Title: Reduced Phosphorus Pollution from Dairies by Removal of Phosphorus from Wastewater through Precipitation of Struvite

Focus Categories:

Keywords: water pollution, phosphorus, dairy waste, TMDL, wastewater reuse

Duration: 1 year, March 1, 2002 through February 28, 2003

Federal Funds Requested: $5,000

Non-Federal Funds Pledged (matching funds): $28,476

Principal Investigator: Amanda Bragg, M.S. candidate

Co-Principal Investigators: Drs. Kevin McInnes and Tony Provin, Soil and Crop Sciences, Texas A&M University, College Station, Texas

Congressional District: 8th

Statement of Critical Regional Water Problems: Phosphorus enrichment of streams and lakes in central Texas is a severe environmental problem. A large portion of the problem phosphorus originates from dairy wastewater. Simplistically, the problem arises from the continued application of dairy wastewater high in phosphorus content to pastures and crops growing on soils already saturated with phosphorus from previous applications. Runoff from these overloaded fields during storms carries phosphorous to streams and lakes. Since phosphorus most often is the limiting nutrient to algal growth, excess phosphorus leads to undesirable eutrophication of surface water resources. If the phosphorus content of the dairy wastewater were reduced to minimal levels, the problem with phosphorous pollution in central Texas would gradually disappear.

Wastewater effluent from dairies in central Texas is stored in onsite lagoons. Typically, this wastewater is applied to Coastal bermudagrass from late spring through early fall. During winter, some lagoon effluent may be used to irrigate wheat or other cereal crops grown for grazing or silage. The nutrient content of this wastewater is such that it provides significantly more phosphorus than nitrogen relative to plant requirement. Wastewater application based upon nitrogen requirement of plants results in excess phosphorus application. It would be advantageous if the nitrogen content of the wastewater could be increased while the phosphorus content was reduced. One way to accomplish this is to process the wastewater before it is applied to the field.

In recent years, the domestic and industrial wastewater treatment industry has developed technology to reduce phosphorus concentrations to minimal levels so that wastewater can be reused while at the same time recovering that phosphorus as a fertilizer source (Driver et al., 1999; Gaterell et al., 2000). Phosphorus and nitrogen are removed from the wastewater by precipitation of struvite, an ammonium-magnesium phosphate.
(MgNH₄PO₄). With the proper stoichiometric concentrations of Mg²⁺, NH₄⁺, and PO₄³⁻, the reaction is very rapid (seconds). The struvite precipitation process is fundamentally different from removing the phosphorus with additions of iron or aluminum as these compounds leave precipitates of little agronomic and economic value. In precipitating struvite for domestic or industrial reuse of the wastewater, magnesium and pH are controlled to drive the reactions so that struvite precipitates while leaving the water with minimal phosphorus and nitrogen. The goal with dairy wastewater is slightly different. Because the wastewater is to be applied to crops or pastures, it is desirable to remove phosphorus as struvite by controlling magnesium, ammonical nitrogen, and pH, but leave the wastewater relatively high in nitrogen so that it has significant value as a fertilizer. Both cool and warm season grasses may be grown in central Texas so the nitrogen in this treated wastewater could be utilized throughout the year. Consistent nitrogen applications as a fertilizer source will reduce nitrogen losses compared to large 1-time applications simply for disposal. To precipitate struvite, stoichiometric amounts of Mg²⁺, NH₄⁺, and PO₄³⁻ must be present in the wastewater and the pH must be within the range where struvite dominates as the solid phase.

While the solution chemistry for struvite formation in relatively clean wastewater is well known (Scott et al., 1991), the effects of the organic materials and high levels of carbonates in the dairy lagoon wastewater on the reactions has not been investigated. Both carbonates and organic materials influence pH and pH buffering. Knowledge of pH and pH buffering are important because they determine the speciation of the key ions. This proposed research would determine the optimum chemical environments to precipitation struvite from dairy wastewaters while at the same time leaving the wastewaters relatively high in ammonical nitrogen so that they have nutritional value to plants.

Concentration of phosphorus in dairy wastewater tends to be high, generally 20 to 100 ppm. We would like to reduce them to <1 ppm by precipitating struvite. This should not be difficult as it is routinely reduced to considerably less than 1 ppm in domestic and industrial wastewater by precipitating struvite. In addition, we would like the resultant wastewater to have <50 ppm ammonical N and to have magnesium concentrations low enough so as not to have a salting effect on the crop and soil. Since ammonical nitrogen concentrations are usually <5 ppm, we will have to add significant nitrogen to the wastewater, as the molar ratio of N:P in struvite is 1:1. After adding the nitrogen, most likely as anhydrous ammonia, the stoichiometric requirement for precipitation may be met by adding MgCl₂ or Mg(OH)₂. These chemicals are readily available and relatively inexpensive.

Nature, Scope, and Objectives of the Research: Representative samples of dairy lagoon wastewater will be collected from private dairies near Stephenville, Texas, in the Bosque River watershed. Research has shown that eutrophic phosphorus levels in water bodies within the Bosque watershed are linked to high levels of phosphorus in soils, sometimes >100 ppm. High levels of soil phosphorus are related to long-term application of dairy wastewater. These samples will be stored in 50-gallon plastic containers. A series of tests will be conducted on subsamples taken from these containers of
wastewater. First, the ionic composition and pH buffer capacity of the bulk wastewater will be determined. Analyses for ionic composition will be done by the Soil, Water, and Forage Testing Laboratory at Texas A&M University. Hydrogen ion concentration will be determined with a Radiometer Precision pH meter. Hydrogen ion buffer capacity will be determined by two sequential serial titrations. The first titration will quantify the bicarbonate and organic buffering. The second titration, after the carbonates have been removed as carbon dioxide, will quantify organic buffering. The initial ionic concentration data, pH, and pH buffer capacity will be entered into a computer program that simultaneously solves the above set of equilibrium and solubility equations. Then the concentrations of magnesium, ammonical nitrogen, and hydrogen ion will be altered in the model to determine a range of near optimum concentrations for struvite precipitation while maintaining our target residual ammonical nitrogen and magnesium concentrations. Concentrations of magnesium, ammonical nitrogen, and hydrogen ion in the actual wastewater solution will be altered by additions of MgCl₂ (or Mg(OH)₂) and NH₄OH such that the range of predicted near optimum concentrations for struvite precipitation will be evaluated. After the solutions have had time to equilibrate, any precipitate will be removed and the remaining wastewater will be analyzed again for ionic composition. New amounts of magnesium and ammonical N to add will be determined based on the empirical data.

**Results Expected from this Project:** Methodology to remove phosphorus from dairy wastewater while increasing the fertilizer value (nitrogen content) for cool- and warm-season grasses will be developed. This methodology will then be scaled up to allow removal of phosphorus from dairy lagoon wastewater before it is applied to pastures or crops. It is envisioned that the technology will be widely accepted and utilized to reduce phosphorus pollution from the application of dairy wastewater in sensitive watersheds such as the Bosque and Leon watersheds in central Texas. The technology is already being used to remove and recover phosphorus from domestic and industrial wastewater (Driver et al., 1999; Gaterell et al., 2000) and from calf manure (Schuiling and Andrade, 1999) so this outcome would not be a high-risk endeavor. The struvite formed from the dairy wastewater would be removed from the watershed and used for a slow-release phosphorus fertilizer where needed. Its fertilizer value has already been evaluated and found to be favorable (Mikkelson and Nelson, 2001).

**References:**


BUDGET BREAKDOWN

Proposed start date: March 1, 2002
Proposed completion date: February 28, 2003

Project Number:

Project Title: Reduced Phosphorus Pollution from Dairies by Removal of Phosphorus from Wastewater through Precipitation of Struvite

Principal Investigator(s): Amanda Bragg, Dr. Kevin McInnes, and Dr. Tony Provin, Department of Soil and Crop Sciences, Texas A&M University

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Budget Justification: Funds are requested for chemical supplies, glassware, and plasticware ($900) to conduct the struvite precipitation experiments. Laboratory analysis of wastewater samples before and after treatment will be done by the Soil, Water, and Forage Testing Laboratory at Texas A&M University for $25 per sample. I expect to generate at least 400 samples. I am requesting $2,500 to analyze 100 of these samples. Tuition and fees cost about $5,400 per year at Texas A&M University. I am requesting $1,600 to cover part of these costs.