RELATION OF SOIL REACTION TO AVAILABILITY OF MAGNESIUM FROM DIFFERENT SOURCES

Thesis for the Degree of M. S.
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Miguel A. Gonzalez

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by

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AN ABSTRACT OF A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

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MAGNESIUM FROM DIFFERENT SOURCES

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Greenhouse and laboratory studies were conducted with two Michigan soils. The availability of magnesium from dolomite, sulfate of potash-magnesia and epsom salts was studied in relation to soil reaction.

Liming an acid soil decreased the ammonium acetate extractable magnesium from dolomite. It was theoretically proposed that dolomite dissociation is directly proportional to the square of the hydrogen ion concentration and inversely proportional to the carbon dioxide pressure of the soil air.

In general, dolomite applications increased the pH in the soil, while sulfate of potash-magnesia and epsom salts decreased soil pH. Ammonium acetate extractable magnesium did not give a true measure of the magnesium status of either the original soils or the soil to which soluble magnesium had been applied. Either 0.1 N sodium chloride or 0.1 N alpha-naphthylamine-HCl removed larger quantities of magnesium from the samples studied than did 1.0 N ammonium acetate. This suggests that the magnesium not removed by ammonium acetate is trapped in the interlayer spaces of vermiculite, montmorillonite and chlorite.

Yield response of barley plants was related to the sodium chloride extractable magnesium in the soils. Magnesium fertilization significantly increased the magnesium content in plants grown on the low magnesium soil.

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INTRODUCTION

Magnesium is one of the essential elements in the growth of plants. It is widely distributed in the earth's crust as the carbonate, silicate, sulfate, and chloride. Two and one-half percent of the lithosphere is magnesium which places it seventh in order of abundance of the elements.

Aluminosilicate minerals such as biotite, augite, hornblende, and montmorillonite contain varying quantities of magnesium. In regions of limited rainfall, dolomite, magnesite (M_gCO_3), and epsomite ($M_gSO_4 . H_2O$) may constitute appreciable sources of this element.

In general, mineral soils contain a sufficient supply of available magnesium for most of the crops commonly grown. Plants obtain their magnesium supplies from the primary minerals in soils or from magnesium ion present in exchangeable form on the surface of finer soil particles.

Although the magnesium ion concentration usually exceeds that of potassium on the exchange complex of most soils in the humid region, it is normally lower than calcium and potassium in percent composition of plant ash.

Magnesium has at least two general functions in the plant: (1) as a structural constituent of the chlorophyll molecule (66), and (2) as an activator for many enzyme reactions involving phosphate transfer and carbohydrate development (32). Although the chlorophyll molecule contains 2.7 percent magnesium, this is only a small part of the total magnesium content of leaves.

Conditions which are generally associated with the development of magnesium deficiencies are low pH (5.5 or lower), sandy, highly leached soils, and heavy fertilization, especially with materials which are lacking in magnesium and are high in potassium.

In 1956, Satyapal (48) studied thirteen representative Michigan soil types. Greenhouse studies on the surface soils indicated that there was little possibility of magnesium deficiency occurring in crops of soybeans, millet and wheat. However, very little information on field response of crops to supplemental magnesium had been reported. It was also known that some soils appeared to be low in exchangeable magnesium.

Field studies on thirty-seven different soil types of Michigan were made by Tobin (53) from which he concluded that the application of soluble magnesium on most agronomic crops on the fine textured soils of Michigan was not necessary at that time (1960). However, results obtained in the central testing laboratory at Michigan State University would indicate that some response to magnesium fertilization may be expected in many of the coarse textured soils in Michigan.

The objective of this study is to evaluate the effect of pH in two coarse textured soils of Michigan as a factor which influences the magnesium uptake and plant yields when three magnesium fertilizers, namely, dolomitic limestone, sulfate of potash-magnesia and epsom salts, are used under greenhouse conditions.

REVIEW OF LITERATURE

Magnesium Content of Soils

In recent times considerable attention has been focussed on magnesium fertilization of various agricultural soils. The results of many of these experiments appear to be contradictory, indicating that several factors may be involved in magnesium fertilization.

When Loew (28) formulated his theory of the optimum calcium-magnesium ratio in the soil for plant growth, it was at first thought that magnesium fertilization might be especially needed on soils neutral or alkaline in reaction. However, very sandy soils and highly weathered soils of the tropics have been found to contain the least magnesium. In such soils, values as low as 0.2 percent magnesium oxide are not uncommon. In contrast, as high as 4 to 5 percent magnesium oxide have been reported in some of the brown, chestnut, and black soils of semiarid parts of the world (4).

In a study made by Bear *et al.* (6) of New Jersey soils, it was found that the total magnesium content ranged from less than 0.02 percent to as much as one percent. After several years of study of the cation content of New Jersey soils in relation to crop needs, it was suggested that the exchange complex of the "ideal soil" should be occupied by about 20 percent hydrogen, 65 percent calcium, 10 percent magnesium, and 5 percent potassium on an equivalent basis (5). Crop response from magnesium application was obtained whenever the amount of the element on the exchange complex was below 6 percent (44). In Missouri, Graham, et al. (16) suggested that a response to magnesium fertilization could be expected when the percent magnesium saturation of soils was below 10 percent of the exchangeable cations.

Analyses of several Michigan soils by Lawton (26) showed that exchangeable magnesium ranged from 0.23 to 2.21 milliequivalents per 100 grams of soil; and Tobin (53) in his study of thirty-seven different soil types of Michigan found that over one-half of the coarse textured soil contained less than 5 percent magnesium on the exchange complex while the fine textured soils generally had a magnesium saturation percentage of ten to twenty.

Bear (6) states that at a low pH the magnesium uptake by plants is more closely related to available supplies than at a higher pH, because hydrogen replaces magnesium on the colloids rendering it more available to plants.

On the basis of their experimental evidence, Bower and Truog (8), and Babcock et al. (2) have postulated that in neutral soils, calcium and magnesium form monohydroxyl ions, that is $CaOH^{+}$, and $MgOH^{+}$, and are then absorbed as monovalent ions.

There are indications that magnesium may become deficient in heavier textured soils. Albrecht et al. (1) have noted that on Missouri soils when productivity is increased with lime and fertilizers, the percent of magnesium saturation of the soil colloids was decreased.

Magnesium Content In Plants

Magnesium occurs in plants in combined forms in chlorophyll and in protoplasm, as well as in soluble form in cell sap (6). It is closely associated with phosphorus assimilation (46) and protein production. A high content of magnesium in a given plant implies youth, active nuclear cell division, rapid growth, and a high percent of protein (30, 66).

According to the investigations of Willstätter and Stoll (62), as reported by Meyer and Anderson (34), the chlorophyll content of leaves is seldom the limiting factor in photosynthesis of vascular plants. External factors such as light and carbon dioxide concentration of the air, or internal factors other than chlorophyll generally become limiting first. There appears to be no quantitative relationship between chlorophyll content and photosynthesis in leaves.

Javillier and Goudshaux (22), as reported by Zimmerman (66), concluded that chlorophyll magnesium represents only a small fraction of the total leaf magnesium in twenty-two plants which they examined. Carolus (11) reported that only ten percent of the magnesium in the green part of the potato plant was found in chlorophyll. Garner _et al_. (15) found that in order to prevent chlorophyll breakdown in tobacco, the total magnesium content of the leaf must be much greater than the quantity present in the chlorophyll. McMurtrey (33) reports that when the magnesium supply becomes inadequate in tobacco, the chlorophyll pigment is the first to suffer. Apparently the non-chlorophyll role of magnesium has priority in the magnesium supply of the plant.

Foy and Barber (14) found that magnesium deficiency symptoms in corn were not accompanied by reduction in yield on two acid Indiana soils and stated that the supply of magnesium in deficient plants was adequate for the nonchlorophyll role, but not for normal chlorophyll production.

Calcium-Magnesium Ratios in Soils and Plants

The hypothesis of Loew (28) that a definite calcium-magnesium ratio in the soil is required for optimum growth of each crop has prompted considerable discussion and research. A calcium-magnesium ratio of 5 to 4 was thought to be detrimental to plant growth. The emphasis on the calcium-magnesium ratio was also supported by Novak (40) after an exhaustive survey of the European literature on the subject. However, Lipman (27) and Moser (36) came to the conclusion that there is no "best" calcium-magnesium ratio in the soil for any crop. Some years later, Hunter _et al_. (20) stated that a calcium-magnesium ratio of 6.5 to 1 in the soil was best for optimum plant growth. Vlamis (58) demonstrated that yields of lettuce and barley were dependent upon calcium saturation up to a level of about twenty percent, above which no further response to calcium was obtained. He also indicated that the principal reason for the infertility of serpentine soils is their low calcium-magnesium ratio or low calcium saturation. Robinson _et al_. (45) concluded that a high magnesium content in some infertile soils favored the toxic influence of chromium, nickel, and perhaps cobalt. Hunter (19) did not find any influence on the yield of alfalfa when the calcium-magnesium ratio varied from 1 to 4 to 32 to 1. This was also demonstrated by

Tucker (55) who found little change in the yield of soybeans when the calcium-magnesium ratio varied from 1 to 5 to 50 to 1. However, this ratio influenced yields on soils with a low cation exchange capacity, This may indicate that the ratio of calcium to magnesium is not important as long as there are sufficient amounts of calcium and magnesium in the soil. Zimmerman (66) states that at high levels of fertility, calcium can be harmful unless accompanied by adequate magnesium.

Sanik et al. (47) studied the calcium-magnesium ratio in relation to some of the minor elements and concluded that for the particular soil studied the best ratio for the uptake of boron was 4 to 1, for copper and manganese, 2.6 to 1 and for zinc, 2 to 1.

Studies by Camp (10) on citrus trees in Florida, indicated that a calcium-magnesium ratio in the soil of between 5 to 1 and 8 to 1 would be best. Elgabaly (13) found that the maximum shoot growth of barley plants occurred when the ratio was 7 to 3.

An investigation by Longstaff (29) using soybeans showed that the calcium content in the plants increased proportionally to the uptake of magnesium.

Halstead et al. (18) determined that a narrow calcium-magnesium ratio did not have an adverse effect on the yield of alfalfa.

Perkins and Stelly (41) demonstrated that neither milliequivalents of exchangeable calcium and magnesium in the soil, nor percentage of calcium and magnesium saturation in the soil showed any correlation with the uptake of calcium or magnesium, or percentage of calcium and magnesium in oats and crimson clover. However, the work by Hunter, _et al_. (20) indicated that the plant uptake and soil supply of exchangeable calcium and magnesium are related.

Recently, Jacoby (21) found severe magnesium deficiencies in citrus when excess of calcium was present and the magnesium level kept constant.

Potassium-Magnesium Relationships

It is well known that the potassium ion, particularly if present in high concentrations, may reduce absorption of other cations by plants.

Investigators are generally agreed that the concentration of soil potassium is one of the most important factors in determining magnesium deficiency (5, 6, 24, 31, 37, 38, 39, 52, 56, 59, 60, 61, 64, 66). The negative correlation between magnesium uptake and exchangeable potassium is frequently better than the positive correlation between magnesium uptake and exchangeable magnesium (14). Magnesium deficiencies are likely to develop under conditions in which the ratio of potassium to magnesium in the soil's exchange complex exceeds 1 to 2 (6).

Field experiments conducted by Foy and Barber (14) revealed that 100 to 500 pounds of potassium per acre induced magnesium deficiency symptoms on corn. This condition was confirmed by low magnesium and high potassium content in leaves.

Magnesium Fertilization

Zimmerman (65), as reported by Bear and Prince (5), stated that for crops grown on acid soils at pH values of about 5.2, a larger percentage of the exchange complex must be occupied by hydrogen, and less by calcium, magnesium and potassium. Under such conditions, magnesium uptake by plants is more closely related to available supplies of the element than at higher pH values and fertility levels.

In his study in 1951, Prince (43) found that the yields of sweet potatoes, Irish potatoes, snap beans and okra grown in magnesium deficient soils were greatly increased by magnesium applications. Sul-Po-Mag, Actomag, epsom salts, and finely pulverized dolomitic limestone were used as magnesium carriers. The soluble forms tended to be more effective the first year of the test on soil that had been limed to pH 6.5 with calcium carbonate. The magnesium of both dolomitic limestone and Actomag was immediately useful for the Irish potato and sweet potato crops grown on the soil at pH 5.5. The evidence indicated a need for the more soluble forms of magnesium for immediate correction of magnesium deficiency.

Not all crops on soils apparently deficient in magnesium have responded to magnesium applications. Usually, however, the magnesium content of the plant has been found to increase as a result of magnesium fertilization (14, 50, 53, 56, 62). Other investigators (3, 7, 35, 49, 53, 54) have either corrected magnesium deficiency symptoms or increased magnesium content of crops by applications of fifteen pounds or more of elemental magnesium per acre. Tobin (53) found that little or no yield response from magnesium applications was obtained in his study; however, he concluded that application of dolomitic limestone on the coarser textured soils of Michigan as an insurance against possible magnesium shortages occurring in the future may be important.

METHODS AND MATERIALS

Greenhouse Procedures

Two Michigan soils were selected for this study based on soil analysis from the central testing laboratory. These soils were selected from fields which were mapped as Karlin loamy sand, both testing the same in exchangeable magnesium by routine soil analysis, and with different pH values. Both soils were taken from the Mission Peninsula in Grand Traverse County. Some of the physical and chemical characteristics of the soils are given in Table 1.

Bulk soil samples, representative of the superficial soil (0 to 6 inches), were air-dried, passed through a one-fourth inch sieve and thoroughly mixed.

Number ten tin cans lined with plastic bags, were filled with 4000 grams of air-dry soil. The fertilizer treatments, given in Table 2, were added and thoroughly mixed with the soil. Each treatment was replicated three times. Nitrogen, phosphorus and potassium were kept constant for each treatment, while source and rate of magnesium were varied. Potassium fertilization was calculated on the basis of the potassium content of the middle rate of sulfate of potash-magnesia. Nitrogen was added in two applications, half of the rate at the beginning of the experiment and the other half four weeks later.

Twenty barley seeds, variety Trail, were planted in each pot on December 22, 1961, and harvested March 2, 1962. Each pot was

TABLE 1

Physical and Chemical Characteristics of the Two Michigan Surface Soils Used in Greenhouse Studies

Parameters Measured	Soil I Karlin Loamy Sand	Soil II Karlin Sand
pH	6.4	5.4
Mg in ppm	46.0	19.0
Ca in ppm	683.5	358.0
K in ppm	19.0	17.0
Sand percent	88.54	93.36
Silt percent	9.90	5.67
Clay percent	1.56	0.97
Clay minerals[1]		
Kaolinite (%)	x	x
Illite (%)	x	x
Montmorillonite (%)	-	xx
Vermiculite (%)	xxx	xx
Chlorite (%)	xx	xx

1. Legend: x = 0-20 percent
xx = 20-40 percent
xxx = $\not<$ 40 percent

Table 2

Fertilizer Treatments For Greenhouse Experiments

Treatment Number	Fertilizer Materials Applied (lbs./acre)					
	Dolomite[1]	Sulfate of Potash-Magnesia[2]	$MgSO_4 \cdot 7H_2O$[3]	N[4]	P[5]	K[6]
(1)	-	-	-	100	86	154
(2)	500	-	-	100	86	154
(3)	1000	-	-	100	86	154
(4)	2000	-	-	100	86	154
(5)	-	444	-	100	86	154
(6)	-	888	-	100	86	154
(7)	-	1776	-	100	86	308
(8)	-	-	496	100	86	154
(9)	-	-	993	100	86	154
(10)	-	-	1986	100	86	154

1. Dolomitic limestone, 33.4 percent $MgCO_3$ equivalent.
2. Sul-Po-Mg, 18.3 percent K, and 18 percent Mg.
3. $MgSO_4 \cdot 7H_2O$, 9.8 percent Mg.
4. Ammonium nitrate
5. Super phosphate
6. Potassium chloride

watered with distilled water once or twice daily as needed. Twice a week each pot was brought to field capacity by weight. After the third week of growth artificial illumination was provided from fluorescent lights for twelve hours per day, as natural light did not satisfy the necessary conditions for maximum plant growth. Approximately ten weeks later, when the first symptoms of heading occurred, the first crop was harvested.

Fifty gram samples of soil were taken for laboratory determinations, and a second crop of barley grown in the same pots from March 11, 1962, to May 19, 1962. No additional magnesium was used at this time in order to evaluate the residual effect of the magnesium carriers in the soils. Nitrogen, phosphorus, and potassium were added in the same amounts as those used in the first experiment.

The plant material was dried for three days at 60 degrees centigrade, plant weights were recorded, and each sample was ground and saved for plant analysis.

Soil Analysis

The original soils were analyzed for pH, and exchangeable magnesium, calcium and potassium, after both the first and second crops.

Soil pH was measured with a Beckman (Model G) potentiometer using a 1 to 1 soil to water ratio.

Mechanical analysis was determined by the pipette method (25).

Qualitative identification of the clay minerals in each soil was made by X-ray diffraction analysis. Forty to fifty milligrams of clay were deposited from suspension onto a porous plate and washed with three increments of a 0.1 N $CaCl_2$ solution which contained three percent glycerol by volume. The deposit was dried in a desiccator, then mounted on a Norelco X-ray spectrometer and analyzed using nickel filtered copper radiation. After the first X-ray exposure the calcium-saturated, glycerol-solvated, clay deposit was potassium saturated by washing with 0.1 N KCl, the excess KCl washed out with distilled water, and dried at 110 degrees centigrade. The X-ray analysis was repeated. The sample was then heated to 550 degrees centigrade and a third X-ray analysis made.

Normal ammonium acetate solution adjusted to pH 7.0, was used as the leaching solution for the extraction of magnesium, calcium and potassium. Acetate in the extract was eliminated by the method described by Dean (12).

Magnesium was determined by the Beckman DU flame photometer, equipped with a photomultiplier, at a wave length of 285.2 Angstroms. Calcium and potassium determination were made by the Coleman (Model 21) flame photometer.

Plant Analysis

Samples of the plant material were wet digested with nitric and perchloric acid as described by Piper (42) and the residue was dissolved in 0.1 N HCl.

Magnesium, calcium and potassium were determined by flame photometry as described for soil analysis.

Solubility Determination of Dolomite

A laboratory study was conducted in an attempt to determine the effect of soil pH on the solubility of dolomite. A surface soil sample of Hillsdale sandy loam from the Michigan State University soils farm, as well as the two soils used in the greenhouse study, was used in this experiment.

The Hillsdale sandy loam soil was selected on the basis of soil reaction. The original soil pH was 4.0; consequently, a wide range in soil pH existed between the original soil and its limed counterpart.

Soil samples from the three soils were air-dried and mixed with the equivalent of 1000 pounds of dolomitic limestone per acre.

Lime requirement to increase soil pH to 6.8 was determined for the Hillsdale sandy loam soil as described by Shoemaker _et al_. (51). Pure calcium carbonate was added to this soil as the liming material prior to adding the dolomite treatments.

Fifty gram samples of soil were weighed out and placed in filter tubes, the bottom of which were plugged with glass wool. Sufficient distilled water was added to bring each sample to field capacity. The samples were incubated at a constant temperature (20 degrees centigrade) and under well aerated condition. Distilled water was added periodically to maintain the moisture level at field capacity.

After different periods of incubation each treatment was leached with 1 N ammonium acetate (pH 7.0). Suction had to be applied during the extractions. Check samples without calcium carbonate and dolomite were run for the Hillsdale sandy loam soil and for the greenhouse soils. Each treatment was replicated twice.

RESULTS AND DISCUSSION

Dolomitic limestone has the dual property of serving as both a liming agent and a source of magnesium which makes this compound very important in correcting magnesium deficiencies under acid soil conditions. Several factors which affect the solubility of magnesium carbonate will be discussed in the following paragraphs.

Magnesium carbonate dissociates to form Mg^{++} and $CO_3^{=}$ ions. The solubility product constant for magnesium carbonate, according to Johnston (23) is:

$$Keq = (Mg^{++})\ (CO_3^{=}) = 1.2 \times 10^{-4} \text{ moles/liter} \qquad (1)$$

The concentration of carbonate ions in the soil is regulated by the dissociation of carbonic acid and bicarbonate ions. The concentration of carbonic acid is dependent on the partial pressure of carbon dioxide in the soil. The concentration of carbonic acid may be obtained as a function of carbon dioxide partial pressure from the following relationships:

$$H_2CO_3 \rightleftharpoons H_2O + CO_2 \qquad (2)$$

$$Keq = \frac{(H_2O)\ (P_{CO_2})}{(H_2CO_3)} \qquad (3)$$

and $$(H_2CO_3) = C \cdot P_{CO_2} \qquad (4)$$

where $C = \dfrac{\alpha}{22.4}$, α is the absorption coefficient of CO_2 (23) and P_{CO_2} is the partial pressure of CO_2 in the soil.

Carbonic acid dissociation proceeds as follows:

$$H_2CO_3 \rightleftharpoons H^{+} + HCO_3^{-} \qquad (5)$$

$$Keq_1 = \frac{(H^+)\ (HCO_3^-)}{C P_{CO_2}} = 3.44 \times 10^{-7} \text{moles/liter} \qquad (6)$$

and

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (7)$$

$$Keq_2 = \frac{(H^+)\ (CO_3^=)}{(HCO_3^-)} = 6.0 \times 10^{-11} \text{moles/liter} \qquad (8)$$

By combining equations (6) and (8) and solving for $(CO_3^=)$, the following equation can be obtained:

$$(CO_3^=) = \frac{20.64 \times 10^{-18}\ C\ P_{CO2}}{(H^+)^2} \qquad (9)$$

The concentration of magnesium in the soil solution may be obtained by substituting the value for $CO_3^=$ ion concentration from equation (9) into equation (1).

$$(Mg^{++}) = \frac{5.94 \times 10^{11}\ (H^+)^2}{C\ P_{CO2}} \qquad (10)$$

It is therefore concluded that the solubility of magnesium carbonate in the soil is a function of the partial pressure of CO_2 in the soil air and the hydrogen ion concentration of the soil. The concentration of magnesium from magnesium carbonate should be inversely proportional to the partial pressure of carbon dioxide and directly proportional to the square of the hydrogen ion concentration.

When a saturated solution of magnesium carbonate or calcium carbonate is at equilibrium, under laboratory conditions, the pH of the systems is approximately nine and a little dissociation of magnesium carbonate or calcium carbonate occurs. This fact may be related to the slow solubility of dolomitic limestone in some soils.

There exists the possibility of the formation of an alkaline environment in the immediate vicinity of the particles of dolomite, which would slow down the rate of dissolution of the dolomite. The importance of this effect is undoubtedly dependent upon the hydrogen buffer capacity of the soils. If a soil contains a large quantity of hydrogen ions this effect could be quite small and dolomite would be very soluble. On the other hand, if a soil is near neutral before addition of dolomite the environment surrounding each individual particle may be very slow to change and the solubility of dolomite may be very small.

Under alkaline conditions magnesium may precipitate as magnesium hydroxide. Bower and Truog (8) and Babcock *et al*. (2) stated that at nearly neutral conditions magnesium hydroxide dissociates forming monohydroxy magnesium ions, that is $Mg(OH)^+$, which may be held by soils or assimilated by plants in this form.

Magnesium in sulfate of potash-magnesia and in epsom salts is present as magnesium sulfate, which is a very soluble salt (71 grams of $MgSO_4$ will dissolve in 100 milliliters of water at 20 degrees centigrade). Magnesium sulfate fertilization may be of importance in the correction of magnesium deficiencies in both alkaline or acid soils since its solubility is not dependent on hydrogen concentration in soils.

Effect of Liming on the Solubility of Dolomite

The results of the laboratory experiment to determine the effect of soil pH on the solubility of dolomite are given in Figures 1 and 2.

Figure 1 shows the effect of liming a soil with original pH 4 on the solubility of magnesium carbonate from dolomite. A comparison of curves A and B shows that nearly all of the 48 parts per million of magnesium added from dolomite was ammonium acetate extractable after one week of incubation. A remarkable decrease in ammonium acetate extractable magnesium was caused by liming. When the soil was limed to neutrality, approximately 80 percent less magnesium was extracted as compared to the percentage extracted when only dolomite was added to the soil.

Little variation occurred in the amount of magnesium extracted at the different periods of incubation from the unlimed soil to which dolomite was added. A general decrease in the amount of magnesium extracted from the other treatments may be seen in Figure 1.

These results agree very closely with the theorical considerations, where it was pointed out that magnesium solubility in a system is directly proportional to the square of the concentration of hydrogen ions and inversely proportional to the partial pressure of carbon dioxide.

Solubility Studies of Dolomite in the Greenhouse Soils

Incubation studies were conducted to determine the solubility of dolomite on the two soils used in greenhouse studies.

Some physical and chemical properties of these soils are presented in Table 1. The pH of these soils is intermediate between the acid Hillsdale sandy loam soil and its limed counterpart.

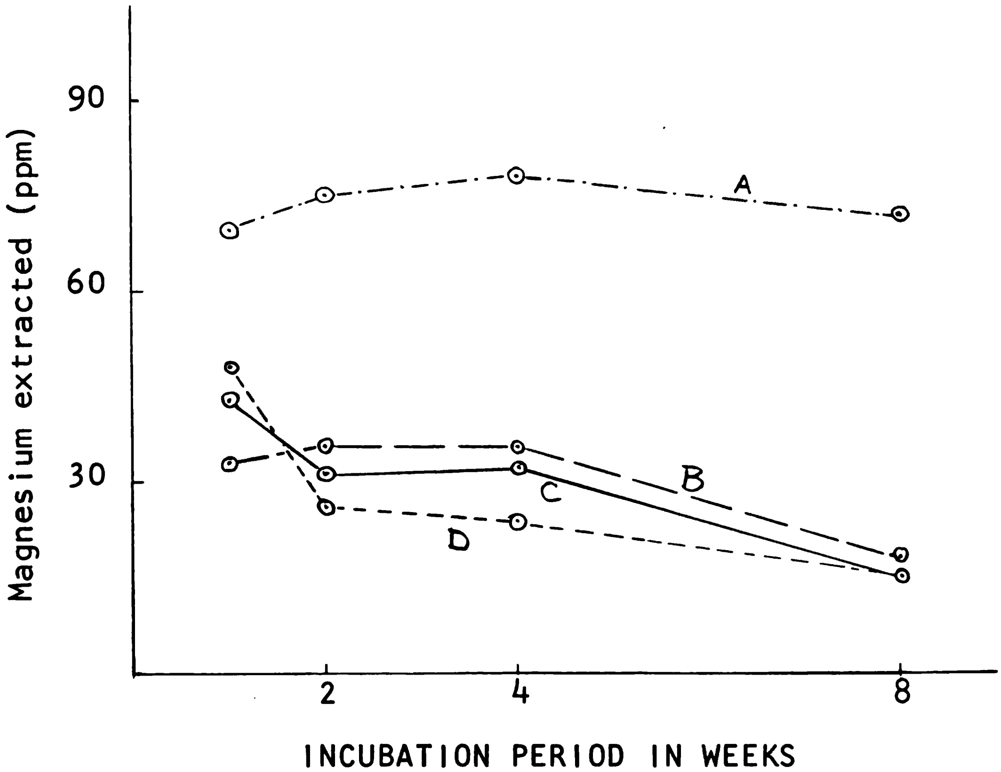

Figure 1. Effect of liming on the solubility of dolomite in a Hillsdale sandy loam soil

A. Unlimed soil ≠ dolomite
B. Unlimed soil
C. Limed soil ≠ dolomite
D. Limed soil

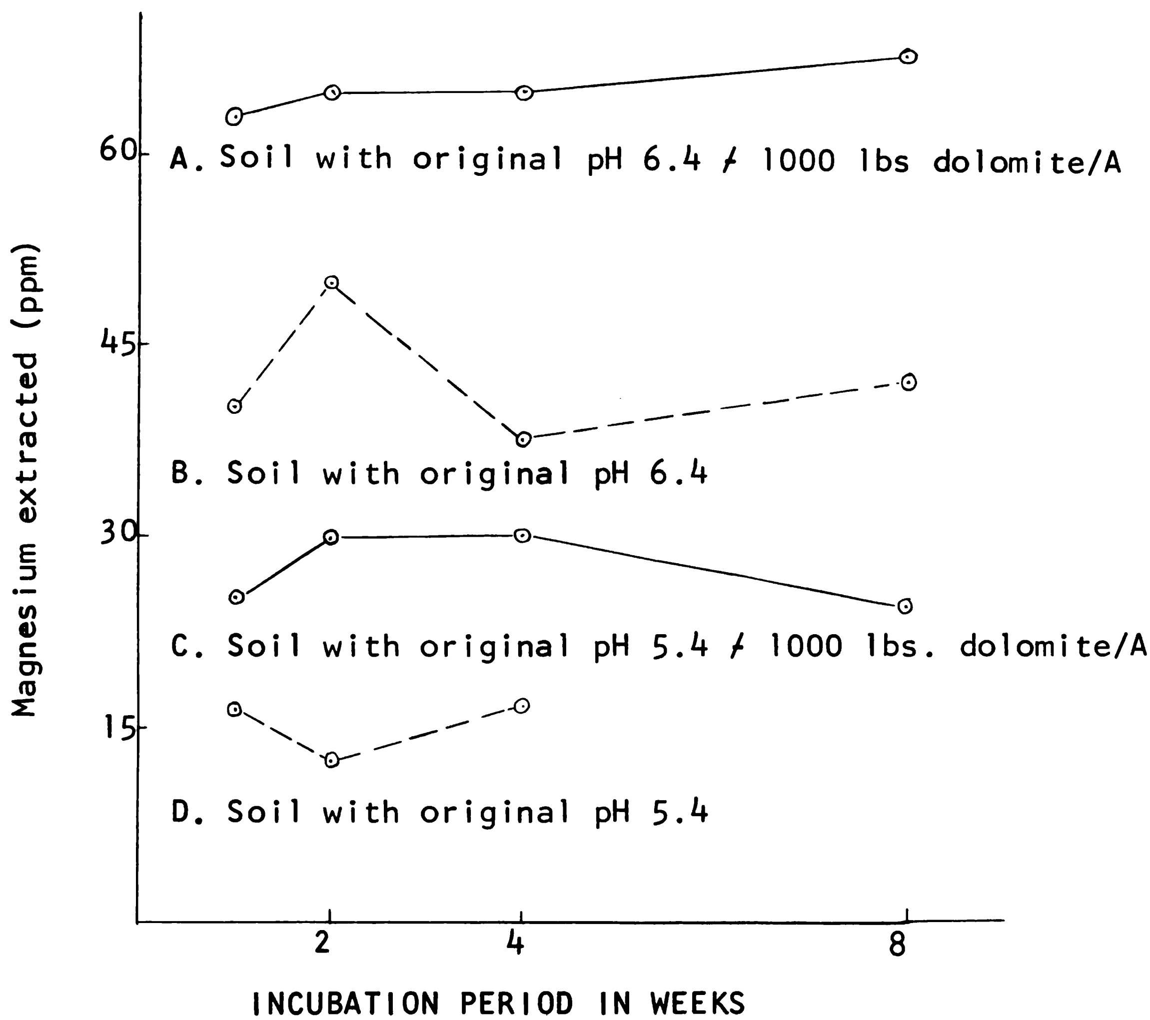

Figure 2. Effect of dolomitic limestone applications on the concentration of extractable magnesium from greenhouse soils at different periods of incubation

Figure 2 shows the amount of ammonium acetate extractable magnesium in the soils after several periods of incubation. The greatest quantities of magnesium were extracted from the soil with pH 6.4 which had dolomitic limestone applied. As it can be seen from Table 1, this soil had an original magnesium content higher than the soil with original pH 5.4. A considerably lower amount of magnesium was extracted from the soil with original pH 5.4 to which the same rate of dolomite was added.

From the clay mineralogy analysis, it was found that vermiculite, montmorillonite and chlorite are present in the soil with the lower pH. Caillere, Henin, and Mering (9), and Grim (17) indicate that magnesium ions can be fixed by montmorillonite with the development of a chlorite type structure under certain conditions and concentrations of magnesium ion. Due to the fact that vermiculite, montmorillonite and chlorite, are present in this soil, the lower magnesium concentration of the extracts from this soil may be related to a fixation of magnesium by montmorillonite into a chlorite structure. The soil with original pH 6.4 also has vermiculite and chlorite in the colloidal system, but no evidence of montmorillonite was found.

A general "retention" of magnesium appears to have occurred in both soils since the final concentration of the extracts does not agree with the applied rate of dolomite (96.3 pounds of magnesium per acre) plus the original extractable magnesium in the soils. This retention will be discussed later in the thesis.

Sufficient soil was not available to determine magnesium from soil with original pH 5.4 after eight weeks of incubation.

Results of Greenhouse Studies
Relationship Between Magnesium Source and Soil Reaction

Physical and chemical properties of the two soils studied in the greenhouse are given in Table 1. In subsequent discussions in this thesis these soils will be referred to as soil I and soil II.

The relation between the different magnesium treatments and soil pH are shown in Figures 3, 5, and 7 for soil I and in Figures 4, 6, and 8 for soil II.

The maximum increase in pH in soil I was obtained with the first rate of application of dolomite; no further increase was obtained for this soil when dolomite was applied at the higher rates.

Dolomite applications produced an increase of pH from 5.45 to 6.4 in soil II. The increase in pH was portional to the quantity of dolomite applied. There was a slight decrease in soil pH at each level of dolomite during growth of the second crop of barley. Applications of sulfate of potash-magnesia and epsom salts decreased soil pH approximately one-third of a pH unit in both soils.

Although the effect of the various magnesium carriers on soil reaction is to be expected, this result may have practical significance. In acid or slightly acid soils dolomite may be used to correct acidity as well as magnesium deficiency. On the other hand, if the magnesium

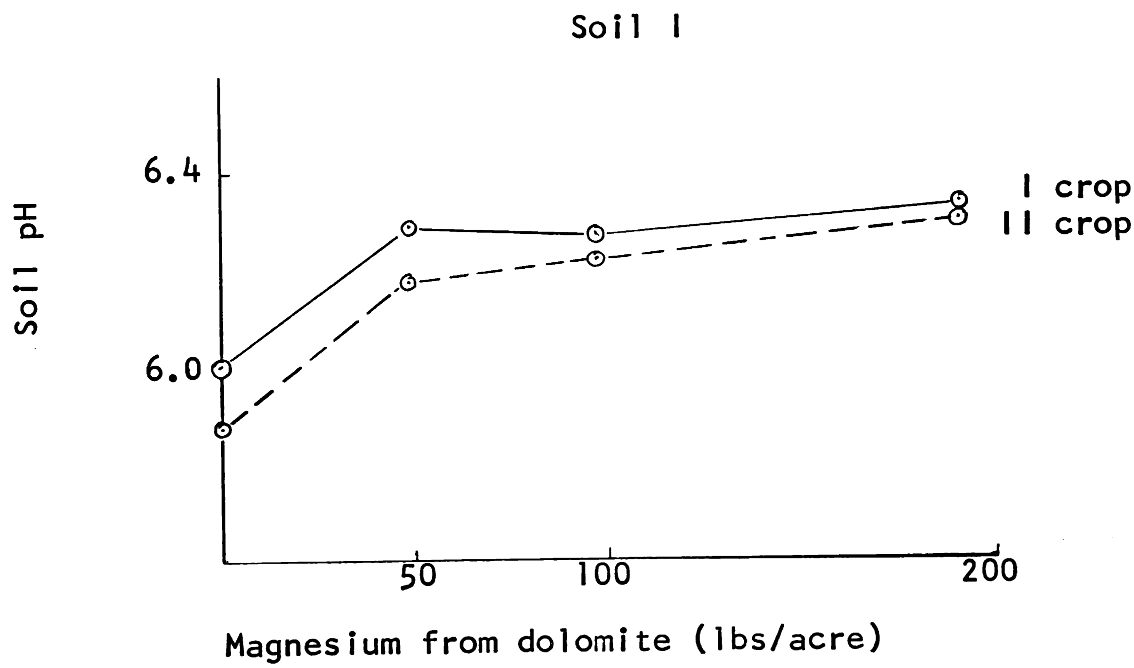

Figure 3. Soil pH after each crop of barley as affected by dolomite applications.

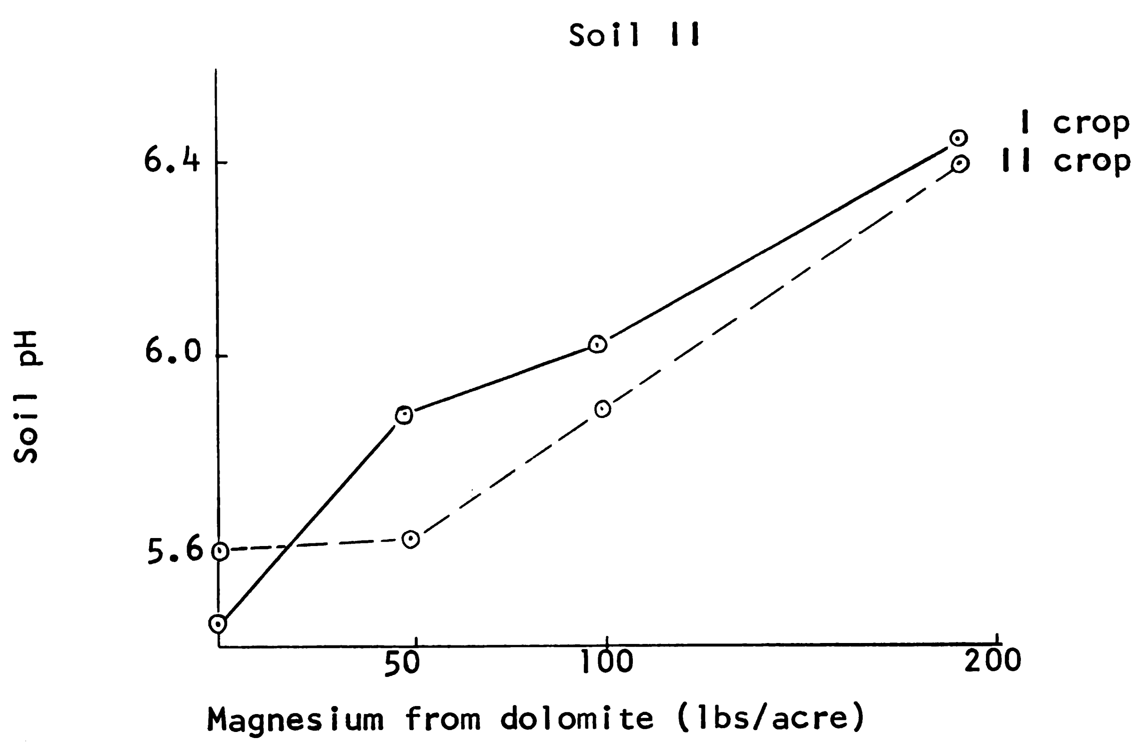

Figure 4. Soil pH after each crop of barley as affected by dolomite applications.

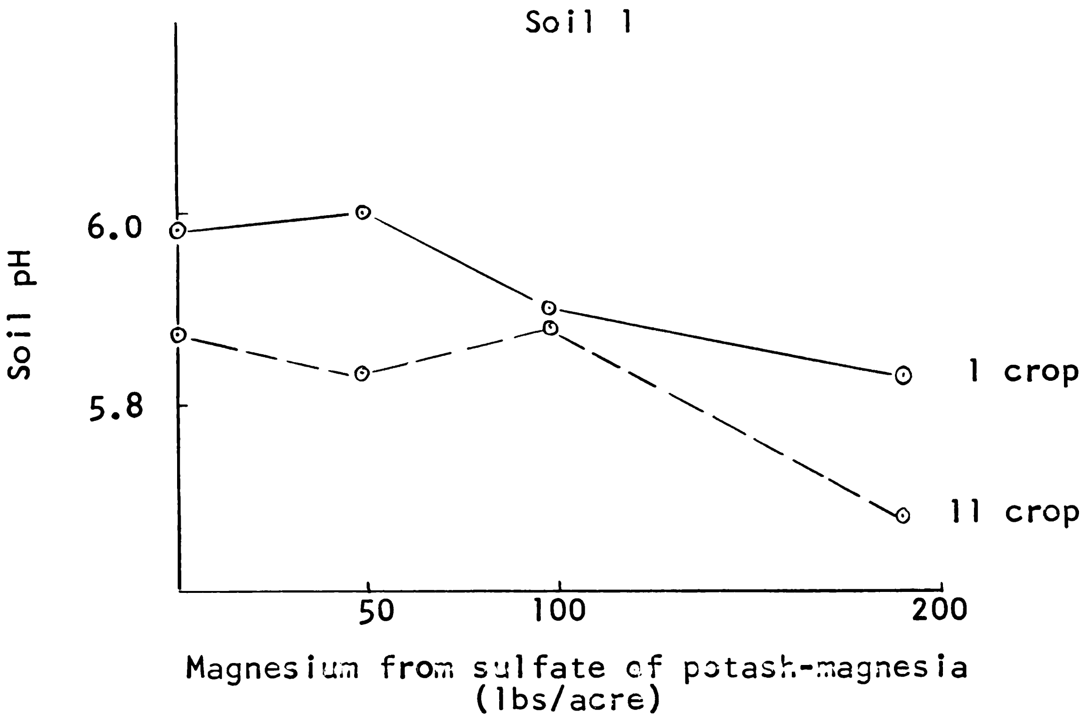

Figure 5. Soil pH after each crop of barley as affected by sulfate of potash-magnesia applications.

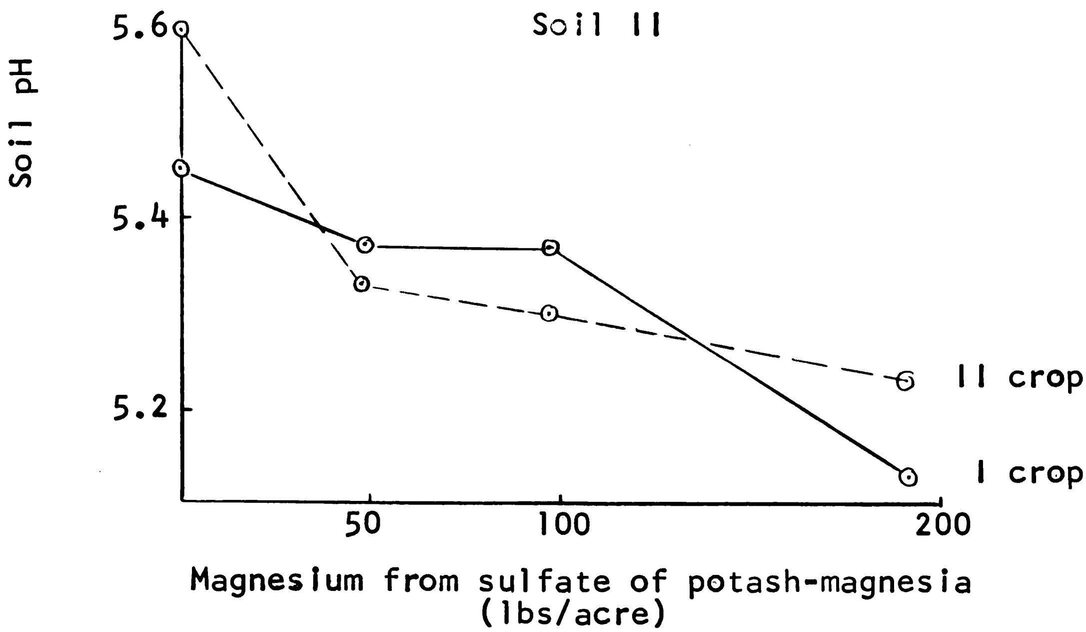

Figure 6. Soil pH after each crop of barley as affected by sulfate of potash-magnesia applications.

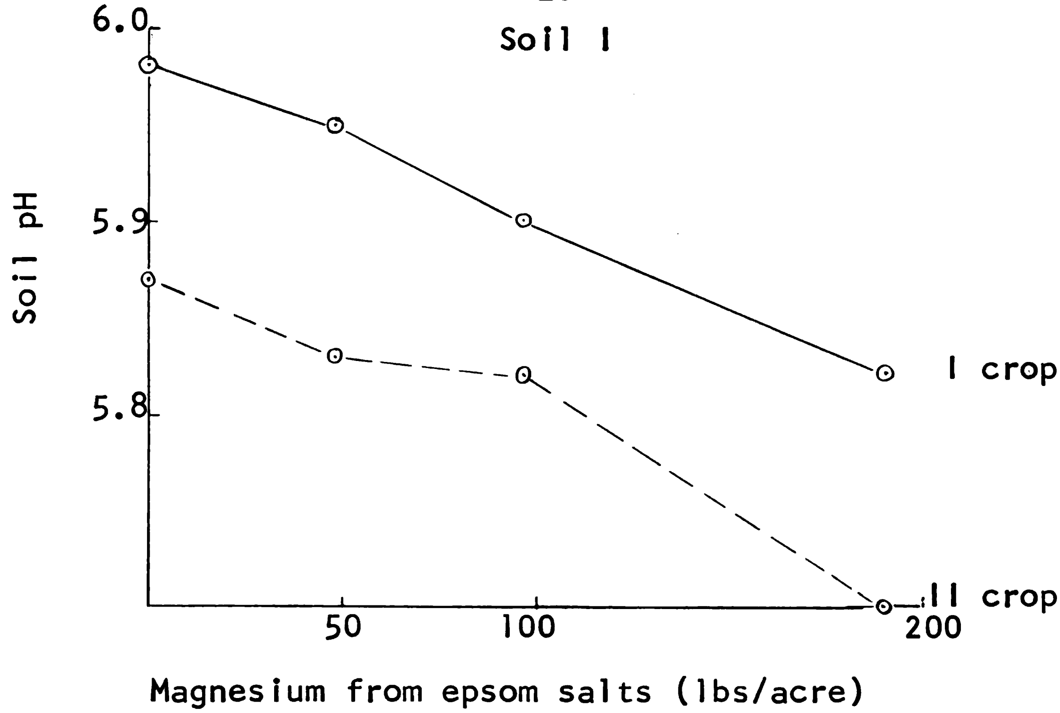

Figure 7. Soil pH after each crop of barley as affected by epsom salts applications.

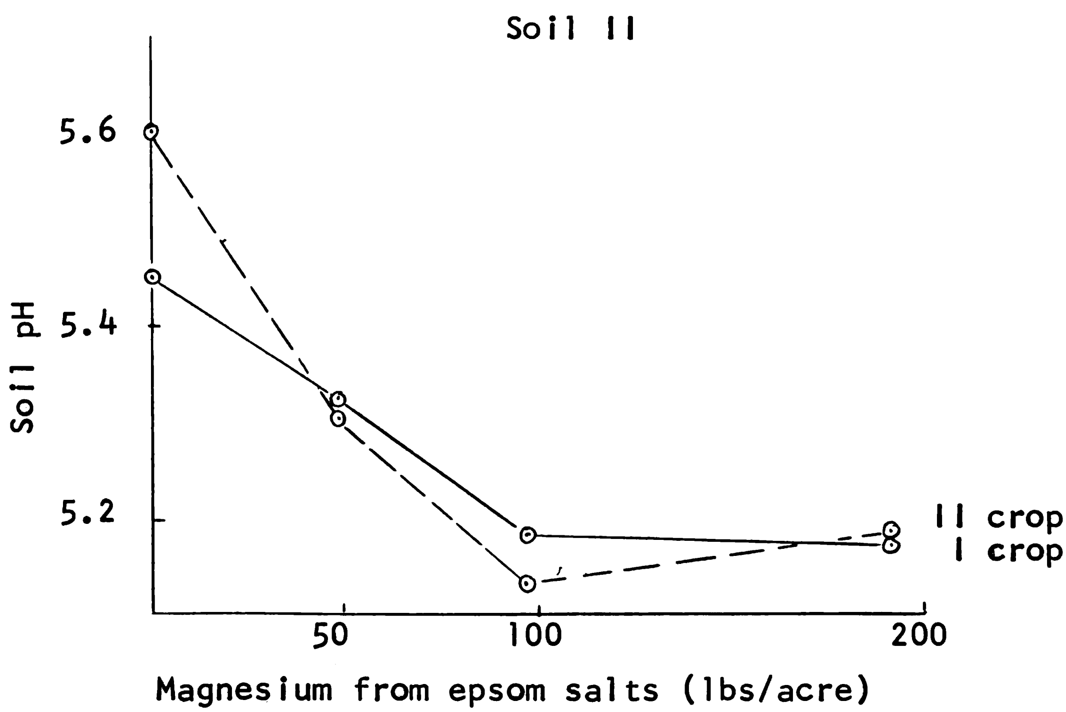

Figure 8. Soil pH after each crop of barley as affected by epsom salts applications.

deficiency is found on leached, acid soils, a soluble source of magnesium such as epsom salts may further increase the acidity.

Evaluation of the Magnesium Status of Soils

Ammonium acetate is commonly used to extract cations from a soil sample. The method used in the Michigan State central testing laboratory to determine "exchangeable" magnesium is to extract 2.5 grams of soil with 20 milliliters of 1.0 N ammonium acetate buffered at pH 7.0. The results for 1.0 N ammonium acetate extractable magnesium are given in Figures 9 and 10 for soil I and in Figures 11 and 12 for soil II.

The ammonium acetate extractable magnesium from soil I after the first crop of barley appeared to be independent of the rate of dolomite applied. As it was pointed out earlier in this discussion, the low dissociation of magnesium carbonate from dolomite may be related to the formation of an alkaline environment around the dolomite particles as the following reaction proceeds in the soil.

$$\begin{smallmatrix}H\text{-}\\H\text{/}\end{smallmatrix}\text{Clay} + MgCO_3 \longrightarrow \text{Mg-Clay} + H_2O + CO_2 \qquad (11)$$

It would then appear that the amount of magnesium carbonate dissociation would be a function of time. Some evidence of this is given in Figure 10 where it is shown that after the second crop of barley the ammonium acetate extractable magnesium from dolomite treatments is proportional to the amount of dolomite applied.

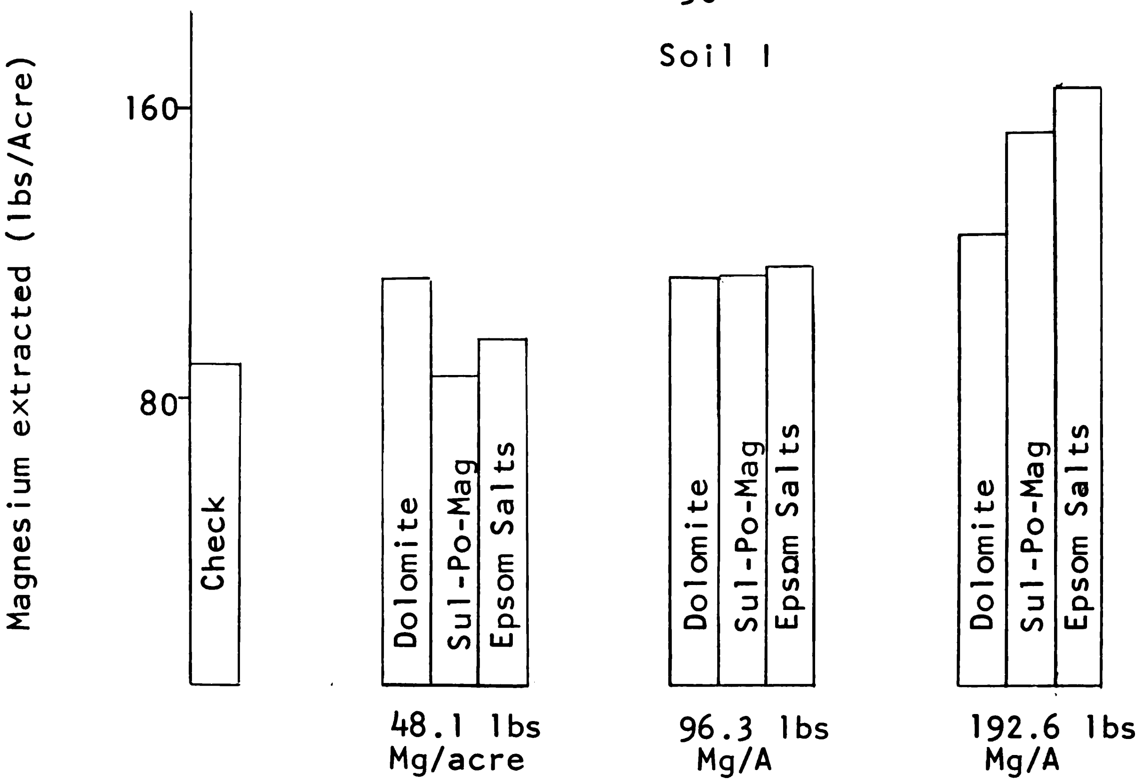

Figure 9. Ammonium Acetate Extractable Magnesium After first crop of barley

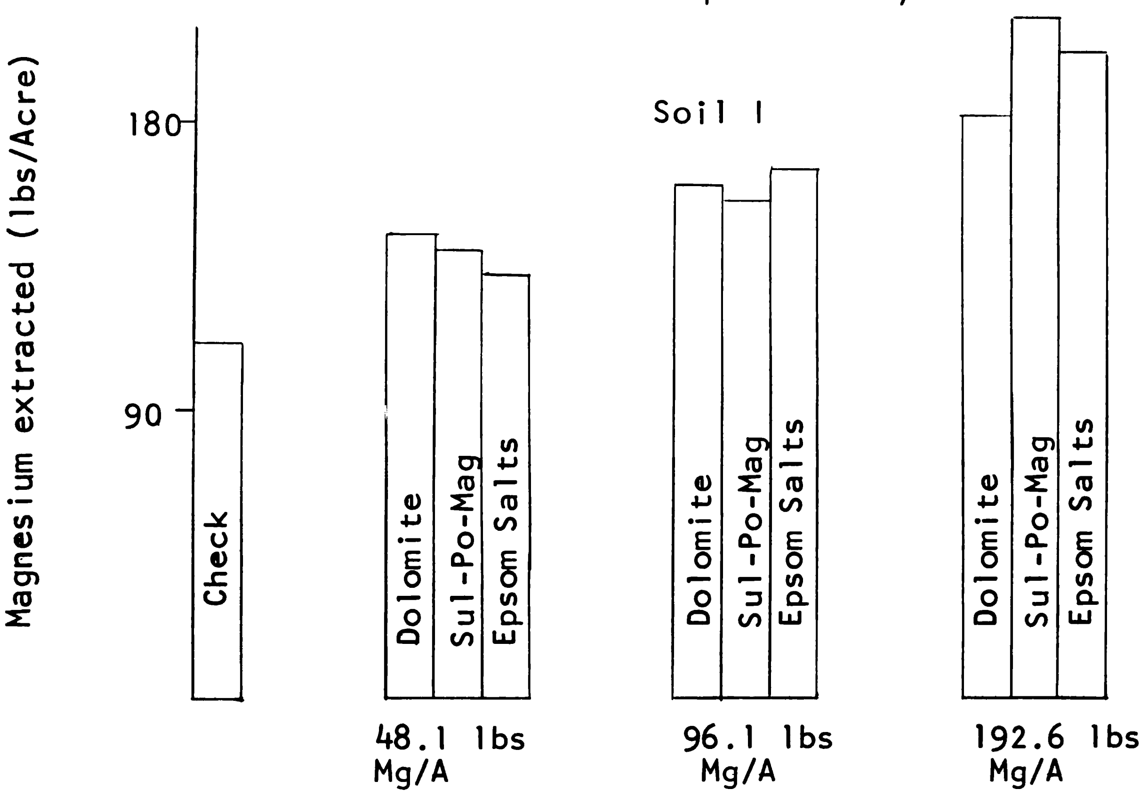

Figure 10. Ammonium Acetate Extractable Magnesium After Second Crop of Barley

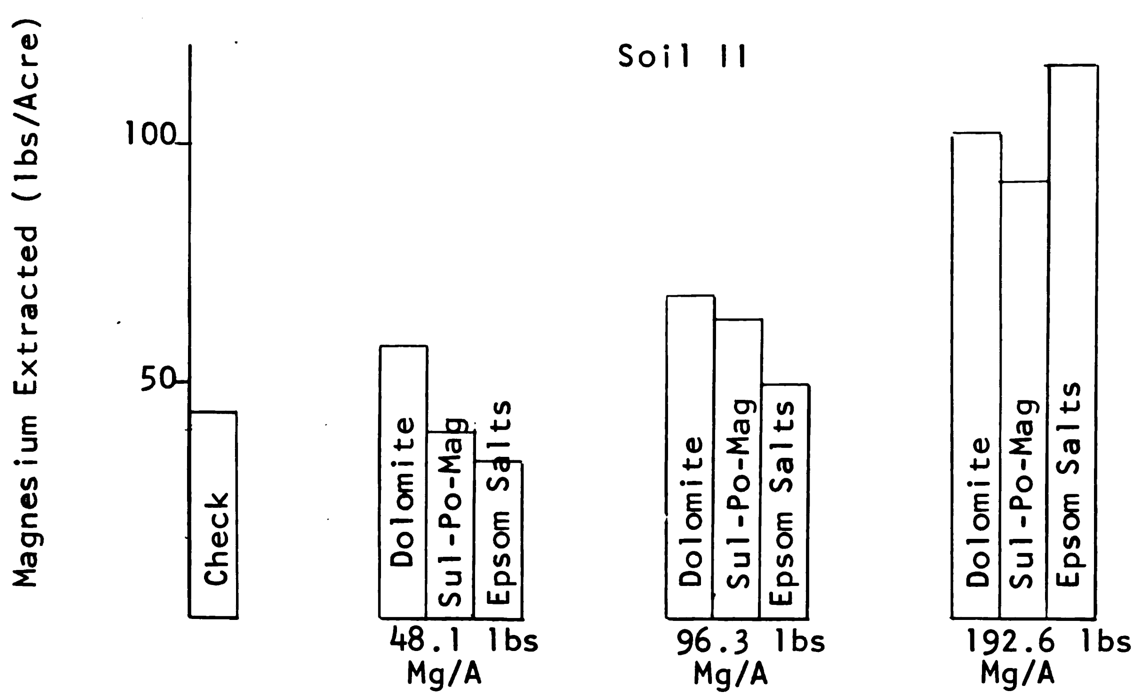

Figure 11. Ammonium Acetate Extractable Magnesium After First Crop of Barley

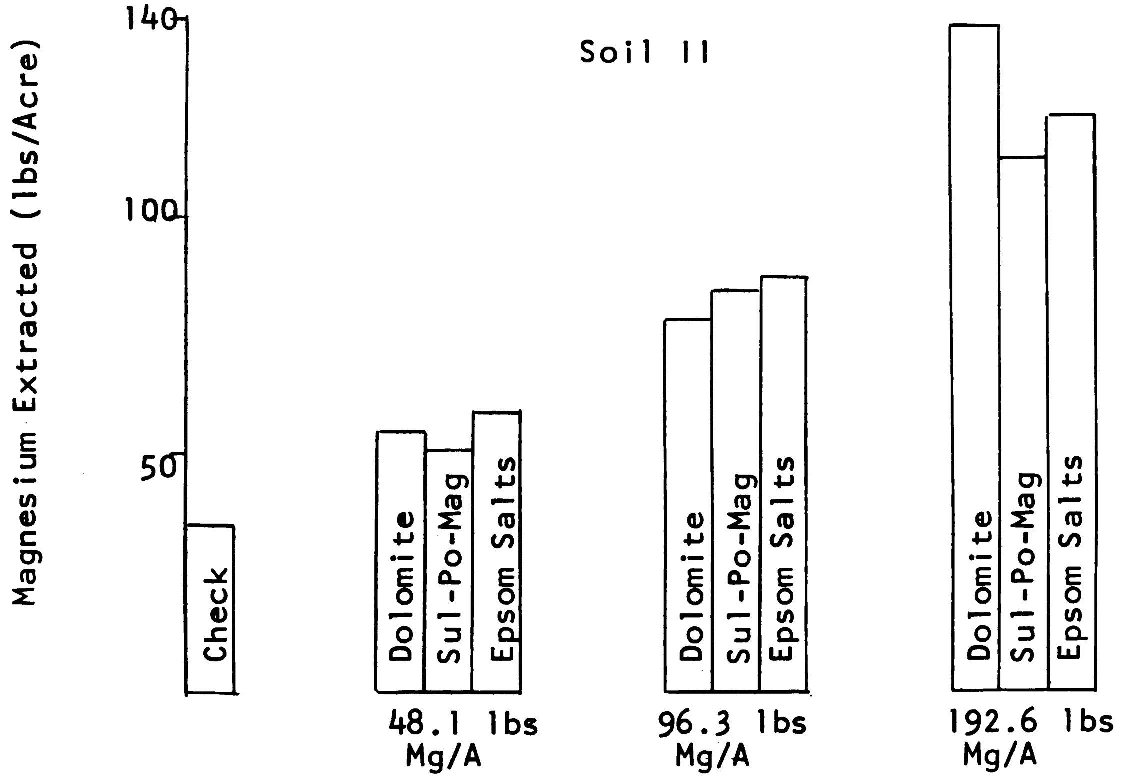

Figure 12. Ammonium Acetate Extractable Magnesium After Second Crop of Barley

In soil II the amount of ammonium acetate extractable magnesium was proportional to the rate of application of dolomite after both the first and second crops of barley. This is attributed to the higher quantity of hydrogen ions in this soil.

The soluble magnesium sources, sulfate of potash-magnesia and epsom salts, increased the concentration of extractable magnesium from both soils at the higher rates of application; however, at the low rate of application the magnesium extracted did not differ from the control.

From Table 1, it can be seen that vermiculite type clay minerals are present in the two greenhouse soils. This clay mineral, as described by Grim (17) is composed of silicate layers bound together mostly by magnesium and calcium ions, with an interlayer aperture which is dependent on the size and hydration state of the ion present. In the case of magnesium in the fully hydrated form this space is approximately 10.7 Angstroms. The ions, potassium and ammonium are capable of collapsing vermiculite plates and preventing expansion upon hydration. Consequently, when an ion such as ammonium is in contact with vermiculite minerals a partial or total enhancement of magnesium present in interlayer positions may be produced as the result of ammonium ions plugging the external sites of the interlayers of vermiculite. Therefore, an ammonium acetate extraction may not give a true reflection of the total amount of exchangeable magnesium present in a soil.

The quantity of magnesium replaced may be a function of the time of contact. When more potassium was added and a new equilibrium established during the second cropping, more magnesium was ammonium acetate extractable.

Additional extractions were carried out on some of the soil treatments as shown in Table 3 to determine if other extracting agents might give a better measure of the magnesium status of the soils. Some evidence has been obtained that indicated that alpha-naphthylamine-HCl may be effective in removing interlayer potassium from soils.[1] Sodium chloride is very effective in maintaining clay mineral structures in an expanded, hydrated condition. Therefore, these two materials were used to study the amount of magnesium that may be contained in the interlayer positions of the clay minerals contained in soils.

Two grams of the soil samples studied were weighed out and fifty milliliters of 0.10 N alpha-naphthylamine-NCl or fifty milliliters of 0.10 N sodium chloride solutions were added to the soil samples previously placed in centrifugue tubes. The samples were shaken for 24 hours. The treated samples were then centrifugued and magnesium concentration determined by use of the Beckman D.U. flame photometer, equipped with a photomultiplier.

A comparison of magnesium extracted by these two extractants and by normal ammonium acetate is given in Table 3.

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1. Ellis, B.G. and Mortland, M.M. Personal Communication.

Two points in Table 3 are of considerable interest. First, more magnesium was extracted from the soil which had received no magnesium treatment with both 0.1 N alpha-naphthylamine-HCl and 0.1 N sodium chloride than was extracted with 1.0 N ammonium acetate. If this is interpreted as being magnesium from interlayer exchange sites, it must be concluded that ammonium acetate extractable magnesium is not a good measure of available magnesium. Secondly, the extracting agents which remove interlayer magnesium more nearly account for the magnesium which was applied to the soil than does the ammonium acetate extraction.

Although the few results reported in this thesis only point out trends in the quantities of magnesium extracted from the soil with different extracting reagents, they do emphasize the need for further research in this area.

Effect of Magnesium Fertilization on Yield and Magnesium Uptake by Barley

Detailed data, together with statistical analysis, from the greenhouse experiment are given in Tables 1, 2, 3, and 4 of the appendix.

A summary of the yield of barley grown in the greenhouse is given in Table 4. The magnesium content of the barley is summarized in Table 5. Since there appeared to be little influence of rate of magnesium application on yield or composition of the barley, all rates of a particular carrier were averaged for the summaries.

Neither yield nor magnesium content of barley grown on soil I were increased by magnesium fertilization. However, additions of magnesium sulfate appeared to decrease yields slightly. Two factors

TABLE 3

Magnesium Extracted from Soil II by Various Extracting Agents[1]

TREATMENTS	EXTRACTING SOLUTION					
	1.0 N ammonium acetate		0.10 N -naphthylamine HCl		0.10 N NaCl	
	Crop		Crop		Crop	
	1	2	1	2	1	2
Check	43.34	35.66	91.66	90.00	145.00	101.76
96.3 lbs. Mg/A as dolomite	68.00	78.34	203.34	133.34	191.76	136.66
96.3 lbs. Mg/A as $MgSO_4.7H_2O$	49.34	87.76	160.00	115.00	191.76	150.00

1. Each value is in pounds Mg per acre and represents a mean of three replications.

may account for the lack of response to magnesium fertilization on this soil. First, when interlayer magnesium is accounted for, this soil contains approximately 240 pounds of exchangeable magnesium per acre. This quantity is normally considered sufficient for plant growth. Secondly, the clay mineral analysis showed that considerable quantities of chlorite are contained in the clay fraction of this soil. Magnesium is undoubtedly released from this mineral during the growing season, consequently, furnishing more magnesium for plant growth.

A significant difference at the 0.10 level was found between the means of yield of plants grown on soil II. A general response to magnesium fertilization can be observed from Table 4. The dolomite treatments gave a slightly lower yield than the soluble magnesium sources on the first crop. However, this trend was reversed in the second crop. This effect may be related to the rate of dissolution of the dolomite.

Yields were consistently lower for the second crop of barley grown on soil II as compared to the first crop; however, the relative response to magnesium was greater for the second crop.

Simultaneous comparisons of the individual means by the method described by Tukey (57) showed that, in general, the magnesium content of the plants from the low rate of magnesium fertilization were not different from those grown in the control. The two higher rates of dolomite, sulfate of potash-magnesia, and epsom salts significantly increased the magnesium content of plants as contrasted

TABLE 4

Summary of the Yield of Barley
in the Greenhouse as Affected by Magnesium Application

Soil	Crop	Yield (gm.)			
		Control	Dolomite*	Sul-Po-Mag*	Epsom Salts*
I	1st	16.5	16.3	16.5	15.7
I	2nd	13.8	14.8	14.3	13.2
II	1st	14.9	15.2	16.0	15.8
II	2nd	6.8	10.5	8.7	9.1

*Average of three rates of application

TABLE 5

Summary of the Magnesium Content of Barley Grown
in the Greenhouse as Affected by Magnesium Application

Soil	Crop	Magnesium Content (%)			
		Control	Dolomite*	Sul-Po-Mag*	Epsom Salts*
I	1st	.31	.30	.31	.33
I	2nd	.30	.29	.28	.29
II	1st	.22	.30	.31	.32
II	2nd	.22	.29	.29	.32

*Average of three rates of application

TABLE 4

Summary of the Yield of Barley
in the Greenhouse as Affected by Magnesium Application

Soil	Crop	Yield (gm.)			
		Control	Dolomite*	Sul-Po-Mag*	Epsom Salts*
I	1st	16.5	16.3	16.5	15.7
I	2nd	13.8	14.8	14.3	13.2
II	1st	14.9	15.2	16.0	15.8
II	2nd	6.8	10.5	8.7	9.1

*Average of three rates of application

TABLE 5

Summary of the Magnesium Content of Barley Grown
in the Greenhouse as Affected by Magnesium Application

Soil	Crop	Magnesium Content (%)			
		Control	Dolomite*	Sul-Po-Mag*	Epsom Salts*
I	1st	.31	.30	.31	.33
I	2nd	.30	.29	.28	.29
II	1st	.22	.30	.31	.32
II	2nd	.22	.29	.29	.32

*Average of three rates of application

to the no magnesium treatment. There appeared to be a trend for greater magnesium uptake from epsom salts as compared to the other sources of magnesium. However, this increased uptake was not statistically significant.

SUMMARY AND CONCLUSIONS

Greenhouse and laboratory studies were conducted with an acid Hillsdale sandy loam (pH 4.0), a moderately acid Karlin sand (pH 5.4) and a nearly neutral Karlin loamy sand (pH 6.4) to determine the relation of soil reaction to availability of magnesium from dolomite, sulfate of potash-magnesia and epsom salts.

Barley plants were grown on the Karlin soils to determine yields and magnesium uptake at three levels of magnesium fertilization.

Magnesium was extracted from the soils with 1.0 N ammonium acetate. Certain soil samples were also extracted with 0.10 N alpha-naphtylamine-HCl and 0.10 N NaCl.

The following conclusions may be drawn from the results of this investigation:

1. Theorical consideration of solubility products show that magnesium concentration in the soil solution as a result of dolomite dissociation is directly proportional to the square of the hydrogen ion concentration and inversely proportional to the carbon dioxide pressure of the soil air.
2. Liming an acid soil decreased the solubility of dolomite as determined by normal ammonium acetate extractions.
3. Ammonium acetate extractable magnesium did not give a true measure of the magnesium status of either the original soil or of the soil to which soluble magnesium had been applied.

4. Either 0.1 N sodium chloride or 0.1 N alpha-naphtylamine-HCl removed larger quantities of magnesium from the samples studied than did 1.0 N ammonium acetate. This suggests that the magnesium not removed by ammonium acetate is trapped in the interlayer spaces of vermiculite, montmorillonite or chlorite.
5. Applications of dolomite increased soil pH while applications of sulfate of potash-magnesium and epsom salts decreased pH. This result may be important for selecting the proper magnesium fertilizer.
6. A yield response of barley grown in the greenhouse was obtained on the soil which contained 123 pounds per acre of sodium chloride extractable magnesium. No yield response was obtained on the soil which contained 240 pounds per acre of sodium chloride extractable magnesium.
7. Magnesium fertilization significantly increased the magnesium content in plants grown on the low magnesium soil. The highest uptake was produced by the highest rate of epsom salts.

Although the purpose of this investigation was not to study methods for determining available magnesium in soils, the results indicate that extracting agents other than 1 N ammonium acetate may yield more reliable values for available magnesium. The results would suggest that more detailed studies are needed to obtain an extraction which would correlate well with field response to magnesium fertilization.

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TABLE 1

Effect of Three Magnesium Carriers on pH and Ammonium Acetate Extractable Magnesium, Calcium and Potassium in Soil I[1]

Treatment			pH		Mg (ppm)		Ca (ppm)		K (ppm)	
			Crop		Crop		Crop		Crop	
Source	lbs/A	Mg lbs/A	1	2	1	2	1	2	1	2
Check	0	0	6.0	5.9	44.3	56.0	537.	521.	12.8	17.8
Dolomite	500	48.1	6.3	6.2	56.8	73.2	525.	546.	11.5	18.7
"	1000	96.3	6.3	6.2	57.0	80.0	525.	562.	13.0	17.5
"	2000	192.6	6.3	6.3	62.8	91.0	533.	562.	12.8	20.7
Sul-Po-Mag.	444	48.1	6.0	5.8	43.0	71.3	512.	537.	14.2	19.8
"	888	96.3	5.9	5.9	57.3	76.8	495.	504.	14.0	17.0
"	1776	192.3	5.8	5.7	77.5	106.7	483.	442.	18.7	20.3
Epsom Salts	496	496	5.9	5.8	48.7	68.5	496.	502.	12.7	23.8
"	993	993	5.9	5.8	58.3	82.3	508.	508.	12.0	15.0
"	1986	1986	5.8	5.7	83.0	100.5	483.	504.	13.3	17.7
L.S.D. 0.05			0.3	0.4	21.19	20.5				
L.S.D. 0.01			0.4	0.5	25.92	25.2				

1. Each value is the average of three replications

TABLE 2

Effect of Three Magnesium Carriers on Yield and Composition of Barley Grown on Soil I[1]

Treatment			Yield (gms)[2]		Mg (Percent)[2]		Ca (percent)		K(percent)	
			Crop		Crop		Crop		Crop	
Source	lbs/A	Mg lbs/A	1	2	1	2	1	2	1	2
Check	0	0	16.5	13.7	0.37	0.30	0.78	0.27	3.2	2.7
Dolomite	500	48.1	17.0	14.6	0.32	0.29	0.81	0.31	3.3	2.5
"	1000	96.3	16.2	15.7	0.31	0.28	0.77	0.25	3.6	2.4
"	2000	192.6	15.7	14.0	0.27	0.30	0.71	0.28	3.3	2.5
Sul-Po-Mag.	444	48.1	15.9	13.3	0.31	0.28	0.76	0.31	3.5	2.4
"	888	96.3	16.6	15.3	0.31	0.28	0.69	0.23	3.4	2.2
"	1776	192.3	17.2	14.3	0.30	0.29	0.55	0.25	4.8	2.6
Epsom Salts	496	496	16.1	12.8	0.33	0.27	0.77	0.27	3.6	2.5
"	993	993	15.5	12.4	0.34	0.29	0.73	0.31	3.6	2.6
"	1986	1986	15.4	14.2	0.32	0.30	0.62	0.29	3.5	2.4

1. Each value is the average of three replications

2. Differences are not significant

TABLE 3

Effect of Three Magnesium Carriers on pH and Ammonium Acetate Extractable Magnesium, Calcium and Potassium in Soil II[1]

Treatment			pH		Mg (ppm)		Ca (ppm)		K (ppm)	
			Crop		Crop		Crop		Crop	
Source	lbs/A	Mg lbs/A	1	2	1	2	1	2	1	2
Check	0	0	5.4	5.6	21.7	17.8	118.	126.	10.5	20.3
Dolomite	500	48.1	5.9	5.6	28.5	27.7	119.	142.	8.0	16.3
"	1000	96.3	6.1	5.9	34.0	39.2	143.	166.	9.3	15.3
"	2000	192.6	6.4	6.4	51.0	70.2	167.	189.	9.2	13.3
Sul-Po-Mag.	444	48.1	5.4	5.3	19.3	25.5	114.	120.	7.0	18.3
"	888	96.3	5.4	5.3	31.3	42.2	109.	104.	10.3	17.7
"	1776	192.3	5.1	5.2	46.5	56.0	90.	89.	15.3	17.5
Epsom Salts	496	496	5.3	5.3	16.2	29.5	113.	102.	8.8	20.3
"	993	993	5.9	5.1	24.7	43.8	110.	113.	7.5	19.2
"	1986	1986	5.2	5.2	58.0	60.7	87.	126.	9.0	18.3
L.S.D. 0.05			0.3	0.4	17.5	21.4				
L.S.D. 0.01			0.4	0.5	21.4	26.2				

1. Each value is the average of three replications

TABLE 4

Effect of Three Magnesium Carriers on Yield and Composition of Barley Grown on Soil II[1]

Treatment			Yield (gms)		Mg (percent)		Ca (percent)		K (percent)	
			Crop		Crop		Crop		Crop	
Source	lbs/A	Mg lbs/A	1	2	1	2	1	2	1	2
Check	0	0	14.9	6.75	0.22	0.22	0.52	0.43	3.7	3.1
Dolomite	500	48.1	16.3	9.36	0.26	0.30	0.49	0.30	3.6	3.2
"	1000	96.3	15.6	11.19	0.31	0.27	0.49	0.17	3.4	2.8
"	2000	192.6	13.6	11.03	0.33	0.30	0.49	0.19	3.4	2.9
Sul-Po-Mag.	444	48.1	15.4	8.21	0.29	0.25	0.42	0.29	3.6	3.5
"	888	96.3	15.8	8.90	0.32	0.30	0.42	0.30	3.7	3.3
"	1776	192.3	16.7	8.89	0.31	0.32	0.27	0.18	5.0	3.8
Epsom Salts	496	496	15.3	9.03	0.29	0.28	0.44	0.29	3.6	3.4
"	993	993	15.8	9.38	0.32	0.31	0.39	0.23	3.7	3.1
"	1986	1986	16.3	8.90	0.35	0.38	0.30	0.19	3.5	3.4
			S	S	**	**				
L.S.D. 0.05					0.08	0.07				
L.S.D. 0.01					0.09	0.08				

1. Each value is the average of three replications

Legend: S = significant at the 0.10 level
** = significant at the 0.01 level

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