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Title THE EFFECT OF CHLORIDE ON THE UPTAKE OF MANGANESE BY BUSH BEANS AND SWEET CORN

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The effect of Cl, lime, and K on the uptake of Mn by bush beans and sweet corn was investigated under field and greenhouse conditions on poorly drained acid soils. Lime at rates up to three tons per acre with Cl and K treatments was applied in factorial combination in the bush bean experiments. All treatments received a uniform application of N, P, and S. The fertilizer materials applied at planting were all banded.

The effect of an application of K on the uptake of Mn was dependent upon the source of K. The application of KCl significantly increased the Mn content when compared with the other sources of K or to the check treatment where no K was applied. This increase was observed in both the bush bean and the sweet corn experiments and, in general, was great enough to cause Mn toxicity in the bush bean experiments. The application of $K_2SO_4$ and $K_2CO_3$ had little or no effect on the uptake of Mn.

The application of Cl always increased the uptake of Mn. All bean plants on the zero lime treatments that had received an application of Cl developed severe Mn toxicity symptoms in the 1963 field experiment and in the 1964 greenhouse experiment.

The application of lime consistently reduced the Mn content with the greatest reduction occurring on the treatments where Cl had been applied. The Mn content of the bean leaves on the limed treatments was below suggested toxic levels and the plants did not show any toxicity symptoms at the time the leaf samples were taken for chemical analyses.

A mechanism has been presented to explain the effect of the Cl salt on the availability of Mn. In this reaction Cl has acted as an electron donor causing a chemical reduction of the manganic-Mn oxides to the plant available manganous-Mn ion.

These experiments offer a possible explanation for some of the reductions in yields that have been observed from the band applications of KCl. They also emphasize the importance of evaluating the effects of individual treatments on the whole range of elements present in the soil that can have detrimental as well as beneficial effects on plant growth.

# THE EFFECT OF CHLORIDE ON THE UPTAKE OF MANGANESE BY BUSH BEANS AND SWEET CORN

by

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# THE EFFECT OF CHLORIDE ON THE UPTAKE OF MANGANESE BY BUSH BEANS AND SWEET CORN

## INTRODUCTION

Soil fertility problems associated with the production of processing crops on some of the poorly drained soils in the Willamette Valley have been recently emphasized in a study initiated by the Soils Department at Oregon State University. Vegetable crop production has been predominantly concentrated on the soils where drainage was not a management problem. However, the future expansion of intensive agricultural production in the Willamette Valley will depend upon the utilization of some of the poorly drained soils which are currently being used for the production of grass seed.

Approximately 800,000 acres in the Willamette Valley are naturally imperfect or poorly drained. Profile development has resulted in a heavy-textured B horizon beginning 15 to 30 inches beneath the surface on much of the older alluvial material. This horizon becomes nearly impervious when wet, creating ideal conditions for the reduction of Mn during the winter months. The impervious nature of the B horizon restricts the growth of plant roots to the area above limiting the storage of available moisture that can be exploited by plants. This low moisture reserve causes droughty conditions to exist during the summer months unless these soils are irrigated.

These soils are typically acid with the dominant pH range from 4.9 to 6.3. They are commonly deficient in available P and most non-legume crops respond to an application of N. The soils are relatively low in exchangeable K and the application of lime is beneficial for crops that do not tolerate acid soil conditions. Concretions of Fe and Mn oxides are present throughout the profile.

Field and greenhouse experiments were established to evaluate the effects of lime, K, and other fertilizer treatments on the production of bush beans and sweet corn on these soils. The effect of excessive amount of Mn on plant growth became evident as the experiments progressed.

# OBJECTIVES

The major objective of this investigation was to evaluate the effect of fertilizer materials on the uptake of Mn in poorly drained acid soils. Bush beans were used as the primary indicator plant with supporting evidence being obtained from sweet corn. Emphasis was placed on the evaluation of the following effects:

A. The effect of source of K on the uptake of Mn.

B. The effect of Cl on the uptake of Mn.

C. The effect of lime on the uptake of Mn.

# LITERATURE REVIEW

Manganese was first demonstrated to be essential for plant growth by J. S. McHargue in 1922. It is known to serve as an activator of certain enzyme systems and is thought to be involved in N transformation in both soils and plants. Manganese is absorbed by the plant system in the divalent form and has been found to concentrate in the region of highest physiological activity. Very small quantities of Mn are essential for plant growth with larger amounts being quite toxic.

Manganese is generally considered to exist in soils in one or more of the three following valence states; (1) divalent Mn which is soluble and may be present as an adsorbed cation or as an ion in the soil solution, (2) trivalent Mn which supposedly exists as the reactive oxide, $Mn_2O_3$, and (3) tetravalent Mn which is generally present as an inert oxide in soils. The divalent form is favored by reducing conditions and a pH below 6.5, while the two latter forms are favored by oxidizing conditions and higher soil pH's.

The moisture status is the main physical characteristic of soils which has an influence on the availability of Mn. Both past and present moisture conditions influence the amounts of available Mn present. Piper (1931) has shown that a period of waterlogging favored the reduction of the unavailable form of Mn to the plant available form and that this may be one way to increase the amounts of available Mn in some soils. Pearsall (1950) attributed this effect to an alteration of the chemical and biological processes caused by a scarcity of available $O_2$. This type of alteration may liberate large amounts of exchangeable cations particularly Fe, Mn, and Al. In a recent publication Dhein (1962) has attributed a temporary Mn injury on clover to the chemical reduction of the higher valency oxides of Mn to the plant available form during a period of waterlogging.

Fujimoto and Sherman (1945) found that the level of exchangeable Mn was decreased when dry soils were moistened to approximately their field capacity under non-saturated conditions. This type of fixation was also observed by Rich (1955) and Christensen, Toth, and Bear (1950) to occur only in well-drained soils. The extractable Mn was increased in soils upon air-drying according to Fujimoto and Sherman (1945), Zende (1954), and Rich (1955). Zende (1954) found that the increase was greater in soils that had a higher organic matter content, a higher content of active Mn, and a pH of less than 6.3. This increase of extractable Mn could be explained by the dehydration of the complex Mn oxide, $(MnO)_X(MnO_2)_Y(H_2O)_Z$, as hypothesized in the Mn cycle of Fujimoto and Sherman (1948).

Some investigators have included soil temperature as a factor affecting the availability of Mn. Mederski and Wilson (1955) showed that foliar deficiency symptoms of Mn developed on soybeans at low soil temperatures and at high soil moistures. They also found that increasing the soil temperature increased the uptake of Mn and reduced the deficiency symptoms in the soybeans. This would indicate that the higher soil temperature either increased the availability of Mn or increased the plant activity.

The availability of Mn has been found to be closely related to the pH of the soil and to pH changes resulting from the application of fertilizer materials and soil amendments. Snider (1943) found that the amounts of soluble and exchangeable Mn in soils were more closely related to the $H^+$ ion concentration than to the amounts of exchangeable bases in the surface layer. He concluded that any increase in soil acidity was followed by an increase in the availability of Mn and that some fertilizers and their constituents affected the availability of Mn in this way. An increase in soluble Mn was measured by Funchess (1918) following the application of $(NH_4)_2SO_4$ in an acid soil. The addition of the acid-residual materials, $NH_4NO_3$, $(NH_4)_2SO_4$, urea, and HCl, were shown by Conner (1932) to benefit oats that were deficient in Mn. According to Berger and Gerloff (1947) the addition of any fertilizer which lowered the pH of the soil caused Mn toxicity to occur in potatoes where the level of available Mn in the soil was near the critical level. Jacobson and Swanback (1932) reported that there was an increase in the uptake of Mn by tobacco plants and an increase in the active Mn in the soil following a decrease in the pH of the soil. The increased availability of Mn from the application of superphosphate was attributed to an increase in the $H^+$ ion concentration by Steckel, Bertamson, and Ohlrogge (1948). This effect was later confirmed by studies made with monocalcium phosphate monohydrate (Lindsay and Stephenson, 1959).

Garey and Barber (1952) corrected Mn deficiency on an alkaline soil with the addition of elemental S. They attributed this effect to an oxidation-reduction reaction involving S and Mn and from a possible increase in soil acidity. The increase of soluble and exchangeable Mn from the addition of sulfur has also been reported by Funchess (1918) and Fujimoto and Sherman (1948).

The beneficial effect of an increase in soil pH on plant growth may result from a decrease in the amounts of available and exchangeable Mn present in the soil. Sherman and Fujimoto (1946) decreased the exchangeable Mn in an Hawaiian soil to about one-fifth the amount found in the unlimed soil by applying two tons of hydrated lime per acre, thereby increasing the pH from 4.6 to 6.7. They also indicated that plant growth was increased and the uptake of Mn was reduced from the application of the hydrated lime. Morris (1948), Lingle et al. (1961), and Hortenstine and Ozaki (1961) all reported a reduction in the uptake of Mn by plants from the application of lime. Mann (1930) applied different amounts of

$CaCO_3$ and $MgCO_3$ and found that the solubility of Mn was decreased by both carbonate sources. Bortner (1935) attributed the abnormal growth of turkish tobacco on a Bera soil of pH 4.5 to large amounts of soluble Mn being present and found that the application of lime reduced the toxic condition of excessive Mn in both field and greenhouse experiments. Crinkle leaf (Mn toxicity) of cotton was prevented by the application of lime or $Na_2CO_3$, but the application of a neutral Ca salt had no effect on the prevention of the toxicity symptoms (Adams and Weir, 1957). Fried and Peech (1946) compared the effect of lime and gypsum applications on acid soils and found that the improved growth of plants was not necessarily due to a lack of available Ca, but that the main effect was an increase in pH resulting from the application of lime. The effect of the application of lime or gypsum on Mn toxicity was also compared by Schmehl, Peech, and Bradfield (1950). The results that they obtained were similar to those of Fried and Peech (1946), except for a detrimental salt effect resulting from the application of gypsum.

Some evidence is available which indicates that the application of a Cl salt increased the uptake of Mn by plants (York, Bradfield, and Peech, 1954; Foy, 1964). York, Bradfield, and Peech (1954) after applying NaCl or KCl observed nearly a 200% increase in the Mn content of alfalfa on an unlimed soil that had a pH of 5.0. They have attributed this to a salt effect, i.e., a cation exchange of Na or

K for H and Mn. Alfalfa yields were severely decreased by the application of $CaCl_2$ on an acid soil in the experiments of Foy (1964). The $CaCl_2$ was applied to supply Ca to the growing plants although an increase of Ca in the plants was not evident from his data. The application of $CaCl_2$ caused the Mn toxicity symptoms, the Mn uptake by the plants, and the exchangeable Mn in the soils to increase. The application of $CaCl_2$ appeared to have little effect on the uptake of Mn by cotton when a Mn toxicity situation already existed, although a slight increase in water-soluble Mn was shown by the data of Adams and Weir (1957).

The addition of glucose has been shown to increase the amounts of divalent Mn present in the soil (Mann and Quastel, 1946; Christensen, Toth, and Bear, 1950). The influence of the glucose was limited to its period of decomposition in a limed soil. In an acid soil or an unlimed soil they found that the Mn status was indirectly influenced after the initial decomposition, i. e., a slower return of the divalent Mn to the insoluble form. The influence from the addition of an organic material on the availability of Mn was dependent upon the moisture conditions at the time of the addition according to the results of Sanchez and Kamprath (1959). They found that the addition of peat caused an increase in the available Mn in a soil that was low in organic matter and in a moistened condition; but if the soil was dry, the increase did not occur.

The effect of superphosphate has been reported in the literature to both increase and decrease the availability of Mn. Page, Schofield-Plamer, and MacGregor (1963) reported an increase in the uptake of Mn by oats from a superphosphate treatment. Messing (1960) reported similar results from studies on lettuce and also measured an increase in the water-soluble and exchangeable Mn in the soil. These results can be explained by the decrease in pH following an application of superphosphate (Lindsay and Stephenson, 1959).

Other investigators have found that the toxic effect of Mn was reduced by the application of superphosphate (Hawkins, Brown, and Rubin, 1951; Lamb, 1961). Bortner (1935) attributed the decrease in the Mn content of tobacco from an application of superphosphate to an immobilization of Mn within the plant. Foy (1964) also suggested that the additional phosphate may be necessary to provide some protection against Mn injury by a similar reaction.

Manganese can either be reduced or oxidized by microorganisms depending upon the availability of $O_2$. In the presence of low available $O_2$, Pearsall (1950) reported an increase in the divalent form of Mn. Microbiological oxidation has been observed to occur in soils as acid as pH 4.8 and as alkaline as pH 8.9 (Leeper and Swaby, 1940).

The intensity of light may have an influence on the amount of

Mn taken up by some plants. McCool (1935) has shown that the Mn toxicity symptoms and Mn content of soybeans and buckwheat were decreased as the light intensity decreased. Sutton and Hallsworth (1958) were able to induce Mn toxicity in forage legumes under conditions of high light intensities and a low Ca supply. However, they suggested that the light intensity effect may be dependent on the Fe/ Mn ratio.

Evidence has been presented above which indicates that a Mn cycle is present in soils involving the divalent, tetravalent, and probably other valent states of Mn. In this cycle two general processes occur which influence the availability of Mn. The first is an oxidation-reduction process and the second is the hydration-dehydration process of the Mn oxides. The dominant process and form of Mn present is controlled by soil pH changes, availability of $O_2$, availability of organic matter, biological population, soil moisture status, and soil temperatures.

# EXPERIMENTAL METHODS

## Soil Characteristics

The experiments were conducted on soils that have been classified as Planosol and as belonging to the Dayton series. The recent reclassification scheme of the 7th Approximation would classify these soils as a Typic Albaqualf.

These soils have developed on the poorly drained terrace sediments of the Willamette Valley. Iron-manganese concretions occur throughout the profile and are concentrated in the lower parts of the $A_2$ horizon. Below this horizon is a very compact and clayey horizon which becomes almost impervious when moist. This impervious nature causes the upper horizons to become waterlogged during the rainy season from mid-fall to mid-spring. Ideal conditions for the reduction of Mn occur on these soils for approximately five months (Conner, 1918; Piper, 1931).

A summary of some of the chemical characteristics for the individual experiments is given in Table 1.

## Design and Application Methods

All experiments were designed as randomized blocks with a different order of randomization being used for each. The treatments in the bush bean experiments were arranged in factorial

Table 1. Soil Characteristics from the Experimental Locations.*

| Location | Lime rate T/A | pH | P ppm | me/100 gms. K | Ca | Mg | Mn | CEC |
|---|---|---|---|---|---|---|---|---|
| Bush bean field | 0 | 4.9 | 19.8 | 0.11 | 2.6 | 1.4 | - | 11.3 |
| experiment-1963 | 3 | 6.6 | 20.2 | 0.14 | 11.0 | 1.5 | - | 11.3 |
| Greenhouse | 0 | 5.0 | 7.2 | 0.18 | 2.8 | 1.1 | 0.67 | 11.6 |
| experiment-1964 | 3 | 6.5 | 8.2 | 0.22 | 8.5 | 1.4 | 0.17 | 12.1 |
| Bush bean field | 0 | 4.9 | 12.5 | 0.14 | 2.9 | 1.3 | 0.10 | - |
| experiment-1964 | 1.5 | 5.2 | 12.7 | 0.14 | 4.5 | 1.3 | 0.07 | - |
| | 3 | 6.0 | 12.4 | 0.16 | 8.6 | 1.4 | 0.04 | - |
| Sweet Corn Exp. -1964 | | | | | | | | |
| 1. 426 | 0 | 5.5 | 16.0 | 0.25 | 7.0 | 1.9 | 0.06 | 18.0 |
| 2. 427 | 0 | 5.2 | 11.0 | 0.16 | 4.3 | 1.2 | 0.13 | 12.3 |

* All values are the means of the replications from the respective experiment.

combination and the lime rates in the bush bean greenhouse experiment were included in the factorial design. The lime rates were considered as main plots and all other treatment combinations were considered sub-plot units in the bush bean field experiments. The sub-plots were planted continuously across all main plots within each replication. This type of design increases the precision with which the interactions can be evaluated and decreases the precision on the main effects.

All fertilizer materials except for lime were banded about two inches to the side and two inches below the seed at planting time. Hydrated lime was broadcast and disced into the soil on the field experiments and mixed by hand into the soil used for the greenhouse experiment.

Soil Sampling and Analyses

Soil samples were taken from all of the replications in the field experiments immediately before planting. The samples were then air-dried, ground, and stored until sub-samples were taken for analyses. All of the methods used for the soil analyses except for the method used in the determination of the extractable Mn were those used by the Oregon State University Soil Testing Laboratory (Alban and Kellogg, 1959).

Freshly obtained soil samples were used for the determination of the available (extractable) Mn. The samples were allowed to air-dry to a workable condition and were then extracted immediately because the drying of a moist soil has been shown to increase the amount of available Mn (Fujimoto and Sherman, 1945).

The procedure for the extraction and determination of the available Mn is as follows:

> Thirty ml. of 1N $CaCl_2$ were added to ten grams of fresh soil in a 250 ml. wide-mouthed polyproylene bottle. The sample was then shaken for ten minutes and centrifuged, and the supernatant liquid was removed by filtering. This process was repeated three times for each sample. The amount of soluble Mn in the combined filtrate was then determined with an atomic absorption spectrophotometer.

Plant Sampling and Analyses

The most recently matured trifoliate bean leaves were sampled for chemical analyses when the plants were at early flowering on the 1963 experiment and when the first trifoliate bean leaves reached maturity on the 1964 field experiment. Six weeks after planting, the greenhouse experiment was terminated and all trifoliate leaves were collected for chemical analyses. Whole tops were taken six weeks after planting from the sweet corn experiments.

All plant samples were dried and ground. Sub-samples were digested with $HNO_3$ and $HClO_4$. The determination of Ca, Mg, Mn, Zn, and Fe in the plant digests was done with an atomic absorption spectrophotometer. Potassium was determined on a flame photometer and P was determined according to the method as described by Barton (1948).

# RESULTS AND DISCUSSION

## Bush Bean Field Experiment-1963

This experiment was primarily designed to investigate the effect of fertilizer treatments on plant growth and possible interactions resulting from the application of lime. All plots received 50 pounds of N per acre as $(NH_4)_2SO_4$. Rates of 0, 26, and 52 pounds of P per acre were applied as $Ca(H_2PO_4)_2$ and KCl was used to supply rates of 0, 50, and 100 pounds of K per acre. Lime was applied three weeks before planting at rates of zero and three tons per acre.

Yield data and chemical analyses of the trifoliate leaves are given in the Appendix. Values used in evaluating the application of K, P, and lime on plant growth and nutrient content are presented in Tables 2 and 3. Primary consideration has been given to the effect of the fertilizer materials on the uptake of Mn.

All plants became extremely chlorotic shortly after emergence regardless of the fertilizer treatment. The first visible leaves, the primary leaves, became stunted and exhibited a severe marginal chlorosis which extended into the interveinal areas. These leaves became crinkled and spotted with numerous small yellowish necrotic spots. The symptoms were later associated with Mn toxicity because of the similarity to the Mn toxicity symptoms as described on

Table 2. Effect of K and Lime on the Yield and Uptake of Mn by Bush Beans in the 1963 Field Experiment.*

| | Lime zero | | Lime 3T/A | |
|---|---|---|---|---|
| K rate (lbs/A) | Mn ppm | Yield T/A | Mn ppm | Yield T/A |
| 0 | 798 | 5.16 | 528 | 3.61 |
| 50 | 1190 | 2.61 | 772 | 7.02 |
| 100 | 1048 | 2.05 | 610 | 6.17 |

| Least Significant Differences (5% level) | Yield (T/A) | ppm Mn |
|---|---|---|
| Comparing the effect of lime at constant K | 1.64 | 458 |
| Comparing the effect of K at constant lime | 2.10 | 482 |

* All values are the means of 4 replications.

Table 3. Effect of P and Lime on the Yield and Uptake of Mn by Bush Beans in the 1963 Field Experiment.*

| | Lime zero | | Lime 3T/A | |
|---|---|---|---|---|
| P rate (lbs/A) | Mn ppm | Yield T/A | Mn ppm | Yield T/A |
| 0 | 745 | 2.61 | 530 | 5.38 |
| 26 | 988 | 2.46 | 702 | 6.02 |
| 52 | 1048 | 2.05 | 610 | 6.17 |

| Least Significant Differences (5% level) | Yield (T/A) | ppm Mn |
|---|---|---|
| Comparing the effect of lime at constant P | 1.64 | 458 |
| Comparing the effect of P at constant lime | 2.10 | 482 |

* All values are the means of 4 replications.

the French bean (Löhnis, 1951; Fergus, 1954). The plants remained in this stunted stage of growth for approximately one week; at this time, the first trifoliate leaves appeared and most of the chlorotic primary leaves dropped off.

All treatments that had not received an application of KCl recovered much faster than the treatments that did and, in general, the limed treatments were better than the unlimed. However, some toxicity symptoms were still evident on some KCl treatments at harvest. The severity of the Mn toxicity symptoms increased as the rate of K increased.

The data given in Table 2 shows that the yield of beans in this experiment could be related to the Mn content of the bean leaves except on the treatments where a K deficiency situation was accentuated by the application of lime. The increase in the Mn content that was associated with the application of K was greater at the zero lime rate than at the three ton rate. The application of K in the presence of lime increased the yield even though this increase was accompanied by an increase in the Mn content. Also, the yield decrease from the first rate of K (50 pounds per acre) in the absence of lime was much greater than the decrease in yield when the rate of K was increased from 50 to 100 pounds per acre. The application of 50 pounds of K always coincided with the application of 45 pounds of Cl.

The application of lime reduced the Mn content in the bean leaves at all levels of K and P (Tables 2 and 3). The decrease in the Mn content was associated with an increase in soil pH from 4.9 to 6.6, possibly causing a decrease in the availability of Mn (Sherman and Fujimoto, 1946; Morris, 1948; Lingle et al., 1961). Lime may have also been more effective at the earlier stages of growth if it could have been applied sooner.

The addition of lime increased the yield of beans significantly where K was applied but decreased the yields where K was not applied (Table 2). The reduction in yield from the application of lime probably was not associated with the small reduction in the K content, 1.05% to 0.96%, but to the wider Ca/K ratio mainly caused by the increase of Ca in the bean leaves from 1.42% to 1.80%. Similar lime by K interactions have also been observed by Van Itallie (1938) and Lucas and Scarseth (1949).

The application of K increased the K content of the bean leaves approximately 1% on all treatments. The increase from the first rate of K (50 pounds per acre) was much greater than the increase between the first and second rate of K (100 pounds per acre). It would appear that the first rate of K was adequate to supply the plant's growth requirement for K in this experiment.

The effect that the application of $Ca(H_2PO_4)_2$ had on the uptake of Mn is shown in Table 3. In general, the application of P increased the Mn content of bean leaves at both levels of lime with the increase being more pronounced at the zero lime rate. The application of P decreased the yields in the absence of lime and increased the yields in the presence of lime. Both changes coincided with a small increase in P content. The increase of P and Mn in the bean leaves and the yield changes were not significant.

Plant samples from the above treatments were analyzed for Ca, Mg, and Zn. The application of lime increased the Ca content and decreased the Zn content on all treatments. The values found for the Ca, Mg, P, and Zn contents do not appear to be in either the deficiency or the toxicity range.

When it became apparent that the severity of the toxicity symptoms were closely associated with the application of KCl, a supplemental non-replicated experiment, immediately adjacent to the main experiment, was established in the middle of the growing season to evaluate which ion was responsible for the effect, the $K^+$ or the $Cl^-$. This experiment consisted of a simple comparison between KCl and $K_2SO_4$ at two rates of P and lime. Even though it was relatively late in the growing season, it was evident that the toxicity symptoms on the primary leaves were considerably more severe on all the KCl treatments than on the $K_2SO_4$ treatments. A comparison made between the sources of K showed that the Mn content of the plants on the KCl treatments was almost 50% greater than the Mn content of the plants on the $K_2SO_4$ treatment. Whole plant samples collected at bloom showed that the Mn content of the plants was reduced two and one-half times by the application of lime (Appendix Table 1b).

The observations and plant analyses data from the supplemental treatments and the main field experiment suggested the following greenhouse experiment.

Bush Bean Greenhouse Experiment-1964

The greenhouse experiment was designed to determine the effect of different sources of K and Cl on the uptake of Mn in the absence and presence of lime. The arrangement of treatments and materials is shown in Table 4. The K materials were banded immediately before planting at a rate per inch of row that would correspond to 41 pounds of K per acre for a 30 inch row spacing. The amount of Cl that was supplied by the $CaCl_2$ treatment was equivalent to the amount supplied by the KCl treatment. All treatments had the equivalent of nine pounds of P and eight pounds of N per acre applied with the banded materials.

Table 4. Arrangement of Fertilizer Materials and Treatments in the 1964 Bush Bean Greenhouse Experiment.

| Fertilizer material | Lime zero | | Lime 3T/ A | |
|---|---|---|---|---|
| | $-CaCl_2$ | $+CaCl_2$ | $-CaCl_2$ | $+CaCl_2$ |
| Check | X | X | X | X |
| KCl | X | X | X | X |
| $K_2SO_4$ | X | X | X | X |
| $K_2CO_3$ | X | X | X | X |

The soil that was used in this experiment was taken from the 1963 experimental site when wet from winter rains. The sample was dried enough to facilitate handling, screening, mixing with lime, and potting. The soil was then kept under saturated conditions in the greenhouse for four weeks to re-establish reducing conditions. It was also allowed to dry slightly before planting to help prevent the occurrence of damping-off during seedling emergence.

The toxicity symptoms that appeared in this experiment were very similar to those described for the 1963 field experiment. The first visible signs of Mn toxicity appeared on all plants that had received an application of Cl regardless of source. The chlorotic symptoms were pronounced on all zero lime treatments and the application of Cl increased the severity of the symptoms.

The effect that the fertilizer treatments had on plant growth five weeks after planting can be seen in Figures 1 and 2. The plant growth that occurred on the treatments corresponded inversely to the Mn content of the bean leaves (Table 5).

Figure 1 compares the effect of the different sources of K and $CaCl_2$ on plant growth in the absence of lime. Figure 2 compares the effect of adding $CaCl_2$ to the sources of K. The check treatment in Figure 2 did not receive any fertilizer treatment. Comparison of Figures 1 and 2 shows that the plant growth was severely decreased from the addition of $CaCl_2$ on the K treatments. No evaluation of the treatment effects on plant yields was made in this experiment; however, the effect of the treatments on plant growth could serve as an indication of the respective yields as shown for the zero lime treatments. The growth of the plants on the limed treatments corresponded very closely to the check treatment in Figure 2.

Chemical analyses for the trifoliate leaves taken at the time the experiment was terminated are given in the Appendix. The values for ppm Mn, percent K, and percent Ca for the respective treatments are given in Table 5.

In the absence of lime the increases in the Mn content of the bean leaves from the application of Cl, either as KCl or $CaCl_2$, were highly significant in comparison to the check treatment where no Cl was applied. The difference between the Mn content on the $CaCl_2$ and KCl treatments was statistically significant in the absence of

Table 5. Effect of Lime and Fertilizer Materials on the Mn, K, and Ca Content of the Bush Bean Leaves in the 1964 Greenhouse Experiment. *

| Fertilizer material | Nutrient content | Lime zero | | Lime 3T/A | |
|---|---|---|---|---|---|
| | | $-CaCl_2$ | $+CaCl_2$ | $-CaCl_2$ | $+CaCl_2$ |
| Check | ppm Mn | 300 | 2192 | 68 | 231 |
| | % K | 0.74 | 2.01 | 0.79 | 1.05 |
| | % Ca | 0.61 | 1.55 | 1.29 | 1.91 |
| KCl | ppm Mn | 1165 | 2125 | 154 | 393 |
| | % K | 3.07 | 3.30 | 3.64 | 2.77 |
| | % Ca | 1.13 | 1.71 | 1.80 | 1.92 |
| $K_2SO_4$ | ppm Mn | 258 | 1783 | 110 | 90 |
| | % K | 1.89 | 3.25 | 1.75 | 2.01 |
| | % Ca | 0.52 | 1.48 | 0.80 | 1.53 |
| $K_2CO_3$ | ppm Mn | 467 | 990 | 120 | 89 |
| | % K | 1.66 | 2.33 | 2.17 | 2.42 |
| | % Ca | 0.50 | 1.00 | 1.43 | 1.23 |

| Least Significant Differences (5% level) | Mn ppm | K % | Ca % |
|---|---|---|---|
| Comparing 2 treatment means | 635 | 0.63 | 0.44 |

* All values are the means of 3 replications.

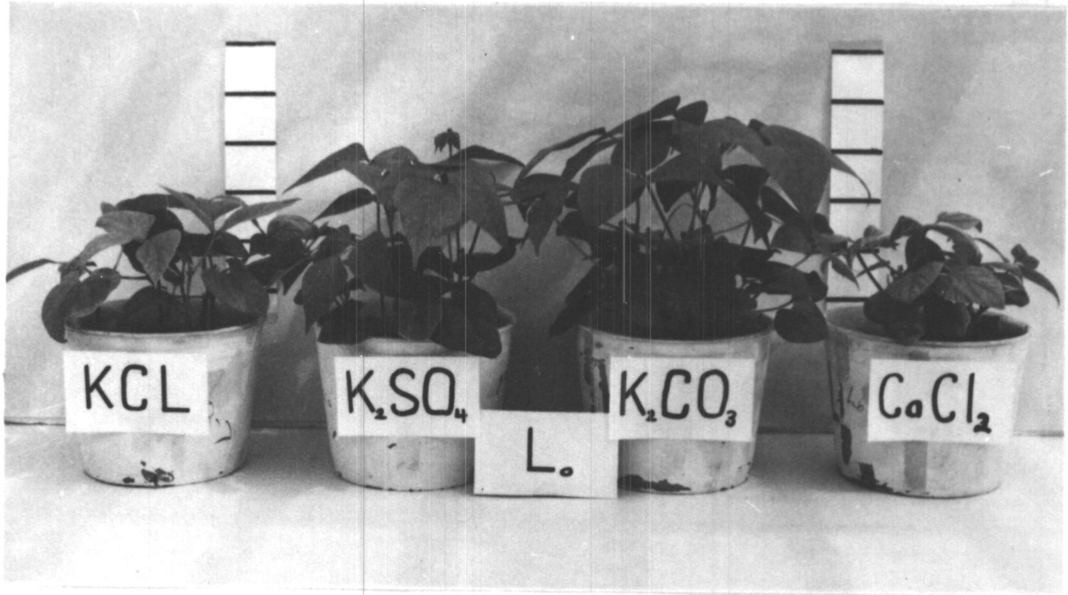


Figure 1. The Effect of the Different Sources of K and $CaCl_2$ on Plant Growth in the Absence of Lime. Greenhouse Experiment 1964.

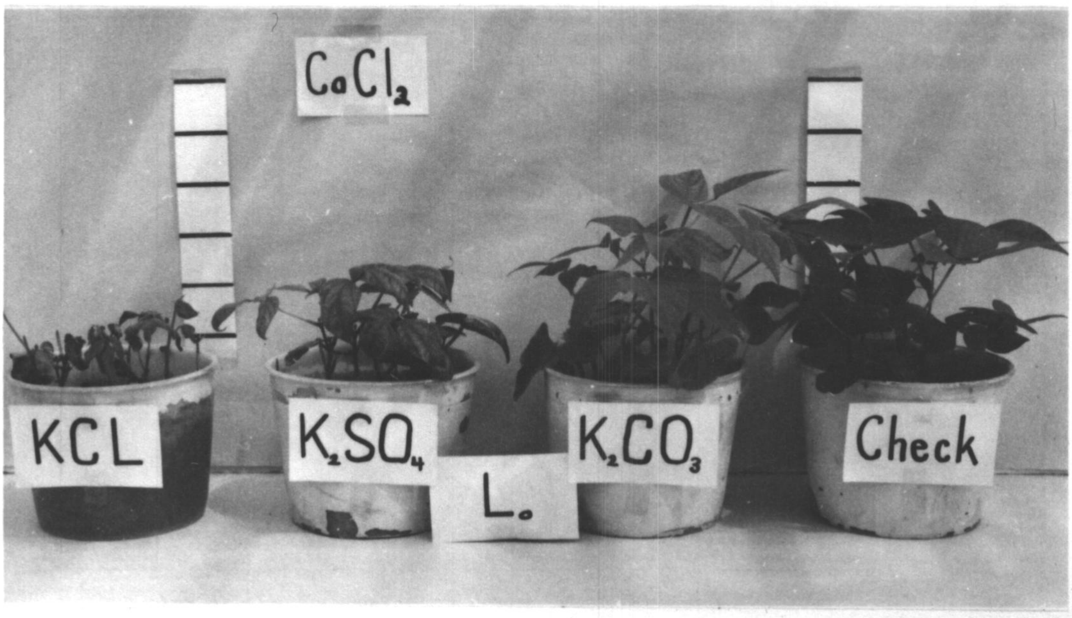


Figure 2. The Effect of Adding $CaCl_2$ to the Sources of K in the Absence of Lime. Greenhouse Experiment 1964.

lime although it is doubtful if much significance should be attached to this difference because of the abnormal growth resulting from the excessive amounts of Mn present. The addition of Cl, as KCl, $CaCl_2$, and KCl plus $CaCl_2$, in the presence of lime still showed a slight increase in the Mn content.

Potassium chloride was the only K fertilizer material that significantly increased the Mn content of the leaves in the absence of lime and $CaCl_2$. This increase was significantly higher when compared to either the check or to the other sources of K. The application of $K_2SO_4$ or $K_2CO_3$ decreased the Mn content in either the presence or absence of lime on the treatments where Cl had been applied. The decreases from $K_2SO_4$ or $K_2CO_3$ may have resulted from an antagonistic effect of K on the uptake of Mn or from a dilution effect.

The application of lime reduced the Mn content in all treatment combinations with the greatest reduction occurring on the treatments that had received an application of $CaCl_2$. All reductions were highly significant on the treatments that had received an application of Cl.

The application of K, regardless of source, increased the K content of the bean leaves when compared orthogonally with the treatments where K was not applied. In general, the K content of the bean leaves was the highest on the treatments that had received KCl. The majority of this increase could probably be attributed to the growth reduction that occurred on these treatments. The K content of the leaves was adequate on the $K_2SO_4$ and $K_2CO_3$ treatments to prevent K deficiency. Potassium deficiency symptoms were not present on any treatments at the time the experiment was terminated although a deficiency situation would have probably developed on the K zero treatments if the plants would have been allowed to mature.

The addition of $CaCl_2$ increased the K content of the bean leaves on all treatments that had not received an application of KCl. The detrimental effect of a Cl salt on plant growth has been previously discussed and the dilution effect may have been the principal factor responsible for this increase. The decrease in the K content of the leaves from the application of lime corresponded to an increase in the Ca content. All K content reductions from liming were significant in the presence of $CaCl_2$ except where $K_2CO_3$ was applied.

The application of K reduced the Ca content except where growth was abnormal on the Cl treatments. The Ca content of the bean leaves was increased by the application of $CaCl_2$ and lime. In general, the Ca content was slightly lower than the levels found in the field experiments.

The K and Ca relationships of this experiment may be summarized as follows: The addition of Ca, from either $CaCl_2$ or lime, increased the Ca content and probably decreased the K content of the bean leaves. In general, the addition of K increased the K content and decreased the Ca content. Similar Ca by K interactions have also been observed by Van Itallie (1938) and Lucas and Scarseth (1949).

The level of the other nutrients in the bean leaves would not indicate a deficiency or toxicity situation. All plant samples collected were analyzed for Mg and P. Selected samples were analyzed for Zn.

Leaves were dying and dropping from the more severely affected plants at the time that this experiment was terminated. This wide degree of senescence between treatments and the high levels of Mn in the plant leaves may have resulted in considerable variation in the chemical composition and attributed to a higher error term. However, there can be little doubt that Cl resulted in marked increases in the Mn content of the bean leaves in the absence of lime or that the application of lime reduced the Mn contents even where Cl had been applied.

Additional experiments were conducted during the summer of 1964 on different field experimental sites. One experiment was conducted with bush beans to provide additional information on the factors affecting the uptake of Mn under field conditions. Two additional experiments were carried out with sweet corn to substantiate the effect of Cl on the uptake of Mn.

Bush Bean Field Experiment-1964

Additional information concerning the effect of Cl on the uptake of Mn by bush beans under the influence of field conditions was the main objective of this experiment. The treatments were arranged so that orthogonal comparisons could be made between the two Cl sources, the two sources of K, the sources of $SO_4$, and the Ca salts.

Potassium was applied at the rates of 0, 50, and 100 pounds per acre from either the KCl or the $K_2SO_4$ source. One source of K was used in each 3 by 3 unit and the Ca salt of the anion of the other K source was used in the same unit, i. e., KCl and $CaSO_4$ were used in one unit and $K_2SO_4$ and $CaCl_2$ in the other unit. Three rates of Cl, 0, 45, and 90 pounds per acre, were applied from either the $CaCl_2$ or KCl source. The $K_2SO_4$ and $CaSO_4$ materials supplied 0, 20, and 40 pounds of S per acre. The amount of Ca that was supplied from either the $CaCl_2$ or the $CaSO_4$ source was considered to be non-significant although 25 and 50 pounds of Ca per acre were supplied by each material at the higher rates. The above treatment combinations are shown in Table 6.

Table 6. Treatment Combinations in the 1964 Bush Bean Field Experiment.

| Treatment No. | Materials and Rate (lbs/A) | | | |
|---|---|---|---|---|
| | KCl(K) | $CaSO_4$(S) | $K_2SO_4$(K) | $CaCl_2$(Cl) |
| 1 | - | - | - | - |
| 2 | 50 | - | - | - |
| 3 | 50 | 20 | - | - |
| 4 | 50 | 40 | - | - |
| 5 | 100 | - | - | - |
| 6 | 100 | 20 | - | - |
| 7 | 100 | 40 | - | - |
| 8 | - | 20 | - | - |
| 9 | - | 40 | - | - |
| 10 | - | - | - | - |
| 11 | - | - | 50 | - |
| 12 | - | - | 50 | 45 |
| 13 | - | - | 50 | 90 |
| 14 | - | - | 100 | - |
| 15 | - | - | 100 | 45 |
| 16 | - | - | 100 | 90 |
| 17 | - | - | - | 45 |
| 18 | - | - | - | 90 |

Thirty-five pounds of N per acre was broadcast as $NH_4NO_3$ before planting and an additional 35 pounds was banded as $(NH_4)_2SO_4$ at planting. In addition, 26 pounds of P per acre was banded on all treatments at planting as $Ca(H_2PO_4)_2$. Zero, 1.5, and 3 tons of hydrated lime per acre were applied and disced into the soil the previous fall.

Manganese toxicity symptoms did not appear as soon after seedling emergence as was observed in the previous bush bean experiments. The late appearance of the toxicity symptoms may have been partially accounted for by the unusually dry spring causing the amounts of available Mn to be lower than that in the other experiments at planting. However, toxicity symptoms were present on all treatments that had received an application of Cl before the appearance of the trifoliate leaves. All treatments that had received an application of lime were not severely affected and recovered very rapidly.

It soon became apparent that the design of the experiment was inadequate to account for the soil differences present. The replications, as designed, were arranged to account for the gradient between the soil series present. However, the location of a drainage ditch along one side of this experiment was instrumental in causing better drainage conditions in approximately one-half of the experimental plots. Treatments that were located on this side of the experiment had a lower level of Mn in the bean leaves and, in general, had larger vegetative growth than the corresponding treatments on the other side. A statistical evaluation of the treatments on the separate sides or the influence of the drainage ditch on plant growth could not be made because of the high degree of classification present in the basic design.

Chemical analyses were carried out on the first mature trifoliate leaves and the results are given in the Appendix. The following conclusions are probably justified from the treatment effects which were observed in this experiment.

The application of Cl from either the KCl or the $CaCl_2$ source increased the Mn content of the bean leaves in comparison to the treatments where Cl was not applied. The increase from the application of Cl as $CaCl_2$ was probably greater than the increase resulting from the application of a similar rate of Cl from the KCl source (Table 7).

The effect from an application of $SO_4$ appeared to be dependent upon the source. The Mn content was increased from the application of $CaSO_4$ and decreased when $K_2SO_4$ was applied.

The Mn content of the bean leaves was reduced from the application of lime in all treatment combinations (Table 7). The decrease was highly significant at the three ton rate.

Potassium deficiency symptoms developed on all treatments that did not receive an application of K. The severity of the deficiency symptoms increased with an increase in the lime rate corresponding to a decrease in the K content and to an increase in the Ca content of the bean leaves. Potassium deficiency symptoms developed on all plants that had less than 1.40% K in the bean leaves when sampled at this stage of growth. All levels of Ca found in the bean leaves are assumed to be adequate in this experiment.

The amounts of Zn, P, Fe, and Mg present in the leaves were also determined. The level of these nutrients appeared to be adequate for plants sampled at this stage of growth.

Table 7. Effect of Lime and Fertilizer Materials on the Mn Content of the Bush Bean Leaves in the 1964 Field Experiment.*

| KCl (lbs K/A) | Lime rate (T/A) | | CaSO$_4$ (lbs S/A) 0 | 20 | 40 | Ave. |
|---|---|---|---|---|---|---|
| | | | ppm Mn | | | |
| 0 | 0 | | 435 | 433 | 446 | |
| | 1.5 | | 292 | 306 | 259 | |
| | 3 | | 205 | 188 | 192 | |
| | | | | | | 306 |
| 50 | 0 | | 519 | 550 | 516 | |
| | 1.5 | | 304 | 399 | 391 | |
| | 3 | | 221 | 242 | 275 | |
| | | | | | | 379 |
| 100 | 0 | | 416 | 497 | 815 | |
| | 1.5 | | 292 | 304 | 381 | |
| | 3 | | 214 | 218 | 322 | |
| | | | | | | 383 |
| | | Ave. | 322 | 348 | 399 | |

| $K_2SO_4$ (lbs K/A) | Lime rate (T/A) | | $CaCl_2$ (lbs Cl/A) 0 | 45 | 90 | Ave. |
|---|---|---|---|---|---|---|
| | | | ppm Mn | | | |
| 0 | 0 | | 505 | 742 | 561 | |
| | 1.5 | | 258 | 441 | 383 | |
| | 3 | | 188 | 244 | 242 | |
| | | | | | | 393 |
| 50 | 0 | | 436 | 436 | 547 | |
| | 1.5 | | 305 | 382 | 368 | |
| | 3 | | 220 | 221 | 287 | |
| | | | | | | 355 |
| 100 | 0 | | 325 | 591 | 585 | |
| | 1.5 | | 206 | 328 | 359 | |
| | 3 | | 172 | 231 | 264 | |
| | | | | | | 340 |
| | | Ave. | 290 | 398 | 399 | |

* All values are the means of 4 replications.

## Sweet Corn Field Experiments 426 and 427-1964

These experiments were carried out to evaluate the effects of different sources of K on the uptake of Mn by sweet corn. The K treatments were applied in a randomized block design with a different order of randomization being used for each experiment.

KCl, $K_2SO_4$, and $K_2CO_3$ were banded at rates of 0, 50, and 100 pounds of K per acre at planting. Ninety pounds of N per acre was broadcast as $NH_4NO_3$ before planting. Sixty pounds of N as $(NH_4)_2SO_4$ and 52 pounds of P as $Ca(H_2PO_4)_2$ per acre were banded at planting on all treatments.

Early field observations indicated a reduction in plant growth and vigor where KCl had been applied as a source of K on both experiments. In general, the plant growth on all treatments was less on the 427 site than on the 426 site. Soil chemical analyses from the two sites indicated that the level of extractable Mn at planting time may have influenced the amount of growth on the experimental sites.

Chemical analyses data for the whole plant tops taken six weeks after planting are given in the Appendix. The Mn contents for the respective treatments are given in Table 8.

The application of KCl increased the Mn content of the plants in comparison with either the check or the other sources of K in

Table 8. Effect of Source of K on the Mn Content of the 1964 Sweet Corn Experiments. *

Experiment 426

| lbs K/A | Source of K | | |
|---|---|---|---|
| | KCl | $K_2SO_4$ | $K_2CO_3$ |
| | ppm Mn | | |
| 0 | 88 | 88 | 88 |
| 50 | 109 | 76 | 72 |
| 100 | 134 | 79 | 82 |

Experiment 427

| lbs K/A | Source of K | | |
|---|---|---|---|
| | KCl | $K_2SO_4$ | $K_2CO_3$ |
| | ppm Mn | | |
| 0 | 247 | 247 | 247 |
| 50 | 331 | 247 | 210 |
| 100 | 403 | 215 | 217 |

| Least Significant Differences (5% level) | Exp. 426 | Exp. 427 |
|---|---|---|
| Comparing 2 treatment means (ppm Mn) | 30 | 81 |

* All values are the means of 3 replications.

both experiments. This increase was highly significant at the 100 pound rate of K. The application of $K_2SO_4$ or $K_2CO_3$ did not significantly affect the Mn content in either experiment.

The application of K from all three sources resulted in a significant increase in the K content for both sweet corn experiments. This increase was highly significant for the KCl treatment on experiment 427 which may have been partially related to the reduction in growth which occurred on this treatment. All increases in K were significant at the 1% level in experiment 426.

Plants samples were analyzed for Ca, Mg, P, Zn, and Fe. The level of these nutrients appear to be adequate for corn plants at this stage of growth.

The level of Mn which is associated with toxicity in sweet corn is not available in the literature nor can it be evaluated in these two experiments. In most treatments there was some reduction of yield occurring with an increase in the Mn content. However, the effect of this increase cannot be evaluated satisfactorily because of a boron deficiency which delayed maturity and prevented filling of the ears. This problem also limited the valuation of increasing the K content.

# GENERAL DISCUSSION

The surface horizons of the soils used in this study normally contain numerous concretions of Fe and Mn oxides. They are also naturally acid and saturated from the winter rains for at least five months of the year. This waterlogged condition and the abundance of Mn oxides result in conditions which tend to restrict the growth of plants which are sensitive to high amounts of available Mn. The Mn oxides are reduced during the period of waterlogging and the half-cell reactions for the most likely reaction describing this reduction are as follows:

| Reaction | $E^o$(volts) | |
|---|---|---|
| $MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{++} + 2H_2O$ | +1.230 | (I) |
| $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ | -1.229 | (II) |
| $2MnO_2 + 4H^+ \rightleftharpoons 2Mn^{++} + 2H_2O + O_2$ | +0.001 | (III) |

All half-cell reactions and their standard oxidation potentials are from the Handbook of Chemistry and Physics, 40th Edition (1959). This reaction is very near to equilibrium in standard state conditions. However, the natural acidity of these soils, the relative abundance of the Mn concretions, and the decrease of the partial pressures of oxygen are all factors which tend to drive this reaction to the right. Oxygen can also be removed from the system by the metabolism of aerobic microorganisms and in pure cultures, where oxygen was absent, manganic-Mn has been shown to function as an electron acceptor (Hochster and Quastel, 1952).

The toxic nature of these soils was reduced by lime. The application of lime caused a marked reduction in the uptake of Mn, increased plant growth, and raised the soil pH from 5.0 to above 6.0. The main effect of liming was probably the reduction of the hydrogen ion concentration. This decrease would bring about a shift in the equilibrium of reaction III to the left under both aerobic and anaerobic conditions. There should be less build-up of available Mn during the period of waterlogging in the limed as compared to the unlimed soil, even though the reaction would still proceed to the right where there was a lack of available oxygen.

The additional Ca supplied from the lime may have had an antagonistic effect on Mn absorption. Calcium has been found by Williams and Vlamis (1957) to reduce the Mn content of the leaf tissue of barley. Löhnis (1960) has also reported that Mn injury could be reduced by fertilizing with Ca. It should be mentioned that their work was done with culture solutions and not under field conditions. However, this may be part of the mechanism by which lime reduces Mn uptake.

The naturally high level of Mn created an ideal situation in which Mn could become quite toxic if its availability were increased. Potassium chloride and $CaCl_2$ appeared to have this effect since the uptake of Mn was increased following the application of these materials. The effect was more apparent on the non-limed treatments again suggesting that the hydrogen ion concentration played an important role.

The effect of the Cl salt on the availability of Mn may be partially due to the high salt concentration in the fertilizer band. A high concentration of soluble salt would displace hydrogen ions from the exchange complex causing the concentration of the hydrogen ions to increase in the soil solution with a corresponding shift in the equilibrium of reaction III to the right. Manganous-Mn may also be increased in the soil solution through a similar exchange reaction. However, the major part of the Mn increase does not appear to be due to this reaction since the application of $K_2SO_4$ and $CaSO_4$, salts of a strong acid, or $K_2CO_3$ had essentially no effect on the uptake of Mn in the greenhouse nor in the field experiments.

Chloride may also be functioning as an electron donor in an oxidation-reduction reaction involving manganic-Mn in acid soils. In order to evaluate this possibility, it would be informative to look at the half-cell reactions of one of the possible reactions. The first half-cell reaction involves the reduction of manganic-Mn and the second the oxidation of Cl. All standard oxidation potentials are given for standard state conditions.

$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{++} + 2H_2O \qquad \underline{E^o\text{(volts)}} \;\; +1.230 \qquad (I)$$

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \qquad -1.358 \qquad (IV)$$

$$MnO_2 + 4H^+ + 2Cl^- \rightleftharpoons Mn^{++} + 2H_2O + Cl_2 \qquad -0.128 \qquad (V)$$

The emf of the combined reaction indicates that there is a slightly greater tendency for the Cl electrode to give off the electrons thus oxidizing manganous-Mn. However, the conditions existing in these soils might be displaced considerably from the standard state. The concentration of the Cl in the fertilizer band or immediately around a KCl or $CaCl_2$ particle could be quite high and may provide a considerable driving force for the reaction. The abundance of Mn in these soils makes it highly probable that a given fertilizer particle would be lying in close proximity to a Mn concretion. The concentration of hydrogen ions in solution would increase through an exchange reaction, creating an additional driving force. Also the concentration of chlorine would be very low because of its removal in the form of a gas or through a secondary reaction with water. In addition, $MnO_2$ and $H_2O$ should have little effect since they are normally very near to their standard states. From these considerations, it seems reasonable to conclude that Mn availability might be quite high in the vicinity of a Cl salt particle.

Another possibility of a Cl reaction would be the following half-cell reactions.

| | $E^o$(volts) | |
|---|---|---|
| $MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{++} + 2H_2O$ | +1.230 | (I) |
| $Cl^- + 4H_2O \rightleftarrows ClO_4^- + 8H^+ + 8e^-$ | -1.360 | (VI) |
| $4MnO_2 + 8H^+ + Cl^- \rightleftarrows 4Mn^{++} + ClO_4^- + 4H_2O$ | -0.130 | (VII) |

This would give a combined reaction with an emf of -0.130 volts which is only slightly more negative than the emf for reaction V. Additional oxidation-reduction reactions involving Cl and Mn have greater negative emf's and would, therefore, be less likely to occur in soils.

Sherman, McHargue, and Hageman (1943) have studied the influence of an addition of a halide salt on the oxidation equilibrium of Mn in soils. They found that the addition of KI to an acid soil, to which manganic-Mn had been added, increased the manganous-Mn and released iodine. This reaction may have occurred in the following way:

| | $E^o$(volts) | |
|---|---|---|
| $MnO_2 + 4H^+ + 2I^- \rightleftarrows Mn^{++} + 2H_2O + I_2$ | +0.694 | (VIII) |

The positive standard emf indicates that this reaction should occur spontaneously as written. The effect of a Br salt application was not clear from their results although the standard emf of an oxidation-reduction reaction would indicate that Br could also reduce manganic-Mn (reaction IX).

$$MnO_2 + 4H^+ + 2Br^- \rightleftharpoons Mn^{++} + 2H_2O + Br_2 \qquad \frac{E^o\text{(volts)}}{+0.165} \qquad \text{(IX)}$$

This reaction may be important in soils because compounds containing Br such as ethylene dibromide and methyl bromide have been applied to some soils as organic pesticides.

Plant samples were taken from each bean experiment at a different stage of growth for chemical analyses. The correct time for plant sampling does not appear to be a critical factor in the identification of a toxicity situation (Löhnis, 1960; Single and Bird, 1958). Manganese toxicity can be adequately identified by visual symptoms and toxic levels can be established from the analyses of the most recently matured trifoliate leaves. A content of 1,000 ppm has been suggested as a Mn toxicity level for the French bean (Fergus, 1954; Löhnis, 1951); however, the observations in this series of experiments would indicate that Mn toxicity may be present when 700-900 ppm of Mn are present in the trifoliate leaves. It should be mentioned that this toxic level is comparable only for plants grown under similar conditions because of the large number of factors affecting the availability and uptake of Mn.

# SUMMARY

The effect of fertilizer treatments on the uptake of Mn was investigated under field and greenhouse conditions. The experiments were conducted on poorly drained acid soils, classified as Planosols. Drainage was restricted on these soils because of a B horizon which becomes nearly impervious when wet thus creating ideal conditions for the reduction of Mn during the winter months. The soils contained numerous concretions of Fe and Mn oxides. The addition of S, K, N, and P has usually been necessary for maximum plant growth and yields on these soils.

Bush beans were used as the primary indicator plant and supporting evidence was obtained with sweet corn. Plant samples for chemical analyses consisted of the most recently matured trifoliate leaves from the field experiments and all trifoliate leaves from the greenhouse experiment. Whole plant tops were taken six weeks after planting from the sweet corn experiments.

The treatments were arranged in factorial combinations for all bush bean experiments. Hydrated lime was broadcast and disced into the soil at rates up to three tons per acre in the bush bean experiments. Sources of K and Cl were compared and Cl was applied at rates up to 90 pounds per acre. All treatments received a uniform application of N, P, and S and all fertilizer materials

applied at planting time were banded.

The effect of an application of K on the uptake of Mn was dependent upon the source of K. The application of KCl significantly increased the Mn content when compared to either the other sources of K or to the check treatment where no K was applied. This increase was observed in both the bush bean and the sweet corn experiments and, in general, was great enough to cause Mn toxicity in the bush bean experiments. The application of $K_2SO_4$ and $K_2CO_3$ had little or no effect on the uptake of Mn.

The application of Cl, as KCl or as $CaCl_2$, always increased the uptake of Mn. The increases were much greater on the unlimed than on the limed treatments. The application of $CaCl_2$ significantly increased the Mn content of the bean leaves on the zero lime treatments in the 1964 greenhouse experiment. All bean plants on the zero lime treatments that had received an application of Cl developed severe Mn toxicity symptoms in the 1963 field experiment and in the 1964 greenhouse experiment. The application of Cl also increased the Mn content in the 1964 field experiments.

The application of lime consistently reduced the Mn content with the greatest reduction occurring on the treatments where Cl had been applied. The Mn content of the bean leaves on the limed treatments was below suggested toxic levels and the plants did not show any toxicity symptoms at the time the leaf samples were taken for chemical analyses.

A toxicity level of Mn cannot be established for all conditions since the availability and uptake of Mn are controlled by a number of factors. However, the observations in this series of experiments would indicate that Mn toxicity may be present when 700-900 ppm Mn are present in the mature trifoliate leaves. It should be mentioned that this toxic level is comparable only for bean plants grown under similar conditions.

A mechanism has been presented to explain the effect of the Cl salt on the availability of Mn. In this reaction Cl has acted as an electron donor causing a chemical reduction of the manganic-Mn oxides to the plant available manganous-Mn ion.

These experiments offer a possible explanation for some of the reductions in yields that have been observed from the band applications of KCl. They also emphasize the importance of evaluating the effects of individual treatments on the whole range of elements present in the soil that can have beneficial as well as detrimental effects on plant growth.

# BIBLIOGRAPHY

1. Adams, F. and J. I. Weir. Manganese toxicity and soil acidity in relation to crinkle leaf of cotton. Soil Science Society of America Proceedings 21:305-308. 1957.

2. Alban, L. A. and Mildred Kellogg. Methods of soil analysis as used in the Oregon State College soil testing laboratory. Corvallis, 1959. 9 p. (Oregon. Agricultural Experiment Station. Miscellaneous Paper No. 65)

3. Barton, C. J. Photometric analysis of phosphate rock. Analytical Chemistry 20:1068-1073. 1948.

4. Berger, K. C. and G. C. Gerloff. Manganese toxicity of potatoes in relation to strong soil acidity. Soil Science Society of America Proceedings 12:310-314. 1947.

5. Bortner, C. E. Toxicity of manganese to turkish tobacco in acid Kentucky soils. Soil Science 39:15-33. 1935.

6. Christensen, P. D., S. J. Toth, and F. E. Bear. The status of soil manganese as influenced by moisture, organic matter, and pH. Soil Science Society of America Proceedings 15:279-282. 1950.

7. Conner, S. D. Factors affecting manganese availability in soils. Journal of the American Society of Agronomy 24:726-733. 1932.

8. Dhein, A. The effect of phosphate and potash fertilizing on yields, botanical composition, and manganese injury in grassland on water-logged soils. Zeitschrift für Acker-und Pflanzenbau 116:75-87. 1962. (Abstracted in Soils and Fertilizers 26:no. 942. 1963)

9. Fergus, I. F. Manganese toxicity in an acid soil. Queensland Journal of Agricultural Science 11:15-27. 1954.

10. Foy, C. D. Toxic factors in acid soils of the Southeastern United States as related to the response of alfalfa to lime. Fayetteville, 1964. 25 p. (Arkansas. Agricultural Experiment Station. Production Research Report No. 80)

11. Fried, M. and M. Peech. The comparative effects of lime and gypsum upon plants grown on acid soils. Journal of the American Society of Agronomy 38:614-623. 1946.

12. Fujimoto, C. K. and G. D. Sherman. Behavior of manganese in the soil and the manganese cycle. Soil Science 66:131-145. 1948.

13. Fujimoto, C. K. and G. D. Sherman. The effect of drying, heating, and wetting on the level of exchangeable manganese in Hawaiian soils. Soil Science Society of American Proceedings 10:107-112. 1945.

14. Funchess, M. J. The development of soluble manganese in acid soils as influenced by certain nitrogenous fertilizers. Auburn, 1918. 78 p. (Alabama. Agricultural Experiment Station Bulletin 201)

15. Garey, C. L. and S. A. Barber. Evaluation of certain factors involved in increasing manganese availability with sulfur. Soil Science Society of America Proceedings 16:173-175. 1952.

16. Hawkins, A., B. A. Brown, and E. J. Rubin. Extreme case of soil toxicity to potatoes on a formerly productive soil. American Potato Journal 28:563-577. 1951.

17. Hochster, R. M. and J. H. Quastel. Manganese dioxide as a terminal hydrogen acceptor in the study of respiratory systems. Archives of Biochemistry and Biophysics 36:132-146. 1952.

18. Hodgman, C. D., R. C. Weast, and S. M. Selby (eds.) Handbook of chemistry and physics. 40th ed. Cleveland, Chemical Rubber Publishing Company, 1959. 3456 p.

19. Hortenstine, C. C. and H. Y. Ozaki. The effect of liming on the availability of iron, manganese and on soil calcium and the pH on Darie fine sand. Soil and Crop Science Society of Florida Proceedings 21:44-50. 1961.

20. Jacobson, H. G. M. and T. R. Swanback. Manganese content of certain Connecticut soils and its relation to the growth of tobacco. Journal of the American Society of Agronomy 24:237-245. 1932.

21. Lamb, J. G. D. A case of manganese toxicity affecting a cold house tomato crop. Irish Journal of Agricultural Research 1(1):17-20. 1961.

22. Leeper, G. W. and R. J. Swaby. The oxidation of manganous compounds by microorganisms in the soil. Soil Science 49:163-169. 1940.

23. Lindsay, W. L. and H. F. Stephenson. Nature of the reactions of monocalcium phosphate monohydrate in soils: I. The solution that reacts with the soil. Soil Science Society of America Proceedings 23:12-18. 1959.

24. Lingle, J. C., R. H. Sciaroni, B. Lear, and J. R. Wight. The effect of soil liming and fumigation on the manganese content of brussels sprouts leaves. Proceedings of the American Society of Horticultural Science 78:310-318. 1961.

25. Löhnis, M. P. Effect of magnesium and calcium supply on the uptake of manganese by various crop plants. Plant and Soils 12:339-376. 1960.

26. Löhnis, M. P. Manganese toxicity in field and market garden crops. Plant and Soils 3:193-222. 1951.

27. Lucas, R. E. and G. D. Scarseth. Potassium, calcium, and magnesium relationships in plants. Journal of the American Society of Agronomy 39:887-896. 1947.

28. Mann, H. B. Availability of manganese and iron as affected by application of calcium and magnesium carbonates to the soil. Soil Science 30:117-141. 1930.

29. Mann, P. J. G. and J. H. Quastel. Manganese metabolism in soil. Nature 158:154-156. 1946.

30. McCool, M. M. Effects of light intensity on the manganese content of plants. Contributions from the Boyce Thompson Institute 7:427-437. 1935.

31. McHargue, J. S. The role of manganese in plants. Journal of the American Chemical Society 44:1592-1598. 1922.

32. Mederski, H. J. and J. H. Wilson. Effect of soil temperature and moisture on manganese absorption by soybean plants. Soil Science Society of America Proceedings 19:461-464. 1955.

33. Messing, J. H. L. Manganese toxicity. Annual Report of the Glasshouse Crops Research Institute, Littlehampton, England, 1960:54-55. 1960.

34. Morris, H. D. The soluble manganese content of acid soils and its relation to the growth and manganese content of sweet clover and lespedeza. Soil Science Society of America Proceedings 13:362-371. 1948.

35. Page, E. R., E. K. Schofield-Plamer, and A. J. MacGregor. Studies in soil and plant manganese: IV. Superphosphate fertilization and manganese content of young oat plants. Plant and Soil 19:255-264. 1963.

36. Pearsall, W. H. The investigation of wet soils and its agricultural implications. Empire Journal of Experimental Agricultural 18:289-298. 1950.

37. Piper, C. S. The availability of manganese in the soil. Journal of Agricultural Science 21:762-779. 1931.

38. Rich, G. I. Soil factors effecting the availability of manganese for peanuts. Virginia Journal of Science (n. s.) 6:229-230. 1955.

39. Sanchez, C. and E. J. Kamprath. Effect of liming and organic matter on the availability of native and applied manganese. Soil Science Society of America Proceedings 23:302-304. 1959.

40. Schmehl, W. R., M. Peech, and R. Bradfield. Causes of poor growth of plants on acid soils and beneficial effects of liming: I. Evaluation of factors responsible for acid-soil injury. Soil Science 70:393-410. 1950.

41. Sherman, G. D. and C. K. Fujimoto. The effect of the use of lime, soil fumigants, and mulch on the solubility of manganese in Hawaiian soils. Soil Science Society of America Proceedings 11:206-210. 1946.

42. Sherman, G. D., J. S. McHargue, and R. H. Hageman. The influence of halides on the oxidation of manganese in soils. Soil Science 56:127-134. 1943.

43. Single, W. V. and I. F. Bird. The mobility of manganese in the wheat plant: II. Redistribution in relation to concentration and chemical state. Annals of Botany 22:489-502. 1958.

44. Snider, H. J. Manganese in some Illinois soils and crops. Soil Science 56:187-195. 1943.

45. Steckel, J. E., B. R. Bertamson, and A. J. Ohlrogge. Manganese nutrition of plants as related to applied superphosphate. Soil Science Society of America Proceedings 13:108-111. 1948.

46. Sutton, G. D. and E. G. Hallsworth. Studies on the nutrition of forage legumes: I. The toxicity of low pH and high manganese supply to lucerne, as affected by climatic factors and calcium supply. Plant and Soil 9:305-317. 1958.

47. Van Itallie, T. H. B. Cation equilibrium in plants in relation to the soil. Soil Science 46:175-186. 1938.

48. Williams, D. E. and J. Vlamis. Manganese and boron toxicities in standard culture solutions. Soil Science Society of America Proceedings 21:205-209. 1957.

49. York, E. T., Jr., R. Bradfield, and M. Peech. Influence of lime and potassium on yield and cation composition of plants. Soil Science 77:53-63. 1954.

50. Zende, G. K. The effect of air-drying on the level of extractable manganese in the soil. Journal of Indian Society of Soil Science 2(1):55-61. 1954. (Abstracted in Soils and Fertilizers 17:no. 2337. 1954)

# APPENDICES

Appendix Table 1a. Chemical Composition of the Mature Trifoliate Leaves and Yield of Beans. Bush Bean Field Experiment 1963. Means of 4 Replications.

| Treatment* N | P | K | Lime rate T/A | Yield T/A | Mn ppm | K % | Ca % | P % | Mg % | Zn ppm |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 0 | 0 | 5.16 | 798 | 1.05 | 1.42 | 0.354 | 0.548 | 29 |
| | | | 3 | 3.61 | 528 | 0.96 | 1.80 | 0.341 | 0.600 | 20 |
| 1 | 2 | 1 | 0 | 2.61 | 1190 | 2.06 | 1.68 | 0.347 | 0.535 | 41 |
| | | | 3 | 7.02 | 772 | 1.82 | 1.99 | 0.319 | 0.480 | 25 |
| 1 | 2 | 2 | 0 | 2.05 | 1048 | 2.03 | 1.69 | 0.323 | 0.511 | 40 |
| | | | 3 | 6.17 | 610 | 2,14 | 1.95 | 0.312 | 0.475 | 27 |
| 1 | 0 | 2 | 0 | 2.61 | 745 | 1.79 | 1.57 | 0.315 | 0.489 | 33 |
| | | | 3 | 5.38 | 530 | 2.09 | 2.04 | 0.281 | 0.533 | 26 |
| 1 | 1 | 2 | 0 | 2.46 | 988 | 1.92 | 1.67 | 0.321 | 0.514 | 38 |
| | | | 3 | 6.02 | 702 | 2.20 | 2.00 | 0.292 | 0.459 | 27 |

* Fertilizer rates: N at 50 pounds per acre, P at 0, 26, and 52 pounds per acre, and K at 0, 50, and 100 pounds per acre.

Appendix Table 1b. Chemical Composition of Whole Plant Tops. Supplemental Bush Bean Experiment 1963. One Replication.

| Treatment* N | P | K | Lime rate T/A | Mn ppm | K % | Ca % | P % | Mg % | Zn ppm |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | KCl | 0 | 1730 | 6.20 | 2.10 | 0.620 | 0.515 | 32 |
| | | | 3 | 1120 | 5.85 | 1.96 | 0.585 | 0.400 | 25 |
| 1 | 2 | KCl | 0 | 2450 | 2.85 | 1.74 | 0.274 | 0.615 | 63 |
| | | | 3 | 540 | 2.74 | 1.85 | 0.285 | 0.435 | 78 |
| 1 | 1 | $K_2SO_4$ | 0 | 1270 | 4.75 | 1.62 | 0.475 | 0.620 | 37 |
| | | | 3 | 720 | 6.25 | 1.92 | 0.625 | 0.750 | 42 |
| 1 | 2 | $K_2SO_4$ | 0 | 1900 | 3.07 | 1.58 | 0.307 | 0.550 | 34 |
| | | | 3 | 500 | 6.45 | 1.70 | 0.645 | 0.485 | 38 |

* Fertilizer rates: N at 50 pounds per acre, P at 26 and 52 pounds per acre, and K at 50 pounds per acre.

Appendix Table 2. Chemical Composition of All Trifoliate Leaves. Bush Bean Greenhouse Experiment 1964. Means of 3 Replications.

| Treatment | Lime rate T/A | Mn ppm | K % | Ca % | P % | Mg % | Fe ppm | Zn ppm |
|---|---|---|---|---|---|---|---|---|
| Check | 0 | 300 | 0.74 | 0.61 | 0.219 | 0.289 | 92 | -- |
| | 3 | 68 | 0.79 | 1.29 | 0.279 | 0.358 | 103 | -- |
| KCl | 0 | 1165 | 3.07 | 1.13 | 0.349 | 0.290 | 161 | 42 |
| | 3 | 154 | 3.64 | 1.80 | 0.383 | 0.286 | 144 | 40 |
| $K_2SO_4$ | 0 | 258 | 1.89 | 0.52 | 0.245 | 0.213 | 74 | 30 |
| | 3 | 110 | 1.75 | 0.80 | 0.217 | 0.201 | 78 | 19 |
| $K_2CO_3$ | 0 | 467 | 1.66 | 0.50 | 0.193 | 0.231 | 91 | 24 |
| | 3 | 120 | 2.17 | 1.43 | 0.248 | 0.267 | 108 | 20 |
| $CaCl_2$ | 0 | 2192 | 2.01 | 1.55 | 0.442 | 0.353 | 136 | 42 |
| | 3 | 231 | 1.05 | 1.91 | 0.375 | 0.378 | 109 | 26 |
| KCl + $CaCl_2$ | 0 | 2125 | 3.30 | 1.71 | 0.335 | 0.333 | 138 | -- |
| | 3 | 393 | 2.77 | 1.92 | 0.318 | 0.267 | 104 | -- |
| $K_2SO_4$ + $CaCl_2$ | 0 | 1783 | 3.25 | 1.48 | 0.289 | 0.286 | 123 | -- |
| | 3 | 90 | 2.01 | 1.53 | 0.253 | 0.224 | 105 | -- |
| $K_2CO_3$ + $CaCl_2$ | 0 | 990 | 2.33 | 1.00 | 0.235 | 0.256 | 96 | -- |
| | 3 | 89 | 2.42 | 1.23 | 0.242 | 0.217 | 120 | -- |

Appendix Table 3. Chemical Composition of the First Mature Trifoliate Leaves. Bush Bean Field Experiment 1964. Means of 4 Replications.

| Treatment* KCl | $CaSO_4$ | Lime rate T/A | Mn ppm | K % | Ca % | P % | Mg % | Zn ppm | Fe ppm |
|---|---|---|---|---|---|---|---|---|---|
| - | - | 0 | 435 | 1.33 | 1.31 | 0.53 | 0.559 | 41 | 303 |
| | | 1.5 | 292 | 1.27 | 1.63 | 0.50 | 0.618 | 43 | 339 |
| | | 3 | 205 | 1.23 | 1.96 | 0.53 | 0.609 | 35 | 343 |
| 50 | - | 0 | 519 | 2.35 | 1.32 | 0.52 | 0.428 | 38 | 394 |
| | | 1.5 | 304 | 2.30 | 1.47 | 0.46 | 0.429 | 40 | 431 |
| | | 3 | 221 | 2.63 | 1.86 | 0.48 | 0.473 | 32 | 484 |
| 50 | 20 | 0 | 550 | 2.11 | 1.47 | 0.51 | 0.470 | 40 | 468 |
| | | 1.5 | 399 | 2.41 | 1.68 | 0.51 | 0.433 | 38 | 553 |
| | | 3 | 242 | 2.40 | 1.61 | 0.47 | 0.413 | 32 | 473 |
| 50 | 40 | 0 | 516 | 2.49 | 1.52 | 0.56 | 0.442 | 41 | 285 |
| | | 1.5 | 391 | 2.48 | 1.70 | 0.52 | 0.454 | 41 | 380 |
| | | 3 | 275 | 2.46 | 1.86 | 0.49 | 0.490 | 36 | 409 |
| 100 | - | 0 | 416 | 2.16 | 1.40 | 0.34 | 0.404 | 38 | 636 |
| | | 1.5 | 292 | 2.53 | 1.60 | 0.38 | 0.407 | 32 | 663 |
| | | 3 | 214 | 2.56 | 1.92 | 0.45 | 0.434 | 30 | 484 |
| 100 | 20 | 0 | 497 | 2.61 | 1.43 | 0.46 | 0.405 | 36 | 499 |
| | | 1.5 | 304 | 2.33 | 1.70 | 0.43 | 0.439 | 33 | 468 |
| | | 3 | 218 | 2.92 | 1.89 | 0.46 | 0.415 | 31 | 381 |
| 100 | 40 | 0 | 815 | 2.04 | 1.58 | 0.44 | 0.432 | 34 | 658 |
| | | 1.5 | 381 | 2.64 | 1.54 | 0.47 | 0.416 | 37 | 548 |
| | | 3 | 322 | 2.85 | 1.84 | 0.47 | 0.425 | 32 | 550 |
| - | 20 | 0 | 433 | 1.25 | 1.34 | 0.56 | 0.582 | 40 | 341 |
| | | 1.5 | 306 | 1.15 | 1.60 | 0.52 | 0.616 | 46 | 364 |
| | | 3 | 188 | 1.25 | 1.85 | 0.60 | 0.615 | 37 | 408 |
| - | 40 | 0 | 446 | 1.26 | 1.31 | 0.57 | 0.592 | 41 | 374 |
| | | 1.5 | 259 | 1.16 | 1.69 | 0.52 | 0.665 | 43 | 334 |
| | | 3 | 192 | 1.07 | 2.06 | 0.56 | 0.706 | 38 | 409 |
| - | - | 0 | 505 | 1.25 | 1.39 | 0.53 | 0.566 | 41 | 479 |
| | | 1.5 | 258 | 1.07 | 1.45 | 0.51 | 0.630 | 40 | 480 |
| | | 3 | 188 | 1.23 | 1.60 | 0.58 | 0.612 | 48 | 441 |

* Pounds per acre of K and S respectively.

Appendix Table 3 (continued).

| Treatment* $K_2SO_4$ | Treatment* $CaCl_2$ | Lime rate T/A | Mn ppm | K % | Ca % | P % | Mg % | Zn ppm | Fe ppm |
|---|---|---|---|---|---|---|---|---|---|
| 50 | - | 0 | 436 | 2.39 | 1.22 | 0.60 | 0.460 | 42 | 321 |
| | | 1.5 | 305 | 2.10 | 1.39 | 0.51 | 0.450 | 41 | 356 |
| | | 3 | 220 | 2.64 | 1.54 | 0.52 | 0.459 | 37 | 345 |
| 50 | 45 | 0 | 436 | 2.38 | 1.42 | 0.52 | 0.420 | 41 | 383 |
| | | 1.5 | 382 | 2.36 | 1.75 | 0.50 | 0.453 | 39 | 405 |
| | | 3 | 221 | 2.39 | 1.69 | 0.49 | 0.436 | 39 | 491 |
| 50 | 90 | 0 | 547 | 2.04 | 1.62 | 0.38 | 0.415 | 36 | 505 |
| | | 1.5 | 368 | 2.70 | 1.75 | 0.51 | 0.413 | 35 | 533 |
| | | 3 | 287 | 2.49 | 1.76 | 0.47 | 0.418 | 31 | 425 |
| 100 | - | 0 | 325 | 2.75 | 1.21 | 0.50 | 0.430 | 37 | 435 |
| | | 1.5 | 206 | 2.73 | 1.17 | 0.49 | 0.411 | 40 | 365 |
| | | 3 | 172 | 2.73 | 1.39 | 0.47 | 0.443 | 36 | 379 |
| 100 | 45 | 0 | 591 | 1.96 | 1.48 | 0.49 | 0.501 | 39 | 478 |
| | | 1.5 | 328 | 2.67 | 1.41 | 0.48 | 0.394 | 38 | 672 |
| | | 3 | 231 | 2.98 | 1.72 | 0.45 | 0.439 | 32 | 676 |
| 100 | 90 | 0 | 585 | 2.21 | 1.54 | 0.40 | 0.451 | 36 | 565 |
| | | 1.5 | 359 | 2.71 | 1.74 | 0.46 | 0.405 | 34 | 542 |
| | | 3 | 264 | 2.73 | 1.90 | 0.48 | 0.428 | 32 | 393 |
| - | 45 | 0 | 742 | 1.44 | 1.62 | 0.58 | 0.579 | 43 | 358 |
| | | 1.5 | 441 | 1.10 | 1.91 | 0.54 | 0.622 | 42 | 383 |
| | | 3 | 244 | 1.40 | 2.30 | 0.53 | 0.618 | 37 | 323 |
| - | 90 | 0 | 561 | 1.46 | 1.95 | 0.40 | 0.542 | 34 | 602 |
| | | 1.5 | 383 | 1.38 | 2.34 | 0.47 | 0.565 | 38 | 548 |
| | | 3 | 242 | 1.56 | 2.12 | 0.61 | 0.553 | 35 | 373 |

* Pounds per acre of K and Cl respectively.

Appendix Table 4. Chemical Composition of Whole Plants Tops. Sweet Corn Field Experiments 426 and 427-1964. Means of 3 Replications.

| Material | #K/A | Mn ppm | K % | Ca % | P % | Mg % | Fe ppm | Zn ppm |
|---|---|---|---|---|---|---|---|---|
| | | | | Experiment 426 | | | | |
| - | 0 | 88 | 1.87 | 0.462 | 0.475 | 0.397 | 248 | 54 |
| KCl | 50 | 109 | 3.37 | 0.460 | 0.436 | 0.328 | 525 | 61 |
| | 100 | 134 | 3.91 | 0.455 | 0.400 | 0.321 | 278 | 56 |
| $K_2SO_4$ | 50 | 76 | 3.18 | 0.424 | 0.520 | 0.393 | 280 | 53 |
| | 100 | 79 | 3.73 | 0.425 | 0.403 | 0.330 | 325 | 48 |
| $K_2CO_3$ | 50 | 72 | 3.08 | 0.418 | 0.445 | 0.291 | 185 | 52 |
| | 100 | 82 | 3.80 | 0.375 | 0.395 | 0.270 | 293 | 50 |
| | | | | Experiment 427 | | | | |
| - | 0 | 247 | 1.94 | 0.420 | 0.521 | 0.436 | 300 | 52 |
| KCl | 50 | 331 | 3.15 | 0.353 | 0.423 | 0.326 | 305 | 44 |
| | 100 | 403 | 3.49 | 0.431 | 0.428 | 0.371 | 235 | 59 |
| $K_2SO_4$ | 50 | 247 | 2.27 | 0.354 | 0.420 | 0.339 | 348 | 48 |
| | 100 | 215 | 2.87 | 0.371 | 0.410 | 0.325 | 487 | 54 |
| $K_2CO_3$ | 50 | 210 | 2.97 | 0.356 | 0.400 | 0.347 | 272 | 42 |
| | 100 | 217 | 3.37 | 0.375 | 0.420 | 0.337 | 420 | 57 |