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Effect of gypsum on potassium and iron release from phlogopite under laboratory conditions

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Abstract

This study estimated the effects of gypsum on the potassium and iron release rate from phlogopite under laboratory conditions. A randomized design with the factorial arrangement and three replications was utilized to run the current experiment. Treatments included different levels of gypsum (0, 2, 5, 12 and 25%) and eight different time periods (12 hours, 1, 2, 4, 8, 16, 32 and 64 days). The result of this study indicated that the rate of potassium and iron release were faster initially, and it slowed down thereafter. As gypsum content increased, potassium and iron concentrations decreased which is haply due to immense presence of calcium ions. Calcium ions change the equilibrium of K by increasing the amount of gypsum. The results revealed that the potassium and iron release rate from phlogopite is drastically declined in the presence of gypsum.

Keywords: Nutrient release, micaceous mineral, weathering, DTPA, ammonium acetate

Introduction

Potassium (K) is an integral nutrient that plays an essential task in enzyme activity, protein synthesis and photosynthesis in plants (Cakmak, 2005; Singh *et al*., 2010). Soil K is commonly categorized into four sections including soluble, exchangeable, fixed, and structural K (Lalitha and Dhakshinamoorthy, 2014). There is equilibrium among different forms of soil K that affects the amount of soil K at any specific time. Soil K forms in the order of their accessibility to plants are the solution > exchangeable > nonexchangeable > mineral (Sparks, 2000). Soil K status extremely depends on the amount of non-exchangeable K (Benipal and Pasricha, 2002). K release from different minerals is affected by the dissolution of crystal structures and the exchange of interlayer K with hydrated cations (Ogaard and Krogstad, 2005). The presence of minerals in the soil can supply K to the plants by weathering (Natale *et al.*, 2001).

Iron (Fe) is one of the most significant micronutrient (Gyana and Sahoo, 2015). The silicate minerals or Fe oxides and hydroxides create the extensive division of Fe in soils (Sterflinger, 2000). Fe in soil fundamentally exists as Fe^{3+} chelate forms and the plant root cannot absorb it under a high potential of hydrogen (pH) in alkaline soils (Cesco *et al.*, 2010). Iron solubility is affected by several parameters. Primary minerals containing Fe (II) are unstable in soils and slowly weather in the presence of atmospheric oxygen (Singh *et al*., 2011).

Phlogopite is a phyllosilicate mica that contains some essential elements such as K, Fe. Exchangeable K of mica is a suitable source of K for plants (Noruozi and Khademi, 2010), and Fe(II) in the octahedral layer of phlogopite mineral is oxidized to Fe(III) by weathering process (Sterflinger, 2000). The extraction of K and Fe from various layers of minerals can be changed at different time periods and they cannot be measured in a short time. Some scholars investigated the release rate of K from various fertilizers during various time periods without any limitation of gypsum and lime. Holcomb indicated that a stable release rate of K was not observed during various time periods (Holcomb *et al*., 2008).

Gypsiferous soils were first identified and presented by a German researcher in 1871 (FAO, 1990). By and large, as pH proliferates due to the presence of gypsum in the soil, the weathering of phlogopite lessened (Sterflinger, 2000). Gypsum is identified to affect the availability of K and Fe elements. Changes in soil K and composition of mineral specifies the long-term sustainability of a cropping system (Shaikh *et al.*, 2007). Some researchers reported that the addition of gypsum can raise the solubility of N, K, Ca, Mg, Mn, Cl, and S and lessened the solubility of P, Na, Fe, Cu, Zn, and B ions because of high concentration of Ca^{2+} and SO$_4^{2-}$ in the soil (Elrashidi *et al*., 2010). Elrashidi *et al*. (2010) revealed that gypsum contains high amount of Ca and SO$_4^{2-}$ ions in soil solution, which may negatively affect the solubility of other nutrients, root absorption sites, and plant growth.

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Therefore, gypsum is known to disturb the nutrient balance in soil solution. It is useful to have a great understanding of K and Fe release rate from external and internal layers of phlogopite during different time periods. The over- application of gypsum can disturb rate of Fe and K release in negative way and also iron measurement method can be unable to provide the actual amount of Fe. This study would help the researchers in determining the actual amount of gypsum which positively affects the Fe and K release and modulating the phenomenon which provide the exact Fe amount in future. To the best of our knowledge, there has yet been no study to investigate the effect of time on the release rate of K and Fe from phlogopite under different levels of gypsum at laboratory conditions. Also, no study has been done to determine the impact of gypsum on solubility of nutrients at different time periods. Hence, the objectives of this research were to study the effects of different time periods × different levels of gypsum interaction on the release rate of K and Fe from phlogopite mineral under the laboratory conditions and to investigate the impact of time on mineral weathering.

Materials and Methods

Sample preparation

Phlogopite as a trioctahedral mica was used in this experiment. Phlogopite sample was collected from a mine in Urmia Province, Iran, and examined with X-ray diffraction (XRD) and X-ray fluorescence (XRF) to identify the purity of phlogopite. It was relented and passed through a 140 mesh before being utilized in this experiment. Phlogopite mineral sample was washed with municipal water and distilled water and then dried in an oven at 105 °C.

Gypsum sample was obtained from a mine around 20 kilometers north of Natanz, placed in the Pliocene sediments. The sample was washed with municipal water and distilled water and then dried in an oven at 45°C before being applied in the experiment. Gypsum sample with high purity was ground and then sifted to achieve 74 to 149 µm particle size. Table 1 indicates the elemental analysis of phlogopite utilized in the experiment.

Table 1: Elemental analysis by XRF for micaceous minerals and Hamadan quartz sand used in the experiment (Norouzi and Khademi 2010)

Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O%	Fe_2O_3	FeO	MnO	CaO	LOI	Total
Urmia Phlogopite	0.41	26.41	17.44	38.7	10.13	0.2	2.8	0.07	0.12	3.72	100
Hamadan Quartz	<0.1	0.11	0.36	97.53	<0.1	0.57	--	--	0.61	0.48	99.86

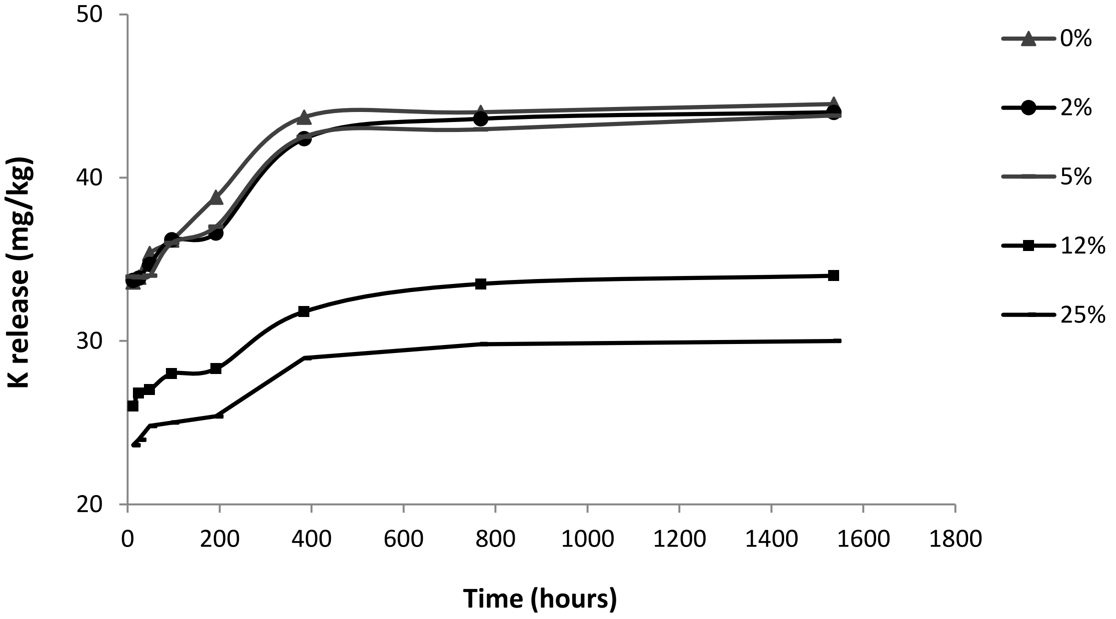

Figure 1: K release from phlogopite by ammonium acetate as a function of time under different levels of gypsum

Laboratory process and analyses

The experiment was done under the laboratory conditions and the samples were kept in incubator for 64 days. All samples were kept under incubation temperature (25°C) in plastic test tube containing a mixture of micaceous mineral (phlogopite), different levels of gypsum including 0, 2(0.02 g), 5(0.05 g), 12(0.12 g) and 25% (0.25 g) and 15 mL ammonium acetate 1 M at pH 7 as an K extractor (Csatho, 1998)/or 15 mL DTPA 0.005 M at pH 7.2 as an Fe extractor (Hanlon and Johnson, 1984). Phlogopite mineral (2 g) was added to each sample. K and Fe of obtained extracts were measured at different time periods (12 h, 1, 2, 4, 8, 16, 32 and 64 days). All test tubes were shaken twice a week by electric shock.

A randomized design with the factorial arrangement and three replications was utilized to run the experiment. Having 5 levels of gypsum content, 8 different time periods and 3 replications, the total number of samples were 240.

Statistical analysis

All the statistical analysis was performed using SAS 9.1 and SPSS software. Means comparison was carried out by the LSD test at $p<0.05$ significance level.

Results and Discussion

Potassium release rate

The results indicate that the amounts of K from ammonium acetate extracts are used as estimates of the K levels of soil. Amounts of K from ammonium acetate extracts can be used as estimates of the K levels of soil that are accessible for uptake by the plant (Omanga *et al*., 2013). The K release at different time periods under different levels of gypsum are presented in Figure 1. By the time, the K release in all samples under gypsum treatments of 0 (control), 2, 5, 12 and 25% increases. The rate of K release from phlogopite in gypsum levels of 0, 2 and 5% is faster than the samples under 12 and 25% gypsum. In all samples, K release showed stable trend after 32 days.

Richard and Bates (1988) stated that in clay minerals having the specific K site, ammonium could displace K from these specific sites, resulting in a higher prevalence of exchangeable K with NH4AOc. A different trend of K release was observed after and before 32 days. K and Fe release increased with the passage of time up to 32 days. Before 32 days, the release rate and amount of K and Fe were higher in the samples containing low amount of gypsum than the samples with high amount of gypsum. The higher rate of K released at the primary stage might be ascribed to external surfaces and edge sites while the slower rate of K release was due to the inter-layer sites involving the slower rate of diffusion (Sparks and Huang, 1985). Brar *et al*. (2008) reported that nonexchangeable K release was faster initially, and it slowed down afterward. The neutral pH (7.00) 1.0 M ammonium acetate (NH4OAc) extraction is the most widely used method to evaluate the soluble and rapidly exchangeable pools of alkali and alkaline elements in soils (Reeuwijk, 2002). Ammonium acetate, whose ionic radius is similar to K^+ and the NH_4^+ ions make possible a sharp rapid separation of K from exchange complex (Hanlon and Johnson, 1984). Only ions with a size similar to K^+, such as NH_4^+ and H_3O^+, can exchange K from wedge zones. (Sparks, 2000).

When the pH neutral ammonium acetate extractor is used on a calcareous soil, it may overestimate Ca^{2+} (Reeuwijk, 2002). K release tends to be sorely slow in samples containing gypsum. Gypsum accumulation in soil may have the limiting effect on nutrient availability due to the decrease in cation exchange capacity (CEC) (Escudero *et al*., 2015; Castillejo *et al*., 2011). Habib *et al*. (2014) revealed that the soils are not deficient in available K owing to the presence of clay mineral.

The cumulative concentration of K released from phlogopite mineral at different time periods under different levels of gypsum is demonstrated in Figure 2. The concentrations of K were not considerably differed owing to three level of gypsum containing 0, 2 and 5%, but 12 and 25% gypsum levels had significant negative impact on Fe concentration in the solution. In the samples containing 25% gypsum, the lowest level of K concentration was obtained. High Ca values resulted in the reduction in K concentrations. The lowest amount of K concentration was found in the samples with gypsum level of 0% (Figure 2). The cumulative concentration of K released from phlogopite in the sample containing 0% gypsum is 302.67 mg kg^{-1} that this amount is respectively 1.2 and 1.4 times greater than samples containing 12 and 25% gypsum. Most amounts of nonexchangeable K were removed from the soil with pH 4.5 but discrepancies in removal between pH 5.5 and 7.0 were small (Islam and Bolton, 2009).

According to the result, the Ca concentration has increased due to the presence of gypsum which may have negative impact on the solubility of K. By increasing levels of gypsum, the K and Fe release have also declined during different time periods. High level of Ca^{2+} ions could lead to substitute for K^+ ions on the exchangeable surfaces of minerals and also K^+ ions trapped as nonexchangeable form (Elrashidi *et al*., 2010).

Iron release rate

The process of Fe released at different time periods under different levels of gypsum is indicated in Figure 3.

Release rate of Fe has decreased by increasing amount of gypsum during different time periods. In the samples containing 0, 2, 5, 12 and 25% gypsum, Fe release increased before 32 days and after 32 days showed stable trend. The presence of calcium and sulfate ions led to the reduction of K and Fe released from phlogopite.

The increase in activity of Ca ion leads to the reduction of Fe release rate from phlogopite mineral (Stegner, 2002). By increasing each pH unit, the Fe^{3+} activity of soil solution

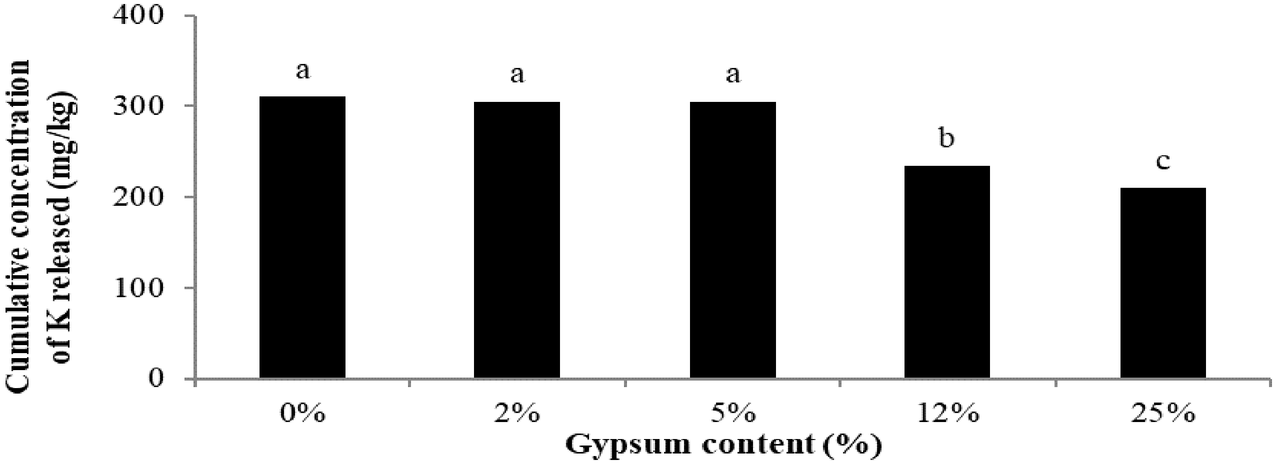

Figure 2: Cumulative concentrations of K released from phlogopite under different levels of gypsum. Means with at least one common letter are not significantly different at *p*<0.05 of LSD test.

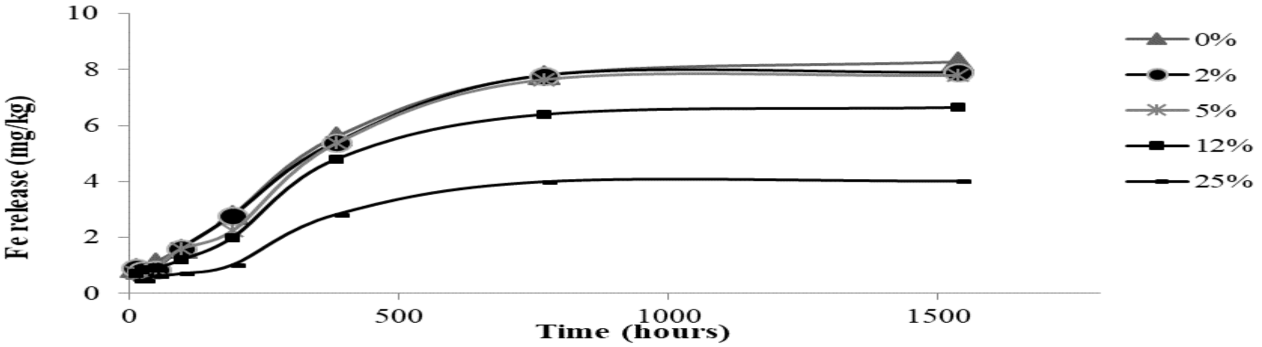

Figure 3: Fe release from phlogopite by ammonium acetate as a function of time under different levels of gypsum.

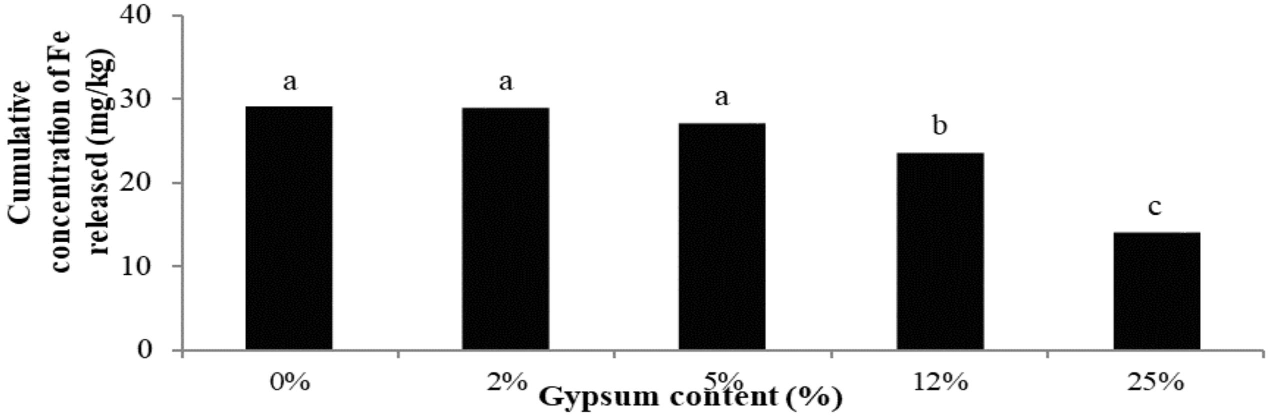

Figure 4: Cumulative concentrations of Fe released from phlogopite under different levels of gypsum. Means with at least one common letter are not significantly different at *p*<0.05 of LSD test.

lessens 1000-fold (Sterflinger, 2000). Mengel *et al*. (2001) manifested that calcareous soils universally contain the high level of Ca concentration in the soil solution. It became clear that Ca competes with Fe for the same binding sites of chelating compounds present in the proximity of the root and availability of iron is thus declined. Stegner (2002) revealed that high level of Ca ion has an antagonistic impact on Fe absorption.

The cumulative concentration of Fe released from phlogopite mineral at the different time under different levels of gypsum is shown in figure 4. The Fe concentrations were not considerably differed at 0, 2 and 5% gypsum while 12 and 25% gypsum level had a considerable impact on the concentration of Fe. The decrement of Fe concentration was shown by raising the amount of gypsum. The highest amount of Fe was found in the gypsum-free samples. Conversely, the lowest concentration of Fe was observed in samples containing 25% gypsum. As the amount of gypsum proliferated, Fe concentrations lessened as such that the samples containing 25 and 12% gypsum demonstrated the highest reduction in Fe concentration.

Gypsum contains high concentrations of Ca and SO_4^{2-} ions in the soil solution (Elrashidi *et al*., 2007), which may decrease the solubility of Fe ions (Elrashidi *et al*., 2010). The concentration of Fe detracts with rising concentration of Ca ion in the soil solution due to the competition between Fe^{3+} and Ca^{2+} ions (Ansari Ezabadi *et al*., 2011; Tisdale *et al*., 2003). Low amount of gypsum did not have extreme impact on nutrient release form phlogopite. But, an extreme reduction was observed in the samples containing high level of gypsum. Sheikhi Shahrivar and Khademi (2017) declared that the low level of gypsum has not considerable impact on the nutrients release from mineral.

A high correlation between K and Fe concentration was observed in all samples. Both K and Fe concentrations lessened by increasing gypsum level (R2= 0.81**, $p<0.01$).

pH change

The pH change range in all samples was 6.5 to 7.5. Also. The pH change range in samples containing 12 and 25% gypsum was 7 to 7.5. A remarkable difference among samples containing various amounts of gypsum was not observed. Some scholars revealed that applying gypsum to the soil will increase the calcium and sulfur amounts, but it will not raise the pH. Also, gypsum has little if any effect on soil pH (Elrashidi *et al*., 2010; Hanlon and Johnson, 1984).

Conclusion

In this study, gypsum is identified to affect the availability of K and Fe elements. High values of added gypsum have negative impacts on K and Fe release from phlogopite. The presence of calcium ions can discompose the balance among the nutrient elements and also decrement in the rate of phlogopite weathering. By increasing level of Ca^{2+} and SO_4^{2-} due to the presence of gypsum, the K and Fe release from phlogopite declined. K and Fe release of all samples increased with the passage of time. In samples containing 0, 2 and 5% gypsum, the rate of K release was faster than samples containing 12 and 25%. At the primary stage of weathering, K was released from external surfaces and edge sites. The slow pace of release of K in the final stages of weathering is due to the fact that K was released from restricted domains such as interlayer sites which are known as structural K. By looking at the processes of Fe release, it can be concluded that the common methods of absorbable Fe measurement which will be done in two hours cannot represent the actual amount of absorbable Fe for plants.

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