

## STRUVITE: A RECOVERED AND RECYCLED PHOSPHORUS FERTILIZER

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Struvite, magnesium ammonium phosphate hexahydrate—is a biogenic mineral of low solubility. For 150 yrs, it has been proposed as a fertilizer but its use has been limited to high-value crops because of the additional cost of manufacture. With the advent of new interest in removing phosphorus from wastestreams before land application, recovery of phosphorus as struvite has gained new interest. Pot studies show that struvite outperforms diammonium phosphate on a unit-for-unit basis in terms of dry matter production, P uptake, and extractable residual P. Various local wastestreams are candidates for struvite removal with little or no chemical additions using molecular templates as nucleating surfaces.

Struvite is a biogenic mineral of the composition magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), with a solubility of 0.2 g/L in water. Humans most often encounter struvite as either urinary sediments or kidney stones, both usually associated with infections of the urinary tract that hydrolyze urea into ammonia and raise urine pH. Struvite is also occasionally encountered in canned seafood, such as lobster, crab, salmon, or tuna, in which (harmless) glass-like slivers form over time, sometimes 5 to 8 mm in length, when ammonia and phosphate released from tissue during processing reacts with magnesium-rich seawater. Struvite is also known as a nuisance in sewage treatment plants (Rawn et al., 1939) when it forms blockages in pipes following anaerobic digestion of solids, a process releasing considerable ammonium and phosphate into the digester liquor. Struvite is also known to form in animal manure, hence its synonym 'guanite', although it is often difficult to determine whether it is present upon excretion or whether it forms upon microbial decomposition of the manure. Presumptive evidence exists for the presence of struvite in poultry manure (Cooperband and Good, 2002) and clear evidence from quantitative x-ray diffraction indicates that struvite and brushite are found in fresh sheep manure in roughly equal proportions and together account for 63% of P in the feces (Shand et al., 2005.) Clearly the presence of so much sparingly-soluble mineral P in the manure will affect the transfer of manure phosphorus to water and runoff.

Struvite contains 5.7% N and 12.6% P by weight; the phosphate is entirely citrate-soluble (Bridger et al., 1962) and the fertilizer analysis in oxide form is 5.7-28.8-0, with 9.9% Mg. As long ago as 1858, struvite has been proposed as potential phosphorus source for agriculture, and repeatedly since then. In fact, struvite appears to form in soil upon fertilization with other ammonium phosphate fertilizers, particularly when neutral or alkaline conditions prevail. Diammonium phosphate (DAP), itself highly water soluble, forms struvite using soil magnesium as the third constituent (Lindsay and Taylor, 1960; Lindsay et al., 1962); struvite formation in soil upon addition of ammonium polyphosphate has also been reported (Ghosh et al., 1996). When struvite is added to soil, phosphorus release appears to be largely the result of microbial nitrification of the ammonium constituent rather than simple dissolution (Bridger et al., 1962). In the 1960s, WR Grace & Co. secured patent rights for manufacture of an ammonium/potassium magnesium phosphate fertilizer, marketed under the tradename of MagAmp as a slow-release fertilizer, made by adding magnesium oxide or magnesium hydroxide to monoammonium phosphate (Peng et al., 1979); cost of production kept this for use in high value-added applications, such as floriculture, only. Alternative methods of producing struvite by the addition of sulfuric acid to rock phosphate and olivine, followed by ammoniation (MacIntire and Marshall, 1959), have not been economically feasible.

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Over the last decade, interest has grown in extracting phosphorus from wastewater and agricultural manure, and struvite has emerged as a strong candidate. The primary motivation for phosphorus recovery is reduction of the phosphorus load when landspreading biosolids and manure on already phosphorus-rich fields, and only secondarily to economically produce high analysis phosphorus fertilizer by recycling instead of manufacture from virgin materials. In most cases, it has been determined that the anaerobic digest liquors and manures are deficient in magnesium and the pH is too low for optimal struvite removal. The addition of magnesium chloride, sodium hydroxide, or magnesium oxide has been frequently proposed, along with carbon-dioxide stripping by sparging to raise the pH. A small number of wastewater treatment plants around the world have built struvite-recovery facilities; the cost of adding magnesium salts and base clearly outweigh the economic value of the struvite as a bulk fertilizer material, but additional savings in prevent struvite obstructions of pipes are convincing (Ueno and Fujii, 2001; Jaffar et al., 2002). A number of struvite-recovery operations have been tested or built for agricultural manure handling operations. Notable are struvite production from veal manure in the Netherlands and pig manure in Japan (CEEP, 2003) and Australia (v. Münch and Barr, 2001). Work in the U.S. at an advanced state are those in Tennessee (Burns et al., 2001; CEEP, 2003) and North Carolina (CEEP, 2004) in piggery manure lagoons. At least in some cases, the precipitate formed upon addition of chemicals is 1:2:0.2 N:P:Mg instead of 1:1:1, indicating that the majority of the phosphate removed was not struvite, but perhaps calcium phosphates along with mixtures of other precipitates. As modern manure handling procedures becomes more similar to wastewater treatment, removal of struvite from agricultural manure becomes more feasible; in fact, the addition of sodium phosphate, as well as magnesium, to dairy manure anaerobic digester effluent has been proposed to remove dissolved ammonium as struvite (Uludag-Dmirer et al., 2005).

Although struvite forms relatively readily from supersaturated solutions, removing struvite crystals from a mixture of suspended solids is problematic since the specific gravity of struvite, 1.6, only slightly exceeds that of common suspended organic solids. The nucleation and crystallization can be localized by use of a molecular template consisting of a densely negatively-charged surface that matches the spacing of the magnesium hexahydrate crystallographic plane of struvite (Barak et al., 2005.) Such templates, whether floating compressed Langmuir monolayers or self-assembling monolayers on a solid substrate, can direct formation of relatively large (0.2 to 2 mm), symmetrical struvite crystals on the treated surface, which can be particularly advantageous in removing struvite products from digester liquors and liquid manure. Additional research has shown that magnesium can be dosed by compulsive ion exchange using cation exchange membranes with magnesium salts separated from the digester liquors and liquid manure.

With the renewed interest in producing struvite—not from virgin fertilizer materials but as a recovered resource from waste streams—examination of struvite as a phosphate fertilizer and comparison against the favored fertilizers of the day becomes an interesting subject. Previous studies have shown struvite to be approximately equal to or surpass monocalcium phosphate and dicalcium phosphate in efficiency (Lindsay and Taylor, 1960; Richards and Johnston, 2001; Johnston and Richards, 2003). However, ammonium phosphates are currently the predominant phosphate fertilizers in the United States, particularly diammonium phosphate (DAP) and a straightforward comparison between ammonium phosphate and struvite seems particularly relevant. The purpose of this study was to analyze the efficiency of struvite as a phosphorus fertilizer in comparison to the synthetic fertilizer DAP using dry matter yield, P concentration in plant dry matter, P uptake in above ground dry matter, and residual Bray P in the soil as measures of comparison.

We conducted a greenhouse experiment in which corn was grown for six weeks in 1.5-kg pots of P-deficient Plano silt loam from Arlington Research Station. Treatments were a control and two rates of DAP (50 and 100 mg DAP-P/kg) and one rate of struvite (36 mg struvite-P/kg): all treatments were brought to a uniform N rate of mg N per kg soil with urea. Pots were brought to field capacity and regularly watered by weight, with no drainage from the pots. Struvite for this experiment was produced in our lab by crystallization from a supersaturated solution of magnesium sulfate and ammonium phosphate, dried, and lightly ground to match the particle size of the DAP.

During the 6-week growth period in the greenhouse, the corn plants grew vigorously and appeared healthy and free of visible pathogens, with healthy and dense roots upon disassembly at harvest. Corn plants grown in the no-phosphorus-added pots were, as intended, visibly phosphorus deficient, with reddish purple tips and leaf margins. Those plants grown in pots that received DAP and struvite were visibly taller than the no-phosphorus controls and phosphorus deficiency symptoms were absent. Statistical analysis showed that the dry matter production of the 36 mg struvite-P/kg was identical to that of the 100 mg DAP-P/kg treatment, and both outperformed the 50 mg DAP-P/kg treatment and the control.

Examination of the amount of phosphorus offtake in the aboveground plant showed (Fig. 1) that the 36 mg struvite-P/kg treatment was equivalent to 42 mg DAP-P/kg, and struvite therefore had a relative efficiency of 117% compared to DAP. Similar analysis for average residual Bray P found that the 36.4 mg struvite-P/kg soil treatment was equivalent to that expected of 64.9 (+/- 12.3) mg DAP-P/kg soil, or 178% equivalency.

We have conducted some chemical analyses of potential local wastewater sources from which struvite recovery could be considered (Table 1). All five samples reflect anaerobic conditions, as evidenced by the very low concentrations of nitrate compared to ammonium. At the Nine Springs Water Treatment Plant (Madison Metropolitan Sewerage District, Madison, WI) we have found that the gravity belt thickener (GBT) feed and filtrate (not shown) are supersaturated with regard to struvite, which is consistent with the tendency of these waters to form pipe obstructions as they leave the anaerobic digesters; the magnesium supply of these waters is relatively small compared to the ammonium and phosphate concentrations and will therefore be limit the amount of struvite formed. In contrast, the supernatant by gravity settling at another part of the plant has a high level of dissolved phosphorus but is not close to struvite saturation. Several working manure lagoons sampled at the Arlington Research Station gave varying results. Those that were slightly acidic were supersaturated with respect to brushite, a dicalcium phosphate dihydrate mineral. On the other hand, the sample that was slightly alkaline (#2) was undersaturated with regard to brushite but very nearly saturated with struvite, which may account for its lower dissolved P concentration. We do not have sufficient information or controlled experimental conditions to allow us to speculate as to the differences between #2 and samples #1 and #3, but clearly struvite formation in the manure samples is favored by an abundant supply of magnesium from the plant diet that is nearly absent in the municipal wastewater. The significance of finding that some wastestreams are struvite-saturated is that the expense of additional chemicals may be avoided, particularly if nucleation of struvite in recoverable forms can be coaxed. Using the self-assembling membrane and compulsive ion exchange technologies of Barak et al. (2005), well-shaped struvite has been formed from GBT filtrate in the laboratory; with self-assembling membranes, crystallites of yet-undetermined composition were formed from the dialyzate from manure lagoon #2.

Taken as a whole, the future looks bright that the phosphorus of various organic waste streams, both municipal and agricultural, may be reduced by recovering a desirable, high-analysis phosphorus fertilizer, struvite.

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Table 1. Chemical analysis (partial report) of selected wastewaters tested for struvite-forming potential by chemical speciation calculations using SPECIES (Barak, 1990). Where the  $pIAP$  (ion activity product) is less than  $pK_{sp}$ , the solubility product for a specified mineral, the water sample is supersaturated with respect to that mineral.

		Nine Springs Water Treatment Plant (MMSD)		Arlington Dairy Manure Lagoons		
		Supernatant, gravity	GBT feed	#1	#2	#3
<i>Analysis of water/dialyzate:</i>						
pH		6.67	7.78	6.14	7.35	6.10
NH <sub>4</sub> -N	mg/L	35.0	624	823	894	859
NO <sub>3</sub> -N	" "	0.03	0.53	0.03	0.06	0.03
Ca	" "	81.1	43.2	375	244	448
Mg	" "	52.9	4.7	282	225	279
Na	" "	265	274	254	370	259
K	" "	20.6	358	2030	2310	2030
PO <sub>4</sub> -P	" "	15.7	204	105	20	93
<i>pIAP (pK<sub>sp</sub>):</i>						
calcite	(8.5)	10.3	8.7	8.8	7.2	8.3
brushite	(18.9)	19.5	18.5	18.7	19.3	18.6
struvite	(13.2)	15.5	12.3	13.6	13.2	13.4

**Figure 1.** Comparison of P uptake in response to struvite application and DAP-P application at three levels (0, 50, and 100 ppm) with quadratic response line drawn among the means and +/- 1 standard deviation of the means. The average P uptake for the 36.4 mg struvite-P/kg soil treatment was equivalent to that expected of 42.6 (+/-4) mg DAP-P/kg soil.

