Leaching of Mg fertilizers in Puerto Rican Ultisols[1]

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ABSTRACT

Laboratory experiments, using disturbed soil columns, were performed to determine solubility and downward movement of surface-applied magnesium fertilizers in three Puerto Rican Ultisols. Leaching of Mg from surface-applied granular magnesium oxide fertilizers was much slower than leaching from Epsom salts and potassium-magnesium sulfate. The inclusion of ammonium sulfate in the MgO fertilizer band resulted in solubilization of Mg from the MgO and allowed greater movement into the soil profile. When ammonium sulfate was applied with MgO, 85% of the Mg dissolved and moved deep into the profile, whereas with MgO applied alone only 15% of the Mg moved. However, in the presence of high concentrations of ammonium sulfate, the extent of Mg leaching through the soil was greater than where soluble magnesium fertilizer was applied without ammonium sulfate. Urea had a lesser solubilizing effect on MgO, and potassium chloride and triple superphosphate were ineffective.

RESUMEN

Lixiviación de fertilizantes de magnesio en Ultisoles de Puerto Rico

Se hicieron seis experimentos en columnas de suelo para determinar la solubilidad y el movimiento vertical de aplicaciones superficiales de sales de Mg en tres Ultisoles tipicos de la zona montañosa de Puerto Rico. La lixiviación del Mg proveniente de la aplicación del fue óxido de magnesio mucho más lenta que la de las sales de sulfato de magnesio y sulfato de potasio-magnesio. La adición de sulfato de amonio a la banda de óxido de magnesio aumentó la solubilidad y el movimiento vertical del Mg en la columna de suelo de 15 a 85%. La urea tuvo un efecto minimo en la solubilidad del óxido de magnesio mientras que el cloruro de potasio y el superfosfato triple fueron inefectivos.

INTRODUCTION

Magnesium is an essential element for plant growth; it forms the center of the chlorophyll molecule and plays important roles in many enzyme systems. The amount of Mg needed for good yields of commercial banana and plantain crops is often larger than the amount that they are

likely to obtain from mountain soils (4, 9). Marked yield responses to Mg applications have been obtained in various crops in Puerto Rico (2, 3, 8). A recent economic analysis of a banana Mg fertilization experiment showed the profitability of heavy applications of Mg in spite of its high cost (5).

Since the uptake efficiency of fertilizer Mg is estimated to be 75% (4), improving management to augment Mg uptake could increase profits by reducing fertilizer costs. Possible environmental side-effects would also be reduced.

Both plant and soil factors contribute to low Mg uptake. Absorption of Mg may be reduced because of limited root surface area, or the ability to take up Mg on a per unit area basis may be reduced by competition from other cations. The soil may not be able to retain adequate Mg if the cation exchange capacity is low or if the concentration of other cations in the soil solution is high. Management practices that reduce Mg retention in the soil include band application, which overloads the soil's cation retaining capacity, and applications of high concentrations of fertilizer salts which compete for retention sites on the clay surfaces. Mg which is not absorbed or is displaced by other cations is subject to leaching loss as water moves downward through the profile.

The incorporation of slow-release Mg sources such as dolomite or granulated MgO at planting time might reduce the excessive concentration of Mg ions associated with band placement. In addition, the low solubility of these sources could help in maintaining a constant and adequate level of Mg sufficient to supply plant needs without promoting serious leaching loss.

Magnesium applications to established plantings of banana or coffee cannot be mechanically incorporated into the plow layer. In this situation farmers normally apply fertilizer on the soil surface near the plant; sometimes the fertilizer is applied in a narrow band with a high concentration per unit area. Surface-applied MgO particles could enter the soil through cracks, or be incorporated to a shallow depth by weeding or cultural practices, but the majority of the insoluble material would remain on or near the soil surface. Published solubility values would indicate that such Mg would not be available. The solubility of MgO in water is 0.0006 g/100 ml whereas that of magnesium sulfate is 71 g/100 ml (10). Thus whereas equivalent of 32 kg/ha Mg as magnesium sulfate applied in a band covering 3% of the surface area of a plantation would dissolve in 0.15 cm of rainfall, it would theoretically require, in the absence of other reactions, 2900 cm of rainfall to dissolve the same amount in the form of MgO. It is possible, however, that magnesium from surface-applied MgO could reach plant roots by solubilization reactions with other fertilizer components present in the same band.

In this paper we report the results of six experiments designed to study the rate of Mg movement from surface applications of various Mg

fertilizers and the effects of heavy applications of fertilizer salts on the solubilization and movement of Mg from MgO applied in concentrations similar to those found in bands under field conditions.

MATERIALS AND METHODS

Soils for the column experiments were air dried, ground and analyzed. Soil pH in water (1:2 soil:H_2O) was measured with a glass electrode. KCl-extractable Al was determined by using an atomic absorption spectophotometer, and exchangeable cations were extracted with neutral 1 *M* NH_4OAc and similarly determined. Table 1 gives properties of soils.

Experiment 1

Non-saturated flow column techniques with small additions of water to simulate natural rainfall (7) were used for leaching experiments. Two columns 77 cm high were constructed of sections of 2.54 cm, (inside diameter) PVC plastic pipe. The sections were of various heights, from 0.2 to 10 cm; the shorter ones were used at the top of the column. The bottom of each column was covered with several layers of nylon net (1 mm openings) supported by a funnel.

The columns were filled with dry Maricao clay soil (Ochreptic Hapludults, clayey, mixed, isothermic). After the columns were moistened we added to one column 0.557 g of Epsom salts ($MgSO_4.7H_2O$), which is the equivalent of 32.5 kg/ha Mg if it were concentrated around plants on 3% of the surface area of a field. To the other column an equal amount of Mg was added as MgO powder (0.094 g of C.P. grade MgO).

A syringe pump driven by a 1 rpm motor was used to slowly drip water onto the soil surfaces at 2.54 cm per day at 2- to 4-day intervals until 7.6 cm had been added. This relatively low rate of water addition was used to minimize macropore movement of water and maximize the effects of fertilizer interaction with the soil (6).

Three days later the sections were taken from the column, and the soil was removed from each section, dried and exchangeable Mg determined.

TABLE 1.—*Soil pH, exchangeable cations and KCl-extractable Al*

Soil	pH	Ca	Mg	K	Al	Effective CEC
		------------------mg/kg-------------------				meq/100g
Maricao clay	4.8	130	300	60	1053	15.0
Corozal clay	6.7	2990	170	650	0	18.0
Humatas clay	5.4	2350	180	300	0	14.0

Experiment 2

Three columns similar to those used in Experiment 1 were prepared with Corozal clay (Aquic Haplohumults, clayey, mixed, isohyperthermic), premoistened with a water spray and passed through a 2-mm sieve. Extra care was needed in working with the Corozal clay because it tends to puddle when it becomes excessively moist. The soil was spooned into the column with periodic tapping. After construction, water was added to these columns, and a fiberglass wick (1.3 cm diameter, approximately 30 cm long) was inserted into the moist soil on the lowest section of the column to provide better drainage by increasing the tension.

Columns A, B, and C each received 0.094 g powdered MgO (C.P. grade), equivalent to 33.5 kg/ha Mg applied in a band covering 3% of the field. Column B received, at the same time, 3.04 g $(NH_4)_2SO_4$ (fertilizer grade) and 2.4 g KCl (reagent grade), equivalent to 360 kg/ha N and 724 kg/ha K applied in a band on 3% of the surface area of a field (approximately four times the recommended trimonthly rate for bananas (1). Column C received one half these levels of soluble salts after the first 2.7 cm water was added and one-half on the eighth day (after 8 cm of rainfall).

Approximately 2.6 cm of water was added to the columns every 2 or 3 days at a rate of about 1 cm per hour until the equivalent of a total of 23.5 cm of rain had been attained. Two days after the last addition of water, the sections were removed from the column; the soil was taken out, dried, and analyzed for exchangeable K and Mg.

Experiment 3

Approximately 0.20 g ground or unground samples of granular Fert-O-Mag[3] MgO fertilizer (American Minerals, P.O. Box 2005, Dunedin, FL 34697) was placed in preweighed small disposable plastic cups, and the exact weight was recorded. Ten millimeters of fertilizer solutions containing 2.2 g of KCl (reagent grade), 3.2 g of $(NH_4)_2SO_4$ (fertilizer grade), 0.14 g of triple superphosphate $[Ca(H_2PO_4)_2.H_2O$, reagent grade] or a mixture of the three were added to each cup.

After 5 days the clear supernatant was removed from half of the cups and the remaining material was washed twice with 30 ml distilled water. After drying, the cups were weighed. The other cups were similarly treated after 10 days. The change in MgO weight was calculated by subtraction. The experiment was run in duplicate.

[3]Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico, nor is this mention a statement of preference over other equipment or materials.

Experiment 4

A sample of Fert-O-Mag MgO fertilizer obtained from the manufacturer was sieved through 1- and 2-mm sieves. Of this sample 64% was retained on the 2-mm sieve and 34% on the 1-mm sieve; 2% passed through the 1 mm sieve. These fractions were designated as coarse, medium, and fine, respectively.

Test solutions were prepared by dissolving 10 g of fertilizer salt [$(NH_4)_2SO_4$, urea or KCl] in 100 ml of water. A control of distilled water was also run concurrently.

Filter papers of 15-cm diameter were weighed and placed in funnels and 1.002 g of coarse, medium or fine MgO fertilizer was placed in each. The bottoms of the funnels were stopped up and 14 ml of test solution was added. Because of the amount absorbed by the filter paper and the amount entering the stem of the funnel, about 4 ml of solution stayed in direct contact with the MgO. After 1.5 hours, the solution was allowed to drain and the paper and remaining MgO were rinsed well with distilled water. After drying for 1 day, the weight of the filter paper plus the MgO was recorded, and the process repeated.

Experiment 5

To investigate the effect of the granule size of MgO fertilizer on the rate of magnesium movement in soils as affected by fertilizer salts, we prepared six soil columns similar to those used in Experiment 1, except that they were 116 cm in height. The columns were filled with Humatas clay (Typic Haplohumult, clayey, mixed, isohyperthermic).

Three individual samples of Fert-O-Mag were analyzed for particle size. The totals for the three samples showed that the finest one-third by weight consisted of 183 particles weighing from 0.001 to 0.010 g each (mean weight 0.0058 g), the medium one-third contained 77 particles of 0.010 to 0.022 g each (mean weight 0.0141 g) and the largest third contained 33 particles of 0.023 to 0.068 g (mean weight 0.0334 g).

Column A served as a check and received 0.898 g fertilizer grade $K_2SO_4.2MgSO_4$ (Sul-po-mag), the equivalent of the application of 59 kg/ha Mg on 3% of a field. Each of the remaining columns received an equivalent amount of Mg in the form of 0.195 g of MgO placed on the soil surface. Column C received 45 fine-size particles, column D received 13 medium-size particles and column E received 5 large particles. Columns B and F received a representative mixture of sizes made up of equal weights of each size fraction to total 0.195 g of MgO. Columns C through F received an additional treatment of fertilizer salts consisting of 1.66 g of fertilizer grade $(NH_4)_2SO_4$ and 1.11 g of KCl. These rates are the equivalent to the application of 196 kg/ha N and 334 kg/ha K on 3% of the field area. Columns A and B did not receive N and K fertilizer salts.

A total of 19.1 cm of water was added intermittently to the column surfaces during a period of 6 days at about 0.32 cm/hr.

A second addition of N and K fertilizer salts was made 10 days after the first addition, followed by 7.3 cm of water added during the following 8 days.

The columns were disassembled section by section, and the soil was dried and analyzed for exchangeable magnesium.

Experiment 6

A conical rubber piston through which a small hole had been bored was inserted in the bottom of a 15.2-cm-tall glass column of 1.6-cm inside diameter. The top of a disposable 0.5-ml glass pipette, 23 cm long with an inside diameter of 3 mm (volume 1.4 ml), was inserted through the hole in the piston and sealed so that the pipette hung downwards from the bottom of the cylinder.

Two 9-mm diameter disks cut from kitchen paper towels were placed in the bottom of the column, covering the top of the pipette. About 0.34 g of small pieces of the same paper toweling 8 mm or less square, were added and tamped down. The apparatus was lowered into distilled water to allow air in the paper to escape upwards while the paper became saturated with water. The wet mass was tamped down to make an air-tight seal. The height of the paper membrane thus formed was 1 cm. The apparatus was lifted out of the water, and checked to verify that the pipette remained full of water, thus providing 24 cm of tension at the surface of the paper toweling.

Moist Corozal clay passed through a 2-mm sieve was added to the cylinder in 1.5-cm increments. After each addition, the soil was compacted slightly. The final height of the soil column was 13 cm, and bulk density was 0.72.

In order to evaluate the effect of $(NH_4)_2SO_4$ on the movement of native magnesium in agricultural soils, we then applied 1.5 g of fertilizer grade $(NH_4)_2SO_4$ to the top of the column. Water was added intermittently to the column one drop at a time for 3 days. We used an Ismatec peristaltic pump (Model 7614-30, Cole-Palmer Instrument Co. Chicago, IL 60648). The rate of addition was slow so that unsaturated flow through or over the surfaces of the soil particles was achieved, rather than saturated flow in water-filled pore spaces. Leachate was collected periodically from the bottom of the pipette and analyzed for magnesium.

A similar run was made with a second column to which 0.228 g of magnesium sulfate was surface applied (equivalent to a field application of 35 kg/ha Mg concentrated on 3% of the surface area). Approximately 25 cm of leachate was collected over a 3-day period.

Following this, approximately 1.5 g of fertilizer grade $(NH_4)_2SO_4$ was added to the column surface, which is the equivalent of applying 450

kg/ha N in a band representing 3% of the field area. Leachate was collected for a 5-day period.

RESULTS AND DISCUSSION

Experiment 1

Experiment 1 was carried out to verify our expectation that MgO would be less mobile in a soil of the tropics than the traditional $MgSO_4$ fertilizer.

Figure 1 shows the results of leaching the highly soluble $MgSO_4$ and low-solubility powdered MgO with the equivalent of 7.6 cm of rainfall. In the MgO column, 78% of the extractable Mg in excess of the original level was located in the top 1.4 cm of the soil. In the $MgSO_4$ column only 15% remained in the top 1.4 cm of the column, while 85% had moved below this depth. These results support the claim that MgO is a long-lasting source of Mg in cultivated soils in which leaching is a problem.

Experiment 2

Experiment 2 was carried out on a Corozal clay soil to examine the possible accelerating effect that fertilizer salts might have on the movement of Mg from powdered MgO applied in high concentrations on the
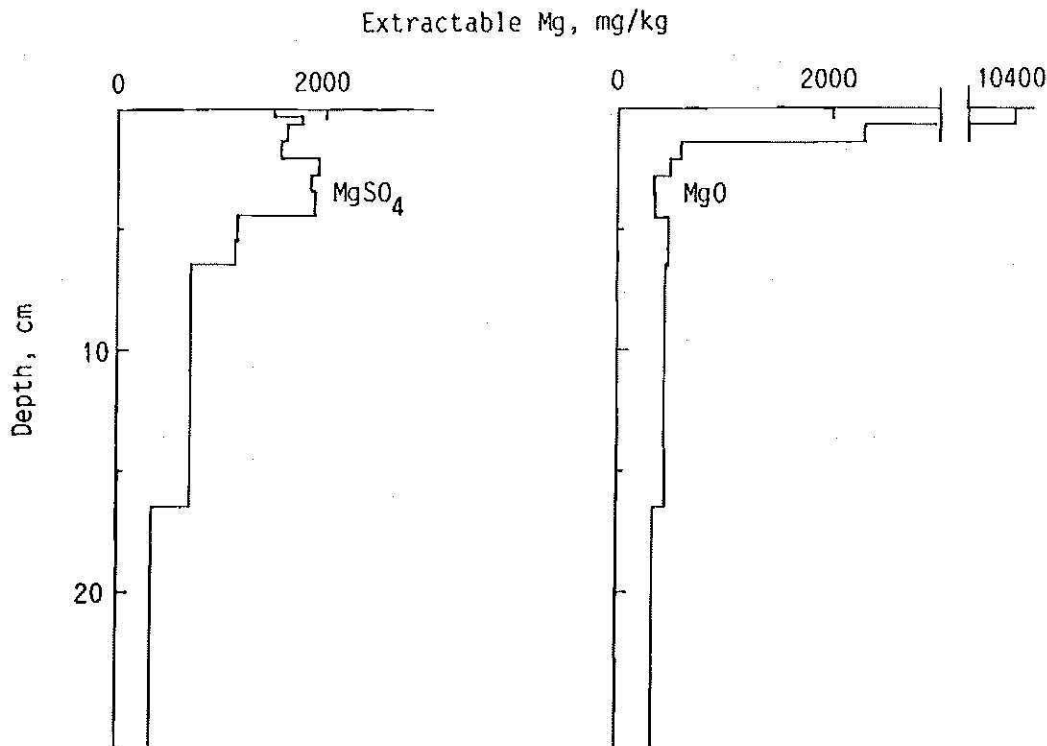

FIG 1.—Exchangeable Mg as a function of depth and Mg source, in a Maricao clay soil.

soil surface, such as might be encountered in bands of fertilizer applied under established plantings of banana or coffee.

After the addition of the equivalent of 23.5 cm of rainfall to the columns there was a clear effect of $(NH_4)_2SO_4$ and KCl on the solubility of the MgO (fig. 2 A vs. B). Approximately 50% of the total Mg applied was mobilized in each of the two fertilizer salt treatments, and moved to the 26 to 66-cm layer. Somewhat more Mg moved deeper in the treatment where the fertilizer was all applied initially (fig 2 B) rather than split into two smaller applications (fig. 2 C).

The results of this experiment support the hypothesis that the fertilizer salts are reacting chemically with MgO to solubilize Mg from the MgO source.

Experiment 3

Experiment 3 was carried out to identify fertilizer components which may be active in solubilizing Mg from a commercial granulated MgO product (Fert-O-Mag) currently being surface-applied as a Mg source in Puerto Rico.

The $(NH_4)_2SO_4$ fertilizer component was much more effective than KCl or triple superphosphate in dissolving the granulated MgO (table 2). Dissolution by $(NH_4)_2SO_4$ was apparently complete by 5 days, as there was no statistically significant additional dissolution in the 10-day treatment (data not shown). Apparently the 5-day period was sufficiently long to eliminate any effect of particle size; 90% of the product was dissolved whether it was ground and applied in powder form or used in the original granule form.

The increase in weight observed when no $(NH_4)_2SO_4$ was applied may be due to the formation of compounds such as magnesium hydroxides or carbonates which are relatively insoluble and heavier than MgO.
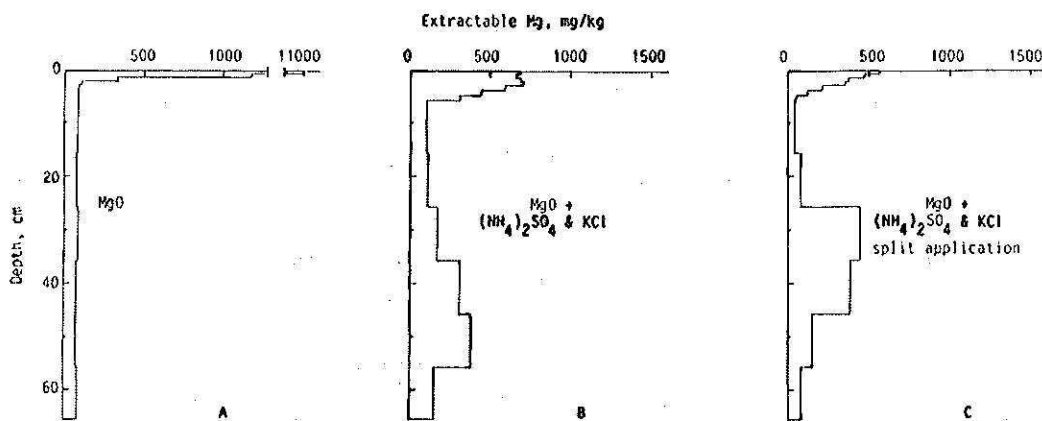

FIG. 2.—Effect of ammonium sulfate and potassium chloride application on movement of Mg from MgO in a Corozal clay.

TABLE 2.—*Weight change (%) of powdered or granular Fert-O-Mag after treatment with various fertilizer solutions*

Treatment	Fineness of Fert-O-Mag		
	Granules	Powder	Mean[1]
	------------------------------%------------------------------		
Triple Superphosphate	+44[2]	+58	+51 a
Water (check)	+24	+46	+35 b
KCl	+25	+45	+35 b
Triple Superphosphate, $(NH_4)_2SO_4$, and KCl	-41	-56	-48 c
$(NH_4)_2SO_4$	-91	-88	-90 d

[1]Means followed by the same letter are not significantly different at 0.05 probability by the Duncan Multiple Range Test.

[2]Values are the means of two replications and two reaction times (5 and 10 days).

Experiment 4

A further experiment was run on granule dissolution to investigate the dynamics of the effects of fertilizer salt effects and granule size on dissolution rate. As figure 3 shows, both urea and $(NH_4)_2SO_4$ dissolved MgO granules. The rate of dissolution with urea was slower than with ammonium sulfate. The fine-sized MgO particles dissolved more rapidly than the coarse particles.

Apparently the dissolution occurs as a result of a chemical reaction between MgO and the $(NH_4)_2SO_4$ or urea fertilizers which produce ammonia. Moistened pH indicator paper held above the funnels showed a strong alkaline reaction, and there was a marked smell of ammonia. If this same reaction occurs in the field and the ammonia volatilized is lost to the atmosphere, it increases the effective cost of the fertilization program for the farmer, because less nitrogen enters the soil for plant use.

The expected reaction between a base, such as MgO, and ammonium sulfate would be the formation of magnesium sulfate and ammonium hydroxide, which is unstable and decomposes to give off ammonia gas. The removal of one of the reaction products as a gas drives the reaction forward and explains why the dissolution process occurs relatively rapidly. A similar reaction might be expected between MgO and urea, which hydrolyzes to form ammonium carbonate. In this case, however, the other reaction product (magnesium carbonate) is sparingly soluble, and less solubilization of Mg is obtained. Where water, KCl or triple
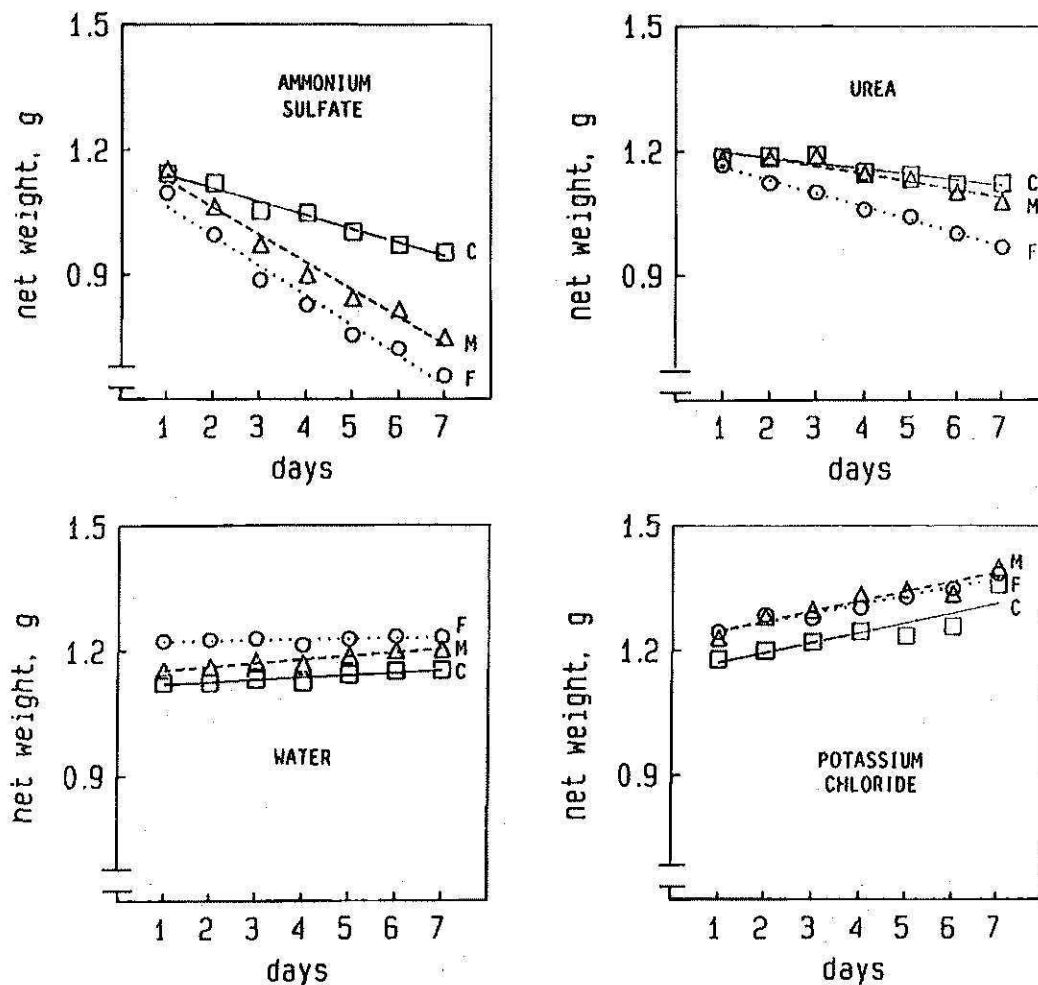
Fig. 3.—Effect of time on weight of granules of Fert-O-Mag MgO soaked 1.5 hours per day in various fertilizer solutions. C = granules retained on 2-mm sieve; M = granules retained on 1-mm sieve; F = granules passing 1-mm sieve.

superphosphate were added, no volatile reaction products would be expected, and if hydrated or carbonated Mg compounds formed, net weight would increase, as was observed.

Experiment 5

Experiment 5 was performed to evaluate, in a Humatas clay soil, the promotional effect of fertilizer salts on the mobilization of Mg from granules of MgO fertilizer in comparison with a soluble source and to investigate whether MgO particle size would have an effect on this process.

The presence of high rates of $(NH_4)_2SO_4$ and KCl had a marked effect on Mg movement (fig. 4 B vs. C-F). The addition of the equivalent of 26.4 cm of rain resulted in movement of 47% of the total Mg applied to
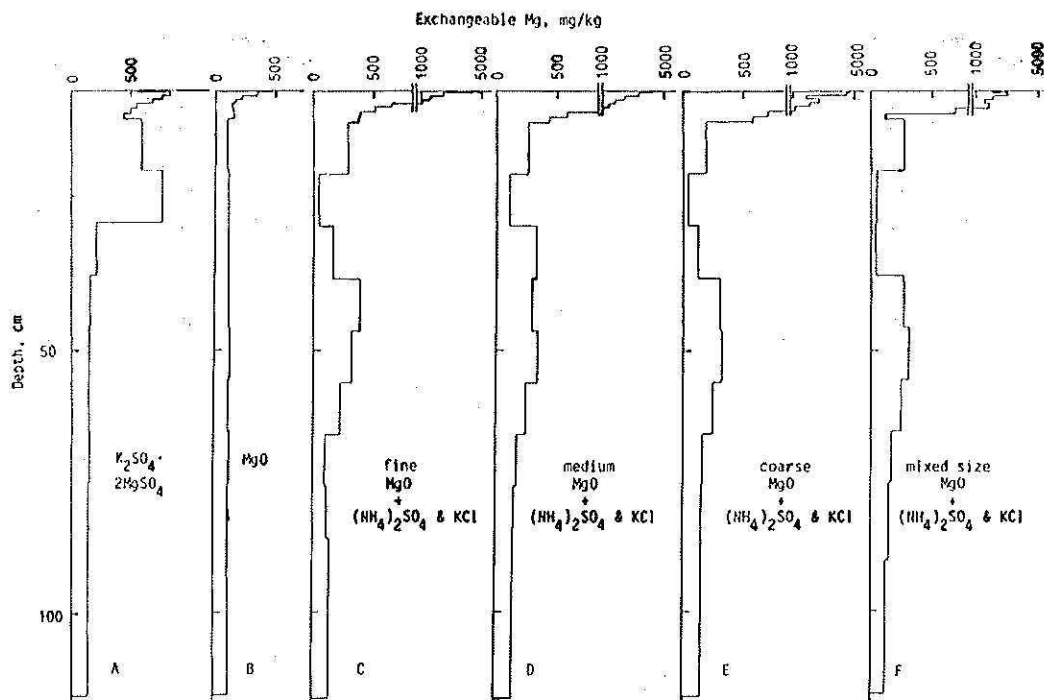
FIG. 4.—Exchangeable Mg as a function of depth, Mg source and size, and nitrogen and potassium fertilizer, in a Humatas clay soil.

depths of 26 cm or more in the column. The second fertilizer salt application mobilized an additional quantity of Mg, indicating that not all the MgO had dissolved with the first application. There was essentially no movement below 2 cm in the column with granular MgO fertilizer alone. Under the conditions of this experiment no clear effect of MgO granule size on dissolution or movement was evident.

Where Sul-Po-Mag (a commonly-used soluble potassium magnesium sulfate fertilizer) was applied alone (fig. 4 A), there was much less Mg movement than where $(NH_4)_2SO_4$ and KCl were applied with MgO. The Mg peak for Sul-Po-Mag moved to 21 cm, while that for insoluble MgO with fertilizer salts was found at 51 cm. This indicates that the high concentrations of fertilizer salts, in addition to dissolving MgO, also enhance the rate of Mg movement through the soil profile.

The low extractable Mg levels found at the 25-cm depth in the fertilizer salt treatment columns (fig. 4 C-F) suggest that the fertilizer salts may also actually displace Mg originally present in the soil as they pass through the column.

Experiment 6

This experiment was initiated to investigate the effect of $(NH_4)_2SO_4$ on leaching of Mg originally present in the soil and Mg added to the soil.

When a heavy application of $(NH_4)_2SO_4$ was washed through a 13-cm soil column with a 2-cm² area by the addition of the equivalent of 6.3 cm of rainfall, 1.7 mg Mg was rapidly leached out (fig. 5 A). This is the equivalent to the loss of 0.72 meq/100 Mg, or about 50% of the total exchangeable Mg initially present.

When a similar column was treated with 10.4 meq/100g magnesium sulfate and the equivalent of 22.5 cm of rainfall, the rate of movement of the Mg peak was much slower (fig. 5 B), and all but 29% of the added Mg was retained, at least temporarily. When the same column then received a surface application of $(NH_4)_2SO_4$, the equivalent of 80% of the added Mg leached out (fig. 5C), and the rate of movement of the Mg peak was two times faster than with the magnesium sulfate alone. This finding supports the observations of Experiment 5 which indicate that heavy applications of $(NH_4)_2SO_4$ may speed up Mg movement through the soil profile and leach out Mg originally present there.

Rates of Mg movement

Rates of Mg peak movement for the various experiments were mathematically adjusted to a common bulk density of 1.0 g/cm³ by multiplying the observed rate by a factor obtained by dividing the actual bulk density of the column by 1.0 g/cm³. The adjusted rates were grouped according to whether or not auxiliary fertilizer salts were present (table 3). The average rate of movement for magnesium in the absence of fertilizer salts was 0.6 cm per cm of rainfall, whereas in the presence of salts it was 2.0 cm/cm. The difference by t-test is statistically significant at the 0.001 level.

The results that we have observed in the three soil series are consistent with what would be predicted on the basis of physico-chemical principles. According to the principle of mass action, the number of magnesium ions retained on an exchange surface should vary according to
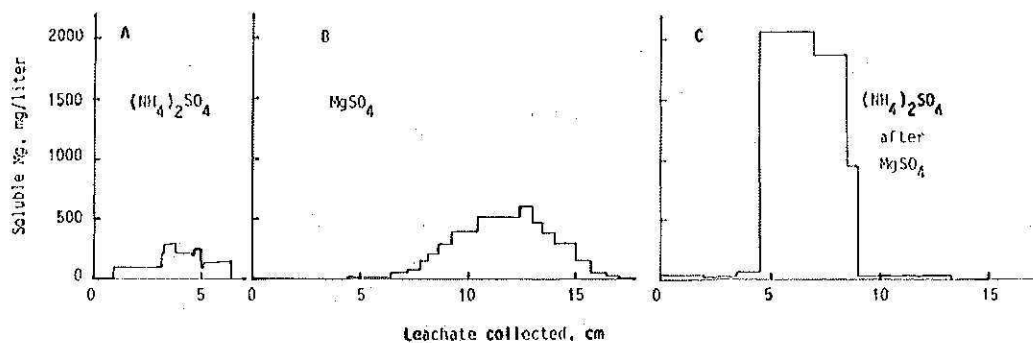

FIG. 5.—Magnesium concentration in Corozal clay soil leachate as affected by surface application of ammonium sulfate (A), and, in a second column, by surface application of Epsom salts (B), followed by ammonium sulfate (C).

TABLE 3. *Rates of Mg peak movement in the presence and absence of $(NH_4)_2SO_4$, adjusted to a common bulk density of 1.0*

Soil	Experiment	Rate of Mg peak movement	
		$(NH_4)_2SO_4$ absent	$(NH_4)_2SO_4$ present
		cm depth/cm rain	
Maricoa clay	1	0.27	
Corozal clay	2		1.80
Corozal clay	6	0.87	2.12
			2.83
Humatas clay	5	0.76	1.93
			1.93
			1.93
Mean[1]		0.63	2.01
(Standard Deviation		(0.32)	(0.40)

[1]The two means are significantly different by t test at $p = 0.001$.

the proportion that they represent of the total number of cations in the soil solution, given that all the cations have equal affinity for the soil. Thus, swamping the system with an excess of ammonium and potassium would be expected to displace most of the Mg from the soil surfaces into the soil solution. Mg in the soil solution is highly subject to leaching losses.

SUMMARY AND RECOMMENDATIONS

Because of the low solubility of magnesium oxide, surface applications of this fertilizer dissolve slowly and would not be expected to supply adequate Mg to rapidly growing plants. However, where MgO is supplied together with $(NH_4)_2SO_4$ in concentrated bands, a considerable proportion of the MgO is solubilized. In the magnesium sulfate form it moves into the soil profile and becomes available to plants, but at the same time it is subject to rapid leaching loss. The reaction of MgO with $(NH_4)_2SO_4$ also forms volatile ammonia which can easily be lost to the atmosphere. Some of the Mg leaching loss could be eliminated by distributing fertilizer more evenly under the plant canopy to decrease overloading of the soil cation retention capacity. Distribution of ammonium sulfate over a greater surface area should also reduce displacement and removal of Mg ions already present in the soil. Perhaps a more efficient approach would be to incorporate MgO or dolomite in the entire plow layer at planting, rather than relying entirely on surface applications made after establishment of perennial crops. These management practices should be investigated under Puerto Rican conditions.

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