A Greenhouse Study Comparing Brushite, MAP, DAP, TSP, and Struvite Using a Phosphorus-Deficient Prairie Soil Tyler Anderson, Phillip Barak, Christy Davidson

Introduction

Over recent decades, monoammonium phosphate (MAP) and diammonium phosphate (DAP) have increased in popularity as phosphorus fertilizers in the US. However, there have been relatively few studies comparing them to each other and to the previously popular fertilizer material, triple superphosphate (TSP), whose active ingredient is monocalcium phosphate. Recent advances in technologies for phosphorus recovery from wastewater may lead to production of the minerals struvite (magnesium ammonium phosphate hexahydrate) and brushite (dicalcium phosphate dihydrate), neither of which is commonly used in large-scale agriculture and for which there is little comparative data. Much can be inferred about the fertilizer implications of these minerals through current understanding of the soil chemistry of P. In noncalcareous, calcium-rich soils, it has long been known that phosphorus solubility is often controlled by brushite within hours of application of any phosphorus fertilizer.

We hypothesized that although MAP, DAP, TSP, and struvite may be more soluble in water than brushite, they are unlikely to be a significantly better fertilizer than brushite. We conducted a simple comparative greenhouse study to examine the effects of these fertilizers on a noncalcareous phosphorus-deficient remnant prairie soil (Plano Silt Loam), holding nitrogen and potassium fertilizer rates constant.

MAP, DAP, and TSP

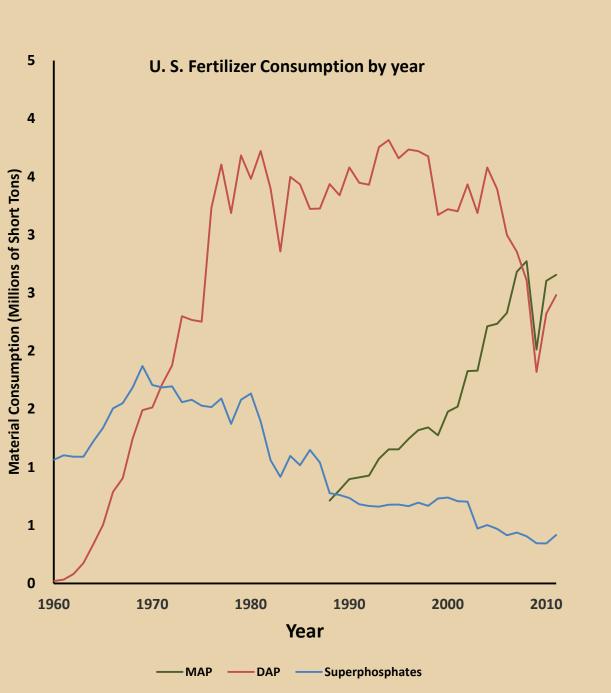


Figure 1: Consumption of, MAP, DAP, and superphosphates

recorded each year since 1960. MAP and DAP have surged in popularity in the last 40 years (USDA).

- Monoammonium phosphate (MAP), diammonium phosphate (DAP), and triple super phosphate (TSP) are derived from mined deposits of apatite, or rock phosphate.
- MAP and DAP have relatively high solubility in water, but in Midwest soils, phosphorus solubility is controlled by less-soluble calcium phosphates.
- MAP and DAP contain N, but little compared to overall crop demands

Fertilizer	% P	% N
MAP	27.0	12.2
DAP	23.5	21.2
TSP	13.2	0.0

Brushite and Struvite

Brushite

- CaHPO $_{A}$ ·2H $_{2}O$
- 18% P by weight
- Readily formed in calcium-rich soils when phosphorus fertilizers are applied to soil
- Controls solubility of phosphorus fertilizers in soil
- Proposed for production from organic acid digest at municipal wastewater treatment plants



Figure 2: SEM image of Brushite (mineralatlas.com)

Struvite

- $NH_{4}MgPO_{4} \cdot 6H_{2}O$
- 12.6% P and 5.7% N by weight
- Precipitates as a nuisance in the pipes of wastewater treatment plants and manure handling facilities
- Currently recovered from municipal wastewater by Ostara Nutrient Recovery Technologies as part of their Crystal Green[®] product

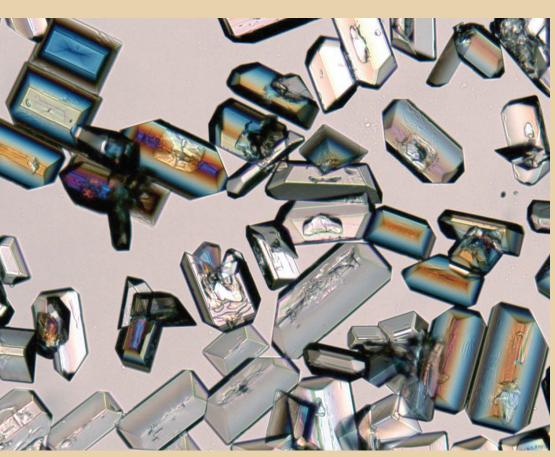


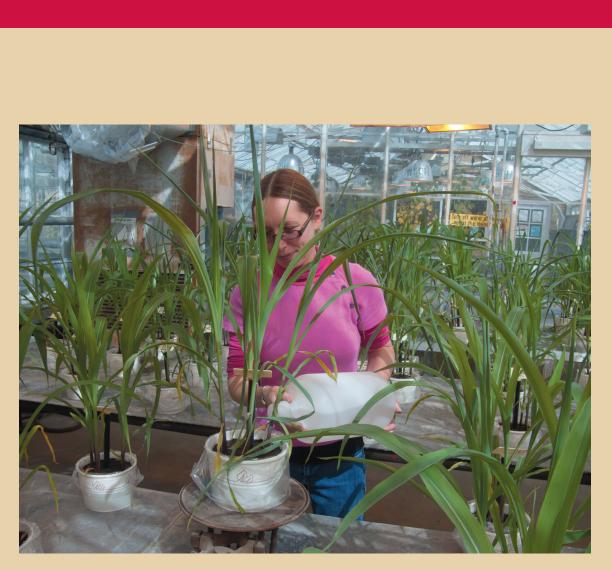
Figure 3: Polarized Light microscope image of struvite

Materials and Methods

Greenhouse

A randomized block pot study was carried out in the UW-Madison King Hall Greenhouses between the dates of Aug 14 and Sept 18, 2014 with four blocks per treatment.

Each pot contained 1.5 kg of Plano silt loam soil collected from an unfertilized and phosphorus-deficient plot at the Arlington Agricultural Research Station in Wisconsin, to which fertilizers were incorporated. Seedlings were thinned to 4 corn plants per pot after 1 week. Pots were watered daily by weight, returning to 25% w/w, field moisture capacity, adjusted for plant fresh weight accumulation.



field capacity. Pictured: Christy Davidson

Fertilizer treatments were MAP, DAP, TSP, struvite, and brushite at rates of 0 (control), 25, 50, 75, and 100 mg P per kg soil. Urea and potassium chloride were applied to equalize nitrogen and potassium concentrations across treatments at 250 mg N and 100 mg K per kg soil.

Results



Laboratory Analysis

Plants in each of the 104 pots were harvested and dried to determine the aboveground dry matter yield per pot. Dry matter was then ground, sampled, ashed, and dissolved in 70% HNO₃. Aliquots were analyzed for phosphorus by ICP-OES at the UW-Madison Soil and Plant Analysis Laboratory (SPAL).

Figure 5: Aboveground dry matter was harvested at the soil surface. Pictured: Tyler Anderson

Greenhouse Pot Experiments Improvements in crop yield with phosphorus fertilizer addition Phosphorus Application Rate (mg kg⁻¹)

Figure 6: Dry matter response rate to P application rate. Brushite, MAP, DAP, and struvite performed similarly.

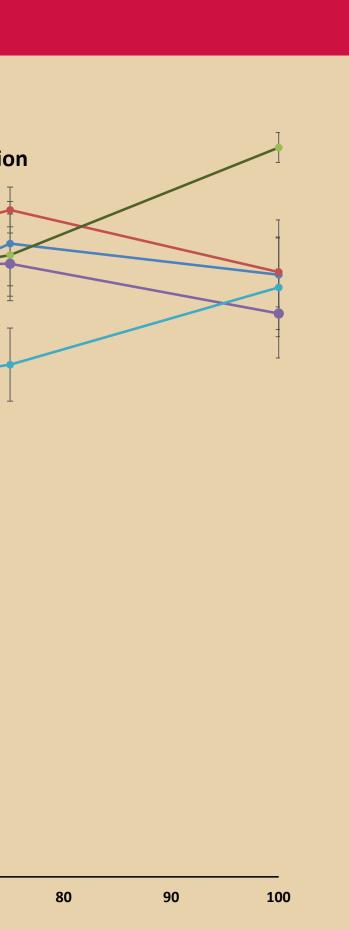


Figure 7: Left. A trial of diammonium phosphate (DAP) applied at 5 different rates (0, 25, 50, 70, and 100 mg P per kg soil from left to right). Right: A similar trial using brushite as the P source. Brushite, though uncommon as a fertilizer, yielded plants of similar height and fullness as the more common DAP fertilizer.

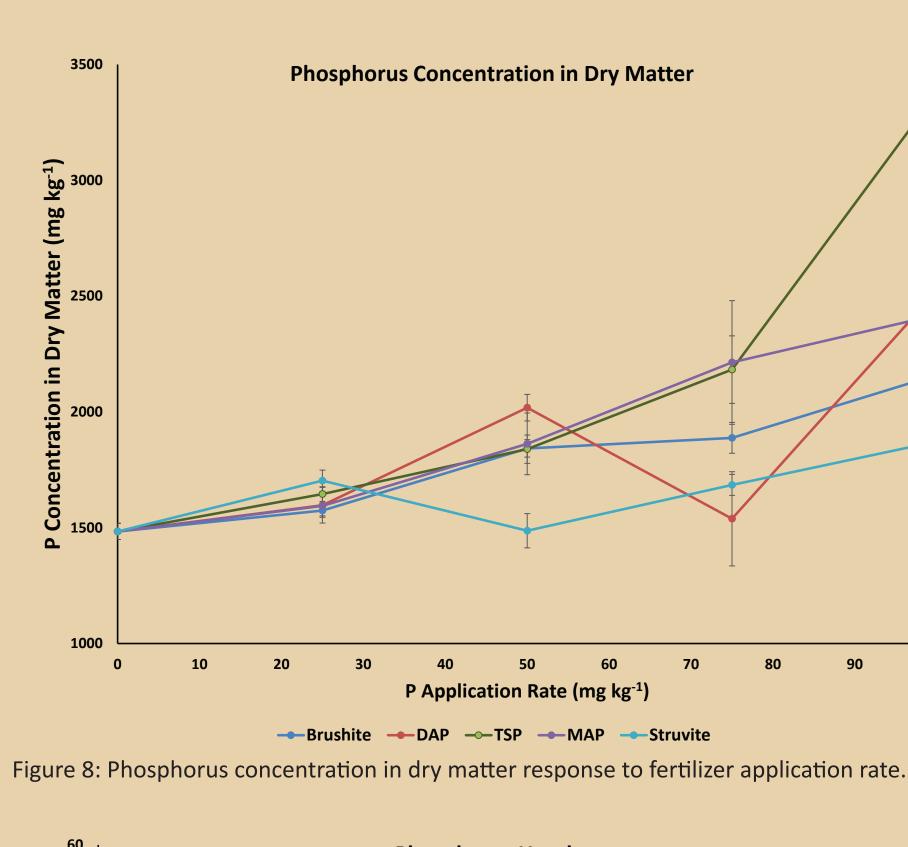
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Results Continued

Figure 4: Plants were watered daily by weight to







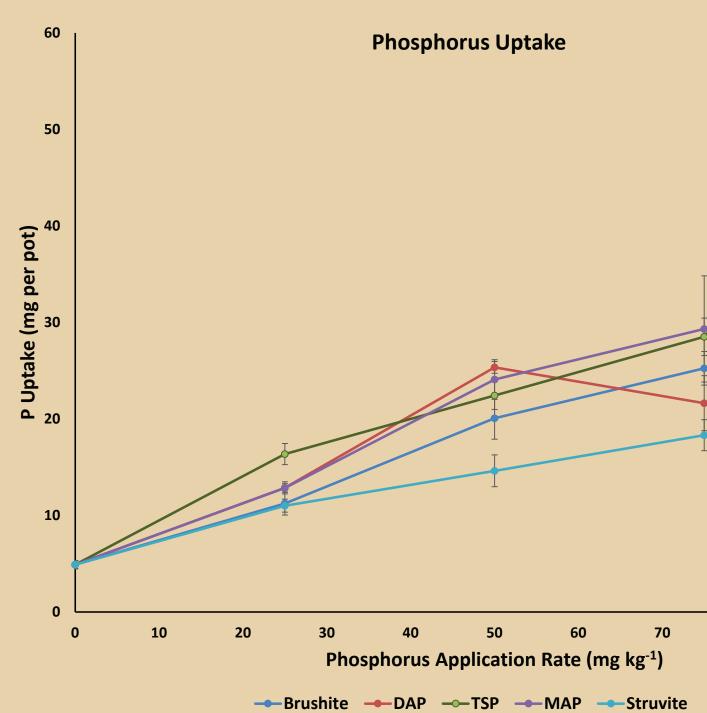


Figure 9: Phosphorus uptake as a response to P application rate for each source. Other than a high uptake in TSP in the highest rate, all treatments took up a similar amount of P, with struvite slightly lagging.

Conclusions

- As expected, the Plano Silt Loam soil exhibited excellent response to P fertilizer with a typical fourfold increase in aboveground dry matter between control and 100 mg P per kg soil treatment.
- Wastewater derived-phosphorus minerals such as **brushite** and **struvite** compare well to more common fertilizers such as MAP, DAP, and TSP.
- Brushite and struvite appear to be viable replacement for common P fertilizers such as MAP, DAP, and TSP, depending on pricing and availability.
- Additional work must be performed to ensure wastewater-derived brushite and struvite fertilizers perform as well as laboratory-synthesized fertilizers. Additionally, field testing will be required to confirm greenhouse findings.

Acknowledgments

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Disclaimer: One of the investigators, Phillip Barak, is inventor and rights-holder of 'Phosphate Recovery from Acid Phase Anaerobic Digesters', U.S. Patent No. 8,568,590 and is co-owner of Nutrient Recovery and Upcycling, LLC, to whom the brushite-forming patent is licensed.



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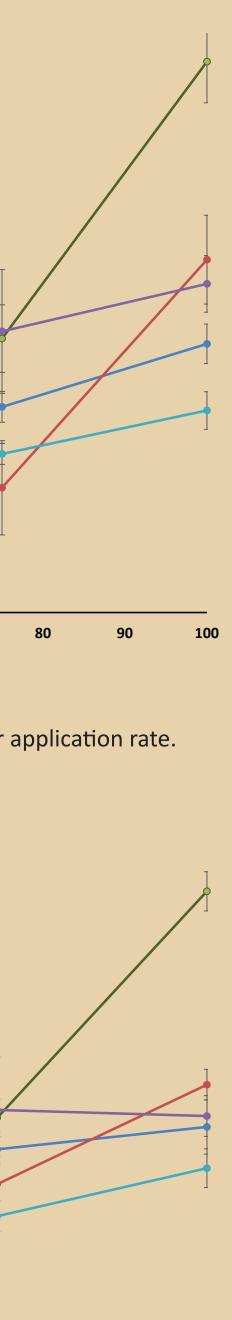




Figure 10: A healthy corn leaf (left) and a leaf showing anthocyanin response to phosphorus deficiency (right).