultivation, plants were irrigated with either a complete or a K-free nutrient solution and distilled water as needed. At the end of the experiment, plants were harvested and their K uptake was measured by flame photometer following dry ash extraction. Micas and their weathering products were separated from the quartz sand to analyze their clay fractions using X-ray diffraction (XRD). Results showed a significant increase in total K uptake in pots containing trioctahedral mica (phlogopite) and OM as compared with non-OM treatments. Addition of OM transformed phlogopite to 2:1 expanding clays but left dioctahedral mica (muscovite) intact with undetectable formation of any secondary minerals. Root activities and OM decomposition appear to have increased rhizosphere acidity which, in turn, facilitated K release from trioctahedral mica (phlogopite) and induced the formation of vermiculite and a minor quantity of smectite and hydroxy-interlayered vermiculite (HIV). In conclusion, the influence of OM on the formation of expanding clays greatly depends on the type of micaceous mineral.

1. Introduction

Potassium (K) is an essential element because it plays an important role in several physiological processes in plant nutrition (Al-Zubaidi et al., 2008; Marschner, 2008). Soil K is often divided into four forms: soluble, exchangeable, non-exchangeable and structural or mineral (Sparks, 1987). The amount of non-exchangeable K is greatly affected by the content and type of clay minerals present in soil (Jalali, 2007). Non-exchangeable K contributes significantly to plant K nutrition (Surapaneni et al., 2002). When soluble and exchangeable K fractions reach low levels as a result of K uptake by crops (McLean and Watson, 1985), non-exchangeable K from the interlayer of mainly illite or mica is released into the soil solution (Tributh et al., 1987). Barré et al. (2007) showed that 2:1 clay minerals serve as a huge and renewable K reservoir. Also, Officer et al. (2006) stressed the importance of 2:1 clay minerals in plant K nutrition by showing a very significant relationship between potentially plant available non-exchangeable K and 2:1 clay mineralogy.

Mineralogical changes in micaceous minerals have been reported after cropping and fertilization (e.g., Robert and Berthelin, 1986; Hinsinger et al., 1992; Velde and Peck, 2002; Norouzi and Khademi, 2010). Plants can promote both the release of K from illite and the formation of 1.4 nm vermiculite layers (Mojallali and Weed, 1978; Hinsinger and Jaillard, 1993; Kodama et al., 1994; Surapaneni et al., 2002). Some authors also observed the smectitization of interstratified illite/smectite clay domains in K depleted conditions (Tributh et al., 1987; Velde and Peck, 2002). Hinsinger et al. (1992, 1993) demonstrated that in the rhizosphere of rape (*Brassica napus*) and ryegrass (*Lolium multiflorum* Lam.), trioctahedral mica (phlogopite), as the sole source of K, rapidly weathered and vermiculitized after root-induced release of interlayer K, which implies that K in solid framework forms could be a source of K for plants. Formation of complexes and production of acid compounds may promote the vermiculite formation mainly by a proton exchange process (Robert and Berthelin, 1986). Also, K uptake by plant roots may decrease K concentration in the soil solution at the root surface, which leads to mineralogical changes, as shown by Hinsinger and Jaillard (1993).

Some soil microorganisms are able to solubilize unavailable forms of K-bearing minerals, such as micas and orthoclase, by excreting organic acids which either directly dissolve K-bearing minerals or

---

* Corresponding author. Fax: +98 311 3913471.
E-mail address: hkhademi@cc.iut.ac.ir (H. Khademi).

0016-7061/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.geoderma.2010.08.003

chelate silicon ions to bring K into solution (Barker et al., 1998; Basak and Biswas, 2009). Berthelin and Leyval (1982) measured K and Mg uptake by plants to demonstrate the ability of rhizospheric microflora of maize (*Zea mays* L.) to weather a trioctahedral mica (biotite). Weathering rate increased when plants were inoculated with nonsymbiotic microflora and an endomycorrhizal fungus, *Glomus mosseae*. Also, Mojallali and Weed (1978) reported that the infection of soybean (*Glycine max.*) roots by *Glomus macrocarpus* accelerated the process of K release from phlogopite in soil. They used X-ray diffraction analysis to show partial weathering of mica to vermiculite.

Dissolved organic compounds have been found to play an extremely important role in weathering processes in forest soils (Pohlman and McColl, 1988; Raulund-Rasmussen et al., 1998). Lundström and Öhman (1990) reported that microorganisms decompose organic materials to compounds that enhance mineral weathering. Khademi and Arocena (2008) indicated that OM led to the formation of a greater quantity of kaolinite from the transformation of palygorskite and sepiolite in the rhizosphere of alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*) and canola (*Brassica napus*).

Soil organic matter is a key attribute of soil quality. Many studies have been carried out on the effect of organic matter on soil physical (Cecil and Tester, 1990; Barzegar et al., 2002), chemical (Cecil and Tester, 1990) and biological (Saha et al., 2008) properties. It affects, directly or indirectly, many chemical, physical and biological properties that control soil productivity and resistance to degradation (Dick and Gregorich, 2004). The OM content of dryland soils decreases more rapidly and to a lower percentage level than in soils of humid zones (Nelson and Oades, 1998). Therefore, to improve the overall biological, physical and chemical conditions of dryland soils, regular addition of OM would be beneficial (Barzegar et al., 2002).

The role of organic compounds in the weathering of K-bearing minerals has been established using pure minerals and specific organic acids such as oxalic and citric acids (Song and Huang, 1988). However, there is no information on the effect of natural OM on the weathering of K-bearing minerals.

The objectives of this study were: (1) to investigate the effect of OM on the transformation of phlogopite and muscovite in the alfalfa rhizosphere, and (2) to examine the influence of OM on potassium uptake from phlogopite and muscovite by alfalfa.

2. Materials and methods

This research was carried out as a pot experiment using pure minerals under greenhouse conditions. Detailed information on growth media, their preparation and different treatments is given below.

2.1. Growth media

A trioctahedral (phlogopite) and a dioctahedral (muscovite) mica, from Hamadan Province, Iran, were chosen as the source of K for plants. Mica samples were ground and sieved and the <60 μm size fraction was collected for the experiment.

Hamadan quartz sand sized greater than 52 μm was used as the plant growth medium. It consisted of almost pure SiO_2 (97.53%) and was free of clay minerals and other substances (Table 1). The quartz sand was washed with 0.2 N HCl, repeatedly rinsed with distilled water until the supernatant solution was chloride-free, oven-dried at 105 °C and used in the pot experiment. The chemical composition of the reference minerals and quartz sand are reported in Norouzi and Khademi (2010).

Cocopeat, a commercial peat made of coconut residues, was used as the OM amendment after washing with tap water on a 1 mm sieve to remove the likely mineral particles. The peat was saturated with NH_4^+ using 1 N NH_4Cl solution, washed with distilled water, oven-dried at 60 °C, and then ground to <60 mesh size prior to usage in the experiment.

2.2. Pot experiment

The experiment was conducted in a greenhouse for 120 days at the Soilless Research Center, Isfahan University of Technology, Iran. Each pot contained 600 g of the growth medium. The experimental design was a completely randomized 3 × 3 × 2 factorial with 18 treatments and 3 replications for a total of 54 experimental pots. The treatments were combinations of 3 growth media, 3 levels of OM addition and 2 kinds of nutrient solutions.

Growth media included quartz sand (control), quartz sand + phlogopite and quartz sand + muscovite. To supply equal quantities of K (0.35% K_2O), 21 g of muscovite or 22.6 g of phlogopite was added to each pot. The three levels of OM treatment were 0% (O_0, control), 0.5% (O_1) and 1% (O_2) on a weight basis. The two types of nutrient solution were K-free (−K) and complete (+K) nutrient solutions prepared according to Stegner (2002).

Before sowing alfalfa (*Medicago sativa* L.) seeds, the growth media were incubated for 30 days at the near field capacity moisture level and at room temperature to initiate the decomposition of OM. Microbial organisms contained in 10 ml field soil extract (including 49 mg/l K) were added to each pot. During the cultivation, plants were irrigated with either the complete or the K-free nutrient solution and distilled water as needed.

2.3. Laboratory analyses

Plants harvested at the end of cultivation were washed with distilled water and dried at 70 °C for 48 h. Biomass was weighed and ashed at 550 °C for 4 h. Each ash sample was dissolved in 10 ml of 2 N HCl and its K concentration was measured by a flame photometer. The same method was also used to determine the potassium content of cocopeat. Nitrogen and carbon contents of cocopeat were measured by Kjeldahl (Bremner, 1996) and Walkley–Black (Nelson and Sommers, 1996) methods, respectively. Potassium uptakes in shoot and root were calculated by multiplying the dry biomass (g/pot) by potassium concentration (mg/g). Total K uptake in each pot was the sum of K uptake in shoot and root.

At the end of the experiment, the particles of mica and its likely weathering products surrounding the roots in each pot were separated from the quartz sand by washing them on a 60 μm sieve and their OM content was removed using 30% H_2O_2. Finally, the clay fraction was separated using a centrifuge.

The mineralogy of the clay fraction was determined by X-ray diffraction (XRD) before and after the pot experiment. Oriented slides

Table 1
The chemical composition (%) of micaceous minerals and quartz sand used in the experiment (after Norouzi and Khademi, 2010).

Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	MnO	P_2O_5	TiO_2	LOI[a]	Total
Quartz sand	<0.1	0.11	0.36	97.53	<0.1	0.61	0.57	–	–	–	0.48	99.86
Phlogopite	0.45	22.54	14.6	42.24	9.29	4.21	4.69	0.11	0.04	0.56	0.9	99.63
Muscovite	0.64	0.08	33.92	48.34	9.98	0.17	1.76	0.06	0.03	0.06	4.5	99.54

[a] Loss on ignition.