## Chapter 3.

# Measuring the effects of potassium application on calcium and magnesium availability in a calcareous sand\*

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#### Abstract

Potassium application can reduce soil and plant calcium and magnesium. However, for calcareous sands with a low cation exchange capacity and excess calcium and magnesium carbonates, the effects of potassium application on available calcium and magnesium are not known. Our objectives were to determine the effects of potassium application on calcium and magnesium concentrations in tissue, and to evaluate the ability of different soil tests to identify potassium-induced changes in extractable calcium and magnesium. We applied potassium at six rates  $(0, 1, 2, 3, 5, and 6 g m^{-2})$ 14 d<sup>-1</sup>) during the 2002 and 2003 growing seasons to L-93 creeping bentgrass [Agrostis stolonifera var. palustris (Huds.) Farw.] grown in a calcareous sand rootzone. Calcium and magnesium were extracted from soil samples using three standard agronomic extraction methods (Mehlich 3, Morgan, 1 *M* ammonium acetate) and two experimental methods (0.01 *M* strontium chloride and 1:5 water). Tissue calcium and magnesium decreased in response to increasing potassium application. The experimental soil tests adjusted to the pH of the soil during the extraction process and detected a decrease in extractable calcium and magnesium, while the agronomic tests did not adjust to the pH of the soil and were unable to consistently detect a difference in calcium and magnesium availability. We conclude that, while changes in calcium and magnesium extracted from this calcareous sand are not always associated with concurrent changes in bentgrass tissue calcium or magnesium concentration, extraction methods which adjust to the pH of a calcareous sand appear more effective in assessing calcium and magnesium availability.

#### Introduction

Potassium (K) is an essential plant macronutrient that makes up from 10 to 30 g kg<sup>-1</sup> of turfgrass leaf tissue dry weight (Carrow et al., 2001). In sand rootzones, K is particularly susceptible to leaching and it is not uncommon for turfgrass managers to apply K to sand rootzones based upon the annual nitrogen (N) rate to address the concern of leaching-induced K deficiency. For example, Carrow et al. (2001) recommend K applications at 125% the N rates when less than 15 g N m<sup>-2</sup> yr<sup>-1</sup> is applied and a N:K ratio of 1:0.83 for higher N application rates. In practice, K is often applied at higher rates than are recommended (Miller, 1999; Snyder and Cisar, 2000) as turfgrass managers attempt to improve the stress tolerance of their swards.

Miller (1999) showed plant tissue and Mehlich 1-extractable calcium (Ca) and magnesium (Mg) decreased with increasing rates of K fertilizer in two non-calcareous soils: a loamy sand and a sand-peat mix. With a fixed number of cation exchange sites in the soil at a given pH, increasing K activity in soil solution through fertilizer applications will invariably result in some exchange for other cations on the exchange sites. As Ca and Mg dominate the cation exchange sites in most soils, a portion of the adsorbed Ca and Mg can be replaced by K. After an initial increase in Ca and Mg in the soil solution following K fertilization, some of this Ca and Mg may be leached from the rootzone. Consequently, regular K fertilization may reduce Ca and Mg availability to roots, and it has been suggested (Miller, 1999) that high K rates increase the potential for Ca and Mg deficiencies in hybrid bermudagrass [*Cynodon dactylon* (L.) Pers. X *C. Transvaalensis* Burtt Davy]. It is unknown if K application would induce a meaningful decrease in available Ca and Mg in calcareous sand rootzones.

Although plant analysis is a useful tool for evaluating nutrient availability to turfgrass grown in sands (Waddington et al., 1994), soil nutrient analysis remains the

primary means of assessing Ca and Mg availability in sand rootzones (Carrow et al., 2001). Common extracting solutions for Ca and Mg include Mehlich 3, Morgan, and 1 M ammonium acetate (NH<sub>4</sub>OAc) (Carrow et al., 2004). These methods extract soluble and exchangeable Ca and Mg from a soil (Wolf and Beegle, 1995). Tests that extract soils at their natural pH include the 1:5 H<sub>2</sub>O extractant that measures water-soluble Ca and Mg, and the 0.01 M SrCl<sub>2</sub> extractant, a modification of the 0.01 M CaCl<sub>2</sub> method, which adjusts to the pH of the soil and has an ionic strength approximating that of soil solution (Van Erp et al., 1998). The performance of these tests with regards to detecting a K-induced change in plant available Ca and Mg in calcareous sands is not known.

Our objectives were to determine the effects of potassium application on calcium and magnesium concentrations in tissue, and to evaluate the ability of the five different soil tests to identify potassium-induced changes in extractable calcium and magnesium.

#### **Materials and Methods**

An experiment was conducted at the Cornell University Turfgrass Research and Education Center (Ithaca, NY) from June 2002 through May 2004 on a 30 cm deep calcareous sand rootzone planted to L-93 creeping bentgrass in 1997. The sand was mined from glacial deposits at Dryden, NY. At the beginning of the study, the sand had a pH of 8.2, cation exchange capacity (CEC) by compulsive exchange (Gillman and Sumter, 1986) of 12 mmol<sub>c</sub> kg<sup>-1</sup>, organic matter of 4 g kg<sup>-1</sup>, and calcium carbonate equivalent of 320 g kg<sup>-1</sup>. Total Ca and Mg were 2.39 mol kg<sup>-1</sup> and 453 mmol kg<sup>-1</sup>, respectively, as measured by EPA Method 3052, a microwave-assisted acid digestion (US EPA, 1999). Potassium (as  $K_2SO_4$ ) was applied at 6 rates (0, 1, 2, 3, 5, and 6 g K m<sup>-2</sup> 14 d<sup>-1</sup>) in a completely randomized design to 3 m<sup>2</sup> plots with 4 replications of each treatment. These rates were chosen to encompass and exceed the ranges of K application rates and N:K ratios applied to creeping bentgrass putting greens (Carrow et al., 2001). Potassium was dissolved in water and applied in solution with a CO<sub>2</sub>-powered backpack sprayer calibrated to deliver 167 ml solution m<sup>-2</sup> at 345 kPa. Plots were irrigated immediately following fertilization to wash the fertilizer solution from the leaves. Thirteen (2002) and twelve (2003) applications of K were made on a 14 day schedule from June through November. Nitrogen and phosphorus (P) were applied in equal amounts to each plot in conjunction with the K treatments. Phosphorus was applied as monoammonium phosphate. In 2002, a total of 19 g N m<sup>-2</sup> and 7 g P<sub>2</sub>O<sub>5</sub> m<sup>-2</sup> were applied, and in 2003, the rates were 13.5 g N m<sup>-2</sup> and 6 g P<sub>2</sub>O<sub>5</sub> m<sup>-2</sup>.

The plots were mowed 6 times weekly at 3.2 mm with a Toro 1000 walking greensmower (Toro Co., Bloomington, MN), and clippings were removed. Leaf tissue was collected each month during the growing season (Table 1) and analyzed for Ca and Mg using the dry ash method of Greweling (1976). Tissue samples contaminated with sand were identified by iron (Fe) concentrations above 1 g kg<sup>-1</sup> and Ca concentration above 312 mmol kg<sup>-1</sup>, and these samples were omitted from the data analysis. Irrigation was applied at the onset of drought stress. Traffic was applied with a golf traffic simulator to mimic 35,000 rounds of golf per year.

Soil samples were collected every 56 days from June through November during the 2002 and 2003 growing seasons (Table 3.1) although in November 2002, frozen soil prevented a planned soil sampling. An additional sampling was done following snowmelt in March of 2003 and 2004. At each sampling, five 19 mm diameter cores  $m^{-2}$  were collected from each plot to a depth of 10 cm. Verdure and thatch were removed from each sample. Soil samples were stored in a freezer at -12°C and thawed, dried and ground to pass 2 mm prior to laboratory analyses.

Tissue Samples	Soil Samples
Collected	Collected
6/4/02	6/4/02
6/30/02	-
7/28/02	7/28/02
8/25/02	-
9/22/02	9/22/02
10/20/02	-
11/15/02	-
-	3/25/03
6/1/03	6/1/03
6/29/03	-
7/27/03	7/27/03
8/24/03	-
9/21/03	9/21/03
10/19/03	-
11/16/03	11/16/03
-	3/29/04
5/30/04	5/30/04

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Table 3.1. Schedule of soil and leaf tissue collection dates in 2002, 2003, and 2004.

Calcium and Mg were measured in each sample using 1 M NH<sub>4</sub>OAc (NCR-13, 1988), Mehlich 3 (Wolf and Beegle, 1995), Morgan (Morgan, 1941), 1:5 H<sub>2</sub>O (Soil

and Plant Analysis Council, 1999), and 0.01 M SrCl<sub>2</sub> substituted for 0.01 M CaCl<sub>2</sub> in the method of Houba et al. (2000). The pH of each extracting solution was measured following extraction with the calcareous sand samples. The Mehlich 3, Morgan, and 1 M NH<sub>4</sub>OAc extractants had a final pH of 5.2, 5.6, and 7.4, respectively, while the 1:5 H<sub>2</sub>O and 0.01 M SrCl<sub>2</sub> extractants both finished with a pH of 8.2. We therefore classify the 1:5 H<sub>2</sub>O and 0.01 M SrCl<sub>2</sub> extractants as adjusting to the pH of the soil during the extraction process, and the Mehlich 3, Morgan, and 1 M NH<sub>4</sub>OAc extractants as non-adjusting.

The experiment was arranged as a completely randomized design between treatments, and as a repeated measures design within treatments. When repeated measurements of the same experimental units are made over time, pairs of repeated measurements on the same experimental unit are likely to be correlated, and the measurements are not independent. The MIXED procedure in SAS/STAT software version 8.2 (SAS Systems, Cary, NC) can be used in a multi-step process to analyze repeated measures data by first modeling the mean structure, and then by specifying an appropriate covariance structure to account for the correlation between repeated measures on the same experimental unit (Wolfinger, 1993). One makes statistical inferences based upon the resultant linear mixed model that incorporates the covariance structure (Littell et al., 2002). This method of analyzing repeated measures data produces accurate maximum likelihood estimators for mean values and accurate standard error estimates that account for autocorrelation between the sampling dates of each experimental unit (Littell et al., 1998).

Our analysis of the tissue Ca and Mg content involved simple linear regression (PROC REG) at each sampling date to determine if increased K rate caused a change in tissue Ca or Mg content. We also fit a linear mixed model using the methodology described in the previous paragraph in order to make inferences about the mean tissue

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Ca and Mg content over the course of the entire study. Similarly, for our tests of whether K application rate caused a change in extractable Ca or Mg from the soil, we used simple linear regression for each extraction method at each sampling date. For the overall tests of K application rate, sampling date, and their interaction on extractable Ca or Mg, we fit a linear mixed model that accounted for the correlation between repeated measurements made on the same experimental units.

#### **Results and Discussion**

#### Available Ca and Mg – Plant

An increase in K application rate caused a significant decrease (p < 0.05) in tissue Ca on 7 of 12 sampling dates while a significant decrease in tissue Mg was seen on only 2 of 12 sampling dates. Averaged across all sampling dates, tissue Ca decreased (p < 0.001) with increase in K application rate as did tissue Mg (p < 0.05). The decrease in mean tissue Ca between the control and the 6 g K m<sup>-2</sup> 14 d<sup>-1</sup> treatment was 56.1 mmol kg<sup>-1</sup> (p < 0.0001), while the decrease in mean tissue Mg was 7.2 mmol kg<sup>-1</sup> (p < 0.0001) (Fig. 3.1).

The mean tissue Mg concentration was statistically decreased by higher K application rates, but the decrease appeared too small to be physiologically meaningful. Optimum plant growth is achieved with Mg between 62 and 144 mmol kg<sup>-1</sup> (Marschner, 1995), and even at the highest K application rates, tissue Mg remained within this range. Although no Ca or Mg fertilizers were applied in this study, and in spite of the high rates of K fertilizer applied in some treatments, leaf tissue levels of Ca and Mg did not fall below the sufficiency ranges presented in Carrow et al. (2001). It appears that, even in this low CEC sand, sufficient quantities

of Ca and Mg were available to preclude any Ca or Mg fertilizer requirements. This finding supports the results of St. John et al. (2003), who found that Ca application to calcareous sands had no measurable effect on turfgrass quality. We investigated only L-93, but creeping bentgrass cultivars may differ in tissue Ca and Mg response to K fertilizer applications; Miller (1999) showed that the magnitude of K-induced decreases in tissue Ca and Mg differed between hybrid bermudagrass cultivars.



Figure 3.1. Mean values for each K application rate of creeping bentgrass leaf tissue Ca and Mg content averaged across all sampling dates. Error bars represent 95% confidence intervals around each mean.

Table 3.2. Effect of K application to a calcareous creeping bentgrass putting green on extractable Ca by 5 different soil extraction methods. Statistical analyses were done for main effects of K application rate (R) and main effects of sampling date (D) as well as their interactions. At each sampling date, the number shown is the slope of the regression line of extractable Ca ( $\mu$ mol kg<sup>-1</sup>) on K application rate in (g m<sup>-2</sup> 14 d<sup>-1</sup>).

Method	R	D	RxD	7/28/02	9/22/02	3/25/03	6/1/03	7/27/03	9/21/03	11/16/03	3/29/04	5/30/04
$1 M \mathrm{NH_4OAc}$	'	***		lSY	SN	NS	NS	NS	NS	NS	NS	SN
Mehlich 3	'	***	,	SN	SN	SN	SN	SN	SN	SN	SN	NS
Morgan		***	,	SN	SN	SN	SN	SN	NS	SN	SN	SN
0.01 M SrCl2	***	***	,	NS	-122*	SN	-135*	-198***	-140*	SN	-136*	NS
1:5 H <sub>2</sub> O	***	***	*	-22*	-29**	-38***	NS	-38***	-43***	-38***	-32***	NS
* p-value < 0.05,	** p-valu	e < 0.01, **	** p-value	< 0.001, †I	o-value > 0.	.05						

Table 3.3. Effect of K application to a calcareous creeping bentgrass putting green on extractable Mg by 5 different soil extraction methods. Statistical analyses were done for main effects of K application rate (R) and main effects of sampling date (D) as well as their interactions. At each sampling date, the number shown is the slope of the regression line of extractable Mg ( $\mu$ mol kg<sup>-1</sup>) on K application rate (g m<sup>-2</sup> 14 d<sup>-1</sup>).

e > 0.05
p-value
< 0.001,
p-value <
[, ***]
e < 0.01
* p-valu
< 0.05, *
p-value

#### Available Ca and Mg – Soil

In samples collected after K treatment initiation, the increase in K application rate did not result in a decrease in Mehlich 3-, Morgan-, or 1 M NH<sub>4</sub>OAc-extractable Ca (Table 3.2) despite the observed decrease in tissue Ca and Mg concentrations. The Mehlich 3 extraction detected no decrease in extractable Mg at any time (Table 3.3). The Morgan extractant detected a decrease in extractable Mg only on 1 of 9 sampling dates, as did 1 M NH<sub>4</sub>OAc.

Contrary to the lack of a response in standard agronomic soil tests for extractable Ca and Mg, an increase in K application rate did cause a decrease in 0.01 M SrCl<sub>2</sub> -extractable Ca on 5 of 9 sampling dates (Table 3.2). The magnitude of the decrease was between 25 and 200 µmol Ca kg<sup>-1</sup> for each increase of 1 g K m<sup>-2</sup> 14 d<sup>-1</sup>. Similarly, the 1:5 H<sub>2</sub>O method extracted less Ca as the K application rate was increased on 7 of 9 sampling dates (Table 3.2). For Mg, 0.01 M SrCl<sub>2</sub> detected a decrease in response to K fertilizer application on 7 of 9 sampling dates, and 1:5 H<sub>2</sub>O detected a decrease on 6 of 9 sampling dates (Table 3.3). Analysis of the soil samples collected prior to K treatment initiation showed that the extraction methods differ from each other in the amount of Ca and Mg extracted (Fig. 3.2). The agronomic soil tests, which extracted more Ca and Mg than either 1:5 H<sub>2</sub>O or 0.01 M SrCl<sub>2</sub>, were less sensitive in the detection of K-induced decreases in extractable Ca or Mg (Fig. 3.3).

The primary source of exchange sites in sand rootzones is soil organic matter, which has pH-dependent charge as the source of its cation exchange sites (Sumner and Miller, 1996). The dissociation of organic acids that comprise the exchange sites in sand rootzones is affected by the ionic strength of the saturating solution (McBride, 1994). Theoretical concepts suggest, particularly for sand rootzones, that extraction methods that adjust to the pH of the soil and have a low ionic strength (i.e. the 0.01 *M*  SrCl<sub>2</sub> and the 1:5 H<sub>2</sub>O extraction methods) have the potential to extract a readily plantavailable fraction of the soil Ca and Mg. The non-adjusting extracting solutions with higher ionic strengths can extract Ca and Mg from less-available pools (St. John et al., 2003), and dissolution of solid-phase carbonates in calcareous sands by non-adjusting extracting solutions may further increase the variability in extractable Ca or Mg. This increased variability associated with non-adjusting extracting solutions can overshadow the effects of K application on extractable Ca and Mg. Our results (Tables 3.2 and 3.3) support this concept.



Figure 3.2. Extractable Ca and Mg from calcareous sand samples (n = 24) collected June 4, 2002 from a creeping bentgrass putting green, prior to initiation of K fertilizer treatments. Error bars represent Tukey's minimum significant difference simultaneously testing differences of all mean values ( $\alpha = 0.05$ ).

Figure 3.3. Extractable Ca and Mg by 0.01 *M* SrCl<sub>2</sub> and 1:5 H<sub>2</sub>O extraction methods from calcareous sand samples collected to a depth of 10 cm from a creeping bentgrass putting green in 2002, 2003, and 2004. Low K is the mean value of the plots receiving the three lowest K rates (0, 1, 2 g K m<sup>-2</sup> 14 d<sup>-1</sup>). High K is the average of the plots receiving the three highest K rates (3, 5, 6 g K m<sup>-2</sup> 14 d<sup>-1</sup>). Error bars show the 95% confidence interval around the mean for each date.



As more and more turfgrass sites are planted on calcareous soils, and as the increasing use of treated or salt-affected irrigation water improves the chances of carbonate mineral precipitation in the soils to which it is applied (Carrow and Duncan, 1998), it would seem that the use of extraction methods which adjust to the pH of the soil could provide a useful tool for Ca and Mg assessment in sand rootzones.

Soil extractable Ca or Mg can only be useful as a tool for fertility management if the data can be related to plant needs and uptake of Ca or Mg. We found that K application reduced tissue Ca and Mg and decreased extractable Ca and Mg from the soil using weak extracting solutions that adjusted to the pH of the soil. However, there was not a clear relationship between soil extractable Ca and Mg and leaf tissue Ca and Mg concentrations on the different sampling dates. Further investigation of the nonacid cation interrelationships in sand rootzones, both in the plant and in plantavailable forms in the soil, is warranted.

The 1:5 H<sub>2</sub>O- and 0.01 *M* SrCl<sub>2</sub>-extractable Ca and Mg were decreased by added K on nearly every sampling date, but the response of tissue Ca and Mg to added K, although still decreasing, was less consistent than was observed in the soil. This suggests that the 1:5 H<sub>2</sub>O and 0.01 *M* SrCl<sub>2</sub> extraction methods detected K-induced Ca and Mg reductions in the soil that were not reflected in the plant content of Ca and Mg. These results differ from those reported by Waddington et al. (1994), who found that for sand rootzones, plant analysis was better able to detect nutritional effects of applied fertilizer than 1 *M* NH<sub>4</sub>OAc or the Baker Soil Test (Baker, 1973). Based on our results, we might suggest that soil analysis with an adjusting extracting solution would be preferable to plant analysis in the assessment of applied K fertilizer on available Ca and Mg. However, further research is needed on sands where K application could decrease tissue levels of Ca and Mg below the critical level.

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### **Summary and Conclusions**

High rates of K fertilizer reduced plant available Ca and Mg in a calcareous sand rootzone. This was evident both in a reduction of Ca and Mg concentrations in the leaf tissue and in a reduction in extractable soil Ca and Mg with increased K fertilizer application when 1:5  $H_2O$  and 0.01 *M* SrCl<sub>2</sub> extractions were used. However, the standard agronomic tests that did not adjust to the pH of the sand failed to detect this response.

The extraction method used for a particular soil sample should be appropriate for the properties of the sample. Extraction solutions that adjust to the pH of the soil and have a low ionic strength offer both practical and theoretical benefits for regular use in the measurement of Ca and Mg availability, but additional work on sands of different mineralogy must be conducted to verify the suitability of these methods.

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