### Assessment of Minnesota's Soil Mineralogy and Impacts on Fertilizer Guidelines Daniel Kaiser Regents of the University of Minnesota Department of Soil, Water, and Climate Email: dekaiser@umn.edu Phone: 612-624-3482 Research Priority Area (select one): Production Stewardship Production Stewardship Option: Soil Fertility/Soil Health Projects Covered: 4159-19SP, 6035-20DD, 6053-21DD

#### **PROJECT SUMMARY**

#### Can soil clay species can be to provide more precise estimates of potassium (K) critical levels?

Analysis of data indicated that corn response to K may vary based on the relative distribution of smectite to illite of soil clays. Data could be separated into two clusters for soils with the smectite:illite ratio of the clay fraction above or below 2.8. For soils with relatively higher illite content (<2.8 ratio), maximum yield was achieved when the air-dried soil test K concentration was near 80 ppm. For soils relatively higher in smectite (>2.8 ratio), maximum yield was achieved when soil test K was closer to 180 ppm. The smectite:illite ratio follows closely to soil parent material and soil texture. The dividing line between soils above and below the 2.8 ratio falls closely with either silt loams or sandy soils (<2.8) and silty clay loam, loam, and clay loam soils.

#### Should cation exchange capacity (CEC) be considered in making K fertilizer guidelines?

Soil CEC is a proxy for soil texture. Soil CEC could be utilized in lieu of the smectite to illite ratio, but it would not provide any better determination of critical soil test K for most soils.

#### How does variable charge impacts K retention and release in low CEC soils?

The data showed little impact of increasing soil pH (by liming) of acidic soils on changes in soil CEC. Soil K retention was affected by liming with lower K retention for limed soils. The lower K retention was not a result in changes in CEC of the soil rather the addition of calcium in the liming source resulted in a displacement of K due to preferential adsorption of calcium on the soil CEC. When calcium was not applied sandy soils were quickly saturated with potassium indicating a low capacity for sandy soils to retain K and a higher likelihood of high rates of K being leached in sandy soils. If liming the soil can change pH the overall impact was low even on sandy soils where variable charge on the CEC should be more important.

### Can soil weathering increase K availability of soils with varying CEC?

Freeze-thaw cycling in soils had little impact on the amount of K that could be leached from sandy soils. Calcium and magnesium in irrigation water had a much greater impact on K leached in sands and the displacement of K by calcium and magnesium could make less available K more strongly held on the soil CEC more available for uptake by corn and could explain a lower relative response to K on irrigated sandy soils.

### **BACKGROUND AND GOALS**

Fertilizer research funding into fundamental soil cycling processes in states like Minnesota has been dominated by nitrogen and phosphorus project while potassium (K) has not been widely researched. Soil testing for K has long been a tool for assessing potential for deficiency in crop production. Analysis of dried soil has been long suggested for determining the availability of K in the soil for crops. Inconsistencies in the soil K test have been noted in Iowa leading to renewed suggestions for analysis of K on undried soil samples. Recent Iowa data has found a better prediction of soil K critical levels using moist soil samples. However, most soil labs are not equipped to handle high throughput analysis of moist soil samples. More recently, North Dakota modified K guidelines based on the ratio of illite/smectite in the soil. In other areas of the U.S. soil cation exchange capacity is utilized as a method to adjust K guidelines while most Midwest states provide one set of guidelines regardless of CEC. Lowering soil test K values and lack of data has resulted in more questions related to K management. Reliable fertilizer guidelines are needed to ensure fertilizer is not over- or under applied.

Minnesota is unique in the diversity of soil types and parent materials representing major growing regions across the state. Soils in Minnesota are represented by high yielding irrigated sandy soils with low cation exchange capacities, loess derived silt loam soils low in K, glacial till soils with varying levels of available K, and high clay lacustrine soils traditionally high in K. Recent unpublished data has shown that current K critical levels may vary based on soil chemical properties and K guidelines need to be more specific to ensure the right rate of K is applied. A basic understanding of clay species present and potential impacts on K nutrition of crops in Minnesota could go a long way for improving fertilizer guidelines. We also need to know whether cation exchange capacity (CEC) should be utilized to improve fertilizer K guidelines. While K application does not post a significant environmental risk research is needed to ensure K is not limiting which could impact the effective utilization of nutrients such as nitrogen which if not utilized by the crop can result in environmental problems.

Minnesota produces corn on roughly 500,000 irrigated acres each year. As previously mentioned, recent data has indicated that critical soil test K levels for corn are likely less on very sandy soils with low CEC. The current question is what break points should be used for CEC in order to be more site specific for K guidelines. Older research from Nebraska pointed to weathering of micas in silt factions in sandy soils may contribute K to crops reducing the need for K to be applied. In addition, a larger majority of the CEC on sandy soils comes from variable charge on organic matter which changes based on pH. Understanding the mineralogy of the sandy soils is important but also K weathering and pH impacts on K retention need to be studied to further our understanding of K dynamics on sandy soils. Low CEC soils can leach K thus over-application is wasteful resulting in reduced profitability and potentially increasing Cl content in groundwater as KCl is the primary source of K fertilizer.

The primary goal of this study is to gain a better understanding of how K cycling varies among soils across Minnesota and to develop a new set of K fertilizer guidelines for corn. Current research projects have been in place focused on corn response to K but funding has not been available to do a more detailed basic analysis of soils to look at mineralogy and K cycling. Soil test data is available comparing K soil test methods, but the current research has not brought

completely clarity to issues related to K availability in soils. A basic chemical and physical analysis of soils highlighting mineralogy would go a long way to our goal of understanding difference in soils and how that impacts K fertilizer guidelines.

# **Objectives and Timeline**

- 1. Determine whether soil clay species can be utilized to provide more precise estimates of K critical levels
- **2.** Determine if soils CEC capacity should be considered in making K fertilizer guidelines and how variable charge impacts K retention and release in low CEC soils.
- 3. Estimate soil K weathering capacity of soils with varying CEC.
- 4. Evaluate the impact of pH on K holding capacity of sandy soils with low CEC.

# MATERIALS AND METHODS

Study 1-Survey of clay species will be conducted across the state of Minnesota in fields where K research for corn or soybean has- or will be conducted. Soil samples archived from past K response trials will be utilized initially but new field studies will be established working with crop consultants either as strip trials where no K and a single non-limiting rate of K is applied or small plots will be established in fields where the K test is at or below the current critical level (160 mg kg<sup>-1</sup> extracted with 1M NH<sub>4</sub>OAC). Small plot trials will consist of four rates replicated four to six times. Soil samples (0-6") will be collected from each plot prior to treatment application, air dried, and analyzed using recommended procedures. Samples from the control (0K) plots will be split where part is kept in a field moist state to be analyzed for K concentration following procedures outlined by Gelderman and Mallarino (1998) for the North-central region, and the remaining soil will be air dried. All new data will be combined with past trial data into a large soil test correlation database which is being developed in Minnesota to provide producers with updated information on critical soil test levels, probabilities of crop response based on soil test classification.

A semi-quantitative analysis of soil clays will be conducted using the Rietveld method (Rietveld, 1969). The goal of this work is to determine if the K response database can be parsed out to better identify critical soil test K levels like work completed in North Dakota. Field sites will be located strategically to allow for mapping of differences in soil clay species across Minnesota. Additional fields and soil types may be sampled in production fields without research trials to provide additional information for constructing coverage maps for clay types. Soil CEC will also be evaluated for each site.

Study 2 was conducted in two phases. Phase I consisted of four differing soil types collected form fields where the water pH was 5.0 or less. Rates of limestone were added to the soil to increase the pH to various levels over a period of 12 to 24 months. Within each soil three soils were selected representing slightly acid, near neutral, and slightly basic pH levels. The three soils selected were then shaken with various concentrations of K to determine soil K sorption. An initial run included a background solution containing 0.01 *M* Ca while the second run contained only K in de-ionized water. Samples were shaken for 16 hours, centrifuged, then filtered into test

tubes to determine the amount of K in solution as a difference between the initial K concentration in solution and the final concentration measured by ICP.

Weathering studies will also be conducted on soils collected for the CEC work along with a few additional sites. Soil cores 1.5 inches in diameter were collected using PVC pipes to a depth of six inches. Multiple cores were taken from withing a 10' diameter area at each site, capped, and were stored in a cold room prior to use. An additional composite soil samples was collected from the around the cores, was dried, ground, and used for lab analysis. Two treatments were utilized for the study arranged in a factorial combination. Factor 1 was temperature regime. Sets of tubes were taken from the cooler and incubated for 1-week intervals either at room temperature (~72°F) while the other set was frozen at 0°F for approximately 14 days followed by 1 day to thaw prior to leaching at room temperature. Factor two consisted of leaching with de-ionized water and simulated irrigation water which contained 40 and 25 mg  $L^{-1}$  of Calcium (Ca as CaCl<sub>2</sub>) and Magnesium (Mg as MgSO<sub>4</sub>), respectively, which approximated the concentration of each element on average for well water samples collected from the Sand Plains Research Center at Becker, MN. To ensure adequate leaching a total of 200 mL of water was applied to each column in a single leaching event. Columns were allowed to drain to approximate field capacity then were either left to incubate at room temperature or were placed back in the freezer. A total of 3 leaching events were completed on each column and each treatment was replicated 3 times. Leachate volume was determined after each leaching event by weighing the flask containing the leachate and assuming a water mass of 1 g mL<sup>-1</sup>. Leachate samples were filtered as needed and were analyzed for total K concentration by ICP. For simplicity, the data in the report is the total amount of K leached over the three leaching cycles.

## **RESULTS AND DISCUSSION**

### Study 1: Field trial and K soil test correlation

A total of 21 farmer field and small plot trials (Table 1) were established to gather K response data to be combined with previously collected data. Field trials consisted of five rates of  $K_2O$  per acre, 0, 40, 80, 120, and 160 lbs. Farmer field trials were established using a Latin square design with five replications. Small plot trials ranged from four to six replicates. Fertilizer potassium was applied at potash (0-0-60). Fertilizer was applied using commercial equipment by establishing blocks in each field where the fertilizer treatment structure was superimposed within fertilizer prescription maps. As applied maps were checked following application to verify fertilizer was applied correctly. Yield data from farmer field trials was collected using combines equipped with calibrated yield monitors.

Soil samples were collected from each replicate as a composite of 10 cores collected to a depth of six inches. Farmer field samples were collected from 0 K plots in June. Soil samples were collected from small plot trials as a composite across each replication before treatment application. Soil samples were dried at air temperature and ground to pass through a 2 mm sieve prior to analysis. Soil was analyzed for extractable potassium by the ammonium acetate procedure (Warncke and Brown, 2011). Semiquantitative mineral identification and clay speciation was conducted using the Rietveld method (Rietveld, 1969). Soil samples for mineralogical analysis were collected from

the field trials outlined in Table 1 as well as additional non-trial locations located in areas of Minnesota to represent major landforms and soil associations.

Year	Location	Trial <sup>1</sup>	STK	Optimal K Rate <sup>2</sup>
			ppm	-lb K <sub>2</sub> O ac <sup>-1</sup> -
2019	Mentor	FF	104	40
2020	Sauk Centre	FF	140	40
	Sauk Centre	FF	118	66
	Morris	FF	161	nr
	Marshall	FF	160	nr
	Granite Falls	FF	185	nr
	Benson	FF	123	79
	Lamberton	FF	171	nr
	Le Sueur	SP	138	93
	Rosemount	SP	81	107
2021	New Ulm	FF	151	71
	New Ulm	FF	113	nr
	Lakefield	FF	162	nr
	Eyota	FF	152	nr
	Belgrade	FF	192	nr
	Belgrade	FF	215	61
	Grand Forks	FF	211	nr
	Rochester	SP	98	78
	Becker	SP	99	66
	Lamberton	SP	109	37
	Rosemount	SP	90	nr

Table 1. Summary of field K response trials established in Minnesota from 2019 to 2021.

<sup>1/</sup> FF, Farmer Field; SP, Small Plot.

<sup>2/</sup> nr, no response

The relative abundance of illite and smectite in soils is estimated across the state of Minnesota in Figure 1. Soils in the southern and western part of the state which are higher in clay tended to have relatively higher smectite concentrations which was expected. Illite abundance was greatest in the SE and the majority of north central Minnesota which corresponds to silt loam and sandy soils where crops historically have responded to K. Major inclusions higher in Illite in Central and Western MN were estimated around major rivers, the Minnesota river valley. Figure 2 summarizes the ratio of smectite:illite which was higher in Central and Western Minnesota and lower in the Southeastern and Central and Northcentral parts of the state.

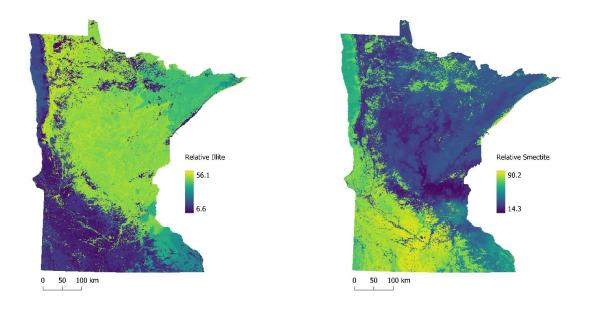


Figure 1. Semi-quantitative abundance of illite and smectite estimated for Minnesota soils.

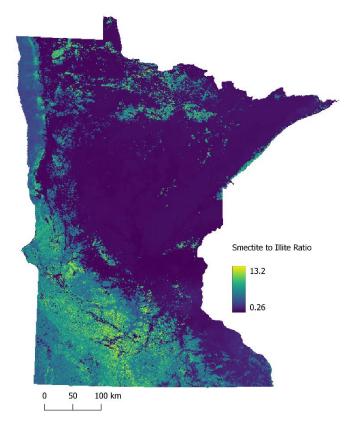


Figure 2. Ratio of smectite: illite for 0-6" soil sampling depth based on a semi-quantitative analysis.

Yield of individual treatments is not show for any of the trial locations given in Table 1. Table 1 contains the average soil test K (STK) and the rate of K that provided maximum yield at sites where a K response occurred. Corn grain yield was increased by K at 11 of the 21 locations. Corn grain yield responses occurred at sites ranging from 80 to 140 ppm with one exception, one site responded with a K test near 260 ppm. Corn grain yield was increased by 80-140 lb  $K_2O$  per acre.

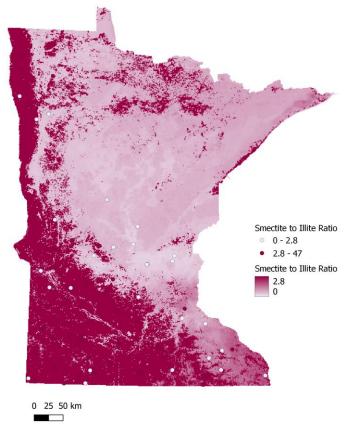


Figure 3. Minnesota state map of soils broken down by soils with smectite to Illite ratios greater or less than 2.8:1.

Analysis of the larger data set indicated that a difference in critical soil test K existed between soils that varied in the ratio of smectite to illite. The split between the data was found at a ratio of 2.8:1 which is different from the ratio currently suggested for use in North Dakota, 3.5:1. Figure 3 was generated using data from Figure 2 indicating where the ratio of smecite to illite was greater than (reddish areas) or less than (pink areas) 2.8:1. The areas of the state greater or less than the 2.8 ratio tend to split out based on soils with higher levels of silt and sand versus soils higher in clay (loam soils to soils with finer textures). While the 2.8 ratio could be used if the data splits based on soil texture it would be an easier concept for the fertilizer guidelines to utilize texture. I have had several questions from growers and consultants regarding the need for them to analyze soils in their fields for the semi-quantitative clay analysis. The data generated by this project should be sufficient and they should not need to analyze soils themselves.

Current trial data was combined with past research to form a database of K response (not shown). The ratio of smectite:illite was calculated for each location along with corn grain yield

response. Figure 4 summarizing corn grain yield response for soils with a smectite:illite ratio of above or below 2.8:1 for both the field moist and air-dried ammonium acetate K extraction. Overall, there was only a very small difference in where corn relative grain yield achieved maximum in both cases. The critical K concentration was determined after fitting a quadratic plateau curve and is defined as the soil test value where 95% of maximum yield was achieved. For soils with a smectite:illite ratio below 2.8, the critical soil K test was 64 ppm (or mg kg<sup>-1</sup>) for air-dry K samples and 51 ppm for field moist. For ratios 2.8 or above the critical soil test K concentration was 108 ppm for air-dry soil and 77 for field moist soil. The soil test value where 100% maximum yield was achieved along with the confidence interval is listed in the test within each figure. I typically have been utilizing the value at 95% and 100% relative yield as the range defining the medium-high categories.

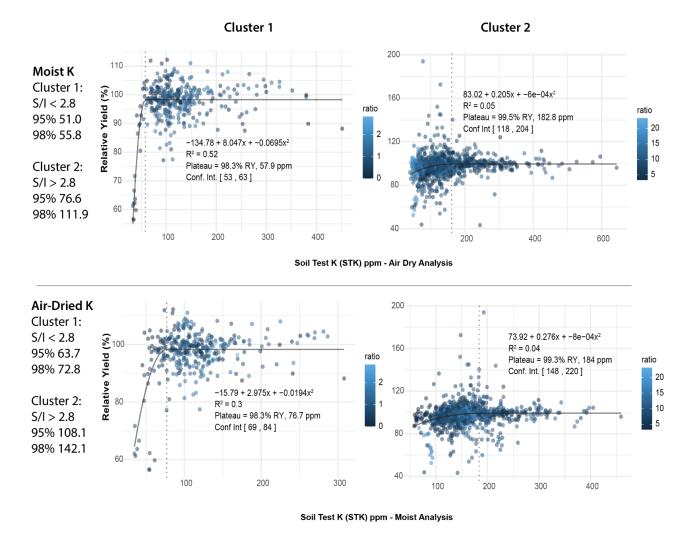


Figure 4. Critical K curves for the moist and air-dried soil analysis clustered by a mineralogy feature, the smectite to illite ratio (S/I). Cluster 1 consists of soils with a S/I > 2.8 and cluster 2 consists of soils with a S/I < 2.8.

The potassium data is more variable than data collected from phosphorus and the models chosen to fit the curves also will vary where the critical levels fall. For example, the moist K results for cluster one contains two sets of points below the 90% relative yield level, but the line fits the lower range of points. While model fitting does help define critical levels the variability of the data can necessitate some re-interpretation of the data. Table 2 contains the proposed ranges for the two areas of the state defined in Figure 3 based on the information collected in this study. Soils with more Illite seem to require a lower critical level which is in-line with the old guidelines. These areas consist of both silt loam and sandy soils.

Table 2. Proposed soil test K classifications based on the ratio of smectite:illite in the soil clay fraction.

Ratio	Very Low	Low	Medium	High	Very High
<2.8:1	0-40	40-80	80-120	120-160	160+
>2.8:1	0-50	50-100	100-150	150-200	200+

The data provided may indicate a lower critical level for soils with a greater abundance of illite. Anecdotally, many field trial locations in the Southeastern part of Minnesota and for irrigated sandy soils have not shown a strong response to K even for Low or Very Low K testing soils. A lower critical level may explain some of the differences that have been observed. It is unclear whether any differences would exist between silt loam versus sandy soils which comprise the bulk of the higher illite soils. This data provides a basis for revision of the corn K guidelines for Minnesota. I still do question whether the ranges need to be lower for sandy soils. Potentially, the Medium class for sands could be 90-120 ppm based on past data but the question I have yet to answer is how different sands are in relation to K retention. The dataset I have developed does not contain enough sandy textured (loamy sands or sandy loams) with responses to K to identify whether a lower critical K concentration is needed. Further research will be required.

The use of the ratio of smectite:illite for K fertilizer guidelines currently is unique to North Dakota. Iowa has modified corn and soybean K fertilizer guidelines, but the Iowa research suggests that the analysis of K on field moist samples is superior to air dried samples. The bulk of the data from Iowa is from higher clay soils likely higher in smectite. While soils in Southeast Minnesota are similar to Northeast Iowa, I don't believe there is much research focused specifically on the Northeast Iowa site loams. All the moist K analysis from Minnesota is combined in Figure 4. A curve was not fit to the data in Figure 4 but I have fit data to the full dataset in the past and the 100% relative yield level typically has fallen around 160 ppm and the coefficient of correlation has typically been better for the field moist test indicating less variation in the data. One other item of note on the field most test is typically the soil higher in Illite have had the tendency to extract greater amounts of K on field moist samples compared to the higher smectite soils that tend to extract more K after drying the soil. It is likely that Minnesota will have some set of guidelines for the field moist test in the future but the adoption by labs likely will be poor due to greater work involved in analysis of field moist soils.

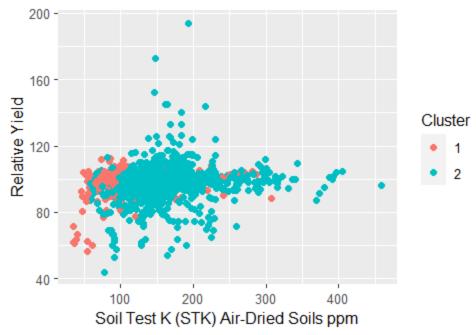


Figure 5. Corn grain yield response to K fertilizer based on soil test K extracted on field moist samples combined for all soils across all smectite:illite ratios.

One item of note is that the analysis of the clay types also contained some analysis of K bearing feldspars which trended higher in soils higher in Illite. The K feldspars also could supply K to crops though weathering. I do not have maps made for this final report, but they will be available online when the final data are available for the clay speciation work. The figures provided in this report do not contain the final dataset submitted to ACT labs in Canada. We submitted additional samples to try to better define soils around the Red River Valley as well as a few gaps in the data from Central MN. My plan is put the final maps online on the nutrient management extension webpage. (https://extension.umn.edu/crop-production#nutrient-management). We also will look at how zip or area code correlate to the clay ratio which could be used by labs to delineate which set of guidelines to use.

## Effect of CEC on guidelines

We have limited data on the CEC at some of the research sites used for some of the historical data. The CEC of the soil should track closely with total clay content and the relative abundance of the clays present. Soils higher in smectite clays will have higher CEC values that those higher in Kaolinite which has little to no layer charge versus illite which is somewhere in-between. Different smectite species can also vary in their CEC values. The procedure used for the determination of the clay species does not allow us to fully quantify exactly what various species of specific clays are present. In theory, CEC could be used for K fertilizer guidelines, but it would be a proxy for the data presented in Figure 3 as there should be a direct linkage between clay and CEC. Soil CEC had significant correlation with clay (r = 0.72), smectite (r = 0.68), and the smectite to illite ratio [r = 0.54 (Figure 6)]. Soil CEC was positively correlated to the relative abundance ratio with higher CEC with more smectite (Figure 7). While CEC could be utilized to

divide soils, it would not provide any further differences in the interpretation provided in Figure 3. The interpretation of the results would be the same.

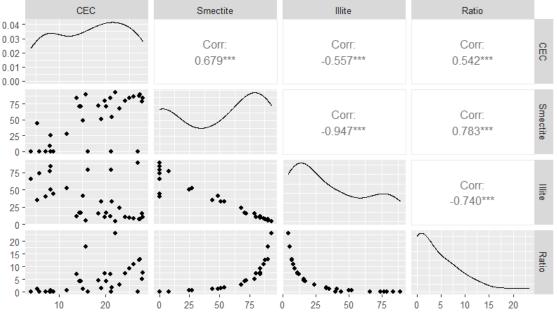


Figure 6. summary of relative abundance factors with soil CEC.

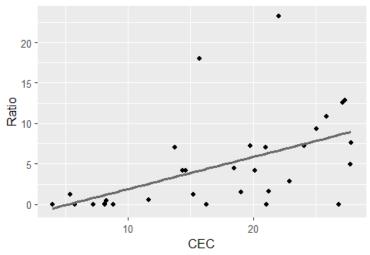


Figure 7. Relationship between soil CEC and the soil smectite:illtie ratio

# Implications to Corn Growers

The primary benefit to corn growers for this work is greater precision to the fertilizer guidelines. When the guidelines were modified increasing the ranges for the K soil test classifications it was done so with data primarily from central and western Minnesota. One item that I did not include in the last update to the fertilizer guidelines were suggestions for K fertilizer application for removal-based guidelines. Based on the information we have in this study building soils to 200 ppm should be targeted to higher smectite soils that will tend to retain K better. The second part

of this study will focus on K retention in soils. If soils will not retain high concentrations of K then building those soils may be impossible. Based on the higher illite soils it is likely that these soils should not be built to more than about 160 ppm. The only question not addressed is sandy soils. Based on past research on loamy sands it is difficult to build these soils to more than 120-130 ppm. Since fertilizer application at soil test levels greater than the critical level (100%) will not increase yield the primary benefit to a refined set of K fertilizer guidelines is cost savings on fertilizer that can be invested into other inputs that may have a greater impact on yield.

One item that could not be address with this project is a recalibration of suggested fertilizer application rates. There was not sufficient data in the field trials that could be utilized to determine whether the suggested application rates in the current corn fertilizer guidelines need to be modified. I will continue to work on recalibration. I currently have a funded trial through AFREC which multiple rates of K applied to corn. If I can get sufficient response data, we should be able to look at the current guidelines. We attempted to target fields where a response was more likely but the issue with K is that the K soil test is not consistent over time. Comparing different sampling timings was not a part of this work but past work has shown significant changes between fall and spring K soil test values. Other research conducted in the past 10 years has compared timing where that component was not needed for this project.

# **STUDY 2 – LAB RESEARCH**

Past research has shown that the amount of K needed on sandy soils has been less than what is current suggested for corn production. The lab research covers basic aspects of K retention in sands. A technical summary of the data will be provided followed by a summary at the end of implications of the lab work for K management in sands. There are two aspects we are looking at for the lab study. The first was the impact that soil pH may have on the cation exchange capacity (CEC) in sandy soils and how this might impact K adsorption. The second portion of this work was to study the potential for K to leach or move using in-tact soil columns. This work was not designed to determine optimal rates and timing of K application on sands.

## CEC, pH and K Adsorption

Soil pH did not significantly impact CEC levels or change CEC levels. There was no evidence that a variable charge was added or lost from soils with the pH change, and visually there was no clear relationship between pH and CEC. In general, the CEC was much higher at Lamberton in comparison to the three other sites (Table 3). Becker was the site closest to significant relationship between CEC and pH (P = 0.09), with a slight increase in CEC with increasing pH level (Figure 8). However, no site exhibited a significant relationship between CEC and pH.

Site	CEC	pН	K (mg kg <sup>-1</sup> )	<b>OM (%)</b>	Texture
Becker	6.14	5.96	93	1.8	Sandy Loam
	[3.15, 8.43]	[4.4, 7.2]	[66, 144]		
Big Stone	8.35	6.0	170	1.7	Sandy ClayL
	[5.27, 10.09]	[4.5, 7.2]	[142, 200]		
Cambridge	4.53	6.26	58	1.3	Sandy Loam
	[3.36, 5.73]	[4.2, 7.4]	[50, 67]		
Lamberton	24.87	5.24	175	4.7	Clay Loam
	[22.99, 28.86]	[4.3, 6.9]	[144, 214]		-

Table 3. The cation exchange capacity (CEC), pH, and soil texture for soils that were limed to create a range of pH levels.

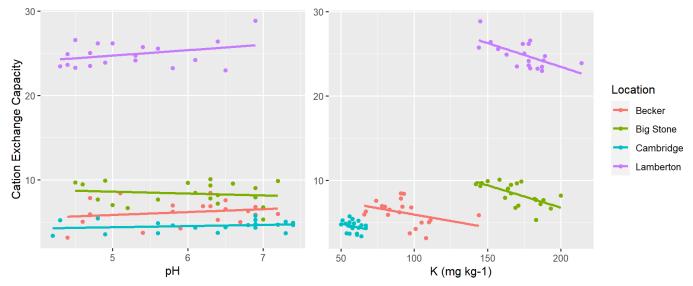


Figure 8. The relationship between cation exchange capacity (CEC) and pH (left) and K concentration (right) for four sites across a range of pH values.

Site		Slope Values	
Site	CEC ~ pH	K (mg kg <sup>-1</sup> ) ~ pH	K (mg kg <sup>-1</sup> ) ~ CEC
Becker	0.34*	-2.56	-4.68
Big Stone	-0.22	1.23	-7.86*
Cambridge	0.14	-0.68	-2.08
Lamberton	0.64	-6.76	-6.99*

Table 4. Linear relationship slopes between CEC, pH, and K concentrations.

\* Indicates significance where  $p \le 0.05$ 

There were no significant relationships between K concentrations and pH levels at any of the four sites (Table 4). However, at both Big Stone and Lamberton there were significant relationships between K concentrations and CEC (P = 0.002 and P = 0.004 respectively). Soil CEC had an inverse relationship with K concentrations, with soil K concentrations decreasing as CEC increased. This was a logical relationship, as with more negative sites available in the soil

complex (higher CEC) one would expect to see less  $K^+$  ions in solution. Rather these  $K^+$  ions would be bound to the soil complex rather than in the soil solution. Becker and Cambridge visually exhibited similar trends, but the relationships were not significant. The difference in significance may have been due to the underlying soil properties like soil texture. Becker and Cambridge are both sandy loams (Table 3). In contrast, Big Stone is a sandy clay loam and Lamberton is a clay loam. The clay presence in these soils likely led to the greater CEC levels at the two sites and potentially influenced the relationship between CEC and K concentration.

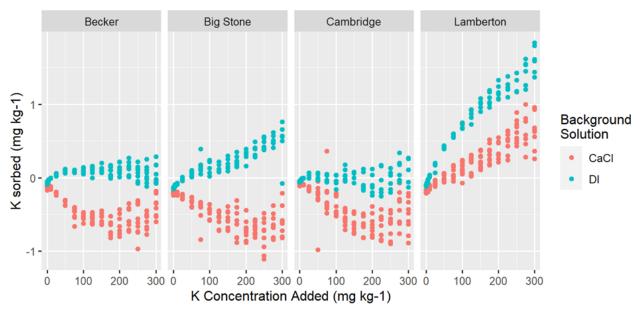


Figure 9. K sorption across 16 K concentrations in a background solution of Calcium Chloride (CaCl<sub>2</sub>) or Deionized water (DI) for soils from four locations.

Sorption isotherms were fitted for the soils from the four locations by measuring the amount of K absorbed across 15 K concentrations from 0 to 300 mg K kg<sup>-1</sup>. Two background solutions with the 16 K concentrations were used: 0.01 M Calcium Chloride (CaCl<sub>2</sub>) and deionized water (DI). There was a dramatic difference in K sorption between the two background solutions with the DI allowing for a significantly greater amount K sorption in comparison to the CaCl<sub>2</sub> solution (P < 0.001) (Figure 9). The CaCl<sub>2</sub> solutions led to the release of K, rather than sorption of K<sup>+</sup> ions, at three sites most likely due to the Ca<sup>2+</sup> ions replacing the K<sup>+</sup> ions on the soil's negative sites. Only soils from Lamberton with a highest CEC (Table 3) absorbed K with a background solution of CaCl<sub>2</sub>. Soils from Lamberton and Big Stone, where the soil is a clay loam and sandy clay loam respectively, sorption with a DI background solution continued to increase with increasing K concentrations. At the other two sites with sandy loam texture, Becker and Cambridge, the soils had little capacity to sorb additional K.

### Influence of pH on sorption

For each location, three pH levels (low, medium, and high) were evaluated for the influence of pH on sorption. The pH levels were created by liming low soils to medium and high levels. The range of pH values between low to high was greatest at Big Stone and smallest at Lamberton (Table 5).

Site		pH levels		
	Low	Medium	High	Range
Becker	4.4	5.9	6.7	2.3
Big Stone	4.8	6.3	6.9	3.0
Cambridge	4.2	6.1	7.2	2.1
Lamberton	4.3	4.9	6.1	1.8

Table 5. Soil pH values for soils limed to 3 levels (low, medium, and high) for soils from four locations.

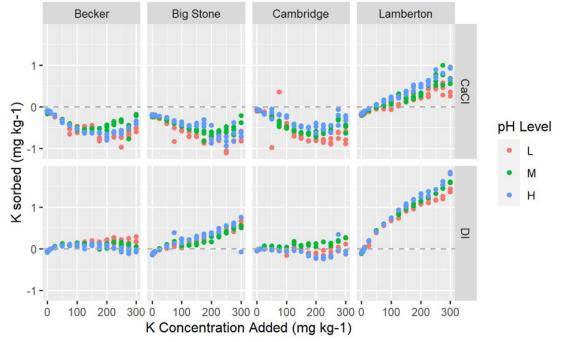


Figure 10. K sorption across 16 K Concentrations for four sites with three pH levels: Low (L), Medium (M), and High (H).

There was evidence of significant influences from pH on K sorption when the background solution was CaCl<sub>2</sub> with all sites pooled in an ANOVA (P < 0.001). Site was also a significant factor (P < 0.001), but there was no significant interaction between site and pH level. When looking at sorption considering only the DI background solution, pH level was not significant (P = 0.812) and Site was the significant factor influencing sorption (P < 0.001). Evaluating each site individually, there was significant differences between pH levels at all locations when CaCl<sub>2</sub> was the background solution (Table 6). Only Becker had significantly different sorption between pH levels when DI was used as the background solution.

	De als ansered -				
Site	Background - Solution -	Low	Medium	High	P value
	Solution				
Becker	CaCl <sub>2</sub>	-0.467b	-0.355a	-0.414ab	0.0472*
Big Stone	CaCl <sub>2</sub>	-0.556b	-0.416a	-0.426a	0.00453**
Cambridge	CaCl <sub>2</sub>	-0.473b	-0.383ab	-0.283a	0.00207**
Lamberton	CaCl <sub>2</sub>	0.087b	0.189ab	0.273a	0.0133 *
Becker	DI	0.099a	0.047b	0.017b	1.13e-06 ***
Big Stone	DI	0.153a	0.146a	0.197a	0.629
Cambridge	DI	-0.033b	0.075a	-0.066b	0.0632
Lamberton	DI	0.640a	0.718a	0.773a	0.653

Table 6. Differences in sorption within sites between 3 pH levels determined by a least significant difference (LSD) mean separation test.

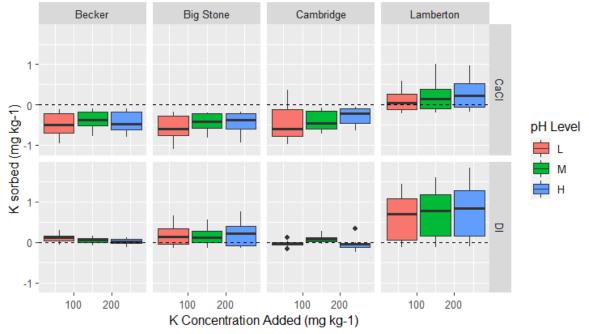


Figure 11. Visual of the trend differences in sorption between 3 pH levels within sites with sorption tests run with two background solutions: 0.01M Calcium Chloride (CaCl<sub>2</sub>) and deionized water (DI).

### **Individual Sites**

At the three sand sites (Becker, Big Stone, and Cambridge), it was evident that the two background solutions resulted in nearly inverse results: the DI solution led to sorption (though it was not a great amount of k sorbed) and the CaCl<sub>2</sub> led to K release. At Lamberton, a clay loam soil, K was sorbed with the CaCl<sub>2</sub> solution but in lesser amounts compared to the DI background solution.

At Becker, the sorption plateau point lowered as the pH level raised, meaning that as pH increased the soil had less capacity to sorb K (in DI solution, Figure 11). K release under the CaCl solution increased as K concentration added to the soil increased, until the K concentration exceeded 127-218 ppm. At these greater K concentrations, the soil released less K. The oversaturation of K in the soil solution may have allowed the K<sup>+</sup> ions to compete with the Ca<sup>2+</sup> ions for soil exchange sites simply due to quantity. A similar trend was observed at the other two sandy soil sites, but it was not as clear across all the pH levels. The M pH level at Big Stone and M pH level at Cambridge exhibited the trend most clearly.

Lamberton, the clay loam, did not reach a plateau point under either background solution (CaCl or DI). The soil had a great capacity for sorbing K ions with the H pH level having the greatest sorption followed by the M and L pH levels respectively. The high CEC levels at Lamberton likely allowed for this soil to sorb K ions at luxury. The lower sorption at the lower pH levels was logical, as you would expect to see a decrease in the net negative charge and an increase in the net positive charge with pH decrease.

### **Other Considerations**

Considering that the soils were limed to achieve a range in pH levels, it is possible that when liming Ca could have already begun to crowd exchange sites in the soil and created a less optimal situation for soil sorption of K. The liming could have also played a role in the lower sorption of K even with the DI water solution in the sandy soils. These facts are evident in the data summarized in Figures 12 to 14 which show K retention for soils based on soil pH values for the three pH values identified as low (L), medium (M), or high (H) and are listed in Table 3. The addition of Ca in the M and H treatments had a greater impact on K adsorption by for the sandy soils but also impacted the other two locations. While we did not look at the K base saturation values of the soils in this study, the impact of Ca on K retention by soils would have some implications on K guidelines based on K base saturation. Some claim that the optimal saturation of K on the CEC should be 2% for all soils to achieve optimal yield and that the extractable K soil test does not predict crop response to K. Other data that I have collected in Minnesota has shown no linkage between K base saturation and the response of any crop to K fertilizer application, which is also supported by other research in the Midwestern U.S.

Extremely high rates of K are typically suggested to change the K base saturation well in excess of the needs of corn. The data we collected would suggest that soils that if these soils are limed the excess Ca and Mg in the limestone would displace some of the K resulting in a lowering of the K base saturation. In effect, it would be very difficult to maintain a specific K base saturation over time, especially on medium to fine textured soils. It may be possible to achieve an optimal K base saturation on sands, but they are also more susceptible to change when Ca or Mg are applied. Based on all the data collected growers should be more concerned about the K soil test from routine tests and critical soil test levels for specific soils compared to the K base saturation.

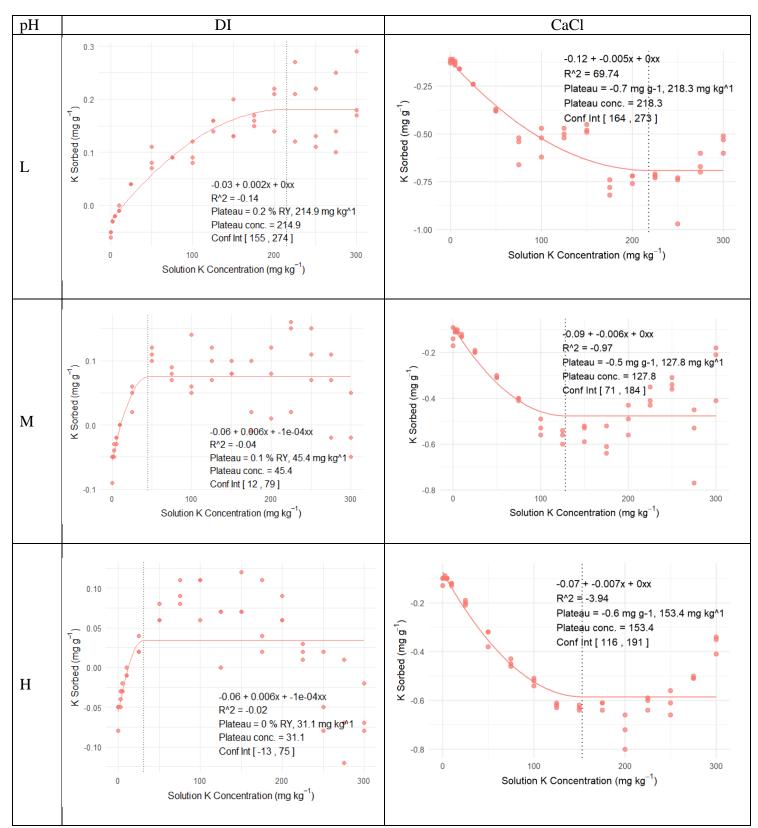


Figure 12. Potassium absorbed by a sandy loam soil collected at Becker for a low, medium, and high soil ph.

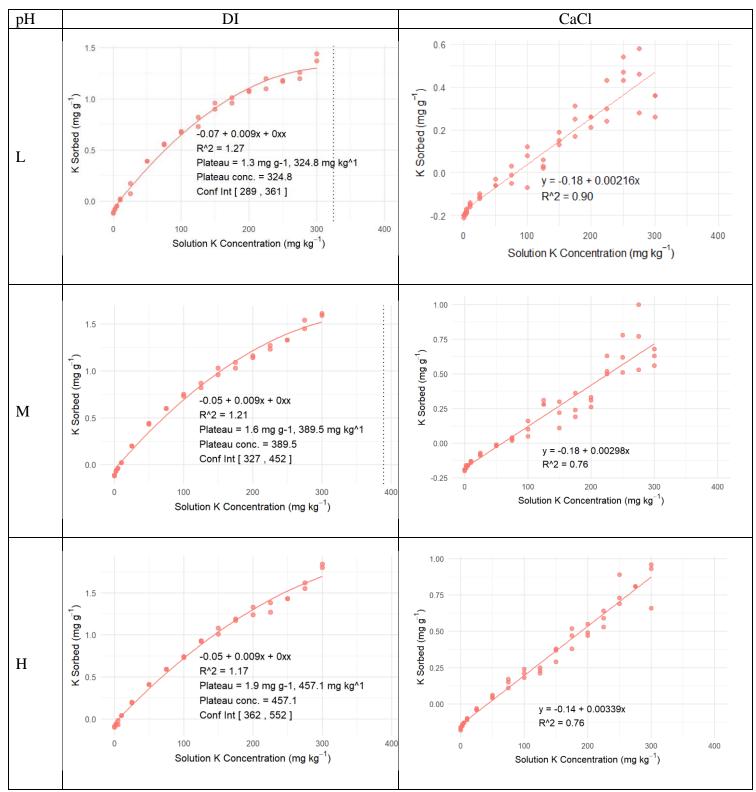


Figure 13. Potassium absorbed by a clay loam soil collected at Lamberton for a low, medium, and high soil ph.

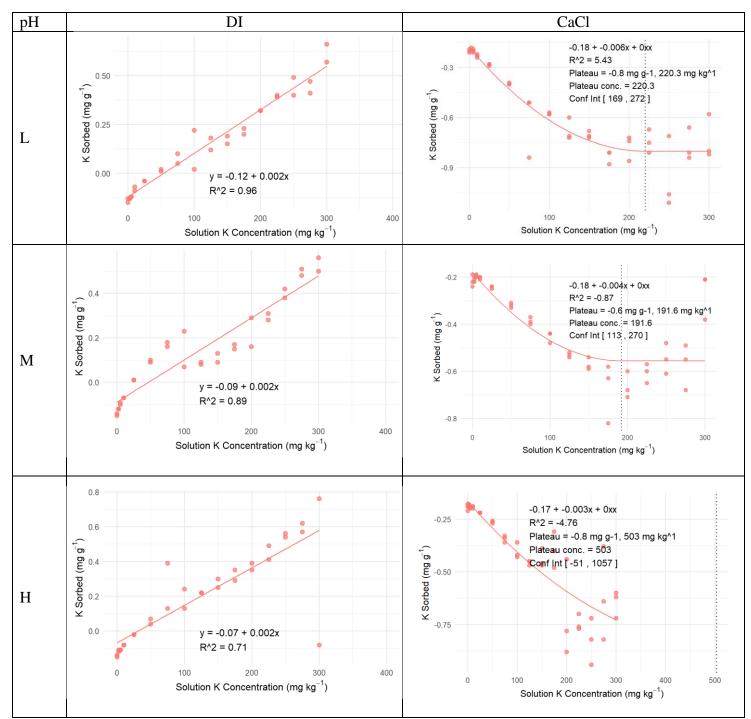


Figure 14 Potassium absorbed by a sandy clay loam soil collected from Big Stone County for a low, medium, and high soil ph.

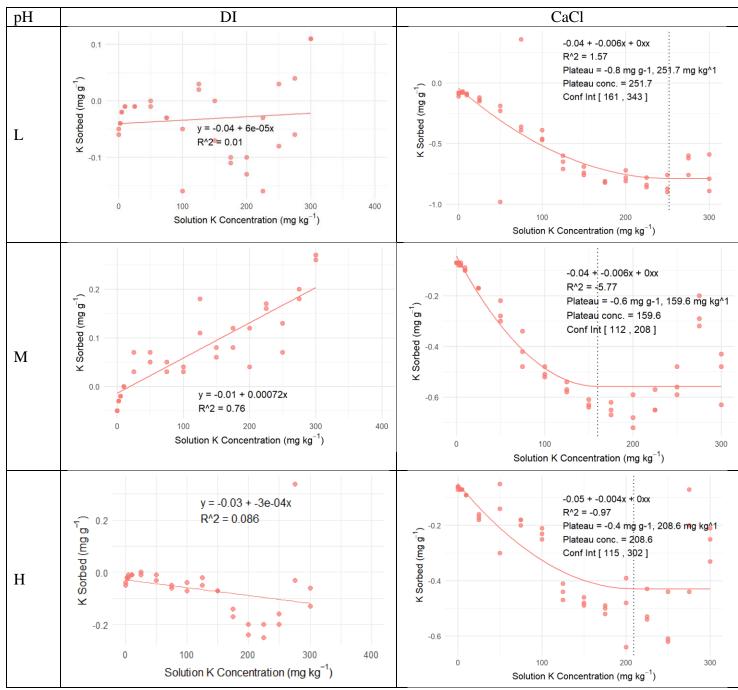


Figure 15. Potassium absorbed by a sandy loam soil collected near Cambridge for a low, medium, and high soil ph.

### Leaching of K from In-tact Soil Columns/Weathering Data

Site	OM	pН	Exch K	Clay	Silt	Sand	- Texture		tive Mi bundaı	
Site	%		mg kg <sup>-1</sup>		···· % 		- Texture -	Smectite	Illite	Kaolinite
Becker	2.0	7.1	121.6	12.5	2.5	85.0	L Sand <sup>a</sup>	0	44	28
Big Stone	1.7	5.2	194.0	12.5	5.0	82.5	Sandy L	0	84	11
Cambridge	1.3	4.9	58.3	7.5	7.5	85.0	L Sand	0	66	17
Crookston	3.5	7.9	171.2	25.0	40.0	35.0	Clay L	72	16	7
Hastings	1.6	5.5	118.6	7.5	10.0	82.5	L Sand	0	74	13
Mentor	1.7	7.2	79.3	7.5	5.0	87.5	L Sand	8	77	9
Rosemount	2.9	5.2	244.6	20.0	47.5	32.5	Clay L	71	17	7
Westport	8.4	5.6	383.0	22.5	27.5	50.0	Clay L	0	89	7

Table 7. Soil properties for eight sites in Minnesota tested for their potential for K weathering.

<sup>a</sup> Indicates a Loamy or Loam soil type

The in-tact soil columns were utilized to determine if freeze-thaw cycles will release potassium from soils. Soil columns six inches in depth were collected from eight locations across the state of Minnesota (Table 7). There were no specific factors that impacted where samples were collected other than representing multiple areas where irrigation is common except for the Rosemount sample which was to compare a medium textured soil. High clay soils were not included as we have had difficulty leaching these soils using the in-tact soil columns in the past. The number of tubes ran required the analysis to be run in different batches such that not all samples were run at the same time. Running the samples at separate times did not appear to impact the results. The volume of water used for leaching was not calibrated to any specific factor related to the soil rather we used a volume that we knew would ensure enough leachate would be available for analysis.

	Water	Source	Temperature		
Site	DI Water Irrigation Water		Freeze/Thaw	Room Temperature	
		ug K leach			
Becker	16.2b	25.7a	23.1	18.7	
Big Stone	32.3	44.7	44.5	32.5	
Cambridge	10.7b	18.2a	14.8	14.1	
Crookston	19.0a	10.8b	13.0	16.7	
Hastings	19.2b	42.9a	36.8a	25.2b	
Mentor	11.0b	22.2a	14.5	18.7	
Rosemount	14.0b	27.2a	24.2a	17.0b	
Westport	11.1b	31.1a	14.7	27.5	

Table 8. Summary of main treatment effects of water source and temperature regime used to treat in-tact soil columns. Data summarized is the amount of K leached when 200 mL of water was applied summed over three separate leaching events.

1 ug K per g of soil ~ 2 lb K per acre

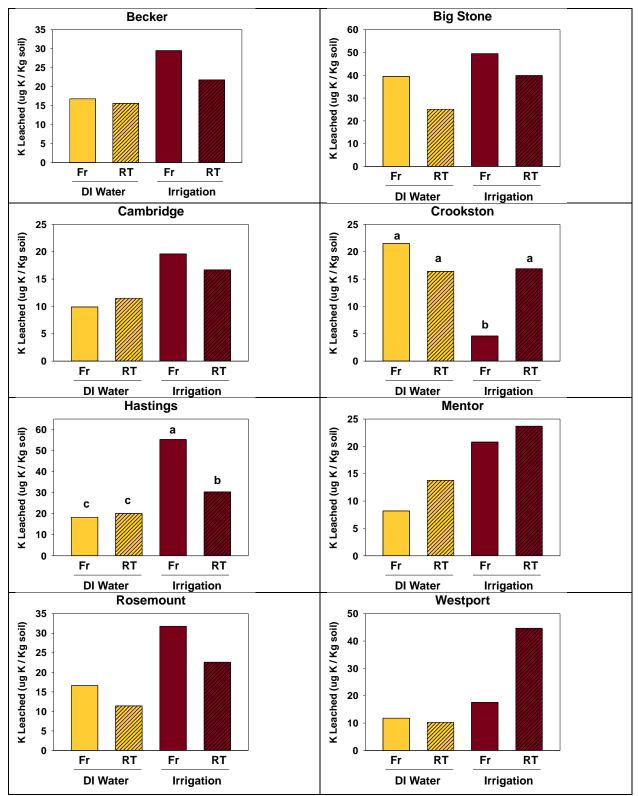


Figure 16. Summary of main treatment interactions of water source and temperature regime used for the K leaching trial on soils collected from eight Minnesota locations.

The design of the experiment allowed for a factorial combination of water source (de-ionized or simulated irrigation water) and temperature. The summary of main effects is given in Table 8 while a summary of the source by temperature interaction is given in Figure 16. Small letters denote significance between or among treatments only when the main effect or main effect interaction was significant. Water source almost always impacted the amount of K leached from the in-tact soil columns with more K leached almost always when the simulated irrigation water was applied. The exceptions were at Crookston where more K was leached with DI water and the soil collected from Big Stone County were water source did not differ. The freeze/thaw cycling only increased the amount of K leached at two of the eight locations. There was no statistical difference at the remaining six locations.

There were only two instances where there was a main effect interaction. At Crookston, the irrigation water treatment under the freeze/thaw temperature cycling resulted in less K leached than the remaining three treatments. The opposite was true at Hastings where the freeze/thaw cycling leached with irrigation water resulted in the greatest amount of K leached followed by the room temperature treatment leached with irrigation water and finally both DI water treatments resulted in the same amount of K leached regardless of the temperature regime. There was no general consistency for the freeze/thaw cycling to lead to more K leached across the soils. This would indicate that it is not likely that K released during freeze/thaw cycles would greatly impact or reduce the need for K fertilizer to be applied on the soils studied. The impact of irrigation water would have a greater impact on K retention which will be discussed more in the next section.

### Implications to Corn Growers

While the data generated for this part of the study is basic there are some implications for K management for corn growers on irrigated sandy soils. The first part of this work was to determine the impact that pH would have on variable charge for the CEC. Clays in soil have what is called a structural charge that is fixed and does not change over time. However, there is some CEC present on soil organic matter and iron oxides in soil which can vary based on pH. The CEC resulting from variable charge from soil organic matter will increase with increasing soil pH. Generally, soil pH is low on sandy soils in Minnesota due to these soils having low buffering capacity and low soil pH maintained for potato grow in the rotation. While it would be expected that changes in pH could impact CEC on sandy soils, the data from this study does not indicated much of an impact of pH on variable CEC charge. This could be because the soils used were generally low in organic matter.

The primary result after increasing pH in the two sandy soils was less K adsorbed which is likely a result of the addition of Ca from the lime treatments. One key point to remember is that not all cations are equal when it comes to how they are adsorbed to the CEC. The Lyotropic series identifies the potential adsorption of cations to the CEC based on the valence (number of positive charges for a specific ion) and the hydrated radius of the ion. The Lyotropic series starts from cations with a greater adsorption strength where  $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > Li^+$ . According to the Lyotropic series Ca has a higher binding strength than K and would displace K easier on the CEC. The data collected supports the higher binding strength of Ca considering the relative amount of K desorbed from the CEC in the sorption work and the lower amount of K

adsorbed at higher pH. The addition of Ca, and possibly Mg, in the simulated irrigation water also flushed out more K from the in-tact soil columns due to Ca and Mg replacing K on the CEC putting more K into solution. If K is being held tightly on the CEC the addition of Ca and Mg through the year in irrigation events might provide a source of available K that the plant may not have had access to in a dryland or rain-fed situation which may reduce the need for K fertilizer to be applied. This theory cannot be fully tested but it is more plausible than changes in variable CEC charge impacted K need for corn.

One additional important result from this work is the lack of K adsorption on the two soils with the greatest sand contents, the Becker and Cambridge soils. In both cases the soils saturated with K at relatively low application levels unlike the Lamberton and Big Stone soils that tended to sorb K as concentrations of K increased in solution. The lack of K adsorption for the sandy soils shows the greater potential for leaching of K in these soils where high rate of applied K is more likely to leach and not be retained near the soil surface. Past research has demonstrated that subsoil K is easier to increase in sandy soils. An AFREC funded study at Becker showed increases in soil test K down to the maximum sampling depth of the study at two feet. While the K is being retained at deeper depths, we do not know how much K is taken up at deeper depths in the soil profile. Fine root hairs which typically take up the bulk of crop nutrients proliferate near the soil surface so while we cannot say that sub-soil K is not taken up it may not be taken up in high quantities. Other research funded previously by the Minnesota Corn growers has shown smaller annual rates of K applied ahead of crops can result in corn grain yields of 250 bushels per acre or more. While it is not known whether the K critical level is lower on sands, the likelihood sandy soils will retain K is lower on loamy sands or sandy loams and more fertilizer is being applied compared to what is needed to maximize yield if current guidelines are used. The lack of retention in general though should indicated that it may not be possible to achieve a soil test K value similar to what can be achieved is silt- or clay loam soils so targeting soil test K concentrations in the medium to high categories is not feasible on irrigated corn acres.

One point that we did not focus on were cation ratios in the soil. With the addition of Ca though we likely did affect the base cation saturation ratio for K and Ca. With the low CEC of the sand a change to the ratio would be much easier but it is still doubtful that the ratio matters. Most previous research on the cation saturation ratios were on sandy soils where it might be more likely that there is an optimal ratio. The impact of the Ca and Mg in the irrigation water though would make it difficult to get a set ratio of K as any K applied could be flushed off the CEC as irrigation water is supplied making it a constant battle to change and maintain an "optimum" cation saturation ratio.

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