Technical Report

Harvesting Soil Salts from Soybean Production Fields: Evaluating a New Method

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Introduction

Soil salinity is a primary soil health concern in North Dakota. The source of this salinity can range from sodium, magnesium, calcium, sulfate, and chloride based salts with some being more difficult to leach from the soil than others (DeSutter and Cihacek, 2009). These different types of salts can greatly influence the ability to ameliorate or remediate areas with high levels of soil salinity using leaching methods.

However, products that modify how salt crystals form have been reported in other industries including those to preserve historically significant buildings. These products disrupt salts to form a crust at surfaces where water evaporates at; but instead makes the salt crystals grow in needles or filaments that can be easily harvested and removed (Selwitz and Doehne, 2002).

At NDSU, we have developed a method that uses a similar product (ferric hexacyanoferrate) to efficiently extract soil salts from brine contaminated soils (Daigh and Klaustermeier, 2016; Klaustermeier et al., 2017). However, we have not yet evaluated the method on naturally occurring surface salts and at concentrations similar to those observed in crop fields. This project will accomplish this and allow for modification of the method to best match soybean producer's needs.

Goals/Objectives

The main goal of this project is to test a new method of removing salts from saline soils to improve soil health and soybean yields. We propose to surface apply ferric hexacyanoferrate, to saline soils, which disrupts the formation of a hard salt crust and allows salt crystals to grow above the soil surface to then be easily harvested. Preliminary data has been collected in the lab demonstrating the proof of concept in extremely high saline soils contaminated with sodium chloride brine solutions. This project will test the product on other salt species commonly observed in naturally occurring saline soils in North Dakota and evaluate any subsequent (i.e., post application) effects on soybean and wheat growth and health as well as soil health.

Methods

Modifications of the original method used for harvesting sodium chloride from brine contaminated soils were performed in the laboratory. Previously, we thought that the early precipitation of calcium, magnesium, and sodium sulfates were responsible for interfering with salt efflorescence after the application of ferric hexacyanoferrate; the interference from a quick forming salt crust. Therefore, the modifications to the original method consisted of including compounds known to increase the solubility of calcium sulfate. If the solubility could be increased, then the formation

of a salt crust would be delayed and the initial nucleation sites of salt efflorescence may have addition time to form due to the ferric hexacyanoferrate.

Field evaluations were planned if the modification of the method of applying ferric hexacyanoferrate to soils to induce harvestable salt efflorescence from the soil surface was successful on salt species other than sodium chloride. However, field evaluations were forgone since a modified method for calcium sulfate, magnesium sulfate, or sodium sulfate was not obtained in the laboratory; therefore providing no proof that field testing would have any chance of success. However, we have already shown this salt-harvesting method to have potential for remediating sodium chloride brine spill, which currently affect soybean and wheat production fields, in North Dakota. Therefore, efforts were focused on identifying subsequent effects that a soil application of ferric hexacyanoferrate may have on soybean and wheat growth and health as well as soil health.

The effects of ferric hexacyanoferrate loading rates on early stage soybean and wheat health were evaluated in a greenhouse using 32 pots arranged in a fully randomized design. Four loading rates of 0 (control), 100, 200, and 1000 g ferric hexacyanoferrate m^{-2} of soil surface. These loading rates will be referred hereafter as 0, 0.5, 1, and 5X loading rates based on recommended rates reported in Daigh and Klaustermeier (2016) and Klaustermeier et al. (2017). Although ferric hexacyanoferrate has been proposed as an in situ remediation method for severely saline soils, the ferric hexacyanoferrate was applied to a non-saline in this greenhouse experiment. This was to eliminate any confounding factors associate with salt stress (osmotic or toxicity stresses) on the soybean and wheat plants. Therefore, any effects on plant parameters and conditions would be due to the ferric hexacyanoferrate loading rates and not due to variable soil salinity levels. Pots were filled with 3kg of air-dried and sieved fine sandy loam soil (Delamere soil series; Coarse-loamy, mixed, superactve, frigid Typic Endoaquolls) that was collected from a soybean production field near Barney, ND.

The upper radius of the greenhouse pots (i.e. at the soil surface) was 9.5 cm, giving a 283.5 cm^2 soil surface to apply the ferric hexacyanoferrate treatments. Suspensions were made using 409 mL of deionized water (DI H_2O), 96 ml of 5% (v/v) ammonia hydroxide solution, and 0, 2.84, 5.67, and 28.35 g ferric hexacyanoferrate to make the 0, 0.5, 1, and 5X loading rates. The ammonia hydroxide is use to dissociate the ferric hexacyanoferrate into Fe and hexacyanoferrate; the latter being the crystallization inhibitor that promotes salt efflorescence. These suspensions were then slowly poured onto the air-dry soil surface of pots in the greenhouse. The 409 mL of DI H_2O with 96 mL of 5% (v/v) ammonia hydroxide solution results in 500.01 g of H_2O applied to each pot. The antecedent air-dried soil contains were 0.03 g/g soil water content. Therefore, the gravimetric soil water content for each pots after applying the ferric hexacyanoferrate suspensions was 0.20 g/g.

After the suspensions were applied to the soil surface, the pots were allowed to incubate uncovered in the greenhouse for 8 d before the soil was thoroughly mixed within each pots and seeds planted the following day on 15 February 2017. Six seeds of either wheat or soybean were planted. Water was then added to the soil surface until the soil was at 1 g/g above field capacity (i.e., 0.14 g/g soil water content corresponding to -0.33 bar matric potential; determined using the plate method). The 1 g/g above field capacity was used to compensate for the addition mass of the ferric hexacyanoferrate treatments. Plastic bags were draped over the pots after seeding until emergence to limit soil evaporation and maintain moist conditions for optimum germination. Once plants had emerged, the plastic bags were removed and pots were thinned to three healthy seedlings. Pots

were weighed daily and water applied to obtain a 15 g/g soil water content as needed to maintain the soil near field capacity conditions. Greenhouse was fumigated twice weekly to control pests and beneficial nematodes were applied to the soil via water on 16 March 2017 to control thrips larva.

Plant height, SPAD meter readings, visual nutrient deficiencies symptoms, pest damage, and vegetative state was determined once a week between 1300 and 1600 hrs standard time. At termination, the root dry biomass and soybean root nodule counts were performed on the belowground portions of the plant. The aboveground portions were analyzed for dry biomass, moisture content, prussic acid, crude protein, acid detergent fiber (ADF), lignin, neutral detergent fiber (NDF), total digestible nutrients (TDN), net energy for lactation (NE_L), net energy for growth (NE_G), net energy for maintenance (NE_M), and mineral contents of Ca, P, Mg, K, Na, Fe, Mn, Zn, and Cu in the stems and leaves. Wheat heads were harvested, heads per pot counted, moisture content, and grain mass determined.

At termination, soil was collected and analyzed for free cyanides, physiologically available cyanides, phospholipid fatty acids (PLFA), pH, electrical conductivity (EC), total N, acid extractable P, K, Zn, Ca, Mg, Na, S, Zu, Cu, Fe, percent base saturation as K, Ca, Mg, and Na, and total organic matter (OM).

The PLFA microbial community analysis included total biomass, 64 biochemical markers, and 12 fatty acids used to quantify total fungi, arbuscular mycrohizae, gram negative and gram positive bacteria, anaerobic bacteria, eukaryotes, actinomycetes, and the ratios of fungi/bacteria, predator/prey, gram positive/gram negative, saturated/unsaturated bacteria, mono/poly, and cyclopropane as a measure of stress on gram negative bacteria.

Findings

In our first column test for this study, with sulfate based salts (calcium, sodium, and magnesium sulfates) which are found in many of North Dakota's naturally saline soils, the salts formed a hard crust at the soil surface and did not allow salts to effloresce (i.e., grow) as anticipated. We had previously tested ferric hexacyanoferrate on sodium chloride brine contaminated soil and observed 30 – 60% of sodium sulfate salts to grow above the soil surface for harvesting. Therefore, we hypothesized that the lack of sulfate based salt growth is most likely due to the low solubility of these types of salts as compared to the very high solubility of sodium chloride. A low solubility salt will form a soil crust earlier than a high solubility salt. We also observed that salt growths (when they do occur for sodium chloride) are strongly related to the amount of salt in the soil water. Therefore, we then also inferred that it would be reasonable to expect this method to work most efficiently on highly saline soils and less efficiently on moderately saline soils. We then conducting more laboratory column studies to evaluate if other additives could be mixed with the ferric hexacyanoferrate to overcome the sulfate salt crusting issue that we had observed. A variety of additives known to increase the solubility of sulfate salts, thus expected to help prevent salt crusting and allowing harvestable salts to effloresce as desired, were evaluated. Unfortunately, such additives did not allow the ferric hexacyanoferrate to effloresce sulfate based salts. After investigating the physical chemistry of hexacyanoferrate in more detail, we conclude that the method is limited to sodium chloride. The physical size and geometry of hexacyanoferrate is practically identical to five clustered sodium chloride ions and has similar charged sizes with the exception of one. This charge mismatch on one side is what likely cause's sodium chloride salts

to effloresce as hopper crystals due to ion blocking (Bode et al., 2012). Therefore, we conclude that the method will not work on sulfate based salts even when their solubility is increased with other chemical additives.

In the greenhouse study, all plant tissue (aboveground and root) and grain parameters were significantly affected by either the main effect of ferric hexacyanoferrate loading rate or its interaction with crop type (Figures 1 and 2). The only exception was for plant root calcium concentrations. Prussic acid concentrations were below detection limits for all plants, indicating that degradation of hexacynoferrate to free prussic acid and subsequent uptake in plants did not occur. Soybean plants at the 1000 g m^{-2} loading rate were significantly slower in growth stages and plant height. However, these plants demonstrated little to no thrips damage while all other plants at lower loading rates showed notable damage. These results are somewhat surprising given hexacyanoferrate's low solubility in water, low and mediated uptake into plants, and slow degradation rate. Ferrocyanides have been considered as plant membrane impermeable, whereas free prussic acid may be taken up via diffusion (Ebbs et al., 2003; Federica and Giartosio, 1983). Plant roots may accumulate ferrocyanides (adsorbed to cell walls) with further byproducts possibly able to be transported from the roots to stems to leaves. However, the uptake has been reported to be transport mediated by transpiration, proteins, and H^+-coupled symporters (Yu et al., 2013; Larsen and Trapp, 2006; Ebbs et al., 2003).

In the greenhouse study, all soil microbial and chemical parameters were significantly affected by either the main effect of ferric hexacyanoferrate loading rate or its interaction with crop type, with exception of total fungi, eukaryotes, fungi/bacteria ratio, predator/prey ratio, monounsaturated/polyunsaturated fatty acid ratio, cation exchange capacity, and soil test Ca and Mg. Soil bacterial communities within the rhizosphere (i.e., gram negative) significantly decreased with loading rates with stress ratios (cyclopropanes vs. monounsaturated fatty acids) significantly increased for both crops. In general, the soil microbial communities appear to be more sensitive (i.e., affected at lower loading rates of ferric hexacyanoferrate) than the plants.

In summary, some effects were positive to the crop except for the highest loading rate in soybean. We conclude that low loading rates (0 to 200 g m^{-2}) does not substantially affect early stages of soybean and wheat growth, but higher rates may cause substantial losses in soybean.

The primary goal of this research was to modify our existing method, originally designed to remediate sodium chloride based brine spills, to also be effective as a means to ameliorate natural saline seeps and road-ditch salinity. Unfortunately, modification of our existing method was not successful and no clear path forward to make such a modification is apparent. Therefore, our salt harvesting method remains limited to sodium chloride dominated brine spills. For example, fracking water spills in northern and western North Dakota. However, this research still benefits ND soybean farmers by providing insights to the impacts the method will have on soybean and wheat grown on farmlands which have been contaminated via a brine spills and subsequently remediated with the existing method. In general, the application of ferric hexacyanoferrate at rates of 200 g m^{-2} (i.e., the recommended rates for remediating brine spill contaminated soils) does not appear to significantly affect soybean and wheat performance. However, the soil microbial community does appear to be somewhat affected at all rates of ferric hexacyanoferrate applications. Moreover, ferric hexacyanoferrate increased stress levels of rhizosphere bacteria. This could mean that soybeans may endure greater stress during drought periods. Since hexacyanoferrate has a substantially slow degradation rate (i.e., hundreds to thousands of years), these microbial stress levels may also persist for a similar period.

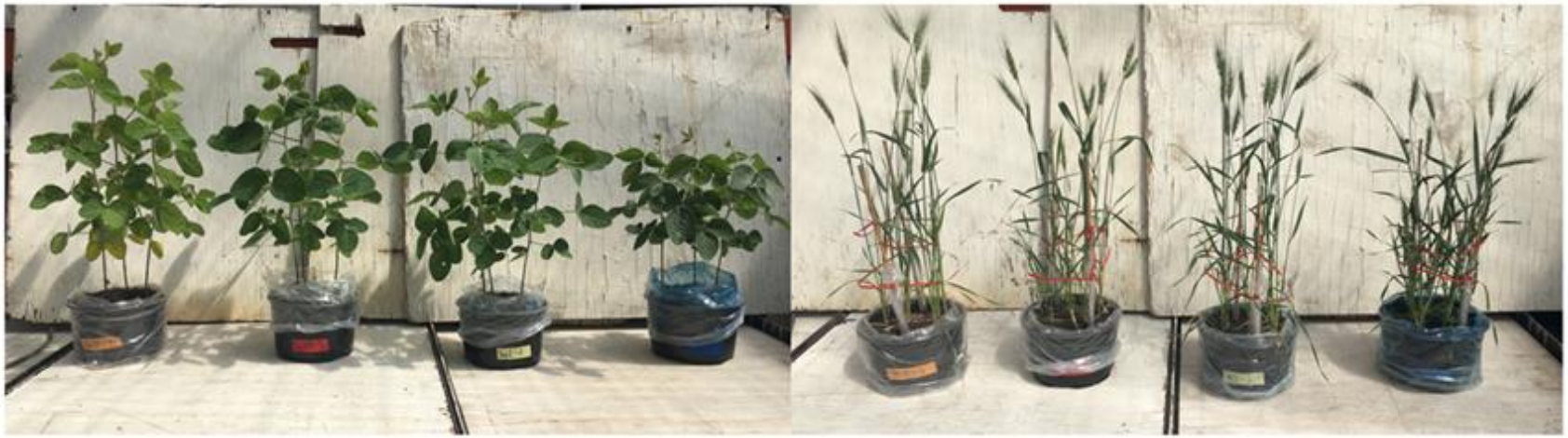

Figure 1. Soybean and wheat plants at termination. Loading rates of ferric hexacyanoferrate, from left to right, are 0, 100, 200, and 1000 g m^{-2}, respectively.

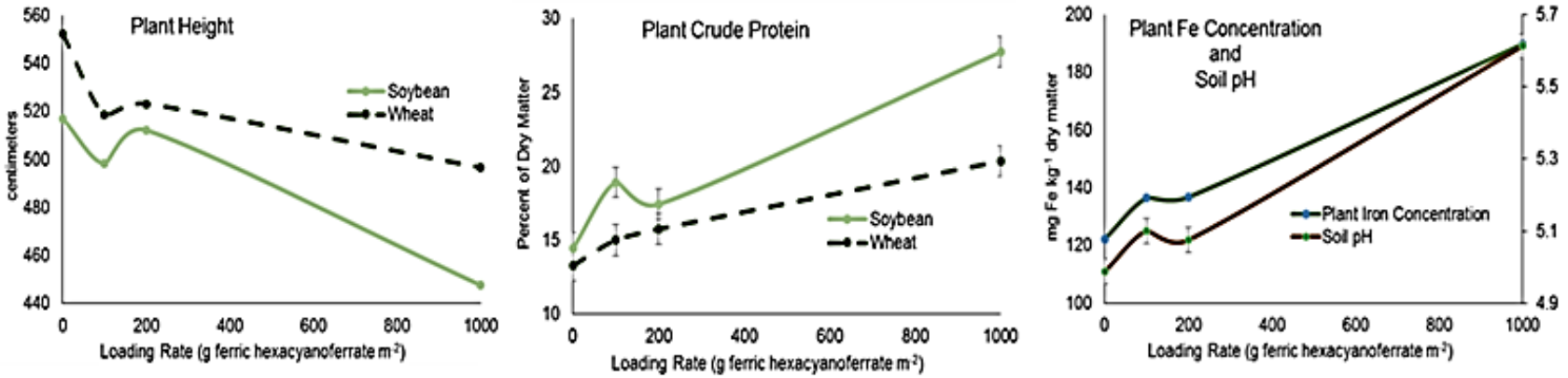

Figure 2. Examples of loading rate effects of ferric hexacyanoferrate on some plant parameters.