THE EFFECTIVENESS OF RECOVERED PHOSPHATES AS FERTILIZER IN SLIGHTLY ACIDIC AND ALKALINE SOIL CONDITIONS

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ABSTRACT

Recovered magnesium phosphates such as struvite ($MgNH_4PO_4 \bullet 6H_2O$) may be useful as a method of improving phosphorus (P) cycling in municipal wastewater treatment and livestock agriculture. However, little work has been done on the re-use of recovered products, and what work has been conducted has focused on low pH soils. This study was conducted to determine if recovered struvite and recovered dittmarite ($MgNH_4PO_4 \bullet H_2O$) are effective fertilizers in alkaline soil conditions, where phosphate rock (RP) is considered to be ineffective. In addition to commercially available triple superphosphate (TSP) and certified organic RP, recovered struvite, dittmarite, and a heterogeneous recovered phosphate were applied as fertilizers for spring wheat (*Triticum aestivum L.*) in a greenhouse study. At a soil pH of 6.5, both dittmarite and struvite increased average plant P concentration over the control. Struvite and dittmarite performance was similar to TSP, especially at the highest application rate. There were no significant differences in plant dry matter (DM) production at pH 6.5. In the limed soil (pH 7.6), many treatments had plant P concentration significantly lower than the control, but all of the fertilizers except RP increased DM production and P uptake over the control, and all of the fertilizers generally performed similarly to each other. These findings support previous work that found recovered phosphates to be effective in acidic soils, and provide evidence that they are also effective P fertilizers in alkaline soils. Recovered magnesium phosphates could, therefore, become a useful alternative for P fertilization in arid and semi-arid environments.

INTRODUCTION

Enrichment of surface waters with phosphorus (P) from municipal wastewater treatment discharge or agricultural runoff is an important water quality concern that can lead to eutrophication (Carpenter et al., 1998). The recovery and use of P by crystallization from municipal and agricultural wastewater has the potential to reduce eutrophication while creating relatively pure, useful byproducts. While it is unclear exactly how long existing rock phosphate (RP) reserves will last, P is a limited resource and its re-use is necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Recovery efforts have focused on wastewater treatment plants (WWTPs), where spontaneous struvite precipitation can be destructive to WWTP facilities (de-Bashan and Bashan, 2004). There exist several full-scale, working examples of WWTPs using crystallization processes for P removal. Depending on the process, the product is either calcium (Ca) phosphate (apatite) or magnesium (Mg) phosphate (struvite, dittmarite, or newberryite) (Driver et al., 1999; de-Bashan and Bashan, 2004). At least one plant sells recovered struvite ($MgNH_4PO_4 \bullet 6H_2O$) as a slow-release component of a commercial fertilizer mix (Ueno and Fujii, 2001).

Recently, on-site P removal from agricultural wastewater has become a focal point of research. Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure an ideal target for P recovery. The same authors also noted that while land application is the preferable method of manure P re-use, application of manure to meet crop nitrogen (N) needs results in the over-application of P. P recovery through crystallization could be used to correct this imbalance. Ideally, a crystalline product would have a high P concentration and could be easily dried and handled, marketable, and transportable at a fraction of the cost of manure or compost.

A number of removal technologies exist, such as that outlined in Bowers and Westerman (2005a, 2005b), which was used to manufacture some of the recovered phosphates in this study. However, very few studies have looked at the use of the recovered products. Many recovery processes focus on Mg phosphates such as struvite, but few applications for recovered struvite have been tested. Its chemical composition makes it impractical for use as a raw material in the modern P industry (Driver et al., 1999; Schipper et al., 2001). Though soil pH was not noted, Bridger et al. (1962) noted the effectiveness of struvite and dittmarite as fertilizer in a variety of situations, such as on turf, on ornamentals and flowers, in forests and orchards, and even on field crops. More recently, Johnston and Richards (2003) compared a variety of recovered phosphate fertilizers in a greenhouse setting, and found recovered struvite to be an effective fertilizer for ryegrass on soils with pH 6.61 and 7.08. Struvite crystallization was also carried out on landfill leachate in Hong Kong, and the product was found to be as effective as commercial fertilizer for vegetables on a nutrient-poor soil with pH 6.2 (Li and Zhao, 2003). Bauer et al. (2007) examined the usefulness of recovered Ca phosphates in a greenhouse setting, on soil with a pH of 4.9, amended with lime to pH 6.5.

There are no studies specifically addressing the effectiveness of recovered phosphates in alkaline or calcareous soils, even though Lindsay (1979) noted that Mg phosphates such as struvite might be more useful than Ca phosphates as fertilizers in such conditions. Rothbaum and Rohde (1976) suggested that struvite dissolution might be increased by an aerobic microbiological mineralization mechanism, though this finding has not subsequently been investigated. Mackay and Syers (1986) found that high Ca concentration in the soil solution inhibited the dissolution of Ca phosphate rock. Increased P availability might make a Mg phosphate alternative a useful tool for P fertilization that is not as inhibited by high Ca concentrations found in calcareous soils.

P fertilization in calcareous soils can be a very challenging problem. This is especially true for certified organic growers, who cannot use conventionally manufactured, more soluble fertilizers such as triple superphosphate (TSP). With the exception of manure and compost, other certified organic P fertilizers such as rock phosphate (RP) and bone meal are not effective in calcareous soils (Elliott et al., 2007; Chien and Menon, 1995) Bolland et al. (1986) even found RP to be ineffective at mildly acidic (pH ~6) soil pH. Therefore, the use of recovered Mg phosphates could improve the sustainability of both livestock and crop production in semi-arid areas such as the western United States. P recovery and re-use from livestock waste could help to alleviate P loading in areas with large numbers of livestock, and provide producers with a valuable resource and potential source of additional revenue.

The successful use of recovered Mg phosphates in calcareous soils, however, hinges on their agronomic effectiveness in these challenging soil conditions. In this study, greenhouse trials were conducted to determine the effectiveness of dittmarite ($MgNH_4PO_4 \bullet H_2O$), struvite, and a heterogeneous recovered phosphate material.

MATERIALS AND METHODS

A low pHsoil with relatively low soil test P was collected from a pristine rangeland in northern Colorado. The soil is a member of the Altvan series, and is classified as a mixed, superactive, mesic Aridic Argiustoll. The surface layer (0-6 in), from which the soil was obtained, is a loam with many fine pebbles. The soil was also relatively high in organic matter, since it was obtained from the surface of a grassland area. Half of this soil was limed from an original pH of 6.5 to pH 7.6 using pure calcium carbonate ($CaCO_3$, Thermo Fisher Scientific, Inc.). The un-limed and limed soils were used for low and high pH fertilizer comparisons. Soil samples were analyzed at Servi-Tech Inc. in Dodge City, KS (Table 1).

Table 1. Soil characteristics of the untreated and limed soils used in the greenhouse trials (n=2). Soil pH and salinity were determined by measurement in a 1:1 soil:water slurry, N was determined by Cd reduction, P was measured by Mehlich-3, and K was measured with the ammonium acetate method. The increase in soil N was likely due to organic matter mineralization during liming.

preparation	pH	NO_3-N (ppm)	P (ppm)	K (ppm)	% O.M.	salts (mmho cm^{-1})
none	6.5	5	31	257	2.4	0.16
lime	7.6	23	44	316	2.4	0.42

In addition to commercially available TSP and certified organic RP fertilizers, three recovered phosphates were applied as P fertilizers. These include crystalline dittmarite from a pump inside a food processing plant in Idaho, crystalline struvite manufactured at a dairy in northwestern Washington, and a mixed product from a phosphorus recovery process at a dairy in Colorado, hereafter referred to as “Colorado product”. The Colorado product consisted mainly of ground apatite seed crystals, recovered magnesium phosphate, and sand grains from the bottom of the dairy manure storage lagoon. Fertilizers were analyzed for total P, Mg, Ca, and K at Ward Laboratories, Inc. in Kearney, NE (Table 2).

Table 2. Bulk fertilizer chemical characteristics. Standard deviations listed in parentheses (n=3). Percentages were determined after a total digest of fertilizer samples. Struvite differs from pure struvite such as that in Bridger et al. (1962) due to Ca phosphate seed crystals, and Colorado product is very heterogeneous in nature due to the presence of sand from treatment.

fertilizer	% P_2O_5	% Mg	% Ca	% K_2O
struvite	28.2 (0.4)	4.2 (0.3)	17.9 (0.9)	0.3 (0.0)
dittmarite	45.4 (0.3)	12.2 (0.6)	0.30 (0.02)	ND
Colorado product	16.2 (0.6)	0.41 (0.01)	18.3 (1.0)	0.5 (0.1)
TSP	48.1 (0.3)	0.61 (0.03)	13.7 (0.7)	0.2 (0.0)
RP	21.7 (0.1)	0.10 (0.01)	25.4 (0.6)	0.2 (0.0)

Fertilizers were applied at two rates, the equivalent of 40 lbs P_2O_5 $acre^{-1}$ and 80 lbs P_2O_5 $acre^{-1}$. The low rate was based on the agronomic rate for P in a broadcast application outlined in Mortvedt et al. (1996), modified for the use of the Mehlich-3 test for soil P. Note, however, that these rates were determined using total P_2O_5, rather than citric acid soluble or “available” P_2O_5. As a result, the same amount of total P (0.05 g or 0.1 g P_2O_5) was applied to each pot receiving a given rate. Fertilizer treatments were mixed thoroughly with 5.5 lbs soil per one-gallon pot, and after treatment application, pots were laid out in a greenhouse in a randomized complete block design. The experiment was performed with a total of 4 replicates (blocks).

"Zeke" hard red spring wheat (*Triticum aestivum L.*) was then planted at a rate of 15 seeds per pot, and after germination excess plants were clipped to a total of eight plants per pot. At one-month intervals, plants were cut approximately 4 inches above the soil. Pots were watered from the bottom with high-quality municipal water approximately every other day, depending on sunlight and greenhouse temperature, in order to maintain the soil at field capacity. A quantity of 30 mL of dilute N solution (0.027 M NH_4NO_3) was applied after the first cutting and approximately every two weeks thereafter to eliminate the possibility of a N limitation of P uptake. For the second and third cuttings, seeds and vegetative growth were harvested separately.

Reproductive and vegetative material were washed in de-ionized water, dried at 70°C, ground, and sent to Ward Laboratories, Inc. for total P analysis. Reproductive and vegetative plant material were weighed and analyzed separately.

Statistical analysis was performed using SAS version 9.1 proc glm. Multiple comparisons were made using Fisher's F-protected LSD at a significance level of $\alpha=0.10$.

RESULTS AND DISCUSSION

Low pH Soil

At low soil pH (6.5), there was no significant difference from the control in total dry matter (DM) production or in DM production at any single harvest. Even TSP did not significantly affect DM production in the low pH soil. The experimental setup was similar (though by no means identical) to Ebeling et al. (2003), but overall variability amongst blocks was much greater than in that study. As a result, treatment effects were more difficult to separate statistically. A major contributor to the lack of differences in DM production was the unusually high amount of seed DM produced in the control pots during the second harvest period. During this period, there was substantially lower seed production in many of the fertilized pots. Though the fertilizer treatments did not significantly increase DM production, several of the fertilizer treatments did result in increased P concentration in vegetative and seed material at low soil pH. Plants treated with TSP, struvite, and dittmarite showed significant increases in P concentration, especially at the higher application rate. In addition to outperforming the control in P concentration, dittmarite performed significantly better than RP and the Colorado product treatments, as well ($p < 0.05$). At the high application rate, TSP also significantly increased P concentration over either RP treatment ($p < 0.01$).

Three factors potentially influencing this outcome in the low pH soil are the P content and P availability of the soil, particularly at pH 6.5, and the soil's organic matter content. At a soil pH of 6.5, P availability is typically optimal for many plants. The optimal pH, coupled with this soil's moderate level of available P (see Table 1), may have led to conditions sufficient for substantial DM production in the un-fertilized pots. Another possibility is that of P release to plants through the mineralization of organic matter over the course of the experiment. The greenhouse in which the experiment was conducted was considered to be abnormally hot, so the temperature coupled with the irrigation of the pots would create ideal conditions for microbiological mineralization of organic matter. Lack of significant differences in plant P content in the last cutting, suggesting increased P availability, could support this conclusion.

Although the addition of fertilizer did not increase DM production at low pH in this experiment, some of the fertilizers did increase plant P concentration both early in the experiment and overall. While RP and the Colorado product had an early effect, the overall average was not significantly different from the control mean P concentration of 0.34%. Struvite and TSP significantly increased plant P concentration at the high application rate, to 0.36% ($p=0.545$) and 0.37% ($p < 0.01$), respectively. Dittmarite increased overall average plant P concentration at both the high and low rates of application to 0.37% ($p < 0.01$). These findings support previous work (Johnston and Richards, 2003; Li and Zhao, 2003) that found recovered Mg phosphates to be effective fertilizers in slightly acidic soils.

High pH soil

One matter of concern regarding the interpretation of plant P concentrations for the limed soil is the high average P concentration for the control, and relatively lower P concentrations in the fertilized plants. Also perplexing is the increased soil test P in the limed soil (see Table 1). These results seem counterintuitive, given the common perception that high pH and the presence of $CaCO_3$ will inhibit P availability to plants, and the application of fertilizer to increase yields and plant P content. Indeed, liming of the soil was selected as a method of controlling overall P availability across both pH values used in this experiment. The addition of large amounts of free Ca may unexpectedly have had the opposite effect, possibly by rendering P bound as iron or aluminum phosphates more soluble. Consequently, comparisons between the low pH and high pH soils are not possible. Liming may be an unsuitable choice to manipulate soil pH for similar experiments in the future.

Even so, all fertilizers except RP and low rate struvite showed significantly ($p < 0.05$) increased total DM production over the control at high soil pH. That RP was ineffective is not a new finding: Mackay and Syers (1986) found that high Ca concentrations inhibit RP dissolution, and Chien and Menon (1995) noted that high pH and high Ca concentration, in addition to other factors, limited the effectiveness of RP in soil. However, since the other treatments all showed increased DM production, the results of this experiment support the conclusion that recovered Mg phosphates can indeed be used as fertilizers on alkaline soils. Field trials and further tests across a wide range of alkaline soil pH and $CaCO_3$ content will help to determine the agronomic effectiveness of these fertilizers under alkaline soil conditions.

Although many of the fertilized pots had lower plant P concentration than the control at high pH, the difference in total P uptake for all of the treatments except RP and low rate struvite was significant ($p < 0.05$). The significant nature of the difference shows fairly convincingly that struvite, dittmarite, and even the heterogeneous Colorado product have the potential to perform similarly to commercial TSP in high pH, high Ca soil conditions. Given the ineffective nature of RP in these particular environments, recovered Mg phosphates might even provide certified organic producers with a viable alternative for P fertilization on calcareous soils.

SUMMARY

The recovery and beneficial re-use of phosphate has the potential to help protect water quality, improve the sustainability and efficient cycling of P (a limited resource), and provide sources of revenue and materials for producers and consumers of phosphate. Several recovery technologies focus on the crystallization of Mg phosphates such as struvite and dittmarite, which cannot be recycled as a raw material for the current phosphate industry but have potential as a fertilizer. A few studies have documented the effectiveness of Mg phosphates in acidic soils, but there is no body of work examining their usefulness in calcareous soil conditions. This study found evidence that recovered Mg phosphates may, in fact, be useful across a broad range of soil conditions. Recovered Mg phosphates increased wheat P concentration in slightly acidic soil conditions, and increased plant DM production in alkaline soil conditions. These results indicate that recovery of Mg phosphates for use as a fertilizer could improve P cycling and water quality, and that recovered Mg phosphate fertilizers could be an effective source of P fertilizer in areas with both acidic and alkaline soils, such as the western United States.

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REFERENCES

Bauer, P.J., A.A. Szogi, and M.B. Vanotti. 2007. Agronomic effectiveness of calcium phosphate recovered from liquid swine manure. *Agron. J.* 99:1352-1356.

Bolland, M.D.A., A.J. Weatherley, R.J. Gilkes, and J.W. Bowden. 1986. Granular reactive apatite rock phosphate is not an effective phosphorus fertilizer in the short term on lateritic soils in south-western Australia. *Aust. J. Exp. Agric.* 26: 217-225.

Bowers, K.E., and P.W. Westerman. 2005a. Design of cone-shaped fluidized bed struvite crystallizers for phosphorus removal from wastewater. *Trans. ASAE* 48(3): 1217-1226.

Bowers, K.E., and P.W. Westerman. 2005b. Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. *Trans. ASAE* 48(3): 1227-1234.

Bridger, G.L., M.L. Salutsky, and R.W. Starostka. 1962. Metal ammonium phosphates as fertilizers. *Agric. and Food Chem.* 10(3): 181-188.

Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Applic.* 8(3): 559-568.

Chien, S.H., and R.G. Menon. 1995. Factors affecting the agronomic effectiveness of phosphate rock for direct application. *Fertilizer Res.* 41: 227-234.

de-Bashan, L.E., and Y. Bashan. 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer. *Water Res.* 38: 4222-4246.

Driver, J., D. Lijmbach, and I. Steen. 1999. Why recover phosphorus for recycling, and how? *Env. Tech.* 20:651-662.

Ebeling, A.M., L.R. Cooperband, and L.G. Bundy. 2003. Phosphorus availability to wheat from manures, biosolids, and an inorganic fertilizer. *Comm. Soil Sci. Plant Analysis* 34(9, 10): 1347-1365.

Elliott, A.L., J.G. Davis, R.M. Waskom, J.R. Self, and D.K. Christensen. 2007. Phosphorus fertilizers for organic farming systems. Colorado State University Cooperative Extension publication no. 0.569.

Greaves, J., P. Hobbs, D. Chadwick, and P. Haygarth. 1999. Prospects for the recovery of phosphorus from animal manures: a review. *Env. Tech.* 20: 697-708.

Johnston, A.E., and I.R. Richards. 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use and Mgmt.* 19: 45-49.

Li, X.Z., and Q.L. Zhao. 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecol. Eng.* 20: 171-181.

Lindsay, W.L. 1979. *Chemical Equilibria in Soils.* 2001 reprint ed. Caldwell, New Jersey: The Blackburn Press.

Mackay, A.D., and J.K. Syers. 1986. Effect of phosphate, calcium, and pH on the dissolution of a phosphate rock in soil. *Fertilizer Res.* 10: 175-184.

Mortvedt, J.J., D.G. Westfall, and J.F. Shanahan. 1996. Fertilizing spring-seeded small grains. Colorado State University Cooperative Extension publication no. 0.534.

Rothbaum, H.P., and A.G. Rohde. 1976. Long-term leaching of nutrients from magnesium ammonium phosphate at various temperatures. *New Zealand J. Exp. Agric.* 4: 405-413.

Schipper, W.J., A. Klapwjik, B. Potjer, W.H. Rulkens, B.G. Temmink, F.D.G. Kiestra, and A.C.M. Lijmbach. 2001. Phosphate recycling in the phosphorus industry. *Env. Tech.* 22: 1337-1345.

Ueno, Y., and M. Fujii. 2001. Three years experience of operating and selling recovered struvite from full-scale plant. *Environ. Tech.* 22: 1373-1381.