

An initial fungal attack on the triazine ring, followed by ammonification and nitrification, may explain why the powdered material degraded at a faster rate than its solution, while the relatively fewer particles in the -8+12 mesh treatments provided considerably less surface area and were thus degraded at the slowest rate. In addition, less nitrogen was released from cyanuric acid perfusing through soil, in a system more conducive to bacterial activity, than from cyanuric acid incubated in the same soil contained in a bottle. Neither metal ion catalysis of triazine hydrolysis in soil nor stimulation of biochemical degradation was observed in experiment 2. Of interest in this connection, however, is the report of Castelfranco and Deutsch (7) on the acceleration of simazine breakdown by polysulfides. Cox (3) has also noted that methylmercapto-triazines have quick action and short persistence in soils. Current work in the authors' laboratory indicates that methoxy- or thiomethoxy-substituted triazines degrade faster than the corresponding chlorotriazines.

Although the few cropping experiments with compounds of the cyanuric

acid series (10) have not shown these materials to advantage, laboratory studies, coupled with their relative ease of production, high N content, and possibility of slow N release in soil, suggest that they are compounds worthy of further study as possible nitrogen fertilizer materials.

Slight modifications of structure may result in materials less resistant to degradation and more amenable to eventual plant uptake of contained N. The dependence of cyanuric acid breakdown on temperature may offer a possible use of this material as a fall-applied nitrogen source supplemented with a readily available source in the spring.

Since materials such as cyanuric acid have been shown to be temporarily toxic to seedlings (10) as well as to inhibit microorganism activity, placing the materials near the seed should be avoided. Further, evaluation of the material as a slow-release nitrogen source should be made only on crops that are expected to respond to smaller amounts of nitrogen added at frequent intervals during the season.

Acknowledgment

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FERTILIZER NITROGEN SOURCES

Crop Response to Urea and Urea Pyrolysis Products

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Availability of nitrogen in urea and urea pyrolysis products for four crops of corn forage and for four clippings of Coastal Bermudagrass grown in greenhouse cultures decreased as follows: urea > cyanuric acid > ammelide > urea pyrolyzate > ammeline > melamine. Cyanuric acid was toxic initially, but most of its nitrogen became available for succeeding crops. Urea formaldehyde was similar in effect to ammeline and urea pyrolyzate for Bermudagrass. In field experiments with wheat, urea pyrolyzate and urea formaldehyde were 33 and 49%, respectively, as effective as urea, and the other sources were even less satisfactory.

PYROLYSIS of urea at moderately high temperature under pressure results in the formation of mixtures of water-insoluble compounds which may have value as nitrogen fertilizers. These compounds are heterocyclic C—N materials and vary in the degree of substitution of amine for hydroxyl groups. The structural formulas of the series (triazines) are shown in Figure 1. Substitution of an NH₂ group for one OH

group in cyanuric acid yields ammelide, substitution of two OH groups yields ammeline, and substitution of all three OH groups with NH₂ yields melamine. Generally, chemical activity of the compounds decreases with increasing substitution. In addition to these compounds, pyrolyzed urea also contains unreacted urea and may contain other compounds as well. Substitution of various organic groups yields other triazine compounds, many of which have been widely used as herbicides.

Kazarnovskii and Malkina (2) studied the kinetics of formation of intermediate

reaction products and melamine. They showed that heat treatment of urea resulted in the formation of ammonium cyanate and its decomposition into cyanic acid and ammonia. Cyanuric acid is formed by the polymerization of cyanic acid. Ammelide, ammeline, and melamine are amination products of cyanuric acid. Kinoshita (3, 4) previously reported on the synthesis of melamine from urea.

Scholl *et al.* (5) found in greenhouse pot tests that response of millet to the nitrogen in melamine nitrate was nearly as great as that in urea and sodium

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nitrate. Responses to melamine phosphate and melamine sulfate were very poor. Only about 1% of the nitrogen in the melamine radical of each compound was converted to nitrate in 13 weeks. Later, Clark *et al.* (7) found that cyanuric acid and sodium and potassium cyanurates nitrified very little during a 6-week period, but had nitrified almost completely after 9 weeks. Urea pyrolyzate produced at 315° F. for 6 hours at atmospheric pressure nitrified less than urea during an initial 3-week period, but almost completely in 15 weeks.

The present paper reports results obtained in greenhouse pot cultures and field experiments with urea and urea pyrolysis products as sources of nitrogen.

Greenhouse Experiments

General Procedure. Reagent-grade cyanuric acid, ammeline, ammelide, and melamine were compared as sources of

nitrogen for crops with urea and with urea pyrolyzate prepared by the TVA Applied Research Branch. Analyses of the various materials are given in Table I. Separate experiments with corn and with Bermudagrass were conducted over a period of several months to study release of nitrogen from the materials with time.

Four successive crops of single-cross hybrid corn were grown in plastic-lined, No. 10 tin cans containing 3 kg. of soil per can. Coastal Bermudagrass was grown in 14- by 14- by 6-inch flats containing 17.0 kg. of soil per flat. A minimum temperature of 70° F. was maintained in the greenhouse. Daytime temperatures ranged as high as 90° F. at times during spring and summer periods. Amounts of plant nutrients applied (mg. per culture or flat) may be converted to pounds per acre (2,000,000 pounds of soil) by multiplying by 0.67 for experiment 1 and by 0.12 for experiment

2. Results reported in Tables II to IV are means of three replicates of each treatment being compared. Dry weights of forage and contents of total nitrogen were determined for each crop or clipping. Adequate phosphorus and potassium were supplied as concentrated superphosphate and potassium sulfate.

Response by Corn (Experiment 1).

The various materials as powders were mixed with 3 kg. of unlimed Hartsells fine sandy loam (pH 5.2) in amounts sufficient to supply the following amounts of nitrogen (N) per culture: urea—100, 200, 400, and 800 mg.; cyanuric acid—100, 400, and 800 mg.; and ammeline, ammelide, melamine, and urea pyrolyzate—400 and 800 mg. Each culture also received 300 mg. of P (680 mg. P₂O₅) and 200 mg. of K (240 mg. K₂O).

Planting and harvest dates were as follows: first crop, June 22 and August 17, 1959; second crop, October 6 and December 7; third crop, February 8 and April 13, 1960; fourth crop, June 21 and August 3. The soil was kept moist between croppings. The first crop received an additional uniform application in solution of 200 mg. of K (240 mg. K₂O); the second crop, 180 mg. of P (410 mg. P₂O₅) and 150 mg. of K (180 mg. K₂O); and the third crop, 360 mg. of P (120 mg. P₂O₅) and 200 mg. of K (240 mg. K₂O).

Yields of dry matter and uptake of nitrogen by the four successive crops of corn grown with urea and urea derivatives are shown in Table II.

FIRST CROP. Yields by the first crop increased curvilinearly up to the 400 mg. rate of nitrogen as urea and then decreased slightly with 800 mg. Uptake of nitrogen by the first crop increased linearly with amount applied as urea. Yields and nitrogen uptake also increased markedly with increase in amount of urea pyrolyzate applied, but effectiveness (based on uptake per 100 mg. of applied N) was only about 35%

Table I. Materials Compared in the Experiments as Sources of Nitrogen

Material	Formula	Experiment No.	Total N, %	Source
Urea	CO(NH ₂) ₂	1	46.3	C. P. Chemical
		2	46.6	C. P. Chemical
Urea pyrolyzate	Mixture	1	46.1 ^a	TVA
		2, field	47.2 ^b	TVA
Cyanuric acid	C ₃ N ₃ (OH) ₃	1	32.1	Eastman Kodak
		2, field	32.3	Food Machinery
Ammelide	C ₃ N ₃ (OH) ₂ (NH ₂)	1	43.3	American Cyanamid
		2, field	42.9	American Cyanamid
Ammeline	C ₃ N ₃ (OH)(NH ₂) ₂	1	49.4	Allied Chemical Corp.
		2, field	52.6	American Cyanamid
Melamine	C ₃ N ₃ (NH ₂) ₃	1	64.9	Eastman Kodak
		2, field	65.3	American Cyanamid
Urea formaldehyde	Mixture	2, field	36.9 ^c	E. I. duPont

^a Urea heated at 500° F. for 1 hour at autogenous pressure. Urea N comprised 33%, water-insoluble N 60%, and biuret N 1.7% of the total N.

^b Urea heated at 525° F. for 75 min. at autogenous pressure. Urea N comprised 25%, water-insoluble N 65%, and biuret N 2.5% of the total N.

^c The A.O.A.C. activity index was 57.

Table II. Yields of Dry Matter and Uptake of Nitrogen by Four Successive Crops of Corn Grown with Various Nitrogen Sources (Experiment 1)

Source of N	Mg. of N Applied per Culture and Crop Number											
	100		200		400				800			
	1	1	1	2	3	4	Total	1	2	3	4	Total
DRY WEIGHT, GRAMS PER POT												
Urea	21.7	32.1	41.4	3.1	10.1	7.1	61.7	39.7	7.7	5.9	7.3	60.6
Urea pyrolyzate	27.9	6.6	9.5	9.3	53.3	35.5	7.8	12.2	13.2	68.7
Cyanuric acid	12.0	...	8.2	13.2	10.6	5.5	37.5	4.0	7.9	19.5	18.4	49.8
Ammelide	13.1	9.9	13.4	9.4	45.8	13.1	11.4	14.8	13.8	53.1
Ammeline	13.4	10.1	11.4	8.3	43.2	12.8	10.0	11.7	12.6	47.1
Melamine	12.1	3.8	5.3	6.4	29.3	12.2	3.9	5.4	6.2	27.7
No N	10.9	3.5	6.0	5.7	26.1					
N UPTAKE, MG. PER POT												
Urea	127	214	389	26	62	42	519	625	47	33	41	746
Urea pyrolyzate	166	46	62	54	328	263	56	75	91	485
Cyanuric acid	112	...	151	154	58	31	394	90	161	217	165	633
Ammelide	116	85	106	56	363	121	112	132	143	508
Ammeline	112	69	72	53	306	108	74	85	83	350
Melamine	90	24	42	37	193	109	35	43	49	236
No N	63	27	32	35	157					

Table III. Percentage of Applied Nitrogen Recovered^a by the First Corn Crop and by Four Crops (Experiment 1)

Material	400 Mg.		800 Mg.	
	Crop 1	Total, 4 crops	Crop 1	Total, 4 crops
Urea	82	91	70	74
Urea pyrolyzate	26	43	25	41
Cyanuric acid	22	59	3	60
Ammelide	13	52	7	44
Ammeline	12	37	6	24
Melamine	7	9	6	10

^a Percentage recovery = $\frac{\text{Total uptake} - \text{uptake with no applied N}}{\text{N applied}} \times 100$.

Table IV. Total Yields of Four Clippings of Bermudagrass (Experiment 2)

Source of N	Yield of Dry Matter (Grams per Flat) with Various Amounts of Applied N (Mg. per Flat)				
	0	200	400	800	1600
No N	18.2				
NH ₄ NO ₃		22.2	25.9	33.4	53.4
Urea		21.0 ^a	...	36.7 ^a	...
Urea pyrolyzate		20.5	...	23.4	...
Cyanuric acid		22.7	...	27.7	...
Ammelide		23.2	...	27.1	...
Ammeline		17.6	...	22.8	...
Melamine		20.8	...
Urea formaldehyde		22.3	...

^a Rates of application were 260 and 1050 mg. of N.

Table V. Yields of Winter Wheat Forage with Fall-Applied Nitrogen at Three Locations in Alabama

Source of N	N, applied pounds per acre	Yields of Dry Forage, Pounds per Acre				Yield increase	Relative Yield Incr., %
		Etowah silt loam, pH 5.9	Greenville sandy loam, pH 5.6	Kalmia sandy loam, pH 5.6	Mean		
No N	0	1095	790	445	780
Urea	25	1520	1180	610	1105	325	27
	50	1715	1630	835	1395	615	52
	100	2170	2185	1455	1970	1190	100
Urea pyrolyzate	100	1650	1220	650	1175	395	33
Cyanuric acid	100	1050	185	425	555	225	...
Ammelide	100	1405	715	495	870	90	8
Ammeline	100	1205	790	695	900	120	10
Melamine	100	1195	865	610	890	110	9
Urea formaldehyde	100	1900	1260	920	1360	580	49
L. S. D., 5% level	...	318	560	250
C. V., %	...	13	29	16

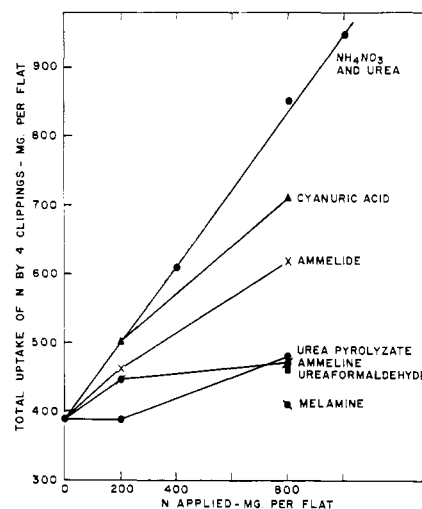


Figure 2. Uptake of N by four clippings of Coastal Bermudagrass

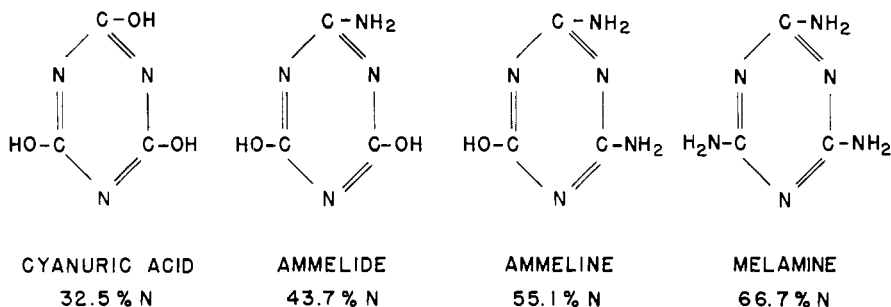


Figure 1. Triazine compounds formed by pyrolysis of urea

that of urea. Results indicated that the water-soluble fraction of this material (probably unreacted urea) comprised most of the plant-available nitrogen.

Cyanuric acid was toxic to the first crop, as indicated by lower yields with increasing amount applied. Ammelide supplied more nitrogen than ammeline, but effectiveness of both of these materials was low. No explanation is apparent for the failure of these materials to supply more nitrogen at the 800- than at the 400-mg. rate of application. Melamine did not supply an appreciable amount of nitrogen to the crop regardless of amount applied.

SUCCESSING CROPS. As expected, there was little residual nitrogen remaining from urea (Table II), even at

the 800-mg. application rate. Ammelide supplied small but fairly constant amounts of N to the second, third, and fourth crops, but again there was little effect of rate of application. Total yields from ammeline were not appreciably different from those for the urea-pyrolyzate mixture, but a larger portion of the nitrogen in the pyrolyzate was released to the first crop and smaller amounts were released to succeeding crops. These data suggest that the pyrolysis of urea under these conditions resulted in a mixture of compounds. Unreacted urea, making up 33% of the total, was readily available. A second portion, probably a mixture of the less soluble materials in the substitution series, was water-insoluble and behaved similarly to ammeline.

The toxic effects from 400 mg. of nitrogen as cyanuric acid observed in the first crop were less obvious in later crops. The second-crop leaves had an abnormal, intense green color, but dry weight and particularly nitrogen uptake increases were substantial. Some evidence of continued toxicity was found with the 800 mg. of N application, as there was some increase in yield over no nitrogen, but lower yields than from 400 mg. There was no obvious evidence of toxicity on the third or fourth crops from either rate, and nitrogen yield from cyanuric acid was above that obtained from the urea pyrolyzate. Total yields, however, were less than those from urea pyrolyzate.

Recoveries of nitrogen from the 400- and 800-mg. rates of applied nitrogen by the first crop and by all four crops are given in Table III.

Response by Bermudagrass (Experiment 2). The test crop for this experiment was Bermudagrass grown in flats containing 17 kg. of Hartsells fine sandy loam lined to pH 6.7. Supplemental fertilizers mixed with the soil were 2.8 grams of P (6.38 grams of P₂O₅) and 1.15 grams of K (1.38 grams of K₂O) per

flat. Five sprigs of Coastal Bermuda-grass were planted per flat on July 31, 1961, and the grass was allowed to spread for two months, during which time it was clipped four times and the clippings discarded. On October 4, the following materials and rates of nitrogen were applied uniformly on the soil surface (mg. of N per flat): ammonium nitrate—200, 400, 800, and 1600; urea—260 and 1050; urea pyrolyzate, cyanuric acid, ammeline and ammeline—200 and 800; urea formaldehyde and melamine—800. Four clippings were made as follows: October 25, November 22, January 23, and April 9.

Total yields of dry matter in the four clippings are given in Table IV and uptakes of nitrogen are given in Figure 2. As the 800-mg. rate of nitrogen was included for all sources, uptakes in the clippings at this rate were used to estimate the apparent recovery of applied nitrogen. Apparent recoveries per 100 mg. of applied nitrogen (total uptake less uptake with no N, divided by 8) were as follows: NH_4NO_3 and urea, 58; cyanuric acid, 41; ammeline, 29; urea pyrolyzate, 12; ammeline, 11; urea formaldehyde, 9; melamine, 3. Cyanuric acid applied at the 800-mg. rate of nitrogen was apparently toxic for the first clipping of grass. Relative values based on yields of dry matter showed the same order of relative availabilities.

As compared with results from soluble nitrogen applied for corn, cyanuric acid was relatively more available for Bermudagrass. Ammelide, ammeline, and melamine showed the same order of availability for both crops. Urea pyrolyzate was similar to ammeline in availability. This preparation was relatively more available, as compared with urea, than that applied for corn in Experiment 1. Actually, relative availabilities can

be changed rather widely by minor changes in pyrolysis conditions.

Field Experiments

Procedure. The various materials were compared as sources of nitrogen for fall-sown wheat on three Coastal Plain soils in Alabama (Table V). Each experiment received a uniform treatment of 500 pounds of 0-6-12 (0-14-14) applied at time of planting. The nitrogen sources were applied with the seed. Planting dates were September 15, 1961, on Etowah silt loam at Alexandria; October 17, on Greenville sandy loam at Prattville; and October 15, on Kalmia sandy loam at Brewton. Each treatment was replicated four times. Wheat was clipped for dry forage yield determinations one or two times during February or early March 1962.

Response by Wheat Forage. Yield results in Table V indicate marked response of wheat forage to urea nitrogen. Yield increases from urea pyrolyzate and urea formaldehyde were 35 and 49% of that from the same amount of nitrogen applied as urea, respectively. Cyanuric acid was toxic in all three experiments, as evidenced by lower yields than from no applied nitrogen. Less toxicity may be noted on the silt loam at Alexandria than on the two sandy loam soils, especially at Prattville. Small, non-significant increases in yields were obtained from ammeline, ammeline, and melamine in these experiments, but mean yields were only slightly higher than yields from no applied nitrogen. These three sources were only about 10% as effective as urea.

Discussion

Availability of the nitrogen in the four triazine compounds—cyanuric acid, am-

melide, ammeline, and melamine—was found to be in the reverse order of the substitution of hydroxyl by amino groups (Figure 1). This results in a decrease in availability of the nitrogen with increasing nitrogen content of compounds in the series. Thus, urea pyrolyzates having the highest possible nitrogen contents may have limited use for grain and hay crops. Cyanuric acid, which is toxic if applied at time of planting, would be expected to be more suitable if applied two weeks or more in advance of planting. Calcium cyanamide, for which the same precautions must be used, has found considerable use as a nitrogen fertilizer.

Ammeline, ammeline, and urea pyrolysis products were equal or superior to fertilizer-grade urea formaldehyde as sources of nitrogen for Bermudagrass. The latter has found considerable use for lawns, where even growth through a season, rather than rapid growth at any one time, is desirable. Another possible use for the triazine compounds may be for tree and shrub fertilization. The less available compounds might supply adequate growth over a period of several years. This potential use should be investigated.

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LIQUID FERTILIZERS

Solubility Relationships in Liquid Fertilizer Systems Based on Superphosphoric Acid

THE NUTRIENT CONTENT of liquid fertilizers is limited by the solubility of the nutrient salts used. A means of increasing concentration is needed to reduce costs of handling, storage, and application. The recent introduction of superphosphoric acid (3, 6) has made this possible; superphosphoric acid is shipped at a concentration of 76% P_2O_5 (33% P), for maximum fluidity, and about half of the P_2O_5 is in nonortho

forms (polyphosphoric acids). Ammoniation of the acid yields ammonium polyphosphates, which are more soluble than the ortho forms of ammonium phosphate.

Effects of superphosphoric acid on solubility in fertilizer systems were discussed by Striplin *et al.* (6). The more extensive study outlined here facilitates estimation of solubilities for all ratios thought to be of practical interest. Solubilities were obtained for "base

solutions" (ammoniated acids) and for N-P-K liquid fertilizers made by adding supplemental nitrogen and potassium to the base solutions. The variables included degree of ammoniation, source of supplemental nitrogen, and ratio of nutrient. Most of the measurements were made at 32° F. Temperature-solubility correlations were derived to permit estimation of solubilities at other temperatures. Similar measurements for

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