

essing behavior, product yield, and nutrient uniformity as any other component of the feed mixture. Decrease in particle size of recycle material favors granule growth and nutrient uniformity in the final product but at the same time reduces processing efficiency and product yields.

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## NUTRIENT AVAILABILITY IN SOIL

# Availability of Minerals from Magnesium Ammonium Phosphates

Soil conditions affecting the availability of minerals from  $MgNH_4PO_4 \cdot H_2O$  have been investigated, and the successful use of this fertilizer as a source of N to produce potted flowering crops from a single preplant application has been demonstrated. Saturation of  $MgNH_4PO_4 \cdot H_2O$  occurs at about 1.7 meq. per liter at 23.5° C. Solubility is only moderately affected in the temperature range from 10° to 40° C. Dissolution is enhanced by acid soil conditions, increased levels of soil moisture, and nitrification. Surface applications result in a slower release of nitrogen than soil incorporations of fertilizer. Particle size of the fertilizer exerts a strong influence on the rate of dissolution at concentrations far from saturation, but the rate of dissolution is also strongly influenced by the saturation deficiency which minimizes the effect of particle size. When incorporated in the soil, the effect of particle size of  $MgNH_4PO_4 \cdot H_2O$  on plant growth was smaller than would be anticipated from surface area considerations.

METAL ammonium phosphates have recently been proposed as long-lasting, nonburning fertilizer sources of N, P, and various metals including Mg, Fe<sup>+2</sup>, Zn, Mn<sup>+2</sup>, Cu, and Co (1). The general formula for this group of compounds is  $MeNH_4PO_4 \cdot xH_2O$ . With the exception of the Zn compound, which is stable under ordinary conditions in the anhydrous state, all compounds are conveniently stable as the monohydrate. Since they are compounds of limited solubility, their utility as fertilizers is particularly attractive in those applications where leaching losses of soluble fertilizers would be high or where low "burn-hazard" or long duration is important. In this respect, this group of fertilizers is of particular interest for the

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production of container nursery stock, flower crops, landscape installations, and turfgrass (5).

This paper reports on several studies of various conditions which may be expected to affect the availability of minerals from metal ammonium phosphates.

#### Methods and Materials

The fertilizer materials used in these studies were commercial products and were classified in various particle size groups as summarized in Table I.

**Solubility.** A series of experiments were conducted to determine the presence of soluble impurities, solubility

at saturation, influence of particle size and temperature on the rate of solution and solubility, and influence of the presence or removal of the products of solution on the dissolution of the minerals. In general, the procedure followed was to add a quantity of the material under investigation to a flask containing distilled water and agitate by aeration in a constant temperature room. Samples of the supernatant were taken periodically for conductometric analysis or for analysis of Mg, P, or NH<sub>4</sub>. Additional pertinent details related to these experiments are given in the discussion or in the figure legends.

**Nitrification.** The influence of nitrification on the amount of dissolution of  $MgNH_4PO_4 \cdot H_2O$  was investigated using

**Table I. Particle Size of Fertilizer Materials Used in This Study**

Material	Mm. Diameter, % Smaller Than:						
	4.7	2.36	1.17	0.59	0.295	0.208	0.147
MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O (8.3% N)							
Coarse granules	42	0	...	...	...	...	...
Medium granules	100	88	26	7	...	...	...
Powder	...	...	...	100	96	74	23
Mg(NH <sub>4</sub> 6/7, K 1/7) PO <sub>4</sub> ·H <sub>2</sub> O <sup>a</sup>							
Medium granules	100	79	2	...	...	...	...

<sup>a</sup> The approximate analysis of the material—N, 7%; P, 17.5%; and K, 3.3% (P<sub>2</sub>O<sub>5</sub>, 40%; K<sub>2</sub>O, 4%)—indicates about 1/7 isomorphous substitution of K for NH<sub>4</sub>.

**Table II. Fertilizer Treatments and Response of Delaware Chrysanthemums Measured at Maturity**

Treatment	Grams N per Pot	Method of Application	Other Additions <sup>a</sup>	Average Flower Diameter (In.)	Average No. of Stems	Leaf Color	Over-all Plant Quality <sup>b</sup>
NUTRIENT SOLUTION <sup>c</sup>							
1	...	Irrigation water	A	5.9	14.3	Dark	Excellent
MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O MEDIUM GRANULES							
2	0.5	Incorporated	B	4.5	11.0	Light	Poor
3	1.0	Incorporated	B	4.9	13.0	Medium	Good
4	2.0	Incorporated	B	5.1	14.0	Dark	Excellent
5	3.0	Incorporated	B	5.2	13.3	Dark	Excellent
6	4.0	Incorporated	B	4.9	15.7	Dark	Excellent
7	8.0	Incorporated	B	4.5	12.3	Dark	Good
POWDER							
8	1.0	Incorporated	B	5.2	14.0	Medium	Good
COARSE							
9	1.0	Incorporated	B	5.0	11.7	Medium	Good
10	1.0	Surface	B	4.6	11.3	Light	Poor
11	3.0	Incorporated	B	4.9	15.7	Dark	Excellent
POWDER							
12	3.0	Incorporated	B	4.6	15.0	Dark	Excellent
FeNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O POWDER							
13	2.0	Incorporated	B	5.2	13.7	Medium	Excellent
MnNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O POWDER							
14	2.0	Incorporated	B	5.1	15.3	Dark	Excellent

<sup>a</sup> (A) 2 grams of single superphosphate and 2 grams of urea-formaldehyde were mixed into each pot prior to planting.

(B) 100 grams of dolomitic limestone and 50 grams of gypsum were added to each cubic foot of the soil mix and 4 grams of heavily coated KCl (supplied by Archer Daniels Midland Co., Minneapolis, Minn.) were added to each pot.

<sup>b</sup> Judgment based on leaf size and color, density of foliage, flower number and size, and general appearance. Marginal leaf necrosis or flower injury reduced quality rating.

<sup>c</sup> Hoagland's (3) nutrient solution No. 2 (5 p.p.m. Fe was supplied as EDTA) was supplied with each irrigation.

a Yolo loam soil. This soil had an initial pH of 5.2 but was adjusted to pH 6.9 by adding to it 1% CaCO<sub>3</sub> and 0.1% NaHCO<sub>3</sub>, mixing, wetting, and allowing it to dry. Ninety grams of the soil thus prepared were mixed with 12 grams of horticultural perlite (approximately twice the volume of the soil) to assure good aeration, and after the additives listed under treatments below were mixed in, the moisture content was adjusted to 15%. Soil samples were placed in loosely capped glass jars which were stored at high relative humidity in a

room at 26.5° C. The samples were incubated for 24 days, and adjusted for small weight changes about midway through the study. At the end of the incubation period, the entire sample was mixed with 100 ml. of 1N MgSO<sub>4</sub>, which was at 11° C., and stirred for about 3 minutes, after which a sample of the solution phase was obtained using a suction filter. This extraction procedure previously had been shown to extract negligible quantities of NH<sub>4</sub> from powdered MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O. The sample obtained was analyzed during

the following 2 days for NO<sub>3</sub> and NH<sub>4</sub>, and the quantities extracted from the soil were computed. Treatment variables, which were replicated four times, were as follows:

Treatment	Additive per 102 Grams of Soil-Perlite Mixture
a	Nothing
b	125 mg. blood meal (13% N)
c	125 mg. blood meal + 2% formaldehyde in the water used to moisten the sample
d	250 grams powder MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O
e	250 grams powder MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O + 2% formaldehyde in the water used to moisten the sample
	Same as "d" except coarse granules MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O were used
g	Same as "e" except coarse granules MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O were used

**Soil Reaction.** The influence of soil pH on the dissolution of MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O was studied by adding various quantities of FeSO<sub>4</sub>·7H<sub>2</sub>O or a mixture of dolomitic limestone and NaHCO<sub>3</sub> to a Yolo soil. The additives were blended into the soil, the moisture content of the soil was adjusted to 13%, and the samples were allowed to incubate for 2 weeks to allow pH values to approach equilibrium. During this period, the soils were mixed occasionally, and the pH of samples was measured by the water-saturated paste method. At the end of this period, the pH values had nearly stabilized. The extreme quantities of reagents required for the pH adjustment of 4650 grams of soil were 30 grams of FeSO<sub>4</sub>·7H<sub>2</sub>O or a mixture of 454 grams of dolomitic limestone and 40 grams of NaHCO<sub>3</sub>, respectively.

At the end of this incubation period, the soil moisture was adjusted to 13.8% (field capacity was 15.7%—the procedure used to adjust soil moisture levels is described below under "Soil Moisture"). Soil samples weighing 573 grams (dry weight) were taken and 10 grams of medium granules MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O were added and mixed into each sample. A series of soil samples without fertilizer served as a control. Samples were stored in a humid environment at 23° ± 3° C. in 1-quart glass jars loosely closed with screw cap lids and mixed twice weekly for aeration.

After 41 days of incubation, the pH and moisture content of a small aliquot of each sample were determined, then the entire sample was transferred to 500 ml. of 1N MgSO<sub>4</sub> (pH 6.75) at 11° C. and stirred vigorously for 3 minutes. Sixty milliliters of filtrate were obtained in 2 to 3 minutes by filtration with vacuum. This procedure dissolved negligible quantities of NH<sub>4</sub> from the fertilizer. The extract was analyzed for NH<sub>4</sub>-N and NO<sub>3</sub>-N, and the total extractable N content of the soil samples was computed.

**Table III. Fertilizer Treatments and Response of Poinsettias Measured at Maturity**

Treatment	Grams N per Pot	Method of Application	Other Additions <sup>a</sup>	Av. Height (In.)	Av. Bract Diam. (In.)	Leaf Color	Relative Leaf Abscission	Evaluation <sup>b</sup>
NUTRIENT SOLUTION <sup>c</sup>								
1	...	Irrigation water	A	18.0	11.7	Medium	Considerable	Poor
MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O MEDIUM GRANULES								
2	1.0 plus nutrient solution <sup>c</sup>	Incorporated and irrigation water	A, B	15.0	12.3	Dark	Slight	Excellent
3	1.0	Incorporated	C	17.9	12.1	Medium	Moderate	Poor
4	2.0	Incorporated	C	14.1	11.2	Dark	Slight	Good
5	3.0	Incorporated	C	8.6	9.2	Dark	Considerable	Poor
6	2.0	Surface	C	20.0	13.8	Medium	Slight	Excellent
7	3.0	Surface	C	19.9	13.5	Dark	Slight	Excellent
8	3.0	1/2 Surface						
		1/2 Incorporated	C	10.5	8.2	Dark	Moderate	Poor
LSD (0.05)				1.67	1.13			

<sup>a</sup> (A) Each pot received 2 grams of single superphosphate, 2 grams of dolomitic limestone, and 1 gram of gypsum.

(B) 2 grams of heavily coated KCl (supplied by Archer Daniels Midland Co.).

(C) 100 grams of limestone and 50 grams of gypsum per cubic foot of soil mix, and 4 grams of heavily coated KCl were added to each pot.

<sup>b</sup> Judgment was based on color and density of foliage, size of plant, size and number of flowers, and general appearance.

<sup>c</sup> Three times weekly irrigation was made with a nutrient solution containing 14 meq. NH<sub>4</sub>NO<sub>3</sub> per liter, 3.5 KNO<sub>3</sub>, and 4.5 Ca(NO<sub>3</sub>)<sub>2</sub>

The moisture content of the soil samples was required at the termination of the study to compute the total volume of the solution from which the sample for analysis was obtained. The average moisture content of samples at the termination of the study was 14.0%—sampling error no doubt was responsible for the disparity between the initial and final moisture content measured. The authors estimate the soil moisture suction at this moisture content to be less than 0.5 bar.

**Soil Moisture.** The influence of soil moisture on dissolution of MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O was studied by incubating fertilized samples of soil of various moisture contents for 36 days, then extracting and analyzing for the NO<sub>3</sub> and NH<sub>4</sub>-N which had been transferred to the soil. The pH of Yolo loam was adjusted to 6.9 as described above, and incubation and extraction techniques were previously described. Moisture levels were originally adjusted approximately to the values listed in Figure 1 by adding the proper amount of water dropwise to samples of air-dry soil spread thinly on a plastic sheet, mixing, and allowing to "equilibrate" 3 days in a tightly sealed jar. The moisture content was determined at the end of this period. Three samples of soil at each moisture level were then weighed out, and into one of these series of soils 10 grams of powder MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O were mixed, while a second series received 10 grams of medium granules, and the third series was unfertilized. The size of the moist samples was such that the dry weight of each was 573 grams.

The field capacity of the soil used was estimated at 15.7%. A value of 9% moisture was obtained for samples equilibrated on pressure membrane apparatus at 5 bars. The permanent

wilting percentage in the soil was expected to occur at about 8 to 8.5% moisture.

Figure 1 indicates the range of moisture levels used in the study.

**Placement of Fertilizer.** The effect of surface application as compared to the incorporation of MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O in soil on the dissolution of the fertilizer was investigated by using columns of soil which were periodically leached with tap water. Krilium-treated (0.1% VAMA) Yolo loam, having a pH of 5.2, was placed in glass tubing, 5-cm. I.D. Eight hundred grams of soil produced a column about 40 cm long. Treatments consisted of: incorporation by uniformly mixing through the soil of 4.5 grams of powder MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O; incorporation in same manner of 4.5 grams of large granules MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O; surface application of 4.5 grams of the powdered fertilizer; surface application of 4.5 grams of the large granules; and nothing added. Each fertilized column thus received 375 mg. of N. Each treatment was replicated twice.

The columns were leached 27 times during a 100-day period after addition of the fertilizer. About 100 ml. of tap water containing about 4 meq. per liter of salts were used for each leaching. The leachate was collected and measured and analyzed for NH<sub>4</sub> and NO<sub>3</sub>.

**Analytical Procedures.** Mg was analyzed by EDTA titration after removal of Ca by oxalate precipitation; P was measured colorimetrically by the vanadate procedure; NH<sub>4</sub> was determined colorimetrically by using Nessler's reagent after distillation with micro-Kjeldahl apparatus; and NO<sub>3</sub> was analyzed colorimetrically by the phenol-disulfonic procedure. Soil reaction was measured with a glass electrode and

electrical conductance was measured with Model RC-16 conductivity meter by the Industrial Instruments Co.

#### Production of Potted Flower Crops.

**CHRYSANTHEMUMS.** Commercially produced rooted cuttings of Delaware chrysanthemum were planted into clay pots having a usable soil volume of 1.2 liters. Five plants were established in each pot. The soil mix used consisted of one half by volume each of fine sand and sphagnum peat moss. Cultural practices were typical for commercial production and included pinching out of the terminal bud 1 week after planting to induce branching. Lateral buds were removed from the branches to produce one large flower per branch. Irrigation was with tap water, usually applied daily. Treatments, replicated three times, consisted of the fertilizer variables listed in Table II.

Flowering occurred about 11 weeks after planting and treatments were evaluated on the basis of flower diameter and number, plant height, general appearance, and foliage color.

**POINSETTIAS.** Commercially rooted poinsettia cuttings, variety Barbara Ecke Supreme, were planted August 31, in clay pots having a usable soil volume of 1 liter. One plant was established in each pot. The soil mix was the same as that used for chrysanthemums. Plants were pinched to induce branching 12 days after planting. Night temperatures in the greenhouse were maintained at 15° C. Irrigation was with tap water, except for treatments receiving liquid fertilization. The fertilizer treatments are listed in Table III. Each treatment was replicated 10 times. Plants matured about December 10. To evaluate response, notes were taken on the relative amount of leaf abscission, leaf color,

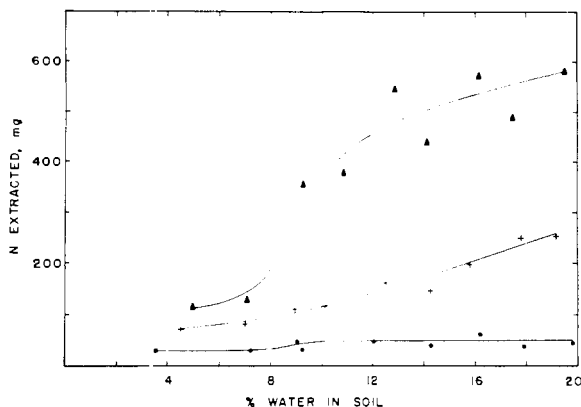


Figure 1. Influence of soil moisture on the total amount of N extracted from soil fertilized with  $MgNH_4PO_4 \cdot H_2O$  after 6 weeks of incubation

▲—▲ soils receiving powdered fertilizer, +—+ soils receiving coarse granules, ●—● unfertilized group

maturity date, and height of plants measured from the base of the main stem to the base of the inflorescence. The maximum diameter of each inflorescence was recorded and an average calculated for each plant.

### Results and Discussion

**Solubility Considerations.** IMPURITIES The electrical conductance developed, as a function of time in various suspensions of medium granules of  $MgNH_4PO_4 \cdot H_2O$  in distilled water is summarized in Figure 2. In Figure 2C, the conductivity of the supernatant liquid approached a constant value of about 0.42 mmho and was independent of the amount of solid phase  $MgNH_4PO_4 \cdot H_2O$  in the suspension. This, of course, is as would be expected for slightly soluble minerals. In Figure 2A, electrical conductivities much higher than 0.4 mmho were observed, which were also related to

the amount of material in suspension, indicating the presence of soluble impurities in the  $MgNH_4PO_4 \cdot H_2O$ . The soluble impurities constituted about 4% by weight of this sample.

**SOLUBILITY.** Analysis of the supernatant liquid of the second resuspension of  $MgNH_4PO_4 \cdot H_2O$  containing 4 grams per liter yielded the following results

pH	Mmoles/Liter		
	Mg	$NH_4$	P
7.97	1.71	1.41	1.68

and the electrical conductivity was 0.42 mmho per cm. at 25° C.

The solubility found corresponds to 22.6 mg. of the anhydrous salt per 100 ml. This is more than 50% higher than the solubility reported by Bridger, Salutsky, and Starostka (7).

The data obtained permit a calculation of the solubility product constant for

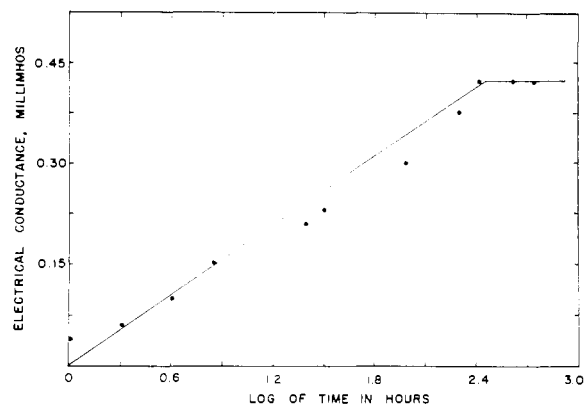


Figure 3. Electrical conductance (corrected to 25° C.) as a function of time of the supernatant liquid of a suspension of 10 grams of  $Mg(NH_4 \ 6/7, K \ 1/7)PO_4 \cdot H_2O$  per liter at 21° C.

$MgNH_4PO_4$ , if the  $PO_4$  concentration is computed using simultaneous equations and the ionization constants for  $H_3PO_4$ .

$$K_{sp} = [Mg] [NH_4] [PO_4] \\ = 1.71 \times 10^{-3} \times 1.41 \times 10^{-3} \times 6.41 \times 10^{-8} \\ = 1.55 \times 10^{-13}$$

This value compares with  $7.1 \times 10^{-14}$  reported by Taylor *et al.* (8), who further concluded that the mineral does not dissolve congruently.

Figure 3 shows the increase in electrical conductivity of a previously washed suspension of magnesium ammonium potassium phosphate versus the log of time in hours. The approach to saturation was approximately linear with the log of time and occurred at about the same concentration as with magnesium ammonium phosphate. That equilibrium is approached so slowly tends to extend the time minerals would become available from this fertilizer.

**PARTICLE SIZE EFFECTS.** Although the particle size of the materials used could not be expected to affect the equilibrium concentration appreciably, particle size does have a large effect on the time required to reach equilibrium. Table IV shows the electrical conductivities of suspensions of coarse, medium, and powdered  $MgNH_4PO_4 \cdot H_2O$  at intervals of 0.5, 1, and 6 hours. The rate at which solution occurs is probably proportional to the relative amounts of surface area exposed when first placed in water, but the rate at which the equilibrium concentration is approached is also affected by the saturation deficit, and this soon causes the direct relationship to surface area to be seriously distorted. After 6 hours, about half as much dissolution of the coarse granules had occurred as had occurred from the powder although the latter solution was only approximately one half of saturation. Discounting the surface area contribution due to surface roughness, the powdered material used in this

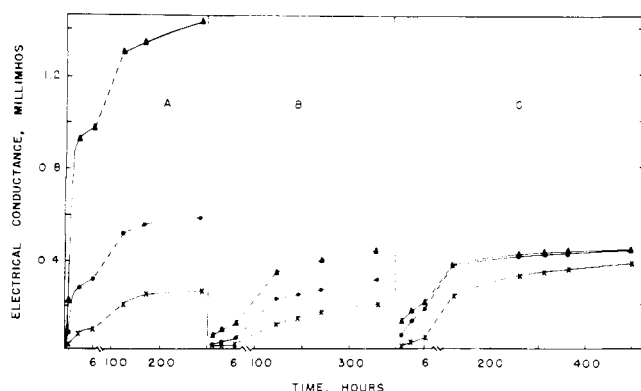


Figure 2. Electrical conductance (corrected to 25° C.) of the supernatant liquid of suspensions of medium granules of  $MgNH_4PO_4 \cdot H_2O$  as a function of time

"B" is a resuspension in distilled water of the granules used in "A", and "C" is a resuspension of the granules used in "B". ▲—▲ represent a suspension at the rate of 16 grams per liter; ●—● represent a suspension at the rate of 4 grams per liter; and X—X represent a suspension at the rate of 1 gram per liter

study had a surface area several hundred times greater than the coarse granules. Particle size is a factor of considerable importance in regulating the availability of minerals from  $MgNH_4PO_4 \cdot H_2O$ ; however, as will be discussed subsequently, the effect is not nearly so large as might be expected on the basis of surface area.

**TEMPERATURE EFFECTS.** The following values of electrical conductance (EC mmhos per cm. at 25° C.) were obtained for the supernatant liquid of suspensions of previously washed  $MgNH_4PO_4 \cdot H_2O$  powder agitated for 48 hours at the indicated temperatures. The suspension concentrations were 10 grams per liter.

Temp. °C.	4	10	21	30	40
EC, mmhos	0.33	0.37	0.42	0.43	0.45

The initial rate of solution (at the end of 30 minutes) was only slightly influenced by temperature. Differences due to temperature were larger at the end of 48 hours than at the end of 30 minutes. Apparently the solubility of  $MgNH_4PO_4 \cdot H_2O$  is influenced somewhat by temperatures but the effect is sufficiently small so that it should not be important in most situations.

**Soil Reactions with  $MgNH_4PO_4 \cdot H_2O$ .** The solubility product principal permits one to anticipate a number of reactions which would affect the dissolution of  $MgNH_4PO_4 \cdot H_2O$ . Any reaction which would tend to remove either Mg,  $NH_4$ , or  $PO_4$  from the solution phase would result in a greater amount of dissolution of the mineral or conversely high solution phase concentration of Mg,  $NH_4$ , or  $PO_4$  would reduce solubility. Thus, the nitrification of ammonium ions would result in greater dissolution of the mineral. Figure 4 illustrates the general effect produced by removing from or adding to the solution phase Mg,  $NH_4$ , or  $PO_4$ . The presence of either an anion or cation exchange resin in the suspension greatly increased the amount of  $NH_4$  dissolved from  $MgNH_4PO_4$ , while 0.05M  $MgSO_4$  depressed the amount becoming soluble.

**NITRIFICATION.** The process of nitrification would be expected to ac-

celerate the solution of  $MgNH_4PO_4$  when  $NH_4$  concentrations become high. Table V summarizes the data obtained in the nitrification study and shows that much more total soluble nitrogen ( $NO_3$  plus  $NH_4$ ) was obtained from powdered  $MgNH_4PO_4$  under nonsterile than under sterile conditions. Nitrite may also have been present in the nonsterile conditions where high levels of  $NH_4$  were present. If so, the data underestimate the influence of nitrification on dissolution of the fertilizer. Where the rate of solution was slow (with the large granules), nitrification did not have a large effect on the total soluble nitrogen obtained, presumably because in the time allowed,  $NH_4$  concentrations did not reach levels high enough to retard the rate of dissolution substantially.

The data in Table V confirm the expectation that when  $NH_4$  production from  $MgNH_4PO_4 \cdot H_2O$  is high, the nitrification process can result in a more rapid dissolution of the mineral than would otherwise be the case. The same result would be expected from other factors which might be removing  $NH_4$  from the soil solution, such as plant or clay adsorption of  $NH_4$ . Likewise soil adsorption of Mg or phosphate would be expected to accelerate dissolution of the mineral for the same reasons.

**SOIL REACTION.** Bridger *et al.* (7) report about a 50% increase in the solubility of  $MgNH_4PO_4 \cdot H_2O$  in 0.001N HCl as compared to water. In an acid soil system, adsorption of soluble Mg,  $NH_4$ , and  $PO_4$  by the solid phase would also be expected to increase the dissolution of  $MgNH_4PO_4 \cdot H_2O$ . On the other hand, nitrification processes in many mineral soils are substantially reduced under moderately acid conditions (2). This tendency per se, considered in the light of nitrification effects previously presented, would be expected to reduce dissolution of  $MgNH_4PO_4 \cdot H_2O$ .

In the alkaline pH range, a number of soil interactions would be expected to affect dissolution of  $MgNH_4PO_4 \cdot H_2O$ . For a given level of soluble P, more  $PO_4$  relative to  $HPO_4$  or  $H_2PO_4$  is found with increasing pH. Soluble levels of Mg

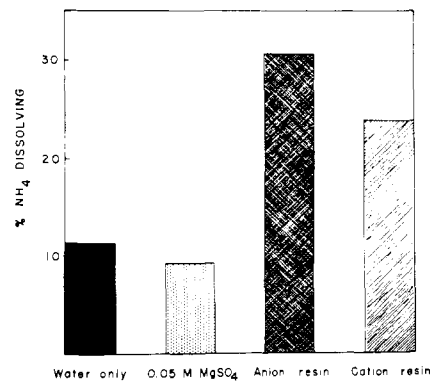


Figure 4. Percentage of  $NH_4$  dissolving from 10 grams of medium granules of  $MgNH_4PO_4 \cdot H_2O$  agitated for 48 hours at 23° C. under the following conditions: (a) 500 ml. of distilled water added, (b) 500 ml. of 0.05M  $MgSO_4$ , (c) 500 ml. of distilled water plus 2 grams of Dowex 1-x2 (a strongly basic anion exchange resin containing adsorbed Cl), and (d) 500 ml. of distilled water plus 2 grams of Dowex 50 W-X2 (a strongly acidic cation exchange resin saturated with Na)

In treatment (d), the  $NH_4$  was exchanged off the resin and added to that in solution in computing the percentage of  $NH_4$  dissolved

often would be higher under alkaline conditions, and this would tend to minimize dissolution. With surface application, loss of  $NH_4$  by volatilization (2) at pH values above 7.5 would tend to hasten dissolution.

The influence of soil reaction on the quantity of nitrogen extracted from  $MgNH_4PO_4 \cdot H_2O$  which had incubated for 6 weeks is summarized in Table VI.

In the unfertilized series, pH values tended to shift toward the range of about 4.4 to 5.0 during the incubation period.  $NH_4$  was found only where pH values remained below 5.2—presumably because nitrification was occurring at higher pH values. The total nitrogen extracted in the unfertilized series averaged about 82 mg. and did not show a trend except that the highest pH treatment was down. Quite probably some

Table IV. Electrical Conductivity of the Supernatant Liquid of Gently Agitated Suspensions (10 Grams per Liter) of Various Size Particles of  $MgNH_4PO_4 \cdot H_2O$  after three Time Intervals

Particle Size	Suspension temperature was 22° C.		
	EC of Supernatant Liquid, $\mu$ mhos		
	After 0.5 hour	After 1 hour	After 6 hours
Coarse	26	44	110
Medium	52	72	145
Powder	134	142	221

Table V. Nitrogen Extracted from Soils Incubated for 24 Days with Several Additives under Sterile and Nonsterile Conditions

Additives	Soil Conditions	Mg. N Extracted per Sample		
		$NH_4$	$NO_3$	Total
Nothing	Nonsterile	0.1	8.2	8.3
Blood meal	Nonsterile	0.2	16.0	16.2
Blood meal + HCHO	Sterile	1.7	1.2	2.9
Powder $MgNH_4PO_4$	Nonsterile	41.5	30.8	72.3
Powder $MgNH_4PO_4$ + HCHO	Sterile	40.0	2.2	42.2
Large granules $MgNH_4PO_4$	Nonsterile	0.6	18.3	18.9
Large granules $MgNH_4PO_4$ + HCHO	Sterile	14.8	4.3	19.1

volatilization of any  $\text{NH}_3$  produced occurred at the three highest pH treatments.

The  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  fertilized series shows well defined treatment effects. The pH shifts were much larger than the unfertilized series and reflected the tendency of  $\text{MgNH}_4\text{PO}_4$  to stabilize around pH 6. Interestingly, no pH shift was observed for the soil originally at pH 5.8, but as soils were initially more acid the higher the final pH became. Very probably this is due to an increasing amount of dissolution resulting from increasing acidity, with the result that the larger amount of  $\text{PO}_4$  produced raised pH values higher. In general, pH reduction in the alkaline range was greater than that which occurred in the unfertilized series and was probably due to the acidulating action typical of  $\text{NH}_4$  fertilizers which undergo nitrification. The  $\text{NH}_4$  extracted was relatively constant in the acid range but declined sharply in the alkaline range probably because of volatilization losses at pH 7.5 and above. Many data are available showing that while ammonia losses may be substantial at pH values of about 7.5 and higher, losses may be reduced when the fertilizer source is covered by several centimeters of soil (2). Very probably nitrogen losses occurring in the alkaline pH range in these laboratory studies are greater than would be encountered under field conditions if the fertilizer were covered by several centimeters of soil. The  $\text{NO}_3$  curve shows a well defined maximum for the treatments near the middle and slightly acid part of the pH range. Deviations from the quantities found at the pH extremes no doubt largely reflect the soil's capability for nitrification.

Apparently increasing the soil pH in the ranges normally encountered in soils tends to reduce moderately the dissolution of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ . The influence of the nitrification process, in the pH range where this transformation is possible, accelerates the dissolution resulting in a broad maximum for the total nitrogen obtained, ranging from about neutrality to around pH 5.5. The fact that the  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  caused substantial shifts in the pH values precludes a more definite statement on pH effects.

The influence of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  on soil reaction is, of course, a matter of considerable practical interest. A comparison between pH changes occurring in the fertilized and nonfertilized series clearly shows the tendency of  $\text{MgNH}_4\text{PO}_4$  to buffer in soils of pH 5.8 to 6.0. The application rate used in this study was several times as high as might typically be used for fertilizer application and consequently the pH changes in normal fertilization practices may not be as large.

**SOIL MOISTURE.** The influence of soil moisture on the total amount of N

extracted from soils fertilized with  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  after 6 weeks of incubation is shown in Figure 1. In the soil used, field capacity was estimated to be 15.7% moisture, and an average value of 9.0% moisture was obtained for samples equilibrated on the pressure membrane apparatus at 5 bars. The permanent wilting percentage in the soil is expected to occur at about 8 to 8.5% moisture. In Figure 1 the quantity of N extracted at the end of the incubation period is plotted against the average of initial and final moisture levels found in the soil. During the incubation period, samples at the four lowest soil moisture treatments lost an average of 1.1% moisture while those on the highest four treatments lost an average of 3.5%.

Soil moisture levels exert a considerable influence on the amount of nitrogen dissolving from  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ . The increase in N dissolving with increasing moisture content was greater for powder than with coarse granules. The higher the moisture content, the greater the volume of water with which  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  attempts to equilibrate. Were this the only consideration, the amount of N dissolving from  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  would be expected to be approximately proportional to the moisture content of the soil. The relationship found for coarse  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  is approximately linear. Nitrification was occurring at such a rate that very little  $\text{NH}_4$  was found except at the three lowest moisture levels. Therefore, the tendency for increased dissolution of coarse  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  with increasing moisture content probably reflects, by and large, the tendency for Mg and  $\text{PO}_4$  to equilibrate with larger volumes of water. The failure to show direct proportionality is probably due to diffusivity effects and soil adsorption.

In the case of the powdered  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , a very large increase in the quantity of N which dissolved occurred in the averaged moisture range of about 8 to 10%. This range coincided with the

moisture range in which there was a large increase in nitrification. Quite probably the moisture effects on solubilization of N with powdered  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  are due both to removal of  $\text{NH}_4$  (from the solution near the mineral) by nitrification as well as to diffusion of the solution phase products of dissolution from the mineral surface. Diffusivity is related to the thickness of moisture films (4), and the removal of Mg,  $\text{NH}_4$ , or  $\text{PO}_4$  from the solid surface would increase by this mechanism with increasing moisture content.

Although moisture levels clearly exert a considerable influence on the dissolution of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , this may not complicate management problems excessively since the large effect occurred in a relatively dry range—about in the moisture range where an irrigation would normally be made.

**MODE OF INCORPORATION.** The results of repeated leaching of soil columns during a 100-day period to which powdered or coarse granules of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  had been added either by incorporation in the soil or as a top-dressing are shown in Figure 5. Particle size and method of application of fertilizer produced large effects on the amount of nitrogen recovered from the columns. Powder forms of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  yielded N more rapidly than granular forms, as would be expected, and the influence of mode of application is also large—surface application yielding nitrogen more slowly than when the fertilizer was incorporated. This effect was no doubt largely due to a tendency of surface applications to dry somewhat between leachings, less diffusion of the soluble components from the fertilizer, and probably less nitrification in the vicinity of the fertilizer. Since leaching was done about twice weekly, the surface-applied fertilizer tended to remain relatively moist and differences in nitrogen release due to application methods would be increased had the intervals between leachings been longer

**Table VI. Initial and Final Soil pH Values Found and  $\text{NH}_4$ ,  $\text{NO}_3$ , and Total Mg. of N Extracted from an Unfertilized Series of Soils and Soils Receiving 10 Grams of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  per 573 Grams of Soil**

Incubation period was 42 days

Unfertilized Series					$\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ Series				
Initial pH	Final pH	$\text{NH}_4^a$	$\text{NO}_3^a$	Total <sup>a</sup>	Initial pH	Final pH	$\text{NH}_4^a$	$\text{NO}_3^a$	Total <sup>a</sup>
3.8	4.2	10.8	32	93	3.8	6.4	207	56	263
4.4	4.4	9.4	63	72	4.4	6.2	196	119	315
5.2	5.1	2.0	107	109	5.2	6.0	191	175	366
5.8	5.4	0.0	83	83	5.8	5.8	193	166	359
7.5	6.5	0.0	74	74	7.5	6.2	143	257	400
8.3	7.7	0.0	78	78	8.3	6.6	63	131	194
8.8	8.0	0.0	84	84	8.8	7.8	22	94	116
9.6	8.2	0.0	64	64	9.6	8.2	26	41	67

<sup>a</sup> Values are milligrams of N extracted per culture.

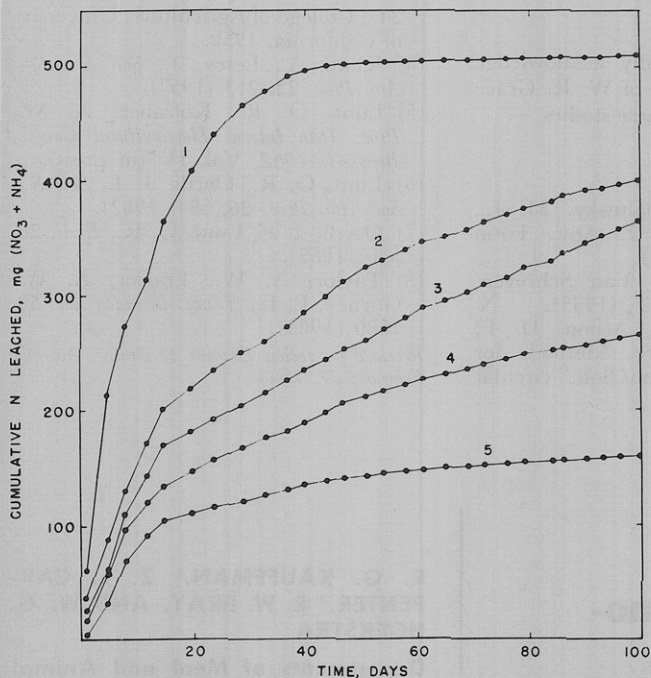


Figure 5. Cumulative removal of N from soil columns by repeated leaching with tap water

Curve 1: 375 mg. of N added from powdered  $MgNH_4PO_4 \cdot H_2O$  incorporated in soil; curve 2: 375 mg. of N added from coarse granules of  $MgNH_4PO_4 \cdot H_2O$  incorporated in soil; curve 3: 375 mg. of N added from powdered  $MgNH_4PO_4 \cdot H_2O$  added to soil surface; curve 4: 375 mg. of N added from coarse granules of  $MgNH_4PO_4 \cdot H_2O$  added to soil surface; curve 5: no fertilizer added

Essentially all of the N was recovered as  $NO_3$  in the leachate, except where powdered  $MgNH_4PO_4 \cdot H_2O$  was incorporated. In this case, when nitrogen recoveries in the leachate were large during the first 30 days, only about 20%, on the average, of the N recovered was in the  $NH_4$  form. This, perhaps, should not be surprising since  $NO_3$  would be much more mobile than  $NH_4$  in the soil column. Where large granules were incorporated 6% of the nitrogen was recovered as  $NH_4$  during the first 30 days. After this date or with the other treatments only traces of  $NH_4$  were recovered.

The data in Figure 5 are interesting on several counts. The steady and prolonged supply of nitrogen becoming available from surface applications of powder or granules or incorporations of granules (curves 2, 3, and 4) is impressive. The data clearly point up the utility of this type of fertilizer under conditions where a prolonged, steady supply of fertilizer is desired, or where leaching losses of soluble fertilizers would be great. By extrapolation, surface applications of large granules might be expected to yield nitrogen at reasonably steady rates for about a year under the conditions of this experiment. The data also clearly illustrate that while particle size does have an effect on the rate of availability, the relationship is far from being proportional to the surface area involved. The large granules when incorporated yielded nitrogen at about  $1/8$  to  $1/10$  the rate of the powder, al-

though the surface area of the powdered fertilizer was presumably several hundred times greater than the large granules. Finally, surface application as contrasted to incorporation in the soil is an effective means of extending the period of supply of nitrogen from  $MgNH_4PO_4 \cdot H_2O$ . Surface application of either powdered or granular fertilizer extends the period of supply to several times as long as when mixed into the soil. Surface applications of coated fertilizers also greatly extend their period of availability (6, 7).

After about 40 days the columns in which powdered  $MgNH_4PO_4 \cdot H_2O$  had been mixed yielded nitrogen at about the same rate as the nonfertilized column. At this time, about 95% of the added nitrogen had been recovered after corrections were made for the original soil nitrogen released during this time.

**Applications of Metal Ammonium Phosphates to the Production of Potted Flower Crops.** Tables II and III also summarize the results for the studies with potted chrysanthemums and poinsettias, respectively.

**CHRYSANTHEMUMS.** Treatment 1, Table II, which received nutrient solution three times per week, produced excellent quality plants, as had been anticipated. One gram of nitrogen per pot was inadequate, while 8 grams was excessive. A comparison of the results obtained with medium, powdered, or coarse granules of  $MgNH_4PO_4 \cdot H_2O$  at suboptimum rates (compare treatments



Figure 6. Typical plants produced on treatments 1, 2, and 7 (left to right) of the poinsettia study (Table III)

3, 8, and 9) of application shows approximately comparable response. Results of the three particle sizes were the same when compared at the rate of 3 grams of N per pot. This shows that effect of particle size on the availability of nitrogen from  $MgNH_4PO_4 \cdot H_2O$  is not really large, when incorporated in soil, and generally substantiates observations made in the laboratory studies. At 4 weeks, the plants on treatment 8 were about 5 to 20% larger than those of treatments 3 or 9, indicating some increased availability of the powdered as compared to the granular fertilizer.

Comparison of treatments 9 and 10 shows that surface placement of the fertilizer, as compared to incorporation, considerably reduces the availability, as would have been expected from the laboratory studies. Differences of about 15% in the size of the plants on these two treatments were observed at the end of 4 weeks.

Development of a very slight to slight interveinal chlorosis on some leaves was observed after about 4 weeks on treatments 2, 3, 4, 6, 7, 8, 9, 11, and 12. Treatment 14 was moderately chlorotic, possibly because of the high level of Mn present. The chlorosis was corrected by the application of 5 p.p.m. Fe as FeEDDHA twice in the irrigation water.

**POINSETTIAS.** The time required for the production of a crop of poinsettias is about one month longer than for most varieties of chrysanthemums. Leaf abscission takes place quite readily if nitrogen levels become low and growth is easily retarded by excessive levels of fertilizer. Consequently, it is more difficult to produce a crop of poinsettias successfully from a single application of fertilizer than is the case with chrysanthemums.

Since particle size of the fertilizer had relatively little effect in the study with chrysanthemums, only one particle size—i.e., medium granules—was used in this study. Comparisons were made with rates and application methods. The liquid fertilizer programs produced poor plants because of considerable leaf drop which occurred presumably because of

inadequate nitrogen supply at some period in growth. Treatment 2, Table III, in which the liquid fertilizer program was supplemented with 1 gram of N from  $MgNH_4PO_4 \cdot H_2O$  incorporated in the mix produced excellent results. The results again substantiate the fact that surface applications are more slowly available and longer lasting than comparable applications incorporated in the soil. Figure 6 shows the appearance of plants produced on treatments 1, 2, and 7.

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## MEAT TENDERNESS FACTORS

### Interrelations of Tenderness, Chronological Age, and Connective-Tissue Fractions of Porcine Musculature

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Tenderness was determined for 206 pork loins from barrows, gilts, and sows 132 to 1173 days old and selected according to five degrees for intramuscular fat. Elastin, acid- and alkali-insoluble collagen, alkali-soluble collagen, and acid-soluble collagen were determined chemically in 20 loins from this group representing all ages but only low levels of intramuscular fat. Advancing chronological age was associated with lower panel tenderness ratings and higher shear-force values; however, the data failed to explain this biochemically. Total quantities of connective tissue did not increase with age, but acid-soluble collagen significantly decreased with advancing age. No significant relations were found between the connective-tissue fractions and various measures of tenderness, suggesting that the physiological age-tenderness relationship may not be a reflection of changes in total quantities of connective tissue in pork muscle.

**P**ALATABILITY characteristics have long been recognized as important yardsticks in determining the acceptance of meat products. Of the various palatability traits, tenderness has received much of the researcher's attention, and the frequency of tough, chewy products undoubtedly accentuates a need for improvement. One approach to the problem has involved the study of connective tissue. The possibility exists that biochemical alterations in the connective tissue may explain at least part of the variation in tenderness of pork products.

Ramsbottom, Strandine, and Koonz (16), Mitchell, Hamilton, and Haines (11), and Bate-Smith (2) have demonstrated large variations in the amount of connective tissue among several anatomical regions of the beef carcass, and have shown the quantity of connective

tissue to be inversely related to tenderness. Bate-Smith (2) indicated that, as an animal grew older, the proportion of connective tissue in total body protein decreased. An increase in collagen concentration soon after birth was followed by a decrease with advancing age. Moran and Smith (12) nevertheless indicated that the degree of meat tenderness was a function of the amount and character of the connective tissue. Research by Wilson (19) has partially refuted such claims, because muscle from young veal calves possessed significantly higher amounts of connective tissue than comparable muscle from steers or aged cows.

In cooking experiments, Cover and Hostetler (5) found that the collagen content of two muscles of differing anatomical location was not related to tenderness and that the moisture in moist-heat cookery was required primarily to obtain high temperatures and not necessarily to convert collagen into gelatin.

Although the characterization of con-

nective tissue is somewhat incomplete, Briscoe and Loring (4), Elden, Noble, and Boucek, (6), and Kao, Boucek, and Noble (9) have made major contributions in medically oriented research on the role of connective tissue in age-related metabolic diseases. A number of soluble and insoluble connective-tissue fractions have been demonstrated and measured quantitatively by Jackson (8). According to Orekhovich and Mazurov (13) and Pierce and Hocott (14), the more insoluble fractions, such as "elastin" and alkali-insoluble "collagen," increase with advancing age. However, little evidence exists that such changes are associated with differences in meat tenderness.

This investigation was made to study the relation of chronological age to measures of tenderness for the longissimus muscle and, secondly, to determine quantitatively two insoluble and two soluble fractions of connective tissue from swine of various ages and to compare changes in these fractions with variations in tenderness.

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