seed (*1, 11*). However, the inert coating will necessarily make up a greater proportion of the pellet weight and thereby will lower the analysis of the original fertilizer.

Optical examinations of fertilizer particles often show extremely irregular surfaces with evidence of pores, crevices, and many small, exposed crystal forms. The nature of this surface including the aggregation of crystals in mixed fertilizers and its polarity must be studied before adequate coatings can be developed. It is more difficult to prepare coatings for granular, single salt fertilizers such as potassium chloride, ammonium nitrate, or urea than for granules involving mixed salt systems. For instance, a very small imperfection in the coating on a granule of KCl allows the potassium to diffuse away rapidly in water or moist soil. With an aggregation of small crystals in a matrix which contains partially soluble salts such as calcium phosphates, the dissolution properties are quite different.

Experimental work indicates that fertilizers can be coated satisfactorily to change the rate at which they dissolve in moist soils. When large quantities of fertilizer are used under farming conditions, this reduction will help to alleviate seed-fertilizer contact injury, reduce leaching losses of fertilizer nutrients in sandy soils, and minimize luxury absorption of potassium by crops.

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AMMONIA LOSSES FROM SOILS

Gaseous Loss of Ammonia from Surface-Applied Nitrogenous Fertilizers

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This work was done to determine if ammonia was lost from urea that was surface-applied to turf or bare soil even in the acid range, or from urea or ammoniates applied to turf which had been surface limed. Volatile loss of ammonia was measured by direct absorption and by crop response. Losses following application of 100 pounds of urea nitrogen averaged 29% for unlimed turf and 39% for limed turf. Respective losses from $(NH_4)_2SO_4$ were 0.4 and 19.7%; and from NH_4NO_3, 0.3 and 3.4%. Losses from urea surface-applied to bare sandy soil averaged 25% in 7 days, while loss from NH_4NO_3 was negligible. Greenhouse cropping of field-treated soil supported the general trend in data obtained by direct measurement. Losses were greater from large pellets than from fine. Dusting with $CuSO_4$ or gypsum did not retard volatile loss. For maximum efficiency under certain conditions, urea, ammoniates, and lime should be incorporated if practical.

GASEOUS LOSS of nitrogen from the soil following application of nitrogenous materials is not a new concept; but only within the last few years has it been recognized to be sufficiently large to justify intensive study. Tests of efficiency of applied nitrogen generally show maximum plant recoveries of between 50 and 75%. Even when leaching losses and residual nitrogen in the soil are considered, there still is a significant amount of nitrogen which cannot be accounted for and must be assumed lost from the soil in gaseous form.

The work of Loewenstein *et al.* (*5*) and Hiltbold and Adams (*4*) shows very definitely that nitrogen, if not kept in the plant utilization cycle, rapidly disappears in gaseous form, except for a fraction held in the soil at equilibrium with the particular type of soil and environment. That major losses as N_2 and N_2O gases occur was shown by the work of Hauck and Melsted using nitrogen-15 (*3*). Thus, to conserve nitrogen, it must be kept in the plant uptake cycle as far as practicable.

The volatile loss of ammonia following surface or shallow application of ammoniacal materials or urea to slightly acid or calcareous soils has been demonstrated by Martin and Chapman (*6*) and Earnst and Massey (*2*). The latter workers also showed the effect of soil moisture in increasing ammonia loss. The factors which have been largely overlooked are the limitations of ammonia-absorbing mechanisms in well developed sods and in light sandy soils in the moderate to strong acid range.

A second major factor which apparently has been ignored is the massive effect of surface liming of grass pastures or other turfs on the pH of the top fraction of an inch of soil, although the soil immediately below may still be acid. The potential loss of ammonia under such conditions may approach that from a naturally calcareous soil.

The primary purpose of this report is to present the latest results of continuing studies on volatile loss of ammonia from turf or bare soils. The approach to the problem of evaluation of volatile loss of nitrogen as ammonia is along two lines: the direct measurement of ammonia as it volatilizes from the soil, and the indirect estimate of this loss by differential crop response to the nitrogen remaining in the soil. The first method became

practical on a large scale with the development of an easily portable static ammonia absorber (7). The principle consisted of absorption of gaseous ammonia by dilute sulfuric acid on a glass wool pad anchored to the bottom of a glass dish about 2 inches deep. This dish is inverted over a treated area. The ammonia absorbed by the acid is then determined at the end of the test period by distillation.

The second and classical method of comparing over-all efficiency of nitrogen sources is to grow a crop and then analyze the harvest to estimate nitrogen absorbed. Obviously, this latter method is subject to serious difficulties in interpretation, because factors such as leaching, nitrification, denitrification to N_2 or oxides of nitrogen, microbiological competition, and plant preference for different forms of nitrogen are involved and may mask losses of nitrogen as ammonia.

The first comprehensive report by the writer (7) was based entirely on the direct measurement of ammonia gas evolved following treatment. In this report it was shown that the application of pelleted urea to four different grass sods resulted in nitrogen losses as ammonia ranging from 13.1 to 23.2% in the 6- to 8-day period following application of nitrogen at a rate of from 25 to 100 pounds per acre. Comparable losses from rates equivalent to 100 pounds of nitrogen per acre applied as crystal urea averaged 29.3%. Loss from Uran, a solution with nitrogen derived about equally from urea and ammonium nitrate, was 11.5%, while a loss of only 0.3% occurred from a comparable amount of pelleted ammonium nitrate used for comparison.

Losses of ammonia nitrogen during 7 days following surface application of urea to bare moist soils increased with decreasing base exchange capacity of the soil and/or increasing soil pH. Volatile loss of nitrogen as ammonia in field and laboratory tests ranged from 17 to 59% of a 100-pound per acre nitrogen application as pelleted urea to acid soils with cation exchange capacities of 7.2 meq. or less per 100 grams. The nitrogen loss from ammonium sulfate used for comparison was generally less than 1%. Losses with Uran solution surface-applied to bare soils were relatively low, unless the cation exchange capacity of the soil was low and the pH relatively high.

Urea hydrolyzes to ammonium carbonate under the influence of the enzyme, urease, which is abundant wherever general microbiological activity exists. Ammonium carbonate rapidly decomposes to ammonia and ammonium bicarbonate and the free ammonia escapes, unless an efficient base-absorbing mechanism is present. It was observed that temperature had a marked effect on volatilization rate. A temperature of

45° F., or lower, largely inhibits urease production or activity, but volatile loss of ammonia increases rapidly as temperature rises above 60° F.

The potential for ammonia loss from urea applied to a soil with an air-dry surface is low as long as high relative humidity or dew is not a factor; however, as little as 1% of moisture in light sandy soils, such as those widely used for citrus in Florida, gave a significant rate of ammonia evolution from urea. It was found for the various conditions tested that any ammonia evolution that did take place was largely complete within 7 days after application of urea, if moisture and temperature were not limiting.

Field tests comparing crop growth response to urea and other nitrogen sources have been quite inconsistent and difficult to interpret for widespread practical recommendations. Soil characteristics, climatic factors, and cultural practices are all intimately related in determining ultimate efficiency of a given material.

A recent report by Volk, Kelly, and Blue (8) on the response of oats and millet to top-dressed nitrogenous materials showed an over-all percentage nitrogen recovery from several tests of 54% for urea and 73% for ammonium nitrate where 25 to 50 pounds of nitrogen were applied per acre. Extensive data by Burton and Jackson (1) covering several years' tests with Coastal Bermudagrass showed nitrogen recoveries from ammonium nitrate to be superior to those from urea. In contrast to these reports, there are numerous published statements by various investigators indicating no consistent differences in response to various top-dressed nitrogenous materials.

Current Research

A possible approach to reduction of volatile loss of ammonia from urea would be the partial inactivation of urease by an inhibitor applied as a constituent of urea pellets. Recent work by the author (9), based on the well known principle that urease activity is inhibited by a heavy metal cation, showed that the rate of hydrolysis of urea was significantly retarded by copper spray residues in the soil. Table I is an attempt to apply this principle to the current problem by dusting urea pellets with copper sulfate prior to application to the soil. According to the data obtained, significant inhibition of urea hydrolysis appears to be impractical by this method, but further study is needed. Apparently, urea diffuses out of the zone of copper effect, thereby rendering the latter ineffective. Copper is readily immobilized by soil, while urea moves freely with soil moisture or by diffusion (9). The possibility of build-up of undesirable

Table I. Effect of Copper Sulfate Dust or Gypsum on Volatile Loss of Ammonia from Pelleted Urea-Nitrogen, Surface-Applied at 100-Pound/Acre Rate in Laboratory Tests on Moist Lakeland Fine Sand, pH 5.6

Treatments, Urea 1 to 2 Mm. Diameter	Replication Number	Nitrogen Loss as NH_3 in 7 Days, %
Urea	1	34.4
	2	36.4
	3	37.9
	Av.	36.2
+ 0.25% Cu by weight of urea[a]	1	32.0
	2	32.2
	3	34.1
	Av.	32.8
+ $CaSO_4 \cdot 2H_2O$ at 1–1 ratio[a]	1	33.6
	2	31.5
	3	38.6
	Av.	34.6

[a] Applied as dry coating to urea pellets 0.4% Cu was similarly ineffective.

Table II. Volatile Loss of NH_3 Following Surface Application of Lime and Nitrogen to Pensacola Bahiagrass Sod on Leon Fine Sand of pH 5.8

Nitrogen Treatment, 100 Lb. N./Acre from:	Field Location	Nitrogen Loss as NH_3, % in 2 Weeks	
		No top lime	1 ton calcic lime on surface, 4 months previously
$(NH_4)_2SO_4$	1	0.5	14.8
	2	0.7	20.9
	3	0.1	22.6
	4		20.5
	Av.	0.4	19.7
Urea	1	28.0	35.0
	2	29.9	37.7
	3	29.1	30.4
	4		41.0
	Av.	29.0	36.0
NH_4NO_3	1	0.3	3.5
	2	0.2	4.1
	3	0.3	3.1
	4		2.8
	Av.	0.3	3.4

levels of copper in the soil must also be recognized.

The use of calcium sulfate on soils in conjunction with urea fertilization is known to reduce activity of free ammonia by forming ammonium sulfate and calcium carbonate by interaction; but, as shown by Table I, mixing of equal weights of urea and gypsum had no measurable effect on ammonia evolution.

Table II presents data to show the effect of surface liming of Pensacola Bahiagrass sod on volatile loss of ammonia from ammonium sulfate, urea, and ammonium nitrate. Certain portions of the area used for these tests were limed 4 months previously and the lime was left undisturbed on the surface, ex-

Table III. Nitrogen Recovery by Greenhouse Cropping Following Surface or Incorporated Application of Pelleted Urea and Ammonium Nitrate in the Field and 12 Days, Exposure without Precipitation, Lakeland Fine Sand, pH 5.6

Treatment, 100 Lb. N/A, 0.39 Gram/Pot, 4 Replicates	Urea			Ammonium Nitrate		
	N, Grams Recovered by:		Net recovery, %	N, Grams Recovered by:		Net recovery, %
	Oats	Millet		Oats	Millet	
Field application to dry surface	0.331	0.034	65.2	0.349	0.037	70.8
Incorporation in field	0.369	0.033	75.3	0.370	0.036	76.3
Incorporation at planting time	0.344	0.035	69.3	0.349	0.037	71.0
Field application of large pellets to dry surface[a]	0.286	0.030	53.0			
Field application of large pellets to moist surface[a]	0.273	0.034	50.3			

[a] Pellets 2 to 3 mm. in diameter used; otherwise range was predominantly 1 to 2 mm. typical of commercial material.

All soils mixed at planting time. L.S.D. (t 0.05) 9.97%.

cept for the effect of rainfall and other natural climatic factors. The effect of liming on ammonium sulfate and urea was readily apparent in increasing loss of ammonia, but the effect on ammonium nitrate was surprisingly low. The latter probably was a result of greater activity of the nitrate ion as compared to the sulfate in holding ammonia in the presence of calcium carbonate. Also, only one half as much ammonia was added in the ammonium nitrate, as compared to other sources. Yield data and nitrogen analysis of forage from these plots of Bahiagrass, and similar tests with Coastal Bermudagrass, are incomplete but yield data obtained to date tend to support the order of findings presented in Table II.

While direct measurement of volatile loss of ammonia by absorbers is considered to be reliable and on the conservative side, it still does not give the practical answer desired by the grower. Data in Tables III and IV are attempts to show that measured volatile loss from the soil will be reflected in yields, if complicating factors such as precipitation within the volatilization period and leaching are eliminated. In these two tests, nitrogen materials were placed on top of the soil as compared to incorporation at the same time or at planting. They were allowed to remain exposed under field conditions for several days. Precipitation and leaching effects were eliminated by supporting covers about 6 inches above the treated areas during periods when precipitation was expected. Data in Table III were obtained by placing the materials on or in soils in small field plots for the exposure period, then placing equal amounts of the field-treated soil in 2-gallon pots and growing one crop each of oats and millet in succession in the greenhouse. Crops were harvested prior to heading out. Root systems were fully developed to the depth of soil in the containers. Data in Table IV were obtained by placing soil in 1-gallon tin containers prior to treatment, then burying the containers to ground level in the field for treatment and exposure. This was followed by mixing the soil in each container and cropping in the greenhouse.

The results supported the general order of data on volatile loss obtained by direct measurement for this soil as previously reported (7). There was greater nitrogen recovery by subsequent cropping where urea was incorporated, as compared to surface-applied. The recovery was relatively unaffected by surface application where ammonium sulfate or ammonium nitrate was used, as would be expected for a soil of pH 5.6. Recovery also was less for large pellets of urea, 2 to 3 mm. in diameter, than for commercial pelleted material. The majority of the latter was in pellets between 1 and 2 mm. in diameter. These and previously reported data suggest that the actual quantity of pelleted urea used per acre probably is not a significant factor in proportionate loss, unless the application is sufficiently large that the micro-environment created by individual pellets overlaps one another in effect. Size of pellets apparently is a critical factor that needs more study.

Table V presents data on tests comparing Uran solution to pelleted ammonium nitrate. Both materials were surface-applied to sodded areas on soil of about pH 5.8. Uran was applied by means of special equipment with the same type nozzles used in commercial application. The solution was applied under constant pressure and speed of equipment. The actual quantity dispensed during total linear travel of equipment over all of the plots was determined. An equivalent quantity of pelleted ammonium nitrate was then calculated and applied. The data are presented because they emphasize the importance of taking into consideration the possible differential effect of different rainfall patterns during nitrogen fertilizer tests.

The order of efficiency for the initial application of ammonium nitrate, as compared to Uran on Area A where 5 days of dry weather followed application, was entirely different from on Area B lying immediately adjacent on which 0.1 inch of rain fell immediately after treatment. A dry period following treatment, or heavy leaching rains occurring before urea had been hydrolyzed would enhance volatile loss or leaching, respectively, from urea as compared to ammoniacal nitrogen. The initial response of the Pensacola Bahiagrass to nitrogen was low and the differential response to refertilization on Area A may be a reflection of carryover of nitrogen from the initial fertilization. While this type of data does not necessarily represent inefficiency as a result of volatile loss of nitrogen, it does show the complex nature of the problem of isolating factors involved in nitrogen efficiency.

That volatile loss of nitrogen as ammonia does exist in quantity under certain conditions must now be accepted and evaluated along with leaching losses, availability rates, and plant preferences for the form of nitrogen present. The fact that one material is

Table IV. Nitrogen Recovery by Greenhouse Cropping Following Surface or Incorporated Application of Various Materials, and Exposure to Natural Insolation without Precipitation, Lakeland Fine Sand, pH 5.6

Treatment 100 Lb. N/A, 0.205 Gram/Can, 4 Replicates	Pelleted Urea, Commercial			Crystal Ammonium Sulfate			Pelleted Ammonium Nitrate		
	N, Grams Recovered by:		Net recovery, %	N, Grams Recovered by:		Net recovery, %	N, Grams Recovered by:		Net recovery, %
	Oats	Millet		Oats	Millet		Oats	Millet	
Surface application, 15-day exposure	0.107	0.049	50.3	0.126	0.051	61.0	0.117	0.065	63.8
Incorporated, 15-day exposure	0.121	0.057	61.8	0.122	0.049	58.0			
Incorporated at planting	0.121	0.058	62.0	0.126	0.049	60.3			

L.S.D. (t 0.05) 6.88%.

Table V. Nitrogen Recovery by Grasses Following Top Dressing with Uran Solution or Pelleted Ammonium Nitrate, Leon Fine Sand, pH 5.8

Treatment and Initial Rains	Coastal Bermudagrass Uran	Coastal Bermudagrass NH_4NO_3	Pensacola Bahiagrass Uran	Pensacola Bahiagrass NH_4NO_3
	Nitrogen Recovered,[a] Net Lb.			
Area A				
54.0 lb. N applied 4/13, 0.93 inch rain on 4/18, cut 5/27	12.9	27.2[b]	7.1	11.5[c]
Refertilized 45.3 lb. N on 6/17, 3.50 inches rain 6/18, cut 7/20	16.8	18.0	18.9	24.4[b]
Area B (Adjacent to *A*)				
45.1 lb. N applied 4/22, 0.10 inch rain immediately, 1.03 inches rain 4/26, cut 5/27	16.8[b]	10.5	8.7	8.7
Refertilized 44.7 lb. N on 6/24, 1.83 inches rain 6/27, cut 7/20	17.3	17.2	17.1	18.4

[a] Av. of six replicates.
[b] Statistically significant difference at 0.01.
[c] Statistically significant difference at 0.05.

subject to greater volatile loss of nitrogen than another material under a given set of conditions does not necessarily imply lower efficiency for crop production. This type of loss is only one of several factors to be considered. However, it does strongly suggest that agricultural practices leading to measurable volatile losses of ammonia, such as surface application of urea to light soils and turf, or of ammoniates to calcareous or top-limed soils, should be taken into consideration and cultural practices adjusted within reason to reduce such losses and thus increase the efficiency of the material in question.

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FOOD ANTIOXIDANTS

Determination of Butylated Hydroxyanisole and Butylated Hydroxytoluene in Potato Granules by Gas-Liquid Chromatography

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A rapid and specific method for the quantitative analysis of low levels of butylated hydroxyanisole and butylated hydroxytoluene in dehydrated potato granules using gas-liquid chromatography with flame ionization detection is described. The method is shown to give analyses with an average error of less than 11% from the true concentration for both antioxidants within the range 0.5 to 10 p.p.m. of antioxidant in the granules.

BHA (2- and 3-*tert*-butyl-4-hydroxyanisole) and BHT (3,5-di*tert*-butyl-4-hydroxytoluene) are used at low levels (<10 p.p.m. of both) in commercial dehydrated potato granules to protect the natural fat of the potato from oxidative deterioration. Many naturally occurring phenolic materials in potatoes interfere with analysis of these antioxidants by colorimetric methods unless a tedious steam distillation procedure (*2*) is used. Even with steam distillation, the authors have found the colorimetric method to be questionable below 10 p.p.m. for BHT.

A gas-liquid chromatographic method (GLC) for BHT in paperboard has been reported (*3*). Thermal conductivity detection was satisfactory for the levels used in paperboard. With the low levels used in potato granules, however, it is impossible to obtain accurate analysis with thermal conductivity detection unless an excessively large sample is taken. The low levels are, however, well within the sensitivity of the flame ionization detector.

Experimental

Materials. Dehydrated Potato Granule Samples. Idaho Russet Burbank potato granules prepared by the conventional add-back process were received directly from the manufacturer—dried to 5.7% moisture—and stored under a nitrogen atmosphere (<0.2% O_2) at 75° F. until the present work, 1 year later. The only additive was sodium bisulfite at a level of 300 p.p.m. of SO_2. Weighed amounts of antioxidants were mixed carefully with granules in the laboratory; first by grinding with mortar and pestle and later with a rotating mixer to give levels used in the analyses—i.e., 0.50 p.p.m., 2.50 p.p.m., 5.00 p.p.m., and 10.00 p.p.m. of each antioxidant. This was done within a day prior to analysis.

Reagents. Petroleum ether, b.p. 40° to 60° C.

BHA (Tenox BHA). Twice recrystallized from petroleum ether, m.p. 59° to 60° C.

BHT (Koppers Food Grade). Purity, 98.7%; m.p. 69° to 70° C.

Standard solution. It contained 0.100 mg. of BHA per ml. and 0.100 mg. of BHT per ml., in petroleum ether.