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Improved Moisture Management Technology for Eco-N-Control Fertilizer

September 2022

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Summary

Three fertilizer technologies to manage nitrogen (N) release rates in soil dominate the market today: 1) *bulk controlled-release technologies*, which use the intrinsic solubility properties of a N-organic co-polymer to control N release; 2) *barrier-based controlled-release technologies*, which use porous polymer or sulfur coatings as a physical barrier to control N release from encapsulated N nutrients; and 3) *slow-release technologies*, which use enzyme inhibitors to chemically slow down the transformation of N nutrients into ammonia (NH₃) or to temporarily reduce populations of bacteria in the soil that are responsible for converting ammonium (NH₄⁺) to highly soluble nitrates. These technologies are expensive and provide only limited control of N-release rates. Also, from another environmental perspective, synthetic polymer coatings do not decompose easily and will accumulate over time with continuous application of fertilizer.

For most of the past two decades we have been developing the Eco-N-Control solid-nitride fertilizer technology, a type of bulk controlled-release technology. With Eco-N-Control, solid-nitride compounds weather like a mineral, slowly releasing N at a rate determined by their composition. Testing by an industrial collaborator, however, showed that earlier versions of Eco-N-Control released at 25% of the desired rate when deployed in unsaturated soils. The overall goal of the current project, therefore, was to strengthen our IP position and the potential for licensing of Eco-N-Control solid-nitride fertilizer technology by developing new ways to manage the level of moisture in contact with the fertilizer when applied to soil thereby ensuring the desired N-release rate.

We achieved this goal by developing a biodegradable polymer cross-linking approach that substantially improved performance of our patented solid-nitride fertilizer. We found that cross-linking an environmentally friendly and biodegradable polymer with a mixture of solid nitrides, other N-nutrient compounds and other additives offers several advantages: 1) mechanical robustness of fertilizer beads, 2) chemical stability during storage, 3) maintenance of sufficient water content in the vicinity of the nitride, and 4) control of N-release rates. We also updated our N-release testing protocol to more realistically simulate the conditions found in soil. Finally, we filed an invention disclosure record to protect these new aspects of Eco-N-Control technology, which offers a potential way to lower both agricultural and industrial pollution by providing an efficient N-delivery mechanism to plants.

Acknowledgments

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1.0 Introduction

Over the past 17 years, we have developed a solid-nitride fertilizer that is designed to efficiently release nitrogen (N) to plants over the course of a growing season with minimal emissions of nitrous oxide. About two years ago two samples of our fertilizer were tested in the greenhouse by one of our industrial partners. A standard N-release test (conducted in our laboratory beforehand) of this solid-nitride fertilizer under saturated moisture conditions resulted in 100% of the desired release rate. In the greenhouse, however, the obtained N-release rates were 25% of the desired rate when compared to ammonium nitrate, a highly soluble form of N fertilizer. Further, parallel testing of a competing controlled-release fertilizer yielded 50% of the desired rate. These results suggested a need to improve the moisture-management at the surface of controlled-release fertilizers for use under the unsaturated moisture conditions found in agronomic soils. Consequently, an LDRD project was awarded to strengthen our IP position and the potential for licensing of solid-nitride fertilizer technology by developing new pathways to manage the levels of moisture in contact with fertilizer when applied to soil thereby ensuring desired N-release rates.

2.0 Methods and Materials

2.1 Preparation of Beads

A wet synthesis approach was developed to produce beads of solid-nitride fertilizer ($\sim 1\text{-}2$ mm in size) containing aluminum nitride (AlN) as the major component, with a biodegradable polymer (BDP) and other additives present at different concentrations. Briefly, for each sample, different amounts of additives were dissolved in deionized water (DIW) and allowed to mix overnight with a magnetic stir bar at room temperature. Then, an aliquot was transferred into a Teflon vessel and different quantities of AlN were added to achieve the targeted N content. The resulting suspension was mixed with a stir bar to produce a homogenous mixture. A 5-mL syringe with needle was used to feed this mixture drop by drop into an aqueous cross-linking solution. Upon contact with liquid the beads formed and settled at the bottom of the beaker. They were recovered after ~ 15 min, washed with copious amounts of water to remove any unreacted cross-linking agent, and dried in an incubator overnight at 30°C . The visual appearance of as-prepared beads is shown in Figure 1. Their microstructure is visualized through SEM images in Figure 2. The sand-colored beads were ~ 1.5 mm in size, had a porous interior with uniformly distributed components, and exhibited an $\sim 2\text{-}\mu\text{m}$ thick, porous layer at the top surface.

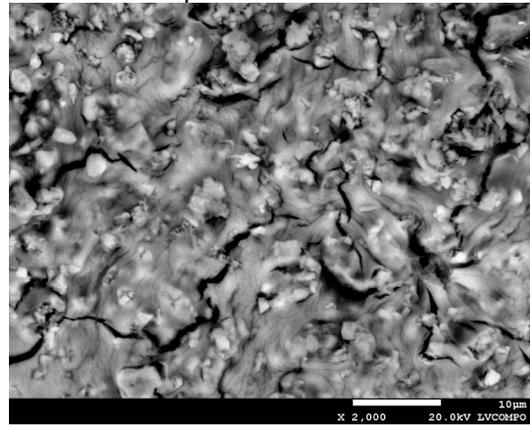


Figure 1. Optical image of produced beads (~ 1.5 mm in size).

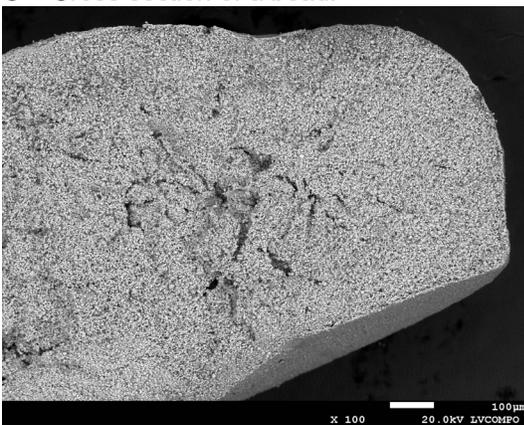
A – Top surface of a bead.



B – Detail of top surface.



C – Cross section of a bead.



D – Detail of cross section close to surface.

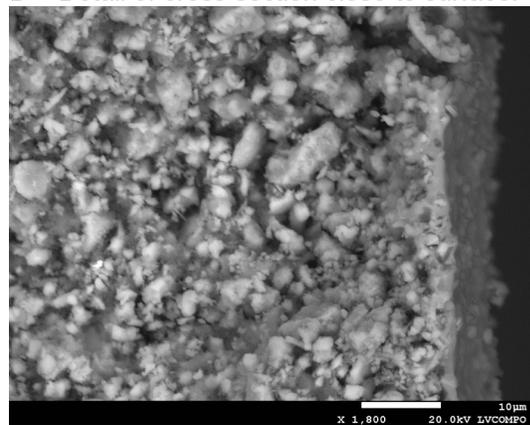


Figure 2. SEM images of beads microstructure.

2.2 Water Uptake at Different Humidity Levels

Samples of three different compositions were produced and their water uptake tested at 100, 75 and 33% humidity for 137 days. These humidity levels were achieved at 24°C by enclosing samples in sealed 500-ml Teflon vessels containing 100 mL of DIW (100% humidity), saturated NaCl solution (75% humidity, 40 g of NaCl dissolved in 100 ml of DIW) or saturated MgCl₂ solution (33% humidity, 156 g of MgCl₂·6H₂O dissolved in 100 mL of DIW). Table 1 shows the composition of the samples in mass% of BDP and AIN and includes the range of initial mass in mg for all samples after drying to constant weight in the incubator at 30°C. Samples were removed from the Teflon vessels at different time intervals and weighed using a 5-digit balance.

Table 1. Composition of the samples in mass% of BDP and AIN and range of initial mass for all the samples.

ID	BDP (mass%)	AIN (mass%)	Mass range (mg)
BDP	100.0	0.0	16-35
BDP/AIN 9/91	9.1	90.9	99-112
BDP/AIN 5/95	4.8	95.2	100-104

2.3 Characterization of N Content and N Release

The total N and carbon (C) contents of the fertilizer materials were determined by dry combustion using a Vario EL cube elemental analyzer (www.elementar.com) equipped with a thermal conductivity detector. Table 2 shows total N and C content in mass% for selected samples.

Table 2. Total N content in mass% for selected samples.

ID	N (mass%)	C (mass%)
BDP/AIN 9/91	30.1±0.2	3.0 ±0.0
BDP/AIN 5/95	31.9±0.8	1.7±0.0
BDP/U/AIN 7/75/18	22.2±1.1	8.6±0.4
BDP/DKP/AIN 5/5/90	25.2±3.8	1.7±0.1

In previous studies, N-release in a synthetic soil (silt-sized glass beads) was measured under saturated conditions, which also happens to be the methodology recommended for assessment of controlled-release fertilizers. As noted in the introduction, however, soils are not saturated when plants are growing in them, and much slower N-release results are obtained from controlled-release fertilizers under these more realistic conditions.

To simulate an unsaturated soil environment, a new low-cost N-release test apparatus was developed. Several iterations of the design were required to ensure it performed as desired. The final version of this apparatus shown in Figure 3 consisted of a “pot-bellied” half-pint jelly canning jar with a thickened lid coated on both sides with an impermeable rubber membrane through which several ports were installed to allow introduction and sampling of liquids/gases. The lid could be sealed to the jar by hand and easily removed to gain access to the contents of the jar. Inside the jar we suspended a porous-bottomed *reaction vessel* to contain the soil above a *leachate-collection vessel* that was open to the atmosphere within the jar when sealed. The various ports through the lid allowed us to add water to the soil to simulate rain events, to remove leachate from the leachate-collection vessel, and to add/remove aqueous boric acid (H_3BO_3) from the bottom of the jar (outside the leachate-collection vessel), which served to trap ammonia gas (NH_3) volatilized from the hydrolysis of the fertilizer. In this way, we could ensure that the soil remained unsaturated, and we could track the fate of the N in the fertilizer under unsaturated conditions, i.e., whether it was volatilized as NH_3 from the soil or leachate, leached as ammonium (NH_4^+) from the soil, or, at the end of the experiment, still in the soil either in its original form or adsorbed to the soil.



Figure 3. N-release test apparatus. Reaction vessel is on right, and leachate collection vessel is inside the jar. Note fine-bore Teflon tubing connected to sampling ports and used to sample leachate and the H_3BO_3 solution outside the leachate collection vessel.

Set-up for a typical N-release experiment consisted of the following steps:

- 1) Separately weighing 10 g of soil (whether synthetic or a natural well-characterized sandy loam) and the N fertilizer sample (N content to equal that of 200-mg of AlN), gently mixing them, and then transferring them to the tared reaction vessel,
- 2) taring the empty jar, lid, and leachate-collection vessel,
- 3) pipetting 20-mL of 5% H_3BO_3 solution into the empty jar and reweighing with lid and leachate collection vessel,
- 4) suspending the reaction vessel inside the leachate-collection vessel and inserting this into the jar
- 5) attaching and sealing the lid to the jar being careful that the various ports (some of which had tubing connected) on the lid were aligned properly with the reaction vessel, leachate-collection vessel, and bottom of the jar to allow irrigation of the soil sample, collection of the leachate, and periodic removal/addition of the H_3BO_3 solution,
- 6) when ready to start the experiment, a pre-determined amount of water was injected through a port onto the soil in the reaction vessel to bring it to the desired level of saturation and the fully assembled apparatus was weighed and incubated at 23-24°C.

Once the experiment was started, the H_3BO_3 solution was collected and replaced periodically (for determination of volatilized NH_3) by opening a vent and attaching a syringe to the appropriate sampling port in the lid of the N-release apparatus. Experiments in which periodic irrigation was conducted with enough water to temporarily saturate the soil required removal of

the leachate solution. Leachate sampling was not needed, however, if completely unsaturated conditions were maintained throughout the experiment.

At the end of the experiment, the N-release apparatus was opened, the reaction vessel removed, and the soil was transferred to a 50-mL centrifuge tube where the reacted N present was extracted with 4 M potassium chloride. The tube was centrifuged to obtain a clear supernatant, which was filtered, and a portion of the filtrate stored. The NH_4^+ in a known volume of filtered extract was then distilled into a separate 5% H_3BO_3 solution by placing it in a reaction vial inside of a 60-mL Teflon bomb, adding solid magnesium oxide to raise the pH, and incubating the bomb at room temperature overnight (modified from Keeney and Nelson 1982, 648-651).

The N present in the H_3BO_3 solutions from the N-release apparatus (volatilized N) and from the distilled extracts (extractable soil N) was then determined by an NH_4^+ -selective electrode method we have developed over the years that uses NaCl as an ionic-strength buffer. Fertilizer N not detected in either of these two solutions was considered to have not reacted.

3.0 Results and Discussion

3.1 Water Uptake

The water uptake over time for BDP, BDP/AIN 9/91, and BDP/AIN 5/95 is shown in Figure 4, Figure 5, and Figure 6, respectively. Cross-linked BDP exhibited parabolic water uptake at 100% humidity and reached a water holding capacity of 3450 mass% after 3288 h (137 days). Significantly lower values of 55 and 18 mass% were obtained at 75 and 33% humidity, respectively. The same trend was observed for the other two samples. After 137 days, the water holding capacities when tested at 100, 75, and 33% humidity, respectively, were 206, 8 and 6 mass% for BDP/AIN 9/91 and 98, 4 and 0 mass% for for BDP/AIN 5/95. Figure 7 shows water uptake with increased concentration of cross-linked BDP after 137 days at different humidity levels. Figure 8 and Figure 9 show the visual appearance of beads of different composition (1-3) at the start and after 137 days, respectively, when tested at different humidity levels (A-100%, B-75%, C-33%). After 137 days at 100% humidity the cross-linked BDP was completely transformed into a gel-like material, while cross-linked BDP/AIN 9/91 and BDP/AIN 5/95 samples exhibited only the initial signs of gelation.

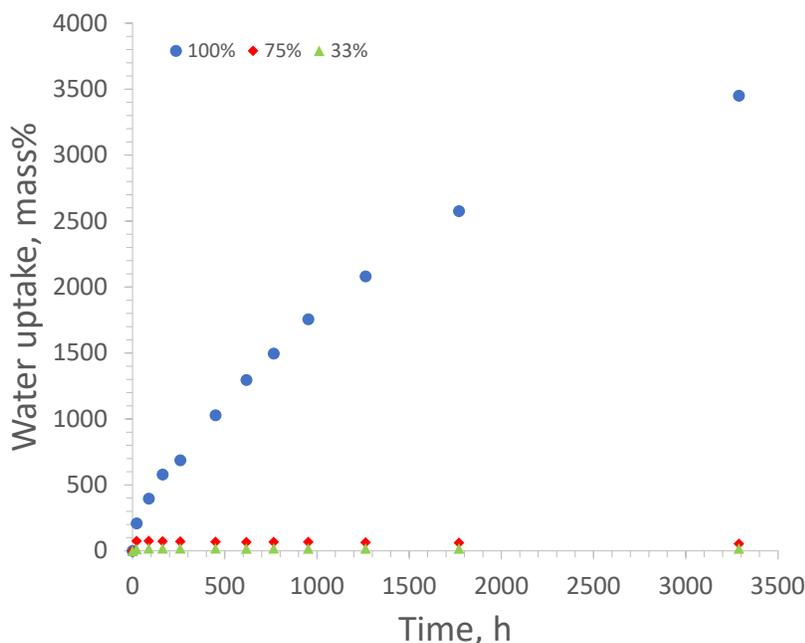


Figure 4. Water uptake over time for cross-linked BDP samples.

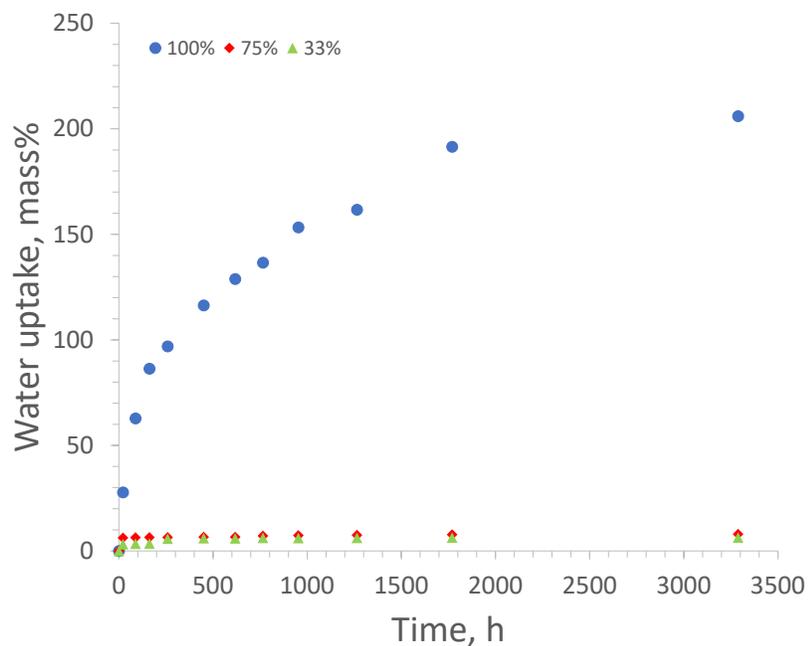


Figure 5. Water uptake over time for cross-linked BDP/AIN 9/91 samples.

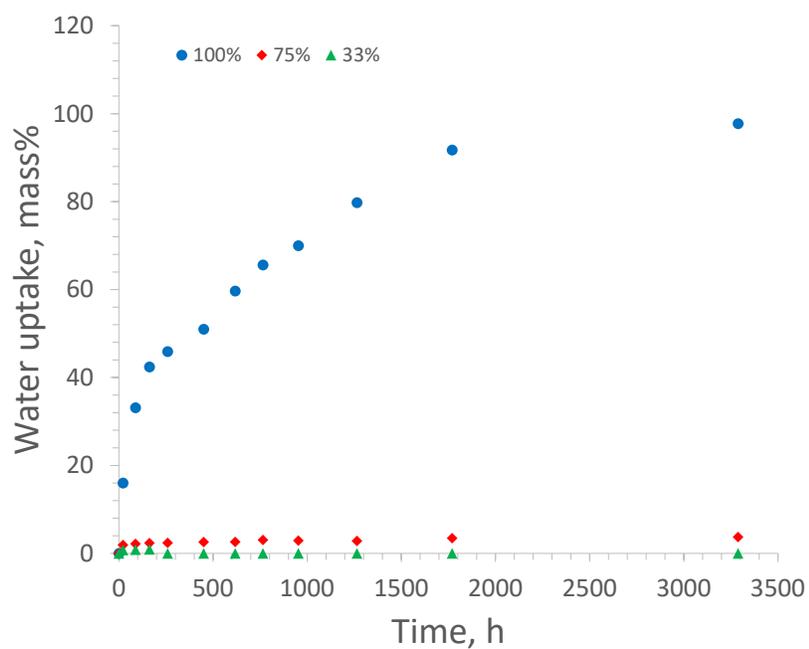


Figure 6. Water uptake over time for cross-linked BDP/AIN 5/95 samples.

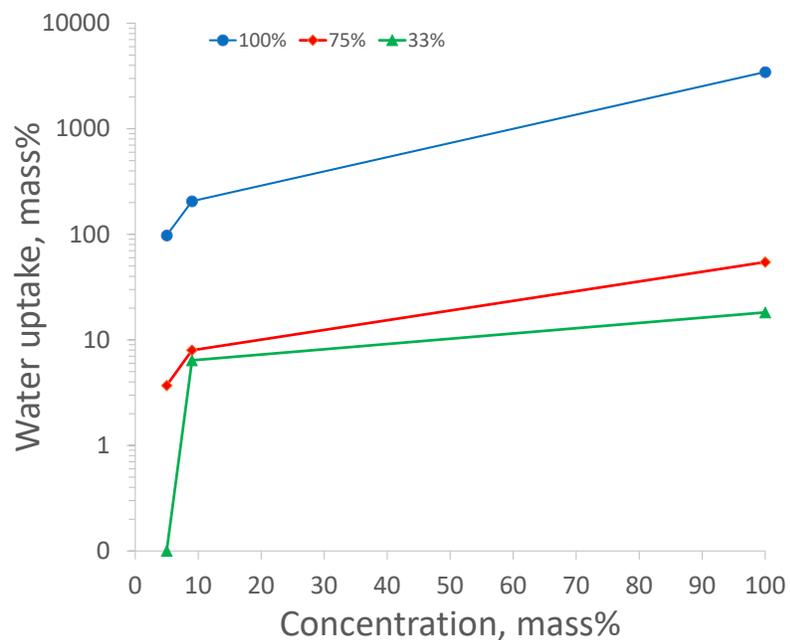


Figure 7. Water uptake as a function of BDP content after 137 days at different humidity levels.

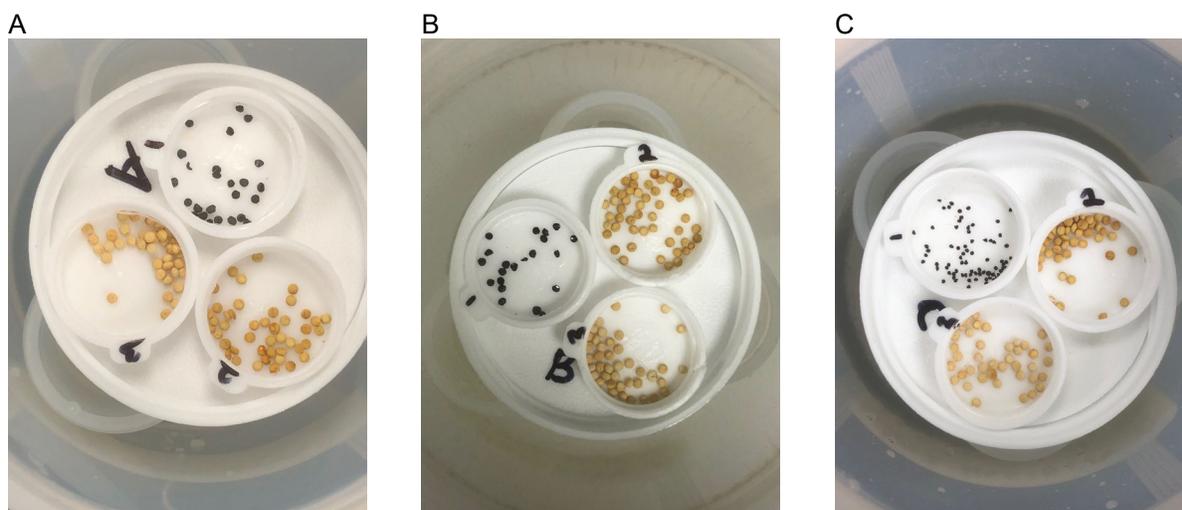


Figure 8. Optical images of beads for samples 1- BDP, 2- BDP/AIN 9/91, and 3- BDP/AIN 5/95 at the start of the water uptake test at A-100%, B-75%, and C-33% humidity.

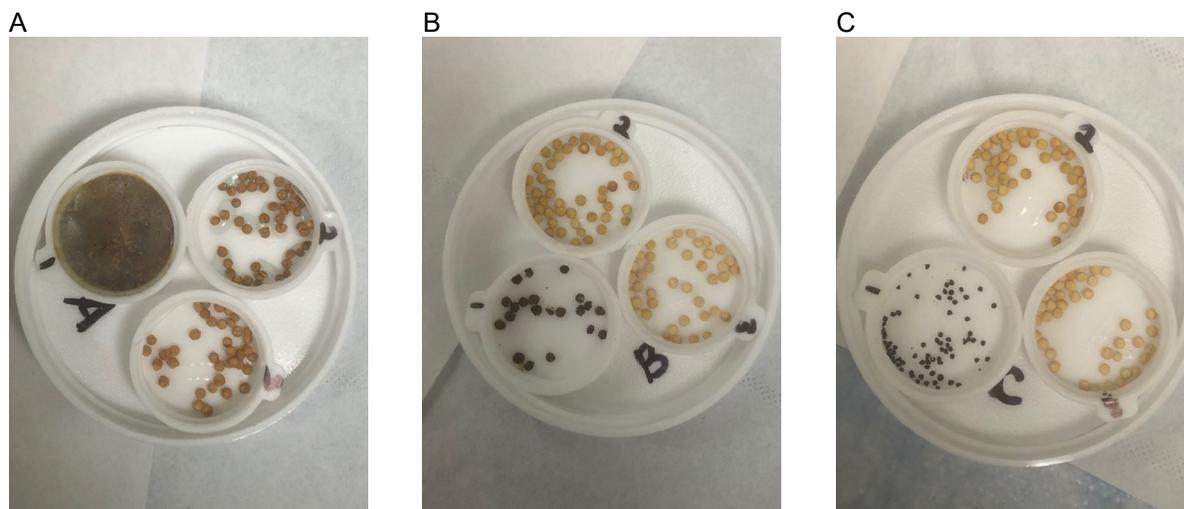


Figure 9. Optical images of beads for samples 1- BDP, 2- BDP/AIN 9/91, and 3- BDP/AIN 5/95 after 137 days of the water uptake test at A-100%, B-75%, and C-33% humidity.

3.2 N Release

We conducted several preliminary N-release experiments on various versions of the cross-linked BDP fertilizer with different levels of urea and AIN present. Here we report results for the final experiment in that series.

Four samples were tested (Table 3), two cross-linked BDP fertilizers (BDP/DKP/AIN 5/5/95, BDP/U/AIN 7/75/18) and two commercial slow-release N fertilizers (a polymer-coated urea (PCU) and a urea-formaldehyde bulk polymer (UF)). The BDP/DKP/AIN 5/5/95 nominally contained 90% AIN and 5% dipotassium hydrogen phosphate (DKP) in a 5% BDP matrix. The BDP/U/AIN 7/75/18 nominally contained 17.5% AIN and 75% urea in a 7.5% BDP matrix. We measured the N contents of the fertilizers and found good agreement between nominal and actual values for the two commercial fertilizers (Table 2), but much lower levels of N in the cross-linked BDP fertilizers than expected. We attribute the lower measured values of N in the cross-linked BDP fertilizers to their high moisture contents, which are not considered in the calculations of nominal mass fraction. Our estimated moisture contents scale with the BDP content as expected from the water uptake results in Figure 4, Figure 5, and Figure 6.

The amount of fertilizer tested was based on the nominal N content of the fertilizer (without including moisture) and was equivalent to the N contained in 200 mg of AIN (i.e., 68 mg N), a common amount we have used in previous studies. Because we did not correct for moisture content of the cross-linked BDP samples, the actual N content tested for these two treatments was less than the nominal level of 68 mg.

Table 3. Properties and amounts of controlled-release fertilizer samples used in N-release experiment.

Trtmt #	Treatment ID	Nominal Mass Fraction, %					Fertilizer sample size, mg	Nominal	Measured	Estimated
		Urea	DKP	AIN	BDP	Other		Initial N Content of Sample	Initial N Content of Sample	Initial Moisture Content
1	BDP/DKP/AIN 5/5/95	0	5	90	5	0	222	31	25	18
2	BDP/U/AIN 7/75/18	75	0	17.5	7.5	0	167	41	22	46
3	PCU	98	0	0	0	2	149	46	46	--
4	UF	83.6	0	0	0	16.4	175	39	40	--

All four fertilizer samples were tested in 10 g (air-dry weight) of a sandy loam soil from western Washington State (Kapowsin Series, 9% clay, 32% silt, and 59% sand). After correcting for the air-dry moisture content of the soil (~2.7%) and adding 1.5 mL of H₂O to the samples when the experiment was started, the nominal gravimetric moisture content of the soil during the N-release experiment was ~18%.

The N-release test involved 6 replicates for each fertilizer treatment. After 3.5, 7, and 14 days, the H₃BO₃ solutions were sampled and replaced with fresh solutions, and 2 replicates of each fertilizer treatment were “terminated” and extracted to determine the amount of reacted N retained in the soil.

The results of the N-release test show much faster release by the BDP/DKP/AIN sample than by the other 3 samples (Figure 10 and Figure 11). This release pattern is typical for AIN samples mixed with small amounts of DKP, which delays the onset of the hydrolysis reaction for a short period of time as seen in Figure 11. After the initial delay, the BDP/DKP/AIN sample releases N much faster than the nominal ideal linear release rate of 1% per day.

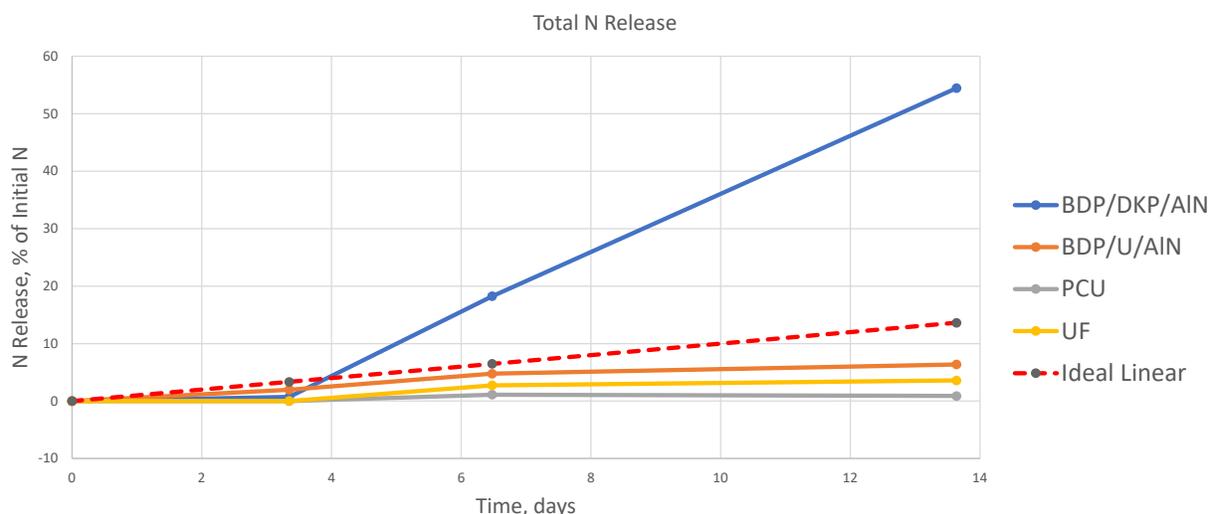


Figure 10. Total N released by the fertilizer samples in natural soil at a moisture content of ~18%.

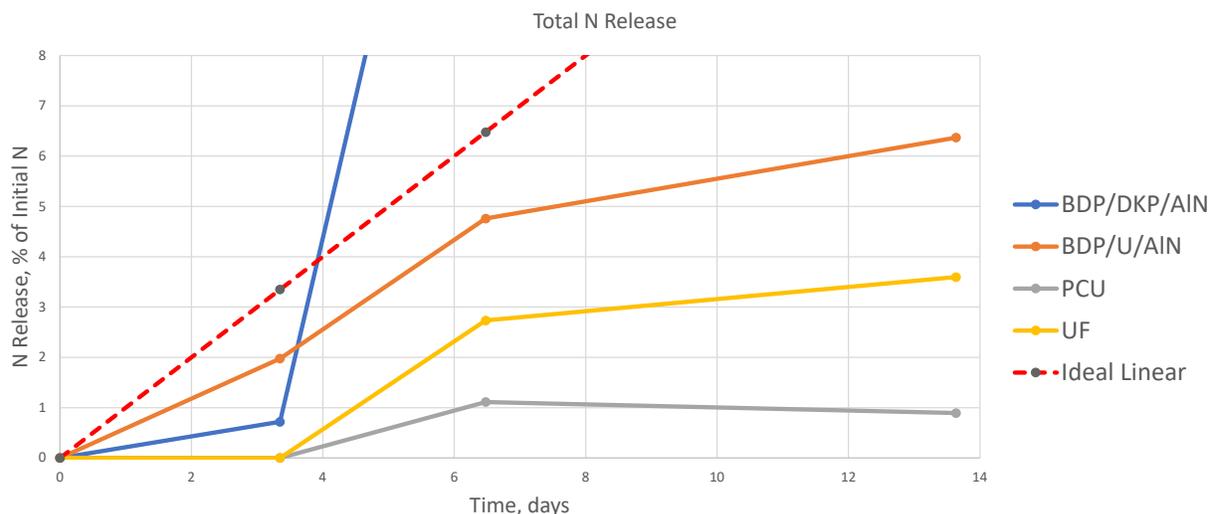


Figure 11. Expanded view of total N release by the fertilizer samples in natural soil at a moisture content of ~18%.

The BDP/U/AIN sample released N at a rate much closer to, and slightly slower than, the ideal rate (Figure 11). We expected this sample to release N much faster than it did due to the labile nature of urea N relative to nitride N, but evidently the nature of this sample conferred substantial stability to the urea N. This result forms the primary basis for our invention.

The two commercial urea-based fertilizers released N more slowly than our BDP fertilizers and the ideal rate, which surprised us. We obtained this result in several of our experiments with both synthetic and natural soil and hypothesize that these fertilizers rely on microbial action to activate their release. In the absence of urease (a soil enzyme generated by microbes and other organisms that catalyzes the conversion of urea to NH_3) urea is quite stable, with a half-life of 3.6 years in aqueous solution at room temperature (Ray et al. 2018, 87). The soil we tested had not been wetted for years (i.e., it is what soil scientists call “lab dirt”) and the microbial community was probably not as well established as would be expected in a freshly sampled “living” soil.

Other insights may be gained from analysis of the fraction of the N released that was “volatilized” relative to that extracted from the soil. We found that the vast majority of N released by the BDP/DKP/AIN sample volatilizes as NH_3 , which is consistent with the AIN hydrolysis reaction that generates alkalinity as it releases N (Figure 12 and Figure 13). As the local pH increases, the aqueous NH_4^+ released by hydrolysis is converted to gaseous NH_3 , which diffuses through the air to the slightly acidic H_3BO_3 solution where it is converted back to aqueous NH_4^+ and thus captured. In contrast, the amount of extractable-N peaked at about 6% after 7 days before dropping to 4% a week later, consistent with an increase in soil pH from the hydrolysis of nitride N. Bounding calculations of the monovalent cation exchange capacity of the soil also suggest a maximum NH_4^+ -retention capacity of about 3.5%. Work by Rochette et al. (2013) on volatilization of NH_3 from hydrolysis of urea when applied to soils suggests that the amount of N in the fertilizer we tested was about 40 times greater than that which could be retained by the amount of soil present.

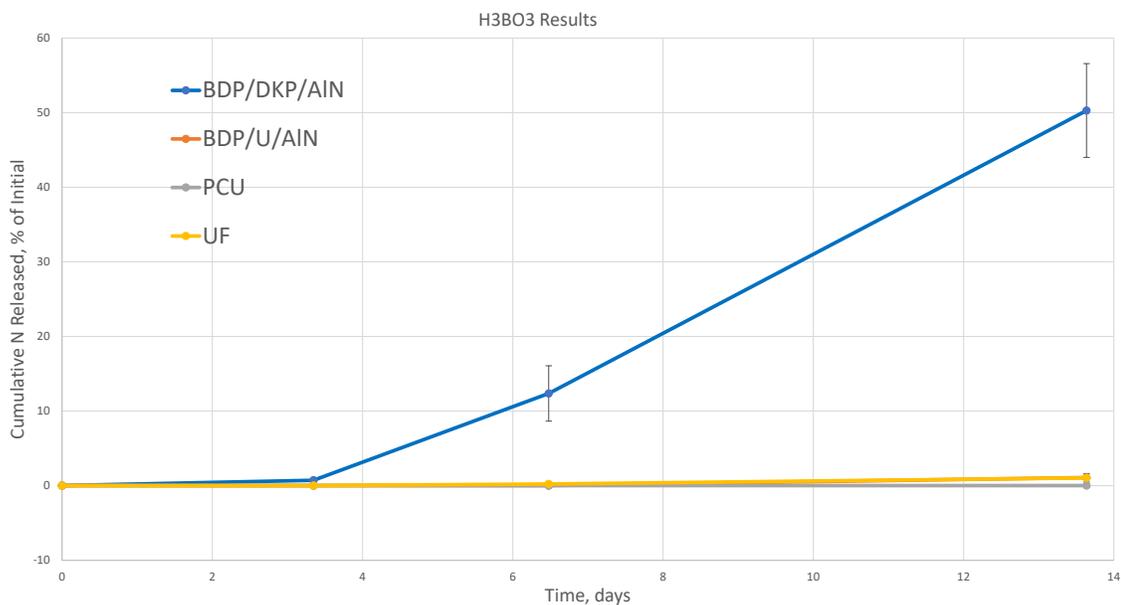


Figure 12. The volatile fraction of N released as NH_3 by the fertilizers.

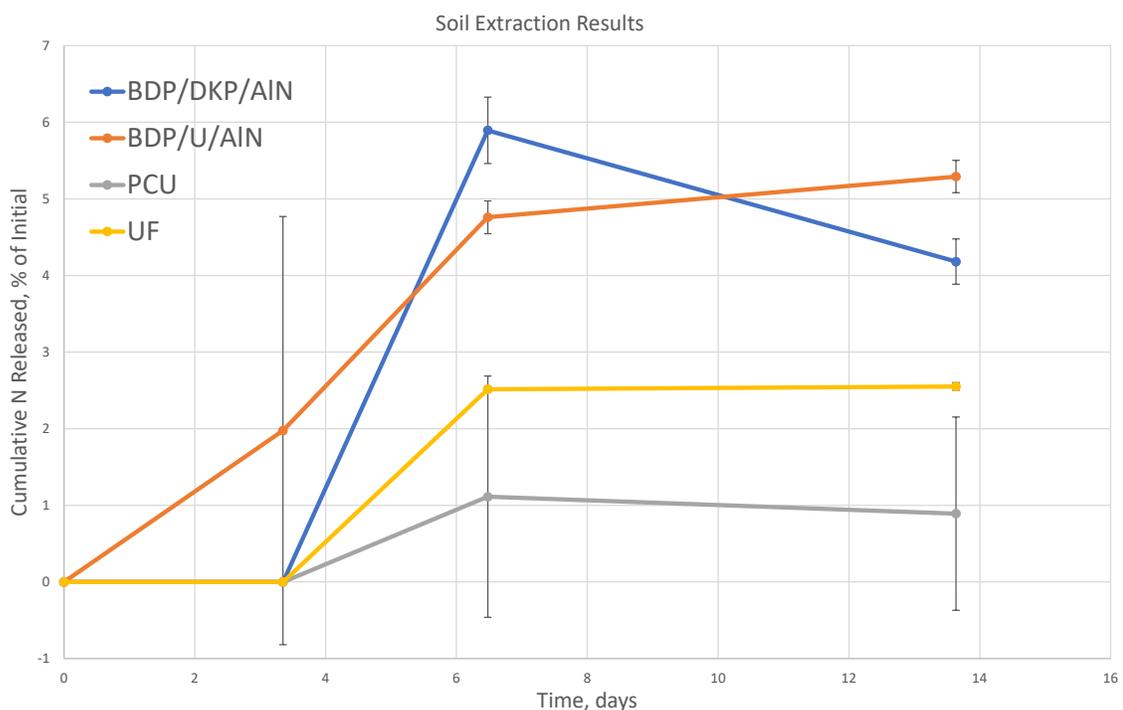


Figure 13. The fertilizer N released and subsequently retained by the soil.

In contrast to the BDP/DKP/AIN fertilizer, the BDP/U/AIN fertilizer did not release any volatile N (Figure 11), which is surprising on two counts. First, urea would be expected to be relatively labile in soil, although as we discussed the urease content of our soil was probably quite low. Second, the AIN present in this fertilizer would be expected to hydrolyze quickly, given the fast

release seen for the BDP/DKP/AIN. The apparent ability to suppress AIN hydrolysis when urea is present is another aspect of the cross-linked BDP technology central to our invention.

N release by the two commercial slow-release fertilizers was predominantly in extractable form, with only the UF showing any NH_3 release at all. As before, we attribute this to the inherent stability of urea in the absence of significant levels of urease and to the low overall levels of N release that did not exceed the NH_4^+ -retention capacity of the soil.

In summary, the results of the N-release study highlight the unique contribution of crosslinking of BDP to slowing the release of N by the solid nitride fertilizer. They also highlight the inherent stability of urea in the (admittedly putative) absence of significant levels of urease. It remains to be seen whether this remarkable stability is retained when urease and an active microbial community are present. It could be that the environment inside the fertilizer offers a new way of controlling N release by urea.

Our results also show that the levels of fertilizer applied per unit of soil in our experiments are far higher than would ever be applied in an agricultural situation and that, consequently, the levels of NH_3 *volatilized* in these experiments do not represent a realistic fertilization scenario. The degree to which the overall N release *rates* measured by our experiments are affected by these high application rates is uncertain. Our sense is that the rates are only slightly, if at all, affected, but only testing with larger quantities of soil, such as performed at the greenhouse scale using plants to harvest the N can confirm this.

Finally, the results of this work demonstrate the fundamentally inorganic nature of the nitride hydrolysis process, in contrast to that of urea, which relies on the presence of urease to make N available to plants. We argue that this aspect of our fertilizer release mechanism makes the solid nitride approach more reliable as a supplier of N to plants.

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