

AN ABSTRACT OF THE THESIS OF

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Title: UREA RELEASE FROM SULFUR-COATED UREA AND
NITROGEN UTILIZATION BY TALL FESCUE

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Sulfur-coated urea (SCU), a slow release nitrogen fertilizer, may be economically competitive with conventional fertilizers, but little is known of the mechanism of urea release from SCU and the environmental factors which affect the urea release rate. Objectives of this thesis were: (1) to determine factors which affect the rate of nitrogen release from SCU; (2) to compare nitrogen utilization by tall fescue (Festuca arundinacea Schreb.), fertilized with urea or SCU.

The rate of urea release from SCU surface-applied to soil was determined during incubation for periods of up to five months under a range of temperatures (5 to 35 C) and soil water potentials (-5 to -30 bars). Three SCU fertilizers with different seven-day urea release percentages and sealants were studied: SCU 4 (wax sealant); SCU 25 (polyethylene-oil sealant, 30:70 w/w); and SCU 23 (no sealant).

In a four-year field experiment (1972-1976), the dry matter and nitrogen yields of irrigated tall fescue fall-fertilized with 200, 400, 600, or 800 kg N/ha/yr as urea, SCU 30, or SCU 4, were measured. Also, urea was applied in five equal increments in the fall and at the first four cuttings each year at annual rates of 980 kg N/ha (1972-1973), 700 kg N/ha (1973-1974), and 800 kg N/ha (1974-1975). Cumulative nitrate leaching losses from tall fescue plots were estimated by analysis of soil solution samples.

Urea release from sealed SCU was slowed by soil sterilization. The rate of urea release from SCU without sealant was unaffected by soil sterilization. After a lag period of 25 days, wax-sealed SCU applied to non-sterile soil at 25 C and -5 bars water potential released urea at a rate of 1.0%/day. In sterile soil, after an initial release of about 10%, no further release occurred. At -15 and -30 bars water potential in non-sterile soil, release took place at 0.5%/day, with a lag period of up to 60 days. SCU sealed with polyethylene-oil released urea at a slightly faster rate at -30 bars than at -5 and -15 bars. Urea release from wax-sealed SCU was more sensitive to temperature than was urea release from the other SCU materials. Following an initial release of 10%, urea release rates from wax-sealed SCU at 35, 25, 15, and 5 C were 1.5, 0.71, 0, and 0%/day, respectively.

The urea release pattern from multi-granule samples of SCU 4, 23, and 25 was shown to correspond to the coating thickness

distribution. The coating thickness distribution can be rapidly determined and is a better indicator of the long-term urea release pattern than the conventional seven-day release test.

In the field experiment, over a four-year period, tall fescue fall-fertilized with SCU produced about 20% more dry matter than fescue fall-fertilized with urea, e. g. , 61 mtons/ha versus 50 mtons/ha at the 800-kg N/ha/yr rate. Fall application of SCU and split application of urea resulted in the same dry matter yield. Residual nitrogen resulted in higher yields by SCU-fertilized tall fescue during the second, third, and fourth years. Four-year nitrogen recoveries by tall fescue receiving fall applications of 800 kg N/ha/yr as urea, SCU 30, or SCU 4 were 43, 58, and 61% respectively.

Over a two-year period nitrate-nitrogen leaching losses from plots fertilized with urea (400 kg N/ha/yr), SCU 4 (400 or 800 kg N/ha/yr) or urea in a split application (average of 800 kg N/ha/yr) were estimated at 65, 20, 19, and 126 kg N/ha, respectively. Nitrate-nitrogen leaching losses were < 10% of the total nitrogen applied.

Urea Release from Sulfur-Coated Urea and Nitrogen
Utilization by Tall Fescue

by

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UREA RELEASE FROM SULFUR-COATED UREA AND NITROGEN UTILIZATION BY TALL FESCUE

INTRODUCTION

Crops frequently recover less than 50% of applied fertilizer nitrogen (Allison, 1965). Denitrification, volatilization of ammonia, and leaching of nitrate from the root zone are in part responsible for this low recovery (Tisdale and Nelson, 1966).

Synthetic nitrogen fertilizers which are not immediately soluble may offer protection against such losses by providing nitrogen at a rate more nearly matching the crop requirement. The development of slow release fertilizers has been reviewed by several writers (Powell, 1968; Hauck and Koshino, 1971; Lunt, 1971; Prasad, Rajale, and Lakhdive, 1971; Hauck, 1972). A number of coated and uncoated nitrogen fertilizers with a slow release character are commercially available, for example, resin-coated urea, ureaform (urea-formaldehyde condensate), and crotonylidene diurea (Hauck and Koshino, 1971). The expense of these products limits their use to high-value markets, such as the nursery and home garden industries. Such products are used for their convenience and low risk of ammonium or salt damage to plants and not because of improved fertilizer nitrogen recovery. Therefore, the exact rate at which nitrogen becomes available to plants from these fertilizers is not critical.

One of the most promising slow release fertilizers is sulfur-coated urea (SCU), first developed by the Tennessee Valley Authority (TVA) in 1961. SCU is produced by spraying molten elemental sulfur onto preheated urea granules. A wax or wax-like petroleum derivative may be applied to seal imperfections in the sulfur coating (Blouin and Rindt, 1967). The resulting product may contain from 10 to 25% sulfur, 30 to 40% nitrogen, and 2 to 3% sealant. Recent improvements in the manufacturing process may have eliminated the need for the sealant material (Shirley and Meline, 1975).

SCU is the first slow release nitrogen fertilizer which promises to have a production cost allowing it to compete with conventional fertilizers in lower-value markets, particularly in those situations where crop recoveries of fertilizer nitrogen are unusually low. Production costs for SCU have been estimated by TVA at 27 to 34% higher per unit nitrogen than for uncoated urea (Young, 1974). During the past ten years, SCU research has centered on the resolution of production problems and on the testing of SCU in field and greenhouse trials on a wide range of annual and perennial crops (Shirley and Meline, 1975; Davies, 1976).

The rate of urea release from SCU in the soil has not been carefully characterized, and the mechanism of urea release has not been determined. Research in this area is needed if SCU is to be tailored, either through modification of the manufacturing process, or by the

bulk blending of fertilizers with different release rates, to provide nitrogen to crops at the rate required for the desired yield.

By convention, SCU fertilizer materials are characterized by the percent of the urea released into solution when the SCU is incubated in water for seven days at 100 F (37.7 C) (Blouin, Rindt, and Moore, 1971). This test measures only the amount of urea immediately released, mainly from granules with broken or defective coatings. It does not necessarily measure the long-term urea release rate of SCU. Furthermore, there is no reason to believe that SCU fertilizers with the same seven-day release percentage will necessarily release urea at the same rate over a longer period of time or respond in the same manner to environmental variables such as soil water content and temperature. Because long-term SCU behavior in the soil has not been characterized, it is difficult to interpret the results of many SCU field and greenhouse experiments reported in the literature.

Furthermore, it has not been conclusively shown that there is any particular advantage in supplying nitrogen to a crop at a steady rate matching plant nitrogen uptake. In fact, a crop can act as its own slow release fertilizer by taking up nitrogen from the soil solution in excess of its immediate metabolic requirements, thereby protecting that nitrogen against denitrification and leaching (Viets, 1965).

Such a phenomenon in forage crops which are harvested more than once a year can result in so-called "luxury consumption". Under some conditions, nitrate accumulates in the plant to levels which can be toxic to animals (Viets, 1965). Also, the removal of nitrogen in one harvest may result in a nitrogen deficiency during the regrowth period. Therefore, forage crops may be one case in which fertilization with a slow release source of nitrogen is superior to the conventional practice.

The general objective of this thesis was to determine the rate of urea release of several SCU fertilizers as a function of soil water content and temperature and to correlate those rates with nitrogen utilization from SCU by a cool-season forage grass (tall fescue).

OBJECTIVES

The specific objectives of this thesis were as follows:

- (1) To determine the mechanisms of urea release from SCU by measurement of urea release from SCU materials as a function of temperature, soil water potential, and soil sterility;
- (2) To develop a rapid method to determine the long-term urea release pattern of a particular SCU fertilizer;
- (3) To compare nitrogen recovery and dry matter yield by tall fescue fertilized with urea and SCU and to compile a nitrogen balance sheet, including nitrate leaching losses;
- (4) To simulate SCU urea release in the field on the basis of experimentally-derived rate constants and to compare the release patterns with the pattern of nitrogen uptake by tall fescue.

RELEASE OF UREA FROM SULFUR-COATED UREA

Introduction

Development of sulfur-coated urea has been hampered by a lack of information in two areas: (1) the influence of environmental factors, particularly soil temperature and water content, on urea release, and (2) the physical properties of SCU which control its urea release pattern. More information is especially needed in the second area to enable the development of practical quality control techniques.

Experiments have shown that release of urea from SCU with wax sealant is very sensitive to temperature. For example, urea release from wax-sealed SCU mixed with soil was delayed at 10 C for 8 to 12 weeks after release had begun at 20 and 30 C (Allen, Hunt, and Terman, 1971). The effect of temperature on SCU urea release has not been satisfactorily explained in terms of a urea release mechanism. Oertli (1973a, 1973b) monitored urea release from wax-sealed SCU incubated in aqueous solutions and observed an effect of temperature similar to that reported by Allen, Hunt, and Terman (1971). He studied the role of microorganisms in the urea release process by comparing the urea release rates in solutions inoculated with Thiobacillus thiooxidans, uninoculated ("normal") solutions, and thymol-sterilized solutions. At 34 C, Thiobacillus inoculation

resulted in an increased rate of release over that observed in the "normal" solutions. However, at 24 C no difference in the release rate of the SCU in the inoculated and "normal" solutions was observed. At both 34 and 24 C, SCU in the inoculated and "normal" solutions released urea faster than SCU in the sterile solution. Oertli (1973a) speculated that microbial degradation of the wax sealant, and not the sulfur coating, was responsible for the observed effect of temperature; but he was unable to increase the urea release rate by inoculation of solutions with a mixed microbial culture obtained from glass slides coated with wax and incubated in soil. This may have been because the population of wax-oxidizing microorganisms in the "normal" solution was already high and therefore not limiting the urea release rate.

Further study is required to clarify the role of microorganisms in release of urea from SCU both with and without wax sealant. The above-cited studies indicate that urea release from SCU is very temperature dependent but do not indicate whether this temperature dependency is due to the presence of the wax sealant.

Soil water potential may influence the rate of urea release from SCU by its effect on degradation of the coating components, absorption of water by urea, and/or diffusion of dissolved urea from the granule. No research has been published which clearly describes either the effect of soil water potential on SCU urea release or the

mechanism of that effect. Furthermore, SCU surface-applied in the field would normally be subjected to fluctuating soil water content and periodic drying, yet there are no reports in the literature of the effects of such conditions on SCU urea release.

Prasad (1976), in what apparently is the only report on the effect of soil water potential on SCU urea release, observed that over a nine-week period, release of nitrogen from two wax-sealed SCU materials mixed with soil increased with increasing water potential in the range from -3.1 bars to -0.01 bars. However, only small differences in release rate as a function of soil water potential were observed when one of the SCU materials was surface-applied. Interpretation of the results of these experiments was difficult due to the small SCU sample size and the failure of the author to include statistical information in the report.

While Prasad's report suggests that SCU urea release will be affected by soil water potential in the range suitable for plant growth, Lunt and Oertli (1962) found that release of nitrogen from fertilizer granules encapsulated with a plastic resin membrane was not affected by soil water potential until it dropped considerably below -15 bars. They speculated that membrane properties controlled the solute transfer at a constant rate over a wide range of soil water contents.

The microbial degradation of sealant and/or sulfur coating components may be essential to SCU urea release (Oertli, 1973b). In

general, soil microbial activity is reduced at water potentials below a few bars (Griffin, 1972). In particular, sulfur-oxidizing bacteria (Thiobacillus spp.) are very sensitive to soil water potential (Burns, 1967). Prasad's observation (1976) that SCU nitrogen release is slowed when soil water potential is reduced from -0.01 bars to -3.1 bars may be due to the effect of water potential on microbial degradation of the coating. It seems likely that sealant-degrading microorganisms are less sensitive to soil water potential than Thiobacillus spp. Because of this consideration and the above-mentioned difficulties in interpreting Prasad's result, further research is required to elucidate the effect of soil water potential on SCU nitrogen release.

The urea release pattern of SCU is a composite of the urea release pattern of individual granules (Hashimoto and Hatfield, 1976). The granules from a particular lot may vary in size, weight, and percent coating. In particular, coating thickness has been speculated to be an important parameter in controlling release (Oertli, 1973a); yet no information on the coating thickness of SCU granules has been published.

The objectives of this research were to determine the range of physical properties of SCU granules and the influence of temperature, soil water content and soil sterilization on urea release patterns.

Materials and Methods

Physical and Chemical Properties of SCU

The following SCU materials were studied in laboratory experiments: SCU 4 (microcrystalline wax sealant, coal tar microbicide in coating); SCU 23 (no sealant, no coal tar); and SCU 25 (sealant consisting of 30% low-molecular weight polyethylene and 70% brightstock oil, no coal tar) (Table 1). Numbers refer to the nominal seven-day release percentage appearing on the fertilizer bag label.

A standard procedure was used to obtain representative subsamples of SCU from bulk containers for all laboratory experiments. A large beaker, 800 to 2000-ml capacity, was filled with SCU from fertilizer bags. The beaker was covered and either rolled or tipped end-over-end. Ten to fifty granules at a time were removed from the beaker with a spatula or spoon, taking care not to allow granules to roll off. It was found that when these precautions were not taken, the SCU became segregated according to granule size. Clumps of three or more granules held together by the coating were discarded, but defectively coated granules were not removed.

The nitrogen contents of the SCU 4, 23, and 25 were determined by placing ten weighed samples, each consisting of 58 granules, in centrifuge tubes containing about 20 ml distilled water and five ppm phenylmercuric acetate (PMA) to inhibit urea hydrolysis. Granules

Table 1. Properties of selected sulfur-coated urea fertilizers.

Fertilizer	TVA lot number	N	S	Sealant	Diatomaceous earth conditioner	Coal-tar microbicide	Seven-day release ¹
					%		
SCU 4	2-11-72B	35.2	18.5	3 ²	2	0.25	4
SCU 23	11-20-73C	33.1	24.0	0	0	0	23
SCU 25	5-8-74A	34.5	23.0	2 ³	2	0	25
SCU 30	7-20-72A	38.2	12.0	3 ²	2	0.25	30
SCU 4 ⁴	4-5-72B	38.2	12.0	3 ²	2	0.25	4
SCU 30 ⁴	7-24-74C	35.9	17.0	2 ²	2	0	30

¹Urea-N released into water after seven days at 38 C.

²Microcrystalline wax.

³70:30 (w/w) mixture of brightstock oil and polyethylene.

⁴SCU used for 1975 fertilizer application in tall fescue field experiment.

⁵Source: Tennessee Valley Authority.

were crushed and the urea was allowed to dissolve for several hours. Coating fragments were separated from the urea in solution by centrifugation and filtration of the supernatant through Whatman No. 1 filter paper. Urea was rinsed from the coating fragments by refilling the tube with distilled water, centrifuging, and filtering two more times. The filtrate was diluted to a 100-ml volume and an aliquot analyzed for urea content by a colorimetric method which uses p-dimethylaminobenzaldehyde (Watt and Chrisp, 1954).

The sample size of 58 granules was selected because of the desire to know the variability in nitrogen content of 58-granule samples used in SCU urea release experiments.

Average granule weights for SCU 4, 23, and 25 were determined both for the 58-granule samples and for five-gram samples containing about 250 to 350 granules. Individual granule weights were determined for 60-granule samples of the three SCU materials.

The urea release from SCU 4, 23, and 25 in sterile solution was measured as follows: Duplicate 50-g samples of fertilizer were placed in erlenmeyer flasks which contained 250 ml of distilled water and five ppm PMA. The flasks were stoppered and incubated at 37.7 C (\pm 1). Two-ml aliquots were withdrawn after 2, 7, 15, and 25 days. Solutions were not shaken but were swirled gently just prior to sampling. The urea content of the two-ml aliquots was determined (Watt and Chrisp, 1954) and the urea in solution was expressed as a

percent of the urea in the original 50-g sample.

Calculation of Average SCU Coating Thickness. If one assumes that granules are spherical and that the density of urea and coating components are known, the average thickness of the sulfur and sealant components can be calculated.

The density of sulfur in the coating was assumed to be the average of the density of crystalline (rhombohedral) S and amorphous S, a value of 2.0 g/cm^3 (Weast, 1972). It has been shown that SCU coatings contain both sulfur allotropes (McClellan and Scheib, 1973).

The density of urea was assumed to equal that of pure crystalline urea, 1.323 g/cm^3 (Weast, 1972). The densities of the wax (0.92 g/cm^3) and polyethylene-oil (0.78 g/cm^3) sealant materials were determined by weighing 20-g blocks of the materials and the water displaced when the blocks were immersed.

The radius (R) of a sphere is related to its volume (V) by the equation

$$R = (3V/4\pi)^{1/3} \quad (1)$$

Volume is equal to mass (M) divided by density (D), and the total SCU granule volume is equal to the sum of its component volumes, that is,

$$V = (M_u/D_u) + (M_s/D_s) + (M_{se}/D_{se}) \quad (2)$$

where subscripts u = urea, s = sulfur, and se = sealant.

The total granule radius is equal to the radius of the urea portion (R_u) plus the coating thicknesses, that is,

$$R = R_u + T_s + T_{se} \quad (3)$$

where T_s and T_{se} are the thicknesses of the sulfur and sealant components, respectively. Substituting Equations (2) and (3) into (1)

$$R_u + T_s + T_{se} = \left[(3/4\pi) \left(\frac{M_u}{D_u} + \frac{M_s}{D_s} + \frac{M_{se}}{D_{se}} \right) \right]^{1/3} \quad (4)$$

where

$$R_u = \left[(3/4\pi)(M_u/D_u) \right]^{1/3} \quad (5)$$

The thicknesses of sulfur and sealant were assumed to be proportional to their volume, and therefore when the value of $(T_s + T_{se})$ had been calculated, the thickness of each component could be calculated:

$$T_s = \frac{(M_s/D_s)(T_s + T_{se})}{(M_s/D_s) + (M_{se}/D_{se})} \quad (6)$$

$$T_{se} = \frac{(M_{se}/D_{se})(T_s + T_{se})}{(M_s/D_s) + (M_{se}/D_{se})} \quad (7)$$

Coating Thickness of Single Granules. Urea was extracted from 60 granules each of SCU 4, 23, and 25 by the following procedure:

Granules were individually weighed to the nearest 0.0001 g and each granule was placed in a 3-ml glass vial which had been weighed to the nearest 0.0001 g. Granules were fractured with a dissecting needle and soaked for 30 minutes in two ml distilled water. The solution was decanted with a pipette and discarded. Care was taken not to remove fragments of insoluble material. Distilled water was added and removed in the same manner two more times to remove the remaining solutes. All vials were dried in an oven at 35 C for 48 hours, cooled to room temperature, and weighed to the nearest 0.0001 g.

For the purpose of calculating the mean coating thickness of each granule, it was assumed that no coating material had been removed in the urea extraction process. Actually, small amounts of the diatomaceous earth conditioner may have been removed.

Because the coating includes sealant material with a density less than that of sulfur (2.0 g/cm^3), the average density of the complete coating is slightly less than 2.0 g/cm^3 . The amount of sealant by weight on each granule probably varies around the average values of 3% and 2% for wax and polyethylene-oil, respectively. Since the sealant and sulfur weights for each granule were not determined, it was felt that the use of 2.0 g/cm^3 would not result in an appreciably larger error in the calculated coating thickness than if the density value were adjusted for an average sealant content.

To calculate the total coating thickness, a modification of Equation (4) was used as follows:

$$T_c = \left[\left(\frac{3}{4\pi} \right) \left(\frac{M_u}{D_u} + \frac{M_c}{D_c} \right) \right]^{1/3} - R_u \quad (8)$$

where T_c = mean coating thickness, M_c = mass of the coating, and D_c = density of the coating (2.0 g/cm³).

Temperature and SCU Urea Release

Woodburn silt loam soil was collected, air-dried to about 13% water, and sieved through a one-mm screen. Reagent grade CaCO₃ equal to 0.4% of the soil by weight was added and mixed thoroughly in a mechanical tumbler. This is equivalent to 11 metric tons/ha mixed to a depth of 20 cm.

The soil was stored in plastic bags for two weeks, at which time the saturated paste pH of the limed soil was 7.0 compared to 5.4 for the unamended soil.

Soil equilibration units were constructed by glueing 4-cm sections of polyvinylchloride pipe (inside diameter 25 cm) to 28- x 28-cm plywood bottoms sealed with black polyethylene plastic.

Four hundred and fourth grams (oven-dry basis) of Woodburn silt loam soil were placed in each sample container and spread evenly to a depth of approximately one cm. One hundred ml of distilled water

was pipetted evenly onto the surface of each soil sample. This amount of water was sufficient to moisten the soil to -0.1 bars water potential and to allow for initial evaporative losses. Five grams of SCU 4, 23, or 25 (equivalent on a surface-area basis to about 350 kg N/ha) was distributed evenly over the soil surface. All samples were sealed in plastic bags and incubated at $35\text{ C} (\pm 1)$ for 35 days. After evaporative losses during sample preparation and the first two days of incubation at 35 C , the soil water potential was about -0.1 bars. During the 35 days, water evaporated at a steady rate of 2 ml/day/sample. After 35 days, all samples were watered to bring them to their initial water content. Samples were then transferred to growth chambers at 5, 15, or 25 C, or left at 35 C.

The percent of the total urea released after 35, 45, 55, and 65 days from the beginning of the experiment was determined by collecting granules with forceps from the surface of duplicate soil samples at each temperature and for each SCU fertilizer. Granules which were partially or completely empty were considered to be released. The fraction of urea released was calculated as equal to released granules divided by the total number of granules. In addition, intact granules were collected for determination of urea content.

In a second experiment, samples were prepared in a similar manner except that soil was initially air-dried to about 3% water and

was not limed.¹ SCU 4 was applied at a rate of 1.44 g to each soil unit. This was equivalent to 100 kg N/ha on a surface-area basis. Units were incubated at constant temperatures of either 5 or 15 C, and urea release was determined on triplicate units by counting intact granules after 5, 42, 60, 90, and 119 days at 5 C, and after 24, 41, 60, 80, and 100 days at 15 C.

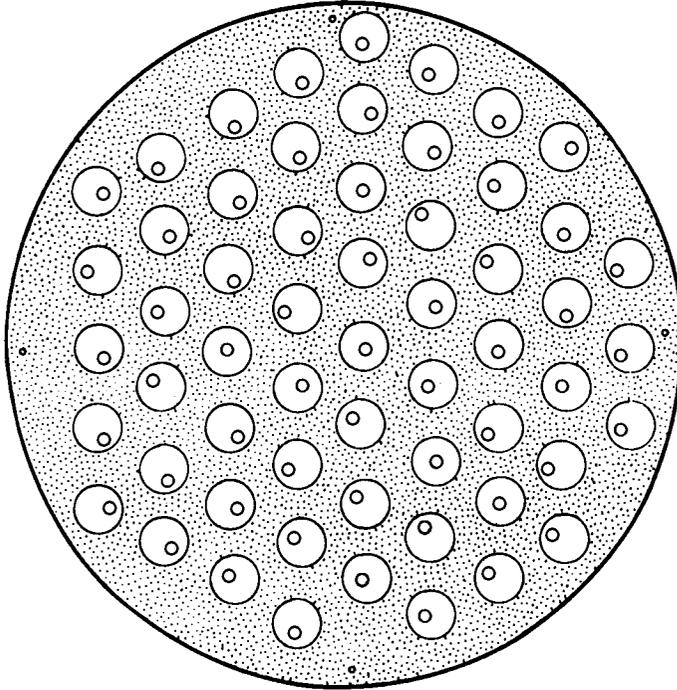
Soil Water Potential and SCU Urea Release

Soil sample holders were constructed from 150- x 10-mm polystyrene petri plates. Melted paraffin was poured into the plate bottoms and allowed to solidify. A hexagonal pattern of 58 holes (1.1 cm diameter x 0.9 cm deep) was melted in the paraffin by pressing the plate onto a hot steel template (Figure 1). These units allowed separation of individual SCU granules so that release of urea from one granule would not influence the environment of adjacent granules by changing the soil water osmotic potential.

Woodburn silt loam soil was air-dried to about 7% water content, crushed, and sieved through a one-mm screen. Sufficient water was added to the soil to bring it to water potentials of -5, -15, or -30 bars. The water contents at potentials of -5 and -15 bars were about 17% and 11%, respectively (Boersma and Simonson, 1970). The water

¹This experiment was conducted jointly with W. M. Jarrell.

TOP VIEW, LID REMOVED



SIDE VIEW, CROSS-SECTION

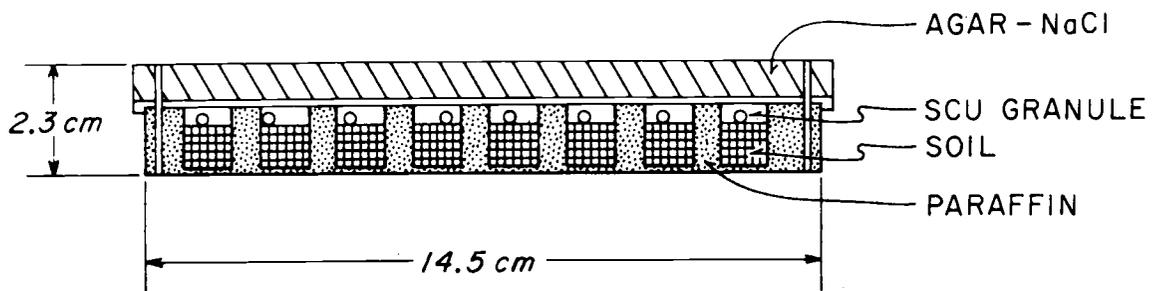


Figure 1. SCU-soil sample containers used to maintain soil water potential.

content at -30 bars was determined by equilibrating small soil samples over a 0.655 m NaCl solution (Lang, 1967) in a vacuum desiccator for two weeks; the water content at that time was 6% by weight.

For the -5 and -15 bar treatments, water was added to the soil by spraying with frequent mixing so that no moist lumps of soil were formed. The moistened soil was allowed to equilibrate for several weeks in sealed plastic bags and was then resieved through a one-mm screen. Soil was poured into the holes formed in the paraffin and distributed evenly by tapping on the edge of the tilted plate so that each hole was approximately two-thirds full. The soil in each hole was tamped with the weight of a glass rod slightly smaller in diameter than the hole.

Soil water potential was controlled by the use of an agar dish vapor equilibrium method (Harris, et al., 1970). This method involves the control of vapor pressure, and hence water potential, by the use of aqueous NaCl solutions of known osmotic potential solidified with agar.

Sodium chloride solutions were made to osmotic potentials of -5, -15, and -30 bars (Lang, 1967), and agar (20 g/l) was melted in these solutions. The solutions were poured into the petri dish lids. The lids were held above the surface of the paraffin by small nails (Figure

1); thus, the agar was positioned several millimeters above the surface of the paraffin.

One fertilizer granule of SCU 4, 23, or 25 was placed in each hole on the soil surface. No attempt was made to prevent granules from touching the paraffin walls of the hole.

Duplicate plates were sealed in plastic "Zip-Lock" bags and placed in a growth chamber at 25 C (\pm 1). Duplicate plates were removed for determination of the percent of urea released after 25 days and every 10 days thereafter for 155 days for SCU 4 and for 125 days for SCU 23 and 25. The urea released was determined by counting intact granules.

Periodic Drying of the Soil and SCU Urea Release

Petri plates (155 mm x 10 mm) were filled with 70 g of Woodburn silt loam soil which had been air-dried to 6% water content and sieved through a one-mm screen. Twenty ml of distilled water was applied to the soil to bring it to about -0.3 bars water potential. SCU 4, 23, or 25 (58 granules) was evenly distributed on the soil surface of each plate. All plates were sealed in plastic bags and incubated at 25 C (\pm 1). After five days and then every ten days the plates were opened and allowed to air-dry for 24 hours. Five days after samples were dried they were rewatered with 20 ml of distilled water. Thus samples were subjected to a five-day-wet, five-day-dry cycle. This

treatment will be referred to as "wet-dry".

Continuously wet (-0.1 to -2 bars) samples were prepared using paraffin-filled petri plates as described in the preceding section but without the use of NaCl solutions to control water potential.

Samples were initially watered by applying about 20 ml of distilled water from a hand-operated sprayer while plates were rotated at about one revolution per second on a turntable. The soil water content appeared to vary among holes, probably as a result of variations in the amount of soil in each hole, as well as uneven application of water. By visual comparison of the soil with soils maintained at -0.3, -5, and -15 bars, it was estimated that the water potential ranged from -0.1 to -1 or -2 bars.

Samples were sealed in plastic bags and incubated at 25 (\pm 1). A beaker of distilled water was placed in the plastic bag to maintain a high relative humidity and reduce evaporative losses from the soil. During the experiment plates were rewatered if the soil appeared to be drying.

Samples were removed at 10- to 20-day intervals for determination of urea release by counting intact granules.

SCU Urea Release in Sterile Soil

Sample containers, soil, and agar-NaCl solutions (-5, -15, and -30 bars; "wet-dry" and "continuously wet" treatments) were prepared

as described in preceding sections. Fifty-eight granules of SCU 4, SCU 23, or SCU 25 were applied to each plate. The sample containers were placed in four-liter plastic "Zip-Lock" bags, two sample containers per bag. Into each bag was placed a glass petri dish containing 15 mls of propylene oxide (Skipper and Westermann, 1972). Bags were immediately sealed and placed in a growth chamber at 25 C (± 1). After 25, 45, 65, 85, 105, and 125 days, duplicate plates for each SCU material were removed from the growth chamber and urea release was determined by counting intact granules. Any samples displaying microbial growth were discarded.

The efficacy of propylene oxide sterilization was tested after 125 days. Thirty SCU granules (five from each of six samples) were aseptically transferred to plates containing nutrient agar (Difco). Plates were incubated for seven days at ambient temperature (about 20 C). No growth was observed on any plates. When granules from non-sterile samples were incubated on nutrient agar, profuse microbial growth resulted.

Scanning Electron Microscopy of SCU Granules

Single granules of SCU 4, 23, and 25 which had been exposed to either sterile or non-sterile soil at -5 bars water potential, and granules which had not been exposed to the soil, were air-dried. Some granules were gently rinsed in 95% ethanol to remove soil particles.

Granules were fixed to sample mounts and coated with a gold-palladium alloy to a thickness of about 1000 Å in a Varian VE 10 Vacuum Evaporator. This unconventionally thick coating was applied to prevent sublimation of sulfur under the vacuum imposed in the microscope sample chamber.²

The coated granules were viewed by scanning electron microscopy (International Scientific Instruments Mini SEM) at an accelerating voltage of 15 kV. Photographs were taken with a 545 Polaroid Land Camera using Polaroid Type 55 film and an exposure time of 30 seconds.

Results and Discussion

Physical and Chemical Properties of SCU

Nitrogen Content. The nitrogen content of SCU 4, 23, and 25, as determined by urea analysis of ten 58-granule samples, varied by several percentage points from the nominal values provided by the Tennessee Valley Authority (Table 2).

The variability of the nitrogen content of SCU samples (Table 2) sets a limit to the variability in the percent urea released from that sample. For example, the coefficient of variability (CV) of the nitrogen content of SCU 4 (58-granule samples) was 2.47% (Table 2), and

²R. Scheib, personal communication.

therefore the CV for the percent urea release must be greater than 2.47%.

Table 2. Mean granule weights and nitrogen contents of SCU 4, 23, and 25.

Fertilizer	Mean granule weight	Nitrogen in 58 granules		Nominal nitrogen content ¹
	<u>mg</u>	<u>mg</u>	<u>%</u>	<u>%</u>
SCU 4	15.86	315.8	34.7	35.2
C. V. ²	3.58%	4.57%	2.47%	
SCU 23	18.16	355.4	33.8	33.1
C. V.	4.01%	2.89%	1.56%	
SCU 25	19.39	353.0	31.4	34.5
C. V.	5.08%	5.12%	2.65%	

¹Source: Tennessee Valley Authority (Table 1).

²Based on ten 58-granule samples.

SCU 4, with a lower total coating weight than the other two SCU materials, had a higher nitrogen content. It also had the lowest seven-day release rate (Table 1); therefore, the seven-day release percentage is not related to the coating weight but instead is probably related to the type and amount of sealant, the number of broken granules, the fraction of granules with very thin coatings, and the number of granules with large holes in the coating.

Granule Weights. The average granule weight, both for five-gram and 58-granule samples varied slightly among the selected SCU

fertilizers (Tables 2 and 3). When 60 granules of SCU 4, 23, or 25 were individually weighed, the weights for each fertilizer were found to be approximately normally distributed (Figure 2). The range of granule weights was greater for SCU 23 and 25 than for SCU 4. This may have been due to the more heavily coated SCU granules (SCU 23 and 25) having a greater range of coating weights.

Table 3. Mean granule weights of SCU 4, 23, and 25.

Fertilizer	Mean number of granules in 5 grams	Mean granule weight	Coefficient of variability ¹
		mg	%
SCU 4	333.4	15.00	2.24
SCU 23	281.6	17.76	4.45
SCU 25	256.4	19.50	3.76

¹Based on ten five-gram samples of each fertilizer.

The variability in average granule weight and nitrogen content (Tables 2 and 3) may have been due to segregation of granules according to size and shape, both during transport and storage of bulk samples and during subsampling. Samples with higher than average granule weights tended to have higher than average amounts of nitrogen; therefore the variability in percent nitrogen was somewhat lower than the variability in granule weight or nitrogen content (Table 2).

SCU Coating Thickness. The average radius of the urea portion and the average thickness of the sulfur and sealant components of

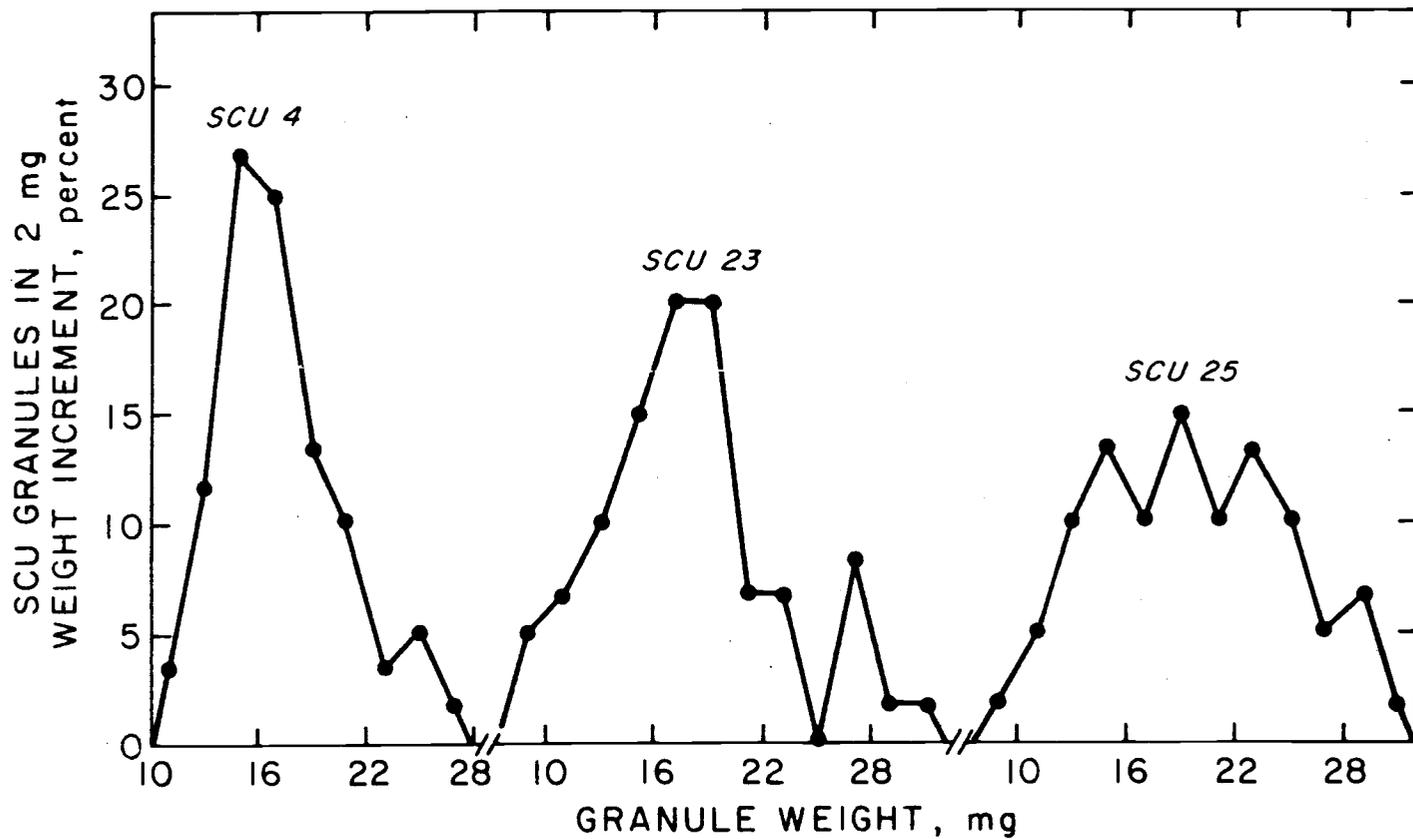


Figure 2. Distribution of individual granule weights for SCU 4, 23, and 25.

the coating were calculated with Equations (5)-(7) using values in Table 4.

Table 4. Urea, sulfur, and sealant in a granule of SCU 4, 23, and 25.

	SCU 4	SCU 23	SCU 25
Ave. granule wt., mg	15.0	17.8	19.5
Nitrogen content, %	34.7	33.8	31.4
Urea content, %	74.4	72.5	67.3
Sulfur content, %	18.5	24.0	23.0
Sealant content, %	3.0	0	2.0
Amount in granule, mg			
Urea	11.16	12.87	13.13
Sulfur	2.78	4.26	4.49
Sealant	0.45	0	0.39

The sulfur coating of all three SCU fertilizers was, on the average, about two-thirds as thick as the sulfur (Table 5). Sealant materials on SCU 4 and 25 accounted for about 26 and 19%, respectively, of the total coating thicknesses (Table 5).

Table 5. Mean thickness of coating components of SCU 4, 23, and 25 granules.

	SCU 4	SCU 23	SCU 25
	- - - - - microns - - - - -		
Radius of urea portion	1263	1324	1333
Thickness of sulfur	64	91	93
Thickness of sealant	23	0	22

The calculation of coating thickness is based on an assumption of spherical geometry; any deviation from a perfect sphere would result in a larger granule surface area per unit volume. Since SCU granules are not perfect spheres, the calculated coating thickness represents a maximum average value.

Also, such calculations provide no information on the variability of coating thickness on a single granule or among granules. Cross-sectional views of SCU granules indicate that coatings on individual granules are not uniform in thickness (Scheib and McClellan, 1976). The urea release pattern for an individual granule may be influenced by both the average coating thickness and the occurrence of thin spots on the coating. It has been suggested that coatings less than 30 microns thick are susceptible to rupture when the urea in the granule absorbs water and swells (McClellan and Scheib, 1973).

Both SCU 4 and SCU 25 are conditioned with diatomaceous earth. Neither the bulk density nor the proportion of the diatomaceous earth which adheres to granules is known. If one assumes that the bulk density of the diatomaceous earth is between 0.5 and 1.0 g/cm³, and that all or the original material (2% by weight) still adheres to the granules, it would form a layer 15 to 30 microns thick. Unlike the sealant, this layer is probably very permeable to water and may even hold water, keeping the granule surface constantly moist.

For granules without thin spots susceptible to mechanical rupture, it is hypothesized that regardless of the mechanism of urea release, the rate of release is controlled by the coating thickness.

Release of Urea from SCU into Sterile Solution

Urea release from SCU 4, 23, and 25 incubated in sterile solution at 37.7 C slowed with time during a 28-day period (Figure 3). Since the urea release during 28 days appears to be unrelated to the calculated thickness of either sulfur or sealant material (Table 5), it is probably a reflection of the percentage of granules with major coating defects or very thin coatings

The seven-day release percentage has become the conventional, arbitrary measure of the amount of nitrogen "immediately available". But the amount of urea released after seven days was only about 80% of the amount released after 28 days (Figure 3).

The seven-day release percentages differed from the nominal values provided by TVA (Table 1). In the case of SCU 4, about twice as much urea (9%) was released in seven days as the nominal release percentage would indicate. The SCU 4 fertilizer used for this experiment was manufactured by TVA in 1972, and the four-year period of storage and handling may have resulted in an increase in granules with broken coatings. The nominal and actual seven-day release values of SCU 23 and 25 are in closer agreement; these materials were

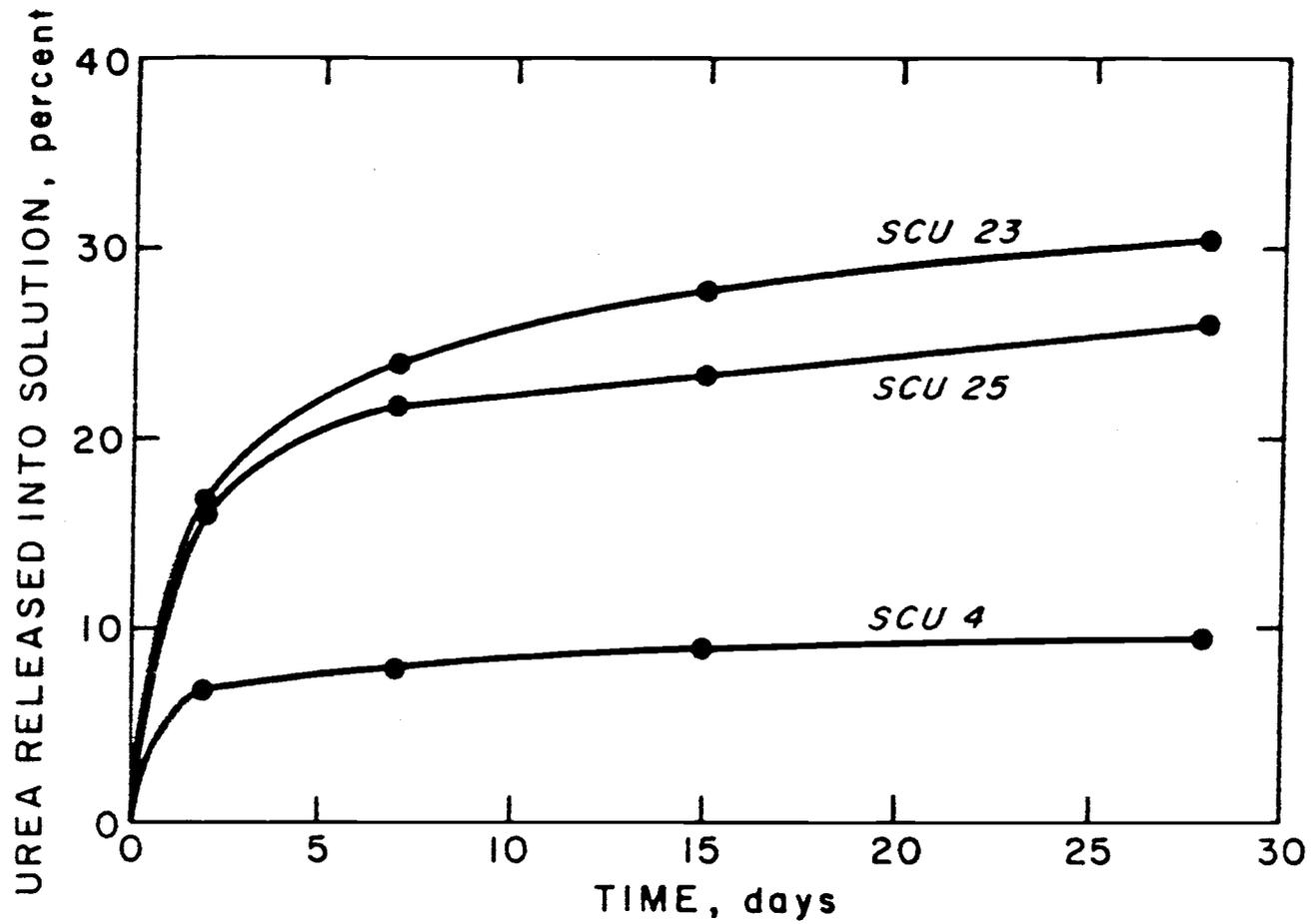


Figure 3. Urea release from SCU into sterile solution at 37.7 C. Percent release expressed as percent of total urea.

manufactured by TVA in 1973 and 1974, respectively.

SCU Urea Release as Determined by Granule Counts
and Urea Analyses

In one of the temperature experiments in which soil-SCU samples were incubated for five weeks at 35 C, then transferred to 5, 15, 25, or 35 C, urea release was determined both by counting empty granules and analyzing intact granules for urea content.

When the granule counts and urea analyses were compared, a close correlation was observed for SCU 4 and 23, but not for SCU 25 (Figure 4). For SCU 25, the granule counts gave a lower percent release than the urea analyses. One possible explanation is that small amounts of urea had diffused from granules which were counted as intact. Also, SCU 25 coatings tended to be physically stronger, and empty granules picked up from the soil with forceps may not have broken. There did not appear to be any effect of the temperature treatments on the difference between granule counts and urea analyses. Since urea analyses were conducted only on selected samples, all urea release data reported in this thesis are based on granule counts. Actual release from SCU 25 may have been somewhat faster.

It should be noted that in most samples, a number of granules were filled with liquid. This liquid may have contained dissolved urea, but in either case the liquid was lost from the very fragile

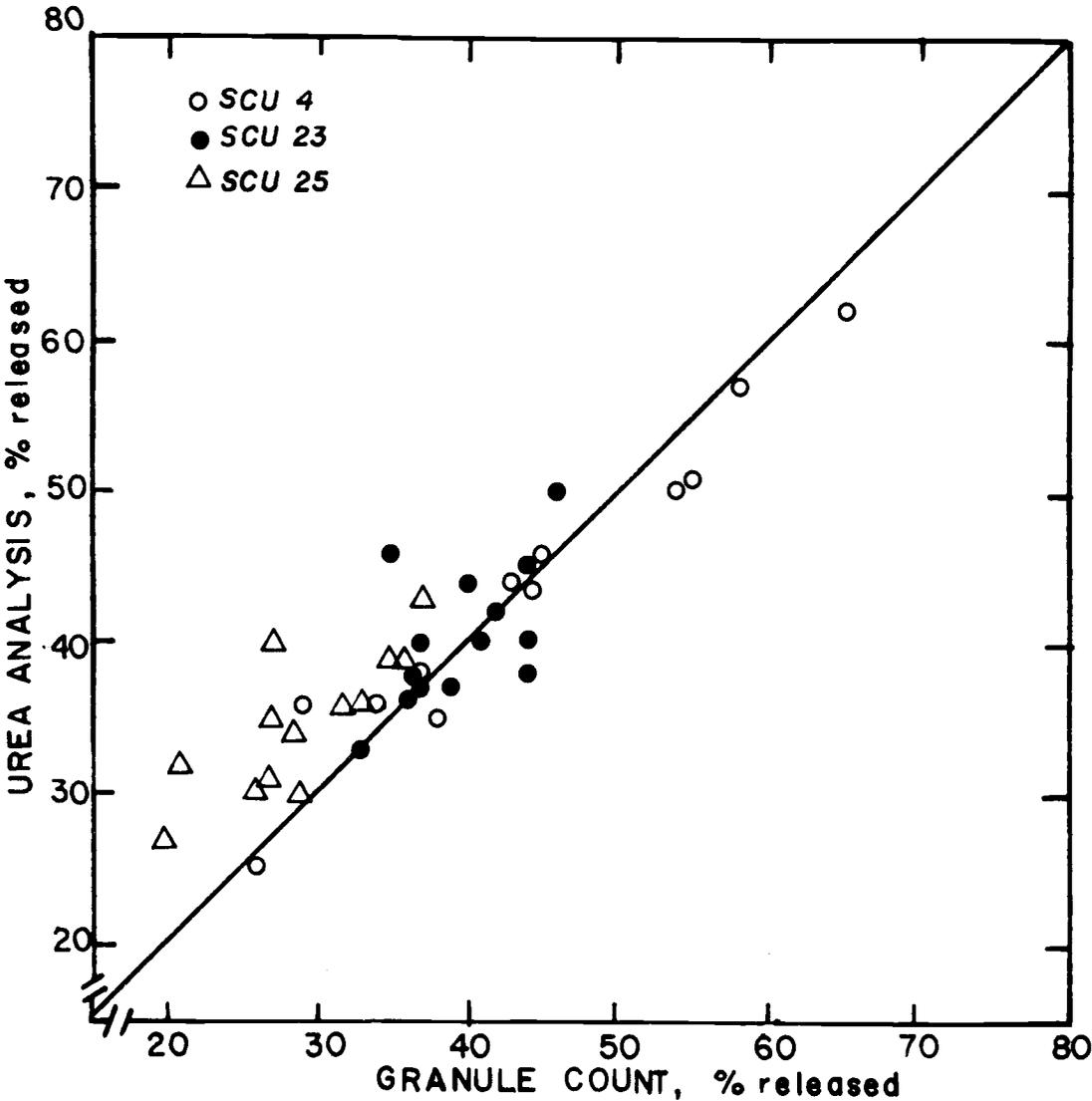


Figure 4. Urea release from SCU as determined by granule counts and urea analyses.

granules before it could be collected for analysis. These granules were therefore counted as released.

Temperature and SCU Urea Release

To determine the effect of temperature on the rate of urea release from wax-sealed SCU (SCU 4) surface-applied to soil, the results of three experiments were compared (Figure 5). In the first experiment (5 and 15 C), SCU 4 was applied at a rate of 100 kg N/ha (surface-area basis). At both temperatures, only about 10 to 14% of the total urea had been released after 80 days (Figure 5). In the second experiment (25 C), SCU was applied to soil in equilibration units in which individual granules were separated (Figure 1). The average surface rate of application was about 450 kg N/ha. After 25 days only about 10% of the urea had been released. Between 25 and 105 days, urea was released at an average rate of 0.71%/day. Only data through the 85th day are shown (Figure 5). In the third experiment (35 C) SCU 4 was surface-applied at a rate of 350 kg N/ha to soil amended with CaCO_3 . Between 35 and 65 days from the beginning of the experiment, urea was released at an average rate of 1.51%/day (Figure 5). Therefore, over the same time period, the average rate of urea release at 35 C was about twice the rate at 25 C, that is, the Q_{10} was about two.

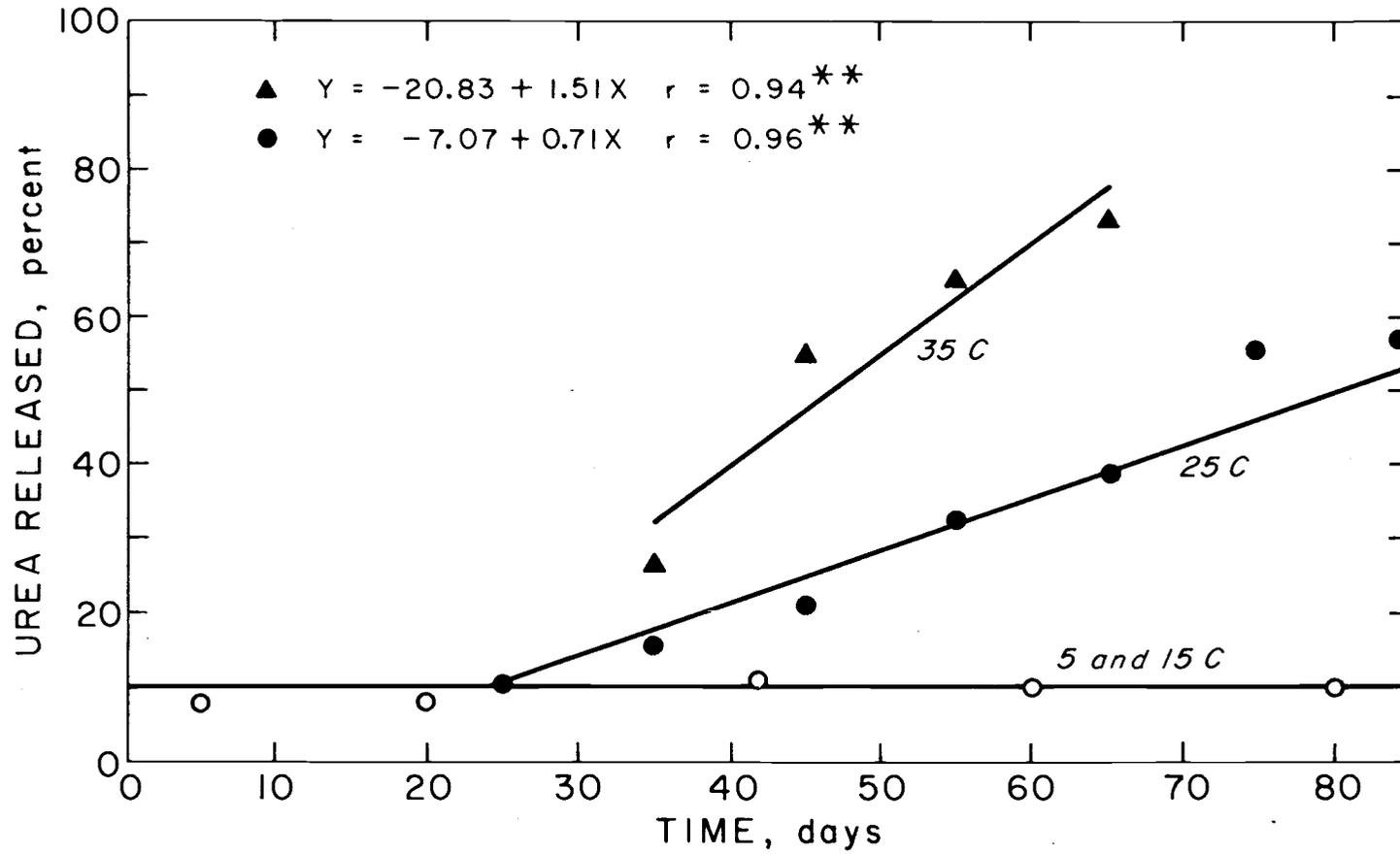


Figure 5. Influence of temperature on urea release from SCU 4 surface-applied to Woodburn silt loam.

At 5 and 15 C, the initial lag period continued for more than 80 days, and it is not possible to compare the average urea release rate over the same stage of release at the four temperatures.

A Q_{10} of two or greater is characteristic of enzymatic or chemical reactions with a high energy of activation, while a Q_{10} near one indicates that some passive process, such as diffusion, is involved (Noble, 1974). Therefore, it appears that urea release from SCU 4 is not strictly a diffusion-limited process.

It may be argued that these experiments were conducted under variable soil conditions (limed vs. unlimed) and SCU nitrogen rates, and that therefore the results are not comparable. It can be speculated, however, that had the SCU rates and soil pH conditions been equivalent, the difference in urea release rates among temperatures would have been even greater than was observed, and therefore the conclusions drawn from the experiments would not be different.

The higher rate of SCU application and faster urea release at 35 and 25 C apparently resulted in more NH_3 production by the urea hydrolysis, as evidenced by higher soil pH at those temperatures. For example, after 60 to 65 days, the soil pH values at 5 and 15 C were 5.6 and 4.9, respectively. Soil pH at 15 C may have been lower than at 5 C because at the lower temperature, nitrification, which would tend to lower the soil pH, was slowed. At 25 C around released SCU granules, the pH ranged from 7.2 to 7.4 and around

unreleased granules ranged from 5.8 to 6.7. At 35 C, the soil pH was 8.4. At that pH, nitrification may actually have been inhibited by the higher NH_3 concentration. It is also possible that at a very high pH such as occurred in the soil at 35 C, activity of microorganisms which degrade the coating was inhibited.

The urea release patterns observed here were similar to those reported by Oertli (1973b). He incubated SCU (40% S, 4% wax) in solutions at 14, 24, and 34 C. At 14 C, almost no urea release occurred during 100 days. At 24 and 34 C, urea release began after a lag period of 20 to 40 days. Urea release after the lag period exhibited a Q_{10} of about two. In agreement with Oertli's observations, Allen, Hunt, and Terman (1971) found that urea release from waxed SCU occurred much faster at 20 and 30 C than at 10 C. Urea release from SCU (total coating weights of 13 and 10%) applied to soil was delayed for 8 to 12 weeks at 10 C, and, following this lag period, was slower than at 20 and 30 C.

The very slow urea release at low temperatures observed and in the literature (Oertli, 1973b; Allen, Hunt, and Terman, 1971) suggests that as the first step of SCU urea release, wax is removed in a temperature dependent process, probably by soil microorganisms. Following wax removal, urea diffuses from exposed pores and channels in the sulfur.

Apparently both the rate of wax removal and urea diffusion control the rate of urea release following the lag period. To determine the effect of temperature on urea release exclusive of its effect on the lag period, SCU 4 was applied to soil and initially incubated at 35 C for five weeks, then transferred to chambers at 5, 15, 25, or 35 C. During the 30 days following transfer, urea release at 5 C levelled off at about 35%, while at 35 C, urea release continued, reaching 72% 30 days after transfer (Figure 6, top). Apparently, at the new equilibration temperature those granules from which wax had already been removed continued to release urea by diffusion--a less temperature dependent process. After 10 days at 5 C, and after 20 days at 15 C, no further urea release occurred, indicating that urea had diffused completely from those granules and that further removal of wax was occurring slowly or not at all (Figure 6, top).

The rates of urea release from SCU 23 (no sealant) and SCU 25 (polyethylene-oil sealant) were also sensitive to temperature (Figure 6, middle and bottom), but interpretation of these results is difficult. At the time of transfer from 35 C to lower temperatures, about 35% of the total urea had been released from SCU 23. After 30 more days, an additional 11% had been released at 35 C, whereas no additional release was observed at 5 C (Figure 6, middle). For SCU 25, about 20% of the urea had been released at the time of transfer. After 30 more days, the SCU 25 transferred to 5 or 15 C had released an

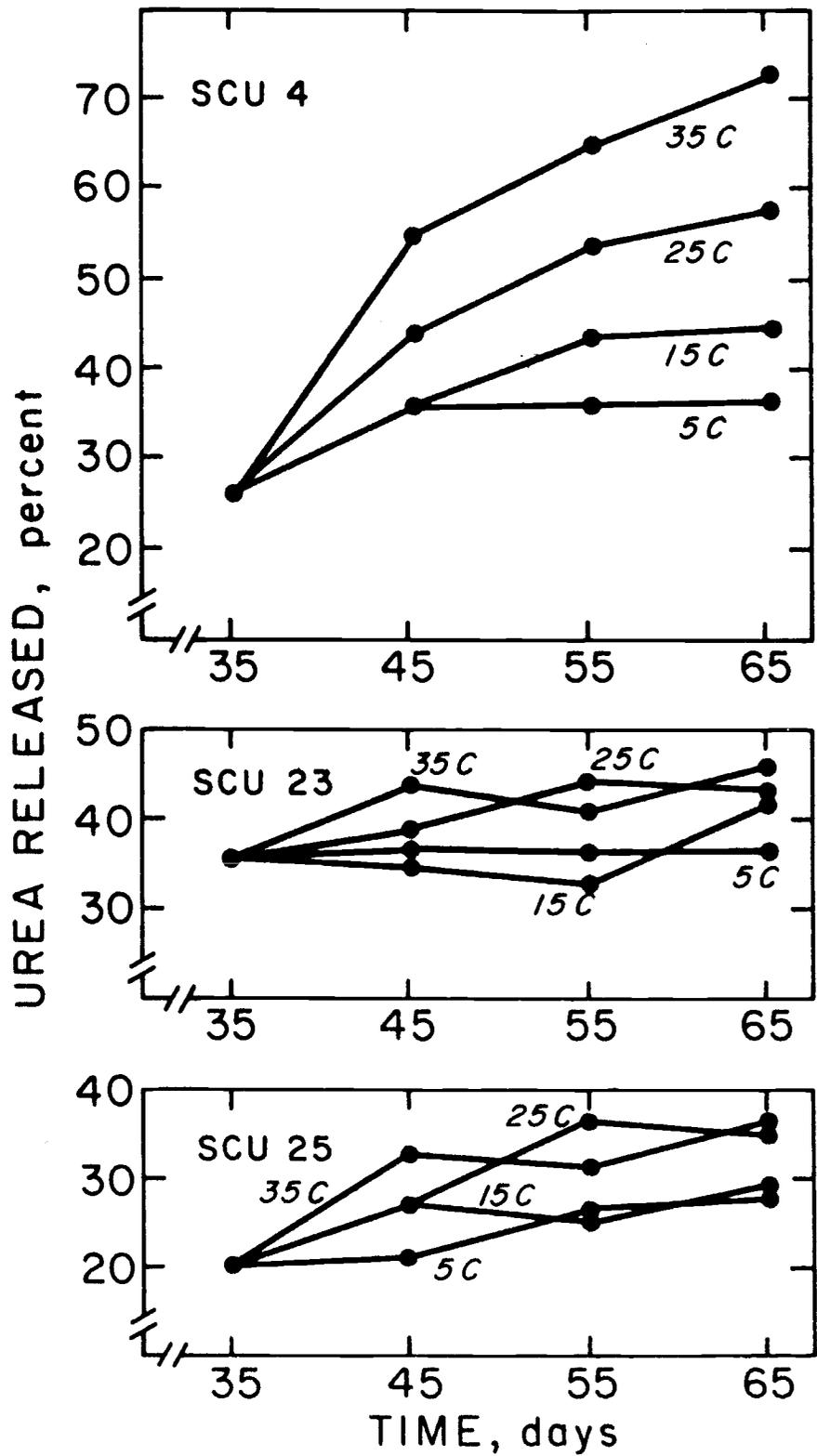


Figure 6. Influence of temperature on urea release from SCU surface-applied to Woodburn silt loam and initially incubated at 35 C for five weeks.

additional 18%, while that transferred to 35 or 25 C had released an additional 25% (Figure 6, bottom). The low rate and high variability of the observed release prevented calculation of Q_{10} values. Both SCU 23 and 25 have thicker sulfur coatings than SCU 4 (Table 5), and this probably accounted for the faster release rate of the latter (Figure 6).

In summary, the urea release rate from SCU with a wax sealant was very temperature dependent, probably as a result of the effect of temperature on microbial wax removal. Urea release over a 30-day period from SCU fertilizers with no sealant and a polyethylene-oil sealant was slower, apparently due to thicker coatings. Therefore, temperature effects on urea release were not as clearly demonstrated for these materials.

Soil Water Potential and SCU Urea Release

Soil water potential may influence the rate of urea release from SCU by its effect on the microbial degradation of sealant and sulfur, the rate of water absorption by granules, the rate of urea diffusion from granules, or by a combination of these effects.

The release of urea from SCU 4, following an apparent lag period, occurred at 1.0%/day at -5 bars water potential compared to 0.5%/day at -15 and -30 bars (Table 6 and Figure 7). While the rate of release after the lag period was the same at -15 and -30 bars, the

lag period was about 50 to 60 days at -30 bars compared to 25 days at -15 bars (Figure 7).

Table 6. SCU urea release rates at 25 C under different soil water conditions and in sterile soil.

Treatment	Fertilizer		
	SCU 4	SCU 23	SCU 25
	- - - - - %/day - - - - -		
-5 bars	1.00 ± 0.11		
-15 bars	0.49 ± 0.08	0.16 ± 0.03 ¹	0.16 ± 0.03 ¹
-30 bars	0.50 ± 0.10		
Wet ²	0.71 ± 0.06		
Wet-dry ³	0.45 ± 0.06		
Sterile	0.00 ¹	0.12 ± 0.03 ¹	0.08 ± 0.03 ³

¹ Average of all moisture treatments.

² Wet = continuously moist; estimated water potential, -0.1 to -2 bars.

³ Wet-dry = moist five days, air-dry five days.

Over a 125-day period, urea release from SCU 23 (no sealant) did not appear to be influenced by soil water potential in the range under consideration; however variability of the data may have obscured small effects (Figure 8).

Urea release from SCU 25 (polyethylene-oil sealant) was actually faster at -30 bars than at -5 and -15 bars; there was no difference in the release rate at -5 and -15 bars (Figure 9).

These results are consistent with the hypothesis that urea release from SCU is mainly a result of microbial degradation of the

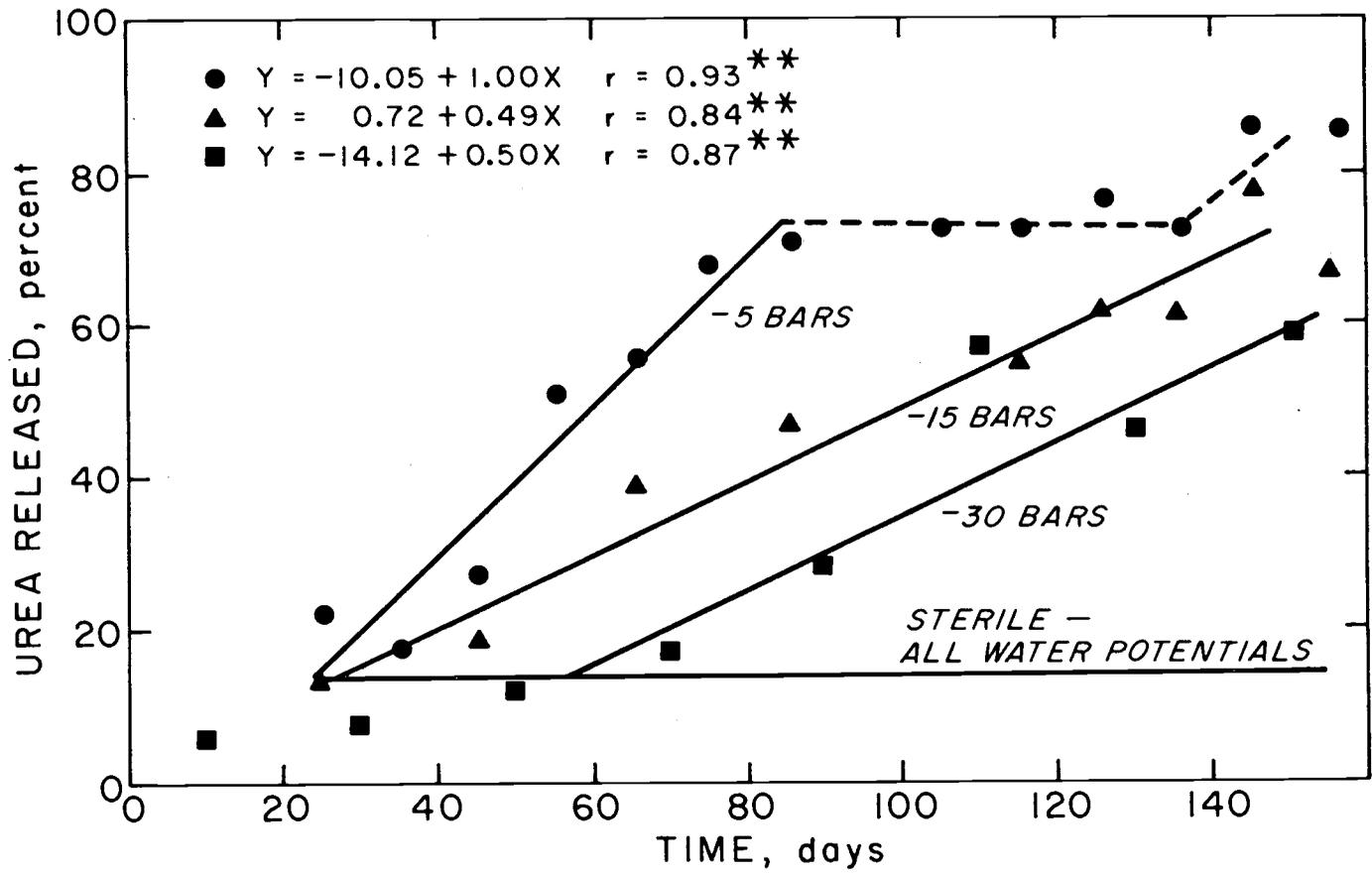


Figure 7. Influence of soil water potential and soil sterilization on urea release from SCU 4 surface-applied to Woodburn silt loam.

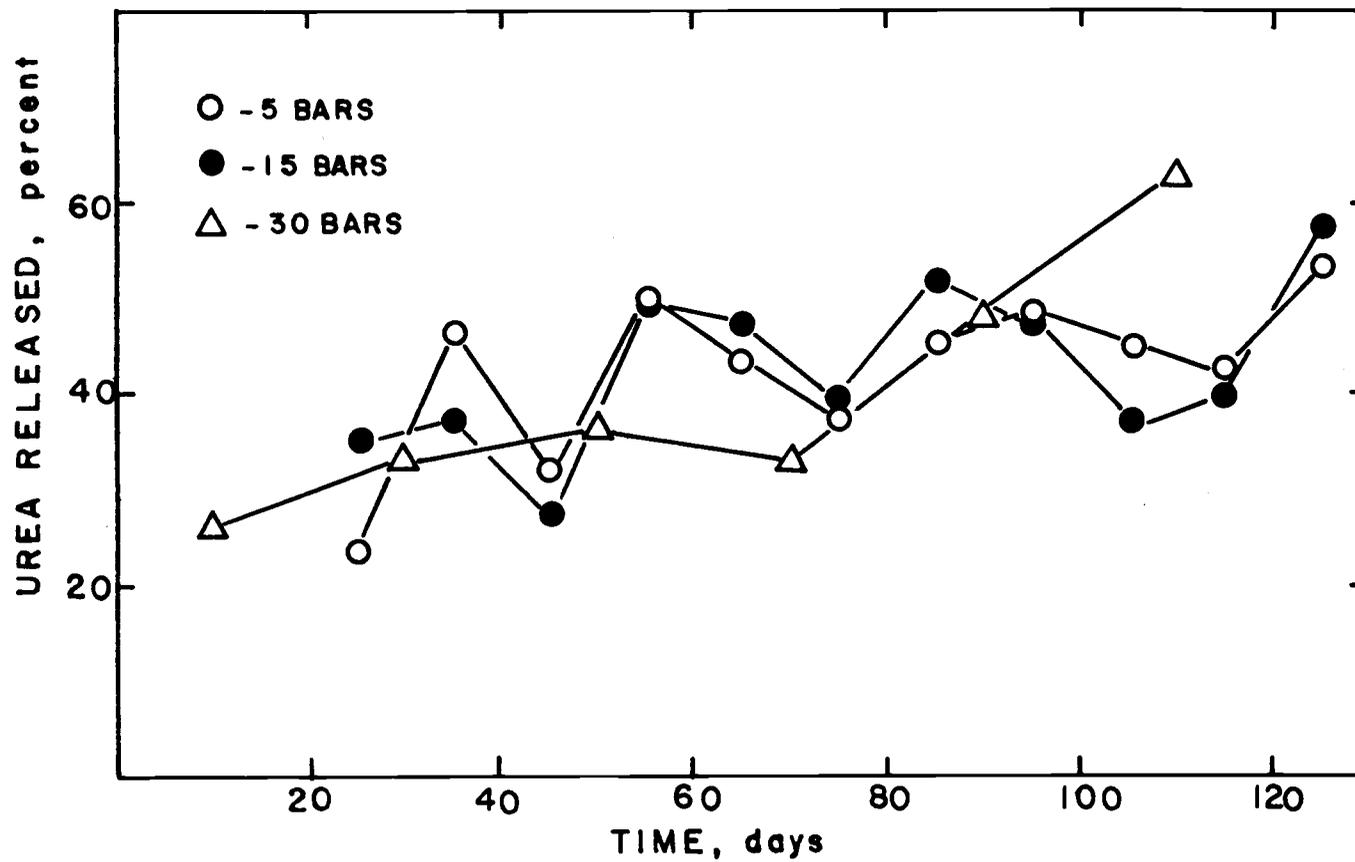


Figure 8. Influence of soil water potential on urea release from SCU 23 surface-applied to Woodburn silt loam.

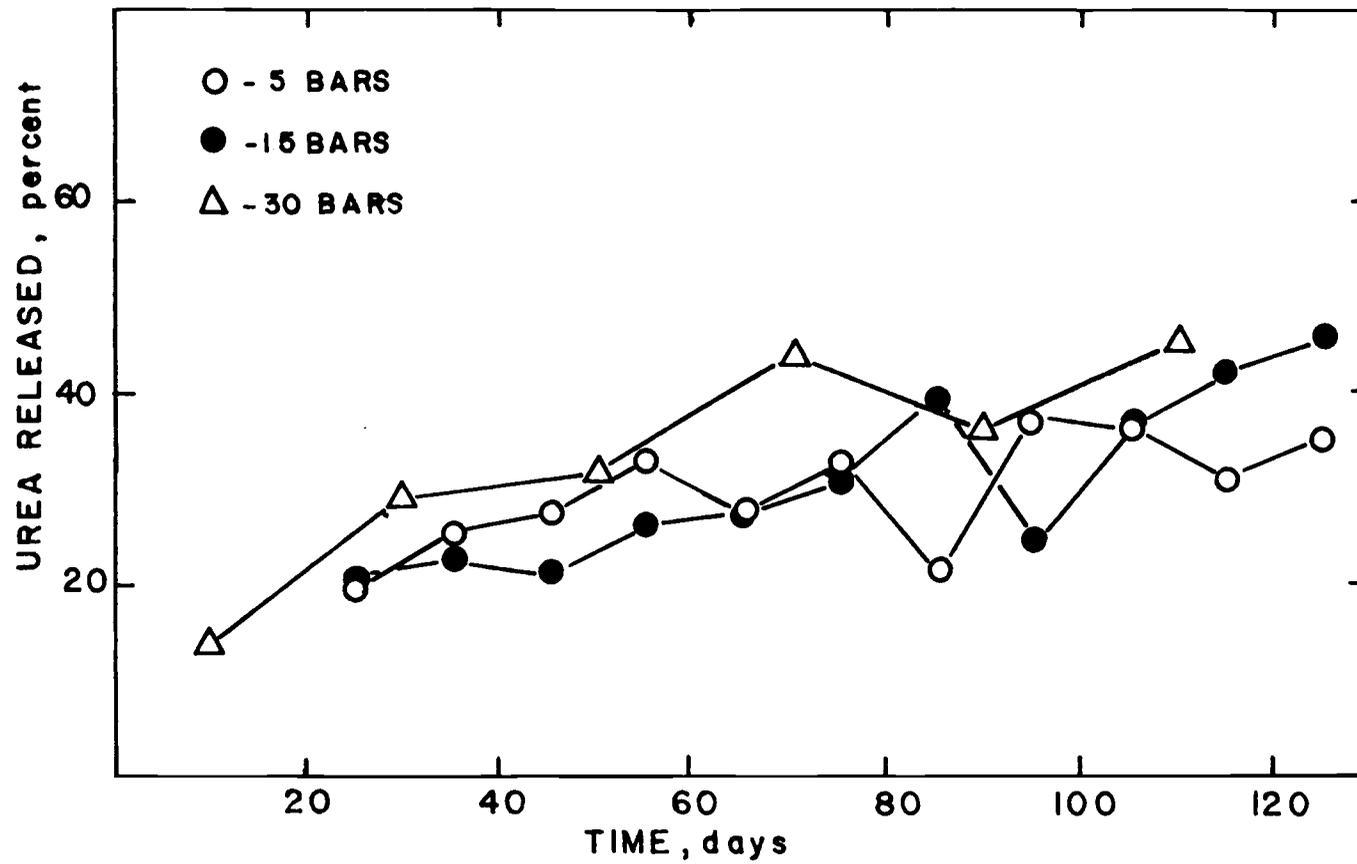


Figure 9. Influence of soil water potential on urea release from SCU 25 surface-applied to Woodburn silt loam.

sealant and not the sulfur. An extensive body of literature indicates that, in general, microbial activity is sharply curtailed below a water potential of -15 bars. For example, Wilson and Griffin (1975) found that bacterial respiration in soil decreased rapidly below a water potential of -3 bars and at -20 bars was very slight. However, many microorganisms remain active at very low water potentials. For example, Fusarium oxysporum f. sp. vasinfectum (a fungus) grows optimally at a soil matric potential of -10 to -15 bars and grows at 50% of the optimum rate at -50 to -60 bars, possibly because of a reduction in antagonism from other soil microorganisms (Cook and Papendick, 1972). This provides one possible explanation for the observed increase in urea release from SCU 25 at -30 bars water potential (Figure 9).

Many actinomycetes are able to remain active in soil water potentials down to -50 bars (Baker and Cook, 1974). Actinomycetes may be involved in the microbial oxidation of the wax sealant on SCU. For example, 48 isolates of an actinomycete, Nocardia asteroides, and 16 other species of Nocardia were isolated from soils by means of a paraffin baiting technique (McClung, 1960). Each isolate was shown to utilize paraffin as its sole carbon source.

The sealant wax and the oil component of the polyethylene-oil sealant, are probably oxidized by a number of species of actinomycetes and fungi (Ellis and Adams, 1961). Some of these species probably

remain active at water potentials of -30 bars, although the overall rate of activity would be less than at higher soil water potentials.

Only a few experiments have demonstrated the effect of soil water potential on bacterial sulfur oxidation. Moser and Olson (1953) measured very low rates of sulfur oxidation at -15 bars water potential in three out of four soils. In the fourth soil, about 33% of the added 100-mesh elemental sulfur was oxidized at -15 bars after four weeks. In general, however, it can be assumed that sulfur oxidation is very slow at water potentials lower than -15 bars (Burns, 1967). It seems unlikely that urea would be released from wax-sealed SCU as rapidly as was observed when soil water potentials were -15 or -30 bars (Figure 7), if the process were dependent on sulfur oxidation.

Urea is very hygroscopic and absorbs water rapidly if the relative humidity is about 80% (equivalent to a water potential of -307 bars at 25 C) (Skujins and McLaren, 1967). Therefore, it is unlikely that absorption of water by urea at -30 bars would be the limiting step in the release of urea.

However, transfer of liquid water or water vapor into a granule through small openings in the coating could be influenced by soil water potential. Also, urea may diffuse from SCU granules in response to a urea concentration gradient, which is determined by the size of openings, coating thickness, and urea concentration at the granule surface. At low soil water contents, the urea concentration

at the granule surface would be higher since the urea would diffuse away from the granule more slowly; therefore diffusion out of the granule would be slower.

Other, indirect effects of soil water potential on urea release from SCU are possible. Urea is rapidly hydrolyzed in soil, liberating carbon dioxide and ammonia. If the urease enzyme is less active at lower water potentials, the urea concentration gradient around granules would not be as steep, resulting in slower diffusion of urea from granules. However, urease activity has been measured at 70% maximal at 90% relative humidity (-142 bars) and 20% maximal at 70% relative humidity (-483 bars) (Skujins and McLaren, 1967). Therefore, it is unlikely that urea release from SCU is limited by urease activity.

In summary, the rate of urea release from waxed SCU at -5 bars was about twice the rate at -15 and -30 bars. Urea release from SCU without sealant was apparently not influenced by water potential. Urea release from SCU with polyethylene-oil sealant occurred more rapidly at -30 bars than at -15 or -5 bars. It is tentatively concluded that soil water potential exerted its effect on urea release primarily by influencing the activity of sealant-degrading microorganisms, but it may also have affected diffusion of urea from granules.

Periodic Drying of the Soil and SCU Urea Release

SCU 4 with wax sealant subjected to continuously moist soil (-0.1 to -2 bars) released urea following a lag period at an average rate of 0.71%/day compared to 0.45%/day when subjected to a "wet-dry" treatment (Table 6 and Figure 10). No treatment effects were observed on the rate of urea release from SCU 23 and 25 over the same period of time (125 days). Release from the latter two SCU materials was sufficiently slow that any treatment effects were masked by data variability.

The effect of periodic drying on the urea release rate from SCU 4 may have been due to both a reduction in the diffusion rate of urea from granules and a lower rate of microbial degradation of the coating. However, a different interpretation of the data is possible. If SCU urea release is related to the time that granules were subjected to moist soil, that is, 50% of the time for the "wet-dry" treatment, the actual release rate for the SCU subjected to periodic drying was $2 \times 0.45\%/day$ or $0.90\%/day$, which is faster than the $0.71\%/day$ release rate of the continuously moist samples. This interpretation of the data suggests that if SCU in a field environment were frequently subjected to short periods of air-drying, the release of urea would be faster than from SCU in continuously moist soil. It is not known by what mechanisms periodic air-drying would increase the urea release

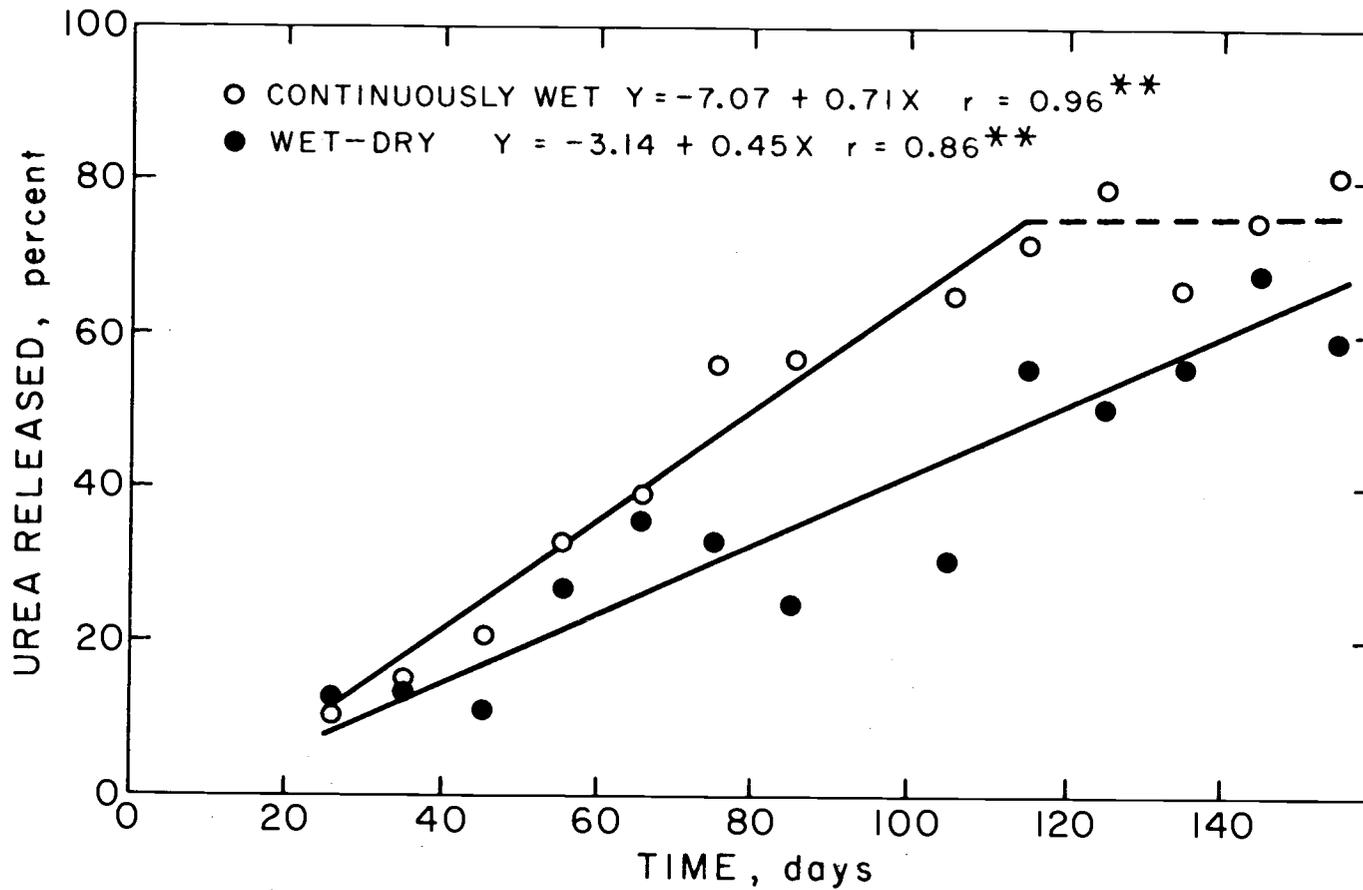


Figure 10. Urea release from SCU 4 surface-applied to continuously wet and periodically air-dried Woodburn silt loam.

rate. Perhaps the rewetting process results in mass movement of water and dissolved urea away from the granule, thereby lowering the urea concentration at the granule surface.

Urea release from SCU 4 was faster at a soil water potential of -5 bars than in a "continuously moist" soil (Table 6). The soil water content in each hole was not controlled. Therefore the soil in any given hole could have been either saturated with water (and therefore anaerobic) or at lower than -5 bars water potential. In either case, soil microbial activity would have been slower than in a well aerated but moist soil environment, and this in turn would have slowed SCU coating degradation.

SCU Urea Release in Sterile Soil

The water potential in the sterile samples could not be controlled, apparently because the propylene oxide sterilant reacted with soil components to form a solute, possibly propylene glycol, which greatly lowered the soil osmotic potential. This resulted in all sterile samples, regardless of original water content, becoming saturated due to water vapor diffusion from the sodium chloride solutions to the soil. Therefore, the results of all sterile water potential treatments for each SCU material were averaged.

SCU 4 incubated in a sterile soil released about 14% of the total urea during 155 days compared to 80 to 85% for the SCU 4 incubated in

non-sterile soil which was continuously wet or controlled at -5 bars water potential (Figures 7 and 10). This confirms the hypothesis that urea release observed in non-sterile soil was the result of microbial activity.

An insignificant difference was observed between the urea release rates of SCU 23 (no sealant) incubated in sterile and non-sterile soil (Table 6 and Figure 11). This suggests that urea release from SCU 23 was controlled by diffusion of urea through small openings in the sulfur coating formed during the manufacturing process or later by a non-biological process.

The rate of urea release from SCU 25 (polyethylene-oil sealant) in non-sterile soil was about twice the rate of release in sterile soil (Table 6 and Figure 12), suggesting that release in non-sterile soil was the result of microbial degradation of the coating.

Because soil sterilization resulted in a decrease in the urea release rate of both SCU fertilizers with sealant while no effect was observed on urea release from SCU without sealant, it is concluded that release from the sealed materials was a result of microbial decomposition of the sealant and not the sulfur. This conclusion conflicts with the previous report that inoculation of solutions in which wax-sealed SCU was incubated with Thiobacillus spp. resulted in an increase in the rate of urea release (Oertli, 1973b). As was previously noted, Oertli observed a temperature x inoculation interaction:

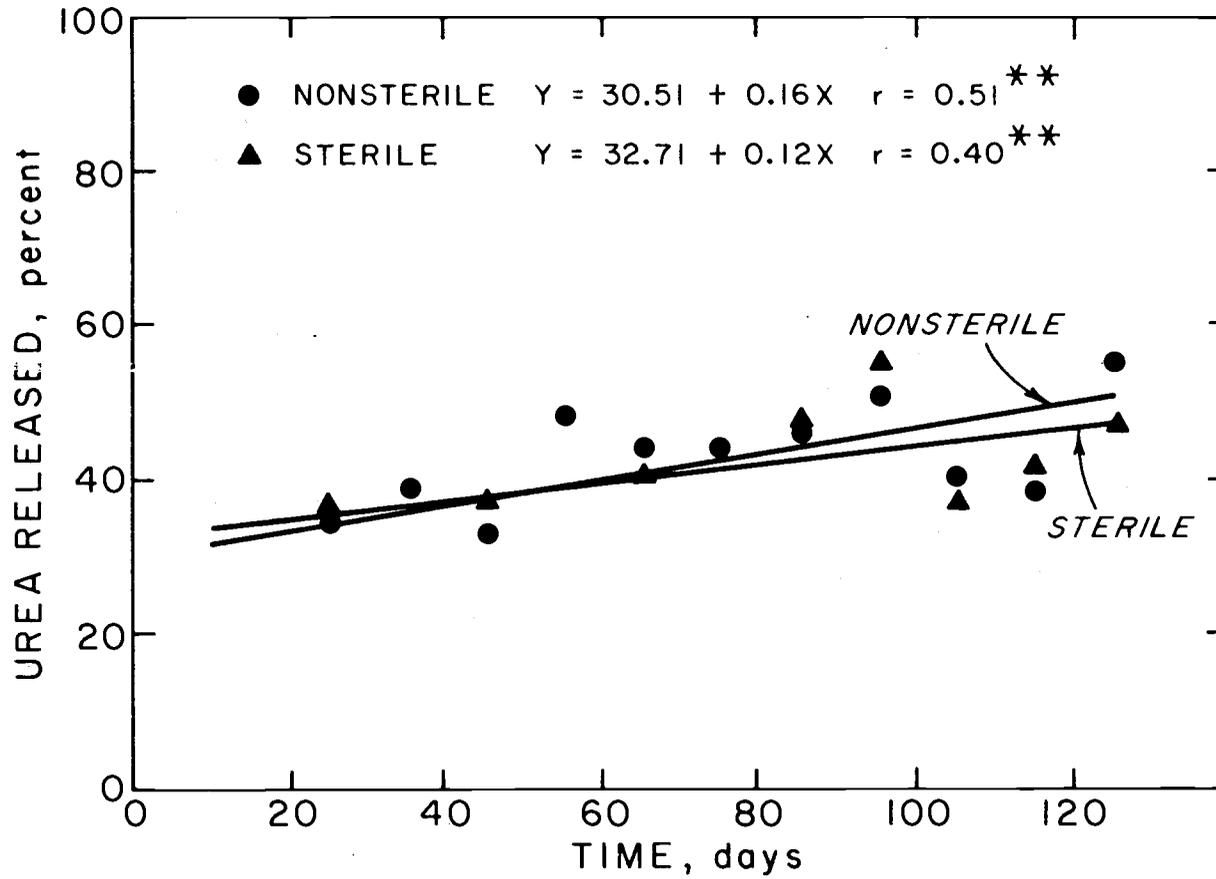


Figure 11. Urea release from SCU 23 surface-applied to sterile and non-sterile Woodburn silt loam.

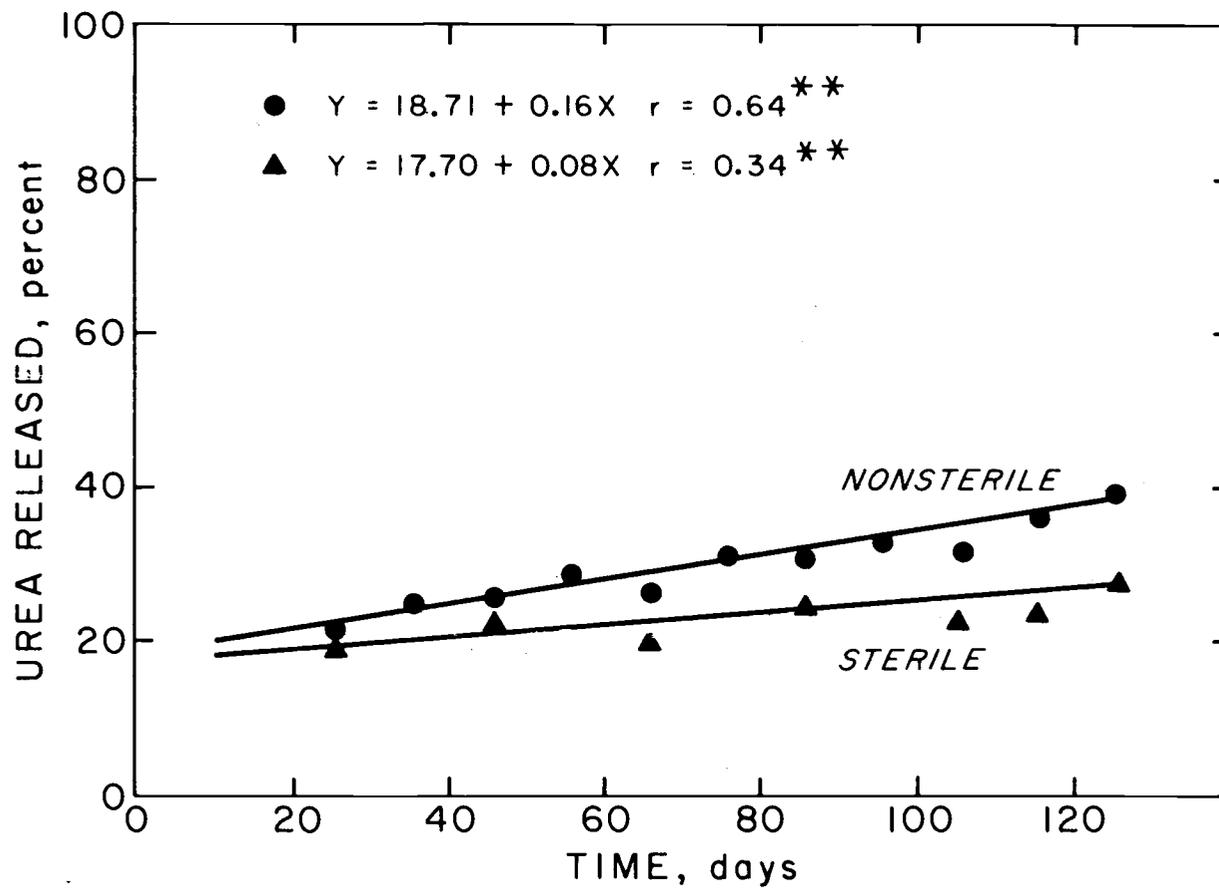


Figure 12. Urea release from SCU 25 surface-applied to sterile and non-sterile Woodburn silt loam.

inoculation enhanced urea release at 34 C but not at 24 C. No explanation for the interaction was given.

Mechanisms of SCU Urea Release

SCU without Sealant. When SCU is placed in water, urea from broken granules is immediately dissolved. Water may also diffuse through small openings in the sulfur coating to dissolve urea. The dissolved urea can then diffuse out the same openings. Alternatively, hydrostatic pressure resulting from the molar volume increase in the urea as it dissolves may rupture the coating, especially where it is very thin (McClellan and Scheib, 1973).

Several types of openings in the sulfur coating may exist:

(1) very fine cracks resulting from improper cooling during manufacture (McClellan and Scheib, 1975) or from mechanical impact after manufacture; (2) small channels or pores between sulfur agglomerates or between the amorphous and crystalline forms of the sulfur; (3) pores which are the result of gaseous inclusions formed in the coating during manufacture.

Examples of the second and third types of opening were observed by scanning electron microscopy (SEM) of SCU granules without sealant (Figures 13 and 14). The pocket (about 15 microns in diameter) may have been a result of a gas bubble inclusion. Small pores (< one micron diameter) between sulfur agglomerates were also

Figure 13. Pore on the surface of a SCU 23 (no sealant) granule before exposure to soil (700X).

Figure 14. Pore on the surface of a SCU 23 (no sealant) granule before exposure to soil (3000X).

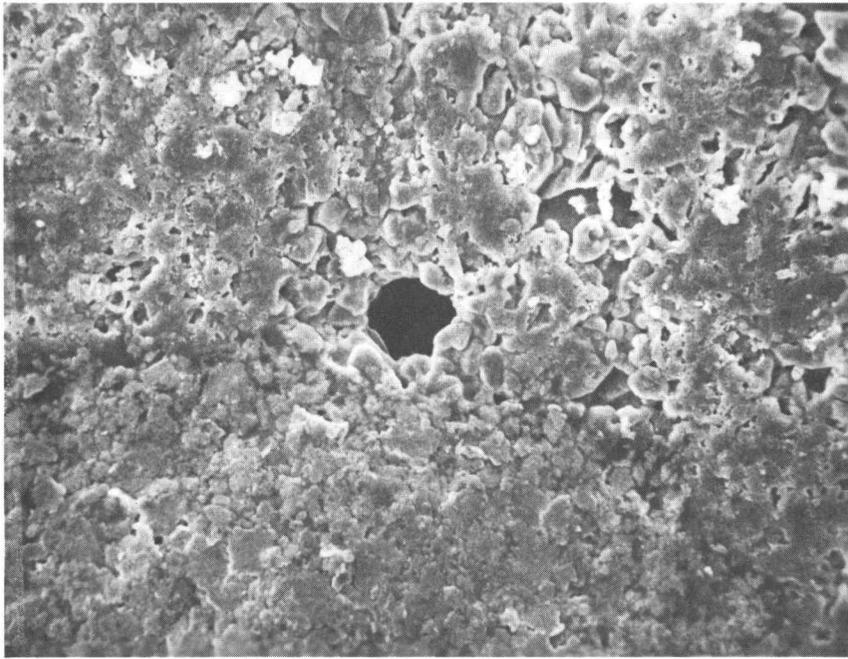


Figure 13

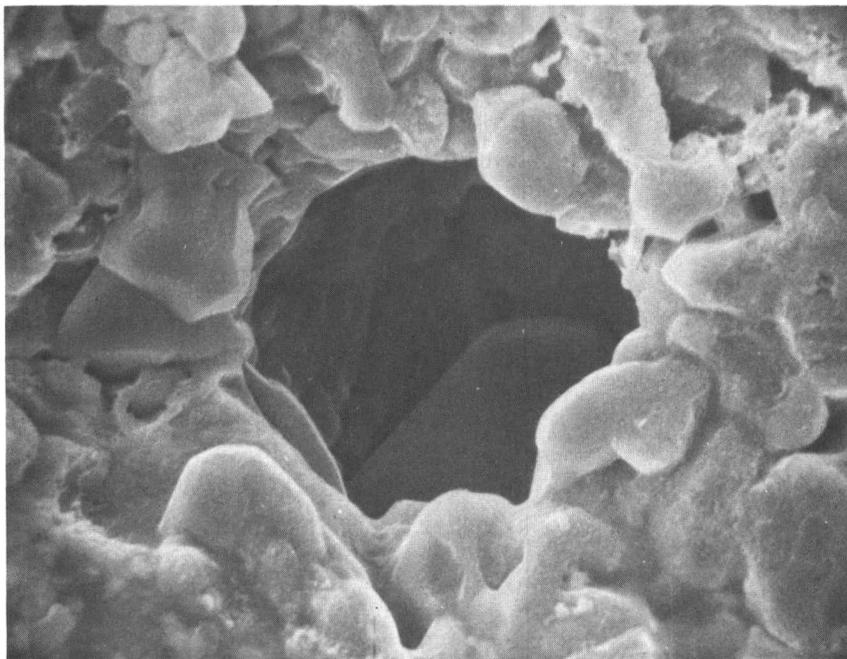


Figure 14

visible (Figures 13 and 14).

The probability that small channels or pores completely penetrate the coating will be a function of coating thickness. That is, granules with thicker coatings will release urea more slowly than those with thinner coatings because (1) the pathway for diffusion is longer, and (2) fewer pores will interconnect the urea solution inside the granule with the surrounding soil solution. In a companion study, Jarrell (1977) has described mathematically the effect of coating thickness on the rate of urea diffusion from individual SCU granules.

This hypothesized release mechanism for individual granules implies that the urea release for a fertilizer sample containing a large number of granules will be a function of both the mean coating thickness and the range in coating thickness.

SCU with Sealant. Petroleum-based wax and polyethylene-oil mixtures have been used by TVA to seal defects and pores in the sulfur coating. Once this sealant is removed, urea release occurs by the same mechanism as it does from SCU without sealant.

SEM views of SCU 4 granules (Figures 15-21) provided visual evidence that wax is removed microbially. The granule surface was initially obscured by the diatomaceous earth conditioner; a number of diatom skeletons were clearly visible (Figures 15 and 16). After 155 days in sterile soil, much less diatomaceous earth was visible, and agglomerates and/or individual crystals of wax were observed

Figure 15. Surface of SCU 4 (wax sealant) granule before exposure to soil (700X).

Figure 16. Surface of SCU 4 (wax sealant) granule before exposure to soil (2000X).

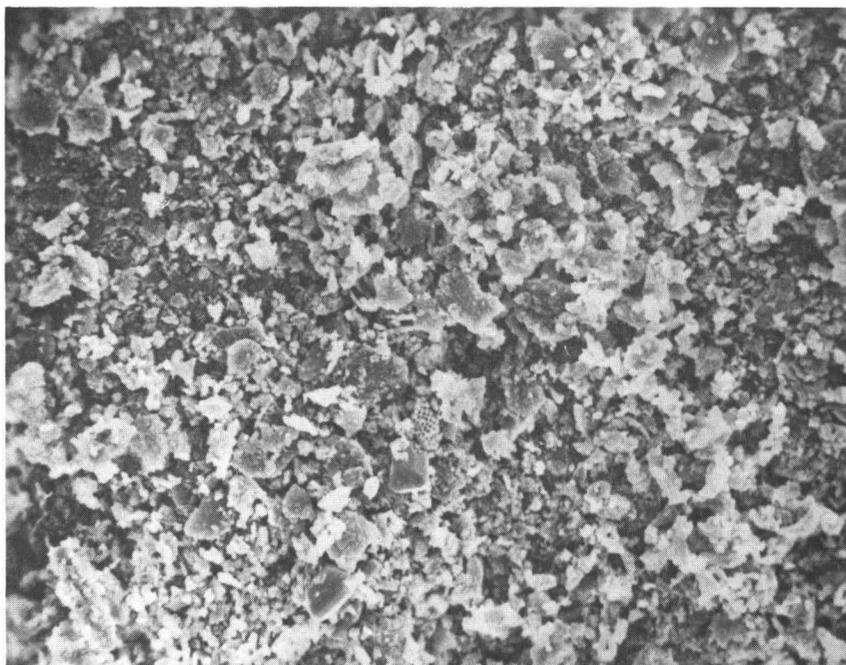


Figure 15

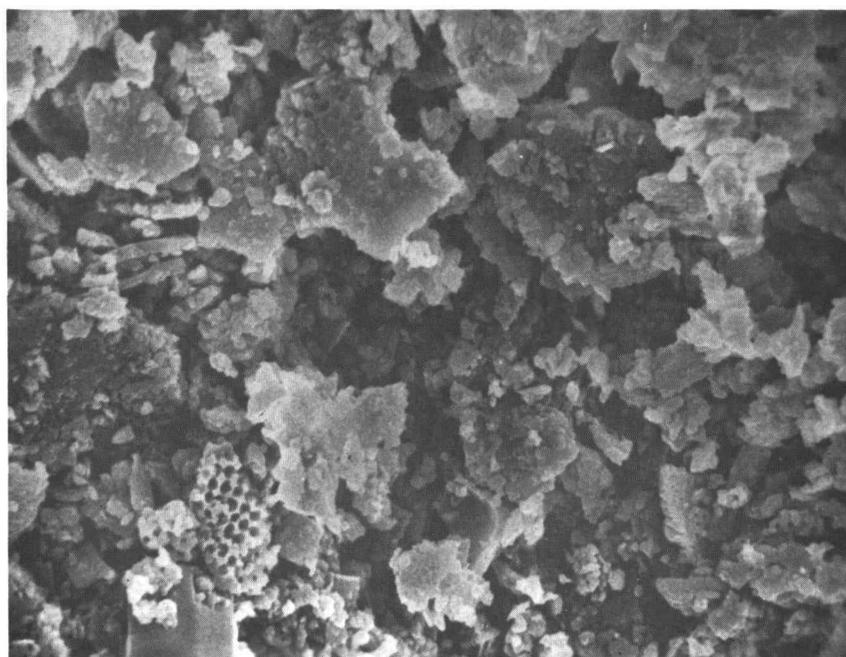


Figure 16

Figure 17. Surface of SCU 4 granule after incubation for 155 days on moist sterile soil at 25 C (700X).

Figure 18. Surface of SCU 4 granule after incubation for 155 days on moist sterile soil at 25 C (700X).

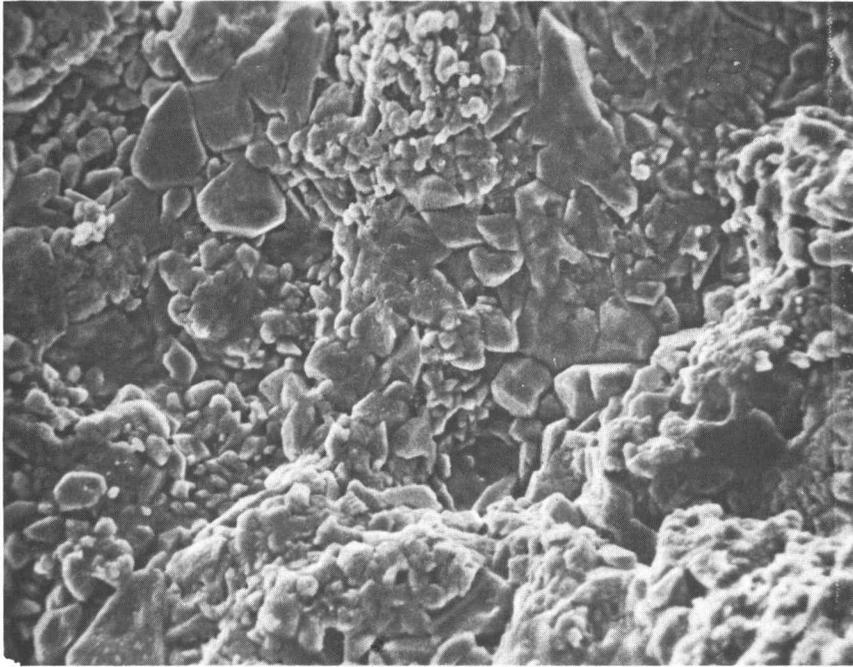


Figure 17

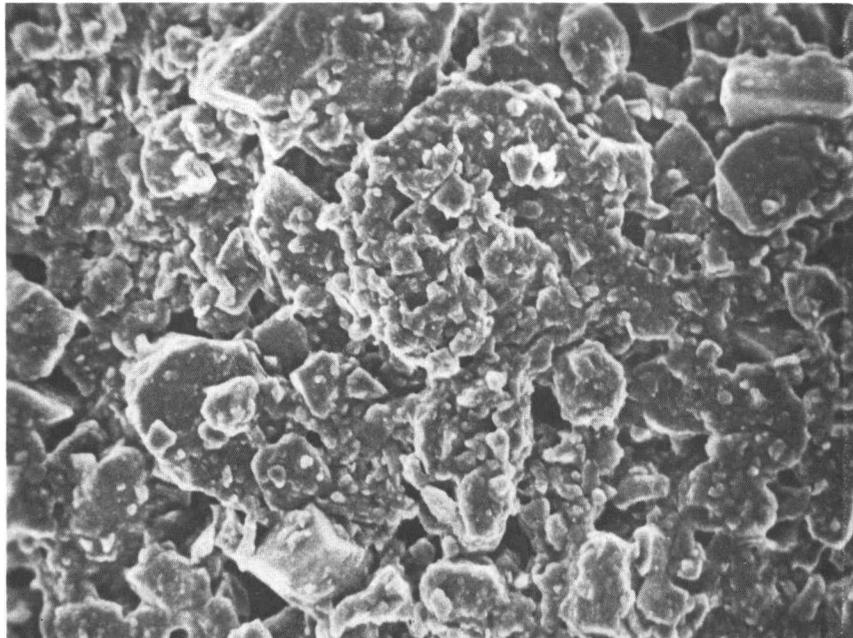


Figure 18

Figure 19. Surface of SCU 4 granule after incubation for 155 days on moist non-sterile soil at 25 C (700X).

Figure 20. Surface of SCU 4 granule after incubation for 155 days on moist non-sterile soil at 25 C (700X).

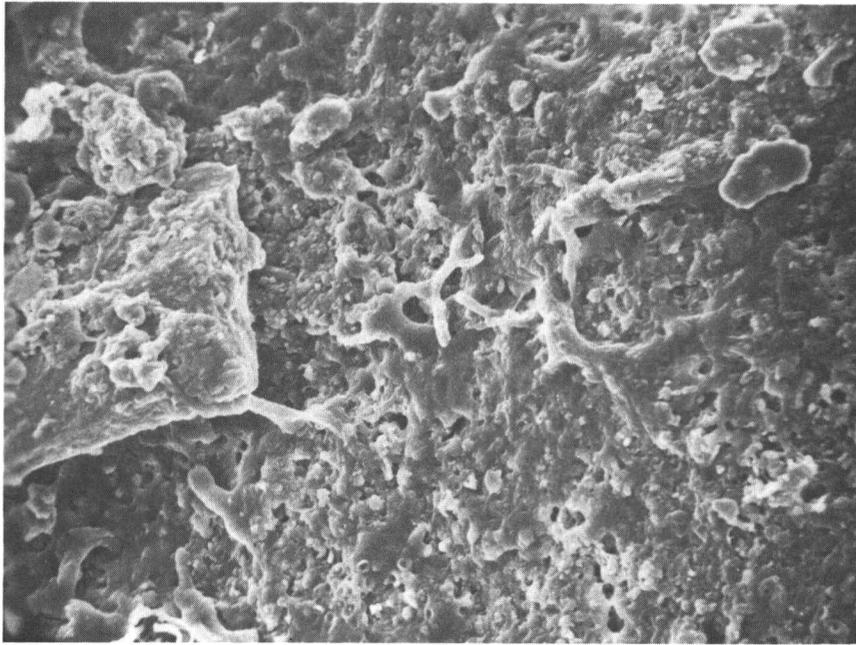


Figure 19

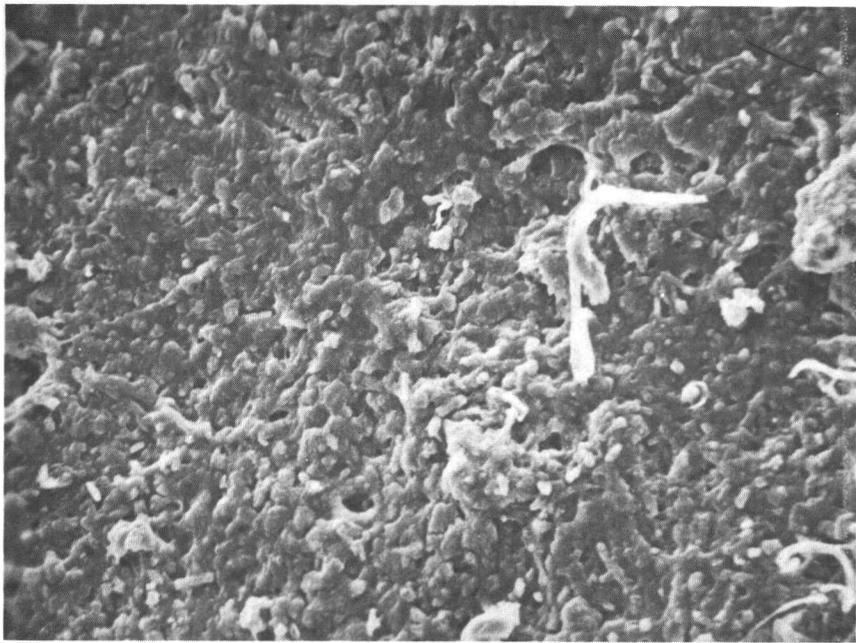


Figure 20

(Figures 17 and 18). After 155 days in non-sterile soil, fungal hyphae were very profuse, and the surface of the granule was much smoother (Figures 19-21), suggesting that at least part of the wax had been removed.

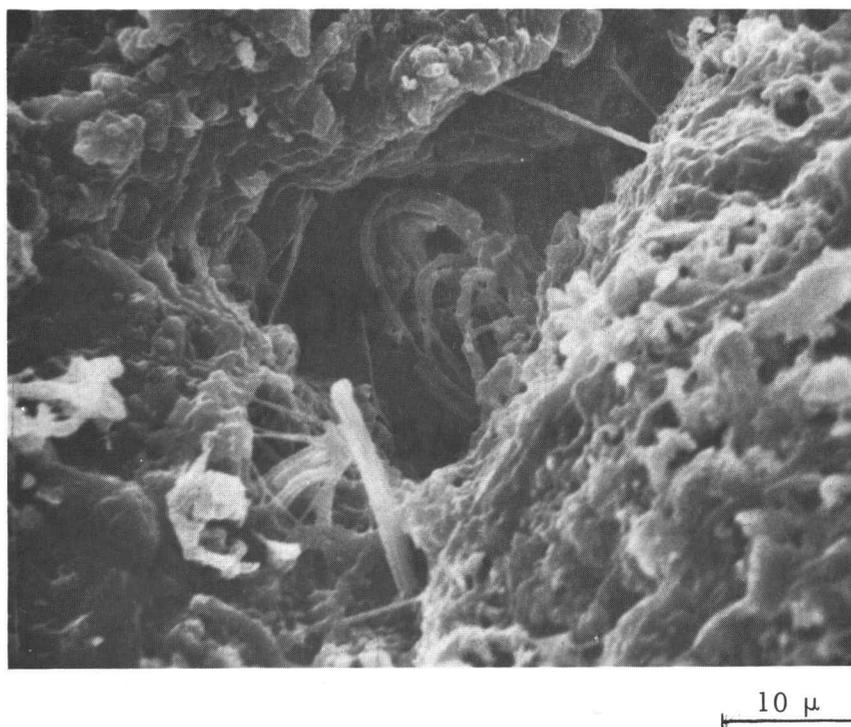


Figure 21. Surface of SCU 4 granule after incubation for 125 days on moist non-sterile soil at 25 C (2000X).

Microbial degradation of the polyethylene-oil sealant is apparently responsible for the urea release from SCU 25 (Figure 12). However, no difference was observed in coatings of granules incubated

for 125 days in sterile and non-sterile soil. The polyethylene-oil is stickier than the wax sealant, and much more diatomaceous earth adhered, obscuring the view of underlying material.

More than 100 species of bacterial, yeast, and fungi can oxidize hydrocarbons (ZoBell, 1969). In contrast, sulfur is oxidized by only a few species of slow-growing, autotrophic Thiobacillus (Burns, 1967). Many soil microorganisms degrade petroleum products, and nearly all petroleum-based compounds will be oxidized by at least one species (Ellis and Adams, 1961). It is very likely that some organisms are able to attack the brightstock oil which comprises 70% of the polyethylene-oil sealant.

SEM was used to compare the appearance of polyethylene-oil samples before and after soaking for 24 hours in toluene to remove oil. The sealant material changed from a dark brown to a light yellow color as a result of the toluene treatment. At 700X magnification, the sealant appeared very smooth before treatment and very porous after (Figures 22 and 23).

The evidence is inconclusive regarding the role of polyethylene-oil sealant in protecting granules and the mechanism by which urea is released from SCU sealed with it. If a polyethylene matrix remains after microbial oxidation of the oil, presumably that matrix is hydrophobic. Diffusion of urea in solution out of granules would be prevented if the channels were composed of a hydrophobic material and

Figure 22. Surface of polyethylene-oil (30:70 w/w) sealant material (700X).

Figure 23. Surface of polyethylene-oil sealant material after soaking in toluene for 24 hours to remove oil (700X).

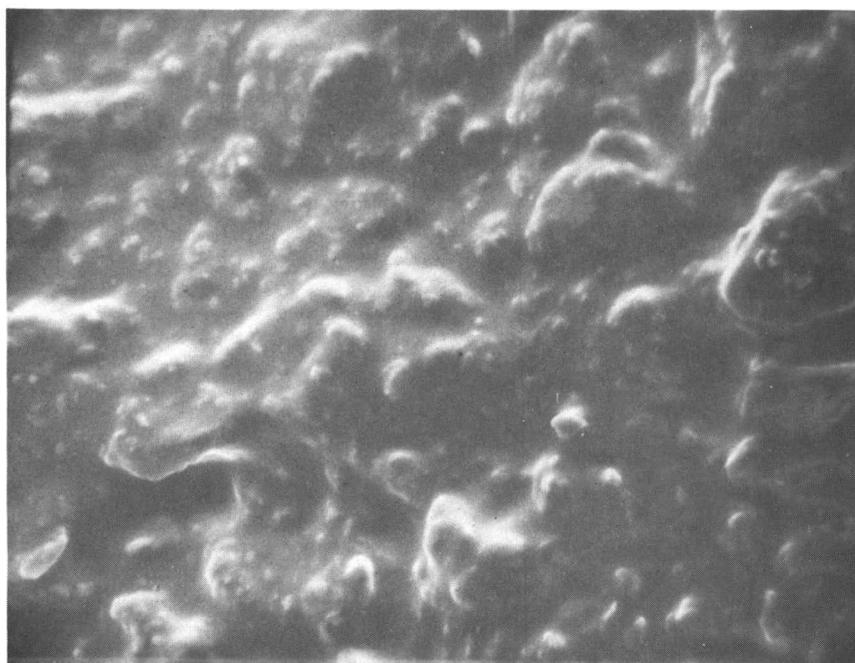


Figure 22

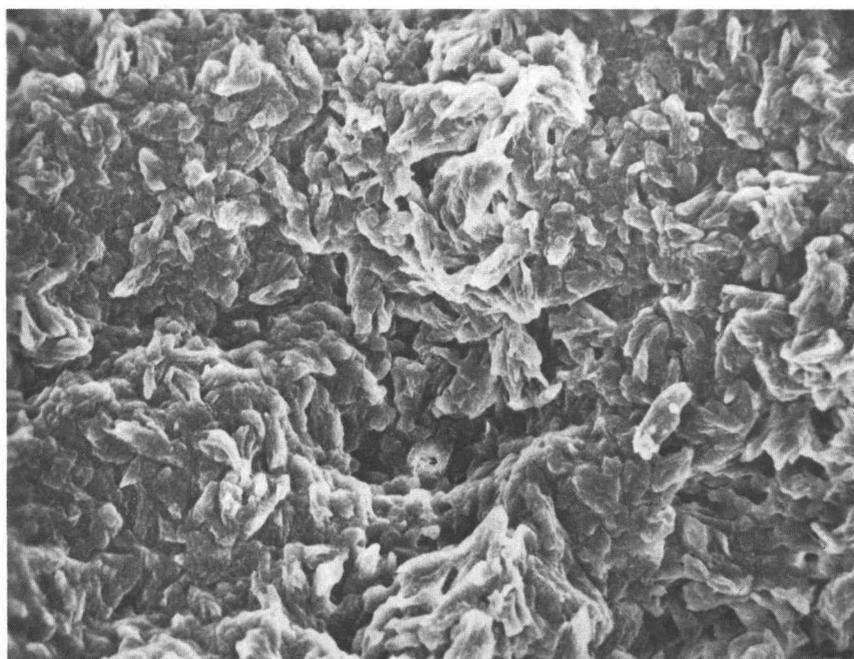


Figure 23

could not become water-filled. Perhaps the internal hydrostatic pressure could overcome this factor.

In summary, SEM studies have provided support for the hypothesis that microbial decomposition of the sealant is essential for urea release from wax-sealed SCU. It has also been shown that small openings in the sulfur coating are present prior to exposure of SCU to a soil environment. Finally, it has been shown that if oil is chemically removed from the polyethylene-oil sealant material, a porous matrix of polyethylene remains through which water may be able to diffuse. However, the actual process of polyethylene-oil sealant degradation was not elucidated.

Proposed Method for Determining the Long-Term Urea Release Pattern of SCU

Evidence has been presented which implies that urea release from SCU is related to the mean coating thickness and the coating thickness distribution or range. This hypothesis suggests that the difference in the urea release pattern for two SCU fertilizer materials will correspond to differences in the coating thickness distributions. Therefore, if the release pattern for one SCU fertilizer were known, the release pattern of a second SCU fertilizer could be determined by comparing the relative amounts of urea with corresponding coating thickness.

To calculate the coating thickness distribution, the total coating weight and urea weight of 60 individual granules each of SCU 4, 23, and 25 were determined (Equations 8 and 9). After the coating thickness for each granule was calculated, the range of coating thicknesses was divided into ten-micron increments, that is, 0-10, 10-20, 20-30, etc. The amount of urea in the granules falling into each increment was totalled and divided by the total urea in 60 granules to obtain the fraction of urea coated with a given thickness. The entire calculation is presented in Appendix III. The cumulative fraction of urea with less than a given coating thickness was plotted against the midpoint of the coating thickness increment (Figure 24). For example, considering SCU 4, about 64% of the urea had a calculated coating thickness of 90 microns or less.

The resulting plot is consistent with the urea release patterns of SCU 4, 23, and 25 (Figures 10-12). SCU 4 incubated in soil at 25 C initially released less urea than SCU 23 and 25, but after about 25 days, urea was released at a faster rate from SCU 4. This corresponds to the fact that although the mean coating thickness of SCU 4 is less than that of SCU 23 or 25 (Table 5), the latter two SCU materials have 10 to 20% urea with thinner coatings (Figure 24). Presumably this more thinly-coated urea is released first.

In the upper part of the release pattern the percent urea released and the corresponding coating thickness correlated reasonably well.

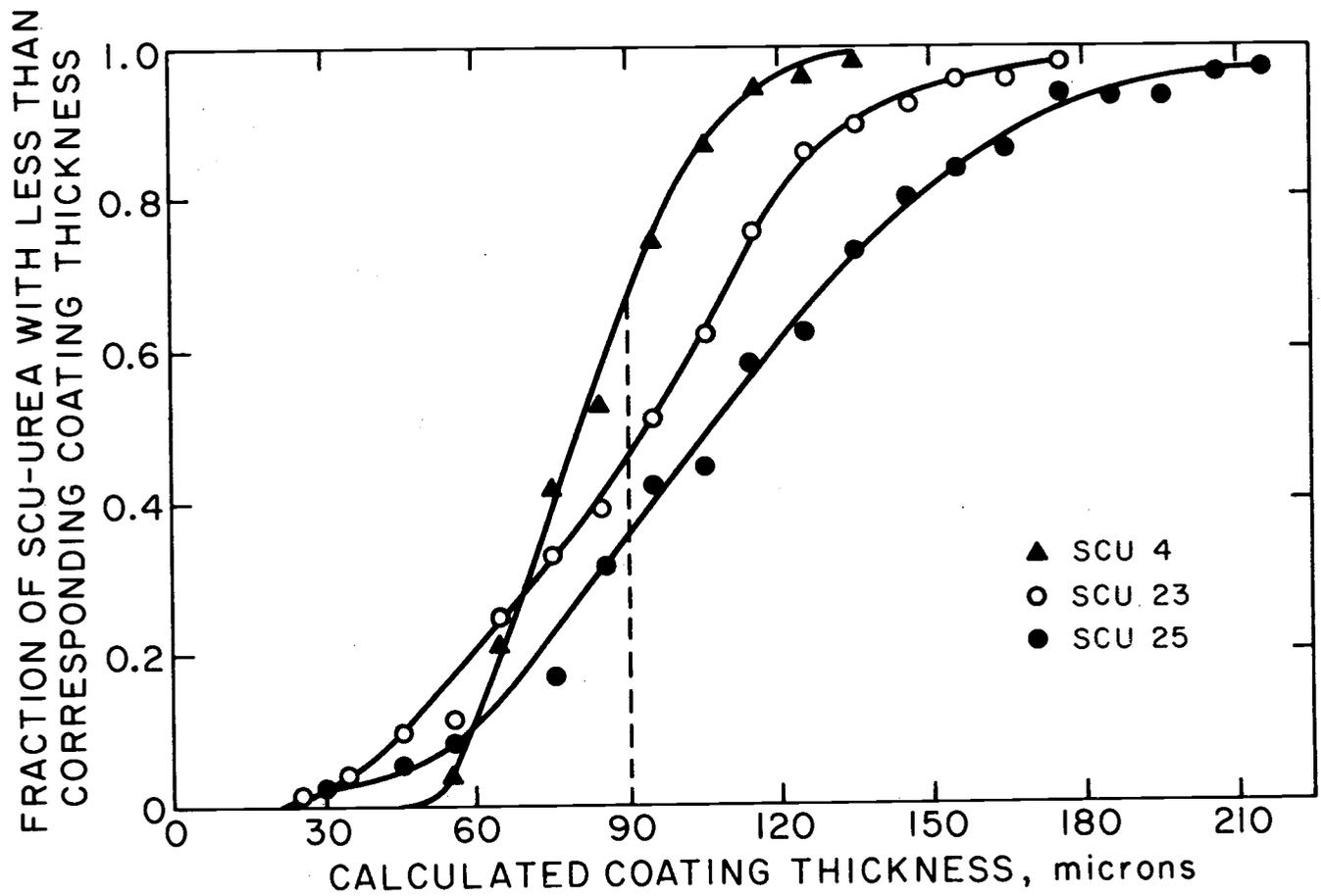


Figure 24. Coating (sulfur plus sealant) thickness distribution of SCU 4, 23, and 25.

For example, after 100 days, about 64, 47, and 35% of the urea had been released from (respectively) SCU 4, 23, and 25 subjected to the continuously wet treatment (Figures 10-12). These release rates correspond to the fraction of urea with a coating thickness of about 90 microns or less for all three fertilizers (Figure 24 broken line).

The correlation among coating thicknesses for the three SCU fertilizers at lower release percentages is not as good, probably because sealant effects are more important in that portion of the release pattern. The term "coating thickness" as used in this discussion refers to a calculated thickness based on the total (sulfur + sealant + conditioner) coating weight but without regard for the different densities of the three coating components. Since microbial degradation of the sealant appears to play an important role in urea release during the first few months after SCU application to the soil, it may be that the sealant thickness distribution and not the total coating thickness distribution will determine the urea release pattern of a particular SCU fertilizer. Possibly, the sealant thickness distribution could be determined by measuring the amount of sealant on a large number of individual granules.

No methods for determining the long-term urea release pattern of SCU have been published. The results of the above calculation suggest that the release patterns of newly produced SCU fertilizers could be quickly determined by a comparison of the calculated coating

thickness distributions of the new fertilizer and a "benchmark" SCU fertilizer. The release pattern of the latter would have been previously characterized for a range of environmental conditions. The comparison could be done in a few hours and would certainly provide a more accurate indication of the long-term release pattern than is now provided by the seven-day release test. It is also possible that manufacturing parameters could be manipulated to produce SCU fertilizers with a given coating thickness distribution and, therefore, a desired urea release pattern.

Summary

The first objective of this thesis was to determine the mechanism of urea release from SCU by measurement of urea release from SCU materials as a function of temperature, soil water potential, and soil sterility. Soil water content, temperature, and fertilizer physical properties were related to SCU urea release patterns over time periods of up to 22 weeks. The conventional seven-day release percentage was not an adequate indicator of the SCU release rate. For example, over a period of 125 days, SCU 4 applied to soil released urea at a faster rate than either SCU 23 or 25. The type of sealant and coating weight correlated with the long-term urea release rate.

It was found that the presence of both wax and polyethylene-oil sealant affected the rate of urea release over a period of four months

or longer. When SCU fertilizers with either of these two sealants were surface-applied to soil sterilized with propylene oxide, the rate of urea release was substantially reduced. In contrast, no significant difference in the rate of urea release from SCU without sealant was observed as a result of soil sterilization.

Both temperature and soil water potential were observed to influence the release of urea from wax-sealed SCU 4. Following a lag period of 25 days, urea was released about twice as fast at 35 C as at 25 C. Also, at 25 C, urea was released about twice as fast at a soil water potential of -5 bars as at -15 or -30 bars. However, the fact that urea release occurred significantly faster at -30 bars (non-sterile soil) than in moist sterile soil, suggests that release was a result of microbial degradation of the sealant and not the sulfur, since the sulfur-oxidizing bacteria (Thiobacillus spp.) would not be expected to be active below a water potential of about -15 bars.

Temperature and water potential effects on the release of urea from SCU 23 (no sealant) and SCU 25 (polyethylene-oil) sealant were less clearly demonstrated. Urea release rates for both products were sufficiently slow that data variability obscured most treatment effects. For both materials, release over a 30-day period was somewhat faster at 35 C and 25 C than at 5 and 15 C. Also, urea release from SCU 25 was faster at -30 bars water potential than at -5 or -15 bars,

possibly due to a reduction in microbial antagonism toward sealant-degrading organisms.

The results indicate that sealant material is removed by microorganisms and that the urea release pattern is determined by the rate of sealant removal and the thickness of the sulfur coating. Because the sealant removal process is microbial, it is more sensitive to environmental factors than the diffusion of urea through the sulfur coating.

The second objective of this thesis was to develop a rapid method to determine the long-term urea release pattern of a particular SCU fertilizer. A method was proposed for characterizing the long-term release rate of SCU fertilizers by calculating the cumulative coating thickness distribution. It was found that for the three SCU materials studied the amount of urea released after 100 days at 25 C corresponded to the amount of urea with a 90-micron or less coating thickness. Implications of this correlation for an improved method of quality control in the manufacture of SCU will be discussed in the final summary and conclusion.

SULFUR-COATED UREA FERTILIZATION OF TALL FESCUE

Introduction

Tall fescue (Festuca arundinacea Schreb.) is an important forage grass because of its ability to grow over a wide range of soil and climatic conditions. It is tolerant of both poor drainage and drought conditions and is one of the best grasses available for poorly drained soils under irrigation (Buckner and Cowan, 1973). It is native to Europe and was introduced to the U.S. by early settlers. The tall fescue cultivars 'Alta' and 'Ky. 31' became widely used in the 1940s (Cowan, 1956).

Tall fescue produces high yields under irrigation and high fertility (Buckner and Cowan, 1973). In early trials at Beltsville, Maryland in 1949-1950, tall fescue fertilized with 270 kg N/ha/yr as ammonium nitrate produced a dry matter yield of 11.0 mtons/ha/yr (Wagner, 1954).

However, as with many crops, the application of high rates of nitrogen fertilizer entails a risk of low nitrogen recovery and stand reduction. For example, in Virginia, an annual nitrogen fertilizer application of 900 kg N/ha resulted in a lower dry matter yield by 'Ky 31' tall fescue than an application of 450 kg N/ha. It was hypothesized by the researchers that the high nitrogen application increased plant respiration, which lowered carbohydrate reserves,

primarily fructosans. This increased susceptibility to frost and drought and reduced the rate of regrowth after clipping (Hallock, Brown, and Blaser, 1965).

Further work showed that stand reduction due to high rates of nitrogen was related to the morphological stage of growth and season. Stands were reduced by high nitrogen rates in the spring but during the summer were only slightly reduced (McKee, Brown, and Blaser, 1967).

The build-up of nitrate in forage to toxic levels has been another problem associated with large fertilizer nitrogen applications. Split applications of fertilizer have been advocated as a way to attain large yields but avoid high plant nitrate concentrations (Wedin, 1974).

Low recovery of fertilizer nitrogen by tall fescue as a result of high nitrogen rates has been reported. In a field experiment in eastern Colorado, irrigated tall fescue which received 90, 180, 360, and 720 kg N/ha each spring recovered 63, 42, 36, and 20% of applied nitrogen, respectively. At the two higher rates, stand loss was estimated at 30% (Dotzenko, 1961). Low fertilizer nitrogen recoveries also may occur because of ammonia volatilization, denitrification, and leaching losses of nitrate, although it is not known whether high levels of nitrate per se in the soil solution contribute to these losses.

It has not been shown whether the efficiency of nitrogen utilization by a crop in producing dry matter could be improved by supplying

the nitrogen at some optimal rate rather than in a single annual application. Hunt (1966) in a study of fertilizer nitrogen utilization by Italian ryegrass (Lolium multiflorum) found that following single applications of fertilizer, nitrogen was used rapidly and reached a maximum level in the plant tissue before a high dry matter level was reached. Raising the level of nitrogenous fertilizer application above 710 kg N/ha resulted in a decrease in dry matter yield, primarily due to lodging and stand thinning. He concluded that the only way to increase the total yield was to develop and grow a grass cultivar with a structure capable of utilizing more nitrogen under optimum light conditions.

Forage fertilization with a slowly available nitrogen source may permit high annual rates of nitrogen to be applied while avoiding stand reduction, low nitrogen recovery, excessive leaching losses, and denitrification losses. Sulfur-coated urea has received attention as a potential slow release fertilizer for forage crops (Tennessee Valley Authority, 1974).

In field experiments with cool season forage grasses, SCU fertilization has resulted in dry matter yields and nitrogen recoveries equivalent to or higher than split applications of ammonium nitrate. In Great Britain, perennial ryegrass (Lolium perenne) received 375 kg N/ha as SCU in a single spring application or as ammonium nitrate in a split application. The SCU-fertilized ryegrass produced higher

dry matter yields, nitrogen yields, and fertilizer nitrogen recoveries at one site, while at another site ammonium nitrate and SCU fertilization gave equivalent results (Davies, 1973).

In field experiments conducted in 1965-1967 by TVA in Alabama, SCU applied at rates of 84 and 168 kg N/ha was compared to ammonium nitrate as a nitrogen source for Ky. 31 tall fescue. The SCU used in these experiments had considerably more sulfur (30 to 44% S) and wax (4 to 5%) than later SCU fertilizers. The dry matter yields of tall fescue fertilized with SCU, urea, and ammonium nitrate were comparable; the main effect of applying nitrogen as SCU was to delay forage production to late-season cuttings (Allen, Mays, and Terman, 1968; Mays and Terman, 1969; Mays, 1970).

In other field studies conducted in Alabama, non-irrigated tall fescue was fertilized with SCU 4, SCU 21, or ammonium nitrate at a rate of 168 kg N/ha/yr (Allen and Mays, 1974). Over a two-year period, the highest dry matter yield resulted from a single SCU 4 application of 336 kg N/ha. A spring SCU 4 application of 168 kg N/ha or ammonium nitrate in a split application resulted in slightly lower dry matter yields. Spring applications (168 kg N/ha) of SCU 21 resulted in even lower yields. During the first year of the experiment, the application of 336 kg N/ha as SCU 4 resulted in a 50% higher yield than that resulting from application of 168 kg N/ha as either SCU 4 or ammonium nitrate, which suggests that the 168-kg N/ha/yr

application rate was considerably below the optimum.

In other experiments in the same report, single applications of SCU 16 and SCU 34 at rates of 84 and 168 kg N/ha/yr resulted in higher tall fescue yields than did split applications of ammonium nitrate. To measure the effect of residual nitrogen, no fertilizer nitrogen was applied the second year. The SCU-fertilized tall fescue produced more dry matter than the ammonium nitrate-fertilized fescue during the second year. The two-year yield totals for the SCU 34- and SCU 16-fertilized tall fescue (168-kg N/ha rate) were 35 and 26% higher than the yield of ammonium nitrate-fertilized tall fescue (Allen and Mays, 1974).

In some experiments, application of SCU resulted in lower forage yields than application of conventional nitrogen fertilizers, possibly due to the use of SCU fertilizers with very heavy sulfur coatings and consequent low release rates. In a greenhouse study in Alabama, nitrogen recovery by ryegrass (Lolium multiflorum) fertilized with SCU was very low (8 to 46%) compared to recovery of nitrogen by ammonium nitrate- and urea-fertilized ryegrass (46 to 59%). In a second greenhouse experiment, apparent nitrogen recoveries by SCU-fertilized ryegrass were much higher than in the first experiment (59 to 77%) and were comparable to recoveries by ammonium nitrate-fertilized ryegrass. The same SCU materials and rates of nitrogen were applied in the two experiments, and no

explanation was provided for the conflicting results (Allen, Terman, and Hunt, 1971).

The above-cited studies of forage fertilization with SCU suffer from one or more of the following limitations: First, only in one experiment (Allen and Mays, 1974) was the effect of residual fertilizer nitrogen measured; in fact, few experiments lasted more than two years. Second, the abundant evidence that very high rates of nitrogen reduce forage grass stands suggests that SCU may be superior to conventional fertilizer nitrogen sources at rates higher than 400 kg N/ha/yr, yet there have been no studies of forage fertilization comparing SCU and soluble nitrogen sources at rates higher than 375 kg N/ha/yr. Third, while nitrogen recovery by the crop is certainly the most important item on the nitrogen balance sheet, other items--in particular nitrate leaching losses--deserve some scrutiny. No studies have been published which compare leaching losses from soil fertilized with SCU and conventional nitrogen sources. This should be of particular interest when high rates of nitrogen are applied. Fourth, in all the studies the SCU fertilizers were inadequately characterized, particularly with regard to the long-term urea release rate in soil. This has made comparison of results from experiments using different SCU materials difficult. Furthermore, as SCU production methods and sealant materials have changed, SCU with similar coating weights may exhibit different urea release patterns.

The following field study was designed to compare dry matter yields and nitrogen recovery of tall fescue and nitrate leaching losses following fertilization with unconventionally high rates of nitrogen applied as urea and SCU.

Materials and Methods

Description of Field Plots and Treatments

The experimental site was located on a nearly level Woodburn silt loam soil (Aqualtic Argixeroll) at the Hyslop Crop Science Field Laboratory, Corvallis, Oregon.

The climate in the mid-Willamette Valley is characterized by warm, dry summers and cool, wet winters. The mean annual precipitation is 100 cm. About 72% of the precipitation occurs during November through March, with only about 2% occurring in July and August (Bates and Calhoun, 1975). The average temperature during November through March is 42.7 F (5.9 C) and from April through October of 59.1 F (15.1 C) (Bates and Calhoun, 1975). The mean annual temperature is 52.3 F (11.3 C).

Plots (1.52 m x 6.10 m) were arranged in a randomized block design with three blocks. All plots received a blanket surface application of 47 kg K/ha in August 1972, 112 kg K/ha in November 1973, and 100 kg K/ha in March 1976.

Two cultivars of tall fescue (Festuca arundinacea Schreb. , var. Fawn and Selection 1000) were seeded in August 1972. Nitrogen fertilizer as either SCU 4, SCU 30, or urea was surface-applied in August 1972, November 1973, and November 1974 at approximate rates of 200, 400, 600, and 800 kg N/ha (Tables 1 and 7). No fertilizer was applied in the fall of 1975 to determine the effect of residual fertilizer nitrogen on tall fescue yield. The urea fertilizer was blended with ammonium sulfate to provide adequate sulfur for tall fescue growth. The blended fertilizer contained 40% N and 4% S. Urea (plus ammonium sulfate) was also applied in five increments during each growing season at annual rates of 980 kg N/ha in 1972-73, 700 kg N/ha in 1973-74, and 800 kg N/ha in 1974-75 (Table 7).

The tall fescue was sprinkler irrigated from June to September each year from 1973 through 1976, receiving about 50 cm of water each summer. The tall fescue was underirrigated so that little or no nitrate leaching below the root zone would occur during the summer months.

The tall fescue was harvested five times in 1973, 1974, and 1975 and three times in 1976 (Table 8). A strip (0.91 m wide x 6.10 m long) was mowed to a height of about five cm. In 1973-74, plots were clipped with a sicklebar mower and raked. In 1975-76, a flail mower was used. The clipped forage was weighed, and the remaining plot area was clipped and raked. No attempt was made to harvest the

Table 7. SCU 4, SCU 30, and urea fertilizer applications to tall fescue grown on Woodburn silt loam soil.

Application date	Treatment, kg N/ha/yr				Split ¹
	200	400	600	800	
	- - - - Actual applied, kg N/ha - - - -				
8/72	196	392	589	785	196
3/73					196
5/73					196
6/73					196
8/73					196
Total	196	392	589	785	980
11/73	200	400	600	800	60
3/74					160
5/74					160
6/74					160
8/74					160
Total	200	400	600	800	700
11/74	200	400	600	800	160
3/75					160
5/75					160
6/75					160
8/75					160
Total	200	400	600	800	800
Grand total 1972-1975	596	1192	1789	2385	2480

¹ Only urea was applied incrementally.

Table 8. Harvest dates for tall fescue plots, 1972-76.

1973	1974	1975	1976
3/21	3/19	3/26	4/6
5/14	5/4	5/14	6/2
6/29	6/14	6/26	8/13
8/15	8/14	8/19	
10/2	9/23	10/15	

grass in the same stage of growth each time, but usually the grass was in the early bloom stage, depending somewhat on the nitrogen fertilizer rate.

Fresh weights were recorded, and one subsample was taken from each of triplicate plots. These subsamples were combined to provide one sample per treatment for dry matter and nitrogen determination. Dry matter content was determined gravimetrically after drying samples for 48 hrs at 70 C.

Total nitrogen content of the tall fescue was determined on each sample using a Kjeldahl digestion method modified to include nitrate-nitrogen (Bremner, 1965).

Statistical Analysis of Dry Matter Yields. Tall fescue dry matter yields were analyzed as a randomized block design with the following factors: blocks, fertilizers, tall fescue cultivars, and rates of nitrogen. The treatments which involved incremental application of urea were excluded to simplify the analysis of variance.

Only cumulative annual yields were subjected to an analysis of variance. Results obtained by Terman (1972) from ten greenhouse and three field experiments indicate that statistical analyses of cumulative yields are usually more meaningful and result in lower coefficients of variability than do analyses of individual clipping yields.

Fertilizer Nitrogen Recovery by Tall Fescue

The apparent recovery of fertilizer nitrogen for the 1973-1976 period was calculated with the following equation:

$$\% \text{ Recovery} = \frac{N_{\text{crop}} - N_{\text{check}}}{N_{\text{applied crop}} - N_{\text{applied check}}} \times 100 \quad (9)$$

where

N_{crop} = N yield of tall fescue (1973-76), kg/ha

N_{check} = N yield of tall fescue (1973-76) fertilized annually with 200 kg N/ha, kg/ha

$N_{\text{applied crop}}$ = N applied (1973-76), kg/ha

$N_{\text{applied check}}$ = N applied (1973-76), to check, kg/ha.

The value for N_{check} represents nitrogen yields of tall fescue receiving the check treatment, that is, the lowest rate of nitrogen fertilizer. Because there were three nitrogen fertilizer sources (urea, SCU 4, and SCU 30), there are three possible values of N_{check} for each cultivar. N_{check} was designated as the lowest of the three values for each cultivar.

Nitrate Leaching Losses

Soil solution samplers were installed on plots seeded to Fawn tall fescue and receiving the following fertilizer treatments:

- (1) SCU 4, 400 kg N/ha/yr, fall-applied
- (2) SCU 4, 800 kg N/ha/yr, fall-applied
- (3) Urea, 400 kg N/ha/yr, fall-applied
- (4) Urea, 800 kg N/ha/yr, incrementally-applied.

Soil solution samples were collected during the second, third, and fourth winters (1973-1974, 1974-75, and 1975-76) from a depth of 91 cm at two- to four-week intervals. The sampling apparatus consisted of a 7 x 4-cm porous ceramic cup (air bubbling pressure = one bar) sealed to a 95-cm length of PVC plastic pipe (4.4-cm inside diameter). The samplers were placed in the soil in a hole slightly larger in diameter than the plastic pipe. The space around the sampler was filled with sieved, dry Woodburn silt loam soil (Figure 25). Two soil solution samplers were installed on each of the triplicate plots.

Soil solution samples were collected by pulling a vacuum on each ceramic cup of about 0.5 bars with a hand pump, waiting for about 24 hours, and then collecting the accumulated water, usually 30 to 100 mls.

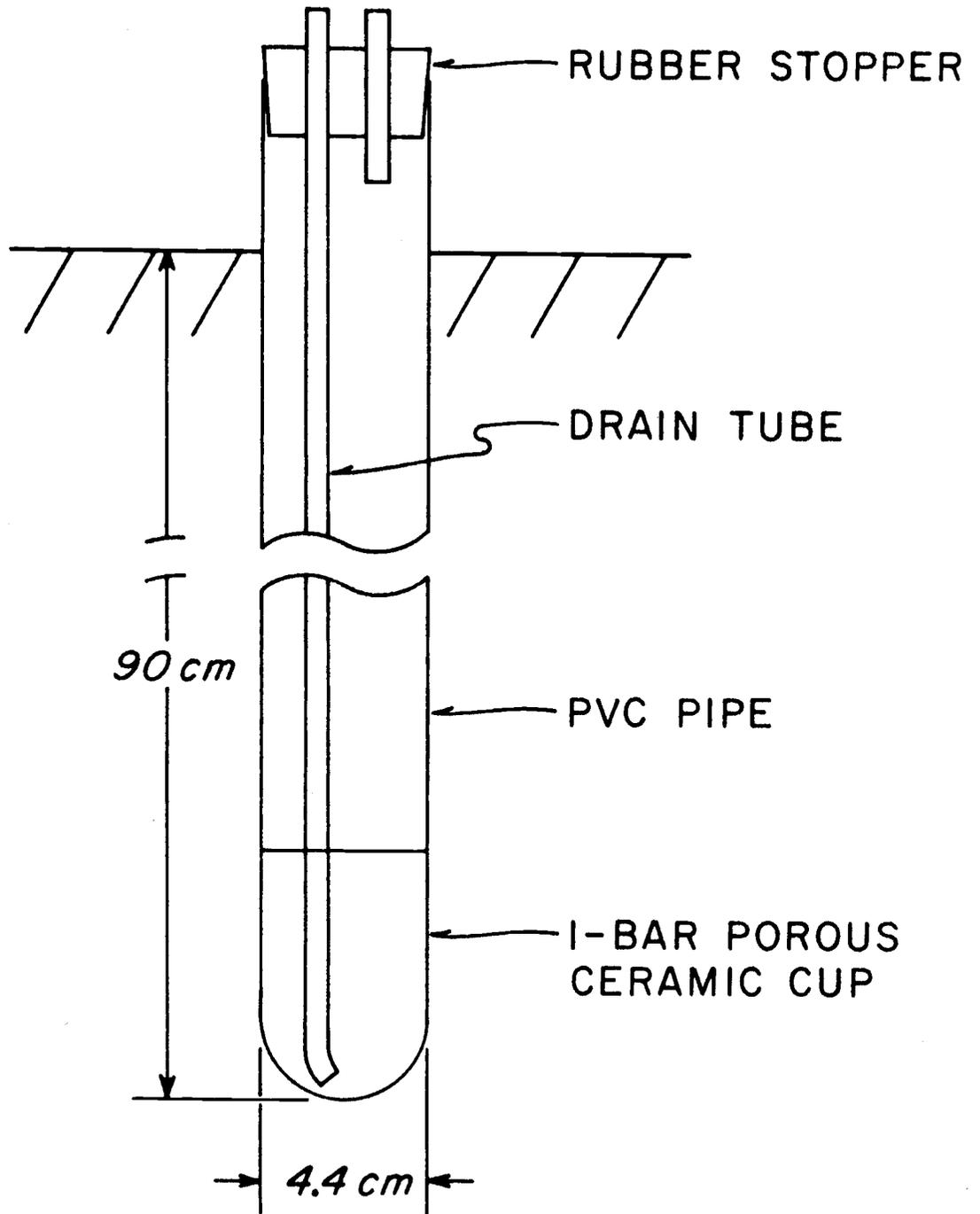


Figure 25. Cross-sectional view of soil solution sampler.

Soil solution samples were stored at 3 C until analyzed for nitrate by a colorimetric procedure using chromotropic acid (West and Ramachandran, 1966). Several drops of 500-ppm phenylmercuric acetate were added to all samples to inhibit microbial activity. Some samples were analyzed with an Orion nitrate-specific electrode. The accuracy of the electrode was verified by comparing the apparent nitrate concentration of selected samples with and without additions of standard nitrate solutions.

The nitrate-nitrogen leached below a depth of 91 cm was calculated with the following equation:

$$\text{NO}_3^- \text{-N lost} = (\text{Rain})(\text{NO}_3^- \text{-N conc.})(0.1) \quad (10)$$

where

$$\text{NO}_3^- \text{-N lost} = \text{leaching loss, kg N/ha}$$

$$\text{Rain} = \text{precipitation during a sampling period, cm}$$

$$\text{NO}_3^- \text{-N conc.} = \text{NO}_3^- \text{-N concentration in sample, mg/l}$$

$$0.1 = \text{factor to convert rain depth into a volume of water per hectare.}$$

The midpoints in time between successive sampling dates were determined. A sampling period was defined as the time between two successive midpoints. The beginning of the first sampling period each year was arbitrarily set at November 1, and the end of the last sampling period was arbitrarily set at March 31.

The lateral movement of nitrate was measured by collection of soil solution samples at different distances from the boundary between a fertilized and unfertilized fallow plot. Plots (3.05 m x 3.05 m) were laid out on fallow soil in a completely randomized block design of three blocks. Three plots received 800 kg N/ha as KNO_3 (5.72 kg KNO_3 /plot). The other three plots received no fertilizer. Soil solution samplers (Figure 25) were installed to a depth of 91 cm as on the tall fescue plots. On fertilized plots, soil solution samplers were installed at distances of 30, 76, 122, and 183 cm from the boundary separating the fertilized and unfertilized plots. Soil solution samplers were installed on unfertilized plots at distances of 30, 76, and 122 cm from the plot boundary. In addition, two samplers were installed on each fertilized plot at a 45-degree angle to the same vertical depth (91 cm). Soil solution samples were collected 31 and 52 days after the KNO_3 fertilizer was applied. During the 31 days, 19.1 cm of rain fell, and 2.1 cm fell during the subsequent 21 days. The nitrate concentration of samples was determined with an Orion nitrate-specific electrode.

Soil Nitrate and Extractable Ammonium

Soil samples were collected in August 1976, following the last harvest from plots which had received the following fertilizer treatments:

- (1) SCU 4, 400 kg N/ha/yr, fall-applied
- (2) SCU 4, 800 kg N/ha/yr, fall-applied
- (3) Urea, 400 kg N/ha/yr, fall-applied
- (4) Urea, 800 kg N/ha/yr, incrementally-applied.

In addition, samples were collected from fallow, unfertilized soil.

Soil samples from 0-30 cm, 30-61 cm, and 61-91 cm depths were collected with a 1.8-cm diameter punch probe. Ten cores were collected from each sampled plot. The moist soils were placed in plastic bags and stored at 3 C for about 24 hours.

The moist samples were mixed thoroughly by hand and subsampled for a gravimetric determination of water content. A second subsample (80 g) was weighed into a 250-ml plastic bottle and shaken for one hour with 150 mls of 2-N potassium chloride. After shaking, the soil suspension was centrifuged at 9000X for 15 minutes, and the clear supernatant was decanted and stored at 3 C for 24 hours until analysis for nitrate- and ammonium- nitrogen content (Bremner and Keeney, 1966).

Soil Total Nitrogen

After subsampling for nitrate and ammonium analysis, the soil samples were air-dried for one week. Three-gram subsamples were then analyzed for total nitrogen (Bremner, 1965).

Soil pH

The pH of the air-dried soil samples was measured with a glass electrode after 50-g samples of the soil were brought to a saturated paste condition with distilled water and allowed to equilibrate for 30 minutes.

Results and Discussion

Tall Fescue Dry Matter Yields

1973. In 1973, annual tall fescue yields (Tables 9 and 13) were generally not affected by fertilizer nitrogen source. An exception was the very high yield of var. Fawn when fertilized with SCU 30 at a rate of 800 kg N/ha. This high yield was primarily due to the high yields in May and June. Also, S. 1000 tall fescue fertilized with a split application of urea (980 kg N/ha) produced more dry matter than then tall fescue fall-fertilized with 800 kg N/ha either as SCU or urea.

The tall fescue generally responded to increases in the rate of nitrogen up to and including the 600-kg N/ha rate, with the exception of var. Fawn fertilized with SCU 4. Both cultivars produced a significantly higher dry matter yield when fertilized with 800 kg N/ha as SCU 30 as compared to 600 kg N/ha. In contrast, neither cultivar responses to the increase from 600 to 800 kg N/ha fall-applied as urea. S. 1000, but not var. Fawn tall fescue, responded to the

increase from 600 to 800 kg N/ha applied as SCU 4.

Var. Fawn tall fescue generally produced more dry matter than S. 1000 when fertilized with SCU 4 or SCU 30, but not when fertilized with urea.

Table 9. Yield of irrigated tall fescue in 1973 grown on Woodburn silt loam.

Fertilizer	N applied kg/ha/yr			
	200	400	600	800
- - Dry matter, metric tons/ha ¹ - -				
<u>Var. Fawn</u>				
Urea	9.00	14.41	17.41	18.91 ²
SCU 30	10.82	14.03	16.88	21.04a ²
SCU 4	10.10	15.12	16.54	17.65
Urea (split) ³				18.49
<u>S. 1000</u>				
Urea	9.88	13.20	17.42a	18.76
SCU 30	9.55	11.69	15.08	17.65
SCU 4	8.85	13.56	15.38	18.00
Urea (split) ³				20.55

¹Total of five cuts; average of triplicate plots.

²Letters indicate a significant difference within rates and varieties at the 5% level as determined by Duncan's multiple range test. $s_{\bar{x}} = 0.63$ mtons/ha, $LSD_{.05} = 1.79$ mtons/ha.

³980 kg N/ha applied from previous fall through 1973 harvest season.

1974. In 1974, following an unusually wet winter (159 cm precipitation from November 1 to April 1), tall fescue fall-fertilized with urea produced lower annual yields than tall fescue which had received SCU 4 or SCU 30 in the fall at rates of 400, 600, and

800 kg N/ha or urea in a split application (Tables 10 and 13). This could have been a result of higher leaching losses from the urea-fertilized plots and carry-over nitrogen from the 1972 application of SCU.

Table 10. Yield of irrigated tall fescue in 1974 grown on Woodburn silt loam.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - Dry matter, metric tons/ha ¹ - -			
<u>Var. Fawn</u>				
Urea	9.02	10.52	11.77a ²	12.57a
SCU 30	10.20	12.09	14.31b	16.61
SCU 4	10.55	14.40a	16.86c	17.86
Urea (split) ³				16.15
<u>S. 1000</u>				
Urea	8.56	7.84a	10.49a	10.29a
SCU 30	9.78	11.39	13.15b	13.77b
SCU 4	8.45	13.06	15.96c	16.42c
Urea (split) ³				14.51bc

¹Total of five cuts; average of triplicate plots.

²Letters indicate a significant difference within rates and varieties at the 5% level as determined by Duncan's multiple range test. $s_{\bar{x}} = 0.68$ mtons/ha, $LSD_{.05} = 1.94$ mtons/ha.

³698 kg N/ha applied from previous fall through 1974 harvest season.

In 1974, larger tall fescue yields were obtained with SCU 4 than with SCU 30 fertilizer applications at the higher nitrogen application rates. More residual nitrogen must have remained on those plots which received the slower releasing SCU 4 in the previous year.

The extent of yield increase with nitrogen application depended on the fertilizer used. Only small, statistically insignificant increases in dry matter yield resulted from fall application of higher rates of urea. In contrast, nitrogen applications up to 600 kg N/ha applied as SCU 4 or 30 resulted in higher yields. Only var. Fawn fertilized with SCU 30 produced a significant response to the increase in applied nitrogen from 600 to 800 kg N/ha.

Var. Fawn produced higher dry matter yields than S. 1000, regardless of nitrogen source or rate.

1975. In 1975, tall fescue fall-fertilized with SCU outyielded tall fescue which received urea in the fall at equivalent rates of nitrogen application (Tables 11 and 13). Application of SCU 4 generally resulted in higher yields than did application of SCU 30 and at the one rate tested resulted in an equivalent yield to that obtained by a split application of urea. As in 1974, the results may be explained by carry-over nitrogen from previous applications of SCU. Precipitation in 1974-1975 was below average (85 cm from November 1 to April 1), and it seems less likely than in the previous year that leaching losses would have contributed to the poor yields of urea-fertilized tall fescue.

Because of rate x variety and rate x fertilizer interactions, the interpretation of tall fescue response to fertilizer nitrogen rate is complex. Generally, S. 1000 was much less responsive to additional nitrogen than var. Fawn. Again, as in 1974, only var. Fawn

fertilized with SCU 30 produced a significant yield increase when the annual rate of nitrogen was increased from 600 to 800 kg/ha. Thus, SCU 4-fertilized Fawn tall fescue outyielded SCU 30-fertilized Fawn tall fescue at 200, 400, and 600 kg N/ha but not at 800 kg N/ha.

The rate x variety interaction also complicates comparison of varietal yields. Generally, at nitrogen rates of 200 and 400 kg N/ha S. 1000 outyielded var. Fawn, while at 600 and 800 kg N/ha there were no significant yield differences between cultivars.

Table 11. Yield of irrigated tall fescue in 1975 grown on Woodburn silt loam.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
- - Dry matter, metric tons/ha ¹ - -				
<u>Var. Fawn</u>				
Urea	8.79b ²	10.34c	12.47c	13.56c
SCU 30	9.85ab	12.83b	14.90b	16.50b
SCU 4	11.32a	14.14a	17.27a	17.07ab
Urea (split) ³				18.26a
<u>S. 1000</u>				
Urea	11.62b	11.11b	12.60c	13.29c
SCU 30	13.68a	14.08a	14.39b	15.52b
SCU 4	11.37b	15.09a	16.51a	17.31a
Urea (split) ³				17.12a

¹ Total of five cuts; average of triplicate plots.

² Letters indicate a significant difference within rate and varieties at the 5% level as determined by Duncan's multiple range test. $s_{\bar{x}} = 0.56$ mtons/ha; $LSD_{.05} = 1.60$ mtons/ha.

³ 160 kg N/ha applied in the fall of 1974 and at each of the first four harvests in 1975 (= 800 kg N/ha total).

1976. To permit measurement of residual nitrogen, no nitrogen fertilizer was applied in the fall of 1975. Total dry matter yields in 1976 were generally less than half the yields obtained in the previous years (Tables 12 and 13). Tall fescue fertilized with urea during 1972-1974 yielded significantly lower than tall fescue which received SCU during those years, indicating there was a substantial carry-over of SCU nitrogen from previous years.

Table 12. Yield of irrigated tall fescue in 1976 grown on Woodburn silt loam.

Fertilizer	N applied, kg/ha/yr ¹			
	200	400	600	800
	- - Dry matter, metric tons/ha ² - -			
<u>Var. Fawn</u>				
Urea	5.30	4.43a ³	4.94a	4.90a
SCU 30	5.82	5.57	6.49	7.18
SCU 4	5.69	5.81	6.60	7.97
Urea (split)				7.31
<u>S. 1000</u>				
Urea	5.84a	5.27a	4.87a	5.13a
SCU 30	7.64b	6.54b	6.75	7.02
SCU 4	6.58ab	5.86ab	6.66	8.21
Urea (split)				7.09

¹Tall fescue not fertilized in fall 1975 or 1976. Split application of urea applied in spring-summer of 1975.

²Total of three cuts; average of triplicate plots.

³Letters indicate a significant difference within rates and varieties at the 5% level as determined by Duncan's multiple range test. $s_{\bar{x}} = 0.40$ mtons/ha, $LSD_{.05} = 1.14$ mtons/ha.

Table 13. Summary of analyses of variance of tall fescue dry matter yields.

Factor	1975	1974	1975	1976
Fertilizer (F)	NS ¹	**	**	**
Variety (V)	** ²	**	**	**
Rate (R)	**	**	**	**
R x F	**	**	**	**
R x V	NS	NS	**	**
V x F	**	NS	NS	NS
R x V x F	NS	NS	NS	NS

¹NS = F value not significant at .05 level of probability.

²** = F value significant at .01 level of probability.

Pooled error term used for determination of all F values.

The tall fescue previously fertilized with SCU 30 did not respond to previous nitrogen applications above 200 kg N/ha/yr, but SCU 4-fertilized fescue did respond to the rate increase from 600 to 800 kg N/ha/yr.

The tall fescue which had received split applications of urea produced yields in 1976 equivalent to the SCU-fertilized fescue. It should be noted that whereas the last fall fertilizer application was in November 1974, the fescue which received the split application of urea was fertilized during the growing season in 1975 (Table 7).

In 1976, as in 1975, S. 1000 produced more dry matter at the two lower rates of nitrogen, while little difference was observed in cultivar yields at the two higher nitrogen application rates.

1973-1976 (Table 14). Fertilization of tall fescue with either SCU 4 or SCU 30 resulted in higher four-year yields than fertilization with fall-applied urea. At all nitrogen application rates, SCU-fertilized tall fescue produced about 20% more dry matter than tall fescue fertilized with urea in the fall. This appears to be a result of carry-over nitrogen on the SCU-fertilized plots and/or losses of nitrogen through leaching, denitrification of ammonia volatilization from urea-fertilized plots. At the one nitrogen rate tested (800 kg N/ha/yr) fall application of SCU 4 and SCU 30 resulted in dry matter yields equivalent to those resulting from application of urea in five increments during the growing season each year.

Table 14. Four-year total yield of irrigated tall fescue grown on Woodburn silt loam, 1973-1976.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
- - Dry matter, metric tons/ha - -				
<u>Var. Fawn</u>				
Urea	32.1b ¹	39.7c	46.6c	49.9b
SCU 30	38.5a	44.5b	52.6b	61.3a
SCU 4	37.7a	49.5a	57.3a	60.6a
Urea (split)				60.2a
<u>S. 1000</u>				
Urea	35.9b	37.4b	45.4b	47.5c
SCU 30	40.7a	43.7a	49.4b	54.0b
SCU 4	35.3b	47.6a	54.5a	59.9a
Urea (split)				59.3a

¹ $s_{\bar{x}} = 1.50$ mtons/ha, $LSD_{.05} = 4.28$ mtons/ha.

If the four-year yield total is considered, SCU 4 was superior to SCU 30 as a nitrogen source at the 400- and 600-kg N/ha/yr rates for var. Fawn tall fescue and at the 400-, 600-, and 800-kg N/ha/yr rates for S. 1000 tall fescue.

Both cultivars produced significant dry matter yield increases with increased nitrogen applied as SCU 4 or SCU 30. When nitrogen was fall-applied as urea, var. Fawn, but not S. 1000, responded to all nitrogen rate increases from 200 to 800 kg N/ha/yr.

The average total yields for the four-year period for all nitrogen rates and sources were 48.5 and 47.0 mtons/ha for var. Fawn and S. 1000 respectively. Large differences in yields of the two cultivars were observed only when 600 or 800 kg N/ha/yr as SCU 30 was applied, in which cases, var. Fawn produced higher yields.

Seasonal Distribution of Dry Matter Yields

In Oregon, tall fescue produces most of its annual yield in the spring months, and although forage quality tends to be lower later in the season, it would be desirable to produce a higher percentage of the total annual yield later in the summer.

In 1974 and 1975, tall fescue fertilized with either SCU 4 or SCU 30 generally produced a higher percentage of its annual yield in the summer and fall harvests than when fertilized with fall-applied urea (Table 15).

Table 15. Dry matter yield of tall fescue harvested at fourth and fifth cutting.

Fertilizer	Year	N applied, kg/ha/yr							
		Var. Fawn				S. 1000			
		200	400	600	800	200	400	600	800
- - - - - Percent of annual yield - - - - -									
Urea	1973	14	21	26	34	20	26	30	33
	1974	12	21	17	23	16	13	18	26
	1975	24	21	25	27	28	20	23	30
SCU 30	1973	19	22	25	28	23	21	25	30
	1974	14	16	27	33	22	19	29	34
	1975	33	34	36	38	40	35	35	36
SCU 4	1973	19	20	23	25	21	24	28	30
	1974	38	35	37	42	32	37	42	42
	1975	38	40	47	44	41	42	49	44
Urea (split)	1973				39				38
	1974				45				50
	1975				46				47

At the 800 kg N/ha/yr application rate, tall fescue fertilized with a split application of urea produced a higher percent of its total dry matter yield at the fourth and fifth (summer and fall) cuttings than did tall fescue fall-fertilized with either SCU or urea (Table 15). In fact, in 1974 and 1975, tall fescue which received the split application of urea produced higher yields at the fourth and fifth cutting than at the first three cuts in the spring, that is, more than 40% of the total yield was produced at the fourth and fifth cuttings.

The temperature dependence of SCU urea release may have contributed to the delay in dry matter production to late season cuttings by the SCU-fertilized tall fescue. No such delay was observed during the first year (1973) (Table 15), possibly because the SCU was applied sufficiently early in 1972 (August 14) that most of the urea was released from granules before the 1972-1973 winter. In contrast, SCU applied in early November in 1973 and 1974 would not have immediately begun to release until late in the following spring because of the low temperatures. This suggests that the optimum application time for a particular SCU material can be determined if the release response of that SCU to environmental factors is known.

Tall Fescue Nitrogen Yields

In general, nitrogen paralleled dry matter yields. In 1973, fall application of urea and SCU resulted in about the same annual nitrogen

yield (Table 16). But from 1974 through 1976, annual nitrogen yields of urea-fertilized tall fescue were much lower than those of SCU-fertilized fescue (Tables 17-19).

The four-year total nitrogen yields for SCU 4-fertilized tall fescue were about 20 to 30% higher than the nitrogen yields of fescue which received fall-applied urea (Table 20). The nitrogen concentration in the harvested portion of the tall fescue generally increased with dry matter yield (Appendix I). This observation is in agreement with the literature (e. g. , Reid, 1966).

Table 16. Nitrogen removal in 1973 by irrigated tall fescue.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - kg N/ha - - - - -			
<u>Var. Fawn</u>				
Urea	161	311	443	563
SCU 30	187	295	399	580
SCU 4	179	294	395	469
Urea (split)				537
<u>S. 1000</u>				
Urea	180	316	442	550
SCU 30	181	243	381	419
SCU 4	158	263	308	454
Urea (split)				599

Table 17. Nitrogen removal in 1974 by irrigated tall fescue.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - kg N/ha - - - - -			
<u>Var. Fawn</u>				
Urea	180	240	277	338
SCU 30	246	315	394	492
SCU 4	199	319	449	545
Urea (split)				438
<u>S. 1000</u>				
Urea	205	182	272	263
SCU 30	239	302	359	394
SCU 4	162	297	417	516
Urea (split)				434

Table 18. Nitrogen removal in 1975 by irrigated tall fescue.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - kg N/ha - - - - -			
<u>Var. Fawn</u>				
Urea	149	219	312	367
SCU 30	191	264	356	428
SCU 4	228	316	448	493
Urea (split)				435
<u>S. 1000</u>				
Urea	252	256	304	343
SCU 30	303	314	373	419
SCU 4	231	319	444	524
Urea (split)				432

Table 19. Nitrogen removal in 1976 by irrigated tall fescue.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - kg N/ha - - - - -			
<u>Var. Fawn</u>				
Urea	83	68	66	67
SCU 30	86	80	106	110
SCU 4	81	87	110	150
Urea (split)				119
<u>S. 1000</u>				
Urea	96	83	66	68
SCU 30	137	103	102	114
SCU 4	102	88	106	148
Urea (split)				111

Table 20. Total nitrogen removal by irrigated tall fescue grown on Woodburn silt loam, 1973-1976.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - kg N/ha - - - - -			
<u>Var. Fawn</u>				
Urea	573	838	1098	1335
SCU 30	710	954	1255	1610
SCU 4	687	1016	1402	1657
Urea (split)				1529
<u>S. 1000</u>				
Urea	733	837	1084	1224
SCU 30	860	962	1215	1346
SCU 4	653	967	1335	1642
Urea (split)				1576

Fertilizer Nitrogen Recovery

SCU 4-fertilized tall fescue recovered from 53 to 74% of the fertilizer nitrogen applied during the four-year period, depending on the rate of nitrogen and source (Table 21). This is in contrast to a recovery of 44% by Fawn tall fescue which received fall-applied urea. Recovery of fertilizer nitrogen by S. 1000 was lower than by var. Fawn for all treatments.

Table 21. Apparent recovery of fertilizer nitrogen by irrigated tall fescue, 1973-1976.

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - Percent ¹ - - - - -			
<u>Var. Fawn</u>				
Urea	--	44	44	43
SCU 30	--	64	57	58
SCU 4	--	74	70	61
Urea (split)				51
<u>S. 1000</u>				
Urea	--	31	36	32
SCU 30	--	52	47	39
SCU 4	--	53	57	55
Urea (split)				49

¹ Apparent recovery defined as percent recovery of increment applied above 200-kg N/ha/yr rate. See text, Equation (9).

The recovery of nitrogen by tall fescue (var. Fawn) decreased as the application rate increased from 400 to 800 kg N/ha/yr (Table 21). Possibly the lower nitrogen recovery by urea - (and to a lesser

extent SCU 30-) fertilized tall fescue at the 400-kg N/ha/yr rate was due to nitrogen loss mechanism unrelated to the grass physiology, for example, ammonia volatilization or denitrification. In contrast, nitrogen recovery by SCU 4-fertilized Fawn tall fescue was higher (74% at the 400-kg N/ha/yr rate) and was limited by the genetic character of the tall fescue, as evidenced by the lower recovery percentage at higher nitrogen rates. The recovery of nitrogen by both tall fescue cultivars was lower when the fescue was fertilized with a split application of urea than when SCU 4 was applied (Table 21).

The apparent nitrogen recovery as discussed here was calculated with Equation (9). For this equation to be valid it must be assumed that the fertilized crop derived the same amount of nitrogen from the soil as the check. If root growth increases at higher nitrogen rates, more available soil nitrogen could be utilized. However, high fertilizer nitrogen rates increase the top-to-root ratio. At very high levels of nitrogen, root growth will be depressed while shoot growth is still increasing (Viets, 1965). If that is the case, the heavily fertilized tall fescue may have obtained less nitrogen from the soil than the check plants; therefore, fertilizer nitrogen recovery would be underestimated.

Rate of Nitrogen Uptake by Tall Fescue

The amount of nitrogen removed by tall fescue during each period of regrowth following clipping was converted to a daily rate of nitrogen uptake (Table 22) to estimate a potential maximum rate of nitrogen uptake during the growing season. Nitrogen uptake rates were calculated only for tall fescue fertilized with SCU 4, SCU 30, and incrementally-applied urea at the highest rate (800 kg N/ha/yr).

Table 22. Rate of nitrogen uptake by irrigated tall fescue, receiving 800 kg N/ha/yr.

Period covered	Days elapsed	SCU 4	SCU 30	Urea (split)
		- - -	kg/ha/day ¹	- - -
<u>1973</u>				
3/21-5/14	54	2.45	2.88	2.53
5/15-6/29	46	2.50	2.81	3.29
6/30-8/15	47	1.25	1.62	2.30
8/16-10/2	48	1.13	1.17	2.66
<u>1974</u>				
3/19-5/4	46	4.14	4.00	2.76
5/5-6/14	41	1.86	1.63	1.26
6/15-8/14	61	2.07	1.32	1.88
8/15-9/23	40	1.79	0.67	2.34
<u>1975</u>				
3/26-5/14	49	2.14	2.02	1.95
5/15-6/26	43	1.49	1.27	1.49
6/27-8/19	54	2.65	1.53	1.59
8/20-10/15	57	1.15	0.64	1.01

¹ Average for var. Fawn and S. 1000.

The maximum nitrogen uptake rate was about four kg N/ha/day in the early spring; this declined to about one kg N/ha/day in September and October (Table 22). No irrigation was applied after mid-August, which may explain the low uptake rate late in the growing season. During 1974 and 1975, the nitrogen uptake rate following the first two clippings was generally higher for the SCU-fertilized tall fescue than for the urea-fertilized tall fescue, whereas the reverse relationship held following the fourth harvest.

The method used to calculate nitrogen uptake only considers the nitrogen removed in the harvested portion of the plant and does not consider nitrogen incorporated into the root mass. During the early spring, nitrogen uptake by the whole plant may be somewhat higher than calculated here because new root tissue will be forming. In the summer, the total root mass will be decreasing, and the actual net nitrogen uptake will be lower than calculated (Troughton, 1957).

Nitrate Leaching Losses

Precipitation during sampling periods and average soil solution nitrate-nitrogen concentrations for a three-year period are presented in Table 23. Nitrate-nitrogen concentrations generally ranged from zero to ten ppm for all samples from SCU-fertilized plots, and slightly higher for samples from urea-fertilized plots. Nitrate-nitrogen concentrations were highest in soil solution from

Table 23. Nitrate-nitrogen concentration in soil solution from Fawn tall fescue plots, 1973-1976.

Date	Precipitation ¹	SCU 4		Urea	
		400 ² fall	800 fall	400 fall	800 split
	<u>cm</u>	- - - ppm NO ₃ ⁻ -N - - -			
<u>1973-1974</u>					
11/1-11/23	40.5	3.1 ³	1.8	1.5	3.6
11/24-12/7	10.9	<1	1.1	1.7	7.3
12/8-12/20	20.9	<1	1.7	5.8	11.0
12/21-1/11	5.7	<1	<1	5.3	8.3
1/12-2/2	33.3	<1	<1	3.0	8.3
2/3-2/18	7.2	<1	1.1	3.2	6.8
2/19-3/15	22.4	<1	1.1	8.7	7.3
3/16-3/31	<u>9.6</u>	<1	<1	5.6	3.8
	150.5				
<u>1974-1975</u>					
11/1-12/9	21.0	<1	<1	<1	1.9
12/10-12/27	16.5	<1	<1	<1	7.0
12/28-1/19	7.4	<1	<1	2.4	8.4
1/20-2/13	12.2	<1	<1	<1	<1
2/14-3/10	8.8	<1	<1	<1	<1
3/11-4/1	10.1	<1	<1	<1	<1
4/2-4/30	<u>9.0</u>	<1	<1	<1	<1
	84.9				
<u>1975-1976</u>					
11/1-1/6	34.7	---	5.1	---	1.7
1/7-1/27	11.7	---	5.7	---	<1
1/28-3/31	<u>29.1</u>	---	2.0	---	1.1
	75.5				

¹ National Oceanic and Atmospheric Administration (1973-1976).

² Annual rate, kg N/ha/yr.

³ Average of four to six samples.

urea-fertilized plots. Nitrate-nitrogen concentrations were highest in soil solution from urea-fertilized plots during 1973-1974 and from SCU-fertilized plots during 1975-1976. The latter may have resulted from carry-over nitrogen applied in the SCU in previous years. This explanation is consistent with the relatively higher dry matter yields by the SCU-fertilized tall fescue in 1976 (Table 12).

The variability in the nitrate concentration of the soil solution from urea- and SCU-fertilized plots was generally sufficiently small that the effects of fertilizer source were not obscured in 1973-1974. During most of the winter, the soil solution nitrate-nitrogen concentrations ranged from about 1.5 to 25 ppm for the plots fertilized with urea at a rate of 800 kg N/ha/yr (Table 24). In contrast, nitrate-nitrogen concentrations generally ranged from 0 to 2 ppm, with a few values as high as 5.5 ppm, for the SCU 4-fertilized plots (Table 25).

Nitrate concentrations were uniformly low during 1974-1975, and no treatment effects were observed. Concentrations were higher in 1975-1976 (Table 23), but treatment differences were not significant (Figure 26).

The cumulative nitrate leaching losses during a two-year period were higher under the urea-fertilized tall fescue than under the SCU 4-fertilized tall fescue (Figure 26). Most of the leaching loss of nitrate occurred during 1973-1974 when precipitation was abnormally high (Figure 26 and Table 23). In the third year (1975-1976),

Table 24. 1973-1974 nitrate-nitrogen concentrations in soil solution from Fawn tall fescue plots receiving 800 kg N/ha/yr as urea (incrementally applied).

Porous ceramic cup sampler	Date							
	11/7	12/1	12/15	12/28	1/26	2/10	2/26	4/10
	- - - - - NO ₃ ⁻ -N, ppm - - - - -							
1	2.8	1.8	5.4	5.4	3.4	4.4	2.4	0.6
2	7.6	9.7	25.0	24.0	18.8	22.8	17.3	5.6
3	2.9	9.3	10.4	6.4	-- ¹	3.6	4.5	5.0
4	1.4	5.6	5.1	1.5	2.8	2.8	6.6	4.3
5	2.6	9.4	9.2	6.4	10.1	11.2	4.8	0.6
6	4.3	8.0	11.1	6.0	6.4	5.2	8.0	5.9
Average	3.6	7.3	11.0	8.3	8.3	6.8	7.3	3.8

¹Missing data.

Table 25. 1973-1974 nitrate-nitrogen concentrations in soil solution from Fawn tall fescue plots receiving 800 kg N/ha/yr as SCU 4 (fall-applied).

Porous ceramic cup ceramic	Date							
	11/7	12/1	12/15	12/28	1/26	2/10	2/26	4/10
	- - - - -NO ₃ ⁻ -N, ppm - - - - -							
1	1.9	2.5	5.4	-	-	-	-	-
2	¹	1.0	3.4	0	0	4.8	0	0
3	1.9	1.2	0.1	0	1.1	0.4	0	2.1
4	4.3	0.4	0.1	0	0	0	5.5	0
5	0.7	1.0	1.2	0	0	0.4	0	-
6	0.2	0.2	0.1	0	0	0	0	0
Average	1.8	1.1	1.7	0	0.2	1.1	1.1	0.5

¹Missing data.

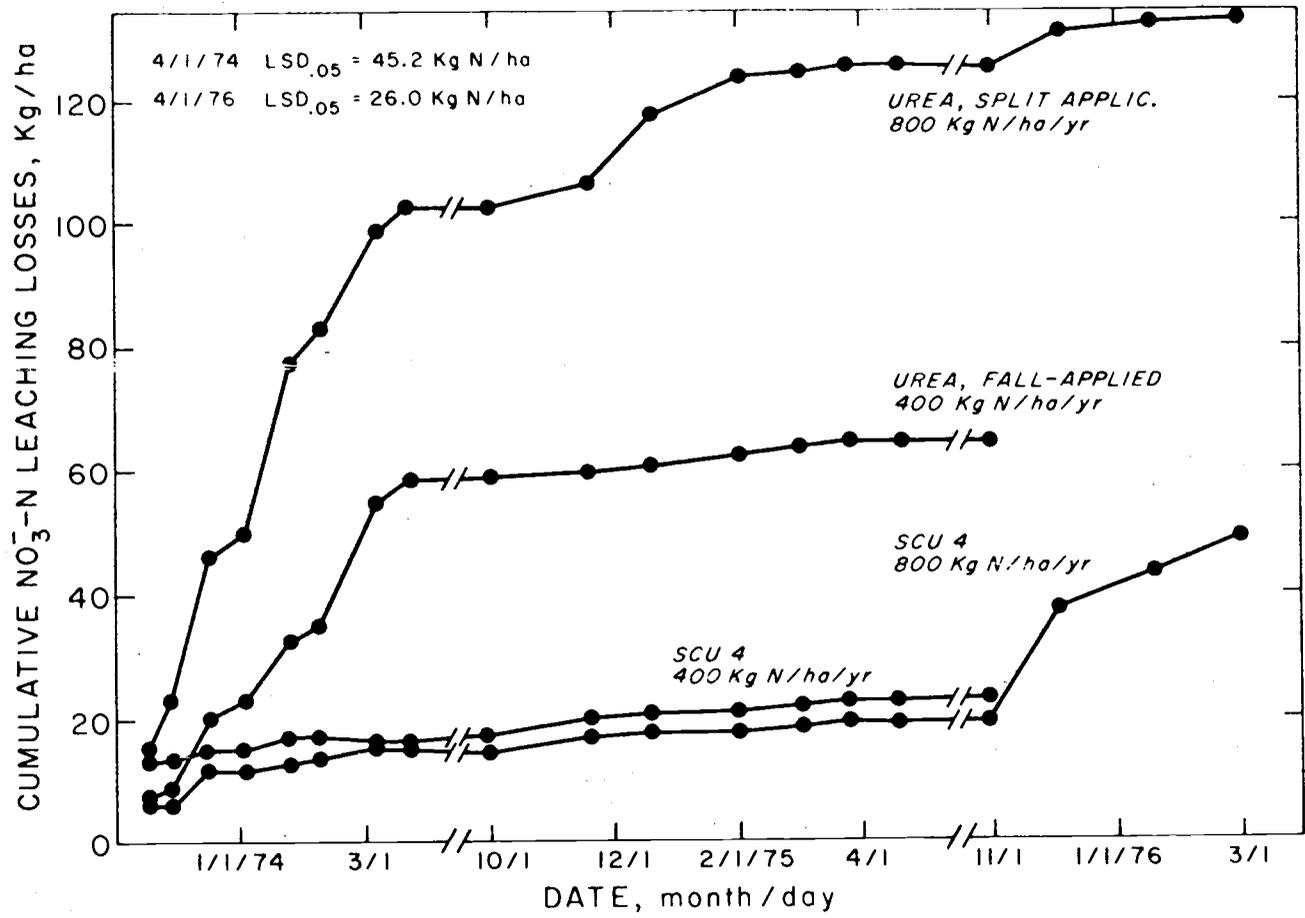


Figure 26. Cumulative leaching losses of nitrate from tall fescue plots fertilized with urea and SCU 4.

cumulative leaching losses from the SCU 4-fertilized plots were higher than from the urea-fertilized plots, possibly due to more carry-over nitrogen on the former; however, the difference was not statistically significant.

The total nitrate leaching losses from the plots fertilized with SCU 4 amounted to just over 2% of the nitrogen applied. The losses from the urea-fertilized plots were 7.0% of the amount applied to plots receiving 400 kg N/ha/yr and 5.3% for the plots receiving 800 kg N/ha/yr (split application). Thus, although nitrate leaching losses were two or three times as high from urea-fertilized plots as from SCU 4-fertilized plots, the losses for all treatments were a small percent of the total amount of nitrogen applied. Apparently, because the urea was applied in the late fall (about November 1) in 1973 and 1974, there was not sufficient time or sufficiently high temperature for the urea to nitrify and percolate downward. It is also possible that denitrification in the early fall could have occurred. The presence of a growing crop may actually increase the rate of denitrification by making the soil more anaerobic or by supplying the denitrifying microorganisms with a carbon source (Woldendorp, 1963). Also, the tall fescue removed considerable nitrate from soil solution during the growing season, and may in addition have taken up nitrate during the winter. Tall fescue root initiation may occur in the winter (Jacques and Schwass, 1956), and therefore even though shoot growth

does not occur, there may be some plant uptake of nitrate.

The nitrate-nitrogen leaching losses discussed here were calculated with Equation (10). For this equation to be valid, the following five assumptions must be made:

- (1) Drainage volume equals rainwater volume;
- (2) Nitrate concentration in a given sample is equal to the actual mean concentration for the entire sampling period;
- (3) Water percolation in the vicinity of the sampler occurs at the same rate as through undisturbed soil;
- (4) Horizontal movement of nitrate between plots due to mass flow or hydrodynamic dispersion is negligible;
- (5) Nitrate transported below the sampling depth of 91 cm is lost to subsequent plant use.

The following is a brief discussion of these assumptions:

From November through March, pan evaporation in the Willamette Valley is very low relative to rainfall. The average total potential evapotranspiration for these five months from 1931 to 1951 in nearby Albany, Oregon was 10.2 cm; of this 4.1 cm occurred in December, January, and February (Boersma and Simonson, 1970). This is very small relative to the total rainfall of 100 cm.

The second assumption could only be proven by more frequent sampling. The nitrate concentration for a given sampling unit did not fluctuate widely from one sampling date to the next (Tables 24 and 25).

This suggests that large fluctuations did not occur over shorter time periods.

The third assumption--that water percolated through the soil at the same rate adjacent to solution samplers and in undisturbed soil--was tested by comparing the nitrate concentration in soil solution from samplers installed on fallow plots vertically and at a 45-degree angle. Presumably, the soil solution collected from the samplers installed at an angle had percolated through relatively undisturbed soil. No differences in the nitrate concentration of samples collected from vertically-installed and diagonally-installed samplers occurred (Table 26), indicating that vertical installation of samplers did not significantly disturb the percolation rate of the soil solution.

Also no differences in the nitrate concentration of the soil solution from fertilized and unfertilized fallow plots occurred as a function of distance from the plot boundary (Table 26). Soil solution nitrate-nitrogen concentrations for fertilized plots ranged from 51.0 to 72.2 ppm and for unfertilized plots from 6.5 to 9.5 ppm. The fact that distance from plot boundary had no effect on nitrate concentration indicates that soil solution nitrate levels in the middle of the 152-cm wide tall fescue plots were not influenced by the nitrate levels of soil solution from adjacent plots.

The last assumption is difficult to validate. Tall fescue is deep-rooted (Buckner and Cowan, 1973), and probably has active roots

below a depth of 90 cm. However, most of the root length is probably in the top 20 cm of the soil profile. Wheat and barley roots may be found at depths of 100 cm, but most of the roots are in the top 10 or 20 cm of soil (Milthorpe and Moorby, 1974).

In summary, the five assumptions required for the validity of the nitrate leaching loss equation appear reasonable.

Table 26. Nitrate concentration in soil solution as influenced by distance from plot border and angle of sampler installation.

Distance inside plot border, cm	NO ₃ ⁻ -N concentration	
	Fertilized plots ¹	Unfertilized plots ¹
	- - - - - ppm - - - - -	
<u>January 17, 1976</u>		
30	55.6 ²	6.2 ²
76	61.0	7.7
122	52.4	7.6
183	52.6	
183 (45 deg angle)	51.0	
<u>February 7, 1976</u>		
30	58.0	7.7
76	72.2	9.1
122	53.8	9.5
183	55.9	
183 (45 deg angle)	51.2	
LSD _{.05}	11.1	

¹Fallow plots. Fertilized plots received KNO₃ (800 kg N/ha) December 16, 1975.

²Average of three replicates.

Soil Nitrate and Extractable Ammonium

The levels of nitrate plus extractable ammonium remaining in soil after four years of nitrogen fertilization were very low (8 to 33 kg N/ha) relative to fertilizer nitrogen applications and crop nitrogen removal (Table 27). No significant difference in nitrate plus extractable ammonium levels was observed in soil from urea-fertilized plots (400 and 800 kg N/ha/yr) and SCU 4-fertilized plots (400 kg N/ha/yr). The available nitrogen content of soils fertilized with SCU 4 at 800 kg N/ha/yr was significantly higher than on other plots (33 kg N/ha versus 8 to 12 kg N/ha). Most of this difference was due to the higher level of extractable ammonium in the top 60 cm in the profile of the plots fertilized with the high rate of SCU 4. This residual nitrogen remained in the soil from previously released granules of SCU 4.

In summary, a small amount of residual ammonium- and nitrate-nitrogen remained in the soil 22 months (two harvest seasons) after the last application of SCU 4 fertilizer. This residual nitrogen was reflected in the higher yield by the SCU-fertilized tall fescue during the last harvest season (Table 12).

Soil Total Nitrogen

The soil total nitrogen at the conclusion of the four-year field experiment was significantly higher on plots which received 800 kg

Table 27. Nitrate- and ammonium-nitrogen in Woodburn silt loam at conclusion of tall fescue field experiment.

Fertilizer	Rate	Depth ¹	NO ₃ ⁻ -N	NH ₄ ⁺ -N	Total ²
	<u>kg N/ha/yr</u>	<u>cm</u>	- - - - kg N/ha - - - -		
Urea	400	0-30	2.3	7.5	9.8
		30-60	0.4	1.0	1.4
		60-90	0.5	0.4	1.0
		Total	3.2	8.9	12.2
Urea	800 (split)	0-30	2.1	4.3	6.4
		30-60	0.7	2.6	3.3
		60-90	0.3	2.0	2.3
		Total	3.1	7.9	12.0
SCU 4	400	0-30	0.9	3.4	4.3
		30-60	0.1	1.5	1.6
		60-90	0.9	0.8	1.7
		Total	1.9	5.7	7.6
SCU 4	800	0-30	3.2	18.2	21.4
		30-60	2.5	5.2	7.7
		60-90	1.5	2.5	4.0
		Total	7.2	25.9	33.1

¹Only var. Fawn plots sampled.

²For NO₃⁻-N and NH₄⁺-N values, $s_{\bar{x}} = 3.24$ kg N/ha,
LSD_{.05} = 9.50 kg N/ha for 30-cm depth increments.

N/ha/yr as both urea and SCU 4 than on plots which received half that rate (Table 28). Total nitrogen levels to a 90-cm depth were 12.2 to 12.5 mtons/ha on plots fertilized with 800 kg N/ha/yr, 11.1 to 11.2 mtons/ha on plots fertilized with 400 kg N/ha/yr, and 10.6 mtons/ha on fallow soil (Table 28). Differences in total nitrogen as a result of nitrogen fertilizer source were not significant. Fallow soil samples were not replicated and therefore were excluded from the analysis of variance.

Because nitrate and extractable ammonium levels were relatively low (Table 27), it is apparent that nearly all of the soil nitrogen was associated with the soil organic matter. Between 52 and 56% of the total nitrogen to a depth of 90 cm was found in the top 30 cm, and 84 to 85% was found in the top 60 cm regardless of fertilizer treatment, reflecting the fact that the soil organic matter levels were higher closer to the surface of the soil.

Soil pH

At the end of the four-year tall fescue experiment, soil pH values ranged from 4.8 to 5.4 (Table 29). On all plots, the pH was 0.1 to 0.4 units lower in the top 30 cm of soil than at lower depths. This may have been due to the acidifying effect of nitrification which would have been more prevalent in the top 30 cm of the soil profile.

Table 28. Total nitrogen in Woodburn silt loam at conclusion of tall fescue field experiment.

Fertilizer	Rate	Depth	Total N ¹
	<u>kg N/ha/yr</u>	<u>cm</u>	<u>kg N/ha</u>
Urea	400	0-30	6,263 ²
		30-60	3,274
		60-90	<u>1,680</u>
			11,174
Urea	800 (split)	0-30	6,533
		30-60	4,156
		60-90	<u>1,822</u>
			12,511
SCU 4	400	0-30	6,234
		30-60	3,160
		60-90	<u>1,665</u>
			11,088
SCU 4	800	0-30	6,704
		30-60	3,544
		60-90	<u>1,907</u>
			12,155
Fallow	0	0-30	5,721
		30-60	3,117
		60-90	<u>1,751</u>
			10,589

¹ Only var. Fawn plots sampled. Average of three replicates x ten cores. Fallow sample not replicated.

² $s_{\bar{x}} = 230$ kg N/ha, $LSD_{.05} = 676$ kg N/ha for 30-cm depth increments.

Table 29. Soil pH of Woodburn silt loam at conclusion of tall fescue field experiment.

Fertilizer	Rate	Depth	Soil pH ¹ (var. Fawn plots)
	<u>kg N/ha/yr</u>	<u>cm</u>	
Urea	400	0-30	4.9
		30-60	5.3
		60-90	5.4
Urea	800 (split)	0-30	5.1
		30-60	5.0
		60-90	5.2
SCU 4	400	0-30	5.0
		30-60	5.1
		60-90	5.2
SCU 4	800	0-30	4.8
		30-60	5.0
		60-90	5.1
Fallow	0	0-30	5.1
		30-60	5.3
		60-90	5.3

¹ Average of triplicate samples.

Differences in pH due to fertilizer source and rate of nitrogen were small and inconsistent (Table 29).

An important question related to soil pH is the possible acidifying effect of SCU due to the oxidation of the elemental sulfur coating. Over a three-year period, approximately 1300 kg/ha of sulfur (40,000 eq/ha of sulfur) were applied to plots which received 800 kg N/ha/yr as SCU 4. Microbial oxidation of sulfur to sulfate creates two equivalents of H⁺ for each equivalent of sulfur (Tisdale

and Nelson, 1966). To neutralize this much acidity would require four metric tons of CaCO_3 /ha, equivalent to 167 kg of CaCO_3 for each 100 kg of nitrogen applied as SCU 4. However, the soil pH values observed suggest that oxidation of the sulfur was slow, probably due to the large particle size of the sulfur coating fragments (Burns, 1967).

Nitrogen Balance Sheet for Tall Fescue

A nitrogen balance sheet was tabulated for the Fawn tall fescue which received 800 kg N/ha/yr as urea (split application) or SCU 4 and 400 kg N/ha/yr as urea (fall-applied) or SCU 4 (Table 30). The total amount of fertilizer nitrogen applied during the four-year experiment was compared to tall fescue nitrogen removal (Table 20), soil extractable ammonium plus nitrate (Table 27), and nitrate leaching losses (Figure 26). Relatively small amounts of nitrogen were leached from the soil profile or remained as residual extractable nitrogen; much more of the applied nitrogen was recovered in the harvested crop (Table 30).

When nitrogen outputs were subtracted from the amount of nitrogen applied, more nitrogen was unaccounted for on the urea-fertilized tall fescue plots (32 and 22% of the applied nitrogen) than on the SCU 4-fertilized plots (27 and 12% of the applied nitrogen) (Table 30).

Table 30. Nitrogen balance for Fawn tall fescue fertilized with urea and SCU 4.

Fertilizer	Urea	Urea	SCU 4	SCU 4
Annual rate, kg N/ha	400	800	400	800
Split or fall-applied	fall	split	fall	fall
	- - - - - kg N/ha - - - - -			
Total applied, 1972-1976	1192	2478	1192	2384
Total removed by crop	838	1529	1016	1655
NO ₃ ⁻ + extractable NH ₄ ⁺ , 0-90 cm, August 1976	12	12	8	33
NO ₃ ⁻ winter leaching losses, first winter excluded	84	132	28	51
Unaccounted-for nitrogen	258	805	140	645
Apparent recovery by crop, % ¹	44	51	74	61

¹ Apparent recovery based on increment above 200- kg N/ha/yr rate.

The missing nitrogen may be accounted for in at least four ways:

- (1) nitrogen incorporation into soil organic matter, including roots;
- (2) leaching losses of nitrate during the first winter (1972-1973) when no data were obtained;
- (3) ammonia volatilization; and
- (4) denitrification.

After four years, plots fertilized with 800 kg N/ha/yr (as urea or SCU 4) had accumulated between 1100 and 1300 kg N/ha (LSC_{.05} = 676 kg N/ha) in the soil more than plots fertilized at half that rate (Table 28). This is probably not statistically different from the 500 to 550 kg N/ha of additional unaccounted for nitrogen at the higher rate. Therefore, the incorporation of nitrogen into soil organic

matter adequately accounts for the missing nitrogen, but it does not eliminate the possibility of other processes such as denitrification or ammonia volatilization.

Also, the unaccounted for nitrogen may have been underestimated if nitrogen was added to the soil by nonsymbiotic nitrogen fixation. Rhizosphere associations between bahiagrass (Paspalum notatum) and Azotobacter spp. have been shown to fix N_2 . Extrapolation of measurements on intact soil cores suggested fixation rates in the field of 90 kg N/ha/yr (Dobereiner, Day, and Dart, 1973). Such an association in tall fescue rhizosphere soil has not been identified; however, Giddens, Adams, and Dawson (1971) concluded that part of an observed increase in soil total nitrogen from 0.047 to 0.088% following five years of tall fescue growth was due to nonsymbiotic N_2 fixation. The tall fescue was fertilized at an annual rate of 34 kg N/ha, and the average annual increase in total soil nitrogen (0-30 cm) was 194 kg N/ha. Nitrogen fixation in soil crusts incubated under illumination was shown by the use of the acetylene reduction technique, and algae capable of N_2 fixation were isolated from the soil and grass leaves. It is not known whether such nonsymbiotic fixation by algae would be affected by high rates of surface-applied fertilizer nitrogen.

Simulated Release of Urea from SCU 4 in the Field

The cumulative release of urea from SCU 4 during a three-year period was calculated as a function of daily minimum and maximum temperatures at the tall fescue field experiment site. The relationship of urea release rate and temperature was determined in laboratory experiments (Figure 5). The rate of urea release at 35 C in those experiments was 1.51%/day.

If the Q_{10} value for a process and the rate of that process are known, the rate at any other temperature may be calculated by the equation

$$Q_{10} = (k_2/k_1)^{10/(t_2-t_1)} \quad (11)$$

where k_2 and k_1 are reaction rates at temperatures t_2 and t_1 , respectively (Salisbury and Ross, 1969). A Q_{10} for Celsius temperatures is equivalent to a Q_{18} for Fahrenheit temperatures. Converting Equation (11) to Fahrenheit,

$$Q_{18} = (k_2/k_1)^{18/(t_2-t_1)} \quad (12)$$

Rearranging:

$$k_2 = k_1 \exp[(t_2-t_1)(\ln Q_{18}/18)] \quad (13)$$

Assuming $Q_{18} = 2$ and that $k_1 = 1.5\%/day = 0.75\%/half\ day$ at

35 C (Figure 5),

$$k_2 = 0.0193 \exp(0.0385t_2) \quad (14)$$

where k_2 = the percent urea released in a 12-hr period at temperature t_2 (deg F). The temperature during each 24-hr period is t_{\max} for 12 hours and t_{\min} for 12 hours, where t_{\max} and t_{\min} are calculated daily maximum and minimum temperatures derived from climatological records (National Oceanic and Atmospheric Administration, 1972-1976). The average temperature (t_{\min} or t_{\max}) for a 12-hr period was arbitrarily set as the average of the daily mean and the daily minimum or maximum temperature. It was felt that the temperatures so calculated would more nearly approximate the average during a 12-hr period.

The amount of urea released in a 24-hr period is k percent, where

$$k = 0.0193 \exp(0.0385t_{\max}) + 0.0193 \exp(0.0385t_{\min}) \quad (15)$$

This equation was used in a computer program (Appendix II) to calculate the cumulative percent urea release from SCU 4 in the field as a function of time. Two assumptions were incorporated into the program: (1) a very rapid, temperature-independent release of 10% when SCU was first applied to the soil; (2) a lag period of 30 days before any further release occurred. These assumptions are

consistent with the release patterns observed in laboratory experiments (Figures 5 and 7).

The cumulative percent urea released from each annual application of SCU 4 was plotted against time (Figure 27). All of the urea was released within nine months after application for all three years, and therefore, there was no SCU carried over to the following year. This is not consistent with the tall fescue field experiment in which SCU-fertilized fescue outyielded urea-fertilized fescue during the second, third, and fourth years but not the first year (Tables 9-11), suggesting that some carry-over nitrogen was present on SCU-fertilized plots.

The calculation probably overestimates the rate of urea release for several reasons. First, the lag period at 5 C and 15 C is longer than 30 days (Figure 5), and secondly, soil moisture effects were not considered. Particularly when the temperature is high, the soil surface will be dry a significant fraction of the time. In previously discussed laboratory experiments, SCU 4 applied to soil subjected to air-drying during five out of every ten days released urea only 63% as fast as SCU applied to soil kept continually moist (Figure 6). It also appears that regardless of treatment the urea release rate decreases when 70 to 75% of the total urea has been released (Figures 7 and 8). The effect of environment on the release rate of the last 25 to 30% of the urea is not known.

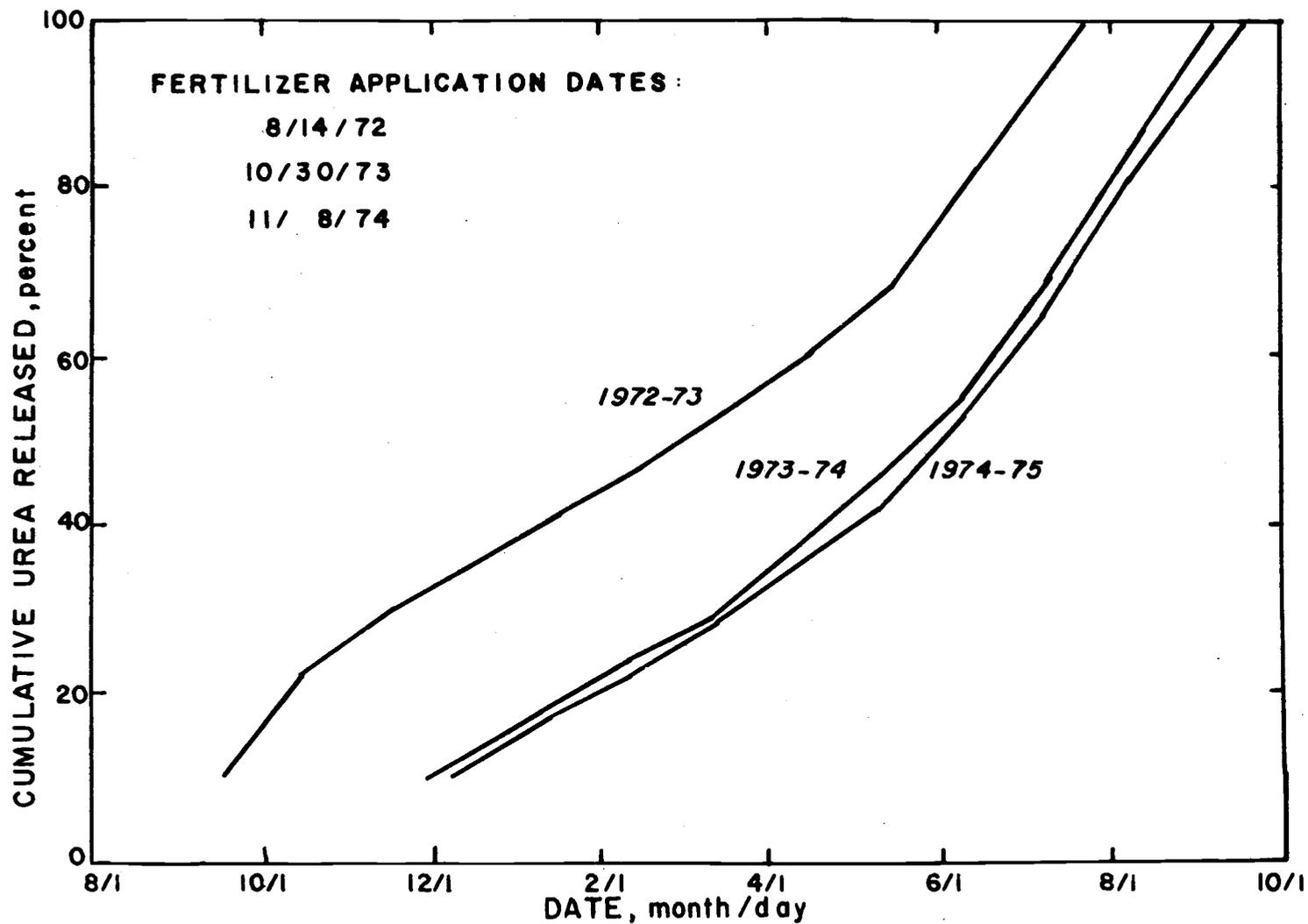


Figure 27. Urea release from SCU 4 simulated as function of daily temperature.

The cumulative amount of urea released from SCU 4 (800 kg N/ha/yr) was calculated for 60-day periods and plotted versus time (Figure 28) to show the amount of urea released during a given time period. The urea release pattern for a three-year period was compared with the nitrogen uptake by tall fescue (Figure 29). The pattern of nitrogen uptake is hypothetical but based on the calculated rate of uptake discussed before (Table 22). The hypothesized uptake rate of nitrogen was 2 kg/ha/day in March, 3 kg/ha/day in April, May, and June, 2 kg/ha/day in July and August, and 1 kg/ha/day in September and October. A total annual uptake of 510 kg N/ha would result from this uptake pattern.

The hypothetical nitrogen uptake rate by tall fescue was superimposed on the SCU 4 urea release pattern (Figure 29). According to the release model, during all three years, substantial amounts of urea-nitrogen were released during fall and winter months when uptake of nitrogen by tall fescue was assumed to be very slow. If nitrogen released from SCU 4 was present in the fall and winter months in excess of that taken up by the tall fescue, it would be lost by the same mechanisms as nitrogen from a conventional source.

Both the SCU urea release and tall fescue nitrogen uptake patterns discussed here are only first approximations. The actual urea release pattern is probably different than that presented here (Figures 27 and 28) because soil moisture effects were not included

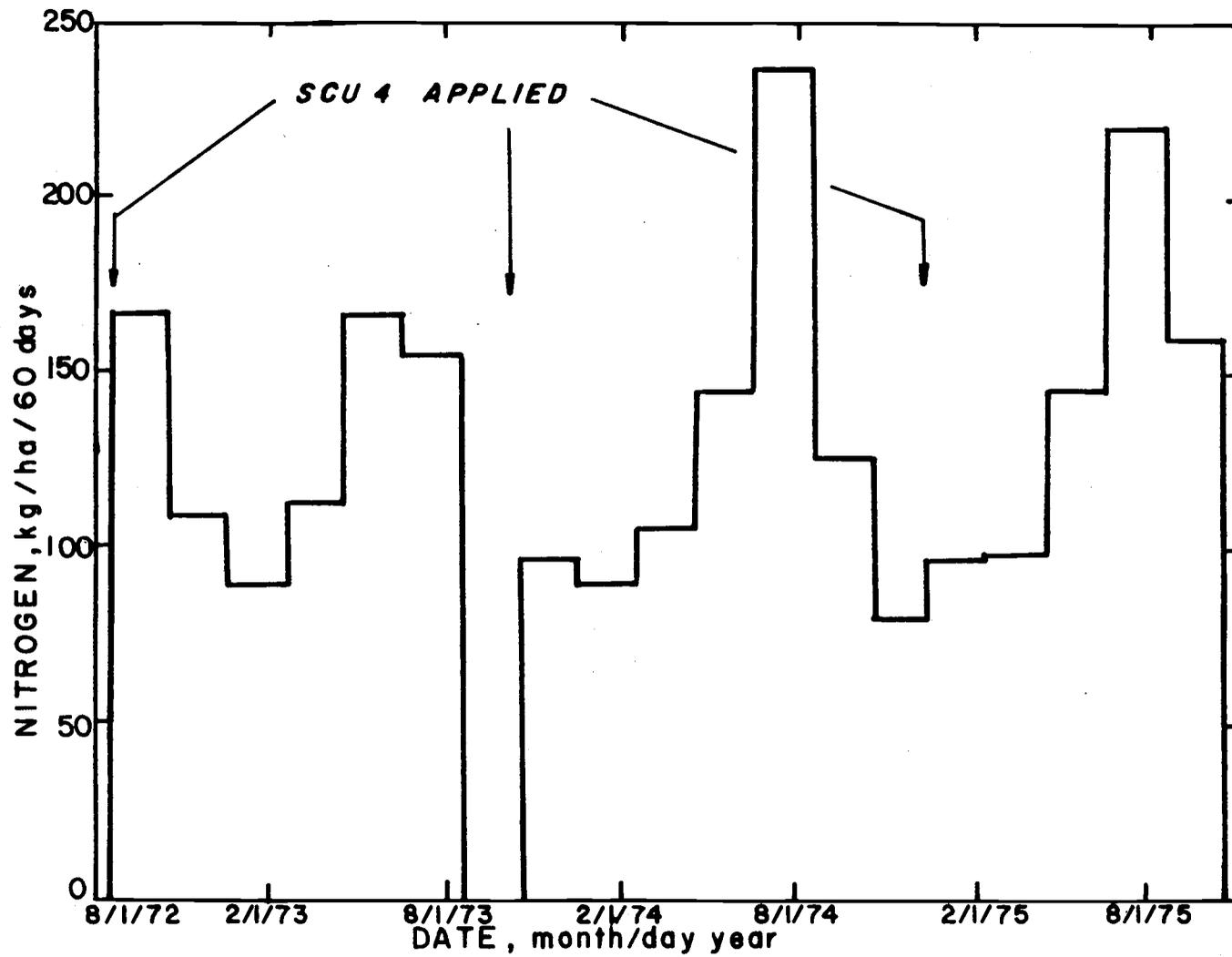


Figure 28. Simulated urea release from SCU 4 applied at 800 kg N/ha/yr.

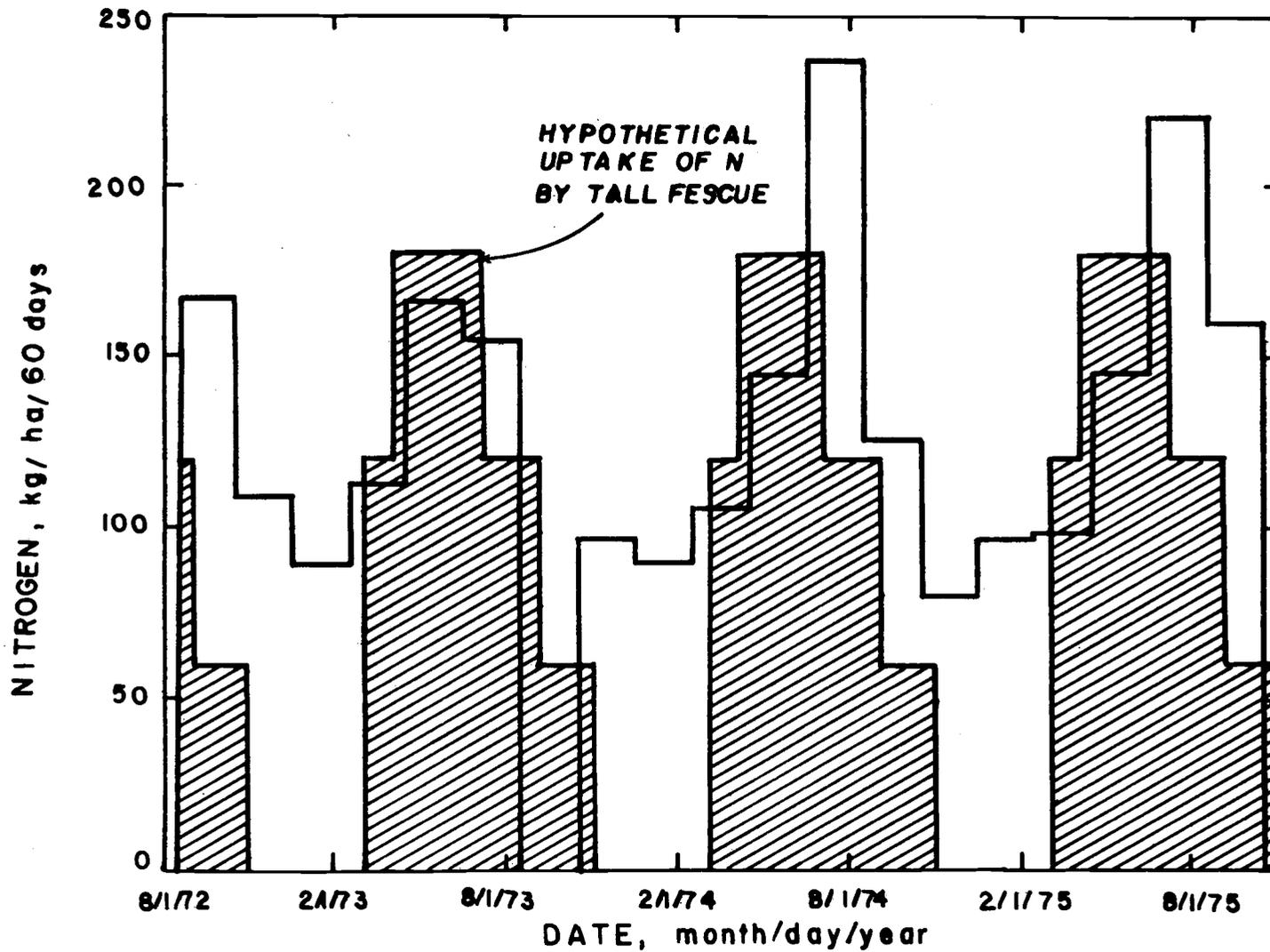


Figure 29. Hypothetical pattern of nitrogen uptake by tall fescue compared to simulated urea release (Figure 28). Hypothetical annual uptake is 510 kg N/ha. Simulated annual urea release is 800 kg N/ha.

in the model. The comparison of tall fescue nitrogen uptake and SCU urea release patterns (Figure 29) suggests that there is much room for improvement in matching the rate of nitrogen supply to the rate of uptake by the crop.

SUMMARY AND CONCLUSIONS

The specific objectives of this thesis were as follows:

- (1) To determine the mechanisms of urea release from SCU by measurement of urea release from SCU materials as a function of temperature, soil water potential, and soil sterility;
- (2) To develop a rapid method to determine the long-term urea release pattern of a particular SCU fertilizer;
- (3) To compare nitrogen recovery by tall fescue fertilized with urea and SCU and to compile a nitrogen balance sheet, including nitrate leaching losses;
- (4) To simulate SCU urea release in the field on the basis of experimentally-derived rate constants and to compare the release patterns with the pattern of nitrogen uptake by tall fescue.

In laboratory studies, the rate of urea release from wax-sealed SCU was temperature dependent and, in sterile soil, very slow compared to the rate in non-sterile soil. Both observations suggest that urea release is the result of microbial degradation of the sulfur or wax when the SCU is applied to moist soil. Soil sterilization also slowed the release of urea from SCU with a polyethylene-oil sealant but did not affect urea release from SCU without a sealant material.

Urea release from wax-sealed SCU was sensitive to soil water potential. At -30 bars soil water potential, urea release occurred at 0.5%/day compared to a release rate of near zero when soil was sterilized. Sulfur-oxidizing microorganisms (Thiobacillus spp.) are generally inactive below soil water potentials of -15 bars, while some species of actinomycetes and fungi (which may be involved in sealant degradation) are capable of activity at much lower water potentials; therefore, it seems that the microbial degradation of the sealant and not the sulfur is required for SCU urea release to occur.

The following SCU urea release mechanism is proposed: When SCU is applied to moist soil, urea is rapidly released at all temperatures from granules with defective coatings. Following a lag period, the sealant is removed from the SCU granules by soil microorganisms. This process is very temperature dependent; at temperatures below 15 C the lag period may be very long (> 80 days). As the coating is removed from granules, urea absorbs water, and the dissolved urea diffuses through existing pores and channels in the sulfur coating, a less temperature sensitive process.

Both the microbial removal of sealant and the diffusion of urea from granules will depend on the thickness of the sealant and sulfur coating components. This hypothesis suggests that the difference in the urea release patterns of two SCU fertilizer will correspond to differences in the coating thickness distributions. To calculate the

coating thickness distribution the total coating and urea weights for 60 individual granules of SCU 4, 23, and 25 were determined. The mean coating thickness for each granule was calculated. The cumulative amount of urea in the 60 granules was plotted against coating thickness to produce a characteristic curve for each SCU fertilizer. It was found that the calculated SCU coating (sealant plus sulfur) thickness distribution for the three materials correlated with the long-term cumulative urea release. For all three fertilizers, the amount of urea released after 125 days at 25 C was equal to that urea having a total coating thickness of 90 microns or less. The coating thickness distribution can be quickly determined and is a quick test to determine the long-term urea release rate. The release pattern over a shorter time period (< three months) may also be related to the sealant thickness distribution. Additional study of both sealant and total coating thickness distribution and their relationship to the urea release pattern for other SCU fertilizers is recommended.

Irrigated tall fescue was grown for four years (1972-1976). At the highest rate of nitrogen fertilizer application (800 kg N/ha/yr), var. Fawn tall fescue yielded a four-year total of 61 metric tons/ha in response to SCU 4 fertilization compared to 50 metric tons/ha in response to urea fertilization (both materials fall applied). Tall fescue fertilized with a split application of urea at the same rate yielded 60 metric tons/ha, not significantly different from the yield

of SCU-fertilized tall fescue.

Nitrogen fertilizer was not applied in the fall of 1975 prior to the last harvest season. In 1976, tall fescue previously fertilized with SCU 4 produced 59% more dry matter than that which had been fertilized with urea, indicating that a substantial amount of fertilizer nitrogen remained on SCU-fertilized plots from the fall 1974 application. An additional 75 kg N/ha was removed by the harvested crop from tall fescue plots which had received 800 kg N/ha as SCU in 1974 above the amount removed by the urea-fertilized tall fescue.

The SCU 4-fertilized tall fescue generally yielded higher than the SCU 30-fertilized tall fescue, except at the lowest nitrogen application rate (200 kg N/ha/yr), suggesting that slower release SCU fertilizers would be especially advantageous at higher nitrogen application rates.

Fertilizer nitrogen recoveries by the tall fescue were calculated using the 200-kg N/ha/yr rate as a check treatment. Four-year nitrogen recoveries by var. Fawn tall fescue after 800 kg N/ha/yr was applied as urea, SCU 30, or SCU 4 were, respectively, 43, 58, and 61%. The fescue receiving the split application of urea recovered 51%.

The seasonal distribution of fescue dry matter yields was influenced by the fertilizer nitrogen source. Fall application of urea tended to result in attainment of a larger percentage of the annual yield in the first three cuts (March, May, and June) than did fall

application of SCU. The split application of urea resulted in an even larger percentage of the annual yield coming in the August and October harvests than did fall application of SCU.

Daily nitrogen uptake rates by tall fescue which was fertilized at a rate of 800 kg N/ha/yr were calculated by dividing the nitrogen yield at the second, third, fourth, and fifth harvest each year by the number of days elapsed since the preceding harvest. Daily nitrogen uptake rates were not consistently different due to nitrogen source. Rates ranged from 2.0 to 4.1 kg N/ha/day after the first harvest in March and from 0.6 to 2.7 kg N/ha/day after the fourth harvest in August.

The nitrate-nitrogen concentration in soil solution from a depth of 90 cm on tall fescue plots generally ranged from 0 to 5 ppm during the winter. During the first year of soil solution sample collection (1973-1974), the nitrate-nitrogen concentrations from the SCU 4-fertilized plots ranged from 0 to 3.1 ppm compared to a range of 1.5 to 11.0 ppm for urea-fertilized plots.

Cumulative nitrate leaching losses (1973-1975) on plots receiving incrementally-applied urea (800 kg N/ha/yr), fall-applied urea (400 kg N/ha/yr), or fall-applied SCU 4 (400 and 800 kg N/ha/yr) were 126, 65, 20, and 19 kg N/ha. Over a three-year period, leaching losses from plots fertilized with SCU 4 amounted to about 2% of the total fertilizer nitrogen applied. Losses from urea-fertilized

plots were 7.0% and 5.3% for the 400- and 800-kg N/ha/yr rates.

At the end of the four-year experiment, 22 and 33% of the applied urea nitrogen (400- and 800-kg N/ha/yr rates) was unaccounted for, compared to 12 and 27% of the SCU 4 nitrogen applied at the same rates. Soil total nitrogen measurements accounted for this "missing" nitrogen but did not eliminate the possibility of denitrification and ammonia volatilization losses.

In summary, in the four-year study, both SCU 4 and SCU 30 fertilizers resulted in greater production of tall fescue dry matter and higher nitrogen recoveries than fall application of urea. At the one rate tested (800 kg N/ha/yr) tall fescue fertilized with SCU and a split application of urea produced equivalent dry matter yields. Leaching losses from urea-fertilized plots were higher than from SCU-fertilized plots, but even the highest losses were not a substantial fraction of total nitrogen applied.

The results of the tall fescue field experiment indicate (1) that fertilization with SCU will result in higher yields than fall application of urea but may not result in sufficient increase to warrant the higher projected cost of the manufacturing process, and (2) that while SCU fertilization does result in substantially lower nitrate leaching losses than does urea fertilization, the tall fescue removes sufficient available nitrogen from the soil so that even at very high rates of application, losses will be a small percentage of the total nitrogen applied.

A simple mathematical model incorporating daily temperatures was derived and used to simulate urea release from SCU 4 in the field. In each of three years, the model predicted that all urea would be released in less than 12 months and therefore did not agree with the observed effect of residual SCU nitrogen on tall fescue yields. The lack of agreement between the predicted and actual urea release was probably due to the failure to incorporate soil moisture effects into the model and the use of a shorter lag period in the model than actually occurs in the field.

A comparison of the hypothetical nitrogen uptake pattern of tall fescue and the simulated urea release pattern of SCU 4 suggests that improvements can be made in matching fertilizer nitrogen supply rate and crop nitrogen demand rate. Whether such improvements will increase yield or crop nitrogen recovery is a very critical, but unanswered, question. While it appears possible to develop SCU fertilizers which maintain the soil solution nitrogen concentration at some desired level, it has not been shown, from the standpoint of crop production, whether this is desirable. Crop species vary both in the rate at which they can take up nitrogen and the rate at which they can incorporate nitrogen into protein.

More research is required to determine whether plants provided with a continuously optimal nitrogen concentration in the soil solution can utilize nitrogen more efficiently in the production of dry matter

than can plants which receive most of their nitrogen at one time. It appears that little progress has been made toward answering this question since 1964 when S. E. Allen (1964) stated, "a great deal of time and money has already been spent on attempts to develop a slow release N fertilizer without actually knowing if our goal is worth achieving."

BIBLIOGRAPHY

- Allen, S. E. 1964. The development of new nitrogen fertilizers, as determined by the nutrient requirements of agronomic crops. pp. 24-30. In Soil and fertilizer nitrogen research: A projection into the future. Tennessee Valley Authority, Muscle Shoals, Alabama.
- Allen, S. E. , C.M. Hunt, and G. L. Terman. 1971. Nitrogen release from sulfur-coated urea, as affected by coating weight, placement, and temperature. *Agron. J.* 63:529-533.
- Allen, S. E. and D. A. Mays. 1974. Coated and other slow-release fertilizers for forages. pp. 559-582. In D. A. Mays (ed.) Forate fertilization. *Am. Soc. of Agron.* , Madison, Wis.
- Allen, S. E. , D. A. Mays, and G. L. Terman. 1968. Low cost slow-release fertilizer developed. *Crops and Soils* 21:13-15.
- Allen, S. E. , G. L. Terman, and C. M. Hunt. 1971. Soluble and slow-release nitrogen fertilizer effects on grass forage, as influenced by rate and placement. *J. Agric. Sci.* 77:397-404.
- Allison, F. E. 1965. Evaluation of incoming and outgoing processes that affect soil nitrogen. In W. V. Bartholomew and F. E. Clark (ed.) Soil nitrogen. *Agronomy* 10:578-606. *Am. Soc. of Agron.* , Madison, Wis.
- Baker, K. F. and R. J. Cook. 1974. Biological control of plant pathogens. W. H. Freeman and Co. , San Francisco.
- Bates, E. M. and W. Calhoun, Jr. 1975. Local climatological data for Oregon State University, 1974. Special Report 177. *Agric. Exp. Stn. Oregon State University.*
- Blouin, G. M. and D. W. Rindt. 1967. Sulfur-coated fertilizer pellet having controlled dissolution rate and inhibited against microbial dissolution. U. S. Pat. 3,295,950; 3,342,577. Assignors to Tennessee Valley Authority.
- Blouin, G. M. , D. W. Rindt, and O. E. Moore. 1971. Sulfur-coated fertilizers for controlled release: Pilot plant production. *J. Agric. Food Chem.* 19:801-808.

- Boersma, L. and G. H. Simonson. 1970. Water tables in Oregon soils with reference to trafficability. Ore. St. Univ., Dept. of Soils. Contract Rep. M-70-1.
- Bremner, J. M. 1965. Total nitrogen. In C. A. Black (ed.) Methods of soil analysis, part 2. Agronomy 9:1149-1176. Am. Soc. of Agron., Madison, Wis.
- Bremner, J. M. and D. R. Keeney. 1966. Determination of isotope ratio analysis of different forms of nitrogen in soils. Soil Sci. Soc. Am. Proc. 30:577-582.
- Buckner, R. C. and J. R. Cowan. 1973. The fescues. pp. 297-306. In M. E. Heath, D. S. Metcalfe, R. F. Barnes (ed.) Forages: The science of grassland agriculture. 3rd ed. Iowa State Univ. Press, Ames, Iowa.
- Burns, G. R. 1967. Oxidation of sulphur in soils. The Sulphur Institute. Tech. Bull. No. 13.
- Cook, R. J. and R. J. Papendick. 1972. Influence of water potential of soils and plants on root disease. Annu. Rev. Phytopathology 10:349-374.
- Cowan, J. R. 1956. Tall fescue. Adv. Agron. 8:283-319.
- Davies, L. H. 1973. Two grass field trials with sulfur-coated urea to examine its potential as a slow release nitrogen fertilizer in the U. K. J. Sci. Food Agric. 24:63-67.
- Davies, L. H. 1976. Slow release fertilizers, particularly sulfur-coated urea. The Fertiliser Soc., London.
- Dobereiner, J., J. M. Day, and P. J. Dart. 1973. Rhizosphere associations between grasses and nitrogen-fixing bacteria: Effect of O₂ on nitrogenase activity in the rhizosphere of Paspalum notatum. Soil Biol. Biochem. 5:157-159.
- Dotzenko, A. D. 1961. Effect of different nitrogen levels on the yield, total nitrogen, and nitrogen recovery of six grasses grown under irrigation. Agron. J. 53:131-133.
- Ellis, Jr., R. and R. S. Adams, Jr. 1961. Contamination of soils by petroleum hydrocarbons. Adv. Agron. 13:197-216.

- Giddens, J. , W.E. Adams, and R.N. Dawson. 1971. Nitrogen accumulation in fescue grass sod. *Agron. J.* 63:451-454.
- Griffin, D.M. 1972. *Ecology of soil fungi.* Syracuse Univ. Press, Syracuse, N. Y.
- Hallock, D. L. , R.H. Brown, and R.E. Blaser. 1965. Relative yield and composition of Ky. 31 fescue and coastal bermuda grass at four nitrogen levels. *Agron. J.* 57:539-542.
- Harris, R. F. , W.R. Gardner, A. A. Adebayo, and L. E. Sommers. 1970. Agar dish isopiestic equilibration method for controlling the water potential of solid substrates. *Applied Microbiology* 19:536-537.
- Hashimoto, I. and J. D. Hatfield. 1976. Dissolution of individual granules of sulfur-coated urea (SCU) in soil. *Agronomy Abstracts.* American Society of Agronomy, Madison, Wis.
- Hauck, R. D. 1972. Synthetic slow-release fertilizers and fertilizer amendments. pp. 633-690. *In* C. A. I. Goring and J. W. Hamaker (ed.) *Organical chemicals in the soil environment.* Vol. 2. Marcel Dekker, Inc. , New York.
- Hauck, R. D. and M. Koshino. 1971. Slow release and amended fertilizers. pp. 455-495. *In* R. A. Olsen, T. S. Army, J. J. Hanway, and V. J. Kilmer (ed.) *Fertilizer technology and use.* 2nd ed. Soil Sci. Soc. Am. , Madison, Wis.
- Hunt, I. V. 1966. The effect of utilization of herbage on the response to fertilizer nitrogen. *Int. Grassland Congr. , Proc. 9th (Sao Paulo)* 9:1113-1119.
- Jacques, W. A. and R. H. Schwass. 1956. Root development in some common New Zealand pasture plants. 7. Seasonal root replacement in perennial ryegrass (*Lolium perenne*), Italian ryegrass (*L. multiflorum*) and tall fescue (*Festuca arundinacea*). *N. Z. J. Sci. Technol.* 37:569-583.
- Jarrell, W. M. 1977. Nitrogen release from granules of sulfur-coated urea. Ph. D. Thesis. Ore. State Univ. , Corvallis. 144 pages.
- Lang, A. R. G. 1967. Osmotic coefficients and water potentials of sodium chloride solutions from 0 to 40°C. *Aust. J. Chem.* 20:2017-2023.

- Lunt, O.R. 1971. Controlled-release fertilizers: achievements and potential. *J. Agric. Food Chem.* 19:797-800.
- Lunt, O.R. and J.J. Oertli. 1962. Controlled release of fertilizer minerals by encapsulating membranes: II. Efficiency of recovery, influence of soil moisture, mode of application, and other considerations related to use. *Soil Sci. Soc. Am. Proc.* 26:584-587.
- Mays, D.A. 1970. Sulfur coated urea: a slow release nitrogen source for grass. *Int. Grassland Congress, Proc. 11th (Queensland, Australia)* 11:428-430.
- Mays, D.A. and G.L. Terman. 1969. Sulfur-coated urea and uncoated soluble nitrogen fertilizers for fescue forage. *Agron. J.* 61:489-492.
- McClellan, G.H. and R.M. Scheib. 1973. Characterization of sulphur coatings on urea. *Sulphur Institute J.* 9(3-4):8-12.
- McClung, N.M. 1960. Isolation of *Nocardia asteroides* from soils. *Mycologia* 52:154-156.
- McKee, Jr., W.H., R.H. Brown, and R.E. Blaser. 1967. Effect of clipping and nitrogen fertilization on yield and stands of tall fescue. *Crop Sci.* 7:567-570.
- Milthorpe, F.L. and J. Moorby. 1974. An introduction to crop physiology. Cambridge University Press, London.
- Moser, U.S. and R.V. Olson. 1953. Sulfur oxidation in four soils as influenced by soil moisture tension and sulfur bacteria. *Soil Sci.* 76:251-257.
- National Oceanic and Atmospheric Administration. 1972-1976. Climatological Data. Oregon. U.S. Department of Commerce. Volumes 78-82.
- Nobel, P.S. 1974. Introduction to biophysical plant physiology. W.H. Freeman and Co., San Francisco.
- Oertli, J.J. 1973a. The effect of coating properties on the nitrogen release from sulfur-encapsulated urea. *Agrochimica* 18:3-9.

- Oertli, J. J. 1973b. Effects of temperature, microbial activity, salinity, and pH on the release of nitrogen of sulfur-coated urea. *Z. Pflanzenernaehr. Bodenk.* 134:227-236.
- Powell, R. 1968. Controlled release fertilizer. Noyes Development Corp., Park Ridge, N. J.
- Prasad, M. 1976. The release of nitrogen from sulfur-coated urea as affected by soil moisture, coating weight, and method of placement. *Soil Sci. Soc. Am. J.* 40:134-136.
- Prasad, R., G. B. Rajale, and B. A. Lakhdive. 1971. Nitrification retarders and slow-release fertilizers. *Adv. Agron.* 23:337-383.
- Reid, D. 1966. The response of herbage yields and quality to a wide range of nitrogen application rates. *Int. Grassland Congr., Proc. 10th (Helsinki)* 10:209-213.
- Salisbury, F. B. and C. Ross. 1969. Plant physiology. Wadsworth Publishing Co., Inc., Belmont, California.
- Scheib, R. M. and G. H. McClellan. 1976. Characteristics of sulphur texture on SCU. *Sulphur Institute J.* 12(1):2-5.
- Shirley, A. R. Jr., and R. S. Meline. 1975. Sulfur-coated urea from a 1-ton-per-hour pilot plant. pp. 33-54. *In* J. R. West (ed.) *New uses of sulfur.* Am. Chem. Soc., Wash., D. C.
- Skipper, H. D. and D. T. Westermann. 1972. Comparative effects of propylene oxide, sodium azide, and autoclaving on selected soil properties. *Soil Biol. Biochem.* 5:409-414.
- Skujins, J. T. and A. D. McLaren. 1967. Enzyme reaction rates at limited water activities. *Science* 158:1569-1570.
- Tennessee Valley Authority. 1975. Use of sulfur-coated urea on forage plants, 1970-1974. TVA Bibliography No. 1445.
- Terman, G. L. 1972. Variability in grass forage clipping experiments comparing fertilizer rates and sources. *Agron. J.* 64:20-23.
- Tisdale, S. L. and W. L. Nelson. 1966. Soil fertility and fertilizers. 2d ed. Macmillan Co., New York.

- Troughton, A. 1957. The underground organs of herbage grasses. Commonwealth Agricultural Bureaux. Farnham Royal, Bucks, England.
- Viets, F. G. Jr. 1965. The plant's need for and use of nitrogen. In W. V. Bartholomew and F. E. Clark (ed.) Soil nitrogen. Agronomy 10:508-554. Am. Soc. of Agron., Madison, Wis.
- Wagner, R. E. 1954. Influence of legume and fertilizer nitrogen on forage production and botanical composition. Agron. J. 46:167-171.
- Watt, G. W. and J. D. Chrisp. 1954. Spectrophotometric method for determination of urea. Anal. Chem. 26:452-453.
- Weast, R. C. (ed.). 1972. Handbook of chemistry and physics. 53rd ed. Chemical Rubber Co., Cleveland, Ohio.
- Wedin, W. F. 1974. Fertilization of cool-season grasses. pp. 95-118. In D. A. Mays (ed.) Forage fertilization. Am. Soc. of Agron., Madison, Wis.
- West, P. W. and T. P. Ramachandran. 1966. Spectrophotometric determination of nitrate using chromotropic acid. Analytica Chimica Acta 35:317-324.
- Wilson, J. M. and D. M. Griffin. 1975. Water potential and the respiration of microorganisms in the soil. Soil Biol. Biochem. 7:199-204.
- Woldendorp, J. W. 1963. The influence of living plants on denitrification. Mededelingen van de Landbouwhogeschool te Wageningen, Nederland. 63:1-100.
- Young, R. D. 1974. TVA's development of sulfur-coated urea. Tennessee Valley Authority Bull. Y-79.
- ZoBell, C. E. 1969. Microbial modification of crude oil in the sea. pp. 317-326. In Proceedings of Joint Conference on Prevention and Control of Oil Spills. The American Petroleum Institute, Washington, D. C.

APPENDICES

APPENDIX I

Tall Fescue Nitrogen Content

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
- - - - - % N - - - - -				
March 21, 1973				
<u>Var. Fawn</u>				
Urea	3.03	3.92	4.18	4.50
SCU 30	3.18	3.63	3.68	4.33
SCU 4	3.36	3.48	3.82	4.02
Urea (split)				3.18
<u>S. 1000</u>				
Urea	3.09	3.80	4.08	4.60
SCU 30	3.17	3.40	4.16	4.42
SCU 4	3.36	3.57	3.90	3.77
Urea (split)				3.24
May 14, 1973				
<u>Var. Fawn</u>				
Urea	1.46	2.01	2.24	2.65
SCU 30	1.44	2.02	2.14	2.57
SCU 4	1.52	1.81	2.53	2.42
Urea (split)				2.50
<u>S. 1000</u>				
Urea	1.68	2.26	2.31	2.66
SCU 30	1.51	1.85	2.36	2.62
SCU 4	1.49	1.72	2.33	2.24
Urea (split)				2.48
June 29, 1973				
<u>Var. Fawn</u>				
Urea	1.49	1.75	2.44	2.90
SCU 30	1.48	1.77	2.02	2.49
SCU 4	1.49	1.60	1.73	2.68
Urea (split)				2.79
<u>S. 1000</u>				
Urea	1.66	2.27	2.62	2.70
SCU 30	1.77	1.92	2.35	2.68
SCU 4	1.38	1.85	2.30	2.31
Urea (split)				3.05

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - % N - - - - -			
August 15, 1973				
<u>Var. Fawn</u>				
Urea	1.54	1.61	2.23	2.72
SCU 30	1.48	1.49	2.00	2.27
SCU 4	1.31	1.49	1.82	1.97
Urea (split)				2.93
 <u>S. 1000</u>				
Urea	1.52	2.00	2.31	2.49
SCU 30	1.47	1.48	1.96	2.20
SCU 4	1.69	1.62	1.82	2.17
Urea (split)				2.81
 October 2, 1973				
<u>Var. Fawn</u>				
Urea	1.70	2.03	2.12	2.48
SCU 30	1.89	1.88	2.12	2.61
SCU 4	1.75	1.95	2.06	2.37
Urea (split)				3.49
 <u>S. 1000</u>				
Urea	1.37	2.16	1.68	2.89
SCU 30	2.20	1.99	2.15	2.28
SCU 4	1.92	2.18	1.74	2.59
Urea (split)				3.34
 March 19, 1974				
<u>Var. Fawn</u>				
Urea	3.95	4.26	4.24	4.57
SCU 30	4.44	4.40	4.58	4.37
SCU 4	3.30	3.97	4.19	4.61
Urea (split)				3.94
 <u>S. 1000</u>				
Urea	4.16	3.97	4.06	4.05
SCU 30	4.10	4.55	4.45	4.50
SCU 4	3.14	3.61	3.49	3.95
Urea (split)				3.24

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - % N - - - - -			
May 4, 1974				
<u>Var. Fawn</u>				
Urea	1.74	2.35	2.30	2.78
SCU 30	2.38	2.83	3.07	3.34
SCU 4	1.83	2.18	2.96	3.32
Urea (split)				2.51
 <u>S. 1000</u>				
Urea	2.00	2.17	2.65	2.67
SCU 30	2.28	2.58	3.04	3.19
SCU 4	1.86	2.23	2.58	3.09
Urea (split)				2.82
 June 14, 1974				
<u>Var. Fawn</u>				
Urea	1.59	1.65	1.80	2.35
SCU 30	1.58	1.66	2.45	2.74
SCU 4	1.93	2.41	2.76	3.05
Urea (split)				2.72
 <u>S. 1000</u>				
Urea	1.77	1.79	1.87	2.32
SCU 30	1.80	2.18	2.32	2.41
SCU 4	1.94	2.47	2.69	3.17
Urea (split)				2.74
 August 14, 1974				
<u>Var. Fawn</u>				
Urea	1.37	1.39	1.39	1.29
SCU 30	1.44	1.38	1.45	2.17
SCU 4	1.54	1.76	1.90	2.47
Urea (split)				2.41
 <u>S. 1000</u>				
Urea	1.52	1.51	1.51	1.52
SCU 30	1.86	1.52	1.76	1.92
SCU 4	1.49	1.85	2.37	2.86
Urea (split)				2.89

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
- - - - - % N - - - - -				
September 23, 1974				
<u>Var. Fawn</u>				
Urea	1.95	2.02	1.94	1.98
SCU 30	2.11	1.99	1.92	2.28
SCU 4	2.19	2.33	2.41	2.77
Urea (split)				3.06
 <u>S. 1000</u>				
Urea	2.19	1.51	2.27	2.16
SCU 30	2.54	2.09	2.40	2.16
SCU 4	2.01	2.20	2.60	3.11
Urea (split)				3.38
 March 26, 1975				
<u>Var. Fawn</u>				
Urea	2.79	3.01	3.61	3.76
SCU 30	2.67	2.95	3.30	3.54
SCU 4	2.96	3.03	3.05	3.32
Urea (split)				2.80
 <u>S. 1000</u>				
Urea	2.65	2.84	3.28	3.39
SCU 30	2.97	2.98	3.39	3.74
SCU 4	2.66	2.84	3.10	3.41
Urea (split)				2.59
 May 14, 1975				
<u>Var. Fawn</u>				
Urea	1.08	1.95	2.55	3.16
SCU 30	2.07	1.97	2.74	3.31
SCU 4	2.07	2.59	2.96	3.32
Urea (split)				2.45
 <u>S. 1000</u>				
Urea	2.12	2.41	2.37	2.64
SCU 30	2.17	2.67	2.98	2.84
SCU 4	2.39	2.39	3.19	3.47
Urea (split)				3.23

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
- - - - - % N - - - - -				
June 26, 1975				
<u>Var. Fawn</u>				
Urea	1.45	1.53	1.69	2.05
SCU 30	1.58	1.80	1.99	1.98
SCU 4	1.71	1.80	2.53	2.46
Urea (split)				2.38
 <u>S. 1000</u>				
Urea	1.78	1.73	1.92	2.12
SCU 30	2.01	1.82	2.07	2.16
SCU 4	1.80	2.01	2.27	2.34
Urea (split)				2.24
 August 19, 1975				
<u>Var. Fawn</u>				
Urea	1.40	1.45	1.73	1.67
SCU 30	1.75	1.71	1.72	1.89
SCU 4	1.83	1.94	2.48	2.81
Urea (split)				2.51
 <u>S. 1000</u>				
Urea	2.15	1.83	1.59	2.03
SCU 30	1.93	1.68	2.14	2.26
SCU 4	1.75	2.00	2.68	3.16
Urea (split)				2.57
 October 15, 1975				
<u>Var. Fawn</u>				
Urea	1.34	1.57	1.66	1.61
SCU 30	1.60	1.63	1.78	1.87
SCU 4	1.90	1.83	2.02	2.38
Urea (split)				1.64
 <u>S. 1000</u>				
Urea	1.83	1.68	1.59	1.83
SCU 30	2.09	1.44	1.65	1.86
SCU 4	1.72	1.14	2.04	2.38
Urea (split)				1.92

Fertilizer	N applied, kg/ha/yr			
	200	400	600	800
	- - - - - % N - - - - -			
April 6, 1976				
<u>Var. Fawn</u>				
Urea	2.69	2.33	2.13	2.27
SCU 30	2.54	2.20	2.46	2.50
SCU 4	1.64	2.49	2.44	3.10
Urea (split)				2.86
 <u>S. 1000</u>				
Urea	2.65	2.47	2.26	2.18
SCU 30	2.35	2.20	2.24	2.42
SCU 4	2.58	2.32	2.47	2.72
Urea (split)				2.59
 June 2, 1976				
<u>Var. Fawn</u>				
Urea	1.53	1.38	1.12	1.12
SCU 30	1.29	1.22	1.34	1.27
SCU 4	1.33	1.25	1.31	1.62
Urea (split)				1.30
 <u>S. 1000</u>				
Urea	1.50	1.45	1.08	1.06
SCU 30	1.73	1.43	1.32	1.47
SCU 4	1.38	1.22	1.31	1.52
Urea (split)				1.27
 August 13, 1976				
<u>Var. Fawn</u>				
Urea	1.91	1.61	--	1.43
SCU 30	-- ¹	--	--	1.44
SCU 4	--	--	1.78	1.41
Urea (split)				1.29
 <u>S. 1000</u>				
Urea	2.00	--	--	--
SCU 30	--	--	--	1.54
SCU 4	--	--	--	1.35
Urea (split)				1.36

¹Missing data.

APPENDIX II

Calculation of Urea Release from SCU 4 as a Function of Temperature

The following Fortran program was used to calculate a cumulative percent release (CUMRLS) of urea from SCU 4 as a function of daily minimum and maximum temperature and time.

```

PROGRAM SCU4RLS
  DIMENSION TEMP(2,625), CUMRLS(625)
C READ DAILY MIN AND MAX TEMP (FAHRENHEIT) INTO ARRAY.
  READ(60,5)TEMP
  5 FORMAT(9X,F3.0,1X,F3.0)
C INITIALIZE CUMRLS DUE TO BROKEN GRANULES.
  CUMRLS(1)=10.
C ADJUST TEMPS HALF DISTANCE TO DAILY AVERAGE.
  DO 3 I-1,625
    IF(CUMRLS(I).GE.100.)GO TO 99
    A=TEMP(1,I)
    TEMP(1,I)=A*.75+TEMP(2,I)*.25
    TEMP(2,I)=TEMP(2,I)*.75+(A*.25)
C Q10=2.WHEN TEMP=95F, 12 HR RLS=.75 PERCENT.
C NOTE, IFQ10=2 IN CELSIUS, Q18=2 IN FAHRENHEIT.
    K=I+1
    X=.0193*EXP(.0385*TEMP(1,I))+.0193*EXP(.0385*TEMP(2,I))
    CUMRLS(K)=CUMRLS(I)+X
  3 CONTINUE
99 WRITE(1,2)(CUMRLS(I),I=1,K,10)
  2 FORMAT(10X,F7.2)
C ONLY EVERY 10TH DAY IS WRITTEN
  END

```

APPENDIX III

Calculation of Coating Thickness Distribution

According to Eq. (8), page 16,

$$T_c = \left[(3/4\pi) \left(\frac{M_u}{D_u} + \frac{M_c}{D_c} \right) \right]^{1/3} - R_u$$

where

$$R_u = \left[(3/4\pi) (M_u / D_u) \right]^{1/3},$$

and

R_u = radius of urea in granule, cm

T_c = total coating thickness, cm

M_u = mass of urea, g

M_c = mass of coating, g

D_u = density of urea = 1.323 g/cm³

D_c = density of coating = 2.0 g/cm³.

Substituting the density values into both equations and combining:

$$T_c = 0.4924(M_c + 1.5117M_u)^{1/3} - 0.5651(M_u)^{1/3}$$

If M_c and M_u are in mg and T_c is in microns,

$$T_c = 492.4(M_c + 1.5117M_u)^{1/3} - 565.1(M_u)^{1/3}.$$

The coating thickness of 60 individual granules of each SCU material was calculated. In the following tables, data have been ranked according to coating thickness.

Urea (M _u)	Coating (M _c)	Coating thickness (T _c)	Coating thickness range	Urea weight in class	Cumulative urea weight	
<u>mg</u>	<u>mg</u>	<u>μ</u>	<u>μ</u>	<u>mg</u>	<u>mg</u>	<u>% of total</u>
<u>SCU 4</u>						
14.6	2.6	52	50-60	46.6	46.6	6.0
8.9	2.0	55				
10.0	2.2	56				
13.1	2.8	60				
15.6	3.2	61	60-70	108.1	154.7	19.9
13.0	2.9	62				
12.4	2.9	64				
13.9	3.1	64				
15.6	3.4	65				
11.6	2.9	67				
10.7	2.8	68				
15.3	3.5	68				
11.7	3.1	71	70-80	187.4	342.1	44.0
12.3	3.2	71				
12.7	3.3	72				
13.5	3.5	73				
16.4	4.0	73				
15.3	3.9	75				
8.7	2.8	77				
17.3	4.4	77				
10.9	3.3	79				
16.1	3.9	79				
15.2	4.1	79				
10.7	3.3	80				
15.9	4.3	80				
10.7	3.3	80				
10.7	3.5	84	80-90	69.4	411.5	52.9
12.0	4.0	89				
11.0	3.8	89				
18.5	5.3	99				
17.2	5.1	90				

Urea (M _u)	Coating (M _c)	Coating thickness (T _c)	Coating thickness range	Urea weight in class	Cumulative urea weight	
<u>mg</u>	<u>mg</u>	<u>μ</u>	<u>μ</u>	<u>mg</u>	<u>mg</u>	<u>% of total</u>
11.9	4.1	91	90-100	171.7	583.2	75.0
12.9	4.3	91				
9.6	3.6	92				
10.5	3.8	92				
8.7	3.4	93				
10.2	3.8	93				
12.6	4.4	94				
15.9	5.1	94				
12.8	4.5	95				
10.0	3.8	95				
19.8	5.9	95				
11.6	4.2	95				
12.7	4.5	96				
12.5	4.6	99				
14.7	5.2	101	100-110	97.6	680.8	87.5
18.7	6.1	101				
9.2	4.0	104				
13.0	5.0	104				
10.5	4.4	105				
19.5	6.7	108				
12.0	5.0	109				
9.1	4.3	112	110-120	59.6	740.4	95.2
9.7	4.5	113				
15.2	6.1	114				
12.3	5.6	120				
13.3	5.9	120				
11.0	5.4	124	120+	37.6	778.0	100.0
16.8	8.0	138				
9.8	6.4	154				
<u>SCU 23</u>						
14.4	1.1	23	20-30	14.4	14.4	1.8
15.3	2.0	39	30-40	25.8	40.2	5.1
10.5	1.6	40				
18.3	2.6	45	40-50	37.5	77.7	9.8
19.2	2.8	47				
11.9	2.2	51	50-60	11.9	89.6	11.3

Urea (M _u)	Coating (M _c)	Coating thickness (T _c)	Coating thickness range	Urea weight in class	Cumulative urea weight	
<u>mg</u>	<u>mg</u>	<u>μ</u>	<u>μ</u>	<u>mg</u>	<u>mg</u>	<u>% of total</u>
14.1	6.0	118				
16.2	6.6	118				
11.5	5.4	120				
11.7	5.5	121	120-130	70.4	685.3	86.4
12.6	5.8	122				
20.4	7.9	122				
12.2	5.9	126				
13.5	6.5	130				
10.3	5.7	135	130-140	26.5	711.8	89.9
16.2	7.7	137				
10.9	6.2	141	140-150	20.4	732.2	92.4
9.5	5.8	143				
12.7	7.4	151				
16.9	9.4	160	150+	60.6	792.8	100.0
19.3	11.6	170				
11.7	9.8	203				
<u>SCU 25</u>						
10.5	1.1	28	20-70	88.4	88.4	11.0
16.3	1.8	34				
7.2	1.3	42				
8.4	1.6	46				
21.9	3.3	51				
24.1	4.8	69				
18.8	4.2	71	70-80	52.5	140.9	17.5
19.6	4.5	74				
14.1	3.9	79				
15.7	4.3	81	80-90	114.2	255.1	31.7
11.4	3.7	85				
17.1	4.8	85				
11.7	3.8	86				
14.1	4.4	88				
9.4	3.4	88				
14.1	4.4	88				
9.0	3.3	88				
11.7	3.9	88				
12.3	4.2	92	90-100	96.6	351.7	43.7
15.9	5.1	94				

Urea (M _u)	Coating (M _c)	Coating thickness (T _c)	Coating thickness range	Urea weight in class	Cumulative urea weight	
<u>mg</u>	<u>mg</u>	<u>μ</u>	<u>μ</u>	<u>mg</u>	<u>mg</u>	<u>% of total</u>
10.0	3.8	95				
12.5	4.5	97				
19.5	6.1	99				
16.6	5.5	99				
9.8	4.0	100				
8.1	3.9	110	100-110	8.1	350.8	44.7
13.5	5.6	113	110-120	106.7	466.5	58.0
12.6	5.4	114				
15.0	6.1	115				
15.8	6.3	115				
17.2	6.8	118				
17.1	6.9	120				
15.5	6.5	120				
9.6	4.9	122	120-130	34.3	500.8	62.2
9.7	5.2	128				
15.0	6.9	129				
11.1	5.9	133	130-140	89.1	589.9	73.3
19.4	8.4	133				
11.8	6.2	135				
19.6	8.6	135				
6.7	4.4	136				
10.8	6.0	137				
9.7	5.7	140				
14.5	7.5	142	140-150	57.3	647.2	80.4
15.7	8.0	144				
11.0	6.5	146				
16.1	8.5	150				
18.0	9.4	154	150-160	31.1	678.3	84.3
13.1	8.0	160				
13.5	8.5	166	160-170	22.1	700.4	87.0
8.6	6.6	170				
11.4	7.9	171	170-180	55.3	755.7	93.9
13.4	8.8	172				
20.2	11.6	174				
10.3	7.7	176				
25.5	16.0	204	180+	49.1	804.8	100.0
5.4	6.6	217				
15.2	13.0	226				
3.0	11.5	427				