

SHINING LIGHT ON NOVEL PATHWAYS FOR POTASSIUM FIXATION IN SOIL

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ABSTRACT

Cotton has a high demand for potassium, and potassium significantly affects both cotton yield and fiber quality. Thus, bioavailability of potassium from the soil is paramount. Bioavailability and leaching of potassium to crops and from soils has been studied since the 1940s. However, problems that confronted agronomists in the 1980s continue to impact growers and crop production, including unpredictable potassium bioavailability and inconsistent plant response to fertilizer application under a variety of soil physical and chemical conditions. Part of the challenge of understanding potassium fixation pathways is the lack of fundamental information on potassium adsorption mechanisms. Our goal is to understand and illustrate at a clay mineralogical (and molecular) level how novel pathways of potassium fixation may be contributing to this persistent potassium problem. Our hypothesis is that the formation of new mineral surface precipitates, which develop on fast time scales, provides access to new adsorption sites for potassium surface complexation, effectively increasing the adsorption capacity of mineral solids and the potential to remove potassium from the soil solution. We present recent results relating to novel surface complexation mechanisms of potassium with layered mineral surface precipitates through a series of wet-chemical and spectroscopic experiments. X-ray absorption spectroscopy (XAS) is applied in these experiments to “shine light” on newly identified adsorption pathways for potassium in oxide mineral systems. Batch adsorption experiments were conducted with potassium, aluminum oxides, and silicon oxide in the presence and absence of co-ions. Overall, our results showed increased amounts of potassium sorption for samples reacted for longer time periods, suggesting that potassium sorption is time dependent. Importantly, we identified novel binding mechanisms of potassium to surface precipitates in the presence of different co-ions and dissolved silicate. Inner-sphere surface complexation to different types of surface precipitates was identified, and an increase of on average 30% in potassium adsorption was observed when silicon oxide was present along with aluminum oxides. Collectively, these results imply that considering only the traditional view of potassium fixation, which heavily relies on potassium incorporation into the interlayer spaces of soil clay minerals already present, could perhaps underestimate the potential of soils to sequester potassium.

INTRODUCTION

The United States has a vital role in the global cotton market and is a critical producer and exporter of cotton fiber. Between August 2019 and July 2020, the US produced about \$7 billion of cotton (USDA, 2022). Cotton has a high demand for potassium, and potassium significantly affects both yield and fiber quality (Oosterhuis et al., 2014). Bioavailable potassium requirements for cotton plants have become even greater with the use of modern, genetically improved cultivars of cotton that partition more nutrients, such as potassium, into the fruit than cultivars from the 1990s (Pabuayon et al., 2020). Thus, bioavailability of potassium from the soil is critical (Suelter, 1985). Potash is a major potassium fertilizer for many crops, including cotton, and the US imports large quantities of potash. Fertilizer prices, including potash, have been near record levels and can fluctuate markedly (Nti & Jones, 2022). The US is heavily dependent on imported potash, and almost all countries rely on just a few countries, mainly Canada, Russia, and Belarus for potassium fertilizer. Disruptions from any of these countries causes serious potassium fertilizer shortages, further increase in prices, and import-export restrictions (Nti & Jones, 2022).

Potassium chemistry in soil has been studied since the early 20th century (Volk, 1934); however, part of the challenge of understanding novel fixation pathways is a lack of fundamental information on potassium adsorption mechanisms (Coyle et al., 2023; Pham et al., 2022). The traditional four “pools” model used to describe potassium in soil (i.e., solution potassium, exchangeable potassium, non-exchangeable potassium, and structural potassium in feldspars) does not capture the dynamics of potassium supply to plants or potassium turnover in soils amended with fertilizers, plant residues, or waste products (Bell et al., 2021; Coyle et al., 2023; Pham et al., 2022; Schmidt et al., 2022).

Specifically, the interlayer space between phyllosilicate clays is often labeled as the culprit for excessive potassium fixation. Illite, for example, is often heavily enriched in potassium, and that potassium is non-bioavailable (Schmidt et al., 2022). Other major sources of non-bioavailable potassium in soil include primary minerals, such as micas or feldspars (Bell et al., 2021). These long-standing concepts, however, may only be partially guilty for potassium fixation. Specifically, they do not account for the rapid fixation of potassium from applied potash fertilizer.

This work aims to address potentially overlooked fundamental mechanisms by which potassium can become bound to newly formed surface precipitates in soil. These precipitates include metal hydroxides and silicated metal hydroxides, whereby potassium can become sequestered or “fixed”. This additional mechanism adds to our understanding of excessive potassium fixation in soil systems. The experimental objective of this research is to examine potassium surface chemistry to identify how it can potentially be incorporated into newly formed surface precipitates (Coyle et al., 2023; Pham et al., 2022).

MATERIALS AND METHODS

Initial studies were conducted using whole soil fractions to determine alterations in potassium chemistry due to traditional soil extraction techniques (Schmidt et al., 2022). Additional studies investigated the extent of potassium adsorption on aluminum and

silicon oxides, where multiple sets of batch adsorption experiments were carried out. Three types of (hydr)oxide minerals used, including two aluminum oxides (boehmite and gamma alumina) and amorphous silicon oxide (Coyle et al., 2023; Pham et al., 2022). The purpose of selecting these minerals was to provide different yet common types of surface adsorption sites (aluminum and silicon surface sites) found in soils. Potassium adsorption experiments were conducted at pH 8.5 at ambient temperature using 0.1 g or 1.0 g of mineral. Minerals were reacted in solutions of 3 mM magnesium, iron, zinc, or nickel nitrate, along with 50 mM HEPBS buffer, 10 mM NaNO₃ background electrolyte, and 1 mM KNO₃ solution. Dissolved elemental concentrations of potassium, aluminum, iron, silicon, nickel, and zinc were measured using inductively coupled plasma optical emission spectrometry (ICP-OES). Thermodynamic modeling was carried out using Visual MINTEQ. Points of zero charge of the mineral surface were determined using a Particle Metrix STABINO Particle Charge Mapping System. Potassium K-edge X-ray absorption near edge structure (XANES) spectra were collected from the reacted, freeze-dried samples at beamline 9-BM-B,C at the Advanced Photon Source (APS). 40 mg freeze-dried sample was pressed into round 7 mm pellets and mounted at 90 degrees incident to the detector an incident beam (Coyle et al., 2023; Pham et al., 2022).

RESULTS AND DISCUSSION

Effects of wet chemical extractants on soil potassium chemistry

We examined how traditional wet chemical extractants (e.g., Mehlich III) affected residual potassium speciation in agricultural soils. Figure 1 is a summary diagram of the molecular-scale processes. The changes in potassium coordination described in Figure 1 were evident in the X-ray absorption spectroscopic data, where the Mehlich III

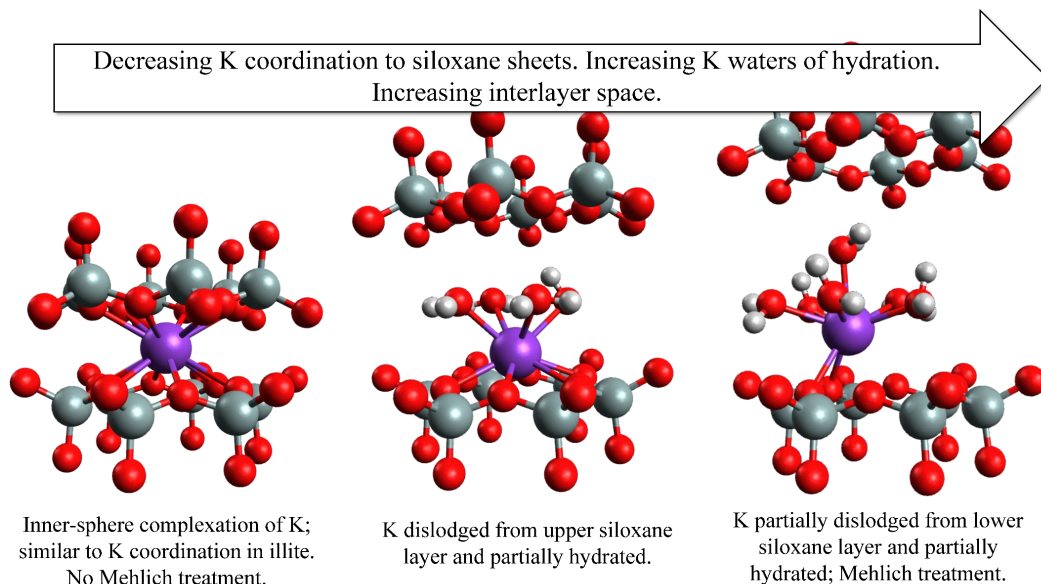


Figure 1. A structural model illustrating the coordination chemistry of potassium bound in the interlayer space of 2:1 clay minerals. During Mehlich extractions, the spectroscopic data indicated that potassium appears to become dislodged from the silica layers and increases in hydration. From (Schmidt et al., 2022), with permission.

extractant caused a dampening in spectra oscillation intensities. This indicated that Mehlich III can dislodge potassium from its inner-sphere siloxane bonds (i.e., the bonds it forms with the silicate molecules that compose clay mineral tetrahedral sheets) (Schmidt et al., 2022). Based on a Linear Combination Fitting (LCF) approach, the amount of potassium associated with montmorillonite increased by 25%. The interlayer space of layered clay minerals, such as smectite (i.e., montmorillonite), served as a sink for potassium. This work made it clear that we cannot directly measure potassium bound to the surfaces of clay minerals due to the high concentration of recalcitrant potassium remaining in the mineral solids. Therefore, to determine the coordination chemistry of surface-bound potassium, we examined the role of silicon and aluminum oxides as well as surface precipitates in potassium sorption (Schmidt et al., 2022).

Potassium sorption to silicon and aluminum surface precipitates

During the adsorption studies and subsequent analyses through X-ray absorption spectroscopy (XAS), and specifically the near-edge X-ray spectra (XANES), a distinct feature in the potassium spectra, i.e., a peak at 3625 eV and a valley at 3632 eV (Figure 2A) was observed (Coyle et al., 2023). The presence of the peak at 3625 eV indicates the possibility that potassium is forming an inner-sphere surface complex with newly formed precipitates, which in this case were layered double hydroxides (LDH) for the nickel and zinc systems. The spectral differences between the systems with and without surface precipitates were evident (i.e., the magnesium-system system did not have any surface precipitates, Figure 2A).

Figure 2B provides a direct comparison between silicon, aluminum, and mixed AlSi systems. Sample notation is as follows: Al, aluminum; Si, silicon; Mg, magnesium; 1M, 1-month. When the single oxide systems (i.e., the AlMg1M and SiMg1M) are compared with the mixed oxide system (AlSiMg1M), the shapes of the white lines are distinct. The doublet is pronounced in the mixed AlSi system compared to single silicon system

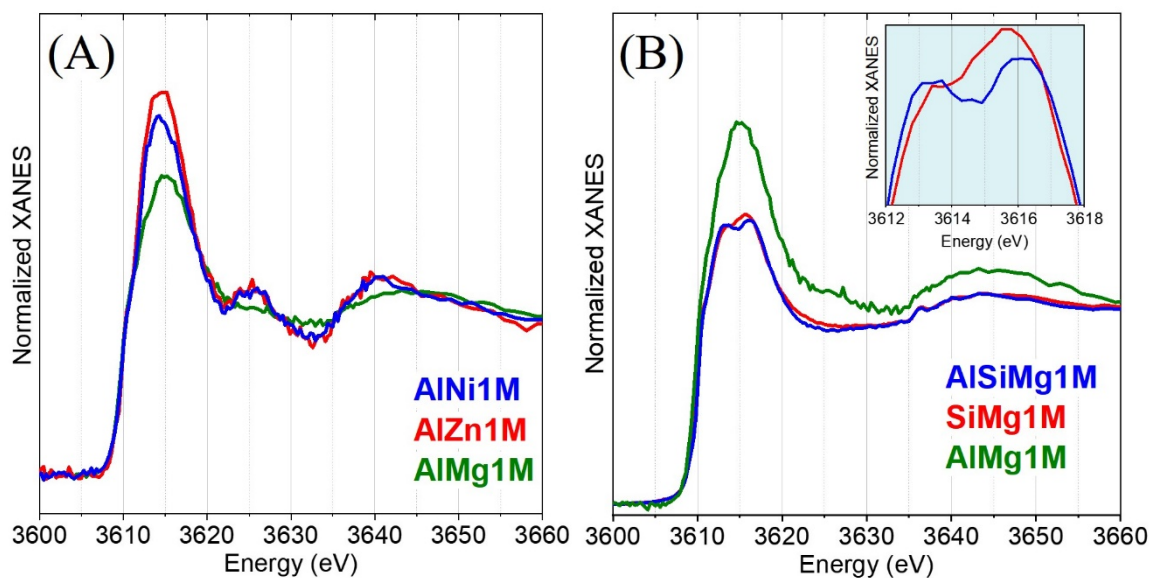


Figure 2A. Potassium XANES spectra for aluminum oxide reacted with different co-ions, and **(2B)** a comparison of XANES for mixed oxide systems. The clear doublet feature is present only in the samples with both silicon and aluminum. From (Coyle et al., 2023), with permission.

(Figure 2B, inset). The pronounced doublet in the AlSiMg1M indicates that the combined presence of aluminum and silicon is affecting the local coordination environment of potassium (i.e., its chemical form, or speciation). These spectra indicate a significant difference in X-ray scattering of aluminum versus silicon as a second nearest neighbor of potassium, and that a distinct bonding mechanism is present in the mixed oxide system which requires the presence of both silicon and aluminum. The sharper features indicate that potassium is more highly coordinated and potentially more tightly bound (Coyle et al., 2023).

CONCLUSION

The experiments indicated that an increase in time also increased the amount of potassium bound to the mineral solids, and that silicon oxide was more reactive than aluminum oxide (Coyle et al., 2023; Pham et al., 2022). This was likely due to the much lower point of zero charge of the silicon oxide. Incorporation of dissolved silicate onto hydroxides may provide new interlayer spaces that can potentially incorporate potassium (Coyle et al., 2023). Surface area by itself did not account for the changes in potassium sorption, and the presence of silicon appeared to promote incorporation into newly formed surface precipitates; overall, a 29% increase in potassium sorption above the predicted amount was observed, and this indicates that dissolved silicate may play a critical role in increasing potassium sorption (Coyle et al., 2023; Pham et al., 2022). The role of dissolved silicate will be pursued in future studies.

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