

Nitrification of Nitrogen Fertilizers. Effect of Nitrogen Source, Size and pH of the Granule, and Concentration

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A measurable granule effect on nitrification was obtained for soluble N fertilizers which hydrolyze to form an alkaline granule environment. Nitrification of an N source can be stimulated or retarded by adjusting the ammonium concentration and pH at the granule site to a favorable or an unfavorable level, respectively. An unfavorable granule environment may lead to considerable accumulation of nitrite. Large granules, high rates of N application, low soil buffer capacity, as well as an alkaline pH of the immediate granule environment, may lead to nitrite accumulation, even in acid soils. An unfavorable granule environment can be modified through incorporation of various salts to the N-containing granule. Nitrogen deficits were obtained from urea added to an acid soil which accumulated nitrite.

WHEN A NITROGEN SOURCE is evaluated by means of nitrification tests, the source material is often added to soil in solution form or as fine crystals. The nitrogen source is thus more uniformly distributed throughout the soil volume, minimizing the local effects of pH and salt concentration found when larger granules dissolve in soil.

With nitrogen carriers of low solubility in water, such as ureaform or oxamide, the size and density of the granule determine its total surface per unit weight and therefore its rate of solution and consequent effect on chemical and biochemical reaction (14). For such materials, the smaller the granule the faster the rate of solution, and, assuming no physiological toxicity, the faster the rate of nitrification.

If the nitrogen carrier is readily water-soluble, which is true for most of the commercially available solid sources, the rates of solution are sufficiently rapid to dissolve more nitrogen than can usually be acted upon biochemically in a short time. The immediate environment of the dissolving granule then becomes a factor in determining how and at what rate the nitrogen is acted upon initially. The differences in the initial reactions may affect the course of subsequent reactions and the eventual utilization of this nitrogen.

One of these initial reactions involves the oxidation of ammonium nitrogen to nitrite. Accumulation of nitrite has been generally associated with neutral or alkaline soils (6, 10, 13, 18). On the other hand, a number of workers have observed an accumulation of nitrite in acid soils which had been treated with anhydrous ammonia (21), or with urea (7, 9, 24-26). Nitrite accumulation

in soils also has been associated with high nitrogen rates at low temperatures or moisture levels (15), high ammonium salt concentrations at high pH (13), and low soil buffer capacity or low nitrifying capacity (7, 14). Damage to plant roots caused by urea and anhydrous ammonia has been reported by Cooke (8), while Court, Stephen, and Waid (9) have suggested that nitrite formed from these fertilizer materials is the toxic agent. Nitrogen deficits have been noted from soils which accumulate nitrite (24), and Clark, Beard, and Smith (7) have studied the extent to which nitrite accumulation in soil influences the recovery of applied mineral nitrogen.

These adverse effects of nitrogen fertilizers appeared to be a function of the extreme conditions that can sometimes occur around an individual nitrogen fertilizer granule or in a close association of granules such as that found in a band placement. The work reported here was undertaken to study the environment of the nitrogen granule site in relation to nitrification and possible gaseous nitrogen loss. Relatively large amounts of nitrogen per weight of soil were used to correspond to actual concentrations of fertilizer observed in band placements, where the ratio of fertilizer to soil influenced by the fertilizer is narrow.

Materials and Methods

Nitrogen Sources Studied. Both reagent-grade and fertilizer-grade materials were used. Information relevant to each source is included in the table pertaining to the experiment in which the source was used.

Granules of a single salt or mixtures of salts were made by intimately mixing

weighed amounts of the appropriate powdered, reagent-grade materials, pelletizing at 10,000-p.s.i. pressure, followed by crushing and screening to the desired size. All materials used were analyzed for total N.

Soils

The two soils used in most of the experiments were Webster silty clay loam (Iowa), pH 8.2, and Hartsells fine sandy loam (Alabama), pH 5.2, or limed to 6.2. Other soils used were Mardin silt loam (New York), pH 6.2, a 1 to 5 mixture of Webster and Mardin, pH 6.9, and 1 to 5 Webster-Hartsells, pH 6.5. The soils varied considerably in nitrifying activity, which is defined for purposes of these studies as the rate at which 50 p.p.m. of N as ammonium sulfate percolating through soil is oxidized to nitrate in a well-aerated perfusion apparatus. The soils, ranked in order of decreasing nitrifying activity, are: Webster - Hartsells > Hartsells 6.2 > Webster - Mardin > Hartsells 5.2 > Mardin.

General Procedures

In all except one experiment, the materials under study were incubated with 30 grams of soil contained in a 125-ml. square milk dilution bottle, or with 100 or 200 grams of soil in a 500-ml. Erlenmeyer flask. Soil moisture was brought to a level predetermined as optimum for nitrification. A one-hole rubber stopper allowed for moderate aeration of the culture while minimizing moisture loss. All cultures were incubated in a moist atmosphere at 30° or 32° C. After incubation, soluble N was extracted from the soil with 0.25% CuSO₄ solution, followed by clarifica-

tion. Nitrate analyses of the diluted extracts were made by a phenoldisulfonic acid method, modified to eliminate nitrite interference. Nitrite was determined colorimetrically by means of a sulfanilic acid and 1-naphthylamine method. All data reported represent averages of two or three replicates.

In the final experiment (Table VIII), the N source was incubated in 10 grams of soil contained in 20- by 50-mm. glass vials. At the conclusion of the experiment, half of the vials with contents were crushed and transferred to 800-ml. Kjeldahl flasks for total N analysis by a reduced iron-permanganate modification of the Kjeldahl method.

Amounts of N and incubation times varied from one experiment to another as suggested by the results of preceding experiments.

Experiments and Results

Application of Urea. A preliminary experiment was conducted in which 50 mg. of urea N was added either as prills or in solution to 200 grams of Mardin silt loam (pH 6.2) and incubated at 30° C. Prolonged storage of this soil had considerably reduced its nitrifying activity. Nevertheless, urea added in solution was readily nitrified, while none of the urea added as prills or granules was recovered as nitrate after 8 weeks (Table I). Nitrification of ammonium released through mineralization was, in fact, inhibited for several weeks in soil

cultures treated with solid urea, as judged from the negative figures obtained for nitrate after correction for control. Spot analyses revealed considerable amounts of nitrite.

These results were contrary to those usually obtained for urea during routine nitrification tests. It was therefore of interest to determine if unusual effects such as nitrite accumulation from a high application rate of urea N could be noted for more actively nitrifying soils. Accordingly, urea prills were added to soil incubation media of high, moderate, and low nitrifying activities, prepared from Webster soil used alone, or in 1 to 5 mixtures with either Hartsells or Mardin soils.

During 26 days' incubation, no urea N was converted to nitrate in either the Mardin or Hartsells soil mixtures (Table II). However, nitrite accumulation was pronounced. In the more active Webster soil, the rapid oxidation of accumulated nitrite is illustrated by the data obtained from samples taken after 24 and 26 days' incubation (Table III).

Granule Size Effects. Since nitrification of urea proceeded differently, depending on whether it was added as prills or in solution, studies on the effect of granule size were of interest. In the next experiment, therefore, urea N as granules ranging in size from -4+6 to -60+100 mesh or as solution, was incubated in either Webster or Webster-Mardin (1 to 5 mixture) soil (Table IV).

In Webster, nitrite accumulation was pronounced after 18 days for all granule sizes and solution. Much of the nitrite already had been further oxidized to nitrate, but significantly less nitrate was found for the largest granule size. There was a slightly higher total recovery of urea nitrogen as nitrate from the solution application after 41 days.

In the Webster-Mardin soil mixture, considerable nitrite accumulated after 18 days, but little or no nitrate. The amount of nitrite which accumulated decreased with decrease in granule size, but was highest for the solution application. Incubation extended to 41 days resulted in continued nitrite accumulation and some nitrate formation from granules of all sizes. More nitrate was produced from solution urea than granular urea after 41 days. However, the lowest recovery of nitrite plus nitrate was obtained after 41 days from urea added as either the largest granule size or in solution, both of which forms had accumulated nitrite at a faster initial rate.

Measurements were also made of nitrite and nitrate accumulation rates from -8+10 mesh urea granules added in two amounts to Webster and Webster-Mardin soils. These rates over a 24-day period are depicted in Figure 1. Both soils accumulated considerable nitrite from 20 mg. of applied urea N (667 p.p.m.). Oxidation of this nitrite was rapid in the Webster soil, whereas nitrate production in Webster-Mardin

Table I. Nitrification of 50 Mg. of Urea N in 200 Grams of Mardin Silt Loam (pH 6.2)

Form of Urea	Granule Size, Mesh	% Found as Nitrate ^a	
		48 days	85 days
Urea N sol., 5000 p.p.m.	...	87	98
Prills	-8+12	-5	65
Granules	-4+6	-1	56
L.S.D., 5%		3.0	3.8

^a Corrected for control. Average of three replications.

Table II. Nitrification of Urea Prills in Three Soil Media^a

Soil	% Urea N Found as	
	Nitrite ^b	Nitrate ^b
Webster-Mardin mixture, 1 to 5	11	-6
Webster-Hartsells mixture, 1 to 5	27	-4
Webster	23	29
L. S. D., 5%	5.4	3.6

^a Incubation at 32° C. for 26 days; 25 mg. of urea N per 30 grams of soil.

^b Corrected for control. Average of three replications.

Table III. Rapid Oxidation of Urea-Derived Nitrite in Webster Silty Clay Loam^a

Nitrite-N ^b		% Urea N Found as Nitrate-N ^b		(NO ₂ ⁻ + NO ₃ ⁻) - N	
24 days	26 days	24 days	26 days	24 days	26 days
44.9	22.8	6.5	28.9	51.4	51.7

^a Incubation at 32° C.; 25 mg. of urea N per 30 grams of soil.

^b Average of three replications.

Table IV. Nitrification of Urea,^a as Affected by Granule Size

Form, or Granule Size, Mesh	% Added N as					
	18 Days' Incubation			41 Days' Incubation		
	NO ₂ ⁻	NO ₃ ⁻	(NO ₂ ⁻ + NO ₃ ⁻)	NO ₂ ⁻	NO ₃ ⁻	(NO ₂ ⁻ + NO ₃ ⁻)
WEBSTER SILTY CLAY LOAM						
-4+6	60	14	74	0	77	77
-6+8	45	27	72	0	75	75
-8+10	58	23	81	0	78	78
-60+100	49	28	77	0	74	74
Solution ^b	56	32	88	0	88	88
L. S. D., 5%	4.5	3.2			3.8	
WEBSTER-MARDIN 1 TO 5 MIXTURE						
-4+6	42	0	42	51	4	56
-6+8	32	0.5	33	71	4	75
-8+10	26	0	26	68	5	73
-60+100	19	0	19	69	5	74
Solution ^b	53	0	53	52	14	66
L. S. D., 5%	6.1			6.3	4.1	

^a 20 mg. of urea N per 30 grams of soil incubated at 30° C.

^b 5000 p.p.m. N.

was almost completely stopped at the 20-mg. rate. At both the 10- and 20-mg. rates, nitrification was preceded by a longer lag period in the less active Webster-Mardin mixture.

Effect of Granule Size, Solution Application, and N Rate. These observations, corroborated by the literature available on the nitrification of urea, suggested that high alkalinity around the hydrolyzing urea granule and rate of nitrite formation were two important factors leading to nitrite accumulation. To determine whether such accumulations could be obtained from solid N sources other than urea, a preliminary study was made in which two amounts of N as $(\text{NH}_4)_2\text{SO}_4$ granules and solution were spot-placed in Webster or Webster-Mardin soil mixture.

Nitrate accumulated in Webster after 18 days' incubation only from a solution application of 10 mg. of N; at twice this amount, nitrite accumulated from both granules and solution (Table V). Either rate of N as $(\text{NH}_4)_2\text{SO}_4$ granules or solution led to nitrite accumulation in Webster-Mardin, coupled with a much slower nitrification rate. Less nitrate was produced after 41 days in either soil from the largest granules (-4+6 mesh) applied.

Quantities of nitrite similar to the above were not obtained in subsequent experiments from $(\text{NH}_4)_2\text{SO}_4$ in non-calcareous soils, although smaller amounts of nitrite did accumulate from spot placements of ammonium sulfate which formed high local concentrations of salt upon solution.

A more comprehensive series of tests was next made in which six N sources were applied to two soils at two to five rates in solution or as granules of four sizes. The large amount of data accumulated can best be summarized by Figures 2, 3, and 4.

Figure 2 illustrates the effect on nitrification of increasing amounts of urea and $(\text{NH}_4)_2\text{SO}_4$ N from 5 to 25 mg. in a fixed volume (represented by 30 grams) of Webster soil. For urea, the percentage of total added N found as nitrite and nitrate decreased with increase in amount added, but the decrease was more pronounced for the large granule than for the solution application. No such difference between solution and granule is noted for $(\text{NH}_4)_2\text{SO}_4$.

Further information on the effect of form of urea and $(\text{NH}_4)_2\text{SO}_4$ (granular or solution) on nitrification at two N rates in Webster soil is given in Figure 3. The difference between solution and granular forms of urea is more pronounced at the 25-mg. rate. Again, no such difference is noted for $(\text{NH}_4)_2\text{SO}_4$ at either N rate.

Figure 4 summarizes the differences obtained in the nitrification of materials which hydrolyze to form either an alkaline or an acid fertilizer-soil environ-

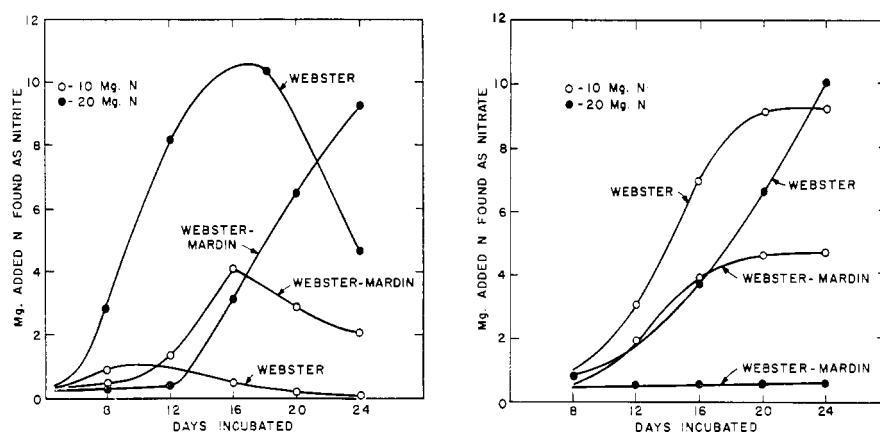


Figure 1. Nitrite (left) and nitrate (right) accumulation from urea in two soils

Table V. Nitrification of Ammonium Sulfate,^a as Affected by Granule Size and Application Rate

Form, or Granule Size, Mesh	Mg. N Added	% Added N as					
		18 Days' Incubation			41 Days' Incubation		
		NO_2^-	NO_3^-	$\text{NO}_2^- + \text{NO}_3^-$	NO_2^-	NO_3^-	$\text{NO}_2^- + \text{NO}_3^-$
WEBSTER SILTY CLAY LOAM							
-4+6	10	<1	61	62	0	82	82
-6+8	10	<1	73	74	0	100	100
Solution ^b	10	22	80	102	0	102	102
-4+6	20	36	27	63
-60+100	20	32	45	76
L. S. D., 5%		5.8	3.1			4.0	
WEBSTER-MARDIN 1 TO 5 MIXTURE							
-4+6	10	23	1	24	3	41	44
-6+8	10	30	3	33	1	45	46
Solution ^b	10	25	20	45	1	59	60
-4+6	20	14	0	14	0	4	4
-60+100	20	31	0	31	15	18	33
L. S. D., 5%		6.2	4.1		5.8	4.3	

^a 10 and 20 mg. of N as $(\text{NH}_4)_2\text{SO}_4$ per 30 grams of soil incubated at 30° C.

^b 5000 p.p.m. N.

Table VI. Nitrification of Nine N-Containing Materials in Two Soils, as Affected by N Rate and pH of N Source

N Source ^a	pH of 1000 P.P.M. N Solution	% of Added N Recovered as $(\text{NO}_2^- + \text{NO}_3^-)^b$							
		Hartsells (pH 6.2)				Webster (pH 8.2)			
		N Added, Mg.				N Added, Mg.			
Urea (after hydrolysis)	>8 ^c	75	30	4	1	99	82	53	20
$(\text{NH}_4)_2\text{CO}_3$	8.6	70	27	...	1	90	78	...	16
$(\text{NH}_4)_2\text{HPO}_4$ (DP)	7.9	58	35	27	3	95	75	59	33
NH_4HCO_3	7.8	...	43	5	2
U-9 ^d	7.6	...	20	29	4	...	63	...	21
U-12 ^e	>8	...	32	25	3	...	74	...	23
$(\text{NH}_4)_2\text{SO}_4$	5.3	13	9	5	4	98	61	53	13
NH_4Cl	5.3	6	4	2	1	88	43	...	4
$\text{NH}_4\text{H}_2\text{PO}_4$ (MAP)	4.5	30	5	3	2	87	25	10	6
L. S. D., 5%		5.6	5.0	3.7	3.6	4.0	4.5	3.6	3.6

^a -8+12 mesh granules added to 30 grams of soil; P added as required to Hartsells to adjust to level in samples treated with DP and MAP.

^b Incubation for 19 days at 30° C. Average of duplicate samples.

^c After hydrolysis.

^d U-9, 30-32-0 urea reactor effluent reacted with furnace H_3PO_4 .

^e U-12, 29-30-0, prilled urea coated with DP from wet process acid.

ment. After 22 days' incubation in Webster soil, no granule size effects on nitrification were noticed for NH_4Cl , and nominal effects for urea, DP, $(\text{NH}_4)_2\text{CO}_3$, MAP, and $(\text{NH}_4)_2\text{SO}_4$. In the less active Hartsells soil (pH 6.2), large granule size effects were obtained for urea and $(\text{NH}_4)_2\text{CO}_3$, both of which materials hydrolyze to an alkaline granule environment.

The effect of granule size on nitrification was apparently more pronounced at higher N rates with the alkaline-hydrolyzing materials. This observation prompted a further series of tests involving nine N sources, three granule sizes, four application rates, and two soils. In these tests, no consistent granule size effect on nitrification was found, probably because of the rather narrow size range (-6+8, -8+16, and -10+16 mesh) used. However, differences between N sources were observed at all N rates. Typical data obtained from the -8+10 mesh granules are summarized in Table VI. The 10-mg. N rate (333 p.p.m.) is comparable to a band placement of fertilizer granules at the rate of 60 pounds of N per acre, as actually observed in the field under static moisture conditions.

Nitrification in the Hartsells soil was favored by the alkaline environment produced by the hydrolyzing granules of urea, NH_4HCO_3 , $(\text{NH}_4)_2\text{HPO}_4$ (DP), and the urea ammonium phosphates. Nitrification of MAP, $(\text{NH}_4)_2\text{SO}_4$, and NH_4Cl proceeded more slowly. These latter compounds hydrolyze in soil in the pH range of 4.5 to 5.5, depending on soil buffering action and on concentration. Less nitrate was produced from NH_4Cl than from any N source tested.

At the 12-mg. application rate (400 p.p.m.), materials hydrolyzing to a pH of about 7.5 nitrified to a greater extent than more alkaline- or acid-forming sources. Experimental N source U-9, a urea ammonium phosphate, appeared to nitrify at a rate intermediate between urea and DP, from which materials it was composed. At higher N concentrations, extreme inhibition of nitrification occurred, especially for the very alkaline- or acid-hydrolyzing materials. Very little nitrification of any N source occurred at a concentration of 800 p.p.m. of applied N in the Hartsells soil.

Differences among sources were also observed at higher concentrations applied to the more active and highly buffered Webster soil. Nitrification of the acid-hydrolyzing MAP was considerably retarded at N concentrations of 400 p.p.m. and above. Increase in concentration tended to have the least relative effect on the nitrification of DP, which maintained a pH slightly above 7.5 around the granule.

Considerable nitrite accumulated in both soils with all materials hydrolyzing to an alkaline pH. As much as 17%

of the urea N applied at the 18-mg. rate to Hartsells was recovered as nitrite after 19 days. In addition, about 2% of the N from $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl added at the 24-mg. N rate was found as nitrite in Webster soil.

Mixtures. The pH at which an N source hydrolyzes was shown in the above experiments to have a marked effect on the nitrification of that source. Of interest, therefore, was whether the nitrification rate of a given N fertilizer could be markedly altered by changing its hydrolyzing pH through addition of acid- or alkaline-forming salts.

Accordingly, -6+8 mesh granules composed of mixtures of either urea or $(\text{NH}_4)_2\text{SO}_4$ with Na_2CO_3 , Na_2SO_4 , and NaH_2PO_4 , were incubated at three N rates in either Hartsells (pH 6.2) or Webster soil. Equivalent amounts of P and S were added to those Hartsells soil cultures which did not receive test granules containing phosphate or sulfate.

Data accumulated from this experiment are summarized in Table VII, from which the following general observations are made. Nitrification of $(\text{NH}_4)_2\text{SO}_4$ was greatly stimulated in Hartsells soil by the addition of alkaline-forming Na_2CO_3 to the N granule.

The largest amount of nitrate was formed from the 50 to 50 mixture (N source/diluent) at the 8-mg. N rate, although this mixture supplied at either the 16- or 24-mg. N rate almost completely repressed nitrification. Excessive alkalinity in the 30 to 70 mixture with Na_2CO_3 also repressed nitrification. High salt concentration was probably a factor in the decreased nitrate production obtained from $(\text{NH}_4)_2\text{SO}_4$ diluted with large amounts of Na_2SO_4 or NaH_2PO_4 .

However, addition of NaH_2PO_4 to urea sometimes enhanced nitrate formation, especially for the 30 to 70 mixture at the higher N concentrations.

The high alkalinity and/or high salt concentrations present around the granule site from some of the treatments resulted in considerable nitrite accumulation in the Hartsells soil. Two of the ammonium sulfate- Na_2CO_3 treatments in which urea was involved resulted in nitrite accumulation. The 30 to 70 mixture of urea with NaH_2PO_4 which produced the most nitrate at the higher application rates accumulated the least comparable amount of nitrite.

In the calcareous Webster soil, a small amount of Na_2CO_3 in the granule stimulated the nitrification of $(\text{NH}_4)_2\text{SO}_4$.

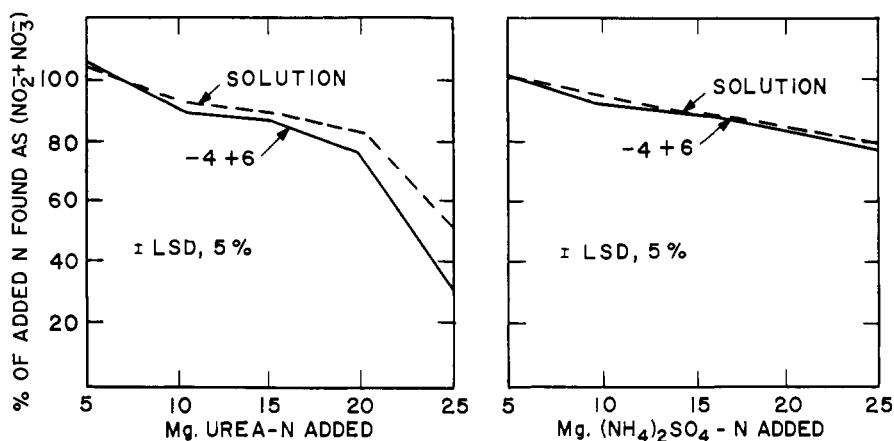


Figure 2. Nitrification of urea and $(\text{NH}_4)_2\text{SO}_4$ after 22 days added as large granules or in solution to Webster silty clay loam, as affected by N rate

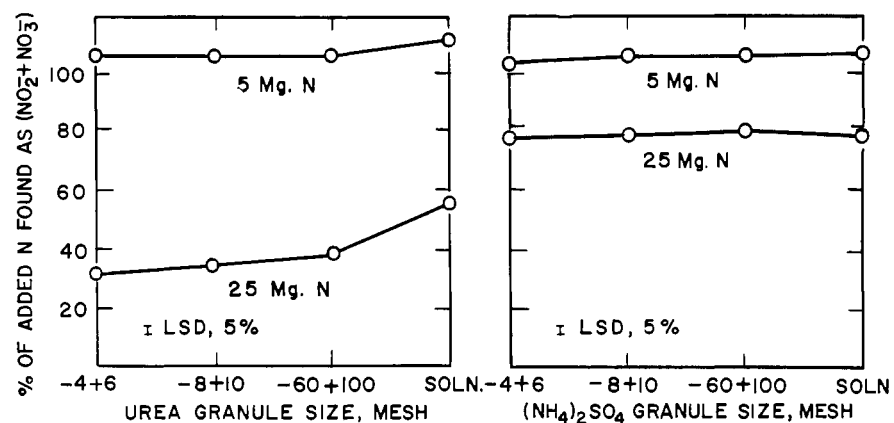


Figure 3. Nitrification of urea and $(\text{NH}_4)_2\text{SO}_4$ after 22 days added to Webster silty clay loam at two N rates, as affected by granule size or solution application

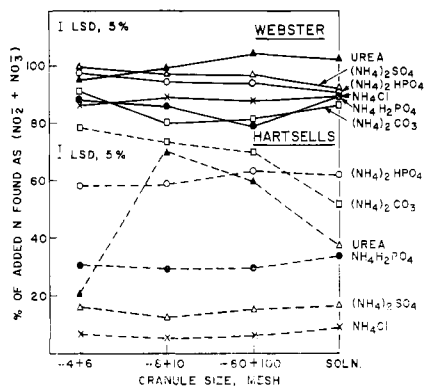


Figure 4. Nitrification of six N sources in two soils, as affected by granule size or solution application

SO₄. Large amounts of Na₂CO₃ with (NH₄)₂SO₄ or Na₂CO₃ in any amount mixed with urea, repressed nitrification. Considerably more nitrate was usually produced from (NH₄)₂SO₄ containing acid phosphate than from comparable mixtures containing the alkaline-forming or neutral salts, Na₂CO₃ and Na₂SO₄.

As much as 65 to 89% of the N applied to Webster was recovered as nitrite in some mixtures containing either (NH₄)₂SO₄ or urea. Nitrite accumulation was negligible only from mixtures of (NH₄)₂SO₄ with NaH₂PO₄, correlating well with the larger amounts of nitrate which were obtained in these samples.

Nitrogen Loss from Accumulated Nitrite. The preceding studies suggested that nitrite accumulation was frequently associated with high concentrations of ammonium at high pH. The stability

of nitrite formed under these conditions was therefore investigated, using calcareous Webster (pH 8.2) and unlimed Hartsells (pH 5.2) as the test soils. Urea or ammonium sulfate in the form of -4+6 mesh granules was incubated at three rates in each soil, followed by analysis of duplicate samples for nitrite, nitrate, and total N, as described under the general procedures (Table VIII).

Accumulated nitrite was observed after 25 days from both urea and ammonium sulfate added at the 600 and 900-p.p.m. N levels to Webster soil and from urea at these two N levels in the Hartsells soil. Almost no nitrification of ammonium sulfate occurred in unlimed Hartsells.

Most of the N added as urea or ammonium sulfate to Webster or as ammonium sulfate to Hartsells was recovered as total N, including that from samples which contained considerable nitrite and nitrate. A higher Kjeldahl error and some ammonia loss are probable explanations for the slightly lower recovery obtained from Webster soil.

However, considerably less total applied N was recovered from urea in the acid Hartsells soil. These results indicate that nitrite accumulating at the alkaline fertilizer granule site may be unstable in the acid portion of the soil environment, leading to gaseous loss of N.

Table VIII. N Loss from Accumulated Nitrite

N Source	N Added, ^a Mg.	% of Added N Recovered as:		
		Nitrate-N	Nitrite-N	Total N
WEBSTER—pH 8.2				
Urea	3	76	0	88
	6	26	54	92
	9	3	67	85
(NH ₄) ₂ SO ₄	3	88	0	99
	6	85	10	103
	9	30	45	93
L. S. D., 5%		3.6	8.0	3.5
HARTSELLS—pH 5.2				
Urea	3	74	0	99
	6	<C ^b	14	58
	9	<C	9	45
(NH ₄) ₂ SO ₄	3	3	0	102
	6	2	0	100
	9	<C	0	101
L. S. D., 5%		3.8	6.3	2.8

^a Indicated amounts added to 10.0 grams of soil. Incubated 25 days at 30° C.

^b Less nitrate than control.

Table VII. Nitrification of N Source-Salt Mixtures in Two Soils, as Affected by Amount of N Applied^a

N Source	Diluent	N Source/ Diluent, % by Weight	pH ^b	% of Applied N as Nitrate				% of Applied N as Nitrite						
				Hartsells		Webster		Hartsells			Webster			
				8	16	24	16	24	8	16	24	16	24	
(NH ₄) ₂ SO ₄	None	...	5.2	20	0	<C ^c	85	65	0	0	0	0	0	31
(NH ₄) ₂ SO ₄	Na ₂ CO ₃	70/30	9.0	51	28	9	98	11	0	0	0	0	3	47
		50/50	9.5	88	0	<C	18	<C	...	16	<1	52	31	
		30/70	10.0	10	<C	<C	3	<C	23	0	0	45	24	
(NH ₄) ₂ SO ₄	Na ₂ SO ₄	70/30	5.3	25	0	<C	84	15	0	0	0	<1	70	
		50/50	5.4	14	<C	<C	43	4	0	0	0	42	56	
		30/70	5.7	5	<C	<C	13	3	0	0	0	59	44	
(NH ₄) ₂ SO ₄	NaH ₂ PO ₄	70/30	3.5	22	0	<C	90	60	0	0	0	<1	4	
		50/50	3.4	16	<C	<C	68	34	0	0	<1	0	2	
		30/70	3.2	3	<C	<C	45	33	0	0	0	<1	<1	
Urea	None	...	>8 ^d	81	5	<C	79	30	0	11	12	8	47	
Urea	Na ₂ CO ₃	70/30	11.3	80	<C	<C	60	18	0	17	3	42	55	
		50/50	11.1	54	<C	<C	32	13	15	21	3	47	67	
		30/70	11.0	11	<C	<C	18	4	28	3	3	89	65	
Urea	NaH ₂ PO ₄	70/30	4.4	86	3	<C	73	19	0	13	14	37	62	
		50/50	4.1	75	4	0	52	11	1	12	12	49	44	
		30/70	3.7	73	34	7	60	15	0	0	6	16	27	
L. S. D., 5%				6.2	6.8	...	5.8	3.9	8.3	6.3	...	7.9	10.0	

^a Figures represent average % of 8, 16, and 24 mg. of N applied to 30 grams of soil found as nitrate and nitrite after 25 days.

^b pH of saturated solution.

^c Less nitrate recovered than from control.

^d Approximate pH after hydrolysis.

Discussion

Stimulation of nitrification by alkaline-forming materials has been reported for applications of anhydrous ammonia (17, 22) and urea (17).

While the optimum pH for nitrification in soil is generally reported to be in the range 7.5 to 9.0 (11, 13, 30), nitrite and nitrate formation observed at pH 13.0 (19) indicates the nitrifying organisms to be relatively insensitive to high OH⁻ concentrations per se. However, large quantities of ammonia may be tolerated by most living organisms only if present in an ionized form—i.e., in an acid medium—and ammonia toxicity increases with increase in pH and consequently un-ionized ammonia (29).

The hydrolysis of urea under conditions similar to those used in studies reported here produced pH values of 8.5 to 9.0 and an apparent partial sterilization of the immediate granule environment. Considerable nitrite, evidence of rapid *Nitrosomonas* activity, was detected at pH 8.1 to 8.3 measured at the extremities of the granule site. Further oxidation of the accumulated nitrite was inhibited, apparently as a result of the high pH and ammonia concentration, and by the nitrite itself. *Nitrosomonas* are reported to be less sensitive to ammonia toxicity than *Nitrobacter* (7). The activity of the latter organisms is evidently restricted to a rather narrow pH range (with an optimum calculated at 7.71) (4). Both nitrate and nitrite inhibit noncompetitively the oxidation of nitrite (4) and nitrite inhibition of its own oxidation has been demonstrated (16) at concentrations as low as 4 mmoles.

These effects leading to nitrite accumulation have been discussed with respect to nitrification in poorly buffered (7) and calcareous (13) soils. Nitrite accumulation was shown in current experiments to be related also to size of granule, to the solution or solid state of the N source, and to concentration of the N source in terms of the ratio of fertilizer to soil influenced by that fertilizer. A large granule of soluble nitrogen placed in soil dominates the soil environment in the immediate vicinity of that granule to a much greater extent than an equivalent amount of nitrogen more widely distributed as smaller granules, or in dilute solution. In one experiment, urea prills produced slightly more nitrate than urea granules of the same size. This can be explained on the basis of more urea per unit volume in the more dense granules, giving rise to a slightly larger area of alkalinity around the granule than the prill, with the consequent effects on nitrification. In this connection, Volk (28) reported greater loss of ammonia from large pellets of urea surface-applied to soil than from fine ones.

For any soil there exists a combination of ammonium concentration and high

pH which will inhibit nitrate formation. Whether this combination is obtained will depend in part not only on the ammonium source, but also on the form in which the source is added. For example, a relatively dilute solution of urea may not result in persistent areas of high local pH and thus nitrifies at a faster rate than an equivalent quantity of urea N added as a solid (Table I). Little difference in nitrification rate is noted, however, for low rates of application of either urea solids or solution in a highly active soil (Figures 2 and 3). A given N source may be added to soil in such a way as to produce a granule environment optimum for nitrification of that source with respect to pH and concentration. The experiments summarized in Tables VI and VII indicate the stimulating effect on nitrification of an N granule environment in the pH range 7.5 to 8.0, and on the accumulation of nitrite above pH 8. Besides the compounds listed in Table V, about 30 other conventional or experimental fertilizer materials were subjected to nitrification tests. All materials which hydrolyzed to an alkaline granule environment, and which usually contained DP, urea, or formamide, nitrified at a faster rate in an acid soil of low nitrifying activity than acid-hydrolyzing materials, and accumulated nitrite when added in sufficient concentration.

Modification of the N source granule environment either to stimulate or retard the nitrification rate is readily accomplished through granulation of the N source with materials hydrolyzing within an acid or alkaline pH range. Drastic modification of this environment, however, usually leads to nitrite accumulation, as the figures in Table VII indicate. A number of investigators (17, 25–28, 31) have reported that acid phosphates can alleviate the toxic effects on crop roots and germinating seeds caused by urea. Mees and Tomlinson (20) found that addition of acid salts or salts which increased calcium in the soil solution decreased ammonia evolution from acid soils. As already noted in Table VII, certain mixtures of either urea or (NH₄)₂SO₄ with NaH₂PO₄ resulted in increased nitrate production. Only part of this latter effect may be the direct result of a lower granule pH on nitrification. Another factor may be precipitation of calcium ammonium phosphates according to the solid phase systems described by Frazier, Lehr, and Smith (12). Such precipitates will reduce the ammonia concentration at the granule site and will allow nitrification to proceed at higher initial N rates. Unpublished TVA greenhouse tests have shown that CaSO₄ mixed with DP reduced plant injury from band applications of the latter.

Precipitation reactions may also explain differences between the nitrification

of MAP and other N sources which hydrolyze to an acid environment (Table VI). MAP nitrified to a greater extent than either (NH₄)₂SO₄ or NH₄Cl in the acid Hartsells soil, but the opposite was true in the calcareous Webster soil. Reactions involving MAP in a calcareous soil may lead to the formation of Ca(NH₄)₂(HPO₄)₂·H₂O (12) which precipitates in the pH range of 5.5 to 8.0, thereby removing ammonium from the soil solution. Such precipitation could occur only with DP if the pH at the granule-solution interface were to drop from around 8 to below 7 as a result of nitrification at the periphery of the granule site.

It is difficult to separate the factors which influence nitrification. These factors include salt concentration per se, possible anion toxicity, precipitation reactions which effectively alter the ammonia concentration, and pH. Further work is required in this regard. One can conclude only that any factor which contributes to the persistence of un-ionized ammonia or extremely high salt concentrations near the granule site may contribute also to nitrite accumulation. Soil factors such as natural or adjusted soil pH, buffer capacity, and rate of nitrification will determine whether nitrite will accumulate at a given concentration of ammonium N in an alkaline environment. The effect of moisture, granule disposition, and geometry of the soil-fertilizer system are factors of importance in determining granule site concentrations. These will be the subject of a succeeding paper.

Current findings now extended to nine soils, show that nitrite accumulation from urea is correlated to the rate at which nitrification proceeds over a short time interval, rather than to the over-all extent of nitrification. Appreciable nitrite accumulated only in those soils in which nitrification was rapid over a 1- to 3-week period, regardless of the percentage of applied N nitrified during this period. A time interval of about 3 weeks usually occurs before application of fertilizer to the field and plant root exploration of the fertilizer zone. Studies during this time period should uncover the significance of nitrite accumulation under field conditions. In this connection, nitrite accumulation was obtained in the field from band applications of mixed fertilizer containing DP in soil as acid as pH 5.2.

The accumulation and persistence of large amounts of nitrite in soil may lead to reduction in N fertilizer efficiency in at least two ways, phytotoxicity and N loss. Phytotoxic effects on agronomic plants from applied urea are reported in several recent studies, un-ionized ammonia (8, 17, 20, 22) or nitrite (9, 25, 26) having been suggested as the toxic agent. Nitrogen deficits from poorly buffered soils that accumulated nitrite

from added urea were reported by Clark, Beard, and Smith (7). Addition of ammonium sulfate to a sandy loam at concentrations corresponding to those found in band application also resulted in gaseous loss of N in forms other than ammonia (5). The data presented in Table VIII demonstrate the loss of N under conditions leading to accumulation of nitrite in an acid soil, and current experiments in larger systems confirm these results. Low and Piper (17) recovered less nitrogen through crop removal from urea prills than from urea solution mixed with an acid soil. Such differences were not observed in limed soil similarly treated. Their results can be explained as possible gaseous N loss from urea prill-derived nitrite accumulating in the acid soil.

The various mechanisms of N loss involving nitrite have been discussed by Smith and Clark (23), Allison (2), and others, and may involve nitrous acid dismutation, or reaction of nitrite with ammonium, amino groups, urea, and other amides.

Most reactions leading to nitrite instability require an acidic medium. A question to be resolved, therefore, is whether nitrous and nitric acid formation at the periphery of the nitrite-producing fertilizer granule site occurs at a sufficiently fast rate to build up the H⁺ ion concentration required to drive the reactions in question. Although pH gradients were measurable at the granule site, no values indicative of micro areas of high pH were obtained. The existence of such areas is postulated from considerable presumptive evidence. This evidence includes N loss from accumulated nitrite in a supposedly alkaline medium, calculations indicating that a relatively large amount of acid is formed from a granule in relation to the small volume of soil influenced by that granule,

and the suggestion that nitrite inhibition of *Nitrobacter* activity is caused by undissociated nitrous acid (4).

About 10% of urea N added to the calcareous Webster soil was not recovered (Table VIII), probably because of loss through evolution of ammonia. The formation and spontaneous dissociation in an alkaline medium of hyponitrite to nitrous oxide are a second possibility (3).

The concentrations of N fertilizers used in the present work appear inordinately high, yet they are no higher than those often obtained from a band placement in the field under static moisture conditions. Rapid movement of the applied N does not occur under such conditions. Further concentration of N may occur as a result of moisture loss. Whether nitrite will accumulate under the extreme soil environmental conditions imposed by high concentrations of N fertilizers will depend very much on the persistence of the affected zone. Accordingly, the work reported here is being continued with larger systems, with the intent of approximating actual band applications of N fertilizers in the field.

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