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Vol. 58:175-178, 1966.

Effect of Temperature and Coating Thickness on the Release of Urea From Resin-Coated Granules¹

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ABSTRACT

Resin coatings are very effective in controlling the availability of N from applied urea in moist soil. In leaching studies, 94% of the noncoated urea was recovered in 1 day, compared to a 49% recovery of the N from coated urea (13.2% resin) in 4 weeks of intermittent leaching.

Release rates are controlled by the thickness of the coating and the temperature of the medium. Coatings averaging 13.2% resin markedly decreased release of urea, compared to coatings of 9.0% resin. In the range between 5 to 35C, increased release of urea accompanied increases in temperature. After 4 weeks of incubation and intermittent leaching totaling 20 inches of water, 25 and 67% of the added N were leached from soil at 5 and 35C, respectively. Increasing the temperature 10C was approximately equivalent to doubling the release time within a 16-week period. Increasing the temperature increases expansion of the capsule and the surface area through which diffusion must take place. This effect is probably supplemental to the effect of temperature on the diffusion phenomena *per se*. Approximately 99% of the capsules were recovered intact after incubation for 16 weeks at four temperatures between 5 and 35C.

LOSSES of nitrogen applied to the soil in fertilizer are frequently large and occur in several ways. Plant-available forms, particularly nitrates, are readily leached from the root zone. Volatilization losses of ammonium and other forms of nitrogen are known to occur. Nitrogen applied to the soil may also be combined to relatively unavailable forms. On the other hand, higher than optimum amounts of available N may be deleterious to plants. Excessive vegetative growth from N application may result in decreased flowering and seed production for certain plants. The high

solubility of N fertilizer salts can result in toxic conditions for germinating seedlings. For these reasons, there is much interest in controlling the release of applied N in fertilizer and, thereby, increasing the efficiency of its use.

Recently, emphasis has been given to methods of coating fertilizer for controlling the release of nutrients. Some of the materials used for coating are polyethylene, resins, vinyl acetate, waxes, paraffin compounds, asphaltic mixtures, and sulfur. Lawton (4) found paraffin and acrylic resin coatings to be superior to several other materials for preventing salt injury during seed germination. Increased yields of corn and increased recovery of N and P when fertilizer granules are contained in perforated polyethylene envelopes were reported by Ahmed et al. (1). Dahnke et al. (2) increased recovery of N by maize in the greenhouse by applying pelleted $(\text{NH}_4)_2\text{SO}_4$ which had been coated with wax.

Lunt, Kofranek, and Oertli (5) showed that coatings of polymeric resin prolonged mineral release from fertilizer over a period of 6 months. In a sand medium through which 7 feet of water had passed, Lunt and Oertli (6) measured a recovery by corn plants of 25 to 45% of the N applied as resin-coated NH_4NO_3 .

Of the commonly used dry N fertilizers, urea is the most toxic to germinating seeds. Gasser (3), in a comprehensive review of the characteristics, behavior, and use of urea fertilizer, emphasizes that the ammonia gas produced in urea decomposition and the contaminant biuret both are toxic in the germination period when urea is banded with seed.

Controlling the concentration of urea in the soil solution by coating granules with resin therefore offers several possible advantages, and the objectives of this study were to measure the effect of temperature and coating thickness on (i) the release of urea from resin-coated fertilizer, and (ii) the leachable N when the coated material was mixed with the soil.

¹Contribution from Soil and Water Conservation Research Division, ARS, USDA, and the California Agricultural Experiment Station. Received Aug. 8, 1965.

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MATERIALS AND METHODS

Two leaching procedures were used. The effect of a resin coating, as well as its thickness, on release of urea was determined by a continuous leaching procedure. Forty granules each of non-coated, light-coated, and heavy-coated urea were weighed, put into a filter-paper envelope, and placed between two thin layers of sterilized quartz sand. Distilled water was passed through the column at 10 to 15 ml per hour.

In the temperature studies, where both release of urea from capsules and leachable N in sand and soil were determined, inverted 500-ml polyethylene bottles were used for leaching columns. Duplicate samples of noncoated, light-coated, and heavy-coated urea (equivalent to 240 mg of nitrogen) were mixed with 320 g of sand or 250 g of soil. The mixture was placed in the lower part of the leaching column and covered with 2.5 inches of sand or soil. Incubation temperatures were 5, 15, 25, and 35°C. Two hundred and fifty milliliters of distilled water were passed through the sand or soil at each leaching, and the leachate was analyzed for urea-ammonium-, and nitrate-N. To determine the amount of urea released through the resin coating in the incubation study, depleted capsules were separated from sand and soil by screening at the conclusion of the experiment. Capsules with their remaining contents were analyzed for N. Urea- and nitrate-N were determined by a modified method of Watt and Chrisp (8) and the phenoldisulfonic method, respectively. A micro-Kjeldahl method was used for determining ammonium- and total N. Untreated soil and sand columns were included, and leachable N from fertilizer was calculated by subtracting values for soil without fertilizer.

To obtain samples for studying effect of coating thickness on release of urea with relatively small fertilizer samples, coated granules received from the manufacturer² were separated according to color saturation. Using the Munsell soil color chart, the light coating was designated as 5Y 8/6 and the heavy coating as 25Y 8/8. To verify the difference in coating thickness, the N content of 13 randomly selected individual capsules was determined for each class. The N ranged from 41.8 to 43.4% for light-coated, and from 39.1 to 41.4% for the heavy-coated urea. The percent resinous membrane was determined by weighing the membrane after removal of urea and also by subtracting the weight of urea determined from the total weight of the coated granule. With the former method, the resin averaged 9.0 and 13.2% for the light- and heavy-coated granules, respectively, and with the latter method, 9.2 and 13.4% respectively. Coated granules of 1.68 to 1.98 mm diameter were used. Samples of noncoated urea, ranging in diameter from 1.65 to 1.68 mm, were taken from a source of commercial urea fertilizer. A No. 20 quartz sand was used in all leaching studies. It was steam-sterilized and vacuum-dried immediately before beginning the incubation studies. The soil was Hanford very fine sandy loam, treated with 0.05% kirlum to facilitate leaching. The cation-exchange capacity of the treated soil was 10.8 meq/100 g of dry soil.

RESULTS

Resin Coating Effect on Release

Resin coatings effectively reduced the mobility of soluble urea. Under continuous leaching in a filter-paper envelope, the noncoated urea was rapidly removed (Fig. 1). Inas-

² Archer-Daniels-Midland Co., Minneapolis, Minnesota.

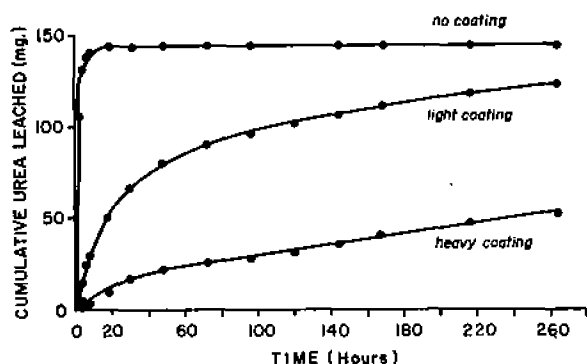


Fig. 1. Effect of coating urea granules with resin of differing thicknesses on rate of urea release under continuous leaching.

much as the quartz sand did not retain nitrogen against leaching, the recovery of nitrogen in the leachate was a measure of the release rate from the capsules. Eighty-eight percent was recovered in the leachate 8 hours after leaching commenced, and recovery ceased after 18 hours when 91% had been recovered. In contrast, 16% of the light-coated and 2% of the heavy-coated urea were recovered in the leachate after 8 hours. After 264 hours of continuous leaching, 67 and 32% of urea had been leached from the light- and heavy-coated materials, respectively. A high rate of urea release occurred initially after wetting. The rate decreased until a nearly constant rate was reached.

Leaching of a sand-fertilizer mixture for a 16-week period showed coating thickness affected cumulative N release for 10 weeks, at which time 96% of the urea had been released from the capsules (Fig. 2). The greatest difference in cumulative release occurred 1 week after leaching was initiated when 100 mg less, or 40% of the total amount, were released from the heavy-coated material. Relatively early during the leaching study, between the first and third weeks, depending on coating thickness, rates of urea release progressively decreased as the capsules were depleted.

Leachability of N from the fertilizer-soil system is of primary interest. Resin coatings on the fertilizer granules markedly reduced the recovery of fertilizer N from the soil columns. After 1 day, 94% of the N from the non-coated urea was leached from the soil (Fig. 2), whereas at the end of 4 weeks, 74 and 49% of the N from light- and heavy-coated materials were recovered, respectively. Rate of recovery was much slower from soil during the earlier part of the leaching period, but when apparent depletion effects were reducing the rate of release in the sand, the rate of recovery of N from the soil was greater. Leaching losses of N would be expected to be less in the soil. A thicker resin coating is an additional factor reducing the leachability of N. The heavier coating continued to effect a reduced nitrogen recovery from the soil throughout the leaching period. Stability of the resin was shown by recovery of all capsules intact at both thicknesses in sand and soil after 16 weeks.

Temperature Effect on Release

Temperature markedly affected the release of urea from the heavy-coated fertilizer in sand (Fig. 3). Although the

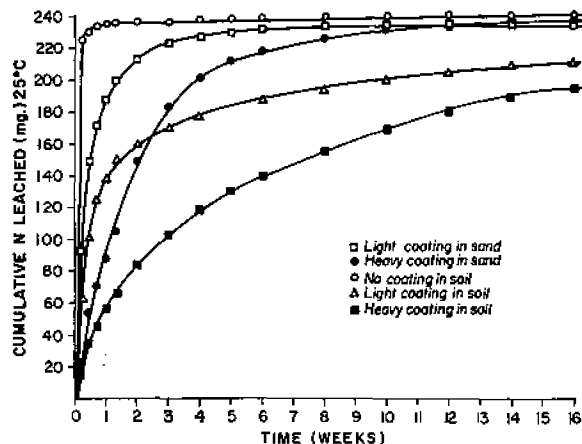


Fig. 2. Effect of thickness of resinous coating on recovery of N from coated urea in sand and soil leaching columns over an extended period.

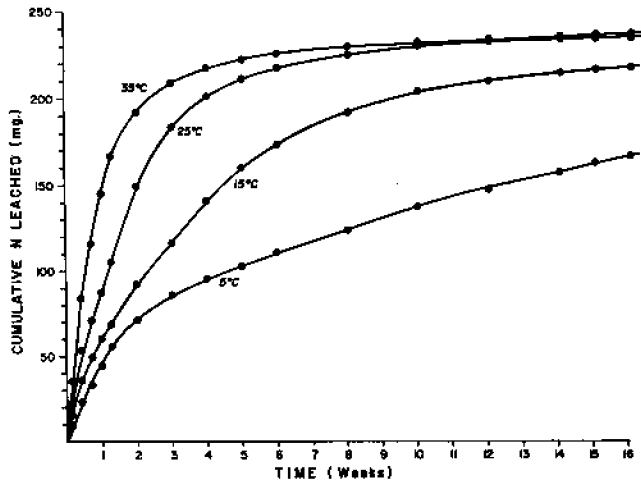


Fig. 3. Effect of temperature on release of urea from heavy-coated granules mixed with quartz sand.

initial period of rapid release prevailed at all temperatures, rates were less and tapered off more rapidly at lower temperatures.

At 1 week, when the rates of release at all temperatures were relatively constant, there was an approximate doubling in the release rate for each 10-degree increase in temperature. Release rates decreased rapidly after 3 weeks at the 25 and 35C temperatures, presumably because of capsule depletion. At 5C, 70% of the urea had been released after 16 weeks of intermittent leaching. Over 3 feet of water had been passed through the sand leaching columns during this period.

Temperature Effect on N Leached from Resin-Coated Urea in Sand and Soil

The leachable fertilizer N from heavy-coated urea was directly related to temperature in soil as well as in sand (Table 1). An increase of 10 degrees in temperature was approximately equivalent to doubling the reaction time in determining the percentage of fertilizer N that was leached for both sand and soil. The greatest departure from this relationship for the period investigated occurred at the 5C temperature after 16 weeks. The effect of the soil in reducing the N leached did not change this time-temperature relationship.

Ten-degree increases between 5 and 35C resulted in similar increased increments of cumulative N leached from soil after the initial rapid release period (Fig. 4). Rates of recovery were fairly constant and similar for a considerable period. For example, between the eighth and tenth week, approximately 12 mg of N were recovered at 5, 15, and 25C, and slightly less at 35C. Apparently the capsule depletion effect was reducing the rate at the higher temperature. As was the case with sand, lower tempera-

Table 1. Effect of temperature and time on the cumulative percentage of N leached from sand and soil to which heavy resin-coated urea was added.

| Time, weeks | Cumulative % N leached | | | | | | | |
|-------------|------------------------|------|------|------|------|------|------|------|
| | Sand | | | | Soil | | | |
| | 5 C | 15 C | 25 C | 35 C | 5 C | 15 C | 25 C | 35 C |
| 1 | 18.6 | 25.0 | 36.7 | 60.7 | 13.0 | 20.2 | 23.7 | 39.5 |
| 2 | 30.0 | 38.6 | 62.5 | 80.3 | 20.0 | 26.2 | 35.0 | 62.2 |
| 4 | 39.9 | 58.9 | 84.1 | 90.9 | 25.4 | 36.0 | 49.5 | 66.6 |
| 8 | 51.8 | 80.7 | 94.4 | 98.2 | 36.2 | 50.4 | 65.0 | 80.8 |
| 16 | 70.0 | 91.5 | 99.7 | 98.7 | 57.6 | 68.5 | 81.8 | 86.9 |

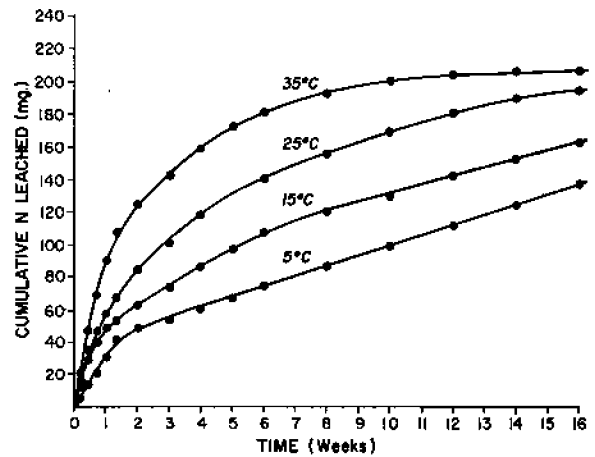


Fig. 4. Effect of temperature on release and recovery of N by leaching soil treated with heavy-coated urea.

tures reduced the rate of N recovery in the leachate and prolonged the period of constant release rate (Fig. 3).

The shape of the N recovery curves in Fig. 4 suggests that the particular sequence of leaching intervals may have influenced the rate of recovery in soil, i.e., lengthening the leaching interval (particularly from 2 days to 1 week) tended to be associated with a slight reduction in recovery rate from the soil columns. Ammonium- and nitrate-N, as well as urea, were recovered in the leachate, indicating that soil conditions were conducive to hydrolysis of urea and nitrification of ammonium-N. Longer intervals between leaching periods would allow more conversion of urea- and ammonium-N, the products of which are susceptible to retention by the soil, particularly ammonium. After 2 weeks of leaching at short intervals (1, 2, 2, 2, 2, and 5 days), 96% of the total urea-N recovered for the 16-week period at 35C was leached (Fig. 5). At the same time, 71% of the ammonium-N and only 40% of the nitrate-N was recovered. When the 1-week leaching interval was initiated, urea recovery decreased to zero, and ammonium-N recovery decreased from 26 to 11 mg of N per week; but nitrate recovery increased from 1 to 8 mg of N per week. Changing to the 2-week leaching interval appeared to further change the rate of removal of these N fractions. The amount of N recovered in the soil leachate is there-

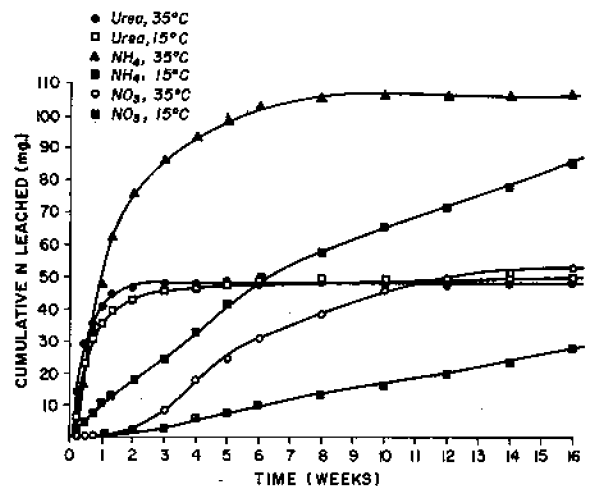


Fig. 5. Effect of two temperatures on N fractions recovered by leaching soil treated with heavy-coated urea.

Table 2. Disposition of fertilizer N applied as heavy resin-coated urea after 16 weeks of incubation in sand and soil.

| Temp. C | % N leached or released | | | |
|------------|-------------------------|----------|---------|----------|
| | Sand | | Soil | |
| | Leached | Released | Leached | Released |
| 5 | 70 | 70 | 88 | 80 |
| 15 | 82 | 83 | 89 | 96 |
| 25 | 100 | 98 | 82 | 88 |
| 35 | 88 | 100 | 87 | 100 |

fore a function of the proportion of the N fraction and its relative retention by the soil, as well as the temperature and resin coating thickness.

The temperature range from 15 to 35C effected a very small difference in N leached as urea (Fig. 5). In contrast, large differences in ammonium- and nitrate-N recovery occurred. Both an increased rate of urea release from the capsule and an increased rate of hydrolysis of urea to ammonium are indicated at the higher temperature. More nitrate-N at 35C than at 15C would be expected, since it is known that higher temperature increases nitrification.

Analyses of leachate for N fractions from the quartz sand columns revealed (i) no recovery of nitrate-N throughout the 16-week leaching period at any temperature, and (ii) a gradual increase in ammonium-N leached which was proportional to temperature level and which totaled 36 mg, or 15%, of total N recovery at 35C.

After the 16-week incubation and leaching period, the resin capsules were recovered from the leaching columns and their contents analyzed for N. An average of 1% or less of the capsules was not recovered from the sand and soil columns. Percent N released from the capsules and the amount of N recovered in the leachates agreed very closely for the sand medium (Table 2). As was expected, the amount of N leached from the soil columns was considerably less than that released, based on final capsule analyses. Release from the resin capsule was similar for the sand and soil mediums at 15, 25, and 35C. The 20% greater release in soil at 5C after 16 weeks is difficult to explain.

Observations of the behavior of the resin capsules on wetting and the size of capsules incubated at different temperatures correlate well with the urea release rates. When the coated granules are placed in contact with a moist surface, the insoluble resin coating softens. The coating appears to act as a semipermeable membrane until osmotic pressure expands the resin capsule to a thinner, more permeable membrane, and the dissolved fertilizer salts diffuse through. Rates of release are highest at this time, when the capsules are under a high internal pressure. Coated urea in its original form and after 19 days in water is shown in the upper left and lower right, respectively, of Fig. 6. The volume of the wetted capsules has increased between two to three times. Coated urea that had been placed on a wet soil surface for 24 hours and dried is shown in the upper right of the figure. Expansion of the resin capsule and the consequent higher initial rate of diffusion are temperature dependent. The larger capsules in lower left of Fig. 6 were taken from soil columns at 35C and the smaller ones from soils columns incubated at 5C. Increased swelling of the capsules at higher temperatures was suggested by Oertli and Lunt (7) as a modifying



Fig. 6. Heavy-coated urea fertilizer capsules magnified 7 times. *Upper left*—in normal storage condition. *Lower right*—after placing in water for 19 days. *Upper right*—removed from surface of wet soil and dried. *Lower left*—recovered from incubation in sand at 35C (upper) and at 5C (lower).

factor in release of salts through the resin membrane. A lighter resin coating or thinner capsule in itself permits a higher rate of diffusion. After initial expansion of the capsule to its maximum volume, water continues to enter and the diffusion rate of urea solution outward remains fairly constant until depletion lowers the concentration gradient.

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