METHYLENE UREA - A CONTROLLED RELEASE NITROGEN SOURCE FOR TURFGRASSES

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The development of nitrogen products derived from condensing urea with formaldehyde represented a significant advance in nitrogen fertilizer technology. This technology provided the basis for developing nitrogen containing fertilizer products with some properties similar to natural organic nitrogen sources. These similarities include (1) a controlled release of nitrogen and (2) a low burn potential. Additional beneficial properties over natural organics nitrogen sources provided by urea-formaldehyde condensation products include (1) high nitrogen analysis (38% vs. less than 10% nitrogen), (2) excellent consistency, (3) improved flexibility in adjusting nitrogen release characteristics, (4) odorless, and (5) economical.

According to a report in Marketing Research Report on Controlled Release Fertilizers by Jeanie H. Ayers, Chemical Economics Handbook, Menlo Park, California (Oct. 1978), nitrogen derived from urea formaldehyde condensation products accounted for 90% of all the controlled release nitrogen consumed in the United States.

While the generic name "ureaform" and ureaformaldehyde has been used for a number of years to describe the condensation products of urea and formaldehyde, it has been suggested (O'Donnell, personal communication, 1976) that methylene urea (MU) would be technically more accurate. This name, methylene urea, shall be used in the discussion to follow.

The early pioneering research carried out at the USDA and reported in 1946 by Yee and Love (Proc. Soil Science Soc. Amer., 11, 389) showed that a nitrogen product with controlled availability could be made by condensing urea with formaldehyde under specific reaction conditions. Following this initial research, two distinct categories of methylene urea products were commercialized. These two categories differed primarily in their solubility characteristics as affected by the distribution of the mixture of methylene urea polymers in the final product plus the level of un-reacted urea.

Manufacturing

Production of methylene urea requires exact control of temperature, pH, reaction time and reaction components. The release characteristics can be controlled by modifying the reaction variables. As shown in Table 1, there are 6 basic components required for production of methylene urea. Urea and formaldehyde are the major components while sulfuric acid, sodium hydroxide and surfactant are only required in molecular quantities.

In the reaction process, urea reacts with formaldehyde to produce monomethylol urea which further reacts with urea to produce methylene urea varying in chain length (2 to 5 urea molecules, or possibly even higher, attached together with methylene groups). (Table 2).

The manufacturing of these products differs relative to the ratio of urea to formaldehyde used and the reaction conditions. Dr. John Hays on the panel will discuss the products common to Category 1 while my discussion will be on the methylene urea products of a second major group, Category 2 (see Table 3).

Chemical Properties

As a basis to give you some background on the two major categories of methylene urea products, typical chemical characteristics are shown in Table 3. A further breakdown on the distribution of nitrogen components within the solubility fractions will also help to characterize differences in these two categories (see Table 4).

The nitrogen release characteristics of methylene urea can be controlled by the method of manufacturing selected. Analytically the release characteristics are classified by the solubility of this product in water varying in temperature. Two temperatures are selected (1) room temperature (22°C) and (2) boiling water (100°C). Based on the solubility at these two temperatures, the biological activity can be predicted. As shown in Figure 1 as the percent of the cold water insoluble nitrogen which is soluble in hot water decreases (NAI), the nitrification rate (conversion of methylene urea to nitrates) decreases. The nitrification rate is dramatically reduced as compared to ammonium sulfate and urea. This rate can be reduced to a point which is relatively biologically inactive.

One of the primary benefits of methylene urea is attributed to its low salt index. As shown in Table 5, the low salt index at equal rates of material is dramatically reduced as compared to conventional fast release N sources. These differences are even more dramatic when compared on an equal nitrogen basis. Since the salt index is a measure of burn potential, it is obvious that on an equal weight or equal N basis, methylene urea would have a much lower burn potential as compared to soluble N sources.

The slow release characteristics of methylene urea are also reflected in the rate of conversion to ammoniacal and nitrate nitrogen in the soil. As shown in Figure 2 and 3, the ammoniacal nitrogen level in the soil solution is up to 4 times higher when treated with urea as compared to the methylene urea. After 6 weeks, the ammoniacal nitrogen level is essentially zero regardless of nitrogen source. In contrast, the nitrate nitrogen level dramatically increases as the ammoniacal nitrogen level decreases. This was only evident if the nitrogen source was methylene urea (Figure 3). The nitrate nitrogen level continues at a high level for 120 days (50-100 ppm) if the soil was treated with methylene urea. In contrast, soil treated with urea never had a nitrate level greater than 30 ppm. Urea readily leaches from the media before conversion of urea to nitrates can be realized.

Biological Properties

Controlled release nitrogen sources are often characterized by improved safety, increased residual, a more uniform growth pattern and less total clipping removal as compared to turf treated with soluble nitrogen sources.

As shown in Table 6 as the percent cold water insoluble nitrogen increases, the degree of injury decreases. These differences are more dramatic when the fertilizer is applied to wet turf, however, still are apparent on dry turf. At a cold water insoluble nitrogen (CWIN) of 42%, injury was not objectional at all rates (1-4 lb. N/M) or methods of application (wet vs. dry foliage). In contrast, complete formulations containing only 2% CWIN caused extreme foliar injury when applied to wet foliage using only 1 lb. of N/1000 sq ft. under the conditions of this study (applied in late August under high temperature conditions).

When comparing methylene urea from Category 1 to Category 2 relative to turf response, a substantial difference in turf color was noted. As shown in Table 7, the spring greening response from a late fall fertilization was very slow when turf was treated with ureaform (Category 1) but was dramatically increased when treated with methylene urea (Category 2). In this same experiment, the nitrogen source IBDU was also included. Initial response was comparable to ureaform while the residual of methylene urea and ureaform was longer than for IBDU (see Table 7).

Spring application of IBDU and methylene urea (Category 2) were compared (see Table 8). In this study, initial greening was very slow when treated with IBDU even though rates of 2 lbs. of nitrogen per 1000 sq. ft. were applied. In contrast, turf treated with methylene urea exhibited a rapid spring greening response. The residual characteristics of these products were similar.

The residual of the methylene urea (Category 2) was compared to urea. As shown in Figure 4, the initial surge of growth was reduced from 1.9 grams for turf treated with urea down to 1.1 grams when the turf was treated with methylene urea (42% reduction in fresh weight). The reduction in initial surge growth is reflected in the residual. These differences are not dramatic from only one application, however. When repeat applications of methylene urea from Category 2 were used, the residual characteristics became more apparent as shown in Figure 5. In this study, the fertilizer program was discontinued in the fall of the 2nd year. Clipping fresh weights in the spring of the 3rd year dramatically reflected the residual characteristics when methylene urea containing 42% CWIN was compared to a product containing 2% CWIN. The color of the turf treated with the controlled release nitrogen source (23-7-7 42% CWIN) was comparable to turf treated with the fast release N source (10-6-4 2% CWIN) in 27 out of 32 observations over a 2 1/2 year period (see Figure 6).

Turf growth is another measure of the controlled release properties of methylene urea. The total fresh weight of clippings can be substantially reduced when turf is treated with methylene urea as compared to urea. As shown in Table 9, clippings removed over a 6 week period was reduced by one third when Kentucky bluegrass was treated with methylene urea as compared to urea. The lower clipping removal is reflected in less tendency for scalping because of delayed mowing, a reduction in mowing frequency and less labor for collecting and removing clippings.

In another experiment, we compared two kinds of methylene urea sources from Category 2 (see Table 10). Two products varying in percent CWIN were applied in early October to Kentucky bluegrass. While it is often reported that methylene urea products will not provide a good color and growth response under cool soil conditions, these results are to the contrary. The product containing 36% CWIN induced better turf color than products containing 50% CWIN suggesting greening response is associated with the percent CWIN in the product. This again illustrates the flexibility in formulating methylene urea products to meet the biological demands of turf.

Summary

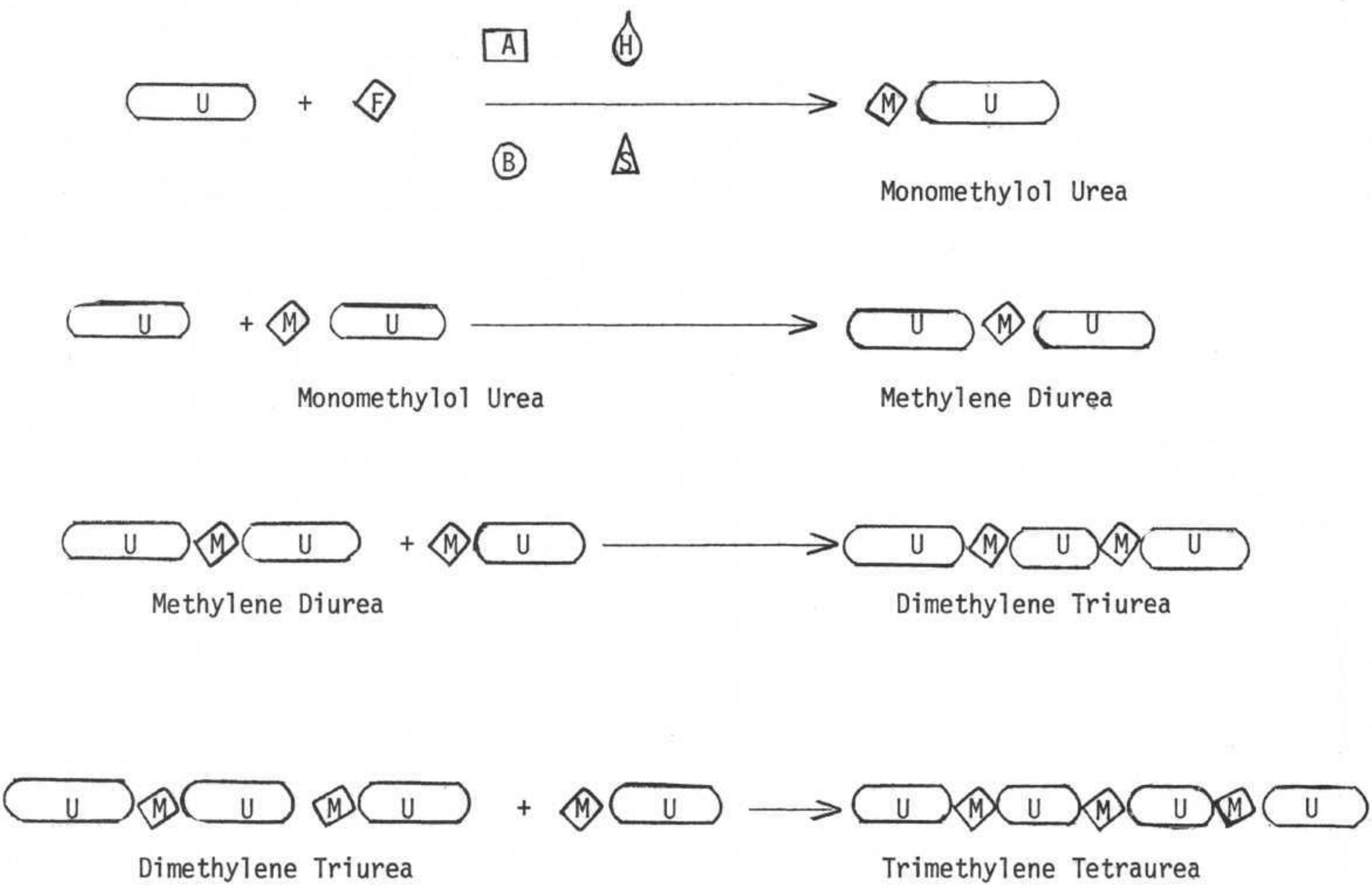
1) The properties of two groups of methylene urea, other slow release nitrogen sources and soluble nitrogen sources vary widely relative to chemical and biological properties.
2) Varying the water soluble and insoluble characteristics of methylene urea of Category 2 (see Table 4) provides substantial flexibility in manufacturing products to meet varied use conditions for turfgrass.
3) The methylene urea nitrogen sources offer advantages relative to turf tolerance, lesser growth response, increased nitrogen efficiency and reduction in pollution potential as compared to soluble nitrogen sources.

This technology has additional benefits which have been overlooked over the years. The pollution potential of nitrogen can be reduced by this technology. This has created a renewed interest in methylene urea in many areas of agriculture.

Table 1. Materials Used in the Production of Methylene Ureas.

Compound	Function	Relative Proportions
Urea	Nitrogen Source	1000
UFC (60% Urea)	Formaldehyde Source (25%)	480
Sulfuric Acid	Catalyst	10
Sodium Hydroxide	Stabilizer	1
Water	Diluent	133
Surfactant	Foaming Agent	2

Table 2. Symbolic Representation of Methylene Urea Condensation Reaction



Symbols U (Urea), F (UFC), A (Sulfuric Acid)

B (Sodium hydroxide), H (Water), S (Surfactant)

M (Methylene Group)

Table 3.

Nitrogen Characteristics of Typical Methylene Urea Products Commercially Available.

Nitrogen Characteristics	Category 1[1/]	Category 2[2/]
	Percent	
Total Nitrogen %	38	38
Nitrogen Active Index (NAI)	33	60
Cold Water Soluble Nitrogen (CWSN)	25	64
Cold Water Insoluble Nitrogen (CWIN)	75	36

1/ Ureaform (Hercules Incorporated and E. I. duPont de Nemours & Company, Inc.)

2/ Methylene ureas (O. M. Scott & Sons)

Table 4.

Approximate Distribution of Methylene Urea Fractions and Urea in Commercially Available Products.

Nitrogen Characteristics	Category 1 1/		Category 2 2/	
	Percent			
Total Nitrogen	38		38	
Nitrogen Active Index (NAI)	33		60	
Cold Water Soluble Nitrogen	25		64	
Urea		8		28
Methylene Diurea		7		27
Dimethylene Triurea		10		9
Cold Water Insoluble Nitrogen	75		36	
Trimethylene Tetraurea		21		22
Pentamethylene Hexaurea		54		14

1/ Ureaform (Hercules Incorporated and E. I. duPont de Nemours & Company Inc.)

2/ Methylene urea (O. M. Scott & Sons)

Table 5. Salt Index of Various Nitrogen Sources.

Nitrogen Source	% N	Salt Index 1/ 2/ Equal Weights	Equal N Levels
Sodium Nitrate	16	100	6.25
Ammonium Nitrate	33	105	3.18
Urea	46	75	1.63
Ammonium Sulfate	21	69	3.29
Methylene Urea	38	4	0.11

1/ Concentration of ions in the soil solution based on sodium nitrate at 100.

2/ Nitrogen is mixed with air dried soil which is brought to 75% of field capacity and stored for 5 days at 5^{o} C.

Table 6. Percent Injury of Merion Kentucky Bluegrass as Affected by Soluble and Partially Soluble Nitrogen Sources Applied to Wet or Dry Foliage 1/.

		Percent Injury 2/ 3/							
		Lbs N/1000 Sq Feet							
		1		2		4		Average	
		Foliage Condition When Applied							
Analysis	% CWIN	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
10-6-4	2	70	0	70	15	100	20	80	12
16-8-8	38	15	0	35	0	80	5	43	2
23-7-7	42	0	0	5	5	0	5	2	3

1/ Waddington, Duich and Moberg, Lawn Fertilizer Test Progress Report 296, June 1969. The Pennsylvania State University, University Park, Penn.

2/ Recorded 2 days after application (August 26, 1966).

3/ Temp. 73, 84, 90°F max. and 52, 59 and 53°F min. on 0, 1 and 2 days after treating, respectively. Relative humidity 39-49%.

Table 7.

Initial and Residual Color Response of Kentucky Bluegrass as Affected by Various Nitrogen Sources Applied in Late Fall (11/22/77).

				Initial Response			Residual Response
				Color (10>1)			
		%	#	Date of Observation			
N Source	Category	CWIN	N/M	12/1	4/7	4/19	5/10
Methylene Urea	2	38	0.9	6.0	5.0*	5.0*	5.7*
Ureaform	1	75	0.9	6.0	3.7	4.0	6.0*
IBDU (coarse)	-	78	0.0	6.0	3.5	4.0	4.3*
Control	-	-	0	6.0	2.5	2.7	2.0
LSD .05				NS	1.6	1.3	1.5

* Significant improvement in color as compared to the check (no fertilizer).

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Table 8.

Initial and Residual Response of Kentucky Bluegrass as Affected by Various Nitrogen Sources Applied in Mid Spring (5-18-77).

			Initial Response		Residual Response
			Color 10>1		
			Date of Observation		
N Source	% CWIN	#N/M	5/31	6/14	7/29
Methylene Urea	38	2.0	10.0	9.3	8.3
IBDU (coarse)	78	2.0	4.3	6.3	7.0
Control	-	0	2.3	3.7	4.3

Table 9. Fresh Weight of Kentucky Bluegrass Clippings Removed from a 10,000 Sq. Ft. Area as Affected by Methylene Urea or Urea.

		Weeks after Application					
		1	2	4	6	Total	%
Product	Lbs. N/M	Lbs. of Clipping/10,000 Sq. Ft.					
Methylene Urea	0.9	1908	1372	2120	64	5464	68 1/
Urea	0.9	2872	2241	2840	84	8037	100

1/ Approximately 1/3 less clippings when turf is treated with methylene urea as compared to urea.

Table 10.

Fall Greening Response of Kentucky Bluegrass as Affected by Two Methylene Urea Sources (Category 2) Applied in Early October (10/2/78).

			Color (10 > 1)				
			Date of Observation				
N Source	% CWIN	# N/M	10/17	10/27	11/14	11/20	Average
Methylene Urea	36%	0.9	8.0	9.0	7.8	6.7	7.9
Methylene Urea	50%	0.9	7.3	8.0	6.3	5.3	6.7
Control	-	0	3.0	4.7	3.0	2.0	3.2

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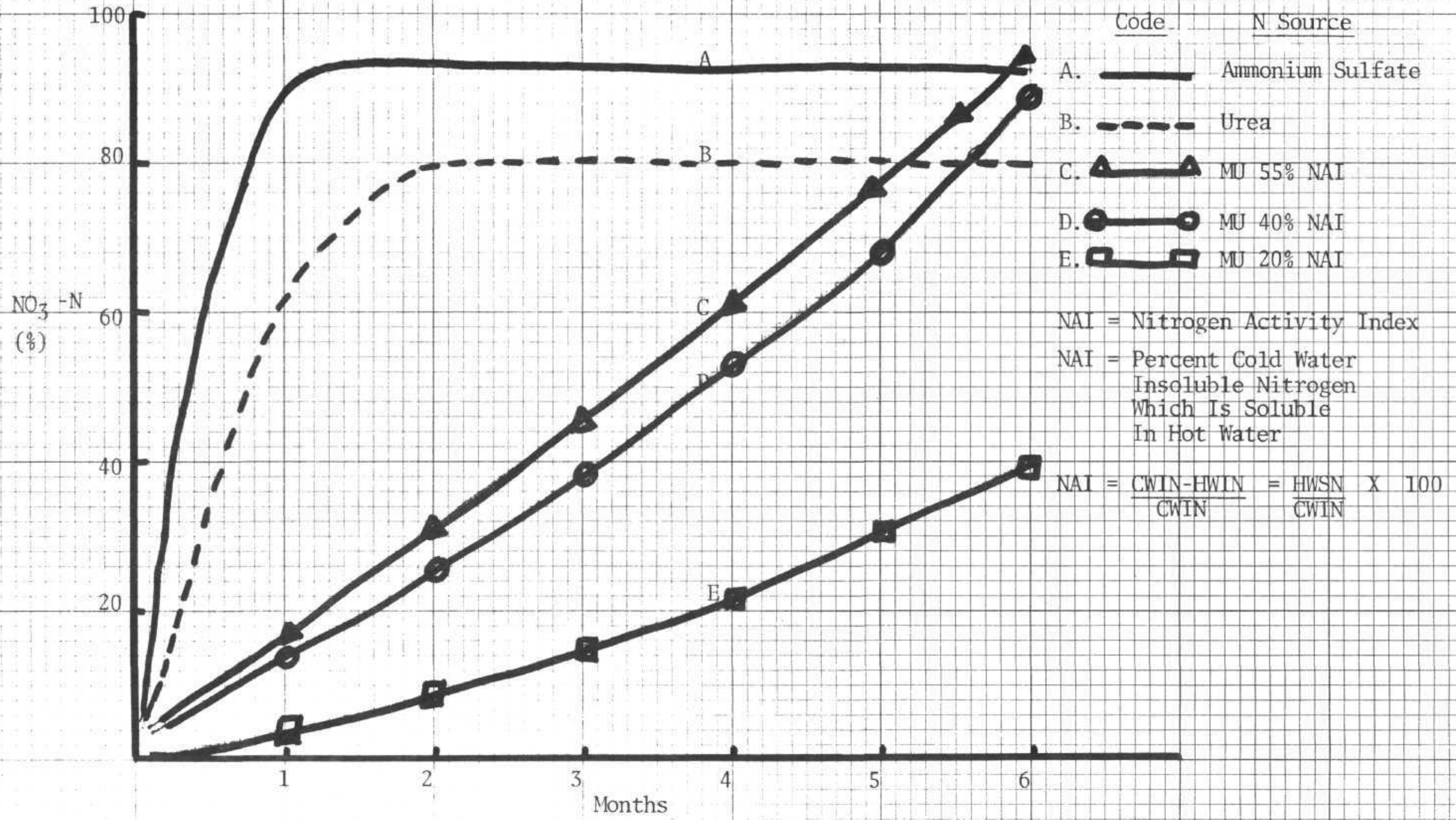
Figure 1. Nitrification Rate of Ammonium Sulfate, Urea and Methylene Urea (MU) As Affected by Time[1/]



1/ R.B. Church (1968) New Fertilizer Materials

Figure 2. Ammoniacal-N Analysis of the Soil Solution as Affected by Urea and Methylene Urea Applied at 2 lbs N/Cubic Yard

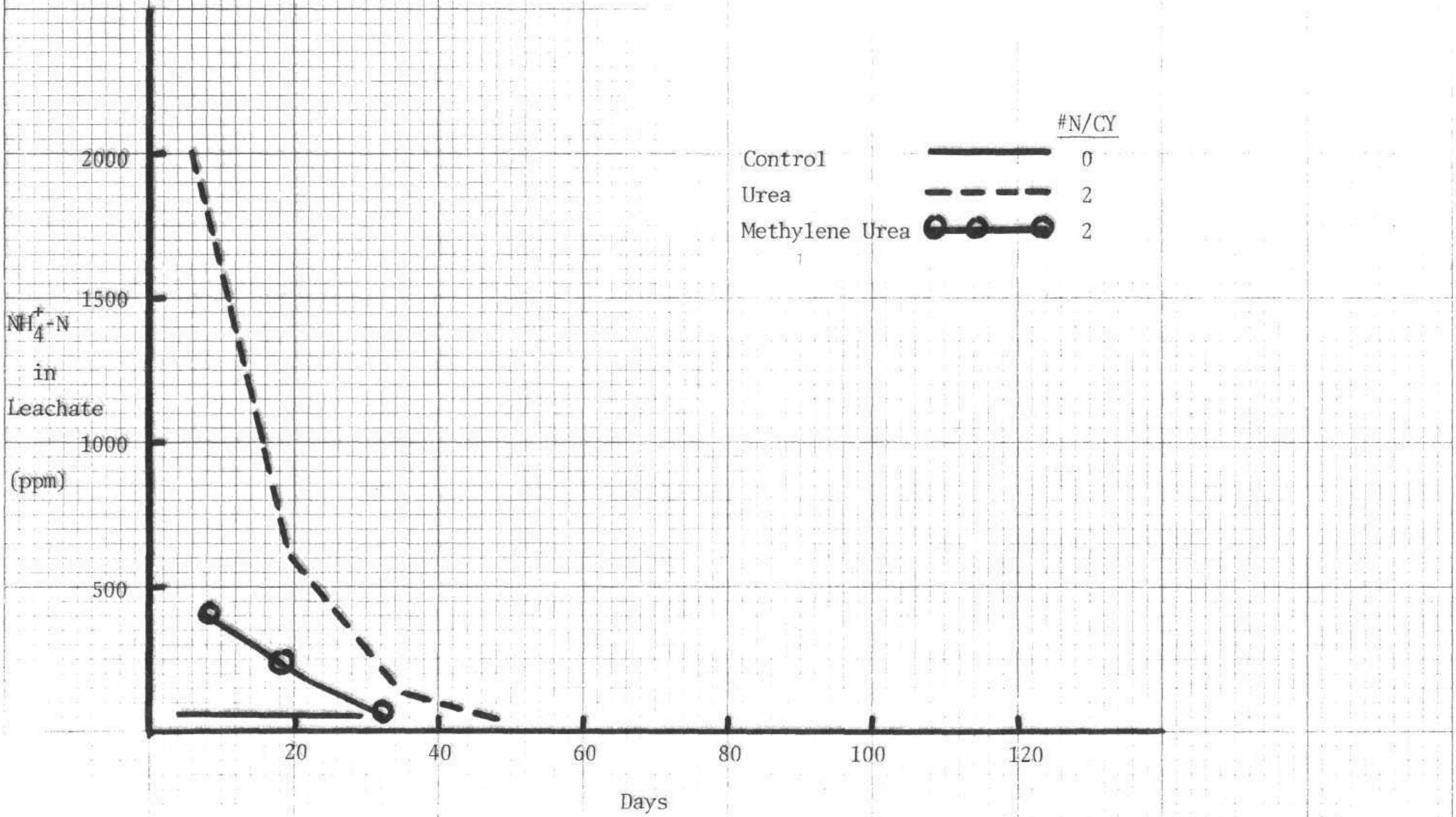


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Figure 3. Nitrate-N Analysis of the Soil Solution as Affected by Urea and Methylene Urea Applied at 2 lbs. N/Cubic Yard

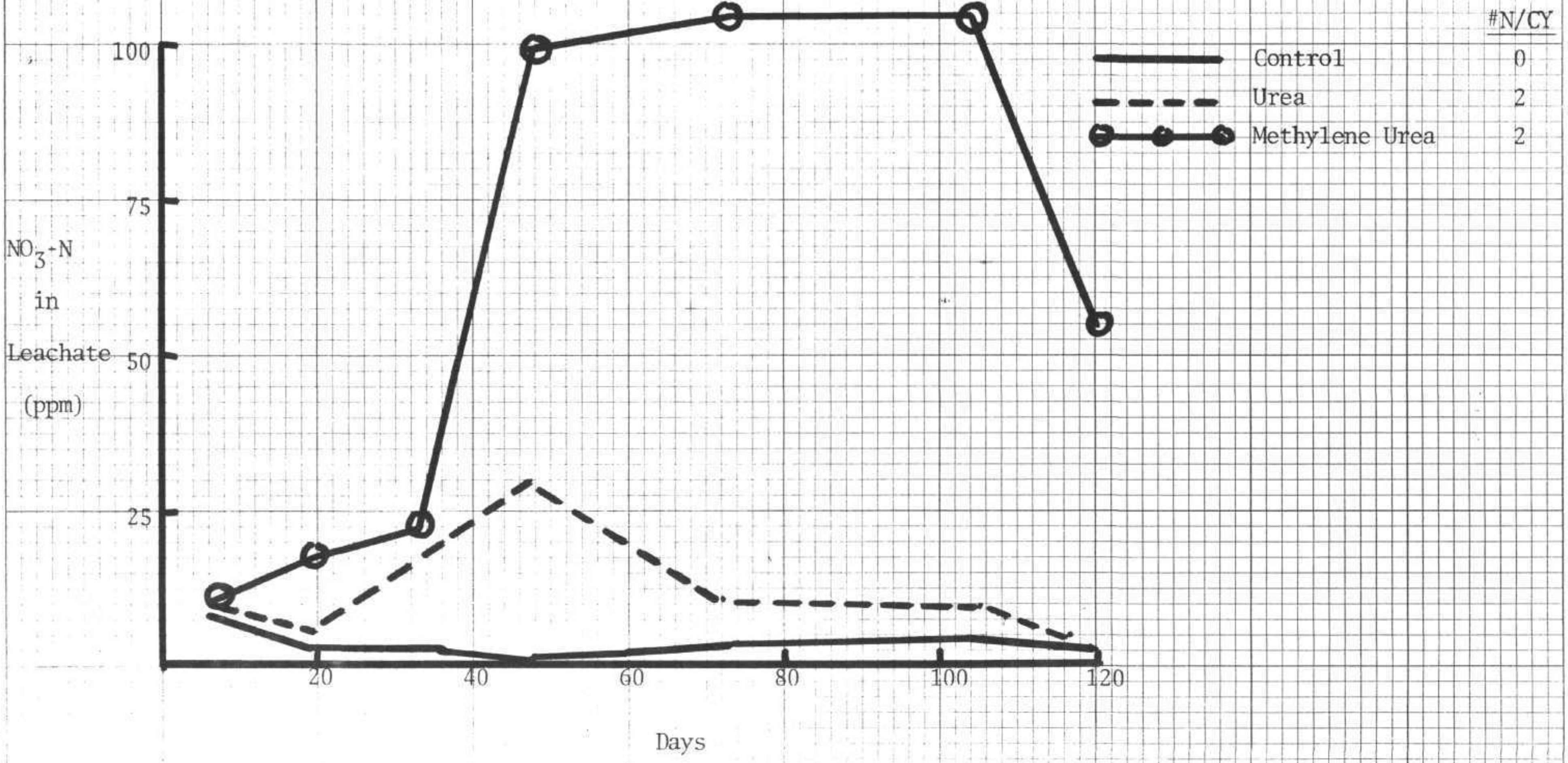

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Figure 4. Fresh Weight of Kentucky Bluegrass as Affected by Urea and Methylene Urea Applied at 1.8 Lbs. N/1000 Sq. Ft.

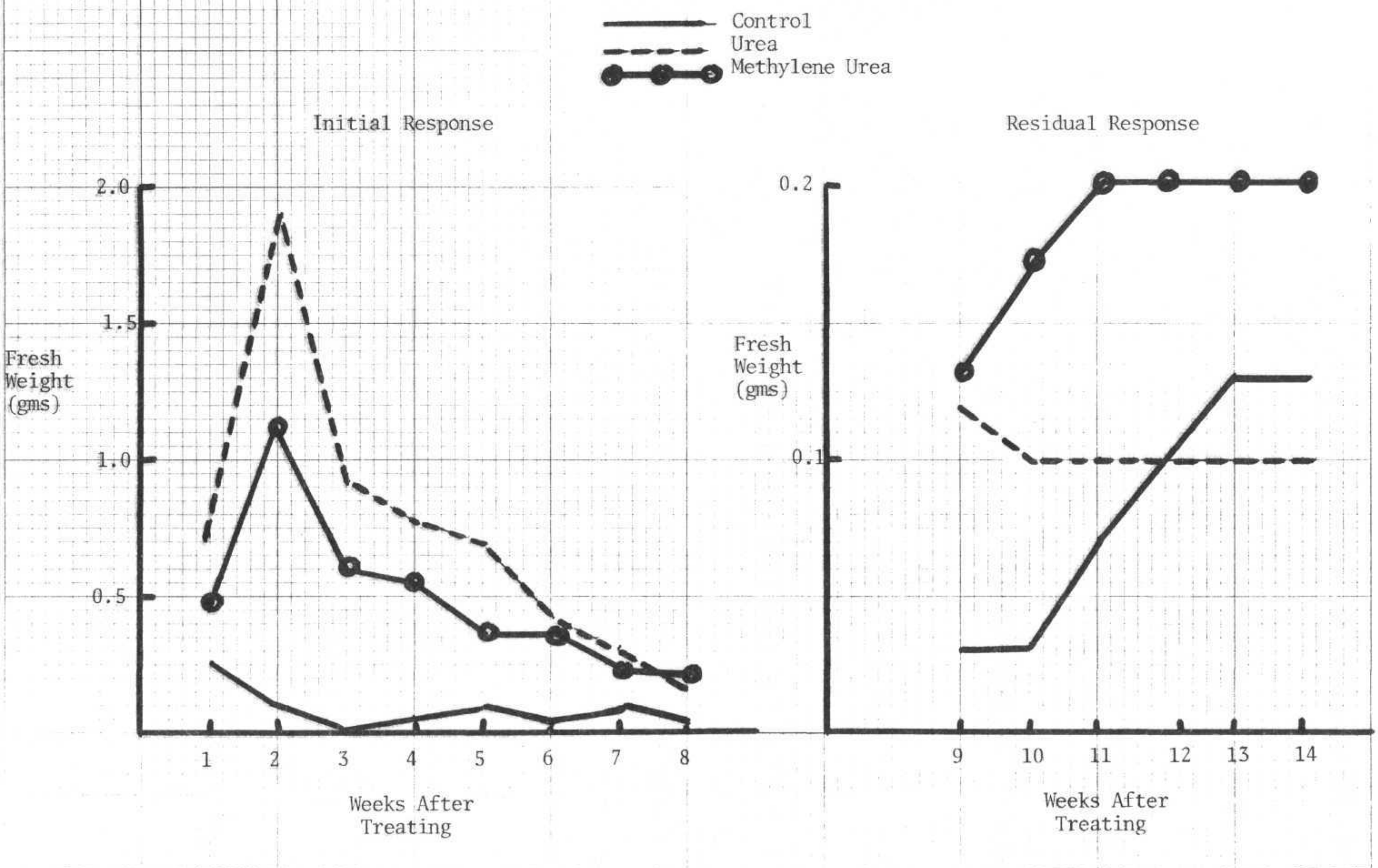

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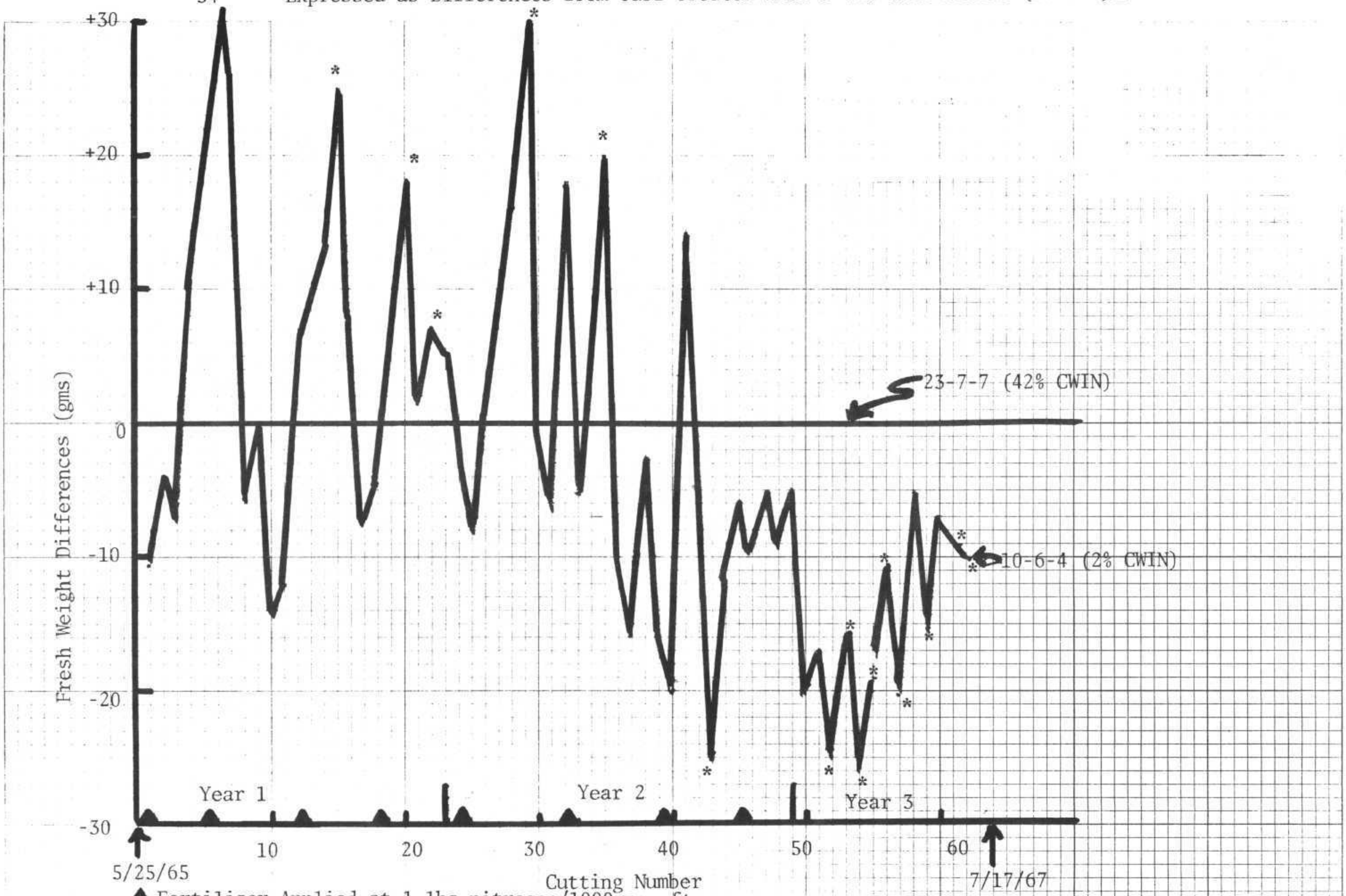
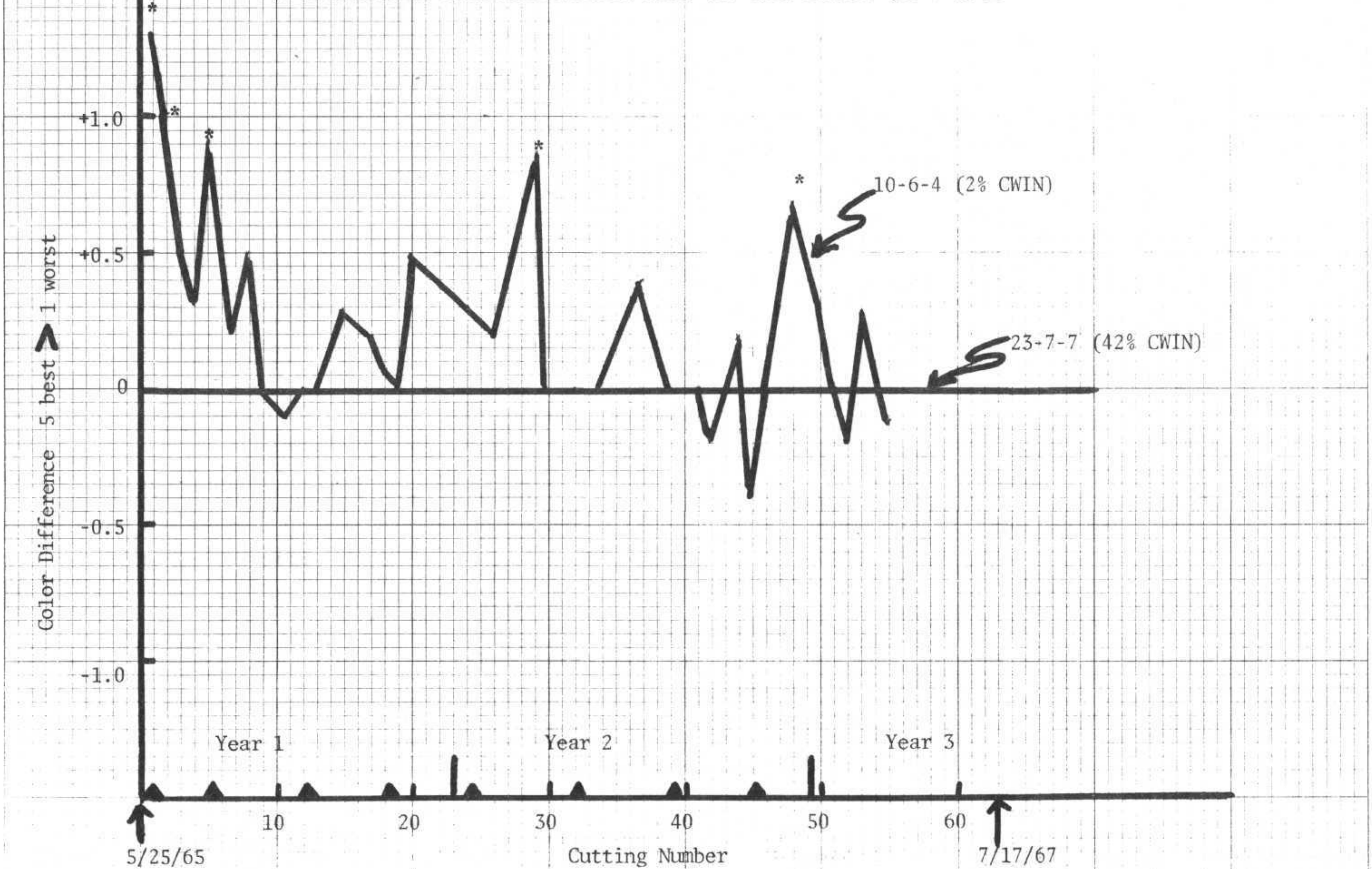
Figure 5. Clipping Fresh Weight of Poa pratensis Treated with a 2% CWIN Source (10-6-4) Expressed as Differences from Turf Treated with a 42% CWIN Source (23-7-7) 1/



▲ Fertilizer Applied at 1 lbs nitrogen/1000 sq. ft.
* Significantly different from 23-7-7 at the 5% level.
1/Waddington, Duich & Moberg, Lawn Fertilizer Test Progress Report 296 June 1969
The Pennsylvania State University, University Park, Penn.

Figure 6. Color of Poa pratensis Treated with a 2% CWIN Source (10-6-4) Expressed as Differences from Turf Treated with 42% CWIN Source (23-7-7) 1/



▲ Fertilizer applied at 1 lb N/1000 sq. ft.
* Significantly different from 23-7-7 at the 5% level
1/ Waddington, Duich & Moberg, Lawn Fertilizer Test, Progress Report 296, June 1969. The Pennsylvania State University, University Park, Penn.