

## LABORATORY AND *IN-SITU* REDUCTIONS OF SOLUBLE PHOSPHORUS IN SWINE WASTE SLURRIES

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### ABSTRACT

Laboratory and field experiments were conducted using magnesium chloride ( $MgCl_2$ ) to force the precipitation of struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) and reduce the concentration of soluble phosphorus (SP) in swine waste. In laboratory experiments, reductions of SP of 76% (572 to 135 mg P l<sup>-1</sup>) were observed in raw swine manure after addition of magnesium chloride ( $MgCl_2$ ) at a rate calculated to provide a 1.6:1 molar ratio of magnesium (Mg) to total phosphorus. Adjusting the pH of the treated manure to pH 9.0 with sodium hydroxide (NaOH) increased SP reduction to 91% (572 to 50 mg P l<sup>-1</sup>). X-ray diffraction of the precipitate recovered from swine waste slurry treated only with  $MgCl_2$  confirmed the presence of struvite. The molar N:P:Mg ratio of the recovered precipitate was 1:1.95:0.24, suggesting that compounds in addition to struvite were formed. In a field experiment conducted in a swine manure holding pond, a 90% reduction in SP concentration was observed in approximately 140 000 l of swine manure slurry treated before land application with 2000 l  $MgCl_2$  (64% solution) at ambient slurry temperatures ranging from 5 to 10°C.

Keywords. Manure, magnesium chloride, phosphorus, struvite

### INTRODUCTION

Excessive loading of phosphorus (P) onto agricultural lands has been recognized as a surface water quality threat in both Europe and the United States [1]. Methods that can reduce either the system P input loading or P movement into surface waters are needed to address this problem. The forced precipitation of struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) from animal waste slurries prior to land application can reduce soluble phosphorus (SP) levels in the manure slurries as well as offer the potential to concentrate and remove P from the system. Using this approach the recovered P could then be transferred to cropping locations that are P deficient [2]. The economical concentration and transport of excess phosphorus to P deficient cropping areas would allow existing operations to remain viable in their current locations.

In the laboratory, soluble phosphorus concentrations have been reduced from anaerobic swine effluent by forcing the precipitation of struvite [2-4]. However, field scale applications of this technology with swine waste have not been documented [3].

The optimal pH for struvite precipitation is 9.0 [5]. The limiting nutrient for struvite precipitation in animal manures is usually magnesium (Mg) [2-4]. The pH range where struvite precipitation occurs in animal waste treatment systems is 7 to

11. Wrigley et al. performed a laboratory experiment to enhance struvite precipitation in anaerobic supernatant from batch and continuously stirred digested swine waste. By increasing the pH to 9.0 and adding Mg, P concentrations in the batch and continuously stirred digested waste decreased by 75 and 90% (respectively); final P concentrations of less than 1 mg l<sup>-1</sup> were achieved [4]. Beal et al. induced struvite precipitation in undigested and continuously stirred digested swine waste. To increase pH and Mg concentration, magnesium oxide (MgO) was added. Magnesium oxide addition increased the pH to 8.5 and decreased phosphorus concentration by 92 and 98% in undigested and digested waste (respectively). The minimum P concentration achieved in the digested waste was 15 mg l<sup>-1</sup> [2].

Waste strength affects struvite solubility [6]. Specifically, struvite solubility is increased in the presence of complexing agents, such as organic acids. The digested waste used by Wrigley et al. [4] had a COD concentration half that used by Beal et al. [2], which had a COD of 24 000 mg l<sup>-1</sup>. In a pilot-plant application recovering struvite from calf manure slurry, Schuiling and Andrade reported that total suspended solids (TSS) interfered with the precipitation process at TSS concentrations above 1000 mg l<sup>-1</sup> [7]. Higher COD levels in animal waste slurries correlate to higher total and suspended solids in the waste. Waste strength and the associated higher

solids concentrations in the waste were the likely cause for the reduced struvite precipitation previously observed in our laboratory [2].

Nelson et al. conducted laboratory tests to precipitate struvite from anaerobic swine lagoon effluent [3]. By increasing the pH to 9.0 and adding sufficient Mg, as MgCl<sub>2</sub>, to achieve a Mg:Total Phosphorus (TP) ratio of 1.6:1, soluble P concentrations were decreased by 62 to 95%. Nelson reported that increasing the Mg:TP ratio both decreased struvite solubility and the pH at which minimum struvite solubility occurred [3]. This supports the hypothesis of Schulze-Rettmer [6] that high Mg concentrations promote struvite formation by overcoming the effects of complexing agents that can bind to Mg.

## MATERIALS AND METHODS

### Laboratory Experiments

Waste was collected from two holding ponds at one swine facility. Samples from the primary and the secondary holding ponds were transported to the laboratory in 19 l sealed plastic buckets and stored at 4°C for 3 weeks prior to the experiment.

Two laboratory experiments were conducted. In the first, manure samples were amended with MgCl<sub>2</sub> (64% solution from *Mineral Research and Development Corp.*, Charlotte, North Carolina, USA). The pH of the MgCl<sub>2</sub> was 5.0. Magnesium chloride was added at a rate to achieve a Mg:TP ratio of 1.6:1. In the second experiment, manure samples were amended with MgCl<sub>2</sub> followed by 1 M NaOH to obtain a pH of 9.0. Magnesium chloride was chosen over MgO due to difficulty experienced by Beal et al. [2] in getting MgO into solution in the swine slurry.

In each experiment, 400 ml of waste was agitated following the addition of the MgCl<sub>2</sub> or MgCl<sub>2</sub> and NaOH for 20-minutes. In each case (primary and secondary waste holding pond slurries), MgCl<sub>2</sub> was added at a rate to achieve a Mg:TP ratio of 1.6:1. Due to differences in the TP concentrations of each holding pond, the primary pond waste was treated with 17 ml of MgCl<sub>2</sub>, and the secondary pond waste with 56 ml of MgCl<sub>2</sub>, per 400 ml of waste. In the experiments where pH was adjusted, NaOH was added until a pH of 9.0 was achieved (30 ml NaOH for primary pond waste, and 50 ml NaOH for secondary pond waste, per 400 ml of waste). Samples were stored in Nalgene® bottles at 4°C and analysis occurred within 24 hours. Samples were analyzed for SP and TP by *QuickChem* Method 12-115-01-1-H and *QuickChem* Method 13-115-01-1-B (*Lachat Instruments*, Milwaukee, Wisconsin, USA), respectively. All pH measurements were made with a calibrated pH electrode (YSI Incorporated Model 63, Yellow Springs, Ohio, USA).

### Field Experiments

In the field study, magnesium was added at 80 l min<sup>-1</sup> to

a secondary swine waste storage pond, while the pond was agitated with a 93 kW Houle® pumping agitator. Approximately 2000 l of MgCl<sub>2</sub> was added to an estimated 140 000 l of liquid swine manure. The pond was agitated for 50 minutes after the beginning of MgCl<sub>2</sub> addition, after which the treated manure was land applied with a Nelson SR-200® irrigation big gun at a rate of 2800 l min<sup>-1</sup>. The ambient air temperature was 1°C at the beginning of the experiment and 9° C at the end. Slurry temperature ranged from 5 to 10° C during the pump-out.

Samples were taken from the waste storage pond, irrigation pump, and field, before, during, and after treatment with MgCl<sub>2</sub>. Prior to analysis for SP, sub-samples were centrifuged at 6000 rpm for 20 minutes then filtered (Whatman 42 paper, Whatman Int. Limited, Maidstone, England) and acidified to pH 2 with concentrated hydrochloric acid (HCl) within 12 hours of collection. Prepared sub-samples were refrigerated at 4°C until analysis. Analyses for SP, TP, and pH were as described above.

Data was analyzed using single factor analysis of variance (ANOVA) using Microsoft Excel. Significance was tested at the 95% confidence coefficient ( $\alpha = 0.05$ ).

### Precipitate Recovery

Before the addition of MgCl<sub>2</sub> to the secondary swine waste storage pond, 15 l of well-agitated swine waste slurry was collected and stored at 4°C in 19 l plastic buckets and transported back to the laboratory. This waste was allowed to warm to ambient conditions in the laboratory (approximately 22°C) and was then treated with MgCl<sub>2</sub> at a rate calculated to achieve a Mg:TP ratio of 1.6:1 in the waste. The treated slurry was allowed to react for 20 minutes following 5 minutes of hand stirring with a wooden paddle. Following this, the slurry was allowed to stand for 20 minutes, allowing solids to settle from the solution. The liquid fraction was decanted off leaving behind the settled solids. The settled material was a black sludge that contained both organic solids and a crystalline precipitate.

## RESULTS

### Laboratory Experiments

Waste collected from the primary holding pond contained 3.5% total solids and had a COD concentration of 21 000 mg l<sup>-1</sup>. Waste from the secondary holding pond contained 11.7% total solids and had a COD concentration of 54 000 mg l<sup>-1</sup>. After the addition of MgCl<sub>2</sub>, the primary and secondary pond waste had a pH of 6.7 and 6.6, respectively. Addition of 1M NaOH raised the pH to 9.0 ( $\pm 0.1$ ).

The initial SP concentration in the primary holding pond was 572 mg P l<sup>-1</sup>. The addition of MgCl<sub>2</sub> solution significantly reduced the SP concentration by an average of 76% to 135 mg P l<sup>-1</sup> (Figure 1). Addition of MgCl<sub>2</sub> solution in

conjunction with 1M NaOH reduced the soluble P concentration by an average of 91%, to 50 mg P l<sup>-1</sup>.

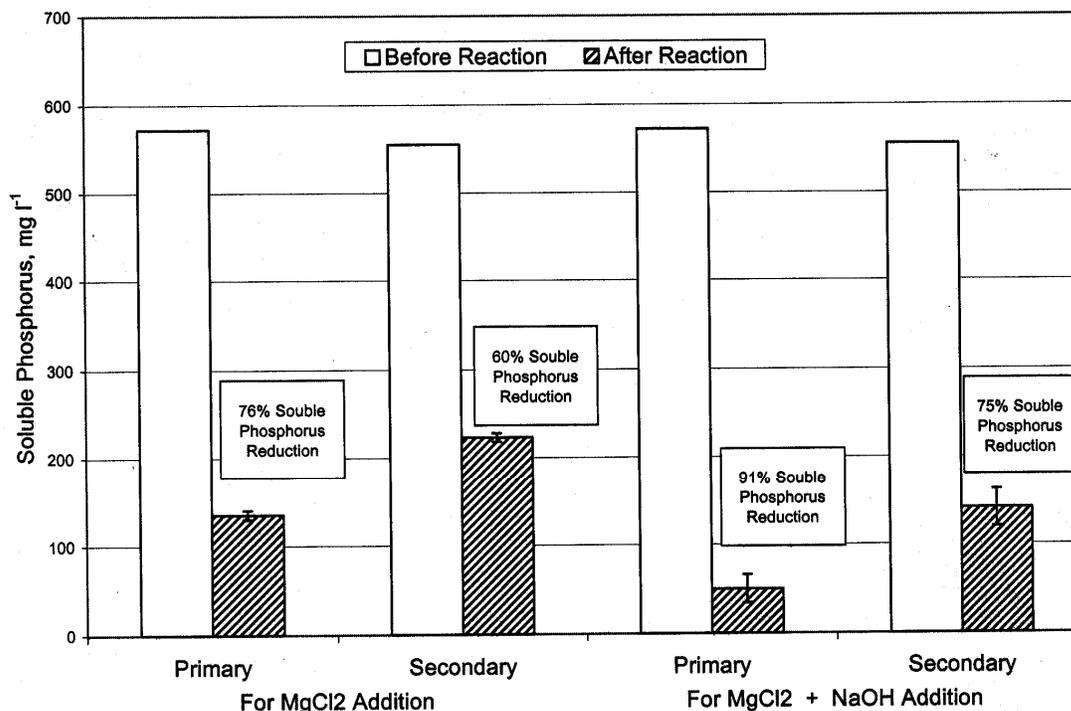


Figure 1. Soluble phosphorus concentrations before and after chemical amendment in laboratory tests. "Primary" indicates swine waste slurry from the primary holding pond and "Secondary" indicates swine waste slurry from the secondary holding pond.

The initial SP concentration in the secondary holding pond was 555 mg P l<sup>-1</sup>. Addition of MgCl<sub>2</sub> solution reduced the SP concentration by 60% to 223 mg P l<sup>-1</sup> (Figure 1). Adding MgCl<sub>2</sub> in conjunction with 1M NaOH (1 M) reduced the SP concentration by an average of 75%, to 141 mg P l<sup>-1</sup>.

#### Field Experiments

Following treatment with the MgCl<sub>2</sub> solution, samples were taken from both the holding pond and in the field. As shown in Figure 2, an 88% reduction in SP (150 to 17.4 mg P l<sup>-1</sup>) was seen when comparing samples from the holding pond before and after treatment. A 90% reduction in SP concentrations was seen (150 to 14.8 mg P l<sup>-1</sup>) when comparing treated samples taken in the field following application with the big-gun system to samples from the secondary waste storage pond prior to treatment. Treatment with MgCl<sub>2</sub> solution decreased the pH of the swine slurry from 7.7 to 6.5.

#### Nature of the Recovered Precipitate

A sample of the settled solids, recovered following

laboratory treatment of the secondary holding pond swine waste slurry with MgCl<sub>2</sub> at a rate calculated to provide a 1.6:1 Mg:TP ratio, was analyzed for total solids (TS) and volatile solids (VS). These analyses indicated that the settled solids contained 15.8% TS and 45.5% VS. Clean water was added to the remaining settled solids and the mixture was "panned" to separate the lighter organic material from the crystalline precipitate that formed following the addition of MgCl<sub>2</sub>. Total solids and VS analyses performed on the crystalline precipitate indicated that it contained 50.4% TS and 16.3% VS. The remaining recovered precipitate was air dried for further analyses.

Both the settled solids and the recovered precipitate were analyzed for total nitrogen (TN) and TP as an indication of their potential value as fertilizer material. Total nitrogen was determined by adding Total Kjeldahl Nitrogen, nitrate and nitrite. Samples were analyzed for TKN by *QuickChem* Method 13-107-06-2-D (*Lachat Instruments*, Milwaukee, Wisconsin, USA). Nitrate and nitrite were determined using a *Dionex Ion Chromatograph* (*DIONEX*, Sunnyvale, California, USA). The settled solids contained approximately 11 000 mg kg<sup>-1</sup> of TN and 7 000 mg kg<sup>-1</sup> of TP. The recovered precipitate contained approximately 26 000 mg kg<sup>-1</sup> of TN and

113 000 mg kg<sup>-1</sup> of TP. The recovered precipitate contained approximately 11 000 mg kg<sup>-1</sup> Mg and was analyzed using an

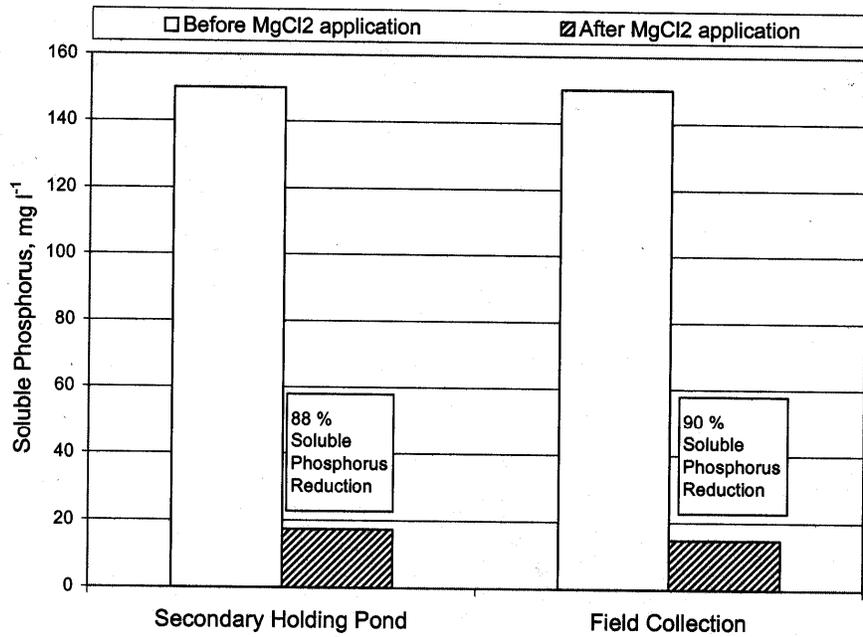


Figure 2. Soluble phosphorus concentrations and percent reductions in the holding pond and field before and after chemical amendment.

atomic absorption spectrophotometer (Perkin Elmer Model 5000). The molar ratio of N:P:Mg in the recovered precipitate was 1:1.95:0.24.

The particle size distribution of the recovered precipitate was categorized using sieve analysis in order to obtain information about the potential to mechanically

recover the material from a liquid slurry in a batch process. Figure 3 shows the particle size distribution of the recovered precipitate as a log-normal plot of sieve mesh opening size versus the cumulative percent of material passing through a sieve of that opening size on a mass basis. The particle size distribution of the material indicates that the potential for

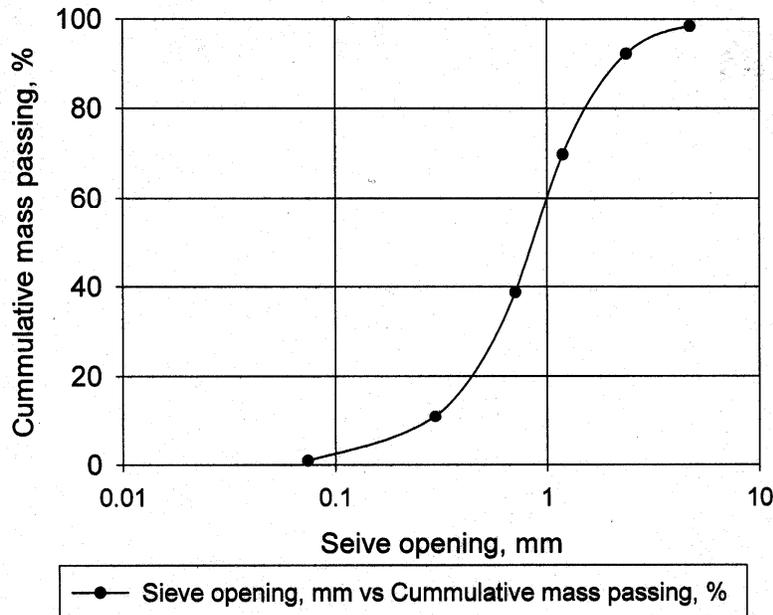


Figure 3. Particle size distribution of recovered precipitate.

mechanical recovery of the precipitate is very good.

The recovered precipitate was analyzed using x-ray diffraction to confirm the presence of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ). The X-ray diffraction indicated correlating peaks for both quartz and struvite. The amount of struvite formed was not quantified.

#### DISCUSSION

Laboratory experiments demonstrated that the SP concentration of swine manure slurry from primary and secondary holding ponds could be reduced by 76 and 60%, respectively, with the addition of  $\text{MgCl}_2$  equivalent to 1.6 times the TP content on a mole basis. Increasing slurry pH in samples from the primary holding pond from 6.6 to 9.0 resulted in a further reduction of SP concentration up to 91%. Increasing slurry pH in samples from the secondary holding pond from 6.7 to 9.0 resulted in a reduction of SP concentration up to 75%.

In the field experiment, reductions in SP of up to 90% were observed following the addition of  $\text{MgCl}_2$ . Before the addition of the  $\text{MgCl}_2$  solution the slurry pH was 7.7, and the liquid waste slurry temperature was 5°C. Following  $\text{MgCl}_2$  addition and agitation for 50 minutes the slurry pH dropped to 6.0 and the slurry temperature increased to 10°C. It should be noted that the experiment began early in the morning and the ambient air temperature increased significantly throughout the experiment.

Soluble P removal in the field exceeded that observed in the laboratory, perhaps because the Mg:SP ratio applied in this holding pond was about twice that used in the laboratory study. The higher Mg:SP ratio applied in the field was due to an over estimation of the swine waste holding pond SP. It is also possible that the differences observed between the field and laboratory results were due to differences in slurry handling and storage between the field and laboratory studies. Either continued anaerobic activity during slurry storage, or aerobic activity following enhanced temperature and incidental aeration of the manure in the laboratory study could have stimulated increased microbial activity and resulted in changes in the forms and quantity of the non-soluble phosphorus and an increase in SP concentration. In the field experiment, the ambient temperature was 15 to 20 °C

cooler than in the laboratory testing.

While the molar ratio of N:P:Mg in the recovered precipitate was 1:1.95:0.24, the expected molar N:P:Mg ratio for pure struvite should be 1:1:1. The fact that the N:P:Mg ratio in the recovered precipitate from this study varied significantly from 1:1:1 indicates that compounds other than struvite were either formed or trapped during the precipitation process.

At present there is no economic motivation for swine producers in the US to reduce the SP content of land-applied swine manure slurry. The future adoption of this technology will depend on the value society places on decreasing P inputs to regional surface and ground water. The overall economics of the process described herein has yet to be evaluated.

#### CONCLUSIONS

Laboratory and field experiments demonstrated that it is possible to significantly reduce the quantity of soluble phosphorus in a swine manure slurry through the addition of  $\text{MgCl}_2$  (64% solution). Soluble phosphorus reductions of up to 76 and 90% were observed in laboratory and field experiments, respectively. X-ray diffraction analysis showed that the recovered precipitate contained struvite. However, the molar N:P:Mg ratio of the recovered precipitate suggest that the recovered material contained compounds in addition to struvite. The economics of this technology have yet to be evaluated. The future adoption of this technology will depend on its cost, and on the value society places on minimizing phosphorus inputs to surface and ground water.

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