Reducing Phosphorus in Dairy Effluent Wastewater Through Flocculation and Precipitation

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Introduction

Background

The association between phosphorus additions and eutrophication of water bodies is well documented (Carpenter et al., 1998; Correll, 1998; Foy and Watts, 1998; Parry, 1998). Loehr (1974) found that undesirable aquatic weed growth occurred in water bodies with excessive phosphorus additions. Phosphorus enrichment of central Texas waters and consequential algal blooms produce environmental problems such as odor emissions, foul tasting water, and fish kills. These problems lead to a decrease in recreational value and an increase in expense of necessary treatment of water resources (TNRCC, 1999). Although the water bodies of concern in central Texas have several sources of phosphorus, runoff of phosphorus from fields irrigated with dairy effluent is most often considered to be the largest source. The North Bosque River in central Texas is one of the affected areas. TNRCC (1999) estimated that over 200,000 people used water originating in the North Bosque River as their primary drinking source. Dairies in this watershed import more phosphorus in feed stuffs than they export in milk products thus P accumulates in the watershed. Unutilized phosphorus in animal excrement applied to crops and pastures is considered the major source of phosphorus that makes its way into streams and lakes of the watershed.

Phosphorus transport

Excrements are typically washed from milking parlors and scraped from feedlots. The effluent carrying the excrement is normally screened to remove large particles then held in a lagoon or series of lagoons until the wastewater can be irrigated to cropland. During storage, larger and heavier particles settle to the bottom of the lagoon(s). Much of finer portion of the solids does not settle out prior to irrigation. Wind, thermal currents, escaping gases, and introduction of fresh effluent provide mixing that limits the settling of these finer particles. A great deal of the phosphorus in water used for irrigation from the lagoons is associated with the suspended solids. Land application of phosphorus in irrigation water from lagoons is generally in excess of the phosphorus requirement for the crop (Daniel et al., 1994; Maguire et al. 2000). The continual land application of effluent in quantities greater than phosphorus uptake has resulted in phosphorus buildups in the soil, thus increasing the potential for phosphorus loss in runoff (Sharpley et al., 1996; Sims et al., 1998).

Phosphorus loss with surface runoff occurs mostly with the loss of sediments containing bound phosphorus, but some is also lost with phosphorus dissolved in the water (Haygarth and Sharpley, 2000). Pietilainen and Rekolainen (1991) suggest that as much as 60-90% of the phosphorus transported from cultivated lands is associated with sediments. Phosphorus pollution of streams begins when rain detaches soil surface particles and carries them and water-soluble phosphorus with runoff water. Consequently, phosphorus in runoff often directly correlates to soil phosphorus (Sharpley et al., 1996). While many in-stream process including biotic uptake and deposition of phosphorus may occur (Edwards et al., 2000), eventually these eroded soil particles and phosphorus are transported to water bodies and slowly released to support plant and algal growth (Gibson, 1997).

The Bosque River and its outlet, Lake Waco, presently are overwhelmed with algal blooms. Since phosphorus is the limiting nutrient for algal growth in freshwater systems, reducing eutrophication caused by algal growth in these water systems is dependant on controlling phosphorus inputs from runoff (Withers and Jarvis, 1998; Little, 1988; Sharpley et al., 1994). If significant levels of phosphorus could be removed from the dairy effluent prior to irrigation, phosphorus content in the soil could gradually decrease with plant uptake and removal, thus reducing phosphorus in eroded sediments.

Flocculation

Principle treatment processes for wastewater reuse include flocculation during which suspended particles join and form aggregates that rapidly settle out of suspension or are of filterable size (Adin and Asano, 1998). Levine et al. (1985) estimated that flocculation processes could aggregate suspended solids with sizes ranging from 0.1 μm to 10 μm. Some research suggests that phosphorus in dairy effluent can be reduced using aluminum sulfate as a coagulant (Hamoda and Al-Awadi, 1996) to reduce suspended solids. Using aluminum sulfate in systems that dispose of water on acid soils may result in reduced plant growth due to aluminum toxicity. The consequences of reduced plant growth are reduced uptake of phosphorus, reduced crop cover, and increased susceptibility of phosphorus runoff with surface erosion.

Polymeric flocculants such as diallyl-dimethyl ammonium chloride (DADMAC) and polyacrylamide (PAM) are widely used in the treatment of wastewater. Use of polymeric flocculants eliminates many of the undesirable consequences associated with use of aluminum sulfate (Rout et al., 1999). DADMAC is widely used as an industrial flucculant. Cationic PAMs have been found to be more efficient than aluminum sulfate and to chemically react with dissolved organics to form colloids (Narkis and Rebhun, 1997). Narkis and Rebhun (1997) also found that a certain form of cationic PAM reacted preferentially with organic matter in solutions. A combination of DADMAC and PAM might be an ideal flocculant.

Precipitation

After suspended solids are removed from dairy effluent, there remains an appreciable amount of organic and inorganic phosphorus in the remaining wastewater. Reduction of the soluble phosphorus concentrations before field application is critical. Phosphate chemistry (Song et al., 2002) suggests that raising the pH of the wastewater remaining after the solids removal would lead to precipitation of one or more calcium phosphate compounds. Struvite, a magnesium-ammonium phosphate, forms readily in human, swine, and poultry wastewater and potentially could be formed in dairy wastewater. Removal of the remaining soluble phosphorous through the formation of insoluble phosphates would produce an irrigation water source acceptable for continual land application to crops and pastures and a sustainable dairy system.

Other benefits of flocculation and chemical treatment

Flocculants remaining in the effluent solution applied as irrigation water may also reduce erosional loss of phosphours by improving the stability of aggregate at the soil surface and by increasing infiltration (Lentz et al., 1992; Lentz and Sojka, 1994; Sojka et al., 1998). Chemical additions during wastewater treatment cause the phosphorus in biosolids to be less soluble and less available to plants (Kirkham, 1982; McCoy et al., 1986; Frossard et al., 1996). Sludges treated with calcium in the form of lime can supply phosphorus more efficiently to plants than Al- and Fe-treated biosolids (Soon et al., 1978). If the solids were kept out of lagoons by a fast-acting flocculation processes, the time between necessary dredging of solids from the lagoon could be extended. Additionally, recent studies indicate that the majority of the solids that enter lagoons are converted to the greenhouse gas methane by microbes and lost to the atmosphere.

Research Objective

The intent of this research project was to determine methods to reduce phosphorus content of water stored in dairy wastewater lagoons.

Materials and Methods

Fresh dairy effluent samples, prior to entering the lagoon, were obtained from a 2000-cow dairy in Comanche, Texas. Samples were collected in 50 gallon plastic drums and transported to Texas A&M University, College Station, and stored in a research laboratory at room temperature (25^{o}C). The drums were vented daily to prevent drum failure. Solids were re-suspended once when the barrels were placed in the laboratory and then allowed to settle with time. Subsamples were withdrawn from the barrels at the time of resuspension and at 15 day intervals for 75 days. A cationic polyacrylamide, PAM, (H2-480Z-C), curtsey of Qemifloc (Qemi International, Houston, Texas) was mixed with diallyl-dimethyl ammonium chloride, DADMAC, in a 1 to 4 (PAM:DADMAC) ratio. This mixture will be referred to throughout the rest of the report as our flocculant. The flocculant was used to remove the organic particles from the effluent. Ammonium hydroxide was used to raise the pH of the effluent to facilitate precipitation of phosphates. Other bases could have been used, but ammonium hydroxide would improve the nitrogen to phosphorus ratio of the wastewater.

The flocculant was added to 40 mL of effluent sample in a 50mL test tube, and the solution was mixed by overturning the test tube, covered with parafilm, three times. The solution was then allowed to settle. After the floccules settled, the clear solution was decanted and analyzed for phosphorus, sodium, ammonium, calcium, magnesium, zinc, manganese, copper, iron, and potassium. Concentrations in flocculated samples were compared to untreated samples. After removing suspended solids from the effluent, ammonium hydroxide was added to increase the pH to levels sufficient to precipitate phosphorus. Each treatment, including a control treatment, was replicated three times, and analyzed along with solution/matrix blanks and standards.

After 75 days, 100 gallons of the effluent was re-suspended. Fifty gallons were treated with flocculant to produce a final concentration of 1.3 mg/L of flocculant. The effluent was then decanted over a 2 mm-mesh to collect the solids. Solids were dried in an oven at 60^{o}C in stainless steel pans. The remaining 50 gallons were allowed to resettle for 7 days. After resettling the barrel was also screened using the same mesh to remove the solids from the solution. These solids were also dried at 60^{o}C. A food processor was used to break dried and caked solids into smaller, more uniform pieces. The water holing capacity of the solids at at 100 kPa, 33 kPa, and 10 kPa was determined via pressure plate. Subsamples also were the solids were analyzed for elemental composition.

The Texas Cooperative Extension Soil, Forage and Water Testing Lab analyzed samples for phosphorous and nitrogen concentrations and cationic composition. The pH of the effluent was measured using a pH probe. Concentration of cations Fe, Zn, Mn, and Cu were also measured to document any accumulations of these elements in the effluent. The laboratory results were used to compare phosphorous removal with the amount of flocculant used, the pH of the effluent, time allowed for the effluent to settle, and removal of specific cations. Identification of the precipitating species was made by analysis of ions removed from solution and X-ray diffraction of the precipitants (XRD).

Results

Effect of settling

Significantly reduced effluent phosphorus concentrations resulted with the removal of suspended solids (Figure 1). This mechanism of separation is slow and results in an accumulation of phosphorus and other nutrients at the bottom of a lagoon. This phosphorus in the bottom of the lagoon then has the potential to mineralize into solution over time. In lagoon settlings, additions of fresh effluent, wind, and thermal currents would prevent the settling of some of these solids.

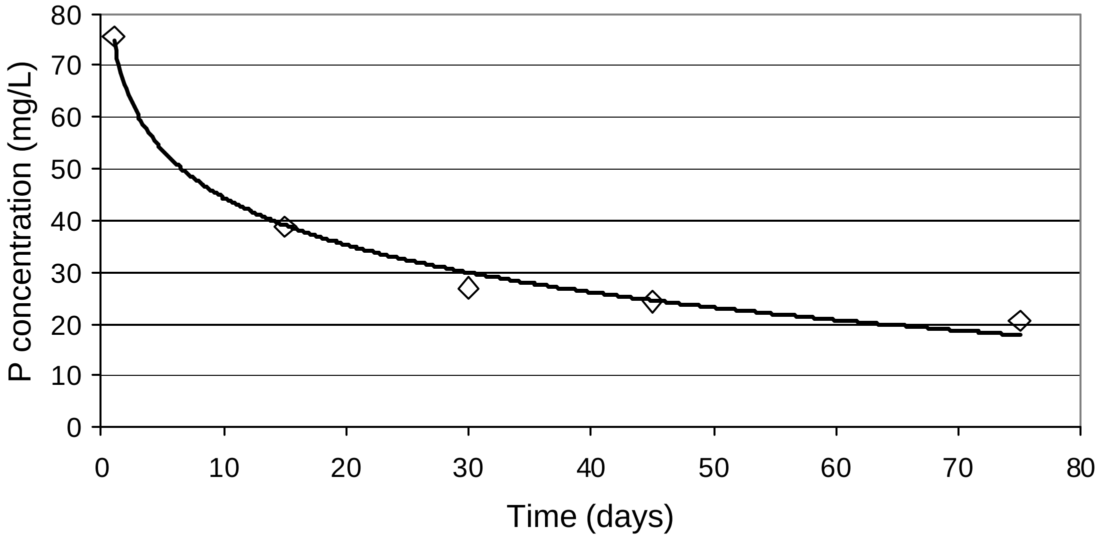

Figure 1: Changes in phosphorus (P) concentration caused by settling of suspended solids over time.

Flocculation

Addition and mixing of the DADMAC/PAM treatment resulted in rapid flocculation. Within minutes, floccules, aggregates of suspended solids, formed and either floated to the top or sank to the bottom of the column, depending on the amount of air entrapment. Larger doses of flocculant were less efficient in reducing concentration of phosphorus as time passed (Figure 2). The decreased efficiency was most likely related to higher surface area of the solids due to microbial breakdown. At flocculant concentrations of 1.3 mg/L and 3.73 mg/L, waiting for settling to occur has little direct advantage; consequently, the earlier the flocculant is added, the greater the potential phosphorus removal..

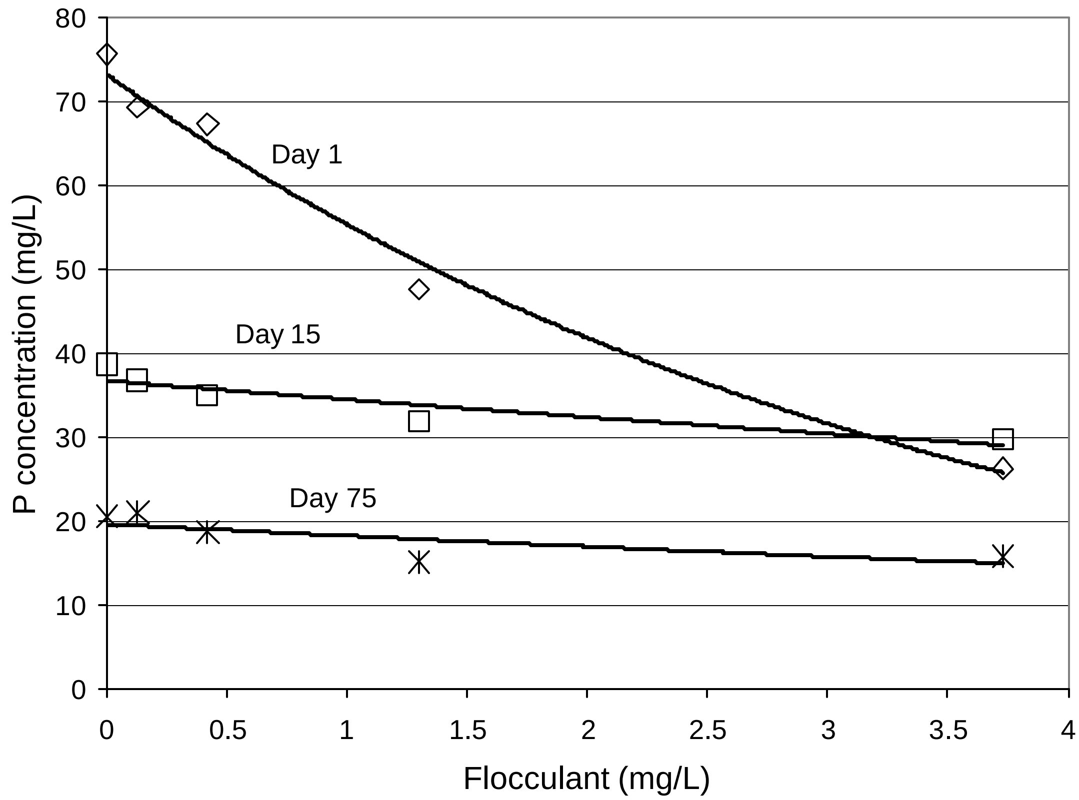

Figure 2: Changes in phosphorus (P) with increasing flocculant added to effluent wastewater.

Precipitation

When effluent pH was raised > 9 with ammonium hydroxide, soluble phosphorus and calcium declined considerably (Figure 3). The concentrations of magnesium did not show a significant change after the pH was raised so the reduction in phosphorus was the result of the precipitation of one or a combination of numerous possible calcium phosphates compounds.

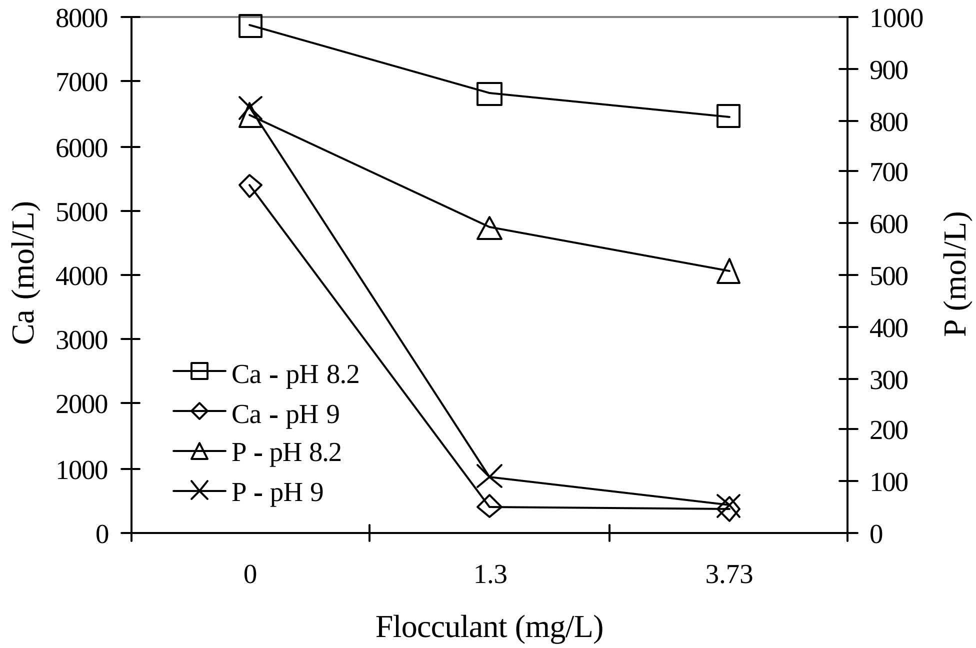

Figure 3: Calcium (Ca) and phosphorus (P) concentrations with pH changes over different flocculant concentrations

From the XRD patterns of the precipitates, several possible minerals were identified. Monohydrocalcite ($CaCO_3 * H_2O$), calcium phosphate ($Ca_3(PO_4)_2$, and struvite (magnesium ammonium phosphate) appear to in the precipitate. Common salts such as sylvite (KCl) and halite (NaCl) also were found in the dried solution.

Solids

The water holding capacity for the flocculated solids was about 0.2 kg water / kg solid greater than the water holding capacity of the settled solids (Figure 4). This observation is consistent with the flocculant removing more of the fine suspended particles from the effluent wastewater.

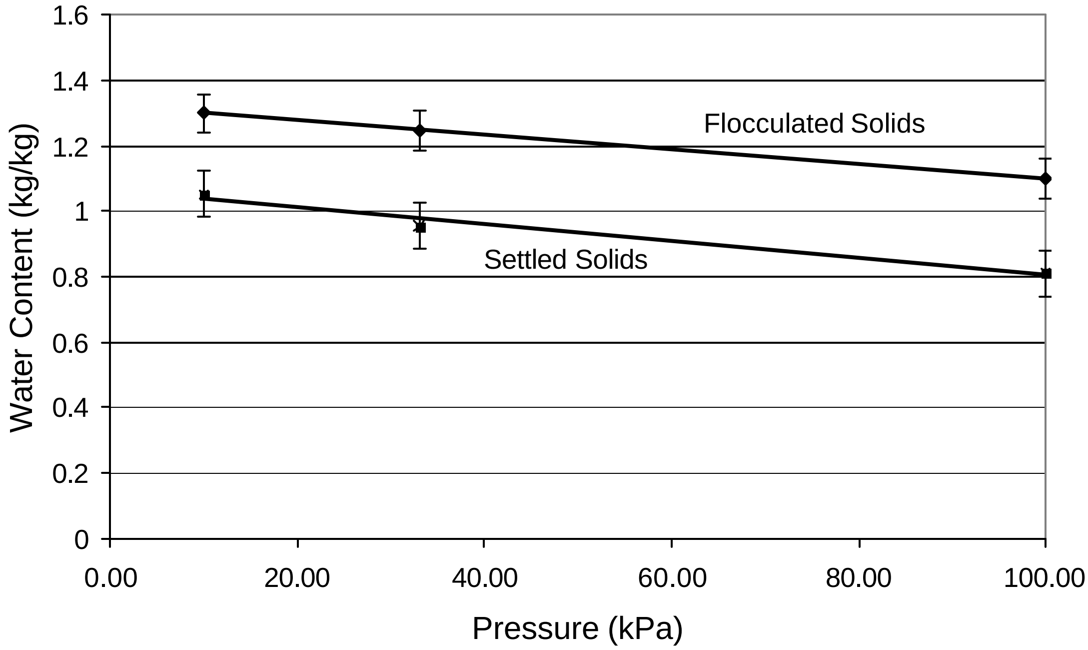

Figure 4: Water holding capacity of the flocculated and settled solids

Conclusion

Combining flocculation and precipitation, dairy farmers can reduce the amount of phosphorus applied to their fields in the form of irrigation. Also, a solid product with concentrated amounts of phosphorus and other nutrients can be produced and transported to a composting facility. These flocculated solids, once composted and applied to gardens, lawns, or landscapes, might increase the aeration and water holding capacity of the soil. As microorganisms in the soil decompose the solids, nutrients will become available to plants. The precipitate removed from the effluent also might be applied to soils to increase fertility.

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