

RESEARCH LETTER

Laboratory studies on dissolution of nitrogen fertilizers by humidity and precipitation

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Abstract

Aiming at improving fertilizer management by assessing fertilizer dissolution, we compared the hygroscopicity of calcium ammonium nitrate (CAN), ammonium nitrate (NS 27-4), and nitrate compounds (laboratory grade). Dissolution of N fertilizers was also studied under simulated rain conditions. All compounds were highly hygroscopic, dissolving within 24 h at 90–99% relative humidity and 25 °C. Addition of 2 mm rain to fertilizer granules (3–4.5 mm diam.) was sufficient to dissolve 50% of the compounds. Dissolution rates by humidity or rain were not the limiting step for plant availability.

1 | INTRODUCTION

Nitrogen (N) fertilizers are nowadays applied with great precision to meet crop demand, using sensor techniques combined with split application (Hooper, Zhou, Coventry, & McDonald, 2015). However, soluble fertilizers applied in split doses require soil water, rainfall, or sufficient air moisture to dissolve and become plant available. Rapid dissolution is critical especially at later stages during crop growth for high N use efficiency. To further improve fertilizer management, knowledge about dissolution dynamics is required.

Literature data show that nitrogenous compounds such as calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] and ammonium nitrate (NH_4NO_3) are highly soluble in water, with solubility of 1.44 g solid g^{-1} H_2O for calcium nitrate tetrahydrate and 2.13 g for ammonium nitrate, which is four- to sixfold higher than for sodium chloride (NaCl) (Lide, 2004). However, studies of the dissolution kinetics of these compounds are scarce. Both are hygroscopic, absorbing water vapor from ambient air, which results in caking and dissolution, a process termed *deliquescence*. Hygroscopicity and deliquescence act simulta-

neously, being dependent on the relative humidity of ambient air. Relative humidity of 50.5% for calcium nitrate and 62.7% for ammonium nitrate has been shown to be sufficient to cause deliquescence at 25 °C (Adams & Merz, 1929). In one study, hygroscopic water uptake of ammonium nitrate used in explosives amounted to 0.15 g water g^{-1} solid during 2 h at relative humidity 87–94% and 28 °C (Harris, 1970).

In this study, we set to examine the amount of water and time required for a fertilizer granule to dissolve. The aim was to determine the dissolution rate of two commercial N fertilizers when exposed to either moist air or precipitation. The hygroscopicities were compared with those of similar chemical compounds. Our specific objectives were (a) to measure the maximum potential of hygroscopicity and dissolution of $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 , and of comparable chemical compounds at high relative humidity, and (b) to quantify the dissolution rates of the two fertilizers under precipitation by simulated rainfall.

2 | MATERIAL AND METHODS

Two granulated and coated commercial N fertilizers, calcium ammonium nitrate (CAN 15.5) and ammonium

Abbreviations: CAN, calcium ammonium nitrate.

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nitrate blended with anhydrite and dolomite (NS 27-4) were used (Yara International ASA) for the hygroscopicity and precipitation experiments. Calcium ammonium nitrate [$5\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$] is a double salt with 15.5% N (14.4% as $\text{NO}_3\text{-N}$ and 1.1% as $\text{NH}_4\text{-N}$) and 18.8% Ca. The NS 27-4 blend [NH_4NO_3 (80%) + CaSO_4 + $\text{CaMg}(\text{CO}_3)_2$] contains 27% N (13.5% as $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ respectively), 3.7% S, and 0.6% Mg. Both fertilizers are coated by a mixture (0.3%) of wax, oil, and resin (Obrestad & Tande, 2016). The reference chemicals used in the hygroscopicity experiment were calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] and ammonium nitrate (NH_4NO_3) (99.4–99.5 purity; VWR Chemicals).

2.1 | Dissolution by hygroscopicity

Hygroscopicity was measured under controlled temperature (25 ± 1 °C) and relative humidity 90–99% in a laboratory setup following the principles of Harris (1970). A 3- to 4.5-mm-diam. fraction of fertilizer granules was selected, representing medium size and aiming for a uniform size distribution. Fifteen granules (total weight 0.6 g) and 0.75 g of reference chemicals consisting of salt crystals (<1 mm) were placed on metal nets (200 mm diam. and 0.5 mm mesh size). Granules were distributed in groups of three and salt crystals in portions of 0.15 g, each at five spots 50 mm apart. Four replicates were used for each treatment except for CANs, where only three replications were successful. Given the relatively infinite supply of water vapor, the fertilizer dose tested was equivalent, but not limited, to 48 kg ha^{-1} .

Plastic cups were attached beneath each metal net to collect the dissolving compound, and nets with cups were weighed on a high-accuracy scale (A&D HF-2000G, A&D Company, Ltd.). Weighing intervals were initially set to every 15 min for chemicals and 60 min for fertilizers, which were then gradually extended to 3 h as the hygroscopicity rates declined. Hygroscopicity on each weighing occasion was expressed as

$$H = \frac{m_a}{m_s} \quad (1)$$

where H is hygroscopicity, m_a is mass of water absorbed, and m_s is initial mass of solid.

The degree of dissolution (D), in percent, was defined based on deliquescence theory by Tereshchenko (2015) as

$$D = H \times s \times 100 \quad (2)$$

where s is the solubility of the compound in water at a given temperature (g solid g^{-1} water). The following solubilities (s) at 25 °C were used in the calculations: 1.439 g for cal-

Core Ideas

- Hygroscopic N fertilizers are dissolved within hours at high air humidity.
- Only a small amount of precipitation is required for dissolution by rain.
- Further dilution of dissolved ions, not dissolution, is the limiting step for plant N uptake.

cium nitrate tetrahydrate (Lide, 2004), 2.5 g for CAN fertilizer (Crystal growing, 2018), and 2.125 g for ammonium nitrate (Lide, 2004). Because a specific solubility value for NS 27-4 was not available, the same value as for ammonium nitrate was assumed despite the presence of slowly soluble dolomite and gypsum.

2.2 | Dissolution by simulated rain

For measurements of dissolution by precipitation, a rain simulator built by Sigtryggsson (2018) was used. The exact weight of intact fertilizer granules was recorded, and the granules were evenly distributed over stainless steel nets similar to those used in the hygroscopicity experiment, covering about 1% of the surface area. Deionized water (21.6 ± 0.5 °C) was sprayed over the granules every 2 min for 40–50 min at a rate corresponding to 18 mm h^{-1} , equivalent to moderate-to-heavy rain intensity. Rainwater drained off from the steel net immediately. Drainage after each spray was collected, weighed, and analyzed for conductivity (inoLab Cond 720, WTW). Each fertilizer compound was subjected to five replicate tests. Conductivity measurements were converted into concentrations using a conversion factor for standards prepared from the same compounds, following a linear relationship (Patten & Bennett, 1962). The 1% coverage of the metal net by granules was equivalent to 180 kg ha^{-1} product, but larger amounts could be added without affecting the outcome of the measurements.

The mass of dissolved salt was computed as

$$m_s = \frac{\sigma V}{X} \quad (3)$$

where m_s is mass of salt in grams, σ is conductivity in S m^{-1} , V is volume of solution analyzed in liters, and X is a conversion factor.

The degree of solid dissolved, expressed as a percentage of weight, was calculated as

$$S_{\text{diss}} (\%) = \left(\frac{m_{s(c)}}{m_{s(\text{end})}} \right) 100 \quad (4)$$

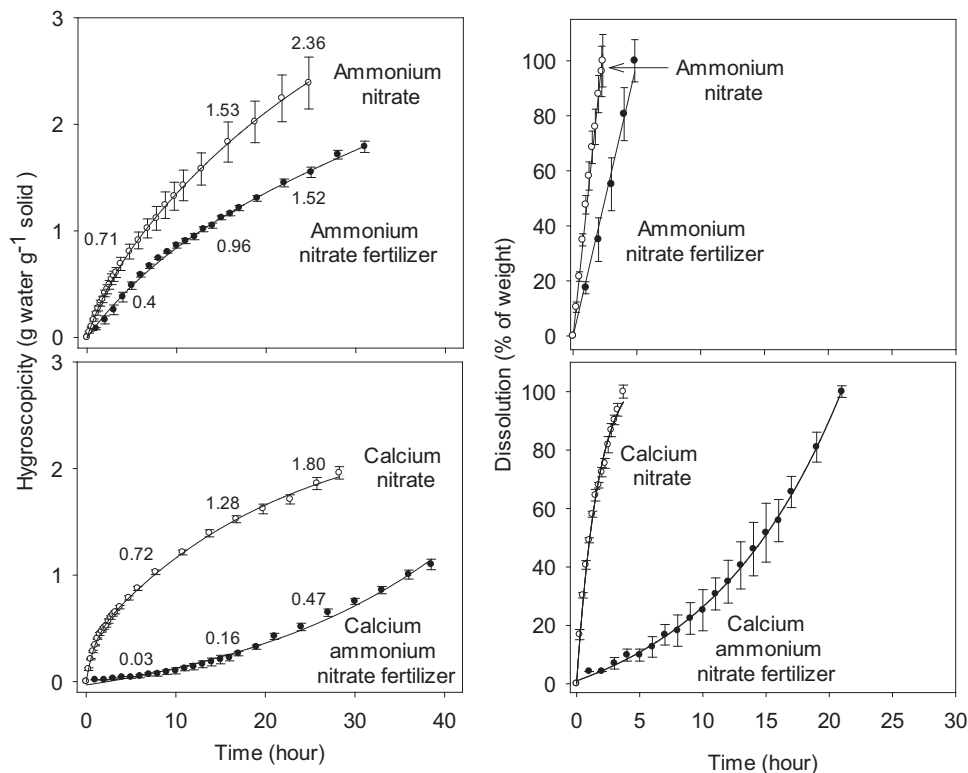


FIGURE 1 Hygroscopicity (left) and dissolution (right) of salt crystals and granules of calcium and ammonium nitrate, ammonium nitrate fertilizer (NS 27-4) and calcium ammonium nitrate fertilizer (CAN) when exposed to air with 90–99% relative humidity at 25 °C, ($n = 4$ [3 for CAN]); mean and standard deviation). Data labels (from left to right) refer to hygroscopicity at 4, 12 and 24 h, respectively

where S_{diss} is the percentage of solid dissolved, $m_{s(c)}$ is the cumulative mass of salt leached, and $m_{s(\text{end})}$ is the amount of salt dissolved and leached at complete dissolution.

3 | RESULTS AND DISCUSSION

3.1 | Hygroscopic water uptake and compound dissolution

Mean values of hygroscopicity and dissolution were fitted to linear or exponential functions using SigmaPlot 12.0 (Systat Software Inc.), resulting in high coefficients of determination, $R^2 = .995\text{--}.999$ (Sigtryggsson, 2018). The two chemicals were more hygroscopic than the two fertilizers tested, probably due to smaller crystal size than granules and to the absence of coating. In 24 h, calcium nitrate absorbed 1.80 g of water, while the CAN fertilizer adsorbed 0.47 g (Figure 1). In comparison, ammonium nitrate absorbed 2.36 g of water and ammonium nitrate fertilizer 1.52 g. Ammonium nitrate had the highest hygroscopicity, absorbing 0.41 g during 2 h, while the ammonium nitrate fertilizer absorbed only 0.16 g.

The hygroscopicity values recorded were higher than those reported for ammonium nitrate and fertilizer salts (Harris, 1970; Mooney, 1924). However, in our study, humidity was

kept constant by continuous water supply. Comparison of rates of dissolution (percentage of weight; Figure 1) showed that within 5 h, all compounds tested except the CAN fertilizer had dissolved completely. The time required for complete dissolution was 2.3 h for ammonium nitrate, 4.3 h for calcium nitrate, 5.0 h for ammonium nitrate fertilizer and 21.1 h for CAN (Figure 1). Relative humidities above 90% occur occasionally under field conditions (NOAA, 2016). Our recorded dissolution rates prove there is a potential for rapid dissolution under high air humidity, even in the absence of rain.

3.2 | Dissolution by rain simulation

In the rain simulation tests, 50% of the two N fertilizers dissolved when they were exposed to about 2 mm of rainwater (Figure 2), which was achieved within 7 min (18 mm h^{-1}). The salts were not completely washed out upon dissolution, so the curves were elongated and flattened out. Complete dissolution was presumably achieved when the curves bent off at the 90% point. This indicates that about 6 and 7 mm of rainwater were required for ammonium nitrate and CAN fertilizers, respectively, to become liquid. Short and intensive exposure was chosen in this study to exclude or minimize the parallel effect of hygroscopicity on dissolution.

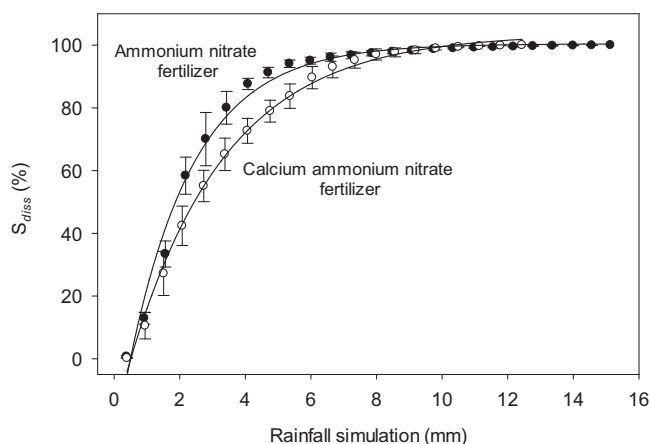


FIGURE 2 Dissolution (S_{diss}) of ammonium nitrate fertilizer (NS 27-4) or calcium ammonium nitrate fertilizer (CAN) by precipitation simulated at a 18 mm h^{-1} rate (each symbol represents four replicates; error bars represent standard deviations of each mean)

3.3 | Impact of enthalpy on dissolution

In addition to the coating and larger particle size of fertilizer granules, enthalpy of solution ($\Delta H_{\text{solution}}$) has an impact on hygroscopicity. The more endothermic a salt is while dissolving, the lower the vapor pressure and the higher the hygroscopicity. Enthalpy of solution (kJ g^{-1}) for the compounds tested is $+0.32$ for ammonium nitrate, $+0.14$ for calcium nitrate, and $+0.08$ for CAN fertilizer (Grishchenko, Druzhinina, Tiflova, & Monayenkova, 2018; Laue, Thiemann, Scheibler, & Wiegand, 2000; Medvedev et al., 1978). Our findings were in accordance with these values, and the relatively weak endothermic properties of CAN could, together with the presence of coating, explain its lower hygroscopicity.

3.4 | Dilution requirement

Dissolution of N fertilizers by humidity and precipitation resulted in high conductivity in solution. For example, conductivity of a single leachate sample from the rain simulator was up to 4.8 S m^{-1} , whereas plant tolerance to ion concentrations is much lower, e.g., for wheat 0.47 S m^{-1} (Amacher, Koenig, & Kitchen, 2000). Compounds dissolved by hygroscopicity had salt concentrations close to saturation, which inhibit ion assimilation by crops and require additional dilution (Marschner, 1986).

4 | CONCLUSIONS

Our experimental results confirm that compared with laboratory-grade salts, fertilizer coatings reduce hygroscopic-

ity as intended. Precipitation and irrigation events exceeding 6 mm , or a 24-h period of $>90\%$ relative humidity at 25°C , was required to incite full dissolution of plant-available N forms from the ammonium nitrate (NS 27-4) and CAN fertilizers. Dissolution can be assumed not to be the limiting step for plant availability of the N fertilizers tested.


ACKNOWLEDGMENTS

The study was sponsored by the Swedish Farmers' Foundation for Agricultural Research (Grant no. O-16-20-761), which we thank.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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How to cite this article: Sigtryggsson C, Hamnér K, Kirchmann H. Laboratory studies on dissolution of nitrogen fertilizers by humidity and precipitation. *Agric Environ Lett*. 2020;5:e20016. <https://doi.org/10.1002/ael2.20016>