

Agronomic Effectiveness of Calcium Phosphate Recovered from Liquid Swine Manure

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ABSTRACT

A new manure treatment technology developed as an alternative to anaerobic lagoons on swine (*Sus scrofa domesticus*) farms includes solid-liquid separation and subsequent recovery of soluble P as calcium phosphate from the wastewater. The objective was to determine the agronomic effectiveness of this calcium phosphate material. A greenhouse study was conducted with annual ryegrass (*Lolium multiflorum* Lam.). Three fertilizer materials were evaluated: the recovered P in two particle sizes (0.5–1.0 and 2.0–4.0 mm), and commercial triple superphosphate (TSP). Fertilizer rates were 0, 22, 44, 88, and 176 mg P kg⁻¹ soil. Three harvests of the ryegrass were made at 2-wk intervals. Total P uptake increased linearly with application rate for all three fertilizer materials. At the highest application rate, total P uptake was 37.8 mg pot⁻¹ for TSP, 26.2 mg pot⁻¹ for the recovered P with small particle size, and 9.0 mg pot⁻¹ for the recovered P with large particle size. Chemical analysis of the recovered P material revealed that over 99% of the P₂O₅ in the recovered calcium phosphate was plant available P, mostly as citrate-soluble, Mehlich-3 extractable soil P at the end of the experiment indicated that little of the large particle size of recovered P material dissolved and became available during this short 10-wk study. The recovered calcium phosphate appears to have potential as a fertilizer source.

REPEATED MANURE APPLICATIONS to land on or around confined animal production facilities has, in some cases, resulted in high soil test P. Overapplication of P can be detrimental to surrounding ecosystems through contamination of surface and groundwaters (Ribaud et al., 2003). Animal waste treatments that include P recovery from manure are a management option that could resolve problems of excess manure P on agricultural lands (Greaves et al., 1999; Smil, 2000).

Recovery of P from animal liquid manures is possible by precipitating it in a variety of chemical forms. These include magnesium ammonium phosphates known as struvites (Webb and Ho, 1992) and calcium phosphates (House, 1999). Much of the literature on recovered phosphates, particularly struvites, from animal liquid manure has been concerned with their production and potential reuse in agriculture (Bowers and Westerman, 2005; Burns et al., 2001; Nelson et al., 2003; Suzuki et al., 2005), but there are very few reports on agronomic effectiveness of recovered phosphates (Johnston and Richards, 2003; Romer, 2006).

A new manure treatment process has been developed for swine farms where the soluble P in wastewater is precipitated into a material containing a relative high concentration of calcium phosphate (Vanotti et al., 2003, 2005). The treatment process applied to systems without anaerobic lagoons consists of three steps which (i) mechanically separates solids from the liquid, (ii) biologically removes N from the liquid, and (iii) precipitates soluble P from the liquid with reduced amounts of hydrated lime (Vanotti et al., 2006). The calcium phosphate-rich precipitate can be dewatered to provide a material that is >90% solids (Szogi et al., 2006b). The resulting dry material contains sufficient P concentration (P₂O₅ > 20%) to be economically transported for fertilizer application or further processing into P containing products.

The high phosphate concentration of this recovered P material suggests it likely has utility as a fertilizer source. Our objective was to evaluate agronomic effectiveness of the calcium phosphate recovered from swine wastewater. The study was conducted under greenhouse conditions with annual ryegrass using two particle sizes of the recovered P material compared with commercial TSP.

MATERIALS AND METHODS

Phosphorus Recovery

The P material evaluated in this study was from a full-scale liquid manure treatment facility located on a 4360-head finisher swine production unit in Duplin County, North Carolina, USA. The treatment facility consisted of three modules. In the first module, the solid phase of the waste was mechanically separated from the liquids. Solids were subsequently converted to compost. The wastewater after separation in the first module was pumped into the second module, where ammonia was converted to dinitrogen gas in a biological nitrification/denitrification reactor. The wastewater then went to the final module, where soluble P was recovered as calcium phosphate precipitate by increasing the pH with controlled amounts of hydrated lime [Ca(OH)₂] (567 mg L⁻¹ wastewater). An average of 39 m⁻³ d⁻¹ of raw manure flushed from the barns was treated in a 9-mo evaluation period. A total of 526 kg of P was recovered from the swine manure (Vanotti et al., 2006). Further details of the process extraction of P from wastewater and dewatering of the precipitate are given in Vanotti et al. (2003, 2005, 2006) and Szogi et al. (2006b).

Greenhouse Study

A greenhouse study was conducted with annual ryegrass as the test crop to evaluate the recovered P material as a fertilizer source. The experiment was conducted twice. Temperature inside the greenhouse was monitored with a HOBO (Onset Computer, Bourne, MA) weather station. Average daily tem-

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perature [(maximum temperature + minimum temperature)/2] was 28.4°C (range 25.3–32.0°C) for the first experiment and 28.6°C (range 24.4–32.0°C) for the second experiment. Artificial lighting was not used.

A sandy-textured soil [Uchee sand (loamy, siliceous, thermic, Arenic Paleudult)] was used in the study. The soil was collected from a wooded area known to be low in P at the Pee Dee Research and Extension Center, Clemson University, Darlington, SC. The soil was passed through a 6.35-mm screen to remove large particles and roots. Two 100-g samples of the soil were air dried on a greenhouse bench, ground, and then chemically analyzed at Clemson University's Agricultural Service Laboratory. Results from this analysis are shown in Table 1. After analysis, a small cement mixer was used to mix Ca(OH)₂ with the sieved soil to raise the pH to 6.5. The soil was then pasteurized (FAMCO, Inc., Model 14 Soil Pasteurizer, Medina, OH) and stored in large plastic containers until it was used.

The dewatered P material from the wastewater treatment facility (Fig. 1a) was ground with a Dynacrush mill (Custom Laboratory Equipment Inc., Orange City, FL), and two particle sizes of the ground material were obtained by sieving for use in the study (Fig. 1b). The two particle sizes were (i) granules that would pass through a 1.0-mm sieve but be retained on a 0.5-mm sieve; and (ii) granules that would pass through a 4.0-mm sieve but be retained on a 2.0-mm sieve. These two particle sizes were selected in an effort to represent sizes commonly used in commercial fertilizer applications (W. Hall, personal communication, 2005).

Treatments were three fertilizer sources (two particle sizes of the recovered P material and commercially-obtained TSP) and five fertilizer rates (0, 22, 44, 88, and 176 mg P kg⁻¹ soil). Nitrogen, potassium, and sulfur were added to all treatment combinations as follows: 1.36 kg soil, 2 g of 15–0–15 (N–P₂O₅–K₂O) fertilizer, and 0.12 g of technical grade (NH₄)₂SO₄ were thoroughly mixed and placed in 15-cm diam. pots on greenhouse benches. Pots were then watered to 100 g water kg⁻¹ soil using a scale and kept moist. About 3 wk later, 1.11 g of annual ryegrass seed was planted in each pot. The soil surface in each pot was kept moist by adding water as needed. At about 5 wk after planting, each pot received 1.00 g of NH₄NO₃.

Three harvests of plant shoot tissues were made in each of the two trials of the experiment. Harvests were made by cutting plants ≈2.5 cm above the soil surface. In the first trial of the experiment, shoot tissue was collected at 19, 34, and 47 d after planting. In the second trial, shoot tissue was collected at 21, 35, and 50 d after planting. Plant tissue samples were dried at 60°C for 3 d and then weighed and ground. After the last cutting in each trial, three 2.5-cm soil cores were collected from each pot and dried on a greenhouse bench. The soil samples were ground for P extraction after removing large roots.

Chemical Analyses

Duplicate samples of the recovered calcium phosphate were analyzed for total P, water-soluble P, citrate-insoluble P, and

Table 1. Chemical properties of the soil used in the greenhouse study before amending with hydrated lime.

| Soil properties | Mean† |
|---|------------|
| pH in water | 4.9 ± 0.1 |
| Cation exchange capacity, cmol kg ⁻¹ | 2.0 ± 0.4 |
| Exchangeable acidity, cmol kg ⁻¹ | 1.8 ± 0.3 |
| Phosphorus, mg kg ⁻¹ | 1.7 ± 0.1 |
| Potassium, mg kg ⁻¹ | 4.8 ± 1.2 |
| Calcium, mg kg ⁻¹ | 22.4 ± 4.0 |
| Magnesium, mg kg ⁻¹ | 4.2 ± 0.4 |

† Mean of two samples ± standard deviation.



Fig. 1. (a) Recovered calcium phosphate precipitate from full-scale wastewater treatment plant. (b) Selected particle sizes after grinding and sieving the recovered phosphate material.

available P (citrate-soluble) as P₂O₅ according to AOAC Official Methods 958.01, 977.01, 963.03 B(a) (AOAC International, 2000). Total C and N contents were determined by dry combustion with a LECO C/N analyzer (LECO Corporation, St. Joseph, MI). Total elemental analysis of the recovered P material was determined with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian Instruments, Walnut Creek, CA) after automated digestion (AutoBlock, Environmental Express, Mt. Pleasant, SC) with nitric acid and hydrogen peroxide (Peters et al., 2003).

Ryegrass shoot tissues were digested with concentrated sulfuric acid (Gallaher et al., 1976) and P concentration determined in the digest by automated ascorbic method adapted to digested extracts (Technicon Instruments, 1977). Total P in the plant tissues at each harvest was calculated by multiplying P concentration by biomass, and total P recovery for the experiment was determined by summing the total P from each harvest. Phosphorus from soils collected at the end of the experiment was extracted using the Mehlich 3 procedure (Tucker, 1992) and P content was determined in the digest using colorimetric analysis.

Statistical Analysis

Experimental design was a randomized complete block and there were four replicates in each experiment. Statistical analysis was performed using the GLM procedure of SAS (SAS

Table 2. Elemental analysis of the recovered phosphorus material.

| Element | Composition [†] |
|---------|--------------------------|
| | g kg ⁻¹ |
| Ca | 318.9 ± 1.4 |
| Total P | 114.4 ± 3.0 |
| Total C | 63.9 ± 0.4 |
| Mg | 17.6 ± 0.2 |
| K | 8.7 ± 0.1 |
| Total N | 6.4 ± 0.1 |
| Total S | 4.9 ± 0.6 |
| Na | 2.5 ± 0.1 |
| Fe | 1.7 ± 0.1 |
| Al | 1.3 ± 0.1 |
| Zn | 0.69 ± 0.01 |
| Cu | 0.33 ± 0.01 |
| Mn | 0.33 ± 0.01 |

[†] Mean of duplicate samples ± standard deviation.

Institute, Cary, NC) over both trials of the study. Phosphorus concentration in plant tissues, total tissue P, and soil extractable P responses to application rate for each fertilizer material were determined using linear regression analysis.

RESULTS AND DISCUSSION

Analysis of Recovered Phosphorus Material

Chemical elemental composition of the recovered P material is shown in Table 2. The two major elemental components of the material were Ca and P. Concentrations of other plant nutrients were low. This indicates that most of the Ca(OH)₂ used in the P treatment module selectively precipitated P in the form of calcium phosphate. Analysis by x-ray diffraction of the same material (Szogi et al., 2006a) indicated that this is amorphous calcium phosphate (ACP), which typically is more soluble than crystalline calcium phosphates such as hydroxylapatite (Valsami-Jones, 2001). Phosphorus availability of fertilizing materials is usually determined using the AOAC “available P” test (AOAC International, 2000). Three fractions are usually determined using finely ground material (No. 40 mesh, < 0.475 mm). A simple extraction procedure with water represents the water soluble P fraction. The filtrate obtained from the remaining water-insoluble material after extraction with neutral ammonium citrate is the citrate-soluble P. What is called “plant available P” is the sum of water-soluble P plus neutral citrate-soluble P. Our results show that the recovered P material had a total P content of 26.22% P₂O₅ (g P₂O₅ per 100 g material, Table 3), which is in between the total P content of single superphosphate (SSP) (16 to 22% P₂O₅) and TSP (44 to 53% P₂O₅). The recovered P was mostly plant available P (99.88% of total P), which is similar to those values

Table 3. Water-soluble, water-insoluble phosphorus fractions and total phosphorus content of the recovered phosphate material.

| Component | Composition [†] | Fraction of total P ₂ O ₅ |
|-------------------------------------|--|---|
| | g P ₂ O ₅ 100 g ⁻¹ material | |
| Water-soluble | 0.15 ± 0.01 | 0.57 |
| Citrate-soluble | 26.04 ± 0.01 | 99.31 [‡] |
| Citrate-insoluble | 0.04 ± 0.01 | 0.15 |
| Total P ₂ O ₅ | 26.22 ± 0.68 | 100.00 |

[†] Mean of duplicate samples ± standard deviation.

[‡] Plant available = water-soluble + citrate-soluble fractions (99.88%).

Table 4. Effect of fertilizer material and rate on ryegrass biomass.

| Material | Rate | Biomass |
|------------------|----------------------------|--------------------|
| | mg P kg soil ⁻¹ | |
| Control | 0 | 4.2 a [†] |
| 0.5–1 mm | 22 | 4.8 ab |
| | 44 | 5.2 b |
| | 88 | 5.2 b |
| 2–4 mm | 176 | 5.7 bc |
| | 22 | 3.8 a |
| | 44 | 4.1 a |
| TSP [‡] | 88 | 4.2 a |
| | 176 | 4.7 ab |
| | 176 | 5.2 b |
| LSD (0.05) | | 0.6 |

[†] Means followed by the same letter are not significantly different (LSD 0.05).

[‡] TSP, triple superphosphate.

of 97 to 100% reported for both SSP and TSP (Follet et al., 1981).

Greenhouse Study

Significant differences in biomass production of the ryegrass were found among treatment combinations in this study. Biomass production was generally lower for plants fertilized with the 2.0- to 4.0-mm particle size of recovered P than for ryegrass fertilized with TSP or the 0.5- to 1.0-mm particle size of recovered P (Table 4). None of the rates of the 2.0- to 4.0-mm particle size differed in biomass production from the control. Only the 176 mg pot⁻¹ rate of TSP had higher ryegrass biomass than the control. In contrast, for plants fertilized with the 0.5- to 1.0-mm particle size, biomass production was greater than the control at the three highest rates.

Similar to biomass production, P concentrations in plant tissues did not change appreciably with increasing P application rate for the 2.0–4.0 mm particle size (Fig. 2). On the other hand, P concentration increased

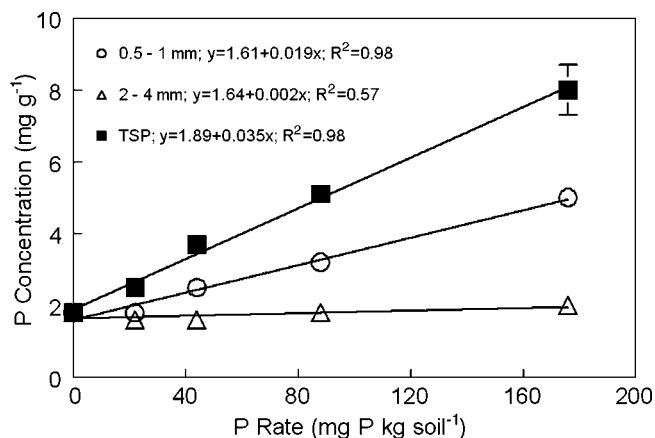


Fig. 2. Phosphorus concentration of ryegrass plant tissues as affected by fertilizer material and application rate. Data are the average of two trials of the experiment. Standard error bars are shown when their size was larger than that of the symbol.

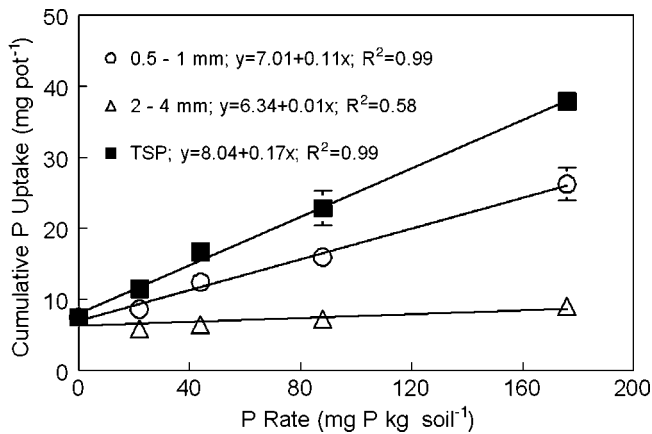


Fig. 3. Phosphorus uptake by ryegrass as affected by fertilizer material and application rate. Data are the average of two runs of the experiment. Standard error bars are shown when their size was larger than the symbol.

steadily with increasing P application rate for TSP and the 0.5- to 1.0-mm particle size of recovered P. At the highest application rate, P concentrations in plant tissues were 5 mg kg^{-1} for the 0.5- to 1.0-mm particle size of recovered P and 8 mg kg^{-1} for TSP.

Phosphorus uptake by the ryegrass was dependent on fertilizer material and rate of application (Fig. 3). Phosphorus uptake with the 0.5- to 1.0-mm particles increased $0.111 \text{ mg pot}^{-1}$ for each mg kg^{-1} increase in applied P. For TSP, plant uptake increased $0.167 \text{ mg pot}^{-1}$ for each mg kg^{-1} increase in applied P. Phosphorus uptake was low for all rates of the 2.0- to 4.0-mm particle size of the recovered P (Fig. 3). Phosphorus uptake in pots containing the large particle size of recovered P increased only 0.02 mg pot^{-1} for each mg kg^{-1} increase in applied soil P. At the highest application rate, total P uptake was 37.8 mg pot^{-1} for TSP, 26.2 mg pot^{-1} for the small particle size of recovered P, and 9.0 mg pot^{-1} for the large particle size of recovered P. This indicates that the recovered P material may have different uses depending on how it is processed. Where a readily available P fertilizer is needed, the finer material (0.5–1.0 mm) is the best choice. On the other hand, coarse granules (2.0–4.0 mm) are better suited for applications that require slow release P fertilizer.

The low P uptake by plants fertilized with the 2.0- to 4.0-mm particle size of the recovered P could be due to low solubility. Mehlich-3 extractable soil P at the end of the experiments is shown in Fig. 4. Mehlich-3 P for the larger particle size of the recovered P was low across all rates (and similar to the controls). Interestingly, the rate response of extractable P concentrations for the 0.5- to 1.0-mm particle size of the recovered P was near the response of TSP. Only at the highest application rate was there a difference in soil extractable P concentration between the small particle size of recovered P and TSP.

The lower solubility of the larger particle size was further confirmed by leaching samples of three particle sizes (<0.15 mm, 0.5–1.0 mm, and 2.0–4.0 mm) of the P

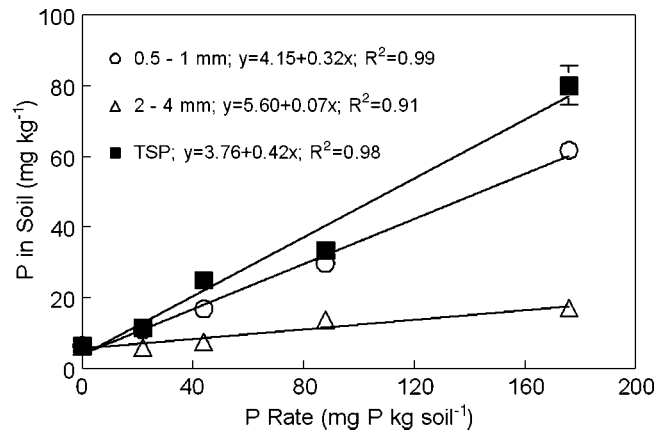


Fig. 4. Mehlich-3 extractable phosphorus concentration remaining in the soil after 7 wk of ryegrass growth as affected by fertilizer material and application rate. Data are the average of two runs of the experiment. Standard error bars are shown when their size was larger than the symbol.

recovered material with Mehlich-3 extraction solution (pH 2.5) and measuring P concentration in the leachate using ICP-AES. The procedure included using duplicate 1.00-g samples and placing the samples in funnels lined with Whatman 42 filter paper and leaching with 10-mL of Mehlich-3 solution. Average P concentration in the leachate was 769 mg L^{-1} for the <0.15-mm particle size, 502 mg L^{-1} for the 0.5- to 1.0-mm particle size, and 267 mg L^{-1} for the 2.0- to 4.0-mm particle size (LSD = 115 mg L^{-1}). These results are in agreement with Tisdale et al. (1985) that grinding of a water-insoluble fertilizer material is essential to ensure a large total surface area exposed for contact by the soil and root system. As a consequence, the P plant availability of the recovered calcium phosphate material is related directly to their specific surface and inversely related to the granule size of the material. Therefore, while citrate-soluble extraction of finely ground recovered P material indicated very high plant availability (>99%, Table 3), its actual availability can be controlled by the size of the granules.

CONCLUSIONS

The recovered calcium phosphate appears to have potential as a fertilizer source without further chemical processing into other P materials, such as the acid treatment typically used to process rock phosphate for fertilizer use. Plants fertilized with 0.5- to 1.0-mm particles of recovered calcium phosphate had P uptake responses almost as good as TSP. Also, soil extractable P after 10 wk in moist soil (3 wk of incubation plus 7 wk with ryegrass) was not that different from soil concentrations when TSP was used as the fertilizer source. When larger particles were used as the fertilizer source; however, there was considerably less P uptake and soil extractable P at the end of 10 wk was still at levels near the control (no added P), even at the highest application rate. Although further research is needed under field conditions and on more soil types for fer-

tilizer application recommendations, it appears that the material may have dual uses depending on how the material is processed. It is potentially a readily available P fertilizer source when ground to a smaller particle size. As large particles, this material may be used for a slow release P fertilizer.

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