Conservation of Nitrogen via Nitrification and Chemical Phosphorus Removal for Liquid Dairy Manure

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Thesis submitted to the faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
In
Biological Systems Engineering

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November 27, 2007
Blacksburg, VA

Keywords: Nitrification, nitrogen conservation, chemical phosphorus removal, alum, ferric chloride, cationic polyacrylamide, dairy manure

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Abstract

The objectives of this study were to (1) determine an intermittent aeration strategy that could be used to conserve nitrogen (N) via nitrification in dairy manure, (2) determine the effect of recycled flush water on the bio-availability of N during nitrification, and (3) determine effective and economical dosages of chemicals to remove phosphorus (P) from liquid dairy manure.

Intermittent aeration strategies, defined in terms of time the aerator is on and off (ON h:OFF h), could be used to conserve N in dairy manure. Testing of four treatments (continuous aeration [100%], 1h:0.33h [75%], 1h:0.67h [60%], and 1h:1h [50%]) showed that only treatments using air provided for 100% and 75% of the time could support nitrification. The 100% and 75% aeration treatments conserved an average of 38% and 25% of influent total ammonia nitrogen (TAN) as nitrite-N+nitrate-N, respectively. Less than 2% of influent TAN was conserved using 60% and 50% treatments. The effect of manure handling technique on N bioavailability and nitrification was tested using flushed and scraped dairy manure. Nitrification was inhibited in scraped manure.

Four aluminum- and iron-based salts and five cationic polyacrylamide polymers were evaluated for P removal using jar tests. Ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2[SO_4]_3 \cdot 13H_2O$, alum), and Superfloc 4512 were selected for further study. Polymer addition enhanced floc size and improved P removal. Treatment of manure (0.89% total solids) from Tank 2 at Virginia Tech's dairy using either $FeCl_3$ or alum in combination with polymer resulted in more than 90% P removal. Chemical treatment and transport of P-rich sludge from a 2,270 m^3 storage tank would result in an estimated 40% cost savings over transport of the entire manure volume offsite for land application elsewhere.

The manure treatment strategies tested provide some solutions to dairy farmers regarding adjustment of N:P ratios so that manure can be applied to meet nutrient needs of crops while adhering to regulations set forth by nutrient management plans.

Acknowledgements

I would like to thank my adviser, Dr. Arogo, for his help, humor, and encouragement throughout this research. Thanks also go out to my committee members, Dr. Knowlton and Dr. Love, for their help and resources. The assistance and support from the entire dairy manure group is appreciated.

I am very grateful to Monika Corbett who faithfully helped me with reactor sampling, manure collection, sample analysis, and disaster cleanup. I would also like to thank Julie Jordan for her help and the use of her laboratory. I appreciate the help from Dr. Mariger and Allen Yoder during reactor construction. I would also like to thank the BSE staff for their assistance.

Thanks go to Jody Smiley for her help with IC analysis. I am also very appreciative of Karen Hall for all of the sample analysis she and her crew did for my project. Thanks also go to Athena Tilley for mineral analysis.

I am very appreciative of Shane Brannock and the folks at the Virginia Tech dairy complex. They have patiently answered my questions and helped me out on many occasions.

I would like to thank Vic Johnson at Kemira Water for providing polymer samples for my jar testing and Tim Rensch from Integrity for his assistance concerning manure treatment.

Finally, I would like to thank my family, especially my parents, who have always encouraged me and supported me in my academic pursuits. I am so blessed to have them. I am also very grateful to my husband. His electronics know-how and muscle have come in handy quite a few times during my research, but I am most appreciative of his love and support. I am also thankful to God for going with me every step of the way, now and always.

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Chapter 1: Literature Review

1 Introduction

Much research has been done in the areas of nitrogen (N) and phosphorus (P) removal from swine manure (Cheng and Liu, 2001; Head et al., 2005; Obaja et al., 2003; Ridenoure, 2004; Vanotti et al., 2003); fewer studies have examined the application of similar treatments to dairy manure. Further, while many studies have focused on complete N removal, this study focused on conservation of N in a non-volatile form, nitrate, to preserve the fertilizer value of dairy manure. This study implemented intermittent aeration strategies to conserve N while minimizing energy costs and a chemical dosing plan to reduce P concentrations. The product of N conservation and P reduction will be a "designer dairy manure" that is a valuable fertilizer with N:P ratios adjusted to meet crop nutrient requirements. The objectives of this study were to

1. develop a cost effective treatment strategy to conserve N in liquid dairy manure by determining the minimum aeration to non-aeration periods required to conserve or concentrate N in the manure;
2. determine the effects of recycled flush water on N bioavailability and nitrification;
3. evaluate the suitability of using chemicals to reduce P concentrations in liquid dairy manure with specific application to the Virginia Tech dairy.

1.1 Manure nutrients

As animal production increases to meet the food needs of a growing world population, so does manure production; therefore, manure management becomes imperative to the sustainability of our environment. Manure is a good source of macronutrients (N, P, and potassium [K]) and minor nutrients (calcium [Ca], magnesium [Mg], sulfur [S], zinc [Zn], copper [Cu], manganese [Mn], sodium [Na], and aluminum [Al]). Usually nutrients in manure are recycled through land-application as a fertilizer. This is an economical alternative to purchasing inorganic fertilizer or disposing of manure in ways that do not utilize the nutrients in the manure.

When manure is applied according to N-based nutrient management plans, over-application of P occurs because manure contains more P than the crops need. P accumulates in the soil due to manure application over time if a nutrient management plan is not followed or is N-based rather than P-based. Losses of P in runoff become more likely as soil reaches its maximum P-holding capacity (Czymmek et al., 2005). P-based nutrient management plans match manure application to the P requirements of the crop. Application of P according to crop needs is intended to reduce loss of P via leaching and runoff. However, P-based management plans limit the amount of manure that can be land applied as fertilizer per unit land area; this results in excess manure and nutrients that may require treatment or export to other farms (Czymmek et al., 2005).

1.2 The need for manure treatment

The encroachment of urban development into formerly agricultural areas and the changing structure of dairy farming in America are contributing to the need for manure treatment. Although the number of dairy operations decreased by 21% from 1997 to 2001 along with a small (1.4%) reduction in dairy cattle numbers, U.S. milk production increased by 6% (USDA-NASS, 2002). Further statistics from the USDA confirm that the current agricultural trends are towards larger operations and higher production (Figure 1).

Dairy operations and other animal feeding operations are centers for high nutrient concentrations. Although manure from these operations can be land applied as fertilizer, this practice is limited by nutrient management plans, the available land area, and the economics of manure transport. The crop area available for application of manure nutrients is becoming more limited due to increasing rural development, urban sprawl, and decreasing farm size.

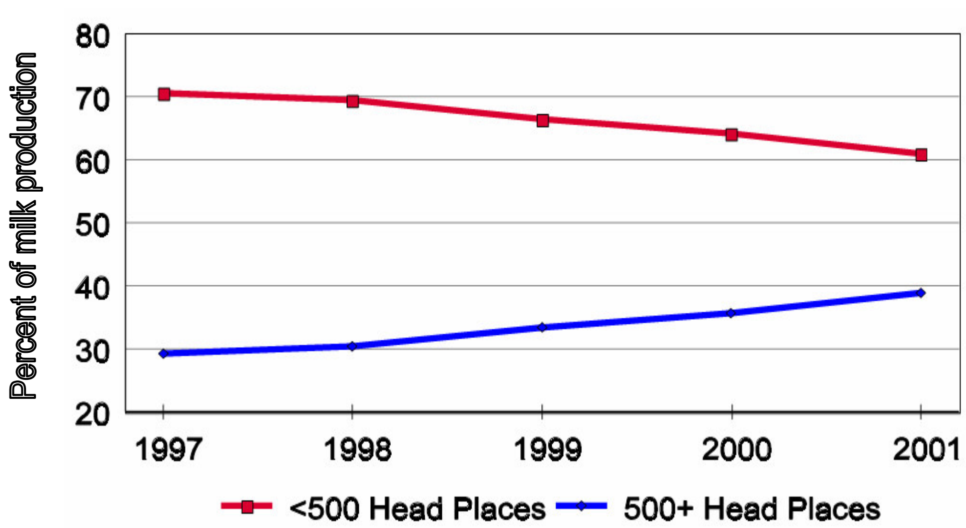

Figure 1. U.S. annual milk production distribution based on dairy cattle numbers per farm (USDA-NASS, 2002)

To handle large manure volumes with high nutrient concentrations, manure can be dewatered (to reduce transportation costs) and applied at nutrient deficient locations off the farm or nutrient concentrations can be chemically or biologically altered so that larger quantities of manure can be land-applied as fertilizer onsite. Chemical or biological treatment is a desirable solution enabling manipulation of nutrient ratios by either conserving N or removing P to match the manure to the needs of the crop.

1.3 Pathways of nutrient loss and environmental concerns

In general, cow manure as excreted contains N and P at a ratio of 6:1 (ASABE, 2005). However, N is subject to loss via volatilization, denitrification, runoff, and leaching (Eghball and Power, 1994; Power, 1994). N loss decreases the fertilizer value of the manure and can impact both air and water quality. The volatilization of ammonia (NH_3) from livestock manure contributes to fine particulate matter in the atmosphere (Panetta et al., 2005). In animal housing, ammonia can cause respiratory problems for both people and livestock. Environmental impacts arise when NH_3 reacts with other compounds in the air to create atmospheric haze and acid rain (Rumburg et al., 2004). When deposited in aquatic ecosystems, NH_3 is toxic to fish and can contribute to eutrophication; NH_3 also consumes dissolved oxygen thus depriving aquatic organisms of the oxygen they need to survive (Obaja et al., 2003).

Implementation of N conservation practices in manure will reduce N loss as NH_3 gas and maintain a high N:P ratio. However, N conserved as nitrate (NO_3^-) can also have negative environmental consequences. NO_3^- in runoff can lead to eutrophication, and leaching of NO_3^- can cause groundwater contamination. NO_3^- in drinking water is a problem because NO_3^- can cause irritation of the bladder and gastro-intestinal tract. More severe cases of NO_3^- toxicity to the body are characterized by nausea, vomiting, and hemorrhagic diarrhea (Strauch, 1987). NO_3^- in drinking water is especially toxic to babies; NO_3^- is reduced to nitrite (NO_2^-) which, when present in the body, causes hemoglobin to be converted to methemoglobin (Greer and Shannon, 2005). Methemoglobin, unlike hemoglobin, cannot carry oxygen resulting in a life-threatening condition called methemoglobinemia. The goal of N-based nutrient management is to apply manure according to the crop's N needs in order to reduce the leaching and runoff of excess NO_3^- which can lead to the problems just described.

Accumulation of P and minor nutrients that are present in manure can also cause soil and water problems. P runoff can contribute to eutrophication of bodies of water. High concentrations of heavy metals such as Zn and Cu cause soil toxicity resulting in reduced soil microbial biomass and increased metal accumulation in plants (Brookes and McGrath, 1984; Singh and Agrawal, 2007). Runoff of metals into waterways can also cause impairment of aquatic communities (Kashian et al., 2007).

2 Nitrogen Conservation

Nitrification can be used to minimize NH_3 volatilization by conserving N through the conversion of NH_3 to non-volatile NO_3^-. In many biological nutrient removal systems, nitrification and denitrification are used in series or simultaneously to obtain complete N removal from NH_3 to dinitrogen gas (N_2). Although N removal is not the goal of this study, N removal by denitrification is inevitable, particularly as low intermittent aeration is used to minimize the cost of energy required for treatment.

2.1 Biological processes for N transformation

Nitrification, denitrification, and simultaneous nitrification and denitrification are typical biological N removal processes. This study will focus on nitrification as a means to conserve N in dairy manure.

2.1.1 Nitrification

Nitrification is a two-step aerobic process by which microorganisms convert NH_3 to NO_3^-. First, ammonium (NH_4^+) is oxidized to NO_2^- by ammonia oxidizing bacteria. The second step is the oxidation of NO_2^- to NO_3^- by nitrite-oxidizing bacteria. The nitrification energy reaction is shown in Equation 1 (Shuler, 1992).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad [1]$$

It is important to note that the stoichiometric ratio of NH_4^+ to NO_3^- in this equation is one to one; the goal of complete NH_4^+ conversion to NO_3^- is practical for this reaction. During nitrification, 4.57 g O_2 and 7.14 g alkalinity as $CaCO_3$ are consumed per gram of NH_4^+-N oxidized (WEF, 2006). Metcalf & Eddy (1991) report that nitrification can occur in wastewater at a dissolved oxygen (DO) concentration of at least 1 mg/L and a pH range of 7.5 to 8.6. However, ongoing studies by Gilmore et al. (In press) have shown that nitrification can occur quite readily at DO as low as 0.3 mg/L.

2.1.2 Denitrification

As previously stated, denitrification is not always a desired reaction because it does not contribute to N conservation. However, treatment strategies involving different aeration and non-aeration periods will sometimes produce conditions that are favorable for denitrification.

Denitrification converts NO_3^- to harmless N_2. Usually heterotrophic microorganisms reduce NO_3^- to N_2 using NO_3^- as an electron acceptor in an anoxic environment. Intermediate products of NO_3^- reduction are the gases nitric oxide (NO) and nitrous oxide (N_2O); like N_2, these products may contribute to N loss. The carbon source, which is organic matter in manure, serves as the electron donor, and denitrification will consume 2.86 g COD/g N where COD is chemical oxygen demand (Metcalf & Eddy, 1991). For denitrification, the pH should typically be from 7 to 8 depending on the type of microorganism at work. A generalized form of the denitrification reaction is as follows:

$$NO_3^- + carbon\ \ source + H^+ \rightarrow N_2 + CO_2 + H_2O \qquad [2]$$

2.1.3 Simultaneous nitrification and denitrification

Simultaneous nitrification and denitrification (SND) is a process that is enabled by the presence of anoxic or anaerobic zones within a reactor or within flocs in the reactor (Daigger and Littleton, 2000; Münch et al., 1996). This is another undesired reaction that may contribute to N loss during treatment.

Though it was once believed that autotrophic bacteria were the sole nitrifiers and that denitrification required anoxic conditions, studies have found heterotrophic microorganisms that nitrify and denitrifiers that nitrify or denitrify during aerobic cycles (Castignetti and Hollocher, 1984; Münch et al., 1996; Robertson et al., 1988; Zhao et al., 1999). Zhao et al. (1999) found that low DO and high organic loading provided favorable conditions for heterotrophic denitrifiers since these conditions typically inhibit autotrophic nitrification. They also reported that SND was responsible for 50% of N removal from municipal wastewater based on influent total N; only 15% of N was removed under fully aerobic conditions (Zhao et al., 1999). Münch et al. (1996) demonstrated aerobic denitrification in sequencing batch reactors with municipal wastewater. In this system, aerobic denitrification was a significant pathway for N removal; it was proposed that at a DO of 0.5 mg O_2/L, the nitrification and denitrification rates would have been equivalent thus enabling complete SND. Although SND is favorable for complete N removal in wastewater treatment, SND results in N loss from an aerated treatment system intended for N conservation.

2.2 Reactor design

The environmental conditions imposed on a microbial community in a reactor determine the type of treatment that will take place. The type of reactor, DO levels, the presence or absence of anaerobic or anoxic zones, and solids retention time (SRT) are parameters that can be manipulated to influence which biological reactions take place.

The two common bioreactor configurations are suspended growth and attached growth. Suspended growth systems allow microorganisms to grow freely in suspension, but these systems require mixing to prevent biomass from settling. Continuous stirred tank reactors, batch reactors, and perfect plug-flow reactors are examples of the suspended growth design. Attached growth systems consist of biofilm growing on a solid support. Structural supports such as plastic packing are used in packed towers or trickling filters; fluidized beds and rotating biological contactors are two other types of attached growth systems that contain media and discs, respectively, for biofilm growth (Grady et al., 1999; WEF, 1998). Microorganisms become attached to the packing (or media) and to each other by excretions of extracellular polymers. Biofilms are irregular and nonuniform structures with both active fractions and debris (Grady et al., 1999). Debris accumulates near the surface of the media while the active fraction grows farther from the media and closer to the nutrient-rich bulk liquid in the system.

SRT is an important criterion when designing a suspended growth nitrification reactor. SRT is the length of time particulate matter (e.g. biomass) stays in the reactor. The recommended SRT for nitrification in an aerobic/anoxic system is 2-15 days depending on temperature (Grady et al., 1999). At room temperature (20°C), minimum aerobic SRT is approximately 2 days. A safety factor of 1.5 is recommended to avoid washout. Washout occurs when the SRT is not long enough to allow the microbial community of interest to become established before being wasted from the reactor. One advantage of attached growth systems compared to suspended growth systems is that the former encourages the development of a nitrifying microbial community with a theoretically infinite SRT thus reducing concern over washout.

While attached growth systems are generally more difficult to model than suspended growth systems due to the complex nature of biofilms, some simplifying assumptions can be made. To understand treatment within the attached growth systems, it is helpful to assume that the system is at steady-state. This implies that biomass will be sloughed off at the same rate as it grows (Grady et al., 1999); therefore, detached biomass also contributes to substrate (or nutrient) removal as it passes from the system as part of the effluent. Flow through the system is also assumed to exhibit perfect plug-flow characteristics; this means that liquid is assumed to move through the length of the column without intermixing with liquid fed earlier or later.

2.3 Intermittent aeration

In manure or wastewater treatment, aeration is used to reduce biochemical and chemical oxygen demands, reduce solids, conserve or remove N via nitrification or combined nitrification/denitrification, and prevent the odors caused by products of anaerobic digestion (Grady et al., 1999). Continuous aeration is the conventional treatment used to provide air to prevent odor and maintain the DO concentration required for nitrification (Burton, 1992; Westerman and Zhang, 1997). However, aeration required for nitrification is energy intensive and costly. For example, Burton (1992) reported that the cost of treating swine manure using continuous aeration was as high as 53% of the profits per pig produced.

Studies on swine manure have shown that intermittent aeration, which involves the use of aeration and non-aeration periods, can lower energy requirements and lead to more effective N removal via nitrification and denitrification (Cheng and Liu, 2001; Head et al., 2005; Mota et al., 2005; Ridenoure, 2004; Yang and Wang, 1999). Ranges of aeration to non-aeration periods resulting in 50 to 85% energy savings have been used to treat anaerobically pretreated swine manure (from a lagoon) with influent total ammonia N (TAN) concentrations of 140 to 220 mg N/L (Head et al., 2005; Mota et al., 2005; Ridenoure, 2004). These studies have shown that aeration for 50% of the time during a 2 h cycle achieved more than 90% TAN removal. Combined NO_2^--N and NO_3^--N production varied from 20 mg/L (Ridenoure, 2004) to 130 mg/L (Head et al., 2005). Aeration 25% and 20% of the time during 2.5 h and 5 h cycles, respectively, achieved about 86% TAN removal with combined effluent NO_2^--N and NO_3^--N concentrations less than 25 mg/L (Ridenoure, 2004). A full scale study of intermittent aeration on swine wastewater by Yang and Wang (1999) resulted in 92% total N removal using aeration for 50% of the time during a 6 h cycle; NO_3^--N was less than 3 mg/L in the treated effluent. Maximum effluent NO_3^--N (343 mg/L) was produced using aeration for 83% of the time during an 11 h cycle which was the highest intermittent aeration strategy tested in that study (Yang and Wang, 1999).

Li and Zhang (2004) used a sequencing batch reactor to study the effects of intermittent aeration on N conservation and N removal from dairy manure. The influent contained a TAN concentration of 690 mg N/L after urea addition. The intermittent aeration treatment provided aeration for 63% of the time during a 12 h cycle; the continuous aeration treatment did not aerate during the 1.5 h settle and decant period. TAN removal was 93% and 95% using continuous and intermittent aeration, respectively. Both treatments produced more than 520 mg/L of combined NO_2^--N and NO_3^--N. Based on these results, Li and Zhang (2004) recommended intermittent aeration for a 30% energy savings compared to continuous aeration for achieving N conservation.

Intermittent aeration can lead to N loss either through incomplete nitrification (causing NH_3 volatilization), incomplete denitrification (loss as NO or N_2O), or complete denitrification (loss as N_2) (Westerman and Bicudo, 2002; Zhang et al., 2006). SND by means of micro-anoxic zones in the reactor or within floc is also a probable pathway that could contribute to N loss (Zhao et al., 1999). Studies are needed to determine the appropriate aeration to non-aeration intervals to minimize cost and maximize NO_3^- production.

2.4 Nitrogen balance

Manure as excreted consists primarily of organic N and NH_3-N. Though the goal of this study is to achieve maximum conversion of TAN to NO_3^--N, some N will inevitably be lost as NH_3 gas, N_2, NO, or N_2O. Some N will be used to form biomass within the reactor. A N balance based on the available data will help determine how much N is unaccounted for and what forms of N may have been lost. Figure 2 shows the forms of N will enter and exit the treatment system.

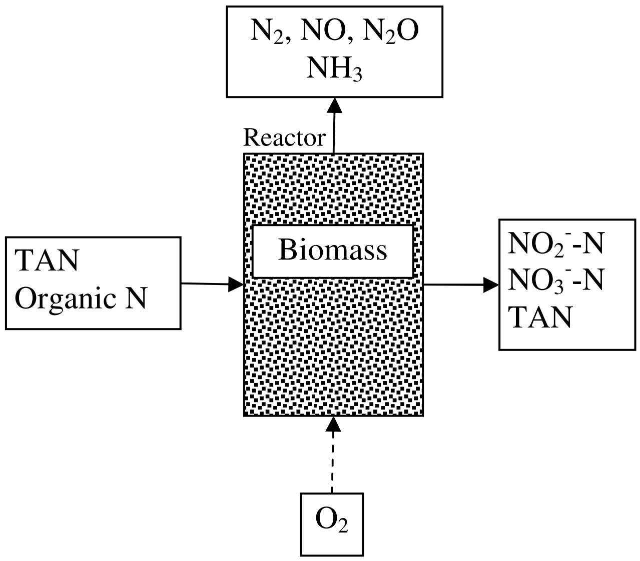

Figure 2. Diagram of N balance including forms of N entering reactor and possible forms exiting

Influent and effluent TAN, total Kjeldahl nitrogen (TKN), NO_2^--N, and NO_3^--N are easily measured so that influent and effluent total nitrogen (TN) can be calculated. Before estimating how much N may have been lost in gaseous forms, it is necessary to first estimate N needed for biomass growth. Grady et al. (1999) elucidated the heterotrophic nitrogen requirement (NR) in an activated sludge system for municipal wastewater as follows:

$$NR = 0.087\left[\frac{(1+f_D \cdot b_H \cdot \Theta_c)Y_{H,T}i_{O/XB,T}}{1+b_H \cdot \Theta_c}\right] \qquad [3]$$

where f_D = fraction of active biomass contributing to biomass debris (0.20 mg TSS/mg TSS);
b_H = heterotrophic decay coefficient (0.18 day^{-1});
Θ_c = solids retention time (days);
$Y_{H,T}$ = true heterotrophic growth yield (mg TSS/mg COD); and
$i_{O/XB,T}$ = mass COD per mass biomass as TSS (1.2 mg COD/mg TSS).

Typical stoichiometric and kinetic parameter values are given for municipal wastewater at 20°C. Given the high total suspended solids (TSS) concentrations in influent manure, it may not be possible to calculate true yield using the following simplistic equation since much of the TSS is not biomass:

$$Y = \Delta TSS/\Delta COD \qquad [4]$$

Assumed values can often be used for heterotrophic growth yields in municipal wastewater treated in activated sludge processes; typical values are 0.5 mg biomass TSS/mg COD removed and 0.4 to 0.8 mg VSS/mg BOD_5 (Grady et al., 1999; Metcalf & Eddy, 1991). It may be appropriate to assume a lower heterotrophic yield for microbial growth in manure.

Whichard (2001) obtained an average Y_H of 0.42 mg biomass COD/mg substrate COD for dairy manure; this is equivalent to 0.35 mg TSS/mg COD. The equation for NR also requires Θ_c, which is the SRT. Since an attached growth reactor does not have an easily measurable SRT, an assumption must be made that accounts for the long retention time of biomass attached to the reactor's media.

Having an estimate for the heterotrophic N requirement and measured concentrations of influent and effluent N forms, the amount of unaccounted-for N can be determined. Assuming the values from Grady et al. (1999) for domestic wastewater at 20°C and a 20 d SRT, NR is calculated to be 0.014 mg N used/mg COD removed. Measured influent and effluent COD values will provide the ΔCOD needed to estimate N consumed for heterotrophic biomass growth in each reactor.

Nitrifier yield during nitrification is typically in the range of 0.06 to 0.2 g VSS/g NH_4^+-N oxidized (EPA, 1993). Nitrogen consumed to produce nitrifier biomass is generally less than 2% of NH_4^+-N nitrified and is usually ignored as an N removal pathway (WEF, 2006).

2.5 Nitrification inhibition by Cu

Heavy metals have been shown to inhibit nitrification in wastewater (Hu et al., 2002; Hu et al., 2004; Madoni et al., 1996). Inhibition by Cu is a specific concern since copper sulfate solution is used at the Virginia Tech dairy for disinfection of cow hooves. Cu inhibition is known to occur at 3.0 mg Cu/L (N. Love, personal communication, 27 November 2007). In a wastewater containing a mixed liquor suspended solids concentration of 1500 mg/L, 26% nitrification inhibition occurred in the presence of 5 mg Cu/L (Kim et al., 2006). Concentrations of 0.01 mM of Cu^{2+} (0.6 mg Cu/L) have been shown to cause short-term inhibition (Hu et al., 2003). The same concentration caused increased inhibition with prolonged exposure.

3 Phosphorus Removal

Biological and chemical methods are both viable options for P removal. Though achieved differently, both processes reduce P in the bulk treatment liquid and produce a P-rich sludge.

3.1 Chemical phosphorus removal

Chemical precipitation is an effective treatment which is known to decrease suspended solids, biochemical oxygen demand (BOD), COD, and nutrients in wastewater effluent due to the reaction of additives with solids in the waste (Metcalf & Eddy, 1991). This treatment can be also applied to remove P from liquid manure. Several studies have been done to evaluate the effects of chemicals on solid-liquid separation and nutrient removal from swine manure (Vanotti et al., 2002; Vanotti et al., 2003; Zhang and Lei, 1998) and dairy manure (Barrow et al., 1997; Sherman et al., 2000; Zhang and Lei, 1998).

3.1.1 Chemical precipitation

Chemical P removal occurs due to the reaction of cations with phosphate to form metal phosphate precipitants. Typical compounds used for chemical P removal include aluminum sulfate ($Al_2(SO_4)_3$, called alum), aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), lime ($Ca(OH)_2$) (Dentel et al., 1993; Metcalf & Eddy, 1991). Soluble P is transformed into an insoluble precipitate upon the addition of a cation such as aluminum (Al^{3+}), iron (Fe^{3+}), or calcium (Ca^{2+}) (Metcalf & Eddy, 1991; WEF, 1998). Ions in wastewater, such as hydroxide, carbonate ions, and phosphate ions, react with metal ions additives to form flocs (Metcalf & Eddy, 1991); flocculation involving metal salts is typically referred to as coagulation. Flocs collect particulates as they sink and settle into the biomass which is removed via sludge wastage. The general equations for phosphate precipitation using Al, Fe, and Ca-based salts, adapted from Metcalf & Eddy (1991) is as follows:

$$Al^{3+} + H_nPO_4^{n-3} \Leftrightarrow AlPO_4 + nH^+ \qquad [5]$$

$$Fe^{3+} + H_nPO_4^{n-3} \Leftrightarrow FePO_4 + nH^+ \qquad [6]$$

$$10Ca^{2+} + 6PO_4^{3=} + 2OH^- \Leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \qquad [7]$$

Despite the 1:1 ratio of metal to P (which is true in the cases of aluminum and iron), wastewater characteristics and water properties such as alkalinity and pH have a significant effect on the reactions above. For instance, carbonate groups, hydroxide ions, and other ligands compete with phosphate groups to react with the metal ions. In practice, the metal to P ratio is rarely 1:1 and bench-scale testing is recommended for determining actual metal dosages (Metcalf & Eddy, 1991).

Chemical P removal produces more primary sludge than biological P removal due to the added mass of the chemical (Metcalf & Eddy, 1991). Compared to biological P removal, the chemical method has higher operating and maintenance costs and requires larger areas for utilization of wasted sludge due to chemicals contributing to sludge volume (Metcalf & Eddy, 1991).

3.1.2 Polymers

Precipitation can be improved by using a two-step process involving coagulation and flocculation. Coagulation occurs by means of the metal ions previously mentioned. Polymers used as secondary additives improve flocculation. Organic polymers used in wastewater treatment are typically cationic and function by destabilizing negatively charged colloidal particles typically found in wastewater (Metcalf & Eddy, 1991). Anionic and neutral polymers are also available; these types of polymers are adsorbed at sites on multiple wastewater particles thus “bridging” the particles. The organic polymers consist of chains of monomers in straight or branched configurations; functional groups along the chain give the polymer its charge (Dentel et al., 1993). High molecular weight polymers combine coagulation and bridging action to facilitate flocculation (Metcalf & Eddy, 1991; Vanotti et al., 2002). Polyacrylamides (PAMs) are a group of polymers commonly used for wastewater treatment. PAMs are neutral but are aminomethylated to gain a positive charge (Dentel et al., 1993). The structure of an acrylamide monomer is shown in Figure 3.

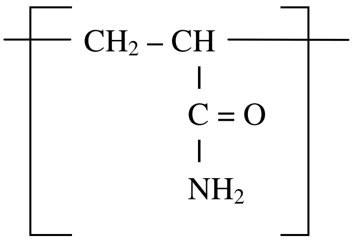

Figure 3. Structure of an acrylamide monomer (Dentel et al., 1993)

Polymers are available in several forms: liquid polymer solutions, liquid emulsion products, and dry forms (Dentel et al., 1993). Liquid solutions consist of polymer dissolved in water. Active polymer concentrations are very low in liquid solutions since high molecular weight polymers are very viscous. The low-concentration product is easy to use, but shipping costs associated with large quantities are not desirable. Polymer emulsions are more stable and more highly concentrated than liquid solutions due to formulation in oil with additives for stability. Polymer is also available as a powder or in other dry forms. These are the most concentrated forms (~95% active product) and are the most economical in terms of shipping. However, proper polymer make-up using dry forms is more difficult. Fish eyes, which are clumps of polymer that will not dissolve, can prevent one from obtaining a homogenous polymer solution.

3.1.3 Studies of chemical P removal

Barrow et al. (1997) evaluated the effectiveness of nutrient and solids removal from dairy manure using a variety of Fe and Ca-based additives. Manure was adjusted to have total solids (TS) concentrations of 0.5, 1.0, or 1.5%. In this early test, ferric salts were found to be more effective than ferrous and Ca additives. At a dose of 278 mg Fe/L using $FeCl_3$, 88% of the total P was removed from a dairy manure containing 1.0% TS.

Zhang and Lei (1998) examined the use of chemicals for solid-liquid separation of swine and dairy manure. The researchers found that there was an optimum $FeCl_3$ dosage for each TS concentration that was tested. Flocculation was tested using varying concentrations of metal ion (0 to 2000 mg/L $FeCl_3$ or 0 to 690 mg/L as Fe) and Magnifloc 255G (0.0025 to 0.125%). Alum was tested using dosages of 400 and 800 mg/L (63 and 126 mg/L as Al). P removal was enhanced when a metal salt and polymer were used together because floc size increased such that particles were retained on a 20-mesh sieve. Flocs produced by metal salts alone were too small to be retained on the sieve.

Vanotti et al. (2002) tested the effects of Magnifloc 234GD, a moderately charged, high molecular weight PAM, on solid-liquid separation by screening in swine manure. The TS of flushed swine manure increased from 4.3 to 24.8 g/L as the pigs grew over the three-month testing period. PAM was dosed at 20 mg/L increments from 0 to 140 mg/L. Dosing was increased to 180 mg/L during the final test with manure at 24.8 g/L TS. Treated liquid was screened, and the solids and nutrient concentrations were measured in the treated liquid fraction.

Treatment resulted in an N:P ratio increase from 5:1 to 11:1 resulting from more than 70% total P removal at PAM doses greater than 100 mg/L (Vanotti et al., 2002).

Sherman et al. (2000) tested the effects of chemical and polymer addition on simulated dairy manure prepared at specific TS concentrations. Alum was tested using dosages from 0 to 317 mg Al/L and $FeCl_3$ was dosed from 0 to 376 mg Fe/L. Two polymers, Magnifloc 234GD and C-494, were dosed using 0 to 4 mg PAM/L, which are far lower concentrations than the 0 to 200 mg PAM/L doses tested by Vanotti and Hunt (1999) in swine manure. Alum provided better P removal than $FeCl_3$ and was recommended as an economical treatment option. Selected alum doses of 0, 53, and 106 mg Al/L were then used in a field test involving batch treatments of 3,500 L of flushed manure. The flushed manure had previously passed trough a sand trap, sedimentation basin, screen, second sedimentation basin, and storage pond before being pumped into the batch treatment reactor. P removal was higher during field tests than laboratory tests because the TS was 0.3 to 0.4% in the field compared to 1.0% in prepared manure for laboratory testing. Treated effluent manure from the field test contained less than 10 mg P/L using the 106 mg Al/L dosage of alum.

Economics are an important factor in chemical treatment of dairy manure. Sherman et al. (2000) analyzed the cost of chemically treating effluent from a dairy producing 800,000 L/d of dilute flush water. Cost recovery in the range of 13 to 59% of expenses could be obtained using an alum dosage of 53 mg Al/L or 18 to 26% using a $FeCl_3$ dosage of 161 mg Fe/L. However, cost recovery depends on the current market value of P fertilizer. The monetary value of P retained in sludge for fertilizer is usually far less than the cost of chemicals used. Improvements in efficiency of P removal must be made so that chemical costs can be reduced making this a more practical treatment technology.

Dosing recommendations for metal salts vary widely. In municipal wastewater treatment, the EPA (1987) has suggested weight ratios of 3.0 Fe:P and 2.0 Al:P for 95% P removal which convert to 1.7:1 and 2.3:1, respectively, as mole ratios. Higher Al:P and Fe:P ratios have been used for treatment of manure due to differences in wastewater quality such as higher organic content. Vanotti and Hunt (1999) used a 2.5:1 Al:P molar ratio for the treatment of swine manure based on preliminary tests that showed this dosing would precipitate more than 90% of P. Oh et al. (2005) used Al:P ratios up to 7.5:1 for dairy manure containing 4% TS. The 7.5:1 ratio resulted in 98% removal of dissolved reactive phosphorus (DRP) from the supernatant compared to 95% removal using a ratio of 5:1; the lower ratio was considered to be optimal.

Several conclusions can be drawn from the studies involving use of chemicals and polymers for treatment of swine and dairy manure. Fe-based chemicals are more effective than Ca based chemicals (Barrow et al., 1997). Al-based chemicals are more effective than Fe-based chemicals and maintain their effectiveness at lower dosages than Fe-based salts (Sherman et al., 2000; Vanotti and Hunt, 1999). As the TS concentration of manure increases, higher chemical dosages are needed to achieve P removal (Oh et al., 2005; Vanotti et al., 2002), and polymer effectively increases P removal when used in combination with chemicals (Vanotti et al., 2002; Zhang and Lei, 1998).

3.1.4 Jar Testing

Wastewater and manure require different coagulant dosages due to varying concentrations of hydroxide ions, carbonate, and phosphate groups that compete for the metal ions. Jar testing is necessary to determine the proper dosage for the matrix being treated.

To conduct a jar test, the chemicals and polymers should be prepared in advance. Polymers may require aging so attention should be given to makeup instructions provided by the polymer supplier (Dentel et al., 1993). A representative sample of the matrix to be treated (500 to 1000 mL) is needed for each jar test. Chemical and polymer doses should be preloaded in beakers or syringes so that all jars can be dosed at nearly the same time. The jar test apparatus should be operated in a manner that simulates mixing as would occur in the full-scale treatment system. High speed mixing at 100 to 200 rpm is needed during chemical addition and mixing; flocculation is performed at 30 to 50 rpm (Dentel et al., 1993; Zhang and Lei, 1998).

3.1.5 Fate of bound P

One concern about the use of chemically treated manure is the availability of P when bound as Fe or Al phosphates (Hyde and Morris, 2004). Soil fertilized with Al- or Fe-treated biosolids has been shown to contain lower concentrations of water-soluble P (WSP) than soil fertilized with untreated biosolids during an incubation study (Maguire et al., 2001). By the end of the 51-day incubation period, soils with chemically treated biosolids had half the WSP as the soils with unamended biosolids. However, even chemically-treated biosolids resulted in some P increase compared to the control soil with no biosolid addition (Maguire et al., 2001).

Hyde and Morris (2004) studied P availability from water treatment residual (WTR) treated with an iron (Fe) based coagulant, Magnafloc 572C, and Magnafloc 1849A. P was added to the chemically treated WTR with the hypothesis that some of the added P would become bound but some would be available for the crop. Hyde and Morris (2004) predicted that available P would be released from the cationic polymer which forms weak electrostatic bonds with P. Lower release was expected from Fe due to the formation of strong covalent bonds. The validity of these hypotheses were not explicitly tested, but lower levels of P amendment were required to enable WTR to supply P to the fertilized crop than were originally hypothesized based on laboratory testing. This suggested that some P release from the Fe- and polymer-treated WTR was occurring, but P amendment was still required to ensure that nutrient needs of the crop were met.

3.2 Biological phosphorus removal

Biological P removal involves P accumulating organisms (PAOs) which accumulate P in excess of typical nutritional requirements. Under anaerobic conditions, PAOs use energy from phosphate bonds to take up acetate which is available as volatile fatty acids (VFAs) (Meyer et al., 2005; 1998); this carbon is stored as polyhydroxyalkanoates (Lee et al., 2001; Metcalf & Eddy, 1991; Obaja et al., 2003). This carbon requirement is easily fulfilled by allowing an anaerobic stage for P removal prior to alternating nitrification/denitrification cycles. It is also to the advantage of the PAOs to take up carbon during anaerobic conditions when heterotrophs do not have their electron acceptor (oxygen) available to be competitive. During an aerobic period, PAOs use stored energy to grow and to accumulate P as polyphosphate at levels beyond what they released during anaerobic conditions. Provided that excess P is available in the environment, this accumulation results in a net P removal known as enhanced biological P removal (EBPR) (1998).

Biological P removal may occur in a batch reactor undergoing intermittent aeration particularly if the first step is anaerobic. Treatment designs intended for P removal or N/P removal often use an anaerobic-aerobic or anaerobic-anoxic-aerobic tank sequences. Similar conditions may be obtained in an intermittently aerated reactor with proper cycle conditions.

Establishing an initial anaerobic period prior to nitrification or maintaining a short solids retention time (2.2 to 3.6 days) helps to prevent growth of autotrophic biomass. Longer SRTs enable nitrification which causes NO_3^-, an electron acceptor, to be returned in the recycle stream to the anaerobic reactor; consequently, heterotrophs can out-compete PAOs for the available carbon thus limiting net P uptake.

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Chapter 2: Effects of aeration time on nitrogen conservation in liquid dairy manure and the impact of nitrogen bioavailability on nitrification

Abstract

Volatilization of ammonia (NH_3) from dairy manure results in the loss of nitrogen (N), thus decreasing the fertilizer value of the manure. Loss of NH_3 by volatilization can be minimized by nitrification, which is a biological process that converts ammonium (NH_4^+) to nitrate (NO_3^-). Continuous aeration, typically used when nitrification of manure is desired, is energy intensive and costly. The objectives of this study were to (1) determine a less energy-intensive aeration strategy to conserve N in dairy manure, and (2) determine the effect of recycled flush water on the bioavailability of N during nitrification.

This study showed that an intermittent aeration strategy, defined in terms of time (ON h:OFF h), could be used to conserve N in dairy manure. Replications of continuous (100%), 1h:0.33h (75%), 1h:0.67h (60%), and 1h:1h (50%) aeration strategies showed that only strategies using aeration for 100% and 75% of the time were able to support nitrification. An average of 38% and 25% of influent total ammonia nitrogen (TAN) was conserved as nitrite-N (NO_2^--N) and nitrate-N (NO_3^--N) using 100% and 75% aeration. Less than 2% of influent TAN was conserved as NO_2^--N and NO_3^--N using aeration for 60% or 50% of time. Although the continuously aerated reactor was more effective at N conservation, the energy savings achieved by using less aeration may warrant use of an intermittent aeration strategy.

The effect of manure handling technique on N bioavailability was evaluated by comparing the extent of nitrification in flushed and scraped dairy manures. The chemical oxygen demand (COD) to total Kjeldahl nitrogen (TKN) ratio was 21 in scraped manure compared to 12 in flushed manure, and copper (Cu) was present in the scraped manure near the 3 mg/L concentration known to inhibit nitrification. Although one reactor achieved nitrification using continuous aeration, the level of scraped manure dilution used was not practical for comparisons with flushed manure regarding the effect of N bioavailability on nitrification.

Intermittent aeration can provide energy savings during nitrification of flushed manure. Differences in N bioavailability between scraped and flushed manure have yet to be compared due to nitrification inhibition by Cu and high COD in scraped manure.

Keywords: nitrogen, nitrification, intermittent aeration, dairy manure, nitrogen bioavailability

1 Introduction

As animal production increases to meet the food needs of a growing world population, so does manure production; therefore, manure management is imperative to the sustainability of our environment. Manure is a good source of macronutrients (N, P, and potassium [K]) and minor nutrients (calcium [Ca], magnesium [Mg], sulfur [S], zinc [Zn], copper [Cu], manganese [Mn], sodium [Na], and aluminum [Al]). Usually nutrients in manure are recycled through land-application as a fertilizer.

In general, cow manure as excreted contains N and P at a ratio of 6:1 (ASABE, 2005). However, N is subject to loss via volatilization, denitrification, runoff, and leaching (Eghball and Power, 1994; Power, 1994). N loss decreases the fertilizer value of manure and can impact both air and water quality. N loss through volatilization of ammonia (NH_3) from livestock manure contributes to fine particulate matter in the atmosphere (Panetta et al., 2005). Environmental impacts arise when NH_3 reacts with other compounds in the air to create atmospheric haze and acid rain (Rumburg et al., 2004). When deposited in aquatic ecosystems, NH_3 is toxic to fish and can contribute to eutrophication; NH_3 also consumes dissolved oxygen thus depriving aquatic organisms of the oxygen they need to survive (Obaja et al., 2003).

Implementation of practices to reduce N loss through NH_3 volatilization will help maintain a high N:P ratio in manure. Nitrification can be used to minimize NH_3 volatilization because the process converts ammonium ion (NH_4^+) to nitrate (NO_3^-) which is a non-volatile form of N. However, NO_3^- can also cause harm to the environment and to aquatic systems (Obaja et al., 2003). Nitrate in runoff can lead to eutrophication, and leaching of nitrate can cause groundwater contamination.

In many biological nutrient removal systems, nitrification and denitrification (conversion of NO_3^- to dinitrogen gas) are used to obtain complete N removal from wastewater (Westerman and Bicudo, 2002; Zeng et al., 2003). Although N removal from manure may not be desirable, N removal by denitrification is inevitable, particularly as low intermittent aeration is used to minimize the energy required for treatment. Simultaneous nitrification and denitrification (SND) is another undesired reaction that may contribute to N loss. SND is concurrent nitrification and denitrification enabled by the presence of anoxic or anaerobic zones within a reactor or within flocs in the reactor (Daigger and Littleton, 2000; Münch et al., 1996).

Aeration is used to reduce biochemical and chemical oxygen demand, reduce solids, conserve or remove N via nitrification or combined nitrification/denitrification, and prevent odors caused by products of anaerobic digestion (Grady et al., 1999). Continuous aeration is the conventional treatment used to provide air to prevent odor and maintain the dissolved oxygen (DO) concentration required for nitrification (Burton, 1992; Westerman and Zhang, 1997). However, continuous aeration for nitrification is energy intensive and costly. For example, Burton (1992) reported that the cost of providing continuous aeration to swine manure accounted for up to 53% of the profits per pig produced.

Studies on swine manure have shown that intermittent aeration, which involves the use of aeration and non-aeration periods, can lower energy costs and can lead to more effective N removal via nitrification and denitrification (Cheng and Liu, 2001; Head et al., 2005; Mota et al., 2005; Ridenoure, 2004; Yang and Wang, 1999). Intermittent aeration strategies resulting in 50 to 85% energy savings have been used to treat anaerobically pretreated swine manure (from a lagoon) with TAN concentrations of 140 to 220 mg N/L (Head et al., 2005; Mota et al., 2005;

Ridenoure, 2004). These studies have shown that aeration for 50% of the time during a 2 h cycle achieved more than 90% TAN removal; combined NO_2^--N and NO_3^--N production varied from 20 mg/L (Ridenoure, 2004) to 130 mg/L (Head et al., 2005). Aeration 25% and 20% of the time during 2.5 h and 5 h cycles, respectively, achieved about 86% TAN removal with combined effluent NO_2^--N and NO_3^--N concentrations less than 25 mg/L (Ridenoure, 2004). In a full scale intermittent aeration study on swine manure, Yang and Wang (1999) reported 92% total N removal using aeration for 50% of the time during a 6 h cycle; NO_3^--N was less than 3 mg/L in the treated effluent. Maximum effluent NO_3^--N (343 mg/L) was produced using aeration for 83% of the time during an 11 h cycle which was the highest intermittent aeration strategy tested in that study (Yang and Wang, 1999).

Li and Zhang (2004) used a sequencing batch reactor to study the effects of intermittent aeration on N conservation and N removal from dairy manure. The influent TAN concentration was 690 mg N/L after urea addition. The intermittent aeration treatment provided aeration for 63% of the time during a 12 h cycle; the continuous aeration treatment did not aerate during the 1.5 h settle and decant period. TAN removal was 93% and 95% using continuous and intermittent aeration, respectively. Both treatments produced more than 520 mg/L of combined NO_2^--N and NO_3^--N. Based on these results, Li and Zhang (2004) recommended intermittent aeration for a 30% energy savings compared to continuous aeration for achieving nitrogen conservation.

To determine if manure handling techniques affected nitrification of dairy manure, nitrification in scraped manure and flushed manure were compared. Flushed manure contained recycled liquid with a potentially high fraction of organic N which would not be immediately available for nitrification. Low NH_3-N concentrations were expected in the recycled flush liquid due to losses by volatilization, immobilization, or nitrification and denitrification during treatment and storage of the liquid. Scraped manure was expected to have a higher NH_3-N concentration.

Intermittent aeration is a proven energy-saving strategy for N removal from both swine and dairy manure, but its application to N conservation in dairy manure requires study to determine if further energy savings could be achieved and if scraping versus flushing affects nitrification. The objectives of this study were to (1) determine the effect of aeration time on the conservation of N as NO_3^- and (2) determine the effect of recycled flush water on N bioavailability during nitrification.

2 Materials and Methods

2.1 Manure collection and preparation

Dairy manure used in this study was obtained from the Virginia Tech dairy complex.

2.1.1 Virginia Tech dairy

The Virginia Tech dairy facility stores recycled flush liquid for flushing alleys of the barn. The dairy barn holds about 190 cows that produce approximately 13 m^3 of wet manure per day (ASABE, 2005). The barn is flushed four times per day (0600 h, 1200 h, 1800 h, and 2400 h) using a daily total of 152 m^3 of flush liquid. The milking parlor is cleaned with 46 m^3 of fresh water. Manure from the barns and milking parlor passes through a rotary separator consisting of mesh screen with 0.79 mm openings and brushes to move manure across the screen surfaces (Integrity Nutrient Control System, Nutrient Control Systems, Inc., Chambersburg, Pa.). The separated liquid is transferred to the settling basin as shown in Figure 4. Overflow from the settling basin enters Tank 1, a 2,220 m^3 circular storage tank. Tank 1 is pumped into Tank 2 which is the same size as Tank 1. Tank 2 is pumped into Tank 3 which has a volume of 4,165 m^3 and the effluent from which is used as flush liquid. All three tanks undergo some mixing and aeration by aerators for odor control. Liquid in Tank 3 is stored for flushing and irrigation.

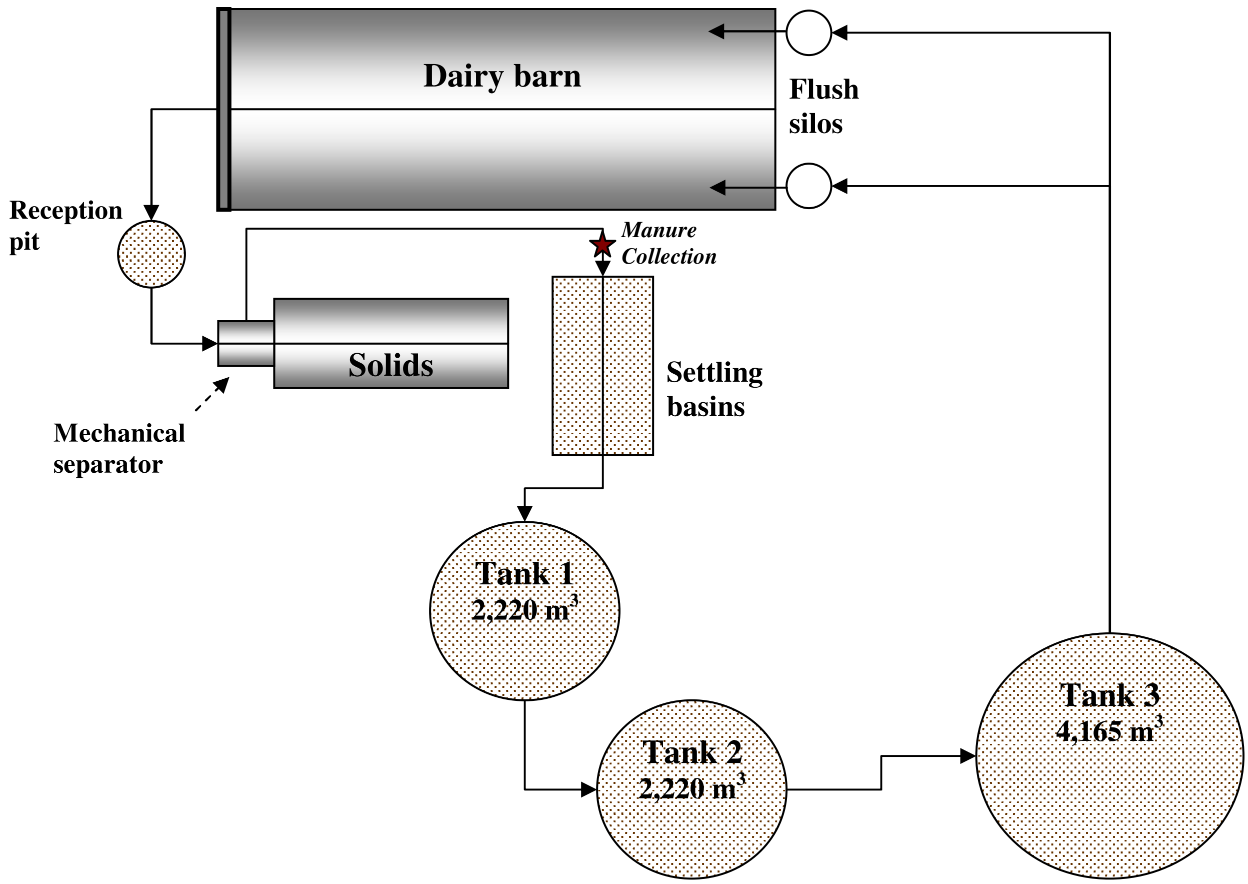

Figure 4. Schematic of the Virginia Tech dairy complex

2.1.2 Flushed manure

Separated liquid manure used in this study was obtained before it entered the settling basins; the collection point is labeled in Figure 4. Approximately 76 L of liquid manure was collected twice a week after the 1200 h flush and transported to the Biological Systems Engineering laboratory where it was pumped into the feed tank for the reactors.

2.1.3 Scraped manure

Scraped manure was obtained by manually scraping feces and urine as deposited on the barn floor with minimal bedding material. The manure was diluted 1:2 by weight (1 part manure to 1 part tap water) and separated using a small 1:4 scale mechanical separator representative of the rotary separator used by the dairy. The screen size in the small scale separator was 3.18 mm. Batches of scraped manure were stored in 20 L containers and frozen at -22°C until use. Further dilution was done in the laboratory to match specific characteristics of flushed manure.

2.2 Reactors

2.2.1 Design

Three reactors, each 90 cm long and 20.3 cm in diameter, were constructed from PVC piping. The working volume of each reactor was approximately 16 L. Clear tubing (9.5 mm inner diameter) was connected along the side of each reactor to observe the reactors' filled volumes. Each reactor had two 25 mm diameter spherical diffusing stones (Fisher Scientific, Columbus, Ohio) attached to a support frame at the bottom of the reactor for aeration. Polypropylene media (Jaeger Products, Houston, Texas) that was 1.6 cm in diameter was contained in a nylon mesh bag set on the structure supporting the diffusers. A diagram of the reactor setup is shown in Figure 5.

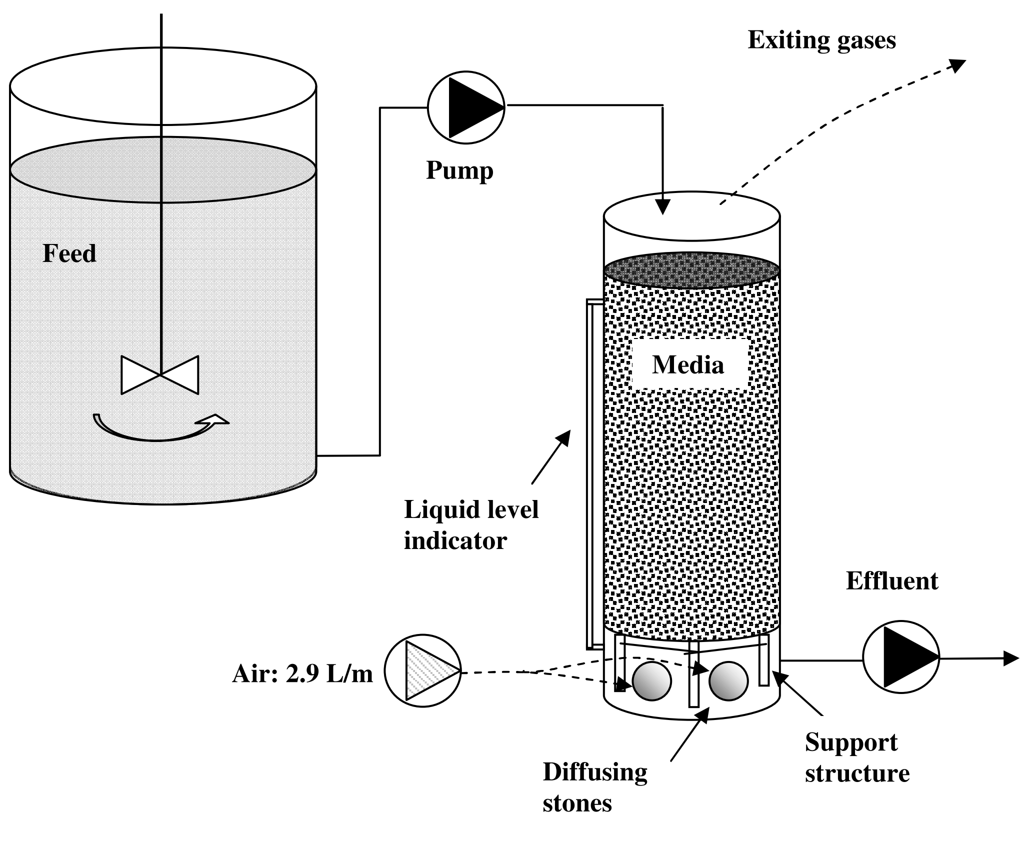

Figure 5. Schematic of an attached growth nitrification reactor

A 3.33 d hydraulic retention time (HRT) was selected based on reports of reactors that had supported nitrification in dairy manure using a 3 to 4 d HRT (Li and Zhang, 2002; Sweetman, 2005). The three reactors had 16 L working volumes, and the HRT was maintained using draw and fill operations that occurred four times per day (Table 1). Effluent (1.2 L) was drawn from each reactor followed by an addition of 1.2 L influent from the 120 L storage tank using peristaltic pumps (Masterflex L/S, Cole-Parmer, Vernon Hills, Ill.) controlled by digital timers (Intermatic, Grainger, Lake Forest, Ill.).

Table 1. Reactor draw and fill schedule

Draw	Fill
0350 h to 0355 h	0400 h to 0405 h
0950 h to 0955 h	1000 h to 1005 h
1550 h to 1555 h	1600 h to 1605 h
2150 h to 2155 h	2200 h to 2205 h

Air for the reactors was supplied using air pumps (Gast, Benton Harbor, Mich., and Barnant, Thermo Fisher Scientific). Influent air flow was maintained at 2.9 L/min using correlated flowmeters with high-resolution valves (Cole-Parmer, Vernon Hills, Ill.). A program was designed using LabView 8 (National Instruments Corp., Austin, Texas) to control solenoid valves (ASCO Red Hat, Grainger, Lake Forest, Ill.) that regulated intermittent aeration strategies. The reactors were operated in a laboratory at room temperature.

2.2.2 Aeration treatments

A range of aeration to non-aeration periods was evaluated to identify the point at which energy use and N loss were minimized. Continuous aeration was used as the control and basis for energy comparisons with intermittent aeration schemes. Three other intermittent aeration schedules were tested as shown in Table 2. Each trial lasted 45 days and each treatment was replicated a minimum of two times.

Table 2. Intermittent aeration strategies defined by time; only a 5 h schedule is shown but aeration treatments were provided continually throughout the 45 d trials

Treatment: % Aeration	Hour 1	Hour 2	Hour 3	Hour 4	Hour 5
100%	**ON**				
75%	**ON**	**OFF**			
60%	**ON**	**OFF**			
50%	**ON**	**OFF**			

2.2.3 Startup

Recycled activated sludge was obtained from the Blacksburg-VPI Wastewater Treatment Plant (Blacksburg, Va.) to inoculate the reactors with nitrifying bacteria. The storage tank was filled with 30 L flushed dairy manure, 30 L recycled activated sludge, and 20 L tap water. The manure to sludge ratio was determined using results of a simulation done in BioWin 2.0 (EnviroSim, Ontario, Canada) to maximize autotrophic biomass. After inoculation, all the reactors were continuously aerated for 19 days prior to the start of the first experimental trial.

2.2.4 Sampling and analysis

Reactors were sampled twice a week by collecting effluent during the morning draw period (0950 h to 0955 h). Temperature and pH of each sample were measured immediately using handheld electronic meters (Accumet AP84, Fisher Scientific, Columbus, Ohio). Well-mixed sub samples from influent and effluents were analyzed for total and volatile solids (TS and VS), total and volatile suspended solids (TSS and VSS), chemical oxygen demand (COD), soluble COD (sCOD), and alkalinity using standard methods for wastewater analysis (APHA, 1998). Total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were analyzed according to validated methods for animal excretions (AOAC, 1984); an analyzer unit was used for TKN analysis (2400 Kjeltec Analyzer Unit, FOSS Tecator, Eden Prairie, Minn.). TAN was measured using an ammonia probe (Orion, Thermo Fisher, Fisher Scientific, Columbus, Ohio) as outlined in method 4500-NH_3 (APHA, 1998). NO_2^--N, NO_3^--N, and orthophosphate were determined by ion chromatography (method 4110) using a Dionex 120 ion chromatography unit (Dionex Corp., Bannockburn, Ill.) (APHA, 1998). Mineral analysis was performed monthly on flushed manure samples using inductively coupled plasma analysis (Spectro CirOS VISION ICP, Model FVS12, Marlborough, Mass.). DO profiles were conducted using a handheld DO meter (Accumet AP84, Fisher Scientific, Columbus, Ohio, and Multi 340i, WTW Inc., West Wareham, Mass.) and a flow-through glass bottle.

2.2.5 Maintenance

After the second trial, the three reactors were disassembled so that air diffusers could be cleaned by manual scrubbing and bubbling in clean water. This maintenance was carried out after each subsequent 45-day trial. The reactors were repacked with the same media and no further attempt was made to slough off biomass beyond that which was loosened by the disassembly and repacking process. Continuous aeration was provided to all reactors two to three days prior to the implementation of intermittent aeration strategies for the following trial.

2.3 Statistical analysis

Statistical analysis was conducted using SAS 9.1 (SAS Institute, Cary, N.C.). Analysis of covariance (ANCOVA) was performed using trial number as a blocking factor and influent manure concentration as the covariate to account for the effect of influent manure characteristics on the effluent. Differences in NO_2^--N and NO_3^--N production were analyzed using analysis of variance (ANOVA). The covariate was absent in this case since oxidized N was not present in influent manure. Differences among treatment means were determined using Fisher's least significant difference (LSD) and were declared significant at $p<0.05$.

2.4 Nitrogen balance

Though the goal of this study was to achieve maximum conversion of TAN to NO_3^--N, some N was unaccounted for and may have been lost as NH_3 gas, N_2, NO, or N_2O. Some N was also retained in the reactor as a component of the biomass which was attached to the media.

Grady et al. (1999) elucidated the heterotrophic nitrogen requirement (NR) for biomass growth in an activated sludge system as follows:

$$NR = 0.087\left[\frac{(1+f_D \cdot b_H \cdot \Theta_c)Y_{H,T}i_{O/XB,T}}{1+b_H \cdot \Theta_c}\right] \qquad [3]$$

where f_D = fraction of active biomass contributing to biomass debris (0.20 mg TSS/mg TSS);
b_H = heterotrophic decay coefficient (0.18 day^{-1});
Θ_c = solids retention time (days);
$Y_{H,T}$ = true heterotrophic growth yield (mg TSS/mg COD); and
$i_{O/XB,T}$ = mass COD per mass biomass as TSS (1.2 mg COD/mg TSS).

Assuming the stoichiometric and kinetic values from Grady et al. (1999) for domestic wastewater at 20°C, a heterotrophic yield of 0.35 mg biomass TSS/mg COD removed (Whichard, 2001), and a 20 d SRT, NR is calculated to be 0.014 mg N used/mg COD removed.

3 Results and Discussion

3.1 Flushed manure

The reactors were operated for four, 45 day, experimental periods. During these experiments, continuous aeration (100%) was replicated four times, 60% aeration three times, and the 75% and 50% treatments two times. It typically took 14 days to achieve steady state when reactors were switched from short aeration periods to long aeration periods. Only results from steady state periods are reported.

Table 3 shows the influent and effluent data averaged over all trials. Although the influent TAN was stable, the TKN of the liquid manure increased significantly over time. The average TKN values over the four consecutive trials were 980, 1,100, 1,210, and 1,420 mg N/L; this increase is apparent in Figure 6. Influent TAN remained constant, but graphs in Figure 6 show that organic N (the difference between influent TN and TAN) increased over time. Linear regression was used to normalize influent TKN data for statistical comparisons.

Reactor performance varied due to influent changes, clogging of the diffusers over time, and other unknown factors. The characteristics of influent manure and treated effluents averaged over all four trials are shown in Table 3; the results are broken down by trial and presented in Figure 6 to show the variations in reactor performance during the four trials.

Table 3. Characteristics of influent flushed manure and treated reactor effluents (means and standard deviations) averaged over all replications of each treatment. Averages with the same letter were not statistically different at a significance level of 0.05.

			Reactor Effluents			
			100%	75%	60%	50%
Parameter	Units	Influent	Continuous	1 h:0.33 h	1 h:0.67 h	1 h:1 h
COD	mg/L	14,120 ± 4,030	11,140^{a} ± 4,110	8,230^{a} ± 2,880	10,510^{a} ± 4,300	8,620^{a} ± 2,810
TS	mg/L	16,160 ± 4,310	15,150^{a} ± 4,240	11,450^{a,b} ± 2,410	17,580^{b} ± 4,330	10,970^{b} ± 3,100
VS	mg/L	10,360 ± 2,850	9,170^{a} ± 2,870	6,750^{a,b} ± 1,780	7,660^{b} ± 3,140	6,350^{b} ± 2,170
TSS	mg/L	10,840 ± 4,330	9,230^{a} ± 4,120	6,400^{a,b} ± 1,860	8,020^{b} ± 5,000	6,160^{a,b} ± 2,790
VSS	mg/L	8,290 ± 3,820	6,720^{a} ± 2,940	4,650^{a,b} ± 1,350	5,970^{b} ± 3,620	4,520^{a,b} ± 1,900
TP	mg P/L	260 ± 130	250^{a} ± 90	240^{a,b} ± 150	170^{b,c} ± 90	190^{c} ± 80
Alkalinity	mg/L as $CaCO_3$	5,610 ± 900	2,510^{a} ± 960	2,690^{a} ± 640	2,910^{b} ± 890	3,930^{b} ± 1,000
pH		8.3 ± 0.2	8.4^{a} ± 0.3	8.5^{a} ± 0.3	8.3^{a} ± 0.30	8.6^{a} ± 0.1
TKN	mg N/L	1,170 ± 210	660^{a} ± 180	500^{a} ± 150	800^{a} ± 210	590^{a} ± 240
TAN	mg N/L	600 ± 110	40^{a} ± 60	30^{a} ± 40	360^{b} ± 190	230^{b} ± 160
NO_2^--N+NO_3^--N	mg N/L		230^{a} ± 100	150^{b} ± 60	20^{c} ± 20	10^{c} ± 10
Total Nitrogen (TN)	mg N/L	1,170 ± 210	890 ± 200	640 ± 180	820 ± 200	600 ± 230

Table 4 shows the mineral concentrations in the flushed manure used to feed reactors. Chloride (Cl^-) has the highest concentration since it is present in tap water used for parlor flushing and in the recycled flush water. K has a high concentration which adds to the fertilizer value of the manure. The K concentration did not change significantly during manure treatment. The Cu concentration in flushed manure was near the known inhibitory level of 3 mg Cu/L (N. Love, personal communication, 27 November 2007).

Table 4. Average mineral concentrations in flushed manure during all replicates of each treatment.

	Cl^-, mg/L	K, mg/L	Ca, mg/L	Na, mg/L	Mg, mg/L	Cu, mg/L	Zn, mg/L
Flush	427	108	72	31	25	1.8	1.9
100%	390	110	77	31	27	1.8	1.9
75%	353	107	56	30	23	1.3	1.4
60%	476	120	33	31	20	0.7	1.1
50%	341	98	39	29	18	0.8	0.8

3.1.1 Treatments using aeration 100% and 75% of time

The Trial 1 graph in Figure 6 shows that aeration for 75% of the time produced slightly higher effluent NO_2^--N and NO_3^--N concentrations than 100% aeration. There was a problem maintaining adequate DO in the continuous reactor at the beginning of Trial 1 which temporarily inhibited nitrification. After the two week startup, there was no significant difference in the average effluent TAN or NO_2^--N+NO_3^--N concentrations using 100% or 75% treatments during Trial 1. However, effluent NO_3^--N from these treatments over all four trials were significantly different with 100% aeration producing higher concentrations of conserved N; the effluent NO_2^--N and NO_3^--N concentrations can be seen in Table 3.

Despite higher NO_3^--N production by the continuous reactor, TAN removal and/or conversion over all replicates was not significantly different using aeration for 100% or 75% of the time. Data from the failure of the 75% treatment during Trial 4 is excluded. TAN reduction of 94% and 96% occurred using 100% and 75% treatments, respectively. Such high TAN reduction suggests that NH_3 stripping was occurring in addition to nitrification. Li and Zhang (2004) observed 93% and 95% TAN reductions while treating dairy manure in sequencing batch reactors operated using continuous and intermittent aeration, respectively, where the intermittent strategy provided aeration for 63% of the time during a 12 h cycle.

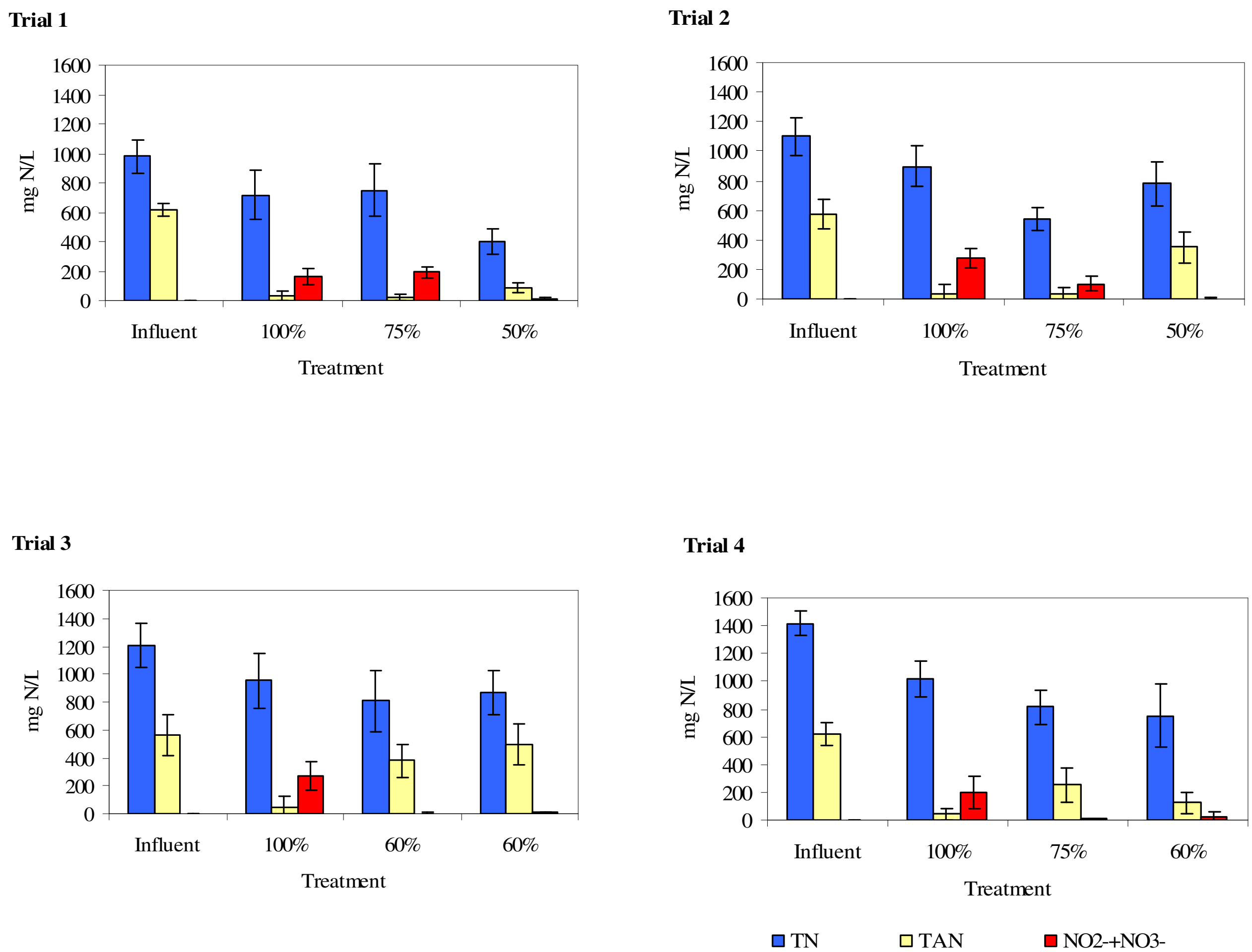

Figure 6. Comparison of influent characteristics (TN and TAN) versus effluent TN, TAN, and NO_2^--N+NO_3^--N for each of the four trials; error bars represent standard deviation

Continuous aeration produced 39% N conversion while aeration for 75% of the time produced 25% N conversion to NO_2^--N and NO_3^--N. This data is summarized in Table 5 where percent reduction is the percentage of influent TAN removed and percent conversion is the percentage of influent TAN converted to NO_2^--N and NO_3^--N. The continuous aeration and intermittent aeration treatments used by Li and Zhang (2004) achieved 80% and 76% N conversion, respectively, with NO_2^--N accounting for up to half of the conserved N. In this study, NO_2^--N accounted for less than 4% of conserved N from either reactor. Conservation of N as NO_3^--N is preferred since NO_2^--N accumulation can lead to production of N_2O, a greenhouse gas, which is one of the intermediate products of NO_3^- during denitrification (Zeng et al., 2003).

Table 5. Summary of average % TAN reduction (influent TAN removed) and % TAN conversion (influent TAN converted to NO_2^--N+NO_3^--N). Italicized data (75% treatment failure during Trial 4) was omitted from the average.

	100%		**75%**		**60%**		**50%**	
	% Red.	% Conv.	% Red.	% Conv.	% Red.	% Conv.	% Red.	% Conv.
Trial 1	95.3	26.4	96.5	30.8			86.3	2.1
Trial 2	93.7	47.7	94.6	18.2			38.9	0.9
Trial 3	91.7	47.3			32.9	0.9		
					12.8	1.2		
Trial 4	93.1	32.0	*59.3*	*1.1*	80.2	4.2		
Averages	93	39	96	25	42	2	63	2

3.1.2 Treatments using aeration 60% and 50% of time

Effluent TAN and NO_2^--N+NO_3^--N concentrations using aeration for 50% and 60% of the time were not significantly different from one another over all trials. These reactors had low effluent NO_2^--N+NO_3^--N concentrations (Table 3) and averaged less than 2% conversion of TAN to NO_2^--N and NO_3^--N (Table 5). Although high N conversion and/or removal has been obtained using similar intermittent aeration periods in swine manure (Head et al., 2005; Mota et al., 2005; Osada et al., 1991), these treatments did not achieve the goal of N conservation in flushed dairy manure. Anaerobically pretreated swine manure used in the referenced studies had sCOD and suspended solids concentrations an order of magnitude lower than the concentrations of flushed dairy manure. Reduction of oxygen demand during pretreatment may have helped reduce competition with nitrifiers by heterotrophic microorganisms.

Inconsistent levels of TAN and TN removal were observed using the 50% and 60% treatments. Although aeration for 50% of the time did not produce significant effluent NO_3^--N or NO_2^--N concentrations during Trials 1 and 2, it is interesting to note the level of TAN removal and TKN reduction by this treatment during Trial 1 (Figure 6 and Table 5). Comparing forms of effluent N in Table 3 shows that effluent organic N decreased as periods of non-aeration increased; therefore, TKN reduction could have been caused by ammonification, the conversion of organic N to NH_3-N. NH_3-N may have been subsequently removed by stripping or by nitrification and denitrification. High TAN removal also occurred using 60% aeration during Trial 4; this result is inconsistent with the results from Trial 3 considering the similarity in influent TAN concentrations during Trials 3 and 4. High TAN removal during Trial 4 skews the average percentage of TAN reduction for 60% aeration shown in Table 5. During Trial 2, TAN removal and/or conversion using aeration for 50% of the time was significantly less than 100% or 75% treatments. Poorer performance by some reactors during Trial 2 may have been due to clogging of the air stones; the reactors were not disassembled for diffuser cleaning until after Trial 2.

3.1.3 Alkalinity and pH

The stoichiometric alkalinity requirement during nitrification is 7.14 g alkalinity as $CaCO_3$/g NH_4^+-N (WEF, 2006). The alkalinity of the influent flushed manure was consistently high enough to meet this requirement. Table 6 shows the alkalinity of influent manure for all four trials; the effluent alkalinity is lower in reactors with higher TAN conversion. Averages of 5.6 and 5.1 g alkalinity as $CaCO_3$/g NH_4^+-N were consumed using 100% and 75% aeration, respectively.

Table 6. Influent and effluent alkalinities for each trial and treatment

	Alkalinity, mg $CaCO_3$/L				
	Influent	100%	75%	60%	50%
Trial 1	4,740	2,740	2,230		3,070
Trial 2	5,510	3,020	3,120		4,740
Trial 3	5,510	1,450		2,390	
				3,580	
Trial 4	6,660	2,830		4,040	

The effluent pH was slightly higher than the influent pH for all treatments. This pH change is consistent with results obtained by Luo et al. (2002) in treatment of swine manure using intermittent and continuous aeration. The pH increase is attributed to aeration which causes the conversion of NH_4^+-N to NH_3-N. Aeration also drives off carbon dioxide which contributes to the pH increase.

Table 7. Influent and effluent pH for each trial and treatment

	pH				
	Influent	100%	75%	60%	50%
Trial 1	8.2	8.4	8.4		8.5
Trial 2	8.5	8.7	8.7		8.6
Trial 3	8.3	8.3		8.5	
				8.1	
Trial 4	8.1	8.1		8.4	

3.1.4 Dissolved oxygen

Airflow in each reactor was controlled at 2.9 L/min during periods of aeration. Several DO profiles were conducted over aeration and non-aeration phases to determine DO levels within the reactors; these profiles were done after the experimental trials had been completed. An average DO of 4.4 mg O_2/L was measured during continuous aeration. Average maximum DO concentrations for 75% and 60% treatments were 3.1 and 4.5 mg O_2/L, respectively. Measured minimums during the non-aeration periods were 0.8 and less than 0.1 mg O_2/L, respectively.

3.1.5 Nitrogen balance

Nitrogen balances were performed for the 100%, 75%, and 60% reactors. The balance on the 100% reactor is described as an example. The average influent TKN was 1170 mg N/L over the seven month period when the four trials were conducted. Using the continuously aerated reactor as an example, approximately 30 mg N/L may have been used for heterotrophic biomass growth (1820 mg sCOD removed/L × 0.014 mg N/mg sCOD removed). Biomass estimates based on sCOD consumption were consistent among treatments. This leaves 1,140 mg N/L available for nitrification and denitrification. If 1,140 mg N/L was oxidized, approximately 230 mg VSS/L of nitrifier biomass could have been produced based on the maximum assumption of 0.2 g VSS/g NH_4^+-N (EPA, 1993). The N consumed to produce this biomass is ignored since it is usually less than 2% of N nitrified (WEF, 2006). Effluent from the 100% treatment contained an average concentration of 40 mg N/L TAN and 620 mg N/L of organic N. Although effluent TAN measurements would include TAN released via the destruction of biomass, biomass debris is a negligible source of effluent TAN since Grady et al. (1999) reported that the N content of biomass debris is likely to be less than that of active biomass. Approximately 230 mg N/L exited the 100% reactor as NO_2^--N and NO_3^--N; therefore, 250 mg N/L may have been lost as gases such as N_2, NO, or N_2O. This N balance and balances for 75% and 60% are shown in Figure 7.

Continuous aeration treatment produced 250 mg N/L of unaccounted-for N compared to 490 mg N/L in the 75% treatment. Higher NO_2^--N+NO_3^--N production, as achieved using continuous aeration, resulted in lower concentrations of unaccounted-for N. Denitrification or SND was a likely pathway for N loss when using aeration for 75% of the time. Its intermittent aeration strategy provided conditions suitable for nitrification and significant NO_3^--N production, but its non-aeration period may have been appropriate for denitrification thus contributing to the highest N losses from either of the reactors. Soluble COD measurements (sCOD) indicate that readily-biodegradable carbon was available to meet the COD requirement of 2.86 g/g N if conditions were suitable for denitrification.

Total average unaccounted-for N using 60% aeration was 320 mg N/L. This high N loss also suggests denitrification, which would cause loss of N as N_2. However, minimal TAN reduction during most replicates suggests that either denitrification was not prevalent or, more likely, that the TAN in the effluent was the result of ammonification. NH_3 stripping may explain part of the unaccounted-for N, and the possibility remains that some N was lost as NO or N_2O but there was little evidence of nitrification or accumulated NO_2^--N.

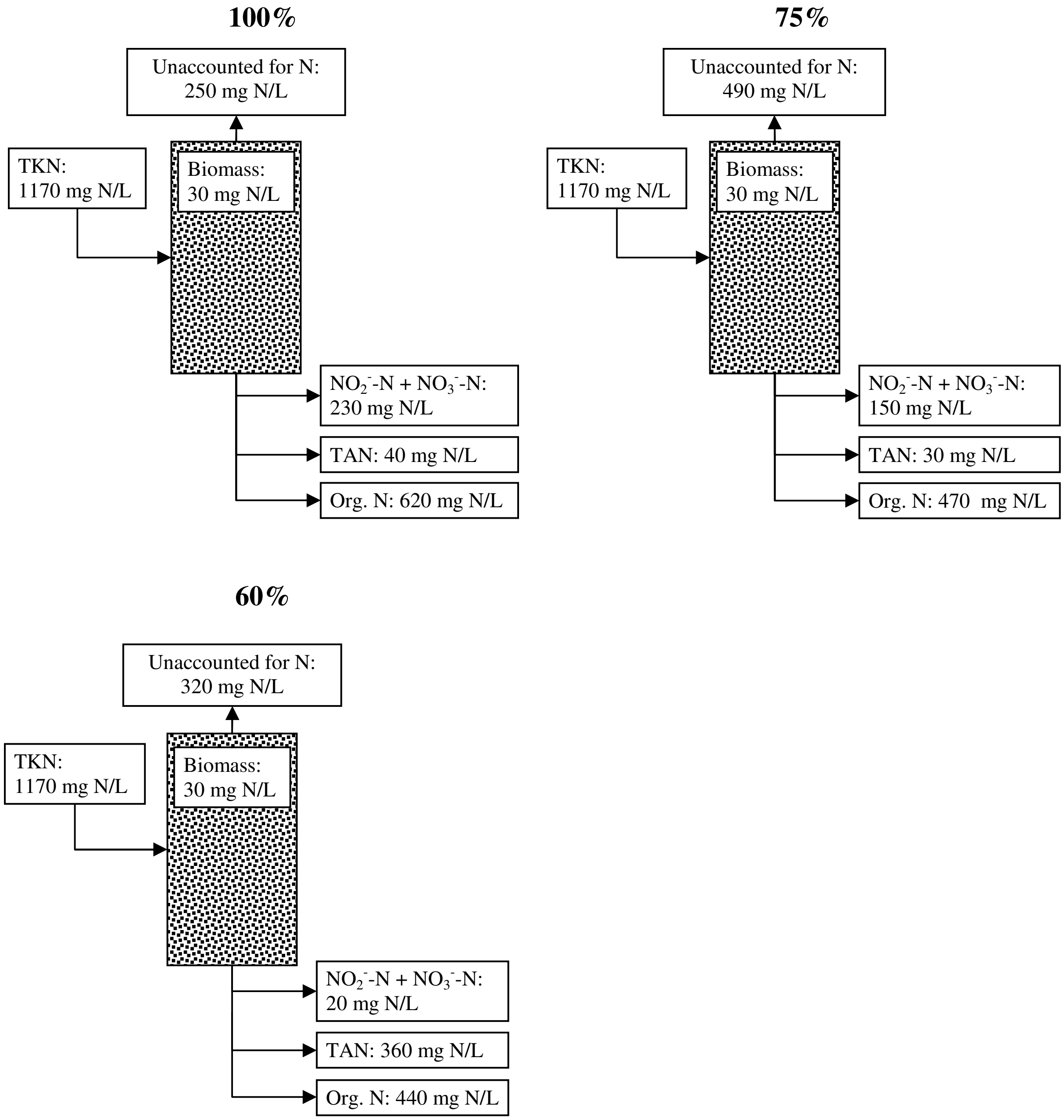

Figure 7. N balances on reactors for using 100%, 75%, and 60% treatments. Concentrations are based on parameters averaged over all trials. Biomass estimates are based on sCOD measurements collected after the four trials; sCOD data is not available for 50% treatment.

3.2 Effects of N bioavailability on nitrification

The effect of N bioavailability on nitrification in flushed versus scraped manure was evaluated by comparing N conversion using the different manures. It was hypothesized that much of the N in flushed manure would be non-bioavailable due to the expectation of bioavailable NH_3 having been volatilized, immobilized (converted from inorganic N to organic forms), or possibly nitrified and denitrified while stored in the three limited-aeration basins at the dairy. Therefore, scraped manure (without recycled flush water) was expected to have a larger fraction of bioavailable N.

The reactors were operated using scraped, separated manure diluted 1:2 (1 part manure to 1 part tap water) resulting in an overall 1:4 dilution since the first dilution was done prior to mechanical separation. The HRT and intermittent aeration intervals were the same as had been used for flushed manure. The 1:4 dilution of scraped manure was first chosen to approximately match the TS of flushed liquid manure.

After two weeks of operating reactors with scraped manure at the 1:4 dilution, no residual DO was present and NO_3^--N was near zero in effluents from reactors using aeration for 100%, 75%, and 60% of the time. Air flow was increased from 2.9 L/min (the flowrate used with flushed manure) to approximately 7 L/min, continuous aeration was implemented in all reactors, and the scraped manure was diluted 1:6 overall. After these changes, effluent TAN measurements from the reactors on the order of 1 mg N/L indicated that either rapid SND was occurring or the high air flow was stripping NH_3-N from the system since neither NO_3^--N nor NO_2^--N was present in the reactor effluents. It was noted that the systems were near the 1600 m^3/m^3 air:liquid ratio for effective NH_3-N stripping (WEF, 1998).

Table 8. Characteristics of flushed dairy manure and scraped dairy manure at the dilutions used in the reactors

Manure type (dilution)	TS mg/L	sCOD mg O_2/L	TAN mg N/L	TKN mg N/L	TAN/TKN
Flushed	16,160	3,410	600	1,170	0.5
Scraped (1:4)	18,220	5,620	310	870	0.4
Scraped (1:6)	12,150	3,110	260	610	0.4
Scraped (1:10)	7,290	2,700	230	330	0.7

The sCOD in scraped manure as separated (1:2 dilution) was 3.5 times higher than that of flushed manure. The average COD/TKN ratio in the scraped manure as separated was 21 compared to 12 for flushed manure primarily because the COD concentrations in the scraped manure were higher. Characteristics of flushed manure and the scraped manure are compared in Table 8. One possible reason for the differences in COD is that the flushed manure was separated with a 0.79 mm mesh whereas the scraped manure was separated using a 3.18 mm screen. The screen size affected the amount of solids and organic material in the liquid manure. Since DO profiles showed that there was no residual DO in the system, it is possible that the high COD concentrations in the scraped manure were causing oxygen to be consumed and thus inhibited nitrifier activity. The continuously aerated reactors operating at the 1:4 overall dilution were undergoing 4,100 to 8,100 mg O_2/L reductions in COD; as a comparison, the average COD reduction in a continuously aerated reactor treating flushed manure was 3,000 mg O_2/L.

It is also interesting to note that the TAN concentrations in the scraped manure did not change much with dilution as would be expected considering the range of dilutions made (Table 8). The reason for this result was unknown since sampling and preservation methods were constant. TKN changed proportionally with the dilutions as would be expected.

The scraped manure was finally diluted 1:10 overall (1 part manure to 9 parts tap water) to more closely match the sCOD of flushed manure. Air flow had been gradually reduced to 2.9 L/min to again match the airflow used in the flushed manure experiments. The DO in all reactors operated using continuous aeration was approximately 3.8 mg O_2/L. The TAN concentration was estimated to be 18 mg N/L at time zero (theoretical concentration immediately after feeding) which left little N available for nitrification. However, one reactor did produce an average of 18 mg NO_3^--N over 15 days of operation using continuous aeration. The result from that reactor points to the possibility of complete nitrification; however, such high dilutions of manure, even if functional, is not practical for dairy manure treatment and does not allow for adequate comparison with nitrification in flushed manure.

The scraped manure may not adequately represent the fecal and urine deposits on the barn floor. The scraping method used was appropriate for collecting solids but did not ensure that urine in the grooved flooring was included. A better collection method is needed to ensure that urine is collected as well as feces. The feed made from scraped manure (1:4 dilution) contained half as much TAN as flushed manure. A two-month survey of TAN in recycled flush water during 2006 showed that the recycled liquid alone contained an average of 550 mg N/L. This TAN, likely a product of ammonification during storage, accounts for the majority TAN in the flushed manure. Higher bioavailable N concentrations were found in the flushed manure and the TAN accounted for a larger fraction of the total N in flushed manure than in scraped manure.

While it was originally believed that the high sCOD/TKN ratio was the primary reason the scraped manure did not readily nitrify, mineral analysis revealed that scraped manure (as separated) had a higher Cu concentration than flushed manure. A copper sulfate solution is used to disinfect cow hooves at the Virginia Tech dairy. The Cu in flushed separated manure was only 1.8 mg Cu/L since the manure is diluted by the use of recycled flush water. However, Cu was 3.08 mg Cu/L in the scraped manure as separated (1:2 dilution) with separate analysis showing that most of the Cu was present in the solids fraction. Therefore, the concentrations were approximately 1.54, 1.03, and 0.62 mg Cu/L in the 1:4, 1:6, and 1:10 dilutions, respectively. These concentrations are below the concentrations of 3-5 mg Cu/L well known to inhibit nitrification (N. Love, personal communication, 27 November 2007; Hu et al., 2004; Kim et al., 2006). However, concentrations of less than 2 mg Cu/L have also been shown to cause a lesser degree of nitrification inhibition (Hu et al., 2003; Madoni et al., 1996). Using the 1:10 dilution, the Cu appears to have been diluted sufficiently to allow nitrification of the small amount of TAN present in the influent manure.

4 Conclusion

Nitrification of dairy manure requires intensive aeration but can be achieved using continuous aeration or aeration for 75% of the time as was found in this study. Aeration for 75% of the time conserved just 33% less N than continuous aeration but reduced energy costs by 25%. Approximately 20 to 40% of the influent N was unaccounted for using 100% and 75%

treatments. It is likely that the non-aeration periods or the potential for anoxic zones within the attached-growth reactors enabled denitrification and/or SND which could have caused N loss as N_2. The 50% and 60% reactors did not conserve N as NO_2^--N or NO_3^--N.

Recycled flush liquid does not seem to hinder nitrification based on the results obtained using the reactors with long periods of aeration. However, the comparison of flushed manure with scraped manure in this study showed that there was nitrification inhibition when scraped manure was used. Cu appeared to be an nitrification inhibitor since it was present at potentially inhibitory concentrations. The COD/TKN ratio in the separated scraped manure was 21 compared to 12 in flushed manure. The high COD concentration necessitated dilution of the scraped manure so that DO would be available for nitrification, yet the 1:10 dilution at which nitrification did occur reduced influent TAN to less than half that in flushed manure. This level of dilution is not practical for dairy manure treatment nor for comparison to the treatment of flushed manure. Use of a finer screen to separate scraped manure may reduce COD such that excessive dilution would not be necessary to approximate characteristics of flushed manure. Finer screening may also reduce the total Cu concentration since most of the Cu is in the solids fraction. However, with a nitrification inhibitor present, nitrification may still not be readily achieved using scraped manure.

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Chapter 3: Chemical phosphorus removal: A case study for the Virginia Tech Dairy Complex

Abstract

The objective of this study was to determine effective and economical dosages of chemicals to remove phosphorus (P) from liquid dairy manure. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferric sulfate ($Fe_2[SO_4]_3 \cdot 5H_2O$), aluminum chloride ($AlCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2[SO_4]_3 \cdot 13H_2O$, alum), and five cationic polyacrylamides were evaluated at varying dosages using jar tests on liquid manure of approximately 0.87% total solids (TS) concentration. Treated manure settled in Imhoff cones and sludge volume was measured; supernatant was analyzed for total phosphorus (TP), solids, and pH. $FeCl_3 \cdot 6H_2O$, alum, and Superfloc 4512, which is an ultra-high molecular weight polyacrylamide, were selected for further testing. Polymer addition enhanced floc size and settleability of sludge and improved P removal. Treatment of liquid manure (0.89% TS) from the second storage tank at Virginia Tech's dairy resulted in more than 90% P removal using either $FeCl_3$ or alum in combination with polymer. The chemical treatment and transport of the P-rich sludge from a 2,270 m^3 storage tank would result in an estimated 40% cost savings over transport of the entire manure volume offsite for land application elsewhere.

Keywords: Phosphorus removal, dairy manure, chemical treatment, alum, ferric chloride, polymer

1 Introduction

Animal feeding operations such as dairies are centers for high nutrient concentrations. Although manure from these operations can be land applied as fertilizer, this practice is limited by nutrient management regulations, available land area, and the economics of manure transport. The crop area available for application of manure nutrients is limited by encroaching urban sprawl and decreasing farm size. Phosphorus or P-based nutrient management plans regulate the application of manure as fertilizer so that P needs of the crop are met but not exceeded. Therefore, economical and environmentally responsible methods are needed to manage the manure that cannot be applied onsite at the animal feeding operation due to P-based nutrient management.

To handle large manure volumes with high nutrient concentrations, manure can be dewatered (to reduce transportation costs) and applied at nutrient deficient locations off the farm; or nutrient concentrations can be chemically or biologically altered so that larger quantities of manure can be land-applied onsite. Chemical or biological treatment is a desirable solution enabling manipulation of nutrient ratios by either conserving nitrogen (N) or removing P to match the manure to the needs of the crop.

The Virginia Tech dairy barn houses about 190 cows that produce approximately 68 kg of manure per animal each day (ASABE, 2005). Flushed manure from the dairy contains an average of 260 mg P/L, 1,170 mg N/L, and 1.6% total solids (TS) after mechanical separation. The P content of the manure is in excess of what can be land-applied onsite. P reduction is a necessary treatment for the Virginia Tech dairy. Chemical P removal is the method of interest due to the relative ease of achieving P reduction.

Typical chemicals used for P removal include aluminum sulfate ($Al_2[SO_4]_3$, alum), aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2[SO_4]_3$), and lime ($Ca[OH]_2$) (Dentel et al., 1993; Metcalf & Eddy, 1991). Soluble P is transformed into an insoluble precipitate upon the addition of aluminum, iron, or calcium cations (Metcalf & Eddy, 1991; WEF, 1998). Competing reactions and water properties necessitate bench-scale testing for determining actual metal dosages (Metcalf & Eddy, 1991). Cationic polymers enhance flocculation via action of colloidal particle charge destabilization and bridging (Metcalf & Eddy, 1991; Vanotti et al., 2002). Polyacrylamides (PAMs) are a group of polymers made up of neutral acrylamide monomers (Dentel et al., 1993). PAMs are neutral, but they are aminomethylated to gain a positive charge. This group of polymers has been used in treatments for P removal from swine manure (Vanotti and Hunt, 1999; Vanotti et al., 2002) and dairy manure (Sherman et al., 2000; Zhang and Lei, 1998). The negative charges of bacteria and colloidal particles in wastewater require the use of cationic PAMs. Vanotti and Hunt (1999) verified this through testing of cationic, nonionic, and anionic PAMs; they found that the effect of nonionic and anionic polymers on swine manure was no different from the untreated control.

Barrow et al. (1997) evaluated the effectiveness of nutrient and solids removal from dairy manure using iron and calcium additives. Ferric salts were more effective than ferrous and calcium additives. At a dose of 278 mg Fe/L using $FeCl_3$, 88% of total P was removed from dairy manure containing 1.0% TS. Vanotti et al. (2002) tested the effects of Magnifloc 234GD, a moderately charged, high molecular weight PAM, on solid-liquid separation by screening in swine manure. PAM flocculation (using doses greater than 100 mg/L) followed by screening resulted in more than 70% total P removal which increased the N:P ratio from 5:1 to 11:1

(Vanotti et al., 2002). Sherman et al. (2000) found that alum provided better P removal from dairy manure than $FeCl_3$ and was more economical since up to 59% cost recovery in terms of the fertilizer value of P could be obtained using alum. Alum was used in field test treatment of a 3,500 L tank with 0.3 to 0.4% solids. An alum dosage of 106 mg Al/L removed 90% of P from dairy manure in the field test.

Chemicals and polymers can also be used in combination treatments. Zhang and Lei (1998) used $FeCl_3$ (0 to 690 mg/L as Fe) and Magnifloc 255G (0.0025 to 0.125%), a high molecular weight polymer, for P removal from swine and dairy manures. Solids removal from dairy manure containing 1.0% TS did not increase significantly beyond an optimum polymer dose of 0.075%; optimum polymer dosages were higher in manure with higher TS concentrations.

In general, the literature suggests that Al-based chemicals are more effective than Ca-based or Fe-based chemicals (Barrow et al., 1997; Sherman et al., 2000). As the TS concentration of manure increases, higher chemical dosages are needed to achieve P removal (Oh et al., 2005; Vanotti et al., 2002), and polymer effectively increases P removal when used in combination with chemicals (Vanotti et al., 2002; Zhang and Lei, 1998).

Chemical choice, dosages, predicted P removal and sludge production, and cost are elements needed to determine the feasibility of a chemical P removal system at the Virginia Tech dairy. The objectives of this study were to determine the most appropriate chemical or chemical/polymer combination for removing P from liquid dairy manure and the corresponding dosages for treatment of Virginia Tech dairy manure. The results of the study will be used to calculate the chemical dosages required to manage P in manure produced at the Virginia Tech dairy complex. By chemically removing P from the bulk liquid manure, a P-rich sludge will be produced that can be transported offsite while the low-P liquid can be applied as fertilizer on the farm in accordance with P-based nutrient management.

2 *Materials and Methods*

2.1 Manure collection and preparation

Flushed and separated liquid manure was obtained from the Virginia Tech dairy. In the laboratory, the manure was diluted with tap water if necessary.

2.2 Chemicals and polymers

Four metal salts and five polymers were tested to determine the most effective and economical dosages for P removal. The chemicals were aluminum chloride ($AlCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2[SO_4]_3 \cdot 13H_2O$, alum), ferric chloride ($FeCl_3 \cdot 6H_2O$), and ferric sulfate ($Fe_2[SO_4]_3 \cdot 5H_2O$) (Fisher Scientific, Columbus, Ohio).

The polymers were provided by Kemira Water (Lakeland, Fla.) and were cationic PAMs: Superfloc 4512, 4516, C-1598, SD-2081, and SD-2083. The 4500-series PAMs contained 39 to 43% active polymer; the C-1500 series and SD-2000 series contained 46 to 50% active polymer. The 4500-series PAMs had linear molecular configurations and ultra-high molecular weights. The other PAMs had high molecular weights, but the SD-2000 series had branched configurations and the C-1500 series was linear (V. Johnson, personal communication, 11 July 2007). These flocculants are recommended for dewatering, gravity settling, coagulant aid, water clarification, and thickening.

2.3 Experiment setup

Bench-scale jar tests were conducted on 1 L volumes of manure using a PB-700 jar tester (Phipps and Bird, Richmond, VA). Manure was analyzed for total and volatile solids (TS and VS) and total and volatile suspended solids (TSS and VSS) according to standard methods for wastewater analysis (APHA, 1998). The pH was measured using handheld electronic meters (Accumet AP84, Fisher Scientific, Columbus, Ohio). The mixing times and speeds used for jar tests are outlined in Table 9.

Table 9. Jar test mixing times and speeds (adapted from Dentel et al. (1993) and Zhang and Lei (1998))

	Coagulation	Flocculation
Chemicals	2 min at 100 rpm	5 min at 30 rpm
Polymers	2 min at 200 rpm	5 min at 30 rpm
Chemicals + polymers	2 min at 100 rpm; (polymer addition) 2 min at 200 rpm	5 min at 30 rpm

Settleability of sludge was measured using 1000 mL Nalgene Imhoff cones. Sludge volume was recorded after 15 and 60 min of settling based on previous research that showed most significant settling occurs during the first hour (Oh et al., 2005). The liquid fraction was decanted and analyzed for TS, VS, TSS, VSS, total P (TP), and pH. Chemically treated samples were analyzed for TP using a spectrophotometer (Hach Odyssey, DR/2500, Loveland, Colo.) and test kits (High Range Total Phosphate Test 'N Tube Kit, 0-100 mg/L as PO_4^{3-}, Loveland, Colo.) which were based on standard methods (4500-P). Flushed manure samples which contained high TP were analyzed according to AOAC (1984). This method was also used to initially verify the results obtained using the TP test kits. The sludge fraction was analyzed for TS and VS.

2.3.1 Chemical dosing

Jar tests were conducted using flushed manure. The original chemical dosing plan is shown in Table 10. When flushed manure with approximately 1.7% TS did not coagulate or settle after treatment, the manure was diluted until treatment produced solid/liquid separation. Appreciable settling did not occur using a 2:3 dilution (2 parts manure and 1 part water), but treatment of manure diluted 1:2 (1 part manure and 1 part tap water) produced solid/liquid separation using the chemical concentrations shown in Table 10. The average TS concentration in the diluted manure was 0.87% over the course of remaining experiments.

The first set of tests using the chemical dosages shown in Table 10 showed that high P removal could be achieved at much lower doses presumably due to the dilution of the manure. Another set of jar tests was conducted using ranges of 100 to 600 mg Fe/L for $FeCl_3 \cdot 6H_2O$ and $Fe_2(SO_4)_3 \cdot 5H_2O$, 60 to 360 mg Al/L for alum, and 100 to 600 mg Al/L for $AlCl_3 \cdot 6H_2O$ were then tested using six dosage increments per range. Increments of 60 mg Al/L were used for alum and increments of 100 mg Fe or Al/L were used for all other chemicals.

Table 10. Original chemical dosing plan for flushed manure prior to implementing manure dilution

Chemical	Dosages, mg Fe/L or mg Al/L										
	0	200	400	600	800	1000	1200	1400	1600	1800	2000
$FeCl_3 \cdot 6H_2O$	x	x	x	x	x	x	x	x	x	x	x
$Fe_2(SO_4)_3 \cdot 5H_2O$	x	x	x	x	x	x	x	x	x	x	x
$Al_2(SO_4)_3 \cdot 13H_20$	x	x	x	x	x	x	x				
$AlCl_3 \cdot 6H_2O$	x	x	x	x	x	x	x	x	x	x	x

	Dosages, mg active polymer/L							
Polymer	0	50	100	150	200	250	300	350
C-1598	x	x	x	x	x	x	x	
SD-2081	x	x	x	x	x	x	x	x
SD-2083	x	x	x	x	x	x	x	
4512	x	x	x	x	x	x	x	
4516	x	x	x	x	x	x	x	

2.3.2 Polymer dosing

Polymers were prepared at working concentrations of 0.50% (5 g polymer/L) by diluting neat polymer with deionized water and aged for 30 minutes according to manufacturer directions. The %TS (% activity) reported by the manufacturer and the polymer density measured in the laboratory were needed to determine the polymer volume needed for preparation of the diluted working solutions. Concentrations from 0.005% (50 mg polymer/L manure) to 0.03% (300 mg polymer/L manure) were tested based on results reported by Zhang and Lei (1998). Polymer dosages were tested in duplicate on flushed, diluted manure collected on two different days.

2.3.3 Chemical and polymer dosing

Combination dosing (chemical + polymer) was applied to both diluted and undiluted flushed manure after the most effective chemicals had been determined. The tests using diluted manure were conducted in duplicate using manure collected on two different days. One set of experiments was conducted using supernatant from jar tests as dilution liquid; this test was done in duplicate using one batch of manure. Supernatant was used to dilute flushed manure in three successive jar tests and supernatant quality was analyzed after each subsequent use.

3 Results and Discussion

3.1 Chemicals

During the first test using undiluted flushed manure, poor settling was observed in the Imhoff cones after 60 minutes. After diluting the manure and testing chemicals at the dosages shown in Table 10, clearer supernatant and better sludge compaction were observed at doses greater than 800 mg Al or Fe/L. The highest dose of $FeCl_3 \cdot 6H_2O$ (2,000 mg Fe/L) produced a red (overdosed) supernatant as shown in Figure 8. Characteristics of the manure prior to treatment are shown in Table 11. The third column shows the average mass of P per gram of total solids.

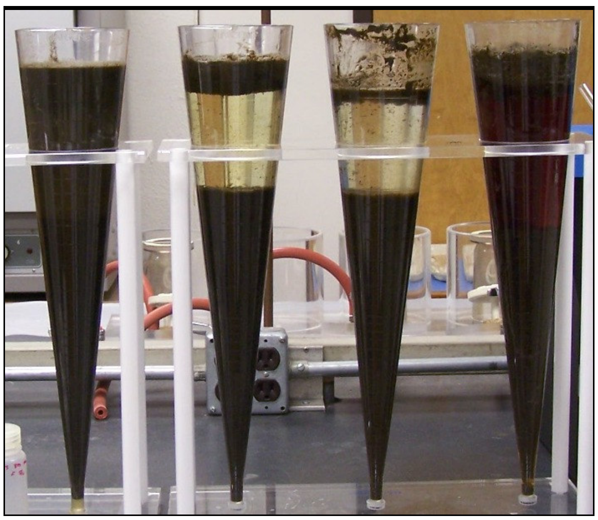

Figure 8. The effect of $FeCl_3 \cdot 6H_2O$ on diluted flushed manure using doses of 800, 1,200, 1,600, and 2,000 mg Fe/L from left to right. Overdosing occurred at the 2,000 mg Fe/L treatment as is evidenced by the red supernatant.

Table 11. Average characteristics of manure used for jar testing

	TS mg/L	**TP** mg P/L	**mg P/ g TS**	**pH**
Flush, 1:2 dilution	8,680	110	13	8.2

All chemicals achieved 90% P removal using less than 600 mg Fe/L of $FeCl_3 \cdot 6H_2O$ or $Fe_2(SO_4)_3 \cdot 5H_2O$, 400 mg Al/L of $AlCl_3 \cdot 6H_2O$, and 240 mg Al/L of alum. The chemical concentrations were then lowered to the ranges described in the methods. This narrowed range of doses corresponded with maximum dosages used in previous studies: 1,750 mg $FeCl_3$/L (605 mg Fe/L) and 800 mg alum/L (126 mg Al/L) in 0.8% TS dairy manure (Zhang and Lei, 1998) and an alum dosage of 317 mg Al/L in 1.0% TS dairy manure (Sherman et al., 2000). The P removal achieved by Al and Fe salts in dairy manure with 0.87% TS is shown in Figure 9..

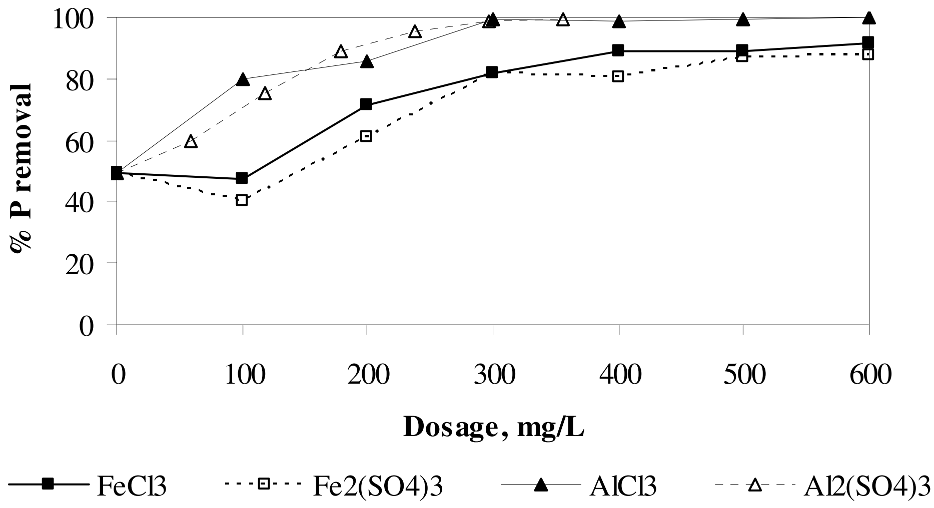

Figure 9. Percentage of P removal from one jar test using diluted flushed dairy manure with 0.87% TS and 86 mg P/L using chemicals as coagulants

Al-based salts outperformed Fe-based salts at all dosages, similar to the results of Sherman et al. (2000). Precipitation by Fe-based salts may be diminished since Fe is redox active, and previous studies have shown the Fe^{2+} salts are not as effective as Fe^{3+} salts (Barrow, 1997). Maximum P removals of 99% occurred at and above dosages of 300 mg Al/L (Figure 9). Fe-based chemicals reached maximum P removals of approximately 90% beyond 400 mg Fe/L. P removal did not increase significantly beyond 300 mg Fe/L and slightly decreased beyond 300 mg Al/L. Alum in the range of 0 to 180 mg Al/L and $FeCl_3 \cdot 6H_2O$ in the range of 0 to 300 mg Fe/L were selected for further testing with polymers due to their common usage and low cost. A summary of results and cost comparisons for maximum doses to be tested with polymer is shown in Table 12.

Table 12. Summary of treatment results for chemicals selected for use with polymer; costs are based on quotes from Univar USA, Inc. (Greensboro, N.C.) and $AlCl_3$ is included for cost comparison

Chemical	Dosage/unit		% TP removed	Normalized mg P rem. / g TS	Sludge, % of trmt vol	% TS removal	Sludge TS, mg/L	Liquid TS, mg/L	pH	Treatment cost, $/1000 L of manure
$FeCl_3$	300	mg Fe/L	82	8.3	63	52	13,230	4,080	7.2	1.1
Alum	180	mg Al/L	89	9.1	73	58	11,750	3,540	7.1	0.9
$AlCl_3$	200	mg Al/L	94	9.6	70	62	12,510	3,210	6.9	3.1

Figure 10 shows how the pH decreased in treated manure as the metal dose increased. The pH decrease was slightly less in the Fe-based chemicals although the pKa value of Fe^{3+} indicates that it is actually a stronger acid than Al^{3+}. However, the redox properties of Fe may have again contributed to this result because reduction of Fe^{3+} would produce Fe^{2+} which is a weaker acid than Al^{3+}.

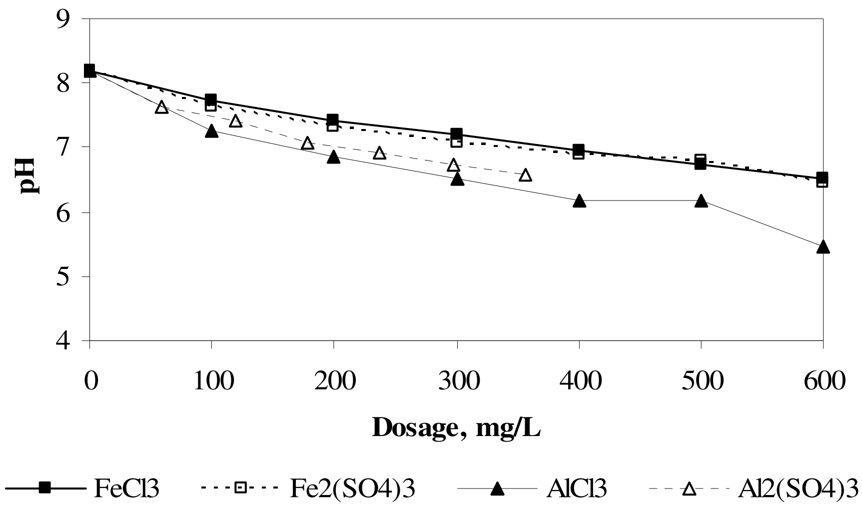

Figure 10. As chemical dose increases, pH of treated manure decreases.

3.2 Polymers

Polymer performance in terms of P removal (Figure 11) and TS removal (Figure 12) did not level out over the range of doses tested. Zhang and Lei (1998) found definite optimum dosages when testing polymers on both swine and dairy manure, but the doses used in their study were much higher than those used here. The optimum polymer dosage they found for dairy manure with 1.0% TS was approximately 0.075% (750 mg/L) which provided 75% TS removal. The maximum 4512 dosage of 250 mg/L shown in Figure 11 achieved 82% P removal and 68% TS removal which is comparable to the results by Zhang and Lei (1998) but at significantly lower doses. The disparity in removal rates between studies may be related to polymers (i.e. different structures or molecular weights) or to other manure characteristics besides TS.

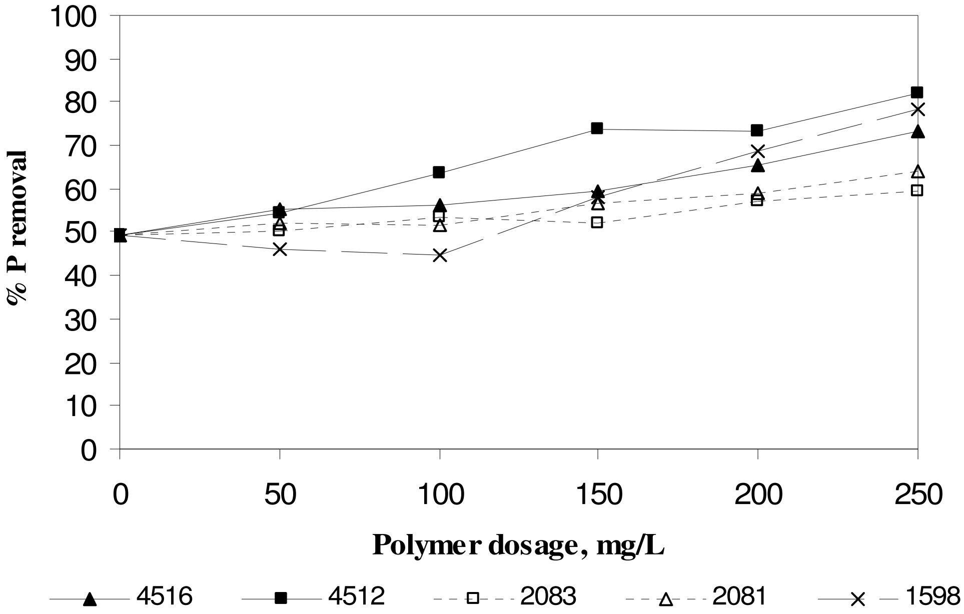

Figure 11. Percentage of P removal from flushed diluted dairy manure treated with polymer

Flocculation was observed using each type of PAM, but the SD-2000 series PAMs exhibited the poorest P removal. The SD-2000 series polymers had branched molecular configurations which would have been expected to promote better flocculation than polymers with linear configurations. However, the C-1500 and 4000-series PAMs, which both have linear configurations exhibited higher P and TS removals especially above 100 mg/L. The 4512 and C-1598 polymers, specifically, showed the greatest increase in P removal as polymer dosages increased. The ultra-high molecular weight polymers (4000-series) may have facilitated higher P removal by virtue of more sites for particles adsorption and longer chain length promoting contact with particles and other polymers for better flocculation. The Superfloc 4512 polymer was selected for further study based on its 82% P removal and exceptional TS removal compared with the other polymers as shown in Figure 12.

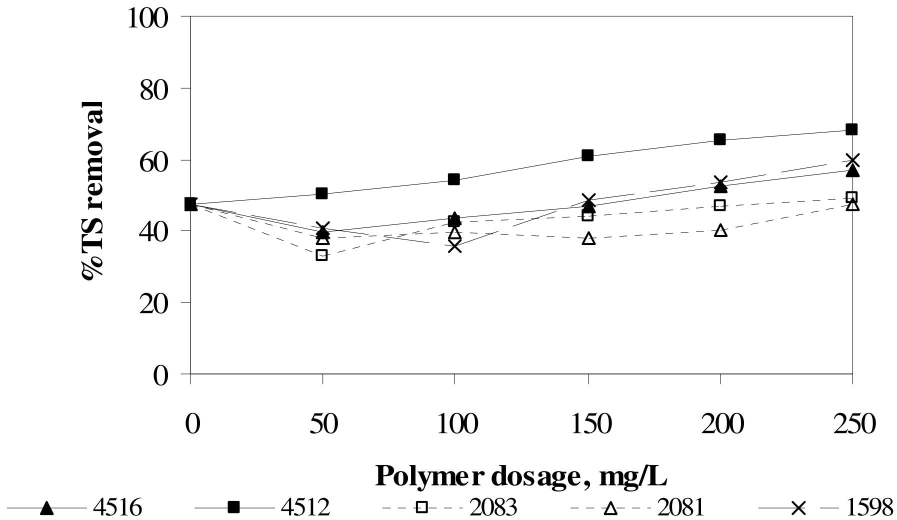

Figure 12. Percentage of TS removal from flushed diluted dairy manure treated with polymer

3.3 Chemical + polymer

The selected chemicals (alum and $FeCl_3 \cdot 6H_2O$) and polymer (Superfloc 4512) were used in combination on flushed diluted dairy manure. The highest P removal and best sludge characteristics did not always occur at the highest dosage. Although P removal was relatively constant for all PAM doses combined with an alum dosage of 180 mg Al/L as shown in Figure 13a, the nature of the flocs produced varied with PAM dosage which would influence the effectiveness of solid/liquid separation. Alum achieved the highest percentage P removal and floc characteristics at a 180 mg Al/L dose with just 100 mg/L of polymer. Higher doses of polymer with alum resulted in an overdosed appearance characterized by smaller, sticky flocs that settled poorly and adhered to the walls of the Imhoff cones.

The most effective $FeCl_3 \cdot 6H_2O$ dosage was determined to be 300 mg Fe/L plus 200 mg/L 4512 based on P removal and floc characteristics. This dosage was more effective than alum+polymer when compared using the graph in Figure 13b which is normalized to account for variations in TS concentration among collections of flushed manure.

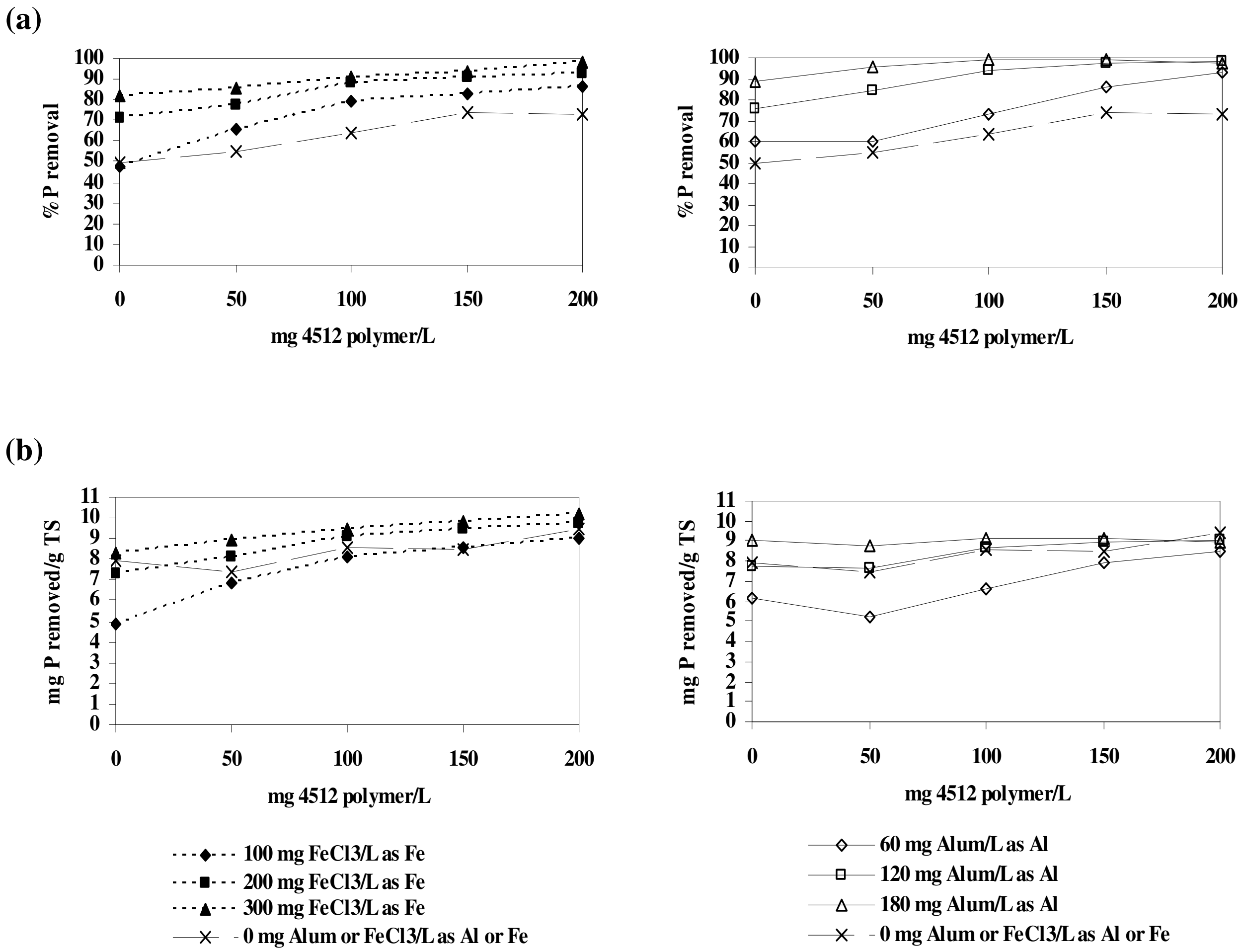

Figure 13. Percent P removal and P removal normalized to TS for treatments using chemicals and polymer combination

The chosen coagulant plus flocculant dosages were applied to full-strength flushed manure. Using manure containing 1.5% solids and 140 mg P/L, the $FeCl_3 \cdot 6H_2O$ combination dosage achieved 80% P removal and alum achieved 90% P removal. The pH and sludge production were the same for both treatments on full-strength flushed manure as shown in Table 13. Sludge production and TS concentrations after chemical treatment are greater for flushed manure than diluted flush as would be expected due to higher initial solids content. The alum treatment can potentially offer a significant cost savings over $FeCl_3 \cdot 6H_2O$ treatment simply due to the lower polymer dosage.

Table 13. Summary of results for chemical and polymer combination treatments on diluted and undiluted flushed manure.

Chemical	mg Fe or Al/L	Polymer 4512, mg/L	% P removal	Normalized mg P rem. / g TS	Sludge as % of trmt vol	% TS removal	Sludge TS, mg/L	Liquid TS, mg/L	pH
				Diluted flushed manure					
$FeCl_3$	300	200		10.2	23	67	44,630	2,680	7.0
Alum	180	100		9.1	25	48	60,350	2,530	7.2
				Flushed manure					
$FeCl_3$	300	200	80	7.1	35	52	70,020	7,230	7.6
Alum	180	100	90	8.0	35	58	61,620	6,430	7.6

The selected metal and polymer dosages (same as those shown in Table 13) were used in jar tests to determine the effects of using treated liquid manure for dilution of full-strength flushed manure prior to chemical treatment; this practice may benefit a dairy operation by reducing the need for storage space due to dilution water while still diluting manure to a treatable level. Prior to dilution, the manure used for this test contained 1.5% TS and 140 mg P/L. The dosages were first applied to flushed manure diluted with water (1 part manure to 1 part water).

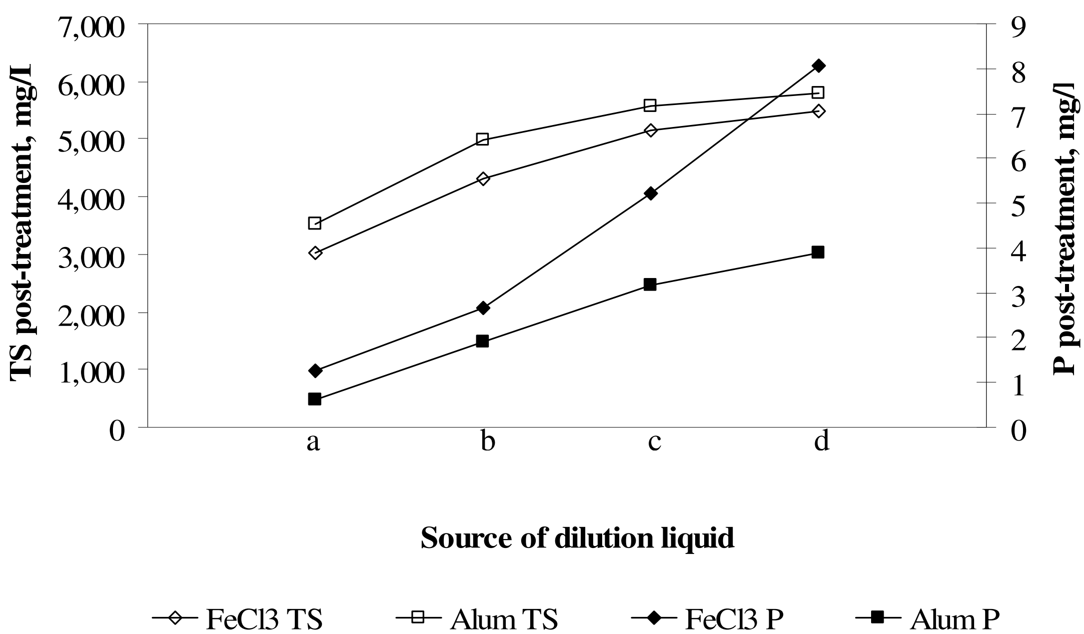

Figure 14. Effect of using supernatant liquid (resulting from chemical treatment) to dilute manure on the effectiveness of chemical P removal. (a) = diluted with tap water; (b) = diluted with (a); (c) = diluted with (b); (d) = diluted with (c).

Supernatant decanted after settling was used to dilute manure in the next jar test (1 part manure to 1 part supernatant). The recycling procedure was repeated three times. The TS concentration increased with reuse of dilution liquid and was higher using the alum treatment (Figure 14). However, P removal was higher using alum which is consistent with previous results from this study. Based on Figure 14, the use of treated supernatant as dilution water had a greater effect on P removal when $FeCl_3 \cdot 6H_2O$ was used. The supernatant became darker after each subsequent jar test and the sludge became less compact as shown in the photograph of subsequent treatments using alum and 4512 polymer (Figure 15). If supernatant was used to dilute manure on a continuous basis, the TS and P in the dilution liquid may become too high to effectively dilute the manure to treatable levels of TS and P. The results of this experiment may differ if a technique besides settling was used to separate supernatant from sludge. In future work, a bench-top belt press will be used to achieve more thorough liquid extraction from the sludge. The belt press may also reduce the TS accumulation that occurred with repeated uses of supernatant separated by settling only.

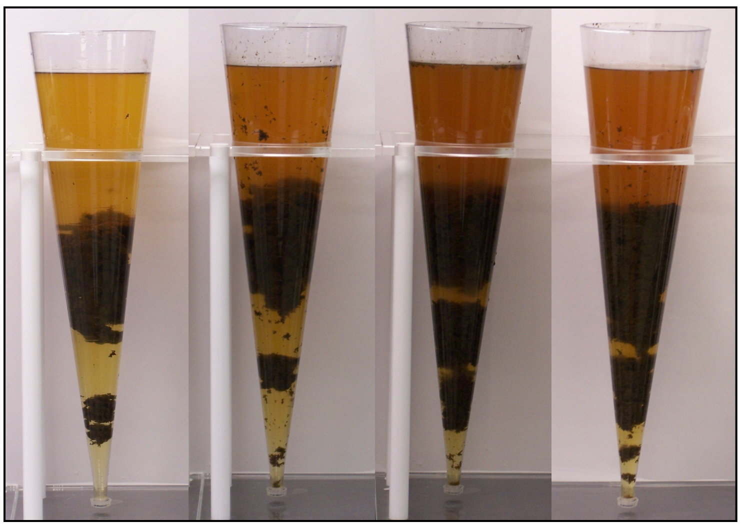

Figure 15. Using treated supernatant as dilution water resulted in successively darker supernatants and less sludge compaction. Dilution 1 (as previously defined) is shown at left, followed by Dilution 2, Dilution 3, and Dilution 4 (far right). The samples shown received alum dosages of 180 mg Al/L and 4512 dosages of 100 mg/L.

An attempt was made to develop a dosing equation so that a dairy could theoretically determine how much chemical was required for a certain level of P removal based on the TS concentration of flushed manure. A practical way to develop the equation would be to plot P removals at mass ratios of metal to solids, such as Al:TS. Since the addition of polymer improves P removal significantly, the graph of Al:TS versus P removal in Figure 16 includes the effect of Superfloc 4512 doses from 0 to 200 mg/L.

Figure 16 implies that any polymer dose with 180 mg Al/L of alum (0.025 g Al:g TS) is acceptable. However, the most effective dosage for alum and Superfloc 4512 was 180 mg Al/L and 100 mg/L polymer. Selection of this dosage cannot be clearly discerned from the graph alone because the dosage was based on both P removal and characteristics of the floc. The size of the flocs and the ability to effectively separate the solids from liquids by screening or other separation techniques changes with polymer dose. Both under-dosing and overdosing polymer resulted in small or sticky flocs that did not have desirable characteristics for solid-liquid separation.

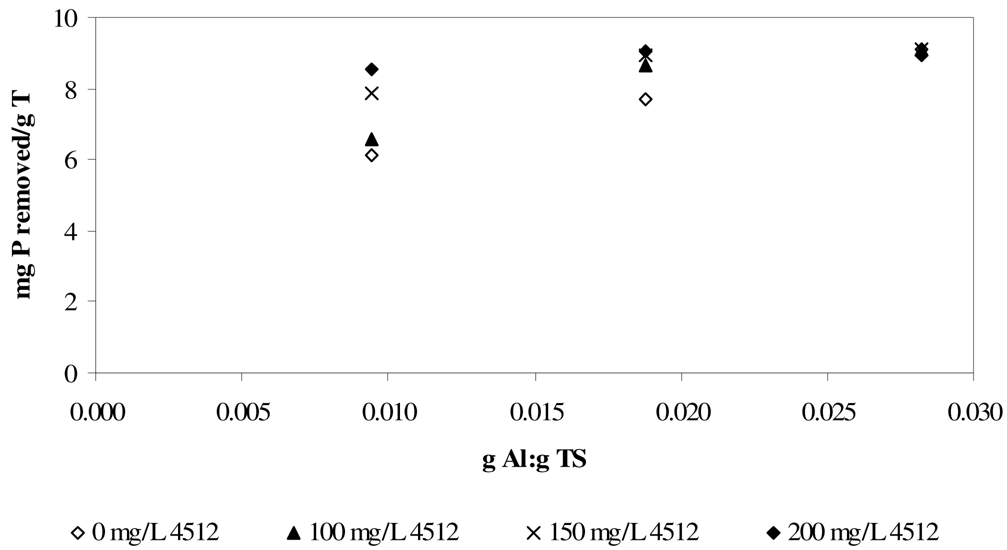

Figure 16. P removal expressed as a function of the Al dose to original TS concentration of manure. Results are based on the average P removal from two tests using flushed diluted manure with 0.64 and 0.79% TS. Alum was dosed at 60, 120, and 180 mg Al/L.

3.4 Application to Virginia Tech dairy

If chemical P removal is implemented at the Virginia Tech dairy, dosing could be done in Tank 2. To determine potential P removal from Tank 2, samples were obtained from the basin. The Tank 2 aerator was out of order and the tank had not been aerated in approximately two weeks when the sample was taken. The Tank 2 manure sample contained 0.89% TS and 70 mg P/L. During aeration, manure from Tank 2 has been reported as having approximately 1.5% TS and 80 mg P/L (K. Knowlton, personal communication, 1 November 2007). Jar tests using the proposed alum and $FeCl_3 \cdot 6H_2O$ doses were conducted in triplicate on the Tank 2 samples.

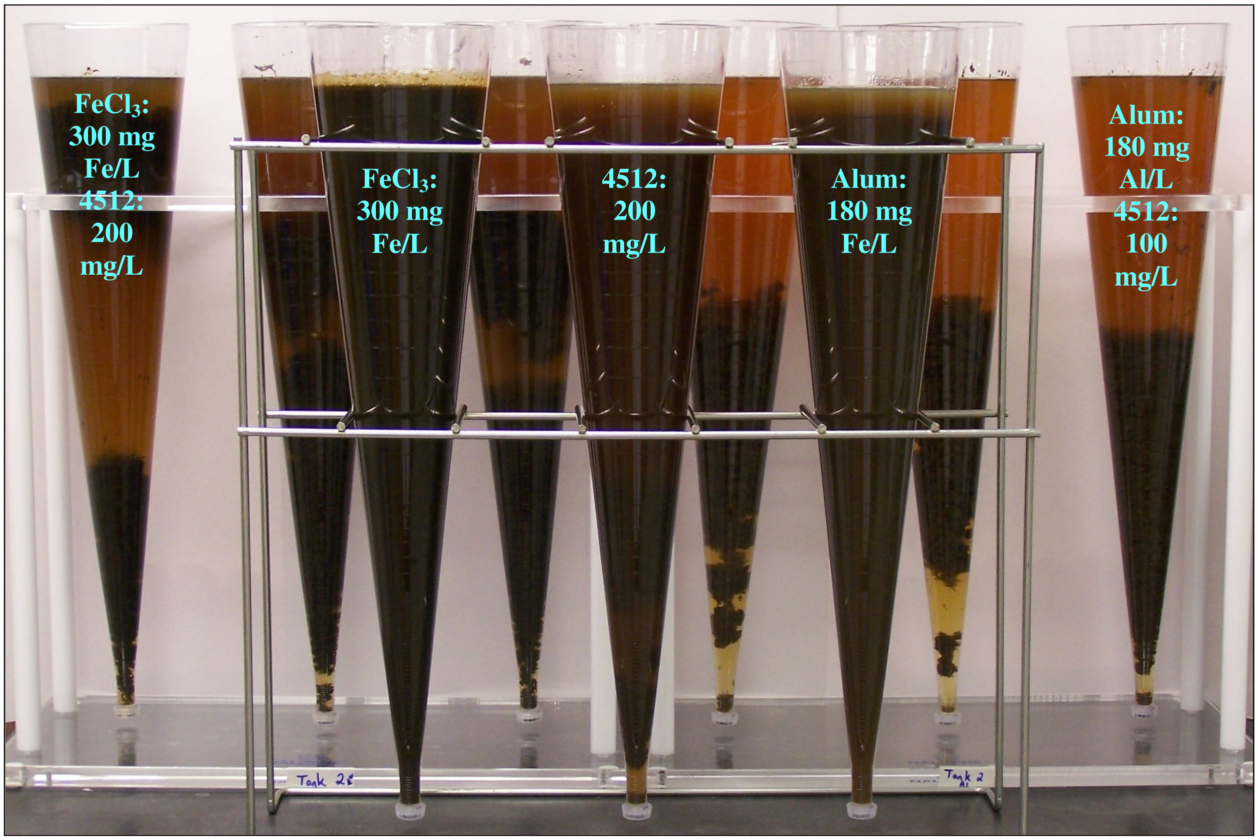

Figure 17. Application of chemical and polymer treatments to manure from Tank 2 (Virginia Tech dairy). The need for combined chemical and polymer treatment is evident since no solid liquid separation is achieved using chemical or polymer alone.

A photograph of manure from Tank 2 after the 60 min settling period is shown in Figure 17. Comparison of the combination treatments with the chemical- or polymer-only treatments shows that polymer is required to achieve solid-liquid separation in the manure samples. The $FeCl_3{\cdot}6H_2O$ and polymer treatment resulted in both floating and settled flocs. It is unknown whether this behavior would persist during full-scale treatment.

Table 14. Results from chemical and polymer treatment of Tank 2 liquid

Chemical	mg Fe or Al/L	Polymer 4512, mg/L	% P removal	Normalized mg P rem. / g TS	Sludge as % of trmt vol	% TS removal	Sludge TS, mg/L	Liquid TS, mg/L	pH
$FeCl_3$	300	200	91	7.1	60	45	16,700	4,750	7.4
Alum	180	100	95	8.0	25	44	21,610	4,870	7.5

Based on laboratory results shown in Table 14, the alum and polymer combination treatment is the clear choice due to its high P removal, lower polymer requirement, and lower overall dosing cost (Table 15). In previous laboratory tests, alum and $FeCl_3{\cdot}6H_2O$ had produced similar sludge volumes; during the chemical and polymer combination treatment on manure from Tank 2, sludge production using alum was less than half that produced by

$FeCl_3 \cdot 6H_2O$. If this dosing was used to treat Tank 2 containing 2,270 m^3 of manure, an estimated 570 m^3 of sludge would be produced. A single chemical dosage using 180 mg Al/L would require 4,370 kg of alum (410 kg as Al) at \$0.49/kg (\$0.22/lb). Use of Superfloc 4512 with the 100 mg/L dosage would require 570 kg of 4512 polymer at \$3.26/kg (\$1.48/lb) for a total cost of \$3,970.

Table 15. Cost of combined chemical and polymer treatment and cost of treating a 2,270 m^3 volume of manure in Tank 2 at the Virginia Tech dairy. Chemical costs were based on quotes from Univar USA, Inc. (Greensboro, N.C.), and polymer cost was obtained from Kemira Water (Lakeland, Fla.)

Chemical			Polymer 4512, mg/L	Cost, \$/1000 L manure			Tank 2
				Chemical	Polymer	Total	Total \$
$FeCl_3$	300	mg Fe/L	200	1.1	1.6	2.8	6,280
Alum	180	mg Al/L	100	0.9	0.8	1.7	3,970

Periodic chemical treatment may provide enough P removal to enable the bulk liquid manure to be used onsite as fertilizer without violating nutrient management plans. It is estimated that transporting 2,270 m^3 of manure offsite would cost \$12,000 (K. Knowlton, personal communication, 20 September 2007). Treating 2,270 m^3 and transporting the estimated 570 m^3 of sludge would cost less than \$7,000. Chemical treatment and sludge transport is more economical than transport of the entire manure volume alone.

4 Conclusions

Chemical treatment has the potential for significant P removal from dairy manure, particularly with combined metal salt and polymer usage. $FeCl_3 \cdot 6H_2O$ and alum in combination with an ultra-high molecular weight polymer were selected as the most efficient and cost effective treatments. After testing on liquid dairy manure with approximately 0.87% TS, the following dosages were selected based on both P removal and sludge characteristics: 300 mg Fe/L of $FeCl_3 \cdot 6H_2O$ + 200 mg/L 4512 polymer and 180 mg Al/L of alum + 100 mg/L 4512 polymer. These metal and polymer combination treatments provided more than 90% P removal from liquid dairy manure obtained from one of Virginia Tech's aerated basins. This shows the potential for high P removal if the basin is treated in the future.

A downside to chemical treatment is the cost of chemicals caused mainly by the need for high chemical dosages needed to treat dairy manure as compared to swine manure or municipal wastewater. However, cost estimates for the Virginia Tech dairy showed that chemical treatment offered a 40% savings compared to the expense of transporting all manure off the farm. Chemical P removal produces a low-P liquid that could be used for continued on-site irrigation and a reduced volume of high-P sludge fertilizer that could be transported to nearby P-deficient sites.

Questions remain about the fate of P bound in the sludge, the effect of polymers on crops, and the potential for odor if alum or other sulfate-containing chemicals are used. Bound P such as $AlPO_4$ or $FePO_4$ may not be immediately bioavailable thus delaying the uptake of P by crops. Maguire et al. (2001) found that soil incubated with chemically treated biosolids had lower water soluble P (WSP) concentrations than soil amended with untreated biosolids. Fertilization with treated biosolids did result in higher WSP than was present in the control (unfertilized) soil.

However, time, soil properties, and biosolids characteristics all have been shown to impact P availability and mobility, and P addition may be necessary to ensure that nutrient needs of crops are met when biosolids or manure containing bound P is used as fertilizer (Hyde and Morris, 2004; Maguire et al., 2001). Though concerns may arise about the effects of polymer on crops, Dentel et al. (1993) stated that there was no evidence to suggest that polymer-treated sludge was harmful to crops or soil microbes. Hyde and Morris (2004) even speculated that polymer may release P more readily than Al- or Fe-based chemicals due to differences in how the P is bound. Finally, studies are needed to determine if treatment of manure with sulfate-containing chemicals will result in odor production during manure storage. Although chemical P removal may not be a long-term solution for dealing with excess phosphorus, it is a highly effective and immediate solution that could be easily implemented, without construction of new treatment facilities, at dairies such as the Virginia Tech dairy facility.

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Chapter 4: Engineering Significance

Increasing animal production, decreasing farm size, encroachment of urban sprawl into rural areas, and the potential for nutrient pollution caused by leaching or runoff of nutrients from animal manure necessitate manure treatment. Removal or reduction of nutrients, specifically nitrogen (N) and phosphorus (P) is widely used in municipal wastewater treatment. This study furthered knowledge regarding N conservation and chemical P removal from dairy manure.

Continuous aeration is the conventional treatment used to achieve nitrification. Though effective, this treatment is energy intensive and costly. To reduce energy requirements, this study found that intermittent aeration, which includes periods of time that aeration is not provided, is an option to achieve N conversion from ammonium (NH_4^+) to nitrate (NO_3^-). To remain competitive with continuous aeration, the air could only be off for very short periods (20 minutes after every 60 min of aeration). Still, this intermittent aeration treatment could provide energy and cost savings which would be beneficial to both the environment and the farm operation.

The goal regarding nitrification was to conserve N as non-volatile NO_3^-. Intermittent aeration or the use of aerobic and anoxic zones during treatment has typically been used to facilitate N removal by nitrification and denitrification. The intermittent aeration strategy that supported nitrification during this study also produced the greatest amount of unaccounted-for N. While it is likely much of the N was lost as harmless dinitrogen gas (N_2) by denitrification or simultaneous nitrification and denitrification (SND), it is possible that N may have been lost as ammonia (NH_3), nitric oxide (NO), or nitrous oxide (N_2O) which have negative environmental effects. The use of intermittent aeration for treatment of dairy manure may need further evaluation to ensure that major forms of unaccounted-for N are not harmful to the environment; otherwise, the energy savings achieved by using intermittent aeration may be canceled out by the release of gases that could contribute to acid rain or global warming.

An attached growth reactor was used for the N treatment system in this study. The use of media for the attached growth is not uncommon in municipal wastewater treatment, but use of an attached growth system would be a novel strategy for a full scale liquid manure treatment system. The benefit of using attached growth reactors in this study was the prevention of nitrifier washout even using a relatively short hydraulic retention time (HRT). The ability to treat large volumes of manure in a short amount of time may be best accomplished using an attached growth system. For full scale treatment of dairy manure, a primary clarifier would be required prior to nitrification in the attached growth reactor to prevent the attached growth system from becoming quickly clogged by the high solids content of the manure.

High P removal was obtained using both iron (Fe)- and aluminum (Al)- based chemicals in combination with cationic polyacrylamides (PAMs). This study showed that polymer in addition to chemicals was necessary to obtain sludge compaction. Sludge compaction and settling are important at the Virginia Tech dairy where treated low-P liquid would be pumped from the surface of the tank and used for fertilizer. This study also showed that polymer allowed a lower dosage of chemical to be used which would help limit undesired metal accumulation in the soil where P-rich sludge is applied.

Appendix

Table A1. Properties of cationic Superfloc polyacrylamides provided by Kemira Water

Polymer	Configuration	Degree of Charge, %	Relative Molecular Weight	Viscosity at 0.5%, cps	Specific Gravity at 25°C	Total Solids, %
C-1598	Branched	55	High	260	1.00-1.06	46-50
SD-2081	Linear	55	High	320	1.01-1.05	46-50
SD-2083	Linear	55	High	280	1.01-1.05	46-50
4512	Branched	10	Very High	360	1.03-1.07	39-41
4516	Branched	40	Very High	340	1.03-1.07	39-43

Vita

Jo DeBusk grew up in Accomack County on Virginia's Eastern Shore. She obtained her Bachelor of Science degree in Biological Systems Engineering from Virginia Polytechnic Institute and State University (Virginia Tech) in 2005. She began her Master of Science work at Virginia Tech in January 2006. Upon graduation in Fall 2007, Jo will continue to work as a research assistant in the Biological Systems Engineering department. In the future, she would like to pursue a career in cooperative extension.