

Availability of Various Fractions of Urea-Formaldehyde

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Cold water-soluble methylene ureas (Fraction I) are rapidly mineralized, but apparently they become available to plants only after internal cleavage and mineralization to ammonium or nitrate. The availability of this fraction was similar to that of ammonium nitrate except for the greater initial flush of growth from ammonium nitrate. Hot water-soluble methylene urea (Fraction II) is mineralized more slowly than Fraction I and is of major concern when discussing slow release properties of urea-formaldehyde. Mineralization proceeds at about 15% per week in the first week or two, but drops to about

1.5% per week in the fourth to sixth month. Hot water-insoluble urea-formaldehyde (Fraction III) is mineralized at a rate of about 10% per year. Only at very high application rates are significant responses observed. Various cropping procedures have been used to measure availability of nitrogen from the various fractions of urea-formaldehyde. Evidence indicates optimally growing grass enhances the rate of mineralization of resistant fractions of urea-formaldehyde by maintaining a more active microbial population.

Commercial fertilizer grade U-F is composed of a series of polymers of condensed urea and formaldehyde. DeJong and DeJonge (1953) concluded that U-F is composed primarily of a mixture of straight-chain polymers of urea and formaldehyde containing as many as six urea residues. They found no extensive ring structures. Partially purified pentamethylene-hexaurea examined by infrared spectrum analysis by Becker (1956) showed branching. All of the lower condensates were unbranched chain molecules. Commercial products also contain from 6 to 10% of unreacted free urea (Hays *et al.*, 1965).

The condensation products are relatively insoluble. Methylene-diurea, the simplest polymer, is soluble to the extent of about 25 grams per liter at 25° C. (Hays and Haden, 1966). Definitive work was done by Long and Winsor (1960) who examined relatively pure preparations of methylene-ureas. They observed 85% nitrification of methylene-diurea and dimethylene-triurea in 3 weeks. Sixty-eight per cent of trimethylene-tetraurea and less than 5% of tetramethylene-pentaurea nitrified in the same period.

Since its introduction more than a decade ago as a nonburning, long lasting fertilizer, the use of urea-formaldehyde (U-F) has expanded steadily in the United States. It is used mostly in turfgrass culture and other specialty horticultural applications, and is commonly included in mixed fertilizers used for landscape purposes. A considerable amount of research has been directed toward evaluating its performance under various conditions (Winsor and Long, 1958). Important questions requiring more definite data concern the rate of mineralization of the more resistant fractions of U-F and the possible direct utilization by the plant of the water-soluble fractions. The research reported here was aimed at answering these questions.

PROCEDURES

Materials. The literature describes U-F on the basis of solubility characteristics. Fraction I: cold water-soluble N (CWSN)—that portion soluble in water at 20–25° C., used in the weight ratio of 250 to 1 of U-F (Association of Official Agricultural Chemists, 1960). The analysis corresponds to a mixture of free unreacted urea, methylene-diurea, and dimethylene-triurea. Fraction II: hot water-soluble minus cold water-soluble (HWSN-CWSN)—that portion dissolving in a pH 7.5 buffered phosphate solution for 30 minutes at 98–100° C. when used in the ratio of 0.1200 gram of cold water-insoluble nitrogen to 100 ml. of buffer. The analysis corresponds to a mixture of trimethylene-tetraurea and tetramethylene-pentaurea. Fraction III: hot water-insoluble N (HWIN)—that portion not dissolved in hot water-soluble fractionation. It is believed to be composed primarily of pentamethylene-hexaurea and longer chain polymers. Commercial fertilizer grade U-F contains roughly equal portions of the three fractions.

The U-F fractions used in these studies were supplied by Hercules, Inc., and were prepared in large scale separations simulating the AOAC procedure. The suppliers obtained the following analyses which help characterize the fractions:

Fraction	Analyses of Whole U-F Used in This Study	
	Wt. %	Av. No. urea residues per molecule
I	31	2.5
II	37	4.7
III	32	7.0

Observations indicate that some additional polymerization occurs during the hot water extraction as shown by the fact that Fraction II is not completely soluble in hot water after separation. A certain amount of back reaction hydrolysis may have also occurred. These reactions, particularly polymerization, appear to have occurred to a greater extent than usual owing to longer exposure to elevated temperatures during the large scale separation.

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For example, 27% of Fraction II used in this work was insoluble in hot water when resubjected to the AOAC procedure. The practical implication of these data relates primarily to Fraction II, where the mineralization rates observed would be expected to be somewhat slower than is characteristic of the Fraction II portion of the whole commercial U-F. All fertilizer materials used in this study were ground and screened to pass a 50-mesh screen and be retained on a 20-mesh screen. The crystalline (presumably pure compounds) methylene ureas were also supplied by Hercules, Inc.

Experiment 1. Alta Fescue (*Festuca arundinacea* var-Alta) was grown in containers holding 1400 ml. of Kriliium-treated Yolo loam to which had been added 25 p.p.m. P as single superphosphate and 286 p.p.m. K prior to seeding. The turf was cropped by clipping until soil N was depleted, growth having been reduced to 20 to 30% of an adequately fertilized treatment. At the end of this period, 32 pots having uniform yields, $\pm 10\%$ of the mean, were selected for treatment. Soil reaction at this time was 6.6.

The pots were divided into eight treatments with four replications of each. Treatments consisted of various sources of nitrogen (Table I). Five soil plugs 2.5 by 10 cm. were removed from each container. Into each Alta Fescue container (with plugs missing) was placed a N treatment prepared by mixing 80 mg. of N (2 lb. of N per 1000 sq. ft.) into soil from spare containers which was then used to refill the holes to within about one inch from the surface. The grass plugs of appropriate length were replanted into the same positions. Thus fertilizer was introduced into established turf of known nitrogen deficiency. Within 3 or 4 days roots permeated the fertilized zone.

The pots were irrigated three times weekly with distilled water. The leachate was caught in plastic dishes and returned to the soil at the next irrigation. Previous experience had shown this irrigation procedure maintained optimum growth.

A separate set of four pots was maintained on a liquid fertilizer program which permitted maximum growth. This provided a reference point with which to compare treatments showing a response to fertilizer treatments.

The fertilized pots were grown in a growth chamber with a night temperature of 18° C. and day temperature of 23° C. Cropping for 26 weeks was accomplished by clipping the turf to a 3³/₄-cm. height, as needed. Clippings were dried, weighed, and analyzed for total N. Analysis of grass tissue was by the micro-Dumas method. Soils also were analyzed for total nitrogen content at the beginning, after 13 weeks for two replications, and at the end of the ex-

periment. To obtain samples for analysis, great care was taken to mix the soils, and six separate determinations were made to obtain an average value.

Experiment 2. This study was conducted in a manner similar to that described above, except that the nitrogen treatments composed of various rates of Fraction III were blended into the soil prior to seeding, and irrigation was with tap water. Leachings were not returned to the containers. Pot size, number of replications, soil, phosphorus and potassium additions, irrigation frequency, and clipping practices were the same as described in Experiment 1. The study was conducted in a glasshouse and continued for over one year. Daytime temperatures were typically in the range of 21° to 30° C., and night temperatures were 13° to 15° C. Fraction III, at rates of 0, 32, 64, 128, and 256 lb. of nitrogen per 1000 sq. ft. constituted the treatment variables. A treatment composed of 5.6 lb. of nitrogen from NH₄NO₃ was included for reference. Availability of Fraction III was evaluated by growth response. Clippings were analyzed for total nitrogen content, as were the soils at the beginning and the end of the study.

Experiment 3. To determine if the soluble fractions in U-F are directly available to the plant, grass was established and grown in Hoagland's No. 1 solution culture until uniform growth was observed. The solutions were then exchanged for nutrient solutions in which NO₃ (as before), urea, methylene-diurea, dimethylene-triurea, or trimethylene-tetraurea were used as the sole sources of nitrogen. Growth was compared with that obtained in the NO₃ solution.

RESULTS AND DISCUSSION

Experiment 1. The technique of introducing plugs of soil containing the fertilizer into established but nitrogen deficient turf proved to be very effective in evaluating the relative availability of the fertilizer nitrogen to the grass by measuring yield response as compared to optimally growing grass. The results are summarized in Figure 1 and Table II. Nitrogen recovery by the clippings is summarized in Figure 2. These data do not account for nitrogen accumulating in the roots and that portion of the plant not clipped off (crown). When the nitrogen availability is so slow that clipping yields are well below maximum, the bulk of the nitrogen being accumulated by the roots is used to sustain the crown. Thus, the data of Figure 2 do not accurately reflect total nitrogen mineralization but are useful for comparative purposes.

The response of Fraction I was very similar to that of

Table I. Nitrogen Sources Used as Treatments in Experiment 1

Treatment	Rate
Fraction I	80 mg. of N per container
Fraction II	80 mg. of N per container
Fraction III	80 mg. of N per container
Fractions II and III	80 mg. of N per container
Whole U-F	80 mg. of N per container
Blank—no N
Irrigated with nutrient solution	10 m.e. N/L
NH ₄ NO ₃	80 mg. of N per container

Table II. Dry Weight of Clippings per Pot Obtained during First 7 Weeks of Cropping, Experiment 1

Nitrogen Source	Grass Clippings per Week per Pot, Mg.						
	Week						
	1	2	3	4	5	6	7
Fraction I	35	320	400	200	80	70	68
Fraction II	28	190	180	130	80	85	80
Fraction III	20	20	20	25	20	25	25
Fractions II and III	28	50	80	85	60	85	85
Whole U-F	43	180	170	100	60	80	80
NH ₄ NO ₃	45	375	375	220	80	60	60
No fertilizer	15	25	15	20	10	15	15
Liquid fertilizer	95	500	860	700	570	620	580

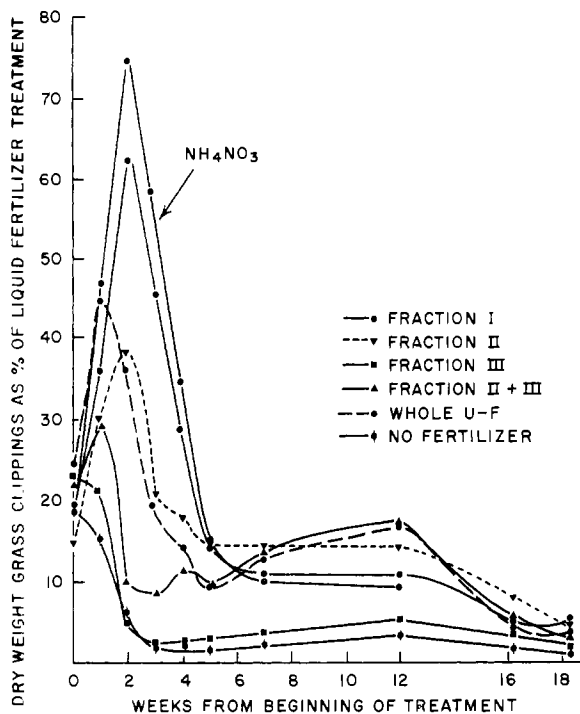


Figure 1. Weekly dry weight yield of Alta Fescue clippings

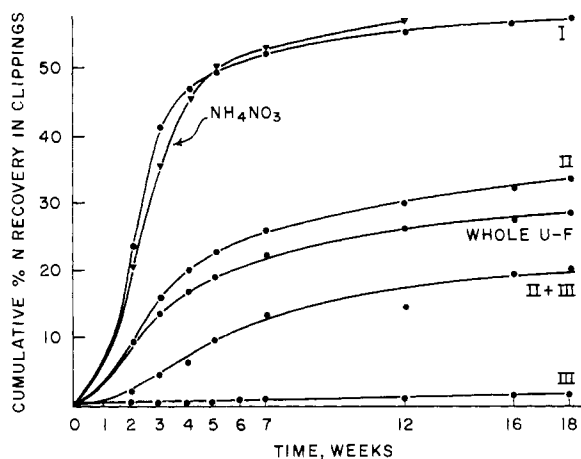


Figure 2. Cumulative per cent N recovery in clippings, corrected for blank

ammonium nitrate in both yield and cumulative per cent recovery, the principal difference being that the initial flush of growth from ammonium nitrate was somewhat greater than that of Fraction I. After 5 weeks, yields had again dropped to less than 20% of maximum. Fraction III and the unfertilized treatment both dropped to a dry weight yield of less than 5% of maximum after 3 weeks. Thereafter, the treatment fertilized with Fraction III was consistently but only slightly better than the blank. Fraction II displayed a modest flush of growth during the first 2 weeks, and after 5 weeks had growth superior to Fraction I or the NH_4NO_3 treatment. At the end of 18 weeks, all treatments were growing at less than 10% of maximum. These data substantiate in general the nitrification data of Long and Winsor (1960), and show that substantial differences in the

rates of availability exist among the different fractions of U-F. The data likewise point out that the tendency for pronounced flushes of growth following an application of fertilizer are much reduced with U-F, and that moderate growth is supported for relatively long periods with U-F. This is enhanced as the levels of Fractions II and III tend to increase in the soil as a result of repeated applications.

Focusing attention on the growth response to whole U-F, during the first week growth was intermediate between that obtained with Fractions I and II. During the second through the fifth week, growth was about two thirds of the average of Fractions I and II, which is about what would be expected if Fraction III were making a relatively small contribution. From the seventh week on, after Fraction I presumably is exhausted, whole U-F performed about as well as Fraction II. Since the treatments received equal quantities of nitrogen, the performance of whole U-F during the period after 7 weeks is better than would be anticipated based on the response to Fraction II. This observation is consistent with the data presented in the Materials section showing that the separation of the fractions resulted in increased polymerization of Fraction II as compared with their composition actually obtaining in whole U-F: It is clear that Fraction III is very much more slowly available than the other fractions.

Clipping analysis for nitrogen confirmed nitrogen accumulation from Fraction I to be about nine tenths of that from NH_4NO_3 during the first 4 weeks. Soil analysis showed 19% of the applied nitrogen (after correction for the blank) to be still in the soil after 13 weeks. This value dropped to 4% after 26 weeks. Comparable values for the NH_4NO_3 treatment were 7 and 0%, respectively. During the week of maximum response (second week) the grass clippings recovered 42% as much nitrogen from Fraction II as from Fraction I. Making reasonable assumptions regarding nitrogen content of crown and roots, based on subsequent analyses, it appeared that the maximum mineralization in any one week was about 15% from Fraction II. At the end of 13 and 26 weeks, 46 and 25% of the applied nitrogen remained in the soil. The soil analyses indicate a mineralization rate of about 1.5% per week during the period from 13 to 26 weeks. In summary, a portion of Fraction II (presumably trimethylene tetraurea) mineralizes relatively rapidly and probably relatively completely in about 4 weeks' time. The longer chain polymers in Fraction II are more slowly mineralized. The present data indicate the mineralization rate is about 1.5% per week. Experiment 2 provides a better basis for estimating the rate of mineralization of Fraction III.

The objective of good turf culture is not high yield production, but maintenance of an adequately dense turf and acceptable color. Generally, these conditions are met sufficiently when growth is about 25 to 75% of maximum. Rapid growth is, indeed, often quite undesirable for good turfgrass culture. Crider (1955) has shown that the removal of more than 40% of the top grass stops root growth within 24 hours. When top growth is rapid, excess removal and scalping of the grass are much more prevalent. Rapid flushes of growth present no problem when mowing is sufficiently frequent. In practice, however, this is not done often and the scalping hazard is greatly increased.

Experiment 2. Data from experiment 2 are summarized in Figures 3 and 4. Where 256 lb. of N per 1000 square feet were added as Fraction III, yields were maintained at approximately a linear rate for over one year. Nitrogen was being mineralized from the hot water-insoluble condensates at rates sufficient to yield maximum growth.

Analysis of the relative growth produced by Fraction III treatments is shown in Figure 4. During the first three weeks, there was a response produced by each increment of nitrogen, although the response curve was flattened out. During the period from 4 to 15 weeks, the growth was almost exactly proportional to the application rate, but thereafter the 256-lb. treatment performed relatively much better than the other treatments. Part of the notable response differential between the 256-lb. rate and the other treatments is attributable to the abundant growth of the grass on the high treatment, which often overflowed the container area and thus intercepted more light. The actively growing grass at the highest application rate also exerted a synergistic effect on the mineralization of Fraction III; the synergism presumably was due to increased production of carbonaceous substrates by the grass roots and the resulting increased microbial population.

An estimate of the rate of mineralization of Fraction III obtained by measuring both soil "residual" nitrogen, and turf accumulation of mineralized nitrogen, indicates a mineralization rate of about 10% per year. It is difficult to obtain this figure with great precision. Soil analysis showed 84% of the applied nitrogen still remaining. The total recovery in the clippings and crown, taken at the end of 57 weeks, showed 8.4% recovery of the applied nitrogen. An independent estimate is obtained by taking the clipping recovery of nitrogen during a period of good growth. It is reasonable to assume the nitrogen in the crown during such a period remains approximately constant. The period of

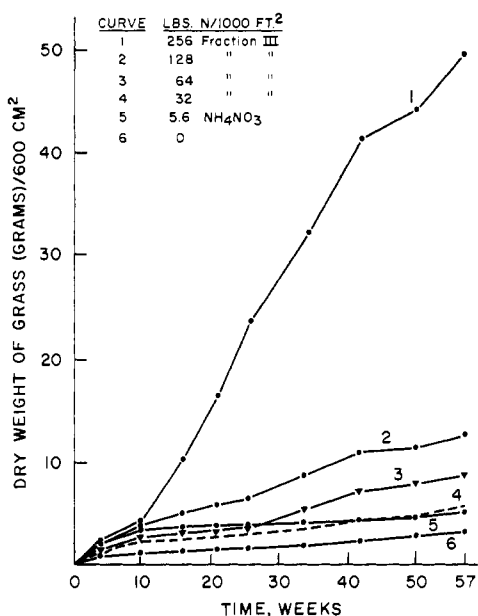


Figure 3. Cumulative dry weight of clippings from large applications of Fraction III compared with NH_4NO_3

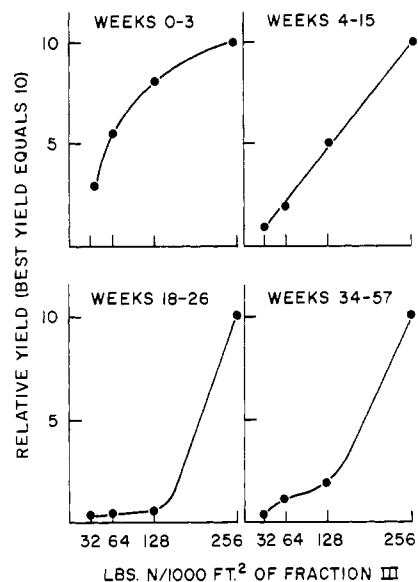


Figure 4. Comparison of yields of four HWIN application rates (on relative scale)

Yields corrected for blank

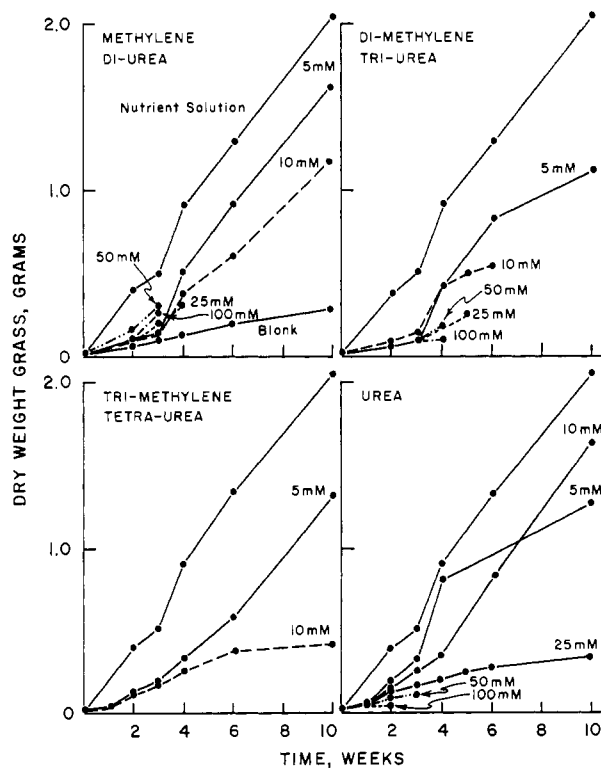


Figure 5. Cumulative dry weight of Alta Fescue clippings from solution culture treatments

11 to 21 weeks showed a 2.05% recovery for the highest Fraction III application which projects to 10.5% per year. An annual mineralization rate of 8.2% is indicated by data from the three lower application rates when examined during the first 8 weeks (a period in which nitrogen supply limited growth moderately) if the assumption is made that the crown and root system had retained about 0.5% of the added nitrogen. The uniformity of these data was good, maximum variation being only about 8% from the mean.

In summary, the plant analyses from several independent observations showed recoveries from Fraction III of about 8 to 10% per year. The soil analyses indicate a maximum mineralization of about 14 to 15% per year (84% remained after 1.1 years). The authors estimate that about 10% mineralization of Fraction III occurs per year under favorable conditions.

Experiment 3. Urea and methylene-ureas as pure crystalline compounds, or as U-F fractions, were used to provide 5-, 10-, 25-, 50-, and 100mM concentrations of nitrogen in an otherwise nitrogen-free nutrient solution. Growth responses were measured by cropping with Alta Fescue (Figure 5).

A delay of one week or more was required for response from methylene-ureas. Then, a rapid increase in growth took place which was followed by the development of toxic effects and, in severe cases, death.

The response of Alta Fescue to crystalline methylene-ureas and urea suggests no direct utilization by the plant of these compounds, as there is a substantial time delay before

achieving a somewhat normal growth rate after being supplied methylene-urea or urea. Breakdown of the condensates by internal cleavage of methylene linkages and release of free urea, or exposure and cleavage of internal amino groups resulting in NH_4 absorption are suggested mechanisms for utilization of these materials by plant roots. Solution analyses indicate the observed toxicity effects were probably due to cleavage to urea molecules and subsequent hydrolysis to ammonia. The relatively high levels of ammonia at the pH levels (pH 4.5–5.5) produced toxicity.

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