

Evaluation of Phosphorus Nitrogen Compounds as Fertilizers

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Thirty-four phosphorus nitrogen compounds were prepared in the laboratory and compared in the greenhouse as high-analysis sources of fertilizer nitrogen and phosphorus for corn. The compounds included phosphonitrilic derivatives, metaphosphimates, metaphosphates, sulfur-containing compounds, and amido- and imidophosphates. The metaphosphates, amidophosphate, thioamidophos-

phates, and phosphoryl triamide were excellent sources of both nitrogen and phosphorus, but metaphosphimates were poor sources. Several of the sulfur compounds were toxic in early growth stages, but thereafter were effective sources of plant nutrients. Of the phosphonitrilic derivatives, only phosphonitrilic hexaamide was an effective source of both nitrogen and phosphorus.

Attempts to develop new and improved fertilizer materials are made with one or more major objectives: to increase the plant nutrient content; to obtain more efficient utilization of the nutrient content by plants; and to decrease the toxicity or salt effect. The economic advantages of higher plant-nutrient contents are indicated by the long-term rise in grades. Efficiency in utilization of fertilizer nutrients has always been lower than desirable—crops seldom recover more than 50% of the applied nitrogen in field tests, although recovery may be as high as 85% in the greenhouse; recovery of phosphorus in the crop immediately following application usually is less than 25%, and residual values are difficult to measure. Hence, increase in utilization of nutrients by crops, as by decreased fixation of nutrients by soil minerals or by decrease of leaching from the soil, would be a significant improvement. Covalent compounds contribute less per unit of plant nutrient to the ionic strength of the soil solution than do the usual ionic fertilizer compounds, and so may offer advantages in the rates and times at which they may be applied.

The highest N-P-K grade of ammonium polyphosphate now produced is about 15-27-0 (N-P₂O₅-K₂O grade, 15-62-0). By further condensation of linear polyphosphates, or by conversion to cyclic compounds, ammonium metaphosphate, which has a N-P-K grade of 14-32-0 (N-P₂O₅-K₂O grade, 14-73-0), is approached as a limit for ammonium phosphates. Further increase in grade can be obtained only with radically different types of compounds, such as those containing covalent P-N bonds and P-N-P linkages, and in which the nitrogen is present as amide or imide rather than as ammonium.

In a search for materials that would offer some of these advantages, 34 compounds were prepared in the laboratory and evaluated in the greenhouse as sources of phosphorus and nitrogen for plants. The study was intended primarily to explore the relation between molecular configuration and agronomic effectiveness. The types of compounds included phosphonitrilic derivatives, metaphosphimates, metaphosphates, and phosphoryl amides, some of which contained sulfur.

PREPARATION OF MATERIALS

The compounds that were tested as potential fertilizer materials are listed in Table I. Compounds that were prepared by methods described in the literature are indicated by references to the published methods; those that were prepared by methods not reported in the literature are denoted by the entry "Text" and are summarized below. Structural formulas for representative compounds are shown in Figure 1.

Phosphonitrilic Derivatives. Phosphonitrilic (or phosphazene) compounds have the general formula (PNR₂)_n. As Allcock (1968) pointed out in a recent review, these compounds resemble organic compounds in the large number of derivatives and polymers that can be formed from them. These characteristics and their fundamental composition of two plant-nutrient elements make these compounds attractive as potential fertilizer materials.

Phosphonitrilic compounds usually are prepared initially as the chloride, (PNCl₂)_n, by reaction of phosphorus pentachloride with ammonium chloride (Shaw *et al.*, 1965). The product is composed largely of 6- and 8-membered rings (*n* = 3 and 4), but contains small amounts of larger rings and straight chains; the monomer (*n* = 1) is unknown. When the phosphorus pentachloride is in excess, the amounts of cyclic compounds are decreased and those of linear polymers terminated with end groups of the elements of HCl and PCl₅ are increased. The cyclic materials can be isolated as essentially single species by fractional crystallization or distillation, but separation of linear polymers into fractions of single chain lengths is difficult.

Phosphonitrilic chlorides react readily with ammonia to form partially ammoniated compounds such as P₃N₃Cl₄(NH₂)₂ (Stokes, 1895), but more vigorous conditions are required for complete ammonolysis. Trimeric phosphonitrilic chloride reacts with ammonia to form phosphonitrilic hexaamide, P₃N₃(NH₂)₆ (Sowerby and Audrieth, 1961), which crystallizes from water as the monohydrate. The anhydrous compound is composed almost entirely of plant-nutrient elements—94.76% (N + P) or 147.69% (N + P₂O₅ equivalent)—and is readily soluble in water.

In a study of the hydrolysis of the ring system of phosphonitrilic hexaamide, Dostal *et al.* (1964) showed that the sequence of degradation products is phosphoryl triamide, diamidophosphate, monoamidophosphate, and diammonium orthophosphate plus free ammonia. The presence of each of these intermediates has been shown by paper chromatography in solutions of the hydrolyzing hexaamide.

P₃N₃(NH₂)₆·H₂O. Anhydrous phosphonitrilic hexaamide (22.8 g) prepared by the method of Sowerby and Audrieth (1961) was dissolved in 200 ml of water and precipitated by addition of 600 ml of ethanol. The precipitate was filtered off, washed with 200 ml of ethanol, and dried in a stream of nitrogen. The chemical composition and water content, as determined by a Karl Fischer titration of the product, showed it to be P₃N₃(NH₂)₆·H₂O.

P₃N₃Cl₆. Commercial trimeric phosphonitrilic chloride (El Monte Chemical Company, Pasadena, Calif.) was purified by distillation and recrystallization from petroleum ether (b 60 to 110° C).

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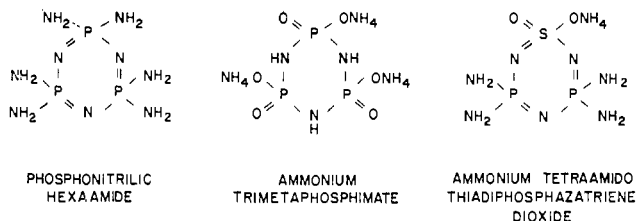


Figure 1. Structural formulas of representative compounds

$P_4N_4Cl_8$. Commercial tetrameric phosphonitrilic chloride (El Monte Chemical Company, Pasadena, Calif.) was purified by distillation and recrystallization from petroleum ether (b 60 to 110° C).

$H_2N[P(NH_2)_2=N]_7P(NH_2)_3FeCl_2$. This linear phosphonitrilic amide was prepared by ammoniation of the corresponding chloride which was prepared by the method of Nichols (1962) from a mixture of 1 mole $FeCl_3$, 10 moles PCl_5 , and 10 moles NH_4Cl . The product was an amorphous orange solid

Table I. Fertilizer Value of Phosphorus Nitrogen Compounds
(Measured in greenhouse with two 7-week crops of corn on Mountview silt loam limed to pH 6.4)

Material	Method of preparation	Composition, wt%		Test No. ^a	Relative performance ^b							
		N	P		Nitrogen response				Phosphorus response			
					Granules		Fines		Granules		Fines	
DM	UN	DM	UN	DM	UP	DM	UP					
Phosphonitrilic compounds												
$P_3N_3(NH_2)_6$	Sowerby and Audrieth, 1961	50.6	38.7	C	72	62	79	80	46	36
$P_3N_3(NH_2)_6 \cdot H_2O$	Text	50.3	37.2	A	86	88	86	86	93	98	50	52
$P_4N_4(NH_2)_8$	Sowerby and Audrieth, 1961	49.5	37.7	B	60	66	20	22
$P_3N_3[N(CH_3)_2]_6$	Keat and Shaw, 1965	31.3	23.3	B	Tox	Tox	4	4
$P_3N_3(NHCSNH_2)_6$	Otto and Audrieth, 1958; Tesi <i>et al.</i> , 1960	34.2	15.0	B	Tox	37	3	5
$P_3N_3Cl_6(NH_2)_2$	Stokes, 1895	20.4	27.7	B	62	74	15	14
$H_2N[P(NH_2)_2=N]_7P(NH_2)_3FeCl_2$	Text	38.1	29.1	C	61	51	48	51	57	38
$P_3N_3Cl_6$	Text	12.1	26.7	B	9	26	8	10
$P_4N_4Cl_8$	Text	11.9	26.7	B	Tox	Tox	7	6
Metaphosphimates												
$(NH_4)_3(PO_2NH)_3 \cdot 0.3H_2O$	Nielsen, 1962	27.0	29.9	A	64	55	61	57	20	22	8	11
$(NH_4)_4(PO_2NH)_4 \cdot 4H_2O$	Text	24.7	27.3	B	54	46	7	7
$CaNH_4(PO_2NH)_3 \cdot 6H_2O$	Text	15.7	26.0	A	22	25	37	31	23	28	8	9
$NaH_2(PO_2NH)_3 \cdot 2H_2O$	Text	14.9	31.3	C	25	23	38	37	20	11
$K_3(PO_2NH)_3 \cdot 0.8H_2O$	Text	11.2	25.5	A	15	10	14	14	24	24	16	14
$H_3(PO_2NH)_3 \cdot H_2O$	Nielsen, 1960	16.8	35.7	B	Tox	Tox	Tox	Tox
$H_4(PO_2NH)_4 \cdot 2H_2O$	Stokes, 1898	16.9	35.1	B	3	0	3	3
$Na_3[(PO_2NH)_2OPO_2]$	de Ficquelmont, 1939	9.3	28.4	B	34	33	16	18
Metaphosphates												
$(NH_4PO_3)_4$	Warschauer, 1903	14.3	31.9	C	98	88	126	124	102	82
$(NaPO_3)_3 \cdot H_2O$	Text	0.0	28.7	B	82	88
Product of reaction of P_2O_5 with NH_4OH	Text	15.1	28.9	C	98	89	148	159	133	108
Sulfur compounds												
$PS(NH_2)_3$	Klement, 1960b	37.3	27.2	A	75	106	80	114	96	106	93	96
$P_2S_2(NH)(NH_2)_4$	Text	34.1	28.9	A	73	80	58	74	72	72	78	75
$P_2S_3(NH)_2(NH_2)_5$	Text	32.5	30.8	A	63	80	34	86	54	60	56	58
$P_nS_n(NH)_{n-1}(NH_2)_{n+2}$	Text	29.1	33.1	A	54	72	70	102	62	62	40	44
$(NH_4)_2PO_3SNH_2$	Falius, 1965	27.7	20.8	C	86	100	108	126	114	91
$(NH_4)_2HPO_3S$	Brois, 1967	18.7	21.0	C	78	107	106	116	128	110
$NaPOS(NH_2)_2 \cdot 3H_2O$	Klement and Koch, 1954	14.9	16.7	C	94	110	118	146	123	109
$NH_4[P_2(NH_2)_4N_3SO_2]$	Becke-Goehring <i>et al.</i> , 1966; Kirsanov, 1952	43.0	24.1	B	74	126	39	44
$SO_2(NH_2)_2$	Text	29.2	...	A	Tox	95	Tox	90
Other compounds												
$PO(NH_2)_3$	Klement, 1960a	43.1	32.2	A	87	92	90	92	104	104	104	103
$NH_4HPO_3NH_2$	Sheridan, 1970	24.5	27.0	B	96	116	82	86
$Na_4P_2(NH)O_6 \cdot 10H_2O$	Nielsen <i>et al.</i> , 1961; Nielsen, 1964	3.2	14.0	C	115	128	102	83
$Na_5P_3(NH)_2O_8 \cdot 6H_2O$	Quimby and Narath, 1960	5.7	19.5	C	58	60	72	46
Product of reaction of P with NH_3	Stock, 1908	5.1	85.9	B	7	12

^a Tests are identified in Table II in which absolute yields and uptakes from reference fertilizer are tabulated. ^b Average of uptake by two crops from two rates of application. Compared as N sources against NH_4NO_3 and as P sources against concentrated superphosphate. Expressed as percent of yield or uptake of nutrient from standard source; DM = yield of dry matter, UN = uptake of N, UP = uptake of P. Granules were minus 6- plus 9-mesh, fines were minus 35-mesh.

whose infrared spectrum indicated the presence of $-\text{NH}_2$ and $\text{P}=\text{N}$ groups.

Metaphosphimates. $\text{K}_3(\text{PO}_2\text{NH})_3 \cdot 0.8\text{H}_2\text{O}$. Potassium trimetaphosphimate was prepared by the action of potassium hydroxide on the ammonium salt. A solution of 0.03 mole KOH in 25 ml of water was added to a solution of 0.01 mole $(\text{NH}_4)_3(\text{PO}_2\text{NH})_3 \cdot \text{H}_2\text{O}$ in 25 ml of water and the mixture was stirred and heated to 60°C . The ammonia was expelled in 90 min, after which the solution was cooled and 150 ml of methanol was added to precipitate the potassium salt. The salt was filtered off, washed successively with 50 ml of methanol and 100 ml of ether, and air dried.

$\text{CaNH}_4(\text{PO}_2\text{NH})_3 \cdot 3.6\text{H}_2\text{O}$. Calcium ammonium trimetaphosphimate was prepared from ammonium trimetaphosphimate and calcium acetate. Solutions of 0.015 mole $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ in 50 ml of water and 0.01 mole $(\text{NH}_4)_3(\text{PO}_2\text{NH})_3 \cdot \text{H}_2\text{O}$ in 50 ml of water were mixed slowly with vigorous stirring. The precipitate was filtered off, washed successively with 50 ml of ethanol and 100 ml of ether, and air dried.

$\text{NaH}_2(\text{PO}_2\text{NH})_3 \cdot \text{H}_2\text{O}$. Monosodium trimetaphosphimate was prepared by treating a solution of the trisodium salt with an ion exchange resin. A solution of 0.1 mole $\text{Na}_3(\text{PO}_2\text{NH})_3 \cdot 4\text{H}_2\text{O}$ in 200 ml of water was added to a suspension of 150 g Amberlite IR-120H resin (H form) in 50 ml of water. The mixture was stirred at room temperature for 1 hr and then allowed to settle. The solution was decanted off and the water was evaporated at room temperature under vacuum to produce an oily liquid. The liquid was dissolved in 75 ml of water, and 150 ml of petroleum ether (b 60 to 110°C) was added. Two liquid layers were formed and 250 ml of ethanol was added carefully to the upper ether layer to avoid mixing of the two layers. On standing in a refrigerator overnight the ethanol diffused into the bottom layer and deposited a white crystalline solid. The solid was filtered off, washed successively with 100 ml of ethanol and 100 ml of ether, and air dried. The identity of the salt was confirmed by its chemical analysis and its x-ray powder diffraction pattern (Herzog and Nielsen, 1958).

$(\text{NH}_4)_4(\text{PO}_2\text{NH})_4 \cdot 4\text{H}_2\text{O}$. Ammonium tetrametaphosphimate was prepared by neutralization of tetrametaphosphimic acid (Stokes, 1898) with an excess of ammonia. Concentrated NH_4OH (30 ml) was added slowly to a suspension of 0.0256 mole $\text{H}_4(\text{PO}_2\text{NH})_4 \cdot 2\text{H}_2\text{O}$ in 150 ml of water. The acid dissolved rapidly on neutralization to form a clear solution to which was added 50 ml of ethanol, whereupon the tetrammonium salt precipitated. The precipitate was filtered off, washed with 100 ml of ethanol, and dried on a clay plate. The product weighed 11.7 g, corresponding to a stoichiometric yield of $(\text{NH}_4)_4(\text{PO}_2\text{NH})_4 \cdot 4\text{H}_2\text{O}$.

Metaphosphates. $(\text{NaPO}_3)_3 \cdot \text{H}_2\text{O}$. Monosodium orthophosphate was heated 5 hr at 550°C and the cooled product was dissolved in water to form a nearly saturated solution. The solution was filtered and acetone was added slowly to the stirred filtrate at 40°C to precipitate $(\text{NaPO}_3)_3 \cdot \text{H}_2\text{O}$ which was identified by chemical analysis and x-ray diffraction. Its pattern was that of Form II of the monohydrate of the trimetaphosphate (Thilo and Hauschild, 1950; Thilo and Wallis, 1953).

Reaction Product. $\text{P}_2\text{O}_5 + \text{NH}_4\text{OH}$. Reagent P_2O_5 (21.5 g) was added slowly and with vigorous stirring to 100 ml of concentrated NH_4OH at 55°C . Addition of 50 ml of ethanol to the cooled solution precipitated a material that was shown by paper chromatography to have its phosphate distributed as ortho- 8%, pyro- 5%, tripoly- 3%, trimeta- 5%, tetrameta- 22%, and more highly condensed phosphates 57%.

Sulfur Compounds. $\text{P}_2\text{S}_2(\text{NH})(\text{NH}_2)_4$. Prepared by heating thiophosphoryl triamide, $\text{PS}(\text{NH}_2)_3$, in a sealed evacuated tube for 16 hr at 120°C .

$\text{P}_3\text{S}_3(\text{NH})_2(\text{NH}_2)_5$. Prepared by heating $\text{PS}(\text{NH}_2)_3$ for 4 hr at 105°C in a tube that was evacuated continuously.

$\text{P}_n\text{S}_n(\text{NH})_{n-1}(\text{NH}_2)_{n+2}$. Longer-chain products, in which n was about 10, were prepared by heating $\text{PS}(\text{NH}_2)_3$ for 5 hr at 175°C in a continuously evacuated tube.

$\text{SO}_2(\text{NH}_2)_2$. Commercial sulfamide (Alfa Inorganics, Beverly, Mass.) was used without purification.

Other Compounds. $\text{NH}_4\text{HPO}_3\text{NH}_2$. Monoammonium monoamidophosphate was prepared by dripping POCl_3 (30.7 g) slowly into a vigorously stirred 10% NH_4OH solution (300 ml) that was maintained at 0°C . When all the POCl_3 had been added, the mixture was stirred for an additional 15 min and then mixed with 1 l. of acetone. Two liquid layers were formed; the bottom layer was separated, adjusted with acetic acid to pH about 6, and diluted with an equal volume of ethanol to precipitate 14.4 g $\text{NH}_4\text{HPO}_3\text{NH}_2$, which corresponds to a 63% yield, based on the phosphorus content.

GREENHOUSE TESTS

The experimental fertilizer materials were evaluated in the greenhouse against ammonium nitrate as sources of nitrogen and against concentrated superphosphate as sources of phosphorus. The tests were made at three different times, and results were expressed in relation to those obtained with the standard fertilizer in the same test. All tests were made in triplicate in plastic pots that contained 3 kg of Mountview silt loam, an infertile acid soil from Tennessee, that had been limed to pH 6.4 with a mixture of 2 parts of calcium carbonate and 1 part of magnesium carbonate.

For evaluation as sources of nitrogen, the compounds were added in amounts to supply 200 or 400 mg N per pot, and phosphorus (as concentrated superphosphate), potassium (as the sulfate), and a micronutrient mixture were added in amounts to ensure that only nitrogen was the limiting nutrient element. All plant nutrients were mixed thoroughly with the soil.

For evaluation as sources of phosphorus, the compounds were added in amounts to supply 60 or 120 mg P per pot, and nitrogen (as ammonium nitrate) and potassium and micronutrients as above were added to ensure that only phosphorus was the limiting nutrient element.

When enough of an experimental fertilizer material was available, it was applied both as fines (minus 35-mesh) and as granules (minus 6- plus 9-mesh). The granules were prepared by pressing the fines in a laboratory press and crushing and screening the pellets.

The pots were planted with corn (*Zea mays*, Funk's G-76) and the forage was harvested 7 weeks after planting. A second crop of corn was planted 2 to 4 weeks after harvest of the first crop, and supplemental nutrients were added as required to ensure that only the nutrient under test was the limiting element. The forage of the second crop also was harvested 7 weeks after planting.

The harvested forage was dried, weighed, and analyzed either for nitrogen by a micro-Kjeldahl method, modified to determine nitrate nitrogen also, or for phosphorus by the vanadate method (Jackson, 1965). In all tests the response to the nitrogen or the phosphorus of the standard fertilizers was more than three times that of the no-nitrogen or no-phosphorus controls, thus assuring valid comparison among the different nutrient sources.

Table II. Crop Response to Reference Fertilizers

(Measured in greenhouse with two 7-week crops of corn on Mountview silt loam limed to pH 6.4. Response of both crops to single initial application)

Test No.	Rate	Nitrogen response ^a		Phosphorus response ^b			
		Fines		Granules		Fines	
		DM	UN	DM	UP	DM	UP
A	Low	32.3	175	36.1	34.5	33.8	34.7
	High	45.8	314	50.0	48.3	44.9	45.9
	Blank	10.9	55	14.9	14.7	14.9	14.7
B	Low	36.1	231	22.3	25.2
	High	50.5	377	32.3	38.0
	Blank	17.8	127	7.9	8.3
C	Low	28.1	248	20.6	18.5	14.9	17.4
	High	36.4	402	33.7	31.1	22.2	30.0
	Blank	10.4	84	7.8	6.6	7.8	6.6

^a NH_4NO_3 was supplied at 200 or 400 mg N/pot. DM = yield of dry matter, g/pot; UN = uptake, mg N/pot. ^b Concentrated superphosphate was supplied at 60 or 120 mg P/pot. UP = uptake, mg P/pot. Granules were minus 6- plus 9-mesh, fines were minus 35-mesh.

The results of the greenhouse tests of the experimental materials are shown in Table I, and the responses to the reference fertilizers, upon which the data in Table I are based, are shown in Table II.

RESULTS AND DISCUSSION

Phosphonitrilics. As shown in Table I, phosphonitrilic hexaamide monohydrate was almost equivalent to ammonium nitrate as a source of nitrogen, and, when applied as granules, equivalent to concentrated superphosphate as a source of phosphorus. When applied as fines, however, it was a less effective source of phosphorus.

The anhydrous hexaamide performed much like the monohydrate but was somewhat less effective, presumably because of a significant content of an insoluble amorphous phase. When applied as fines it was slightly less effective than ammonium nitrate as a nitrogen source and considerably less effective than concentrated superphosphate as a phosphorus source. When applied as granules, it was only slightly less effective than concentrated superphosphate as a phosphorus source; its effectiveness as a nitrogen source was not measured. Granular concentrated superphosphate usually gives better responses in Mountview soil than fine concentrated superphosphate, but the difference is seldom as great as that shown by the hexaamides. The relatively poor performance as sources of phosphorus of both the hydrated and anhydrous hexaamide when it was applied as fines suggests the need for further study of the fertilizer behavior of this compound.

Increase in the size of the phosphonitrilic ring, as to $\text{P}_4\text{N}_4(\text{NH}_2)_6$, decreased the effectiveness of both nitrogen and phosphorus. The hydrolysis of the octaamide has been reported (Moureu and Rocquet, 1936; Pollard *et al.*, 1963) to proceed by way of the tetraammonium tetrametaphosphimate to the diimidotrimetaphosphate. If the octaamide decomposes in soil tests in this way, the availability would be expected to be 75% for nitrogen and 25% for phosphorus. Our crop response was 65% for nitrogen and 20% for phosphorus, in good agreement with the prediction.

The unsubstituted chlorides, $\text{P}_3\text{N}_3\text{Cl}_6$ and $\text{P}_4\text{N}_4\text{Cl}_6$, were either toxic or almost inert. Derivatives of the trimeric phosphonitrilic ring, such as the dimethylamido and thiourea substitutions, were practically inert, particularly as phosphorus sources. The partially ammoniated trimeric chloride, $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$,

was a moderately effective nitrogen source, but a very poor phosphorus source. The linear phosphonitrilic amide was only about half as effective as the standard fertilizer materials. Thus, of the phosphonitrilic compounds tested, only the hexaamide was an effective fertilizer material, and all other phosphonitrilic derivatives were markedly less effective.

Metaphosphimates. All the metaphosphimates tested—the tri- and tetrameric acids and five of their salts, and a diimidotrimetaphosphate—were ineffective as fertilizer materials. It appeared that both the nitrogen and the phosphorus in the metaphosphimate ring were only very slowly available to the plants and that plant response was largely that to the ammonium nitrogens attached to the rings.

The metaphosphimates are unique in that they are water soluble but too stable to be effective sources of plant nutrients. Results of the greenhouse tests thus are in agreement with those of laboratory studies of Quimby *et al.* (1960) who showed that metaphosphimates hydrolyze very slowly *in vitro* even at 60° C. On the other hand linear polyphosphates also hydrolyze slowly *in vitro* (Farr *et al.*, 1967), but hydrolysis is accelerated in the soil to supply sufficient phosphorus for crop growth (Terman and Engelstad, 1966 Hashimoto *et al.*, 1969). In similar tests, Waněk (1969) also found ammonium trimetaphosphimate, $(\text{NH}_4\text{PO}_2\text{NH})_3$, to be less effective fertilizer material than diammonium phosphate.

Metaphosphates. The three metaphosphates tested were all highly effective sources of both nitrogen and phosphorus, and the apparent superiority over concentrated superphosphate as sources of phosphorus, especially of the granular metaphosphates, suggests the need for further investigation. In Mountview soil, ammonium orthophosphates usually are superior to concentrated superphosphate, but the differences seldom are as large as those shown in Table I for the tetrameric metaphosphate and the mixture of linear and cyclic metaphosphates.

Sulfur-Containing Compounds. Thiophosphoryl triamide, $\text{PS}(\text{NH}_2)_3$, was a highly effective source of both nitrogen and phosphorus, but its three condensation products were less effective. Thiophosphoryl triamide and its condensation products were all somewhat toxic to the first crop, but this toxicity disappeared for the second crop. Brief laboratory tests suggested that the toxicity was caused by release of hydrogen sulfide as these materials hydrolyzed in the soil solution.

All three thiophosphates tested were highly effective sources of both nitrogen and phosphorus. $(\text{NH}_4)_2\text{HPO}_4\text{S}$ showed a very slight toxicity soon after emergence, but the symptoms soon disappeared and the crop response was normal.

The six-membered ring compound, ammonium tetraamido thiadiphosphazatriene dioxide, $\text{NH}_4[\text{P}_2(\text{NH}_2)_4\text{N}_3\text{SO}_2]$, that was formed by ammoniation of the product of the reaction of phosphorus pentachloride with sulfamide, was a highly effective source of nitrogen, but a poor source of phosphorus. On the basis of the uptake of nitrogen, sulfamide appeared to be an effective source of nitrogen, but the yields of forage were less than those of the no-nitrogen blank. This effect, which persisted through both crops, shows sulfamide to be highly toxic.

Other Compounds. Phosphoryl triamide and monoammonium monoamidophosphate, both of which are intermediates in the hydrolysis of phosphonitrilic hexaamide, were very effective sources of both phosphorus and nitrogen. The imidodiphosphate was a highly effective source of phosphorus, but the diimidotriphosphate was markedly less ef-

fective; neither compound was tested as a source of nitrogen.

The product of the reaction of elemental phosphorus with ammonia was practically inert; the results lend weight to the assumption that the product was a polymeric form of red phosphorus with elements of ammonia as chain terminators because red phosphorus is known to release phosphorus very slowly to plants (Widdowson and Rothbaum, 1964).

CONCLUSIONS

Phosphonitrilic hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, in which high plant-nutrient content is combined with high effectiveness of both its nitrogen and its phosphorus (when applied as granules), appeared to be one of the most promising compounds encountered in this study. The relative ineffectiveness as sources of phosphorus of both the anhydrous material and the monohydrate when they were applied as fines, and the adverse effect of the polymeric impurity in the anhydrous material are details that require further study. Commercially practicable methods for the preparation of these compounds are being sought.

Although the metaphosphimates have high plant-nutrient contents, both the phosphorus and the nitrogen in the metaphosphate ring were only slightly available to plants. Phosphorus uptake from all the eight metaphosphimates tested was very low, indicating that this class of compounds has little promise as fertilizer materials.

The metaphosphates and the condensed phosphates that were formed by the reaction of phosphoric oxide with ammonium hydroxide were effective sources of both nitrogen and phosphorus. These compounds, although lower in nutrient content than the covalent compounds, are higher than fertilizer materials now in wide use. When applied as granules, these materials were more effective sources of phosphorus than concentrated superphosphate, and this class of compounds is being studied further.

The sulfur compounds present a somewhat mixed picture. Thiophosphoryl triamide and its condensation products have high plant-nutrient contents and generally supplied both nitrogen and phosphorus readily to plants, but the initial toxicity of these materials decreases considerably their attractiveness as fertilizer materials. The thioamidophosphates, although not particularly high-analysis materials, were very effective fertilizers, and further study is being made of this class of compounds.

Phosphoryl triamide and monoammonium monoamido-phosphate are highly promising fertilizer materials. Both have high contents of plant nutrients, and both were highly effective sources of both nitrogen and phosphorus.

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