

Capturing and Utilizing Struvite from an On-Farm Dairy Operation

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Executive Summary

The objectives of sampling Bella Holsteins, sampling three other Colorado dairies, and evaluating the fluidized bed reactor for struvite production were met. Struvite was produced at two dairies, including Bella Holsteins, using a pilot-scale fluidized bed reactor. Phosphorus removal averaged 14% after pre-treatment at both dairies. After accounting for dilution and differences in treatment method, phosphorus removal averaged 14% at Bella Holsteins and 9% at Diamond D Dairy.

Including Bella Holsteins, a total of four dairies were sampled. The wastewater at Bella Holsteins was not found to be “typical” for Colorado dairies, because wastewater characteristics and waste management systems were different at all four locations. However, three locations might be candidates for struvite production. Field testing of struvite production was successfully conducted at two out of these three candidate locations.

The product was analyzed along with other recovered magnesium phosphate materials using X-ray diffraction, and the presence of magnesium phosphates was confirmed with scanning electron microscopy and energy dispersive spectroscopy. Evaluation of recovered phosphates and commercial fertilizers in a greenhouse study also provided evidence that recovered phosphates may be useful fertilizers in both slightly acid (pH 6.4) and slightly alkaline (pH 7.6) soils.

This study has shown that struvite production is possible on Colorado dairy farms, and that the recovered phosphates may indeed be useful as a fertilizer. Some possibilities for improving phosphorus removal in the reactor include utilizing a larger reactor, using a slower flow rate, or treating the wastewater to reduce interference from calcium. A larger reactor or slower flow rate can compensate for the viscosity of dairy wastewater and can also provide longer reaction times, enabling a more complete reaction. Calcium interference has been found to inhibit struvite formation and affect product characteristics, so decreasing calcium in the reactor influent may also improve both removal efficiency and crystal characteristics.

Summary of Contractual Obligations

1. Sample Bella Holsteins at multiple locations to determine if struvite production would work better taking wastewater from the first lagoon rather than from the solid separation unit. Collect and analyze samples and run preliminary bench-top experiments to analyze the efficiency of phosphorus removal.
2. Sample three other dairies to determine if wastewater at Bella Holsteins is representative in phosphorus, magnesium, ammonium, pH, and solids content.
3. Evaluate fluidized bed reactor using brucite mined by ACM-Texas, LLC. Monitor and record the production of struvite. Calculate the amount of phosphorus removed from the dairy's waste stream. Calculate how this process affects a dairy's land base requirements and application rates.

Summary of Actions

I. Objective 1: Bella Holsteins

A. Sampling at Multiple Locations

In the summer of 2006, wastewater at Bella Holsteins was sampled at 7 locations, including the raw influent, and at the inflow locations of each of the four cells then operational in the anaerobic treatment and storage system. The first lagoon had two inflow locations, and a sample was taken from each. In addition, a sample was taken at the far end of the fourth cell. All samples were refrigerated and transported on the same day to Colorado Analytical Laboratories, Inc. in Brighton, Colorado for analysis of total and dissolved phosphorus, ammonia nitrogen, total magnesium, pH, and solids (total, dissolved, and suspended).

B. Preliminary Bench-Top Experiments

Bench-top experiments analyzing the performance of the cone-shaped fluidized bed reactor under laboratory conditions with swine manure were previously documented by Bowers and Westerman (2005b). A bench-scale model of the reactor was not available prior to the beginning of field experiments immediately after dairy sampling in the summer of 2006. Field trials began in summer 2006, and this work proved to be more effective and realistic than bench-top analysis.

II. Objective 2: Sampling of Other Dairies

Wastewater from three other dairies, Diamond D Dairy, La Luna Dairy, and Morwai Dairy, was sampled and analyzed in addition to that of Bella Holsteins. In addition to the 7 wastewater samples from Bella Holsteins, 13 samples were collected from various locations at the other dairies (3 from Diamond D, 6 from La Luna, and 4 from Morwai). Samples were refrigerated and taken to Colorado Analytical Laboratories, Inc. for analysis of total and dissolved phosphorus, ammonia nitrogen, total magnesium, pH, and solids (total, dissolved, and suspended).

III. Objective 3: Evaluate Fluidized Bed Reactor

A. Brucite from ACM-Texas, LLC

Analysis of wastewater samples indicated that magnesium levels in the sampled dairy wastewater were high. Due to literature reports of high magnesium-to-phosphorus ratio actually inhibiting struvite formation (Bowers and Westerman 2005b), brucite was not used as a supplemental magnesium source in the field experiments. However, powdered brucite was evaluated for its ability to raise the pH of the wastewater during the treatment process.

B. Monitor and Record the Production of Struvite

Field trials were performed for a total of 9 days. Pumping difficulties during the first five days of field trials led to a decision to change locations from Bella Holsteins to Diamond D Dairy in order to accurately characterize reactor performance. A total of 108 wastewater samples were collected hourly or semi-hourly from the raw lagoon influent, pre-treated reactor influent, and treated effluent during reactor operation. 89 of these samples were used to analyze reactor performance. The unused 19 samples were taken during preliminary testing and troubleshooting, or during one day of field operation after the lagoon had been diluted significantly, rendering the data statistically unusable due to potential confounding factors. Analysis of this wastewater for total and dissolved phosphorus, ammonium nitrogen, total nitrogen, and metals (including magnesium) was performed at the Colorado Soil, Water, and Plant Testing Laboratory under the direction of Dr. James Self, the laboratory manager. Decreases in phosphorus and magnesium concentrations in the wastewater were interpreted as struvite production.

Samples harvested from the reactor bed were sent to Colorado School of Mines for X-ray diffraction (XRD) analysis to confirm the presence of struvite, and were also examined at Colorado State University using a scanning electron microscope in conjunction with energy dispersive spectroscopy (SEM-EDS).

C. Calculate the Amount of Phosphorus Removed from the Waste Stream

Analysis of wastewater samples from action IIIB, above, allowed the calculation of the approximate amount of phosphorus removed from the dairy's waste stream during reactor operation. For more information, refer to "Summary of Results" below and appendix B.

D. Calculate Changes in Land Base Requirement and Application Rates

Using the results from action IIIC, above, changes in a hypothetical dairy's land base requirement and manure application rates were calculated. Model dairies of herd size 100, 1000, and 10000 were considered. Refer to "Summary of Results", below.

IV. Other Analysis and Experimentation

A. Fertilizer Analysis of Struvite and Other Magnesium Phosphates

Samples harvested from the reactor in Colorado were sent to Ward Laboratories, Inc. in Kearney, Nebraska for elemental analysis of phosphorus, potassium, calcium, and magnesium. Comparative samples of struvite made by Bowers et al. (2007) using a similar process were also analyzed, as were samples of commercial phosphate fertilizers (triple superphosphate and phosphate rock) and a compound similar to struvite obtained from an Idaho food processing plant.

B. Greenhouse Trials Using Struvite and Other Magnesium Phosphates

In order to determine whether the product of the treatment process can be used as a fertilizer, a greenhouse study was conducted. Using the results from the elemental analysis in action IVA, above, the various compounds were applied as phosphorus fertilizers in pots planted to "Zeke" hard red spring wheat (*Triticum aestivum*). Two rates (the equivalent of 40 lbs P_2O_5 acre⁻¹ and 80 lbs P_2O_5 acre⁻¹) and two soil pH levels (slightly acidic and alkaline) were used. Plant dry matter and phosphorus content were measured to evaluate fertilizer performance over the course of the three-month study.

C. Dissolution Study to Examine the Solubility of Struvite in the Laboratory

To supplement the results of the greenhouse trials, the solubility and phosphorus availability of the various fertilizers were compared in low, neutral, and high pH solutions. The percentage of phosphorus dissolved in solution was examined over the course of several months for each of the five fertilizer treatments used in the greenhouse study.

V. Presentations and Publications

A. Articles in Scientific Journals

At this time, 3 articles are in preparation, with the intent to submit them to peer-reviewed scientific journals. Working titles and names of planned journals are listed below:

Massey, M.S., J.G. Davis, R.E. Sheffield, and J.A. Ippolito. Phosphorus recycling on dairy farms using a potentially “organic” treatment process. (Working title.) *Trans. ASABE*.

Massey, M.S., J.A. Ippolito, J.G. Davis, and R.E. Sheffield. Microscopic and macroscopic variations in recovered magnesium phosphates. (Working title.) *Env. Eng. Sci.*

Massey, M.S., J.G. Davis, J.A. Ippolito, and R.E. Sheffield. The use of recovered magnesium phosphates as fertilizer in calcareous soils. (Working title.) *J. Plant Nutrition*.

B. Presentations, Posters, and Other Publications

A total of 2 oral conference presentations, 4 poster presentations at conferences, and 1 newsletter article were used to communicate the results of this research to a broad audience of both specialists and non-specialists. Citations for the conference proceedings, abstracts, and newsletter article are listed below:

Massey, M.S., J.G. Davis, R.E. Sheffield, and J.A. Ippolito. 2007. Reducing dairy effluent phosphorus content through struvite precipitation. In *Proc. Western Nutrient Management Conference 7*: 204-209. Salt Lake City, Utah. Poster.

Massey, M.S., J.G. Davis, R.E. Sheffield, and J.A. Ippolito. 2007. Struvite production from dairy wastewater and its potential as a fertilizer for organic production in calcareous soils. In *Proc. International Symposium on Air Quality and Waste Management for Agriculture*. American Society of Agricultural and Biological Engineers Publication no. 701P0907cd. Broomfield, Colorado. Oral presentation.

Massey, M.S., J.G. Davis, and R.E. Sheffield. The effectiveness of recovered phosphates as fertilizer in slightly acidic and alkaline soil conditions. March 4-5, 2008. In *Proc. Great Plains Soil Fertility Conference*. Denver, Colorado. Poster. (In preparation.)

Massey, M.S., J.G. Davis, R.E. Sheffield, and J.A. Ippolito. 2007. Reducing dairy effluent phosphorus content through struvite precipitation. 1-3 May, 2007. S-1000 annual meeting, Sustainability of Livestock and Poultry Production: Life Cycle Principles and Research. Aguadilla, Puerto Rico. Poster.

Massey, M.S., J.A. Ippolito, J.G. Davis, and R.E. Sheffield. Morphological variation among magnesium phosphates recovered from wastewater. November 4-8, 2007. American Society of Agronomy-Crop Society of America-Soil Science Society of America 2007 International Annual Meetings, New Orleans, Louisiana. Poster.

Massey, M.S., J.G. Davis, R.E. Sheffield, and J.A. Ippolito. Recovery of magnesium phosphates from dairy wastewater and their use as a fertilizer on calcareous soils. November 4-8, 2007. American Society of Agronomy-Crop Society of America-Soil Science Society of America 2007 International Annual Meetings, New Orleans, Louisiana. Oral presentation.

Massey, M., and J. Davis. 2007. Phosphorus recovery in Colorado agriculture. *Colorado Water*, April/May 2007: 16-19.

Summary of Results

I. Objective 1: Bella Holsteins

The results of the analysis of wastewater samples from Bella Holsteins can be found in appendix A. Based on those results, the pilot-scale fluidized bed reactor was set up at the inflow to the third lagoon. This location was chosen because the viscosity of the liquid is an important factor in successful reactor operation. In general, it was hypothesized that the water with the lowest solids content would be the most appropriate for the reactor. If the influent is too thick, proper functioning is impeded. As a result, influent was pumped from the third lagoon, rather than directly from the solid separator.

Over the course of operation at Bella Holsteins, the fluidized bed reactor removed an average of 14% of the total phosphorus in the pre-treated reactor influent. Removal efficiencies over 30% were observed at some times during preliminary experimentation and field testing with the reactor at Bella Holsteins, but these removal rates were not consistent. There was no sample dilution at Bella Holsteins, but the treatment process added significant amounts of nitrogen to the wastewater, possibly leading to increased P removal rates.

Preliminary wastewater sample results were found to be somewhat misleading, however. Due to difficulties pumping the wastewater at Bella Holsteins, experimentation there was ended prematurely. The wastewater was too thick for the pumps in the pilot-scale system. There was no indication of high solids loading in the preliminary wastewater samples for the chosen location (see appendix A).

Experimentation continued at Diamond D Dairy in Mead, Colorado. There were fewer problems pumping the wastewater at this location. However, large amounts of sand were

collected from inside the lagoon during pumping, which led to “contamination” of the reactor bed with sand.

II. Objective 2: Sampling of Other Dairies

The four dairies (including Bella Holsteins) chosen for sampling had very different operations, with very different waste management systems and varying sizes. These four dairies, therefore, can provide an excellent picture of the different characteristics of wastewater. Sample results can be found in appendix A.

Sample results and experience with the fluidized bed reactor demonstrated that Bella Holsteins’ wastewater was at that time not representative of other dairy wastewater, and that the characteristics of the wastewater at Bella Holsteins varied from point to point within the system. The situation was similar at other dairies. Wastewater characteristics were variable throughout the system.

However, at 3 out of the 4 dairies sampled, at least one location might be suitable for struvite production. Phosphorus removal was observed at both of the sites where the reactor was tested (see below). The fourth dairy (listed as “dairy #4” in appendix A) has a very unique waste management system with very high solids content and low orthophosphate throughout, which might make the use of this technology impossible.

III. Objective 3: Evaluate Fluidized Bed Reactor

A. Use of Brucite Mined by ACM-Texas, LLC

Brucite was originally conceived as a magnesium supplement during the wastewater treatment process. However, the wastewater at both Bella Holsteins and Diamond D Dairy was naturally very high in magnesium (see appendix B). Bowers and Westerman (2005b) found excessively high concentrations of magnesium resulting in a high magnesium-to-phosphorus ratio to actually inhibit the formation of usable struvite crystals. For this reason, supplemental magnesium was not added.

Nonetheless, a brucite slurry remains a reasonable candidate for adding supplemental magnesium at locations where magnesium levels are not naturally sufficient for struvite production. Brucite’s effectiveness as a magnesium supplement could not be evaluated in these experiments due to high levels of magnesium already present in the wastewater.

Brucite was also tested for its ability to raise the pH of the wastewater in the treatment process, but the pH response proved to be too small and too slow for the brucite to be used in this fashion.

B. Monitor and Record the Production of Struvite

At both Bella Holsteins and Diamond D Dairy, the fluidized bed reactor removed an average of 14% of the phosphorus and magnesium from the wastewater after pre-treatment with acid. Detailed results are reported in the conference proceedings included as appendix B. (*Note that there are subtle differences in the removal efficiencies calculated in papers included as appendix B and appendix C due to differences in calculation specifics, rounding, or statistical analysis. Practically, these differences are inconsequential.*) Note that the effects of dilution at Diamond D dairy were not considered in the proceedings papers. After compensating for approximately 5% dilution, the fluidized-bed reactor removed an average of approximately 9% of the phosphorus and magnesium at Diamond D Dairy. Removal rates higher than 50% were observed at Diamond D, but these rates were not consistent. Removal of ammonium nitrogen and total nitrogen was also observed when using the new method developed by Massey et al. (2007), in which ammonia was not added during treatment. The method developed by Bowers and Westerman (2005a, 2005b) results in substantially increased nitrogen in the treated wastewater, since gaseous ammonia is added during treatment.

Simultaneous removal of phosphorus, magnesium, and nitrogen from the wastewater was interpreted as production of struvite. Crystalline phases of struvite were not identified in the reactor beds from Bella Holsteins or Diamond D Dairy using XRD, but semi-crystalline and amorphous struvite was identified in these samples using SEM-EDS. Magnesium phosphate, most likely struvite, was produced in the reactor, and magnesium, phosphorus, and nitrogen were removed from the waste stream in the process.

C. Calculate the Amount of Phosphorus Removed from the Waste Stream

Assuming 14% removal and an average phosphorus concentration of 95 mg per liter, approximately 13 mg of phosphorus were removed per liter of wastewater treated. At an approximate average flow rate of 1.9 gallons (7.2 liters) per minute, approximately 94 mg of phosphorus was removed from the waste stream per minute of operation. This rate is equivalent to approximately 5.6 g of phosphorus removed per hour in the pilot-scale system.

Using the dilution-corrected 9% removal rate, 8.55 mg of phosphorus were removed per liter of wastewater treated. This is equivalent to 61.6 mg per minute, or approximately 3.7 grams per hour.

D. Calculate Changes in Land Base Requirement and Application Rates

Table 1 shows the land base requirements for three “model dairies” with phosphorus-based manure application rates based on Waskom and Davis (1999). Manure treated with the fluidized bed reactor would most likely be applied in liquid form, but both the concepts and mathematics are simpler if the calculations are performed for the manure on a dry-weight basis.

Even with only 9% (or 14%) total phosphorus removal, for a large dairy (10,000 head) the fluidized bed reactor system could reduce the phosphorus-based land base requirement by hundreds of acres. Improved removal efficiencies for dairy manure, such as the 30-50% or more observed by Bowers et al. (2007), could reduce the land base requirement even further.

Table 1. Changes in land base requirements for model dairies of different sizes. Assumptions include 7 lbs P per ton of manure, 61 lbs acre⁻¹ P fertilization (based on 35 ton/acre corn silage), 25.9 lbs manure (46% moisture) per 1400 lb cow per day (or 4.73 tons per cow per year).

number of lactating cows	land base requirement without phosphorus removal (acres)	land base requirement with 9% phosphorus removal (acres)	land base reduction (acres)
100	54	49	5
1000	543	492	51
10000	5433	4924	509

IV. Other Analysis and Experimentation

A. Fertilizer Analysis of Struvite and Other Magnesium Phosphates

Elemental analysis of various phosphate fertilizers, including commercial triple superphosphate (TSP), commercial certified organic rock phosphate (RP), and three recovered phosphates revealed clear differences in the bulk characteristics of the material. The three recovered phosphates that were analyzed included struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) produced by Bowers et al. (2007) at a dairy in northwestern Washington, dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, a monohydrate compound otherwise identical to struvite) recovered from a food processing plant in Idaho, and the product of the treatment process performed at Diamond D Dairy in Colorado. The product from Colorado had the lowest phosphorus content of any of the fertilizers analyzed. This was attributed to contamination of the bed material by sand from the dairy lagoon, which “diluted” the overall phosphorus concentration of the material. Dittmarite was similar in phosphorus content to TSP.

Table 2. Phosphorus fertilizer characteristics for 5 different phosphorus fertilizers. Triple superphosphate (TSP) and certified organic rock phosphate (RP) are commercially available fertilizers. Struvite, dittmarite, and the Colorado product are recovered phosphates. Note that phosphorus content is given as total phosphorus, rather than plant-available (citric acid soluble) phosphorus as shown on fertilizer labels.

fertilizer	obtained from	percent P_2O_5
TSP	commercial manufacture	48.1
certified organic RP	commercial manufacture	21.7
struvite	fluidized bed reactor at WA dairy	28.2
dittmarite	recovered from ID food processing plant during cleaning	45.4
CO product	fluidized bed reactor at CO dairy	16.2

B. Greenhouse Trials Using Struvite and Other Magnesium Phosphates

All of the recovered phosphates performed similarly to TSP at high soil pH (7.6) in greenhouse trials, and did increase dry matter production over the control group. Although dry matter production was not significantly different from the control at low soil pH (6.4), struvite, dittmarite, and TSP did in some cases increase phosphorus content of the plants, particularly at the 80 lbs P₂O₅ acre⁻¹ rate. Other investigators have found struvite to be effective at low soil pH (Johnston and Richards, 2003; Li and Zhao, 2003). Though Lindsay (1979) noted that magnesium phosphates such as struvite could theoretically perform better than calcium phosphates at high soil pH, this study is among the first to examine the effectiveness of struvite at high soil pH.

Preliminary results of greenhouse data analysis indicate that recovered phosphates could be viable sources of phosphorus fertilizer across a range of soil pH levels and soil environments, including alkaline and calcareous soils. Selected preliminary results were reported as shown in action VB, and final results will be reported in academic journals, as shown in action VA.

C. Dissolution Study to Examine the Solubility of Struvite in the Laboratory

The laboratory dissolution study confirmed the highly variable nature of the Colorado product (some samples contain large amounts of phosphorus, others contain relatively small amounts), and suggest that other recovered magnesium phosphates are similar in solubility to TSP. Recovered phosphates are generally more soluble than certified organic RP. Final results will be reported in academic journals, as shown in action VA.

References

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Appendices

Appendix A: Dairy Wastewater Sample Analysis

Bella Holsteins

Table 3. Phosphorus, magnesium, and ammonium-N concentrations in wastewater at Bella Holsteins. All concentrations are listed as mg l^{-1} . Analysis was performed by Colorado Analytical Laboratories, Inc.

location	ortho P	total P	magnesium	$\text{NH}_4^+\text{-N}$
before solid separator	46.63	270.49	330.6	551.89
first lagoon, north pipe	31.25	174.13	227.0	424.22
first lagoon, south pipe	35.85	191.81	250.0	447.28
second lagoon	53.92	194.38	238.0	512.36
third lagoon	44.04	137.51	198.1	598.02
fourth lagoon, inflow	34.55	108.73	209.1	625.21
fourth lagoon, west end	33.45	186.25	270.1	626.85

Table 4. Solids and pH for wastewater at Bella Holsteins. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	total solids (%)	total suspended solids (mg l^{-1})	total dissolved solids (mg l^{-1})	pH
before solid separator	4.517	22400	4440	8.29
first lagoon, north pipe	1.686	13140	3960	8.16
first lagoon, south pipe	1.722	14600	4430	8.19
second lagoon	1.719	14350	4360	7.24
third lagoon	0.926	5950	4700	7.39
fourth lagoon, inflow	0.938	4600	5260	7.83
fourth lagoon, west end	1.369	10100	5410	7.90

Diamond D Dairy

Table 5. Phosphorus, magnesium, and ammonium-N concentrations in wastewater at Diamond D Dairy. All concentrations are listed as mg l^{-1} . Analysis was performed by Colorado Analytical Laboratories, Inc.

location	ortho P	total P	magnesium	$\text{NH}_4^+\text{-N}$
before solid separator (holding tank)	232.66	665.09	891.4	779.24
lagoon inflow	208.69	540.67	817.4	462.11
bank opposite lagoon inflow	41.94	183.41	366.2	435.75

Table 6. Solids and pH for wastewater at Diamond D Dairy. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	total solids (%)	total suspended solids (mg l ⁻¹)	total dissolved solids (mg l ⁻¹)	pH
before solid separator (holding tank)	10.032	66900	7220	7.34
lagoon inflow	7.247	78600	8500	7.35
bank opposite lagoon inflow	2.324	19000	7440	8.06

Dairy #3

Table 7. Phosphorus, magnesium, and ammonium-N concentrations in wastewater at Dairy #3. All concentrations are listed as mg l⁻¹. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	ortho P	total P	magnesium	NH ₄ ⁺ -N
before solid separator	10.38	205.35	552.9	187.81
after solid separator	15.68	182.57	546.4	167.22
second lagoon, inflow	4.81	22.98	230.5	98.02
second lagoon, near irrigation pump	5.05	22.76	228.8	99.67

Table 8. Solids and pH for wastewater at Dairy #3. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	total solids (%)	total suspended solids (mg l ⁻¹)	total dissolved solids (mg l ⁻¹)	pH
before solid separator	3.070	36000	5710	7.84
after solid separator	2.616	29000	5630	7.72
second lagoon, inflow	0.414	2600	3050	7.82
second lagoon, near irrigation pump	0.436	1400	2930	7.49

Dairy #4

Table 9. Phosphorus, magnesium, and ammonium-N concentrations in wastewater at Dairy #4. All concentrations are listed as mg l⁻¹. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	ortho P	total P	magnesium	NH ₄ ⁺ -N
before solid separator, barn influent only	2.41	484.84	711.2	897.86
before solid separator, barn and parlor influent	7.34	506.27	714.5	1029.65
after solid separator	6.51	513.29	720.1	1046.13
settling pond	7.83	532.45	731.0	1532.13
storage lagoon	5.33	521.63	923.3	1037.89
recirculation tank	7.77	480.28	796.2	1334.43

Table 10. Solids and pH for wastewater at Dairy #4. Analysis was performed by Colorado Analytical Laboratories, Inc.

location	total solids (%)	total suspended solids (mg l ⁻¹)	total dissolved solids (mg l ⁻¹)	pH
before solid separator, barn influent only	5.425	17740	15400	8.49
before solid separator, barn and parlor influent	6.457	36450	10900	7.56
after solid separator	5.643	31300	11700	7.64
settling pond	6.244	85600	11600	7.67
storage lagoon	5.746	61000	13800	7.38
recirculation tank	5.574	65000	12300	7.65

***Appendix B: Conference Proceedings Detailing Reactor
Evaluation and Performance***

Struvite Production from Dairy Wastewater and its Potential as a Fertilizer for Organic Production in Calcareous Soils

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Abstract. Forced precipitation of struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$) in wastewater treatment has recently received increased attention as a method of phosphorus (P) recycling. While both struvite and phosphate rock (PR) can be used as a P fertilizer on acid soils, PR is ineffective in calcareous soils. Magnesium (Mg) phosphates such as struvite, on the other hand, could be a more useful fertilizer in alkaline soils, especially in organic production where conventional P fertilizers are not an option.

A new organic treatment method, based on an existing process using a cone-shaped fluidized-bed reactor, was developed and field-tested with dairy lagoon wastewater. The pH of the wastewater was adjusted using acetic acid and potassium hydroxide as the water passed through the reactor system. Wastewater samples were analyzed using ICP-AES. Total P (TP) was reduced from an average of 80.6 ppm at the reactor input to 69.0 ppm at the reactor output using the new method (n=30). Total Mg was also reduced from an average of 179 ppm to 155 ppm, and mean total nitrogen (TN) content went from 1123 ppm in the influent to 955 ppm in the treated effluent.

The granular product was harvested and examined qualitatively using XRD and SEM-EDS. SEM-EDS analysis confirmed the presence of amorphous Mg phosphates with approximately a 1:1 molar ratio of Mg:P. These results indicate that the new process did remove TP, Mg, and TN from the wastewater through precipitation of Mg phosphates.

Keywords. Struvite, dairy manure, wastewater treatment, phosphorus, fertilizer, organic

Introduction

The recovery and use of phosphorus (P) by crystallization from municipal and agricultural wastewater has received increased attention in recent years for its potential to improve treated effluent quality while decreasing sludge volume and creating relatively pure, useful byproducts. While there is some question regarding exactly how long existing rock P (PR) reserves will last, it is clear that P is a limited resource and that its recovery and reuse are necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Most efforts have focused on municipal wastewater treatment plants (WWTPs), where spontaneous precipitation of struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$) can be destructive to WWTP facilities and incur expense due to downtime and cleaning (de-Bashan and Bashan, 2004; Shu et al., 2006). Additionally, P releases from WWTPs can cause eutrophication of surface water bodies, so there can be strict regulatory limits on treated effluent. Given the scale and expense of a WWTP, it is easier to justify capital investment in new P removal technologies, so these facilities have naturally been a focus of research. 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) (van Dijk, 1984; Driver et al., 1999; de-Bashan, 2004).

Comparatively little work has been done regarding on-site P removal from agricultural wastewater. Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure

an ideal target for P recovery. According to the same review, while direct land application is the preferable method of P reuse from manure, the application of manure at a rate which meets crop nitrogen (N) needs results in a significant P surplus. P recovery through crystallization could be used to correct this imbalance.

Furthermore, intensive livestock operations are increasingly concentrated in certain regions, potentially overwhelming the capacity of the local land to absorb the quantity of manure generated by such operations. Spears et al. (2003) found that the average dairy in Utah and Idaho had a 6.6 t year⁻¹ surplus of imported P that was not accounted for in product outputs. Due to this local nutrient excess, manure must be transported longer and longer distances for disposal or land application, at significant cost. Recovery of P from agricultural wastewater as a crystalline, easily dried product has the potential to solve some of these issues. P recovery can decrease nutrient concentrations in wastewater while giving livestock producers a valuable resource that can provide extra revenue, is easily handled, and can be transported long distances at a fraction of the cost of manure or compost.

However, there are significant constraints for on-site P removal processes that must be met in order for the technology to be practical. Recovery technology must be relatively inexpensive, and must be economical on a smaller scale than P removal at a typical WWTP. Additionally, the system cannot require extensive monitoring, maintenance, or material inputs. Most importantly, treated effluent must remain suitable for spreading on crops (Greaves et al., 1999). This last requirement imposes the most stringent limitation on the process, as it precludes the addition of certain chemicals, such as sodium hydroxide (NaOH), and the use of certain techniques, such as raising the pH of the wastewater to very alkaline levels. Though these are commonly used in P recovery at WWTPs, high sodium concentrations or pH would render the effluent unsuitable for land application and are, therefore, not suited for treatment of agricultural wastewater. Only a relatively inexpensive, simple technology that preserves the suitability of effluent for application is practical for on-site P removal in an agricultural setting.

The cone-shaped fluidized bed reactor designed by Bowers and Westerman (2005a) is one such technology. In laboratory and field-scale experiments, P was recovered as crystalline struvite from wastewater generated in swine production. The uniquely shaped reactor was used in combination with Mg addition and pH increase using ammonia to reduce total phosphorus (TP) concentration in treated effluent, with mean concentration reductions up to 82% (Bowers and Westerman, 2005b). Even without Mg addition, pH manipulation alone resulted in a mean value as high as 64% for TP removal. The crystalline product was confirmed to be struvite by X-ray diffraction (XRD) analysis.

Unfortunately, few applications for recovered struvite have been developed. Its chemical composition makes it impractical as a raw material in the modern P industry. Ammonium renders struvite unusable in the high-temperature process for the manufacture of phosphoric acid, and Mg interferes with the "wet" manufacturing process (Driver et al., 1999; Schipper et al., 2001). Its potential for use as a slow-release fertilizer has been known for decades, but until recently little scientific work has been conducted. Johnston and Richards (2003) evaluated different recovered phosphates, comparing their relative effectiveness as fertilizer in a greenhouse setting, and found recovered struvite to be an effective fertilizer for perennial ryegrass. 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 (Li and Zhao, 2003).

These studies have documented the usefulness of struvite as a fertilizer in acidic and neutral soil conditions, using soils at a pH between six and seven. However, the particular difficulties of phosphorus fertilization on alkaline and calcareous soils suggest that the same might not be true for struvite as a fertilizer in high-pH environments. For example, the ineffectiveness of phosphate rock as a fertilizer in calcareous soils is well documented (Mackay and Syers, 1986; Chien and Menon, 1995; Elliott et al., 2005). High concentrations of Ca in calcareous soils substantially decrease the solubility of PR, which consists primarily of Ca phosphates such as hydroxyapatite. According to Lindsay (1979), Mg phosphates like struvite are substantially more soluble than Ca phosphates at alkaline pH, and therefore have potential for use as a P fertilizer in calcareous soils.

The development of a sustainable, effective alternative for P fertilization on calcareous soils is especially important for organic agriculture in semi-arid environments such as Colorado. Manure and compost are the only viable options for P fertilization on organic farms with alkaline soils, common in the western United States. PR and bone meal are other options available to organic producers with acid soils, but they are ineffective as fertilizers in calcareous soil. Nutrient availability from manure and compost depends on mineralization of the organic nutrients contained therein, a process that can take weeks or months (Elliott et al., 2005). Furthermore, manure or compost application may not be suitable for all situations, such as fields with high runoff risk or legume production with the goal of maximizing biological nitrogen fixation. An alternative for P fertilization in organic production on calcareous soils would be a welcome addition to any organic producer's arsenal.

Recovered struvite has the potential to be this alternative. In this study, the technique outlined by Bowers and Westerman (2005a) was modified, and a new crystallization process was developed and tested

that is more in accordance with the letter and spirit of the regulations for organic food production. Acetic acid and KOH were used instead of HCl and anhydrous ammonia to adjust the pH during wastewater treatment using a field-scale cone-shaped fluidized bed struvite crystallizer. KOH was selected over NaOH since treated wastewater remains suitable for land application after KOH addition. It is thought that the product of this treatment process could indeed be certified for use in organic production with little or no modification to existing regulations.

In order to test the effectiveness of the product harvested from the reactor, it was applied as a fertilizer to wheat growing in acid and alkaline soils in greenhouse trials. The solubility and structure of recovered phosphates were also examined, but a full report on all of these topics is beyond the scope of this paper.

If the recovered phosphates are more effective than PR as a fertilizer, their potential for use by organic producers could increase their value, as well as their economical transport distance. This could help to alleviate P loading in areas with large numbers of livestock producers, as well as give organic growers a viable option for correcting P deficiency in crops.

Materials and Methods

Wastewater Treatment and Water Analysis

Wastewater treatment using the University of Idaho pilot-scale struvite crystallizer was performed on several different days in August and September 2006 at two separate dairies in northern Colorado. Samples of wastewater were collected at various locations on four dairies and analyzed at Colorado Analytical Laboratories, Inc. From these, two were selected as potential sites for treatment. Two different processes were used: the “conventional” process, which utilizes hydrochloric acid (HCl) and anhydrous ammonia for pH adjustment, and the “new” process, which replaces these chemicals with acetic acid and potassium hydroxide (KOH).

The primary components of the fluidized-bed crystallizer system are a 1000 L holding tank and a large, inverted conical reactor vessel. The reactor cone is initially seeded with a bed of PR material to provide sites for the growth of struvite crystals. During operation, wastewater is pumped from the holding tank into the base of the reactor cone through a manifold. Inside the manifold, other substances such as Mg solution, hydroxide solution, or gaseous anhydrous ammonia can be combined with the effluent stream. The effluent enters the cone, and passes through the bed of material at its base, eventually reaching the top of the reactor where treated effluent is allowed to drain back into the lagoon. A simplified diagram of the treatment process is shown in Figure 1.

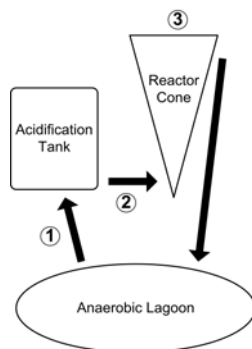


Figure 1. Simplified diagram of the wastewater treatment process. Black arrows show the flow of wastewater from the lagoon into the acidification tank, then into the reactor vessel, and finally back to the lagoon. Numbers denote sample locations: (1) lagoon (untreated wastewater), (2) input (acidified wastewater), and (3) output (treated effluent).

Wastewater was pumped from an anaerobic lagoon into the holding tank, and adjusted to an approximate pH of 5.2 by addition of acid. Acidification increases the concentration of orthophosphate (OP) in the effluent by dissolving inorganic phosphate complexes already present in the water. Liquid in the tank was continuously recirculated and mixed by a small pump at its base, and glass electrodes were used to monitor system pH. Once the target pH was reached, acidified wastewater was pumped at a rate of 410 to 456 L h⁻¹ through the manifold, where a base (either gaseous ammonia or KOH solution) was added to rapidly increase the pH to between 7.5 and 8.3 in order to encourage the precipitation of phosphates as the effluent passed through the bed of seed material. At the above flow rate, the hydraulic retention time (HRT) of the wastewater in the reactor was just over four minutes.

Wastewater samples were taken at three points in the process: prior to entering the holding tank, immediately prior to entering the manifold, and at the top of the reactor vessel near the outlet, referred to as “lagoon”, “input”, and “output” samples, respectively. Input and lagoon samples were taken by opening valves and draining wastewater directly into 1 L sample bottles, while output samples were obtained by transferring liquid from the top of the cone into the sample bottles. Samples were refrigerated and taken to the Colorado State University Soil, Water, and Plant Testing Laboratory. OP was evaluated using the ascorbic acid method (Kuo, 1999). Following digestion of samples with nitric and perchloric acid, TP and metals were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo Jarrell Ash IRIS Advantage, high resolution, dual view). Total N was measured using a LECO TruSpec C/N analyzer, and ammonium N was measured colorimetrically with an OI Analytical Flow Solution 3000 flow injection system.

Statistical analysis was performed using SAS proc mixed, with sampling time as a random effect, and sample location (lagoon, input, output) and date as fixed effects at a significance level α of 0.05.

Reactor Product Analysis

Samples of product harvested from the reactor bed were rinsed, dried, and sent to the Colorado School of Mines for X-ray diffraction (XRD) analysis. Other recovered phosphates, including struvite and dittmarite (magnesium ammonium phosphate hydrate, $MgNH_4PO_4 \cdot H_2O$) were also analyzed via XRD.

The product and other recovered phosphates were further inspected with scanning electron microscopy using energy dispersive spectroscopy (SEM-EDS). Carbon paint was applied to the surface of 1cm x 1cm aluminum stubs, and a small quantity of sample was sprinkled on to the wet carbon paint. Cylinders were allowed to dry for one week prior to examination with SEM-EDS.

Application of Product in Greenhouse Trials

Slightly acidic soil (pH 6.5) was collected from a site in northern Colorado in November 2006. The soil was air-dried and passed through a 1.25 cm screen to remove stones and clumps of plant matter. In order to achieve an alkaline pH, powdered $CaCO_3$ was added to a portion of the soil at a rate of approximately 0.3% by weight. The $CaCO_3$ was mixed thoroughly with the soil, the mixture was then wetted and allowed to air-dry. The soil- $CaCO_3$ mixture was wetted and air-dried several times in order to allow it to reach equilibrium prior to re-analysis and addition of treatments.

Greenhouse trials were conducted to compare the effectiveness of commercially available triple superphosphate (TSP) fertilizer with PR, recovered dittmarite from a food processing facility, crystalline struvite manufactured using the conventional method, and amorphous product made using both the conventional method and the new method. The fertilizers were applied to the acidic (un-limed) and alkaline (limed) soils planted to spring wheat (*Triticum aestivum* “Zeke”). Fertilizer performance was evaluated using dry matter production and P uptake over a growing period of three months. Analysis of greenhouse trial results is in progress as of this writing.

Results

Wastewater Analysis

Wastewater samples were collected at the system input, reactor input, and reactor output during operation in order to track and analyze system performance. Selected results for the new method are presented in Table 1, and results for the conventional method are shown in Table 2.

Table 1. Mean concentrations and removal efficiency for selected elements of the untreated wastewater, acidified influent, and treated effluent using the new process (n=30). Asterisks denote a significant ($\alpha=0.05$) difference between input and output.

	lagoon (mg L ⁻¹)	input (mg L ⁻¹)	output (mg L ⁻¹)	removal, input to output (%)
ortho P (as P)	40.5	60.5	30.8	49*
total P (as P)	85.8	80.6	69.0	14*
total Mg	184	179	155	14*
total N (as N)	1017	1123	955	15*
NH ₄ -N (as N)	323	319	266	16*
total Ca	331	322	301	7*
total K	478	441	610	-38*

Table 2. Mean concentrations and removal efficiency for selected elements of the untreated wastewater, acidified influent, and treated effluent using the conventional process (n=5). Asterisks denote a significant ($\alpha=0.05$) difference between input and output.

	lagoon (mg L ⁻¹)	input (mg L ⁻¹)	output (mg L ⁻¹)	removal, input to
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				output (%)
ortho P (as P)	12.2	25.5	4.77	81*
total P (as P)	99.8	94.9	81.0	14*
total Mg	161	154	136	12*
total N (as N)	718	675	1228	-82*
NH ₄ -N (as N)	379	442	889	-101*
total Ca	311	299	303	-1
total K	357	369	422	-14

The different P removal processes were tested at separate dairies due to difficulties pumping the wastewater at the initial location. Mg and OP concentrations were greater in the lagoon effluent used for the new process, while TP concentration was greater in the wastewater used for the conventional process.

Acidification had the expected effect, raising the OP concentration from the lagoon to the reactor input in both processes. However, dilution due to the addition of acid as well as settling in the acidification tank resulted in slightly lower concentrations in the reactor influent when compared to the lagoon wastewater. A significant difference between lagoon and input samples was present only for TP in the new method ($p=0.043$).

The data show a reduction in OP, TP, Mg, and TN from reactor input to outlet for both the conventional and new processes, with considerably greater Mg being removed than P on a molar basis. On a molar basis, 1.6 to 3 times more Mg was removed than P. OP decreases were greater than TP decreases, and TP reduction was similar in both processes. The conventional process resulted in greater relative OP reduction than the new process.

Product Analysis

Samples of reactor products made using both the conventional (HCl and NH₃) and new (acetic acid and KOH) methods were analyzed using XRD, but no crystalline phases (i.e. struvite) could be identified from the resulting spectra. PR seed samples were also examined using XRD, and showed strong correlation with database spectra for carbonate fluorapatite as well as quartz, dolomite, and calcite.

When product was examined with SEM-EDS, amorphous particles having an approximately 1:1 ratio of Mg:P were identified. While EDS data is only semi-quantitative, the data suggest a strong association between Mg and P in these particles (Figure 2).

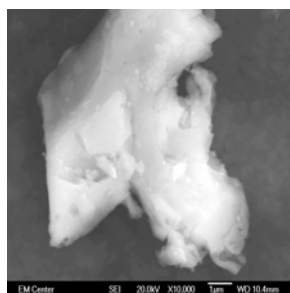


Figure 2. Particle produced using the new (acetic acid/KOH) method. EDS analysis showed molar composition of 16.25% P, 15.14% Mg, 65.25% O, 1.37% K, 0.77% Al, 0.79% Si, and 0.43% Ca (C not included due to background interference).

The structure of the Mg phosphate particles examined using SEM-EDS was highly variable, but in all cases relatively large amounts of both P and Mg were present (Figure 3).

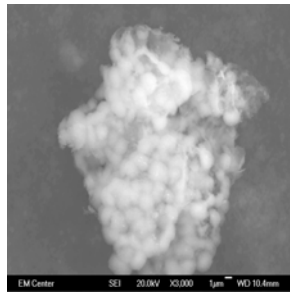


Figure 3. Particle produced using the conventional (HCl/NH₃) method. EDS analysis showed molar composition of 12.91% P, 9.99% Mg, 5.17% Ca, 66.18% O, 2.02% Si, and small amounts of Fe, K, and Cu. Note the globular structures and tendrils extending from the surface, and the relatively high amount of Ca.

Discussion

The mean TP removal efficiency of 14% does not match the 64% removal efficiency shown by Bowers and Westerman (2005b) in experiments using swine wastewater, but does compare more favorably to results obtained by Bowers et al. (2005) for treatment of dairy wastewater in Idaho and Washington (14% reduction in Idaho and 15% in Washington) using the conventional acidified process. Reported Mg and P concentrations in the Idaho dairy wastewater (Bowers et al., 2005) were similar to the concentrations observed in this study. Wang et al. (2005) concluded that the ideal Ca:Mg molar ratio for struvite precipitation is 0.5 or less, and that a ratio greater than one in wastewater can significantly inhibit struvite formation. The Ca:Mg ratio for the reactor influent in the current study ranged from 1.04 to 1.21. Bowers and Westerman (2005b) also found that excessively high Mg concentrations relative to P actually reduced P removal efficiency. They reported that a Mg:TP ratio greater than 1 may reduce P removal efficiency. The molar ratio of Mg:TP in the current study ranged from 2.0 to 3.8, so no supplemental Mg was added during wastewater treatment. It is possible that high concentrations of Mg inhibited struvite formation in the reactor. However, Huang et al. (2006) found that Mg:TP ratios as high as 3.3:1 with Ca:Mg ratios of up to 6:1 were conducive to struvite production from WWTP effluent. Even with these conflicting findings, it is possible that the Ca:Mg or Mg:TP ratio in dairy lagoon wastewater may not have been optimal for struvite crystallization and could explain the low observed efficiency.

Even at decreased efficiency, the observed simultaneous reduction of P and Mg levels in the effluent suggests that Mg phosphates were indeed precipitated out of the effluent in the reactor. On a molar basis, 1.6 to 3 times more Mg was removed than P, so other Mg compounds must be produced in the reactor in addition to phosphates.

According to Bowers and Westerman (2005a), all OP is theoretically available for recovery through struvite crystallization. The TP reduction Bowers and Westerman (2005a) observed was, in some instances, greater than this theoretical maximum. In the current study, however, mean TP reduction was notably lower than mean OP reduction on an absolute basis. This indicates that some potentially recoverable phosphate is being discharged in the treated effluent stream prior to crystallization onto particles in the reactor bed, or that some of the bed particles themselves are being expelled from the reactor. A combination of these processes could also be occurring; the net result is that decreased OP concentration in the treated effluent is reflected only partially by the observed reduction in TP concentration. Bowers and Westerman (2005b) reported that slower flow rates resulted in greater P removal efficiency in field-scale experiments. In the current study, a flow rate between the 341 L h⁻¹ and 568 L h⁻¹ in Bowers and Westerman (2005b) was used with a very similar experimental setup. It is possible that with a slower flow rate or larger reactor, a longer HRT and correspondingly longer reaction time would improve performance and product characteristics over those reported in the current study.

SEM-EDS data shows that amorphous Mg phosphates were formed in the reactor, rather than the regular crystalline morphology observed in laboratory and fieldwork outlined in Bowers and Westerman (2005b). The struvite particles in the SEM images bear no resemblance to recovered struvite crystals in Li and Zhao (2003), for they lack any regular structure. EDS analysis was only possible on very small particles due to the lack of electrical ground on larger particles in the current study, so no comparison can be made with larger struvite particles shown in Huang et al. (2006). However, XRD analysis would likely have identified crystalline phases of struvite if they were present in detectable amounts. This indicates that either the large particles are not crystalline phosphates or that they are not present in high enough concentration to be identified by XRD. SEM-EDS examination of the larger particles is planned.

Observed removal efficiency in the current study was lower than previous studies (Bowers and Westerman, 2005b), and strong evidence exists that the recovered Mg phosphates are in amorphous or semi-crystalline phases rather than crystalline form. These differences could be due to high Mg concentration, interference from Ca or other ions in the wastewater, or incomplete crystallization in the reactor. Allowing for longer reaction time might improve removal efficiency and the crystalline structure of recovered material.

Conclusion

Low removal efficiency compared to that observed in Bowers and Westerman (2005b) and the amorphous to semi-crystalline nature of the Mg phosphate particles examined in the current study point to the necessity for elucidating various reactions occurring inside the reactor under field conditions. Previous studies have shown that P can be recovered by producing struvite crystals in a cone-shaped fluidized bed reactor, but the observed performance and product characteristics in the current study do not match those of previous work. Further research is needed to improve removal efficiency and regularity of precipitate characteristics using actual wastewater under field conditions.

Even though removal efficiencies were comparatively low, the data suggest that Mg phosphates were precipitated from the wastewater in the reactor. Due to the high solubility of Mg phosphate in soil (Lindsay, 1979), the recovered product might indeed prove to be a useful fertilizer on alkaline soils. If so, it could provide a sustainable alternative to PR for P fertilization in organic production.

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***Appendix C: Other Conference Proceedings, Articles, and
Abstracts***

REDUCING DAIRY EFFLUENT PHOSPHORUS CONTENT THROUGH STRUVITE PRODUCTION

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ABSTRACT

Forced precipitation of struvite (magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) in wastewater treatment has recently received increased attention as a method of phosphorus (P) recycling. Dairy lagoon P concentrations can be lowered, and the recovered struvite has the potential to be marketed and used as a fertilizer. Struvite may even be useful in organic production on calcareous soils, where rock P (PR) is not an option.

A new organic treatment method, based on an existing process using a cone-shaped fluidized-bed reactor, was developed and field-tested using dairy wastewater. Wastewater pH was adjusted within the reactor using acetic acid and KOH. Input and output samples were analyzed with ICP-AES. The new process yielded a mean total P (TP) removal of 12% ($\pm 3\%$) at a 95% confidence limit ($n=34$). Magnesium (Mg) reduction of 12% ($\pm 2\%$) was also observed.

The granular product was examined semi-quantitatively using SEM-EDS, which confirmed the presence of amorphous Mg phosphates with approximately a 1:1 molar ratio of Mg:P. Wastewater and product analysis are ongoing, and greenhouse trials are scheduled to test the effectiveness of the recovered P as a fertilizer at various soil pH levels.

INTRODUCTION

The recovery and use of P by crystallization from municipal and agricultural wastewater has the potential to improve treated effluent quality while decreasing sludge volume and creating relatively pure, useful byproducts. While it is unclear exactly how long existing PR reserves will last, P is a limited resource and its reuse is necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Most efforts have focused on wastewater treatment plants (WWTPs), where spontaneous struvite precipitation can be destructive to WWTP facilities (de-Bashan and Bashan, 2004; Shu et al., 2006). Additionally, P releases from WWTPs can cause eutrophication of surface water bodies, resulting in strict limits on treated effluent. Given the scale and expense of a WWTP, it is easier to justify capital investment in new P removal technologies, so these facilities have naturally been a focus of research. 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 Mg phosphate (struvite) (van Dijk and Braakensiek, 1984; Driver et al., 1999; de-Bashan and Bashan, 2004).

Comparatively little work has been done regarding on-site P removal from agricultural wastewater. Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure an ideal target for P recovery. According to

the same review, while land application is the preferable method of manure P reuse, application of manure to meet crop nitrogen (N) needs results in a significant P surplus. P recovery through crystallization could be used to correct this imbalance. The product would also be easily dried, easily handled, marketable, and transportable at a fraction of the cost of manure or compost.

However, there are significant constraints for on-site P removal processes that must be met in order for the technology to be practical. Recovery technology must be economical on a smaller scale than P removal at a typical WWTP. Additionally, the system cannot require extensive monitoring, maintenance, or material inputs, and treated effluent must remain suitable for spreading on crops (Greaves et al., 1999). This last requirement imposes the most stringent limitation, as it precludes the use of processes common to P recovery at WWTPs, such as NaOH addition and raising pH to very alkaline levels. High sodium concentrations or high pH would render the effluent unsuitable for land application, so these techniques cannot be used to treat agricultural wastewater. Only a relatively inexpensive technology that maintains the suitability of effluent for application is practical for on-site P removal in an agricultural setting.

The cone-shaped fluidized bed reactor designed by Bowers and Westerman (2005a) is one such technology. In laboratory and field-scale experiments, P was recovered as crystalline struvite from wastewater generated in swine production. The uniquely shaped reactor was used in combination with Mg addition and pH increase using ammonia to reduce TP concentration in treated effluent, with mean concentration reductions of up to 82% for TP (Bowers and Westerman, 2005b). X-ray diffraction (XRD) analysis confirmed the presence of struvite.

Unfortunately, few applications for recovered struvite have been developed. Its chemical composition makes it impractical as a raw material in the modern P industry (Driver et al., 1999; Schipper et al., 2001). Its potential for use as a slow-release fertilizer has been known for decades, but until recently little scientific work has been conducted. Johnston and Richards (2003) evaluated different recovered phosphates, comparing their relative effectiveness as fertilizer in a greenhouse setting, and found recovered struvite to be an effective fertilizer for ryegrass. 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 (Li and Zhao, 2003).

Previous studies have examined struvite as a fertilizer on acidic or neutral soils. The development of an effective alternative for P fertilization on calcareous soils using recovered P could improve the sustainability of both livestock and crop production in semi-arid areas such as the western United States. By recovering P using a method based on Bowers and Westerman (2005a) that is in accordance with the letter and spirit of the regulations for organic food production, the product could be even more valuable. The use of recovered P in conventional or organic production on alkaline soils could help to alleviate P loading in areas with large numbers of livestock, and provide producers with a valuable resource and potential source of revenue.

METHODS

Wastewater Treatment and Water Analysis

Wastewater treatment using the University of Idaho pilot-scale struvite crystallizer was performed in August and September 2006 at two separate dairies in northern

Colorado. Two different processes were used; the “conventional” process which utilizes HCl and anhydrous ammonia for pH adjustment, and the “new” process which replaces these chemicals with acetic acid and KOH. By using KOH rather than NaOH, treated wastewater remains suitable for land application. The chemicals in the new process are also usable in some areas of organic agriculture, and the product might one day be certified as well.

The primary components of the fluidized-bed crystallizer system are a 250 gal holding tank and a large, inverted conical reactor vessel. The reactor cone is initially seeded with a bed of PR material to provide sites for the growth of struvite crystals. During operation, wastewater is pumped from the holding tank into the base of the reactor cone through a manifold. Inside the manifold, other substances such as Mg solution, hydroxide solution, or gaseous ammonia can be combined with the effluent stream. Effluent then enters the cone, and passes through the bed of material at its base. Treated effluent drains back into the lagoon from the top of the cone.

Wastewater was pumped from an anaerobic lagoon into the holding tank, and adjusted to a pH of 5.2. Acidification increased the concentration of orthophosphate (OP) in the effluent by dissolving inorganic phosphate complexes already present in the water. Liquid in the tank was continuously mixed by a pump at its base, and electrodes were used to monitor pH. Once the target pH was reached, acidified wastewater was pumped at a rate of 1.8 to 2 gal min⁻¹ through the manifold, where either NH₃ or KOH solution was added to rapidly increase the pH to 7.5-8.3 to encourage the precipitation of phosphates as the effluent passed through the seed material.

Wastewater samples were taken at three points in the process: prior to entering the holding tank, immediately prior to entering the manifold, and at the top of the reactor vessel. Samples were analyzed at the Colorado State University Soil, Water, and Plant Testing Laboratory. OP was evaluated using the ascorbic acid method (Kuo, 1996). Samples were digested with nitric and perchloric acid, and TP and metals were determined using ICP-AES (Thermo Jarrell Ash IRIS Advantage, high resolution, dual view). Basic statistical analysis was completed using Microsoft Excel 2003 (full analysis will be performed using SAS).

Reactor Product Analysis

Samples of product harvested from the reactor bed were sent to the Colorado School of Mines for XRD analysis. Product was further inspected using a scanning electron microscope in conjunction with energy dispersive spectroscopy (SEM-EDS). Carbon paint was applied to the face of small aluminum cylinders, and the product was sprinkled on the carbon paint while wet. Cylinders were allowed to dry for one week prior to examination with SEM-EDS.

RESULTS AND DISCUSSION

Wastewater Analysis Results

Wastewater samples were collected at the reactor input and output during operation in order to track and analyze reactor performance. Selected preliminary results for both the conventional and new methods are presented in Table 1.

Table 1. Mean concentrations and removal efficiency for selected elements of the influent and treated effluent using the conventional and new processes. (Conventional n=5, new n=30).

	conventional, input (ppm)	conventional, output (ppm)	conventional removal %	new, input (ppm)	new, output (ppm)	new removal %
OP (as P)	25.5	4.77	81	60.3	31.3	48
TP (as P)	94.9	81.0	14	78.4	67.2	14
total Mg	154.2	136.0	12	175.6	152.1	13
total Ca	299.2	303.2	-1.3	313.8	292.8	7

The different processes were tested at separate dairies due to difficulties pumping the effluent at the first location. Mg and OP concentrations were greater in the effluent used for the new process, while TP concentration was greater in the wastewater used for the conventional process. Additionally, the effluent used for the new process was diluted with irrigation water prior to the last five hours of operation, yielding lower concentrations for this period (not shown in Table 1). This period had notably lower TP removal efficiency. Including these four samples, the mean TP removal efficiency for the new process was 12%, with a 95% confidence interval of $\pm 3\%$. Mean Mg removal efficiency was also 12%, with a 95% confidence interval of $\pm 2\%$.

A reduction in both Mg and TP was observed for both the conventional and new processes, with considerably more Mg being removed than P on a molar basis. On a molar basis, 1.6 to 3 times more Mg was removed than P. OP reductions were also much greater than TP on an absolute and relative basis. Ca concentration increased slightly with the conventional method, while it decreased with the new method. Although TP reduction was similar in both processes, the conventional process resulted in greater relative OP reduction than the new process.

Product Analysis Results

Samples of reactor products made using both the conventional and new methods were analyzed using XRD, but a crystalline struvite phase could not be identified. PR samples were also examined using XRD, and showed strong correlation with database spectra for carbonate fluorapatite as well as quartz, dolomite, and calcite.

When the product was examined with SEM-EDS, semi-crystalline and amorphous particles having an approximately 1:1 ratio of Mg:P were identified from the new and conventional methods (Figures 1 and 2, respectively). While EDS data is only semi-quantitative, it suggests a strong association between Mg and P in these materials. The structure of the magnesium phosphate particles examined using SEM-EDS was highly variable, but in all cases fairly large amounts of both P and Mg were present.

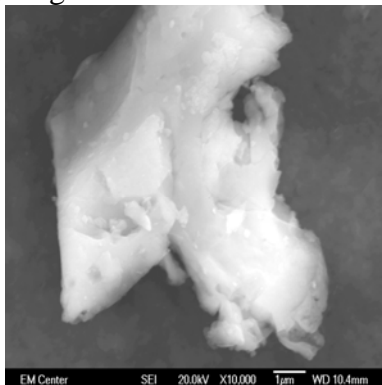


Figure 1. Particle produced using the acetic acid/KOH method. EDS analysis showed atomic composition of 16.25% P, 15.14% Mg, 65.25% O, 1.37% K, 0.77% Al, 0.79% Si, and 0.43% Ca.

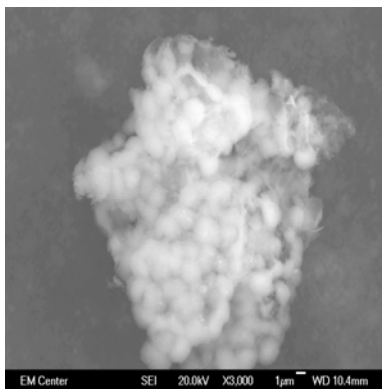


Figure 2. Particle produced using the HCl/NH₃ method. EDS analysis showed atomic composition of 12.91% P, 9.99% Mg, 5.17% Ca, 66.18% O, 2.02% Si, and trace Fe, K, and Cu.

Discussion

The mean TP removal efficiency of 12% did not match the 66% removal efficiency observed by Bowers and Westerman (2005b) in experiments with swine wastewater and no added Mg, but was comparable to results obtained by Bowers et al. (2005) for treatment of dairy wastewater in Idaho and Washington (14% reduction in Idaho and 15% in Washington) using the conventional acidified process. Reported Mg and P concentrations in the Idaho dairy wastewater (Bowers et al., 2005) were similar to the concentrations observed in this study. Wang et al. (2005) concluded that the ideal Ca:Mg molar ratio for struvite precipitation is 0.5 or less, and that a ratio greater than 1.0 in wastewater significantly inhibits struvite formation. The Ca:Mg ratio in the current study ranged from 1.04 to 1.21. Bowers and Westerman (2005b) found that a Mg:TP ratio greater than one may reduce efficiency. The molar ratio of Mg:TP in the current study ranged from 2.0 to 3.8, without supplemental Mg. It is possible that high concentrations of Ca or Mg inhibited struvite formation in the reactor. However, Huang et al. (2006) found that Mg:TP ratios as high as 3.3:1 with Ca:Mg ratios of up to 6:1 were conducive to struvite production in WWTPs. Even given these conflicting results, the Ca:Mg or Mg:TP ratio in the wastewater may not be optimal for struvite crystallization and could explain the low observed efficiency.

Even at decreased efficiency, the observed simultaneous reduction of P and Mg levels in the effluent suggests that magnesium phosphates were indeed precipitated from reactor effluent. On a molar basis, 1.6 to 3 times more Mg was removed than P, so other Mg compounds were probably produced in the reactor in addition to phosphates.

According to Bowers and Westerman (2005a), all OP is theoretically available for recovery through struvite crystallization. The TP reduction they observed was sometimes greater than this theoretical maximum. In the current study, however, TP reduction was notably lower than OP reduction. This indicates that some potentially recoverable phosphate is being discharged in the treated effluent stream prior to crystallization in the reactor bed, or that some of the bed particles themselves are being expelled from the reactor. The net result is that large decreases in OP concentration result in smaller than

expected TP reduction. Bowers and Westerman (2005b) reported that with a similar setup and flow rates of 1.5 gal min⁻¹ and 2.5 gal min⁻¹, the slower flow rate resulted in greater P removal efficiency in field-scale experiments. It is possible that a slower flow rate and correspondingly longer reaction time would improve performance and product characteristics over those reported in the current study.

SEM-EDS data shows that amorphous Mg phosphates were formed in the reactor, rather than the crystalline morphology observed in laboratory and fieldwork in Bowers and Westerman (2005b). The struvite particles in the SEM images bear no resemblance to recovered struvite crystals in Li and Zhao (2003), for they lack any regular structure. EDS analysis was only possible on very small particles due to the lack of electrical ground on larger particles, so no comparison can be made with larger struvite particles shown in Huang et al. (2006). However, XRD analysis would likely have identified crystalline phases of struvite if they were present in detectable amounts. This indicates that either the large particles are not crystalline phosphates, or that they are not present in high enough concentration to be identified by XRD.

Observed removal efficiency in the current study is lower than previous studies (Bowers and Westerman, 2005b), and strong evidence exists that the recovered magnesium phosphates are in amorphous rather than crystalline form. These differences could be due to high Mg or Ca concentration, other ions in the wastewater, or incomplete crystallization. A longer reaction time might improve removal efficiency and the crystalline structure of recovered material.

SUMMARY

Low removal efficiency compared to that observed in Bowers and Westerman (2005b) and the amorphous nature of the Mg phosphate particles examined in the current study point to the necessity to elucidate the reactions occurring under field conditions. Previous studies have shown that P can be recovered by producing struvite crystals in a cone-shaped fluidized bed reactor, but the observed performance and product characteristics in the current study do not match those of previous studies. Further work is needed to improve removal efficiency and regularity of precipitate characteristics using actual wastewater under field conditions.

Though removal efficiencies are comparatively low, the data suggest that Mg phosphates were precipitated from the wastewater in the reactor. Struvite production at dairies can help to correct nutrient imbalances in the western United States while providing a useful byproduct.

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Phosphorus Recovery in Colorado Agriculture

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Introduction

Struvite (magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation in municipal wastewater treatment systems with high phosphorus (P) loading has traditionally been considered a difficult problem in wastewater treatment plant (WWTP) management. To reduce maintenance issues and downtime caused by spontaneous struvite precipitation, and to respond to increasingly stringent regulations on P discharge from WWTPs, wastewater is commonly dosed with iron or aluminum salts to reduce effluent P concentration by binding phosphate in minimally soluble forms. Chemical precipitation, while very effective in reducing P concentration in the treated effluent, also significantly increases the volume of sludge generated in the treatment process. Increased sludge volume increases disposal costs. Furthermore, the insoluble nature of the iron and aluminum phosphates generated by the treatment process makes them unusable for other applications, making disposal the only practical option. In addition to the short-term costs of disposal, the world's dwindling supply of economically extractable phosphate rock makes disposal an increasingly unattractive option for the long term, as well (for more information on P reserves, P recycling, and the commercial P industry, see Schipper et al., 2001, Driver et al., 1999, and Driver, 1998).

Interest in forced struvite precipitation as part of the treatment process has increased in the past ten years. Rather than allowing costly spontaneous precipitation, relatively new processes allow for phosphate to be removed from the waste stream as struvite in a controlled fashion. Other technologies, such as processes for P recovery as calcium phosphates, have also been developed (Van Dijk and Braakensiek, 1984). These technologies can be used to decrease effluent P concentration while simultaneously generating a relatively pure, useful, potentially marketable product; they can also effectively treat effluent without increasing sludge volume and associated disposal costs. However, there are still many barriers that must be overcome before P recovery becomes commonplace in municipal WWTPs. Unresolved issues include P recovery technologies that are still relatively expensive, and markets for recovered P that are not yet well developed.

Agricultural wastewater, such as that found on dairy and swine operations shares many of the same characteristics of municipal wastewater. In Colorado, agricultural wastewater is often applied to fields directly from anaerobic storage and treatment lagoons. The high nitrogen (N) to P ratio of typical agricultural wastewater when compared to plant nutrient needs, however, results in a significant over-application of P to cropland if the effluent is applied at a rate calculated to meet plant N needs. Over the long term, a buildup of P could become a significant risk to water quality through soil erosion or runoff, and contribute to eutrophication of P-enriched surface water bodies. One potential solution to this difficult waste management conundrum is to lower the concentration of P in

agricultural wastewater prior to land application, so that wastewater could be applied to meet plant N needs without applying P in excess of biological requirements.

Due to the similarities between agricultural and municipal wastewater, techniques for municipal wastewater treatment might also be used in the treatment and management of agricultural wastewater. However, there are other constraints that must be met in order to create practical treatment solutions for agricultural settings. A viable technology must be robust, simple, practical on a smaller scale than most WWTPs, and relatively inexpensive to install and operate. Increased sludge volume, such as by chemical precipitation, would likely drastically shorten a waste treatment lagoon's useful lifespan and so is not an optimal solution. P recovery is one possible alternative. Successful application of P recovery processes in agriculture would decrease environmental risk while potentially providing a livestock operation with an additional source of revenue (the product of the treatment process). However, the treated effluent must remain suitable for land application, which precludes the use of certain chemicals such as sodium hydroxide commonly used in existing P recovery processes at WWTPs. Clearly, the additional economic and practical constraints on agricultural wastewater treatment make finding a solution to this already complicated problem even more difficult.

We have been investigating the feasibility of P recovery on Colorado dairy farms since the spring of 2006 thanks to a grant provided by the USDA NRCS through the Farm Pilot Project Coordination, Inc. and Applied Chemical Magnesium Corporation of Loveland, CO. During the summer of 2006, we used a demonstration scale cone-shaped fluidized-bed reactor built by Dr. Ron Sheffield of the University of Idaho to treat anaerobic waste lagoon effluent at two northern Colorado dairy farms. Analysis of the reactor's performance is ongoing, as is examination of the product harvested from the treatment process. In addition, a greenhouse study to assess the potential effectiveness of recovered struvite as fertilizer in Colorado soils began in March 2007. If recovered struvite is shown to be an effective fertilizer, P recovery as struvite for use on local farms and in local gardens might one day become a reality.

Wastewater Treatment

The University of Idaho struvite crystallizer, shown in figure 1, is a cone-shaped fluidized-bed reactor similar to the one designed, built, and tested by Bowers and Westerman (2005). The primary components of the fluidized-bed crystallizer system are a 250 gal holding tank and a large, inverted conical reactor vessel. The reactor cone is initially seeded with a bed of finely ground rock phosphate material to provide sites for the growth of struvite crystals. During operation, wastewater is acidified in the holding tank and pumped into the base of the reactor cone through a manifold. Inside the manifold, other substances such as magnesium (Mg) solution, hydroxide solution, or gaseous ammonia can be combined with the effluent stream. Effluent then enters the cone, and passes through the bed of material at its base. Treated effluent drains back into the waste treatment lagoon from the top of the cone. Bowers and Westerman (2005) used this system along with pH alteration and Mg addition to remove up to 81% of the orthophosphate (OP) and 80% of the total phosphorus (TP) in swine lagoon wastewater.

Our initial experiments used the “conventional” treatment process, which utilizes hydrochloric acid (HCl) to lower the pH of the wastewater in the holding tank, and anhydrous ammonia (NH₃) to raise the pH as the effluent enters the cone. Acidification increases the concentration of OP in the effluent by dissolving inorganic phosphate complexes already present in the water, and rapidly raising the pH encourages the precipitation of phosphates as the effluent passes through the seed material. Though supplemental Mg is added in many existing struvite recovery processes, the dairy wastewater at both locations for this study was very high in Mg, so none was added in our experiments. After initial tests with the conventional method, we developed and field-tested a new process that uses acetic acid in place of HCl and potassium hydroxide (KOH) solution rather than NH₃. The chemicals in the new process are allowed for restricted uses in certified organic food production, and in the future it is hoped that struvite recovered using this process will also be certifiable for organic production. This would improve the economics of P recovery, as well as the environmental sustainability of livestock agriculture and organic food production in Colorado.

During the field experiments, wastewater was pumped from an anaerobic lagoon into the holding tank, and adjusted to a pH of 5.2. Liquid in the tank was continuously mixed by a pump at its base, and electrodes were used to monitor pH. Once the target pH was reached, acidified wastewater was pumped at a rate of 1.8 to 2 gal min⁻¹ through the manifold, where either NH₃ or KOH solution was added to rapidly increase the pH to 7.5-8.3. The rapid pH increase resulted in the precipitation of phosphates on the seed material.

Wastewater Treatment Results

The experiments were performed at two northern Colorado dairies. Samples of the raw lagoon wastewater, acidified reactor input, and treated effluent were taken and analyzed at the CSU Soil, Water, and Plant Testing Laboratory. Selected results of the wastewater analysis are shown in Table 1.

Both the conventional and new processes demonstrated similar performance for TP and Mg removal, though the performance did not match that of Bowers and Westerman (2005) using swine wastewater. The conventional process removed a greater percentage of OP than the new process, suggesting that the new process would benefit from further work in order to achieve optimization. There are a number of potential culprits for the relatively low P removal efficiency observed in our experiments, including interference from high levels of calcium, interference from suspended organic matter present in the waste stream, or a flow rate that was too high, which would have caused incomplete reaction in the reactor vessel.

In addition to low P removal efficiency, X-ray diffraction analysis of the products did not identify crystalline struvite in the reactor material from Colorado. Subsequent examination with an electron microscope did find amorphous Mg phosphate particles in the harvested product. Any of the factors that may have resulted in low P removal efficiency could also have contributed to the amorphous (rather than crystalline) nature of the product.

Though our field tests of the cone-shaped fluidized-bed reactor for P recovery on Colorado dairy farms did not yield ideal results in terms of P removal efficiency or product characteristics, we were able to successfully remove P from lagoon effluent. Further adaptation and refinement of this or other P recovery technologies to suit local conditions may soon enable effective P recovery from agricultural wastes. Successful application of P recovery processes could significantly improve P cycling in agriculture, provide livestock operations with an additional source of revenue, and protect surface waters from pollution risks associated with the over-application of P to cropland.

Fertilizer Evaluation

Because of its chemical composition, recovered struvite is not currently usable as a feedstock by the commercial P industry. The N in struvite would cause serious emission problems during the sintering stage of “dry” P production (Schipper et al., 2001), and the Mg interferes with the chemistry of “wet” phosphoric acid production (Driver et al., 1999). However, several investigators have evaluated recovered P for direct use as a slow-release P fertilizer (for example, see Johnston and Richards, 2003). There are full-scale P recovery facilities at several WWTPs throughout the world, most notably in the Netherlands and Japan. Some of these WWTPs even sell the treatment byproduct in fertilizer mixes (Ueno and Fujii, 2001).

In all cases, however, the effectiveness of struvite has been evaluated on soils of acidic to neutral pH. There is no information regarding struvite use as a fertilizer on alkaline or calcareous soils common to Colorado and the western United States. If economical P recovery from agricultural or municipal wastewater in Colorado is to be realized, local uses must be found for the recovered product.

To that end, a greenhouse trial comparing recovered phosphates with conventional P fertilizers began on March 2, 2007. An acidic (pH 6.4-6.5) rangeland soil with moderate P availability from northern Colorado was treated with powdered CaCO_3 to raise its pH to approximately 7.5, equivalent to that of a slightly calcareous soil. Fertilizers were applied to both the low pH and high pH soils, to evaluate their performance as P sources for wheat (“Zeke” hard red spring variety).

Recovered product made in Colorado from the new water treatment process was applied, as was struvite recovered in Washington using the conventional treatment process, and magnesium ammonium phosphate hydrate (dittmarite, $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) removed from a food processing plant during cleaning. Certified organic rock phosphate and triple superphosphate fertilizer treatments were also included to compare the performance of recovered phosphates against that of more conventional P fertilizers.

Monitoring and analysis of plant growth and P uptake is planned through July of 2007. If the recovered phosphates demonstrate satisfactory performance, the use of P recovered from municipal or agricultural sources as fertilizer on Colorado soils may indeed be practicable.

Conclusion

P recovery from agricultural and municipal wastewater in Colorado is already a technologically feasible and environmentally attractive water treatment alternative. It may become an economically attractive one in the relatively near future, as well, as supplies of P dwindle and strict water quality standards designed to protect surface waters compete with rising waste disposal costs. Struvite production is one option for P recovery, but its effectiveness as a fertilizer on the alkaline, calcium-rich soils commonly found in Colorado is untested. If struvite is found to be an effective fertilizer under local conditions, then P recovery in Colorado, with its associated economic and environmental benefits, will be that much closer to becoming a reality.

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Table 1. Mean concentrations and removal efficiency for selected elements of the influent and treated effluent using the conventional and new processes. (Conventional n=5, new n=30).

	conventional, input (ppm)	conventional, output (ppm)	conventional removal %	new, input (ppm)	new, output (ppm)	new removal %
ortho-P (as P)	25.5	4.77	81	60.3	31.3	48
total P (as P)	94.9	81.0	14	78.4	67.2	14
total Mg	154.2	136.0	12	175.6	152.1	13
total Ca	299.2	303.2	-1.3	313.8	292.8	7

Abstract: Morphological Variation Among Magnesium Phosphates Recovered from Wastewater

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The recovery and reuse of magnesium (Mg) phosphates such as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has the potential to protect surface water quality, extend phosphorus (P) reserves for use in industry and agriculture, and provide facility operators with a potentially valuable byproduct. Recovery technology can be used in wastewater treatment plants (WWTPs), intensive livestock operations, and industrial facilities with high-P waste effluent, and the product of treatment can be applied as a P fertilizer.

Four recovered magnesium phosphates were examined: crystalline struvite produced from livestock waste effluent, amorphous Mg phosphate made using the same method as the crystalline struvite, Mg phosphate made using a modified method, and crystalline dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) recovered from a food processing plant during cleaning. The crystalline samples were clearly identifiable from X-ray diffraction (XRD) spectra, while no crystalline Mg phosphates were identified from XRD spectra of the amorphous samples. Mg phosphate particles of various sizes were identified in all samples using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS).

Many of the particles examined using EDS showed a 1:1 ratio of Mg and P. However, particle morphology ranged from crystalline and regular to semi-crystalline to completely amorphous and irregular. This wide variation in recovered Mg phosphate morphology highlights the need for further investigation into the practical effects of structure on the beneficial reuse of recovered phosphate materials.

Abstract: Recovery of Magnesium Phosphates from Dairy Wastewater and their Use as a Fertilizer on Calcareous Soils

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Forced precipitation of struvite (magnesium ammonium phosphate hexahydrate) in wastewater treatment has recently received increased attention as a method of phosphorus (P) recycling. While both struvite and phosphate rock can be used as a P fertilizer on acid soils, phosphate rock is ineffective in calcareous soils. Magnesium (Mg) phosphates such as struvite, on the other hand, could be a more useful fertilizer in alkaline soils, especially in organic production where conventional P fertilizers are not an option. A new organic treatment method, based on an existing process using a cone-shaped fluidized-bed reactor, was developed and field-tested using dairy wastewater. The amorphous or semi-crystalline product of this treatment process, as well as other recovered Mg phosphates including crystalline struvite and dittmarite (magnesium ammonium phosphate hydrate) were evaluated in greenhouse trials. The recovered Mg phosphates were tested against a control group, commercial phosphate rock fertilizer, and commercial triple superphosphate to compare the various Mg phosphates' effectiveness as a P fertilizer at acidic and alkaline soil pH. If plants show an increased or comparable response to Mg phosphates as compared to other fertilizers, recovered phosphates could have potential as an organic P fertilizer in calcareous soils.