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CHEMICAL ADDITIONS FOR PHOSPHORUS REDUCTION IN LIQUID DAIRY MANURE

By

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ABSTRACT

CHEMICAL ADDITIONS FOR PHOSPHORUS REDUCTION IN LIQUID DAIRY MANURE

By

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Current trends in the dairy industry are for larger production facilities on smaller parcels of land. The trend of increasing herd size and decreasing land base has driven dairy producers to look for alternative treatment and utilization options for manure nutrients. Separation of manure nutrients into a liquid stream high in nitrogen and a solids stream rich with phosphorus allows for more flexibility in storage, transport, and utilization or export of manure nutrients. Treating liquid dairy manure (with an average of 2.85% total solids) with chemical additions in the laboratory and field experiments proved to significantly reduce soluble (SP) and total (TP) phosphorus in the liquid fraction. Chemical coagulants investigated with liquid dairy manure included lime, alum, and ferric chloride. Laboratory experiments using lime, alum, and ferric chloride reduced TP in the liquid fraction by up to 75%, 100%, and 82%, respectively, after 24 hours of settling. Settling for 24 hours with mixing as the only form of treatment decreased TP in the liquid dairy manure by 60%. Field experiments showed that 48 hours of natural settling reduced TP in the liquid by 55%, mixing increased the TP reduction to 73%. Chemical additions of lime, alum, and ferric chloride in the field tests reduced TP by 70%, 81%, and 71%, respectively.

Dedicated to Mom, Dad, Kevin, and Lindsay

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LIST OF ABBREVIATIONS

Al (III)	Aluminum in the +III Oxidation State
ATP	Adenosine Triphosphate
AWWA	American Water Works Association
BOD	Biochemical Oxygen Demand
Ca (II)	Calcium in the +II Oxidation State
COD	Chemical Oxygen Demand
DAP	Diammonium Phosphate
Fe (III)	Iron in the +III Oxidation State
$FeCl_3$	Ferric Chloride
FS	Fixed Solids
G	Velocity Gradient
GAAMP's	Generally Accepted Agricultural Management Practices
GMF	Green Meadow Farms, Inc.
MDEQ	Michigan Department of Environmental Quality
MWPS	MidWest Plan Services
NTU	Nephelometric Turbidity Units
P.A.	Public Act
PAM's	Synthetic polymers derivatives from polyarylamide
PHB	Poly-β-hydroxybutyrate
ppm	Part per million
RTF	Right to Farm Act
SP	Soluble Phosphorus

TP	Total Phosphorus
TS	Total Solids
TSP	Triple Superphosphate
VFA	Volatile Fatty Acid
VS	Volatile Solids

CHAPTER 1

INTRODUCTION

1.1 Industry Scope

The dairy industry is Michigan's leading agricultural commodity with cash receipts from the sale of milk totaling $729 million in 2000 (Michigan Agricultural Statistics, 2001). Michigan currently ranks 8th nationally in milk production. In 2000, there were 300,000 milk cows on 3,500 farms in Michigan. The average dairy cow in Michigan produced 8,626 kg (19,017 lb) of milk in 2000, with a total state production for the year of 2,588 million kg (5,705 million lb). While milk production continues to increase and cattle numbers remain unchanged the total number of dairy farms in Michigan continues to decrease.

A critical component of dairying is manure production. A full grown lactating cow will produce approximately 67 L (17.7 gal) of manure per day (MWPS, 2000) or 24,455 L (6,460 gal) annually. The annual total nutrients contained in the manure of one lactating cow are: 136 kg (300 lbs) of Nitrogen, 69 kg (153 lb) of P_2O_5, and 79 kg (175 lb) of K_2O.

1.2 Statement of Problem

Simply stated, the problem is that dairy farms, regardless of operation size or location, produce an immense amount of nutrients (nitrogen, phosphorus, and potassium) in the manure. Manure as excreted is 88% moisture (MWPS, 2000). Any additional dilution water from rain, cattle waterer's, or cleaning water further dilutes the manure slurry. The end fate of manure on most dairy farms is land application to fallow ground.

Two concerns arise from land application regarding phosphorus in the manure. The first concern deals with applying liquid dairy manure to land with tile drainage. Field tile serves as a direct conduit to fresh water. Saturated soils or well aerated soils with fissures and wormholes, may allow liquid manure to move very quickly to the tile drains and then to surface water. The second concern is with eroded sediment reaching surface water. Phosphorus in its stable form is anionic (negatively charged) and tends to adsorb to the cationic clay particles and iron minerals in the soil solution. Due to biological, chemical, and climatic changes in the soil and surrounding environment, phosphorus is continuously cycled in the soil solution. Often, soil erosion carries soil particles and attached nutrients until deposited in surface waters.

The real concerns arise when the phosphorus reaches the surface water through either drainage or surface water. Phosphorus is the limiting nutrient in the growth of algae. Phosphorus in excess of 0.02 ppm can cause elevated algae populations and accelerate the natural eutrophication of surface waters (Sharpley et al., 1999). In Michigan, surface water is of the highest priority since the Great Lakes system contains 20% of the world's fresh water (Copeland, 1996). In 1981, the Michigan Legislature enacted the Right to Farm Act (RTF), P.A. 93. The act was designed to protect producers from nuisance lawsuits by setting voluntary practices to ensure proper management of natural resources. The practices were written so that, if followed by agricultural producers, environmental quality would not be degraded. The practices, also known as GAAMP's (Generally Accepted Agricultural and Management Practices), provide guidance for manure management and utilization. For example, current voluntary guidelines call for no application of manure to ground that has a Bray P1 test of 150ppm (300 lb/acre) or greater. The traditional practice of disposing of manure in the least cost fashion has elevated soil phosphorus levels above 150 ppm on fields surrounding livestock operations. The 150 ppm phosphorus level is deemed sufficient to meet crop needs, but not so high as to have large quantities of soluble phosphorus free in the soil solution.

1.3 Proposed Solution – Chemical Phosphorus Separation

The present limits for manure application to the cropland, based on phosphorus concentration, reduce the application methods and management options available to producers. Utilizing a phosphorus reduction practice, like chemical phosphorus separation, before storage creates a liquid stream relatively low in phosphorus and a solid (sludge) stream with a high phosphorus concentration. In addition, chemical phosphorus separation has potential to add a profit center to the dairy business by creating a nutrient rich organic material that can be sold or used to replace commercial fertilizers in the cropping program.

Municipal and industrial wastewater treatment systems have long had to address the concern for nutrients in treated wastewater streams. Many approaches to the problem of nutrient removal from effluent have been developed and implemented over the years. Investigating the application of wastewater technologies to liquid dairy manure may offer know-how and information to aid in the development of a system or systems to better manage and reclaim the phosphorus.

1.4 Objectives

Nutrient management is quickly becoming a top priority in animal agriculture. In Michigan phosphorus is the primary nutrient of concern. Phosphorus management prior to manure storage is a relatively untested area that presents an opportunity for improved environmental quality and profitability. Based on this, the objectives of this project are as follows:

1) To evaluate and characterize the effluent stream following the sand and solid/liquid separation systems.

2) To compare the effectiveness of various chemical coagulants, under laboratory conditions, on the coagulation and reduction of phosphorus in the liquid fraction.

3) To apply laboratory findings to a pilot unit under field conditions to see if laboratory results translate to a larger scale reactor.

4) To evaluate the economic viability of a chemical treatment system.

1.5 Thesis Organization

Chapter 2 discusses the current methods for phosphorus removal and management in municipal and industrial wastewater treatment. In addition, recent efforts to reduce phosphorus concentrations in liquid dairy manure are also presented. Chapter 3 focuses on the laboratory methods used to characterize the manure stream and to analyze the phosphorus reduction efforts. The test procedures used in the laboratory and pilot tests are also considered. The results from laboratory and field tests using the pilot unit are presented in Chapter 4. Chapter 5 offers a summary of the study in addition to conclusions drawn from the project.

CHAPTER 2

LITERATURE REVIEW

2.1 General Comments

If phosphorus use continues to increase, worldwide phosphate reserves are expected to be completely depleted near the end of the next century (Driver, 1998). Globally, agriculture uses 85% of the total phosphorus extracted annually for commercial fertilizers and feed additives (Greaves, 1998). With agriculture leading the way in phosphorus use, it is the likely industry to target for phosphorus reduction or recovery programs. Phosphorus in agricultural fertilizers is one area targeted. Educational programs, financial constraints, and activist groups are helping to reduce over-fertilization of croplands. These same pressures are pushing livestock producers to examine how phosphorus is fed and manure is managed. Animal nutritionists have made advances in reducing the use of phosphorus concentrates in diets, but a large portion of the phosphorus fed to livestock remains indigestible and is excreted in the feces. Treatment and management of animal manure is where improvements in the removal, reuse, and management of phosphorus must be made.

With the passing of the Clean Water Act in 1972, municipal and industrial wastewater treatment systems were forced to meet strict standards for discharge to the waters of the United States. Wastewater treatment plants employed many diverse processes for removing phosphorus and other nutrients from the waste stream. Many of these technologies have application potential for dairy manure. In the Great Lakes region, wastewater treatment plants must follow stringent guidelines. Michigan's wastewater treatment facilities must achieve a maximum monthly average of 1 mg/L of total phosphorus in the effluent stream (MDEQ, 1999).

Phosphorus removal systems fall into two broad categories, biological and chemical. Biological phosphorus removal involves two stages, anaerobic digestion followed by an aerobic treatment. On the other hand, chemical phosphorus removal involves the addition of positively charged ions such as lime, ferric chloride, alum, or organic polymers, all of which bind to the phosphate anions forming large dense particles that settle out of suspension. Mechanical solids separation has been investigated as a means for phosphorus removal in agricultural livestock systems (Converse, 2000).

2.2 Agricultural Phosphorus

Since the introduction of commercial fertilizer, manure has long been thought of as a waste material with little value - a byproduct of milk production that should be handled, stored, and disposed of incurring the least expense to the dairy operation. In the mid-1990's, due to environmental pressure and the increased emphasis on profitability and efficiency, livestock producers began to view manure as a valuable fertilizer and soil amendment. Manure is a rich source of organic matter, nitrogen, phosphorus, and potassium. Agriculture is the world leader in phosphorus consumption and the United States is the largest consumer at 13% of the annual global phosphate. Western Europe is second using a combined 12% (British Sulphur Publishing, 1998). The majority of the phosphate used in agriculture is in commercial fertilizers, but a significant amount is used in the formulation of rations for livestock and poultry. Recovery and reuse of phosphorus excreted in the feces of livestock and poultry is essential for the sustainability of the world's phosphorus supply, surface water quality, and a safe and economic food supply.

A study conducted in 1995 on the nutrient balance of Michigan's cropland reported that Michigan is a phosphorus deficient state without the use of commercial fertilizer (von Bernuth and Salthouse, 1999). Using manure as the only source of fertilizer, Michigan would be in a deficit in phosphorus by 24 kg/Ha (21 lbs/ac). The overuse of commercial fertilizers causes an excess of 15 kg/Ha (13 lbs/ac) of phosphorus. Through better management, manure nutrients can be harvested and exported for use in deficient areas.

2.2.1 Phosphorus Transport from Agricultural Fields

Phosphorus is lost from agricultural fields by two processes, surface runoff and subsurface flow. Runoff events carry two forms of phosphorus, that which is bound to sediment and that which is dissolved in water. Sharpley et al. (1992) reported that 60 to 90 percent of the phosphorus lost to runoff is carried by sediment. Dissolved (soluble) phosphorus released from soil particles and decomposing plants comprises the remaining portion of the phosphorus lost to runoff. Soluble phosphorus is immediately available for aquatic plant and animal use, whereas phosphorus bound to sediment is a long-term source of phosphorus not accessible for utilization until released as soluble phosphorus (Ekholm, 1994). Subsurface flow contributes to soluble phosphorus loss in soils with low phosphate holding capacities (Cation Exchange Capacity) or where rapid flow follows macropores and wormholes. Figure 2.1 depicts the routes of phosphorus loss from soil and plants.

2.2.2 Agricultural Phosphorus and Water Quality

It is important to remember that runoff from agricultural fields is only one of several factors that influences phosphorus levels in surface water. The three main factors that influence the supply of soluble phosphorus in surface water are biological turnover, sediment exchange, and phosphorus input from runoff and discharge. Biological turnover and sediment exchange can be classified as recycling of phosphorus within the biological system. The third factor is the only input of phosphorus into the aquatic system. Furthermore, discharge and runoff are not strictly limited to agriculture. Other sources include industry, wastewater treatment plants, and golf courses, just to name a few.

FIGURE 2.1: Phosphorus Release from Soil and Plant Material to Surface and Sub-surface Water (Sharpley, et al., 1999)

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Research on phosphorus in livestock wastes has approached the subject from the standpoint of water quality. Water quality is a top concern for both society and the agricultural industry. Excess phosphorus in surface water wreaks havoc on the natural cycles and habitats. Phosphorus levels exceeding 0.02 ppm (Sharpley et al., 1999) in surface waters have been shown to significantly increase the rate of eutrophication or the natural aging of lakes and streams. Phosphorus contained in the runoff from cropland has been linked to algae blooms that can lead to fish kills and/or neurological damage in humans exposed to the toxins secreted by the algae (Burkholder et al., 1992). In addition to the water quality concerns, the depletion of the world's phosphorus reserves is forcing the entire agriculture industry to look for more conservation of phosphorus in agricultural cycles.

2.3 Physical Separation

Physical separation of manure solids and nutrients, primarily phosphorus and potassium, from manure effluent is based on size and density (Day, 1998). Physical separation is not only the most cost effective and simplest method of separation, it is also an essential characteristic of biological and chemical floc removal. Solid-liquid separation methods include settling (sedimentation), evaporation, and mechanical separation.

2.3.1 Settling

Suspended nutrients have a natural propensity to settle, as there density is generally greater than the density of water. Four types of settling have been identified in

TABLE 2.1: Types of Settling Phenomena Involved in Wastewater Treatment

(Metcalf and Eddy, 1991)

Type of settling phenomenon	Description	Application/occurrence
Discrete particle (type 1)	Refers to the sedimentation of particles in a suspension of low solids concentration. Particles settle as individual entities, and there is no significant interaction with neighboring particles	Removes grit and sand particles from wastewater
Flocculant (type 2)	Refers to a rather dilute suspension of particles that coalesce, or flocculate, during the sedimentation operation. By coalescing, the particles increase in mass and settle at a faster rate	Removes a portion of the suspended solids in untreated wastewater in primary settling facilities, and in upper portions of secondary settling facilities. Also removes chemical floc in settling tanks
Hindered, also called zone (type 3)	Refers to suspensions of intermediate concentrations, in which interparticle forces are sufficient to hinder settling of neighboring particles. The particles tend to remain in fixed positions with respect to each other, and the mass of particles settles as a unit. A solids-liquid interface develops at the top of the settling mass	Occurs in secondary settling facilities used in conjunction with biological treatment facilities
Compression (type 4)	Refers to settling in which the particles are of such concentration that a structure is formed, and further settling can occur only by compression of the structure. Compression takes place from the weight of the particles, which are constantly being added to the structure by sedimentation from the supernatant liquid	Usually occurs in the lower layers of a deep sludge mass, such as in the bottom of deep secondary settling facilities and in sludge-thickening facilities

wastewater: i) discrete, ii) flocculant, iii) hindered (also called zone), and iv) compression (Metcalf and Eddy, 1991). Sedimentation will generally involve multiple settling types at different stages and times. In some instances, all settling types may occur simultaneously. Table 2.1 contains descriptions of the four settling types.

Naturally occurring sedimentation has an impact on total solids and nutrient content of liquid dairy manure in storage. Jones and Brown (2000) reported reductions in effluent total solids of 18% to 35% and total phosphorus of 47% for a two-hour settling period. In other research, twenty minutes of unaided settling was found to remove 65% of the total solids and 60% of the total phosphorus in simulated dairy flushwater (Barrow et al., 1997). The literature, however, does not discuss the stability of the naturally settled sludge or management of the nutrients contained in the sludge. Lorimore et al. (1995) conducted a sediment basin study on feedlot runoff. It that study, it was determined that settling basins with retention times of 10 to 100 minutes reduced total solids by 39 to 53%. This study was conducted using beef manure from an open feedlot, thus gravel picked up in the runoff may have an influence on the sediment efficiency. Chastain et al. (1999) reported that liquid dairy manure in a simulated settling basin with a retention time of 60 minutes reduced P_2O_5 in the effluent by 38%. In addition, he reported that passing effluent from a screen separator through a settling basin removed an additional 14.6% of the P_2O_5.

2.3.2 Mechanical Separation

Mechanical separation is an important treatment method for dewatering animal manure. Dewatering produces liquid and solid fractions that can be better managed to meet the needs of the producer. The liquids may be injected or irrigated, while the solids can be composted or surface applied. Mechanical liquid-solid separators use sedimentation, screening, centrifugation, and/or filtration to remove free water from manure solids. Sloping screens, vibrating screens, screw presses, and centrifuges are commonly used methods for liquid solid separation of dairy manure. Mechanical separators function by exploiting differences in particle size and density to achieve the desired products of separate solid and liquid streams. Mechanical separation, as with most treatment options, is challenged by non-uniform characteristics and production of manure due to differences in species, genetics, age, rations, collection method, dilution, and weather.

Theoretical solids removal using mechanical separation for dairy manure slurries is in the range of 64 to 84% according to Zhang and Westerman (1997). The addition of chemicals to coagulate dissolved solids can result in removal efficiencies over 85%. Hegg et al. (1981) used three screens, vibrating, stationary, and rotating, to remove solids from dairy manure. The rotating, stationary, and vibrating screens removed 8.25%, 7%, and 12% of the dry matter, respectively. In this study, nutrient removal was not evaluated. Huijsmans and Lindley (1984), evaluated the usefulness of the stationary screen for removing solids from liquid dairy manure. They found that the static screen with or without a rinse bar was only able to remove approximately 25% of the total solids. In a more recent study, Zhang (1997), separation efficiencies for liquid dairy manure on stationary and vibrating screens were reported to be 49% and 8 to 16%, respectively. Nutrient removal efficiency for dairy manure was not presented in this study, however, Chastain et al. (1999) stated that 53.1% of the P_2O_5 was removed from liquid dairy manure by a static screen.

In 2000, Converse presented the results of research done on the solids and nutrient removal using screw presses. Converse found that the two screw presses (FAN and Vincent) removed 23.8% and 33.4% of the total solids. The phosphorus (P_2O_5) removal efficiency of the screw press was reported to be 5.7% and 9.7%.

Zhang (1997) states that the economics of solid-liquid separation are based on ease of manure handling, odor control, nutrient management, and manure solids value.

2.4 Phosphorus Removal and Recovery

Past research has focused on binding up phosphorus at various points in the manure or wastewater system. Phosphorus has been bound and settled in storage, thus creating a phosphorus sink in the sludge that settles out during storage. Others have attempted to chemically bind phosphorus in the field. Another approach to phosphate management in the manure stream is that of removal and reuse before storage. In the following sections past research on biological and chemical phosphorus removal will be discussed. Both biological and chemical phosphorus removal allow for several methods for managing and reusing of removed phosphorus. Removal, recovery, and reuse of phosphate in livestock manure is a sustainable and environmentally sound approach to manure management.

2.4.1 Biological Phosphorus Removal

Literature on biological phosphorus removal dates back to India in the late 1950's. Srinath et al. (1959) observed the phenomenon that would become known as "luxury uptake", the uptake of excessive amounts of phosphorus by microorganisms in wastewater when exposed to aerobic conditions following an anaerobic period. Biological phosphorus removal is dependent on a two-stage system where anaerobic conditions are followed by aerobic treatment. Under these conditions, microorganisms can hold approximately 12% phosphorus on a dry weight basis. Van Loosdrecht (1998) states that the advantage of biological phosphorus removal over chemical phosphorus removal is that biological removal systems are highly selective and can achieve low phosphorus concentrations in the system effluent. The drawbacks to biological phosphate removal are system management and collection and utilization of the biomass containing the phosphorus. Management issues associated with the biological system include i) equipment maintenance, ii) monitoring pH, temperature, and acetate levels, iii) correcting for fluctuations in pH, temperature, and acetate, and iv) assuring homogeneity of input stream and proper detention times.

2.4.2 Mechanisms of Biological Phosphorus Removal

Many references including Metcalf and Eddy (1991) and Van Loosdrecht (1998) describe biological phosphorus removal as a two-step process, an anaerobic phase and an aerobic phase. In the anaerobic phase fatty acids accumulate and are stored in the cells, polyphosphate serves as the energy source. Byproducts of this step include methane and limited denitrification of existing nitrate. During the aerobic phase, cell growth occurs with fatty acids serving as the energy source. It is during this period of cell growth that the "luxury uptake" of phosphorus occurs. At the same time, ammonia is converted to nitrate (nitrification). In the following sub-sections, the anaerobic and aerobic phases of biological phosphorus removal will be examined more closely.

2.4.2.1 Anaerobic Phase

Acinetobacter is the primary organism in the phosphorus removing bacteria group know as "bio-P bacteria". During the anaerobic phase, microorganisms use stored polyphosphate for the production of adenosine triphosphate (ATP) (Van Loosdrecht, 1998). In the absence of oxygen or nitrate, the "bio-P bacteria" amass volatile fatty acids (VFA's) using polyphosphate as the substrate. The VFA's storage under anaerobic conditions will serve as a substrate (energy source) for the "bio-P bacteria" during the aerobic phase, thus giving them an advantage over hetertorphs during aeration. The hydrolysis of polyphosphate supplies energy for polymerization of poly-β-hydroxybutyrate (PHB). In addition, the hydrolysis of polyphosphate releases phosphorus during the anaerobic stage, the released phosphorus accumulates until it is shuttled out of the cell by the pH gradient sensitive "carrier". Anaerobic conditions are favorable for the formation of PHB, which serves as a reserve for carbon and energy. Cell membrane activity is strongly influenced by pH, therefore, the transport and ratio of VFA uptake and phosphorus release is dependent on pH (Smolders et al., 1994). Figure 2.2 presents the cycle of the bio-P bacteria during the anaerobic phase.

FIGURE 2.2: Bio P Bacteria During the Anaerobic Phase (Hashsham, 2000)
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2.4.2.2 Aerobic Phase

The energy from the hydrolysis of PHB during the aerobic phase is used in the growth of new biomass and formation of polyphosphate. Normal metabolic phosphorus uptake meets the microorganisms' needs for maintenance, synthesis, and energy transport. Excessive polyphosphate development serves as a phosphorus reserve for future phosphate needs. The wasting or removal of the excess biomass (sludge) produced during the aerobic stage is the route by which phosphorus is removed from the waste stream.

For years, biological phosphorus removal has been an effective method for industrial and municipal waste treatment. On the other hand, very little is known about biological phosphorus removal for animal wastes. Due to the differences in animal and municipal wastes a direct transfer of application could very well fail. Animal manures have nutrient levels that are several orders of magnitude higher than municipal wastes. In addition, municipal wastes are much lower in total solids content than animal wastes. Table 2.2 shows a comparison of municipal and dairy wastewater.

The effects, benefits, and disadvantages of anaerobic and aerobic treatment have been well documented for several types of animal wastes. However, very little information exists on biological phosphorus treatment of animal waste and even less information exists on dairy manure treatment. Recent papers by Sukias, J.P.S. et al. (2000), Moser, M.A. et al. (2000), and Zhang R.H. et al. (2000) looked at the application of anaerobic and aerobic conditions for treating dairy manure.

Biological phosphorus removal is a complex process involving several steps and intensive management. Another disadvantage is the high capital cost associated with new biological treatment facilities.

2.5 Mechanisms of Chemical Phosphorus Removal

Chemical addition as a means of nutrient removal and purification have been used since the late nineteenth century in both water and wastewater treatment. Chemical nutrient removal is dependent on three steps: i) coagulation, ii) flocculation, and iii) settling of the aggregated floc (Francois, 1984). Settling and sedimentation of the floc has been discussed in the Physical Separation section of this chapter. The following sub-sections contain a discussion of coagulation and flocculation as it relates to nutrient removal from liquid dairy manure.

TABLE 2.2: Municipal Wastewater Vs Dairy Manure

Parameters	Municipal[1]	Dairy[2]
	Wastewater	Wastewater
	(mg/L)	(mg/L)
Color	Grey to Black	Brown to Black
BOD_5	250	15,000
COD[*]	500	37,619
Total N	40	6,000
Total P	9	3,000
Total Solids	300	95,000
Volatile Solids	240	81,000

[1] Southwest Biotechnology and Infomatics Center
[2] Mid-West Plan Service-18, 2000
[*] Laboratory experiments conducted during this Thesis project

2.5.1 Coagulation and Precipitation

The terms coagulation and flocculation are used interchangeably in the water treatment literature. Coagulation and flocculation, in theory, refer to the aggregation of particulates. Precipitation is the formation of particulates.

The goal of chemical coagulation is to increase the particle size of suspended material. Coagulation is dependent on two factors, charge neutralization and interaction. Essentially, coagulation is the destabilization of colloidal particles by the addition of coagulants that reduce the repulsion between particles. O'Melia (1970) refers to the Schulze-Hardy rule which states that coagulation is brought about by the ion of opposite charge of the colloid and that the efficacy of this ion increases markedly as its charge or valence increases. According to Schulze-Hardy, each charge on the chemical ion brings about a ten-fold increase in its coagulation ability. As the charge on the coagulant goes from 1 to 2 to 3 its coagulating ability goes from 10 to 100 to 1000 (O'Melia, 1970).

Coagulation is the process by which dense aggregates are formed by the assembly of suspended particles with multivalent ions or organic polymers. In wastewater treatment systems the multivalent ions used for coagulation are generally cationic. After coagulation, the increased densities of the newly formed aggregates cause them to settle. If coagulation alone does not achieve the desired results, the coagulated suspension may pass into a flocculation system where the destabilized particles form larger, denser flocs with the addition of a polymer.

Coagulation takes place in a rapid mix chamber, the chamber is used to create a homogenous mixture and ensure contact between colloids and ions or polymers. Hudson (1967) states that industrial plants use powerful mixing devices with rapid mix chamber detention times of not greater than thirty seconds. The design of rapid mixing for coagulation is based on the velocity gradient (G). The velocity gradient is dependent on the mixing power input, the fluid viscosity, and the fluid volume. The velocity gradient equation developed by Camp and Stein (1943) has become the standard for municipal and industrial treatment plant mixing design. Table 2.3 contains average detention times and velocity gradients for wastewater treatment. The equation for the velocity gradient is (Sievers, 1989):

$$G = \sqrt{\frac{P}{\mu V}} \tag{2.1}$$

where G = mean velocity Gradient (1/s)

P = power (ft·lb/s)

μ = dynamic viscosity (lb·s/ft^2)

V = volume (ft^3)

Sievers (1989) studied velocity gradients in one percent (TS) animal manure slurries. Samples were agitated in a jar test apparatus for 20 minutes, then allowed to settle for 100 minutes. Sievers reported that the optimum velocity gradient (G) for chemical addition to dairy manure was 22.3 s^{-1}. Detention times in this trial ranged from 240 seconds for iron additions to 480 seconds for chitosan. Sievers also reported that chemical coagulation in wastewaters with high organic solids concentrations required less mixing.

2.5.2 Flocculation

As defined by Hemenway (1968), flocculation is the physical mixing of particles destabilized by coagulation in order to form larger floc structures through contact.
In contrast to the rapid-mix chamber utilized for coagulation, which uses high power with a short retention time, a flocculation basin uses low power input with a longer detention

time. Insufficient mixing may result in poor cluster (floc) formation, thus reducing solids and nutrient removal (Sievers, 1989). Excess mixing may cause the flocculation process to become ineffective. This occurs when the shear forces cause the floc to disintegrate because the cohesion strength of the particles has been exceeded. Traditionally the velocity gradient ranges from 30 to 60 s^{-1} for good floc formation in municipal and industrial water treatment as seen in Table 2.3 .

TABLE 2.3: Typical Velocity Gradient (G) and Detention Time Values for Wastewater Treatment Processes (Metcalf and Eddy, 1991)

		Range of values	
Process		**Detention time**	**G value, s-1**
Mixing			
	Typical rapid mixing operations in wastewater treatment	5 - 20 s	250 - 1,500
	Rapid mixing in contact filtration processes	< 1 - 5 s	1,500 - 7,500
Flocculation			
	Typical flocculation processes used in wastewater treatment	10 - 30 min	20 - 80
	Flocculation in direct filtration processes	2 - 10 min	20 - 100
	Flocculation in contact filtration processes [a]	2 - 5 min	30 - 150

[a] Flocculation occurs within granular-medium filter bed

2.5.3 pH Adjustment

It is well understood that pH adjustment of the waste stream can have a significant influence on the effectiveness of chemical coagulants (O'Melia, 1969). In certain cases, coagulation or flocculation can be induced by simply adjusting the pH through the addition of acids or bases. Sievers et al. (1994) investigated the effects of pH adjustment on settling and turbidity removal. Increasing the pH of dairy wastewater and poultry litter was found to have little effect on water clarity. On the other hand, increasing the pH of swine manure drastically reduced turbidity. Metcalf and Eddy (1991) state that there is generally no relationship between turbidity and suspended solids or phosphorus. pH adjustment alone does not appear to be the answer to phosphorus removal from dairy manure, however it may play a role in influencing and improving the efficiency of other coagulants.

2.5.4 Solids and Phosphate Removal using Chemical Additions and Organic Polymers

The most commonly used chemical precipitants in phosphorus removal are calcium [Ca(II)], aluminum [Al(III)], and iron [Fe(III)] and organic polymers. The addition of multivalent metal ion salts to wastewater forms precipitates with soluble phosphates. The

TABLE 2.4: Chemicals Used in Wastewater Treatment (Metcalf and Eddy, 1991)

Chemical	Formula	Molecular weight	Density, lb/ft^3	
			Dry	Liquid
Alum	$Al_2(SO_4)_3 * 18H_2O^a$	666.7	60 - 75	78 - 80 (49%)
	$Al_2(SO_4)_3 * 14H_2O^a$	594.3	61 - 75	83 - 85 (49%)
Ferric chloride	$FeCl_3$	162.1		84 - 93
Ferric sulfate	$Fe_2(SO_4)_3$	400		
	$Fe_2(SO_4)_3 * 3H_2O$	454		70 - 72
Ferrous sulfate	$FeSO_4 * 7H_2O$	278	62 - 66	
Lime	$Ca(OH)_2$	56 as CaO	35 - 50	

[a] Number of bound water molecules will vary from 13 to 18

Note: lb/ft^3 x 16.0185 = kg/m^3

increased molecular weight of the precipitates enhances settling. Table 2.4 from Metcalf and Eddy (1991) presents some common forms of the metal salts used in wastewater treatment. Likewise, polymers are anionic, cationic, or nonionic and work by bridging particles into larger aggregates.

In wastewater treatment, there are three strategies for phosphate removal from the waste stream, including pre-precipitation, co-precipitation, and post-precipitation. Pre-precipitation involves the addition of coagulants or flocculants to the raw waste stream, the phosphate is then settled out in the primary clarifier. Co-precipitation occurs when chemically coagulated phosphate is removed with biological sludge following a biological treatment such as anaerobic digestion. Sievers et al. (1994) discuss using chemical coagulants to treat swine manure for volatile solids removal following anaerobic digestion. Post-precipitation is the addition of chemical coagulants following secondary settling.

2.5.4.1 Calcium

Calcium in the form of lime is frequently used to treat wastewater for solids and phosphate removal. Lime added to wastewater first reacts with the natural bicarbonate alkalinity to form $CaCO_3$. Calcium ions react with phosphate ions above pH 10 to form hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$), a precipitate (Metcalf and Eddy, 1991). The phosphate-calcium reaction is shown by equation 2.2:

$$10Ca^{+2} + 6PO_4^{-3} + 2OH^- \Leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \qquad (2.2)$$

The alkalinity of the wastewater is the main factor that influences the dosage needed. Metcalf and Eddy (1991) state that a good rule of thumb for calcium phosphate precipitates is that lime must be added at a rate of 1.4 to 1.5 times the total alkalinity. Lime as a coagulant can be used in a pre-precipitation or post-precipitation system. Barrow et al. (1997) reported that the addition of hydrated lime to a simulated dairy flush stream reduced total solids by 72.3%. In this same study, little difference was seen in the amount of total solids and nutrients removed by various levels of calcium addition.

2.5.4.2 Aluminum

Aluminum in the form of liquid alum ($Al_2(SO_4)_3 \cdot 14\text{-}18H_20$) is a common coagulant used in wastewater treatment. Unlike lime, alum will precipitate phosphate in a molar ratio of one to one. In addition, aluminum ions are most effective in the neutral to slightly acidic range. The phosphate precipitation reaction that occurs when wastewater is treated with alum can be written as follows:

$$Al^{+3} + H_nPO_4^{n-3} \Leftrightarrow AlPO_4 + nH^+ \qquad (2.3)$$

Due to the many variables including pH, alkalinity, trace elements, and organic matter that influence chemical coagulation, equation 2.3 cannot be used to predict the alum dosage without bench scale confirmation. Laboratory confirmation of chemical doses is done using jar tests with the actual wastewater to be treated. A more in-depth description of jar testing is found in the Chapter 3, Experimental Methods.

A study conducted by Jones and Brown (2000) used alum to treat dairy wastewater. During lab tests, it was observed that a 3 g/L dose of alum reduced ortho-phosphorus in the effluent by 93-99%. The study reported 81% total phosphorus removal using a dose of 3 g/L of alum. Jones and Brown (2000) indicated that at treatment levels higher than 3 g/L the total phosphorus removal actually decreased. In 1998, Zhang and Lei reported that additions of aluminum sulfate improved settling of manure solids by promoting coagulation.

2.5.4.3 Iron

Iron reacts with phosphate in wastewater in much the same manner as aluminum. Several forms of iron are used to treat wastewater for phosphorus removal, the most common are Ferric Chloride ($FeCl_3$), Ferric Sulfate ($Fe_2(SO_4)_3$), and Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$). Phosphate precipitation using iron is represented by equation 2.4:

$$Fe^{+3} + H_nPO_4^{n-3} \Leftrightarrow FePO_4 + nH^+ \qquad (2.4)$$

As with alum, one mole of iron will precipitate one mole of phosphate. Furthermore, the iron-phosphate reactions are also hampered by side reactions, thus laboratory testing should be done to confirm equation 2.4. Unlike aluminum, iron works best in acidic conditions (pH < 6).

Traditionally, iron has been the most popular of the three cations for wastewater treatment. Barrow et al. (1997), Sievers et al. (1994), and Zhang and Lei (1998) all looked into the usefulness of iron for reducing total solids and nutrients in the dairy wastewater stream. Barrow et al. (1997) simulated dairy flushwaters with 0.5, 1.0, and 1.5% total solids to test the usefulness of iron for solids and nutrient removal. Barrow reported that ferric chloride was more effective than ferric sulfate and that 278 mg/L of ferric chloride reduced phosphorus in the effluent by 89%. An interesting finding by Zhang and Lei (1998) is that large solids in animal wastes did not hinder the actions of chemical coagulants. In the same study, Zhang and Lei (1998) found that the optimum dose of chemical coagulant is related to the solids content. The optimum dose for a waste stream with 1.6% total solids was found to be 1000 mg/L.

As with phosphate, iron has been found to be an effective means for removing solids from animal waste streams. Barrow et al. (1997) found that 278 mg/L of $FeCl_3$ reduced total solids by 88.8%. $FeCl_3$ with 358 mg/L of calcium oxide (CaO) increased solids removal to 93%. Sievers et al. (1994) used $FeCl_3$ to remove volatile solids from 1% total solids simulated waste streams of dairy, swine, and poultry manure. It was found that $FeCl_3$ removed 75% of volatile solids from dairy and swine wastewater, but was far less effective for poultry manure.

2.5.4.4 Polymers

Unlike the ionic coagulants discussed previously, organic polymers are commonly used as flocculating agents in wastewater treatment. The polymers can be natural or synthetic, can carry a charge or not, and the molecular weight can be manipulated to meet the desired treatment need. Natural polyelectrolytes are biological derivatives of starch products, cellulose, or alginates. Synthetic polymers are monomers that have been polymerized into high molecular weight chains. Zhang and Lei (1998) state that the majority of synthetic polymers are derivatives of polyarylamide (PAM's). Polyelectrolytes can posses a charge, positive or negative, or can be charge less (nonionic). Molecular weights of organic polymers are generally in the range of 10^4 to 10^6. Polymers have two advantages over metal salts, they are at least partially biodegradable and they do not interfere with further biological processing. However, polyelectrolytes are substantially more expensive at \$7.48/kg than metal salts, which cost \$0.40/kg (Sievers et al., 1994).

Polymers act by several modes of action as seen in Figure 2.3 from O'Melia (1969). The most common is the floc formation, Reaction 2A, where both coagulation and bridging take place. Adding a polyelectrolyte with opposite charge of the wastewater particles coagulates the wastewater. Wastewater particles are generally anionic, thus cationic polymers are used to counteract the charge. Coagulation is carried out in the rapid mix chamber which has short retention time, but uses large amounts of power to assure complete mixing. Bridging occurs in the flocculation chamber and is the attachment of two or more particles to the same polymer chain. As more particles become attached and intertwined in the polymer chain a new particle known as a "floc" forms. Flocculation basins use much less power for mixing, but the wastewater has a longer detention time. Hemenway and Keshavan (1968) suggest velocity gradients of 30 to 60 s^{-1} for floc formation. They also state that gradients of greater than 75 ft s^{-1} cause excessive shear and may cause the polymers to break apart.

FIGURE 2.3:Reactions between Colloidal Particles and Polymers (O'Melia, 1969)
See Michigan State University, Department of Agricultural Engineering Library

Jones and Brown (2000), Zhang and Lei (1998), and Sievers et al. (1994) all used commercially available polymers to treat animal wastes for solids and nutrient removal. Jones and Brown were able to reduce total solids by 85% with polymers, but found little reduction in orthophosphorus using only cationic PAM's. Combining the polymer with alum treatment reduced the amount of polymer used and significantly improved solids and orthophosphorus removal. Zhang and Lei (1998) reported similar results using combinations of ferric chloride and synthetic polyelectrolytes. Sievers et al. (1994) reported 75% volatile solids removal using chitosan, a natural polymer, from cattle slurries.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 General Comments

This chapter describes and discusses the techniques and methods utilized to characterize liquid dairy manure and to test the ability of various additives to coagulate and settle phosphorous. The American Water Works Association (AWWA) standard procedures for determining soluble phosphorous (SP), total phosphorous (TP), chemical oxygen demand (COD), total solids (TS), volatile solids (VS), fixed solids (FS), and turbidity, were used throughout the phosphorous separation study to characterize the manure stream and determine removal efficiencies. Workers in both industrial and municipal wastewater treatment industries accept the AWWA methods.

3.2 Standard Techniques and Procedures

3.2.1 Soluble Phosphorus (SP)

The technique to determine the soluble phosphorus (SP) is AWWA (1993) section 4500-P, direct phosphorus analysis. This analysis looks strictly at the reactive (soluble) phosphorus in the sample of wastewater.

3.2.1.1 Materials

The following equipment was used to determine the soluble phosphorus content of the liquid dairy manure:

250 ml Erlenmeyer Flasks

1.6 Micron Glass Fiber Filter

Fischer Scientific Vacuum Pump, 1/3 Hp

Extech pH/mV/Temperature Meter

Hach test tubes

10 ml Pipette and Pipette Filler

Eye Dropper and Bottle

Milton Roy Spectronic Model and Spectrophotometer

3.2.1.2 Methodology

Soluble phosphorus is the measure of reactive phosphorus, primarily orthophosphate, which responds to colorimetric tests without preliminary hydrolysis or oxidative digestion. Reactive phosphorus can be dissolved or suspended. The preparation procedure for soluble phosphorus analysis includes the following steps:

- Manure samples are diluted 200 to 1 with deionized water. This level of dilution is necessary due to the high phosphorus content of dairy manure and the relatively small range of the stannous chloride colorimetric procedure.
- The diluted sample is then vacuum filtered through the 1.6 micron filter. This step removes the large suspended particulates in the sample.
- 100 ml of the filtered sample is measured into an Erlenmeyer flask and the solution is allowed to reach room temperature.

Colorimetric analysis of the 100 ml filtered sample is carried out using the Stannous Chloride Method, AWWA (1993), 4500-P D. Stannous chloride analysis proceeds as follows:

- 4.0 ml of the Ammonium Molybdate Reagent I and 0.5 ml of Stannous Chloride Reagent I are added to the 100mL filtered sample, care is taken to assure thorough mixing between reagent additions.
- Color development is measured 10 minutes after reagents are added, but before 12 minutes.

Overcash et al. (1974) points out that ascorbic acid, stannous chloride, and vanadomolybdate methods "yield essentially similar results for orthophosphate analysis and have nearly the same variability." The absorbance of the solution is measured photometrically at 690 nm in the visible spectrum using a spectrophotometer. Absorbance measurements are then compared to the calibration curve to get the actual soluble phosphorus of the sample. Calibration curve preparation is discussed later.

3.2.2 Total Phosphorus

The analysis procedure used to measure total phosphorus (TP) is the Persulfate Digestion procedure defined in the AWWA Standard Methods (1993), section 4500-P. Persulfate digestion oxidizes organic matter present in the manure sample and releases the bound phosphorus as orthophosphate.

3.2.2.1 Materials

The following equipment is used to determine the total phosphorus content of liquid dairy manure:

250 ml Erlenmeyer Flasks

Corning Hotplate

Fume Hood

Extech pH/mV/Temperature Meter

Hach test tubes

10 ml Pipette and Pipette Filler

Eye Dropper and Bottle

Milton Roy Spectronic Spectrophotometer

3.2.2.2 Methodology

Total phosphorus is the colorimetric measure of the ortho-phosphate in the sample following oxidation. The procedure for analyzing a sample for total phosphorus is as follows:

- Samples are diluted 200 to 1 with deionized water.
- Sample digestion, 1 ml of sulfuric acid solution and 0.40 g of ammonium persulfate are added to 50 ml of the diluted sample which is then gentle boiled using the hot plate.
- Boiling persists until a final volume of 10 ml is reached.
- Digested sample are then diluted to 100 ml and cooled to room temperature.
- Colorimetric analysis is then carried out using the Stannous Chloride procedure discussed under the soluble phosphorus section.

Analysis results are then compared to the calibration curve to get actual phosphorus concentrations.

3.2.3 Phosphorus and COD Calibration Curve Preparation

The calibration curve is essential to quantifying the results of colorimetric analysis. The calibration curve is a reference point to make comparisons between unknown phosphorus concentrations and known concentrations. In this project, five and four point calibration curves were used for phosphorus and chemical oxygen demand (COD), respectfully.

3.2.3.1 Materials

The materials needed to create a phosphorus calibration curves are the same as for SP and TP analysis.

3.2.3.2 Methodology

The calibration curve is created by carrying a series of orthophosphate and COD standards through the same methods used for SP and TP and COD analysis. Due to treatment differences, separate curves are produced for SP and TP. The points for the phosphate calibration curves are 0, 0.5, 1.0, 1.5, and 2.0 ppm. Similarly, the four point COD curve is created with points at 0, 200, 500, and 1000 ppm. Sample analysis points are then compared to the calibration line, the linear equation for the line is used to calculate the actual phosphorus content of the sample. A new calibration curve is created for every new set of standard reagents. Calibration curves with regression coefficients smaller than 0.980 are considered erroneous, and a new curve is created.

3.2.4 Chemical Oxygen Demand

Chemical oxygen demand (COD), similar to biochemical oxygen demand, is the measure of organic matter in wastewater. COD is the oxygen equivalent of the organic matter content of a sample following oxidation using a strong chemical oxidizing agent in an acidic medium at a high temperature (150°C ± 2°C). Potassium dichromate is the principal oxidizer. The COD oxidation reaction is represented as:

$$C_xH_yO_z + Cr_2O_7^{-2} + H^+ \xrightarrow{Heat} Cr^{+3} + CO_2 + H_2O \qquad (3.1)$$

Overcash, et al. (1974) states that COD is a reliable, quick, and reproducible measure of oxygen demand in animal wastes. Sampling and pipetting errors, which are difficult to control due to the nature of animal waste, in addition to errors associated with the test, account for fluctuations in the results.

3.2.4.1 Materials

The materials utilized in COD analysis are:

HACH 25 tube COD Reactor
Mercury Thermometer
HACH High Range COD Vials (50 – 1500 mg/l COD)
Milton Roy Spectronic Spectrophotometer
Fume Hood

3.2.4.2 Methodology

The standard technique prescribed by the HACH Company for measuring COD follows the AWWA Standard Methods (1993) for Closed Reflux Colorimetric Method, 508 C. COD analysis consists of:

- Preheating COD reactor to 150°C ± 2 °C.
- 2 ml of the manure sample diluted 100 to 1 with deionized water is added to a HACH COD vial.
- The sample and vial contents are mixed by inverting several times.
- Vials are heated in COD Reactor for two hours.
- The vial is removed from the heater and the colorimetric absorbance is measured using a spectrophotometer with a wavelength of 620 nm in the visible spectrum. The colorimetric analysis results are compared to a series of standards to get the actual COD.

3.2.5 Hot Weighing

Solids content is analyzed using methods accepted by the AWWA (1993) and described in sections 2540 B and E. The only change to the standard procedure is that measurements are taken on a "hot basis" instead of "cold basis". 'Hot basis" weights are taken immediately after removing the sample from the oven, "cold basis" weights are taken after the sample is allowed to cool in a desiccant. "Hot basis" measurements are preferable because of the elimination of the potential for a faulty desiccant allowing moisture to accumulate on the beaker.

3.2.5.1 Materials

The following equipment is used to hot weigh samples:

Fisher Scientific Isotemp Oven Model 655°F (±1 °C)
Mettler AE 240 Balance ±0.0001 g

50 ml beaker

3.2.5.2 Methodology

The procedure for hot weighing sample is as follows:

- Clean 50 ml beakers, stored in the drying oven for a minimum of twenty-four hours, are weighed on the Mettler AE 240 Balance.
- The balance is tared to account for the weight of the beaker and the moisture accumulated while measuring.
- Approximately 25 g of sample is measured into the 50 ml beaker, the sample mass is recorded as m_{sample}.

3.2.6 Total Solids Measurement

Total solids (TS) is a measure of the solid material remaining after the moisture is evaporated in a oven with constant temperature between 103 and 105°C. The sum of the TS and percent moisture content is equal to 100% of the sample weight. The procedure for measuring TS is approved by the AWWA Standard Methods (1993), section 2540 B. The only change to the standard method is that sample weights are measured on a "hot basis" instead of a "cold basis" as discussed above.

3.2.6.1 Materials

The equipment used to measure TS is identical to the materials identified for hot weighing.

3.2.6.2 Methodology

The standard procedure for determining TS is as follows:

- Samples weighing between 25 and 50 g are weighed into 50 ml beakers using the hot weight technique.
- Samples are dried at temperatures between 103 and 105°C for a minimum of twenty-four hours.
- After the twenty-four hour drying period, the dried sample mass is measured and recorded.

TS is the ratio of the mass of the dried sample to the mass of the original (wet) sample (equation 3.2).

$$TS = \frac{m_{dry}}{m_{sample}} * 100 \qquad (3.2)$$

where: TS = Total Solids, %

m_{dry} = Sample mass after drying, g

m_{sample} = Initial (wet) sample mass, g

3.2.7 Fixed and Volatile Solids Measurement

Adding the fixed solids (FS) and volatile solids (VS) gives the TS of the sample. FS is the inorganic portion of the sample that remains after the sample has been ignited. Conversely, the VS are composed of the organic material that is burned off during ignition in the muffle furnace. The procedure for measuring FS and TS is outlined in the AWWA Standard Methods (1993) section 2540-E.

3.2.7.1 Materials

The equipment for measuring FS and VS is identical to that for hot weighing, with the addition of a laboratory furnace with a peak temperature of 550°C. In this study the following furnace was used:

Thermolyne Type 30400 Furnace (±1 °C)

3.2.7.2 Methodology

The technique used to determine FS and VS is:

- Hot weigh samples as previously described.
- Ignite samples in Thermolyne muffle furnace at 550°C (also known as ashing) for a minimum of one hour.
- Return samples to the oven to cool to between 103 and 105°C before weighing the remaining ash.

The ash remaining after ignition constitutes the FS, or inorganic material, and can be expressed as equation 3.3:

$$FS = \frac{m_{ash}}{m_{dry}} * 100 \qquad (3.3)$$

where: FS = Fixed Solids, %

m_{ash} = Sample mass after ashing, g

m_{dry} = Sample mass after drying, g

The portion of the sample vaporized during the ashing process is the VS (equation 3.4), and is calculated as:

$$VS = \frac{m_{dry} - m_{ash}}{m_{dry}} * 100 \tag{3.4}$$

where: VS = Volatile Solids, %

m_{dry} = Sample mass after drying, g

m_{ash} = Sample mass after igniting, g

TS is equal to the sum of the fixed solids (FS) and volatile solids (VS).

$$TS = VS + FS \tag{3.5}$$

The FS (inorganic material) is the residue remaining after igniting the sample at 550°C for no less than one hour. Likewise, VS (organic matter) is the measure of the sample weight lost during ignition.

3.2.8 Turbidity

Turbidity is the clarity of a sample of wastewater. Turbidity in wastewater samples is caused by suspended matter such as clay, silt, organic matter, and inorganic particles. Turbidity is a comparison of the light absorbed (scattered) by suspended particles in a sample to the light scattered by a reference sample under the same conditions. The light used in the measurement is a Tungsten-filament lamp with a light travel distance of less than 10 cm, light penetrates the sample at a 90° angle. In generally turbidity cannot be correlated to the weight concentration of suspended matter.

3.2.8.1 Materials

The materials used in turbidity measurements are:

Hach 2100A Turbiditmeter
Hach 50 ml tubes
Hach Stock Turbidity Suspension

3.2.8.2 Methodology

AWWA Standard Method 214 A, the Nephelometric Method for measuring turbidity is the procedure used to analyze the clarity of the liquid dairy manure samples. Calibrating the turbidity meter is the key to reproducible and accurate turbidity measurements. Calibration is done by:

- Preheating turbidity meters for 24 hours.
- Creating a 400 NTU (Nephelometric Turbidity Units) standard solution by combining as directed in Method 214A
- Diluting 10 ml of the 400 NTU solution with 100 ml of deionized to produce a 40 NTU solution.

  Note: all calibration and sample solutions are shaken well before turbidity testing to assure that no settling has occurred.
- Calibrating the turbidity meter in the 100 NTU range with the 40 NTU solution.

- Filling the 50 mL tubes with samples and placed in the turbidity meter for analysis.
- Calibration is continuous during analysis.
- Reporting turbidity readings from 10 to 40 NTU's to the nearest 1 NTU.

3.2.9 Temperature and pH Analysis

In addition to testing other characteristics, manure samples were also analyzed for pH and temperature.

3.2.9.1 Materials

The meter used to measure temperature and pH is:

EXTECH pH/mV/Temperature Meter

3.2.9.2 Methodology

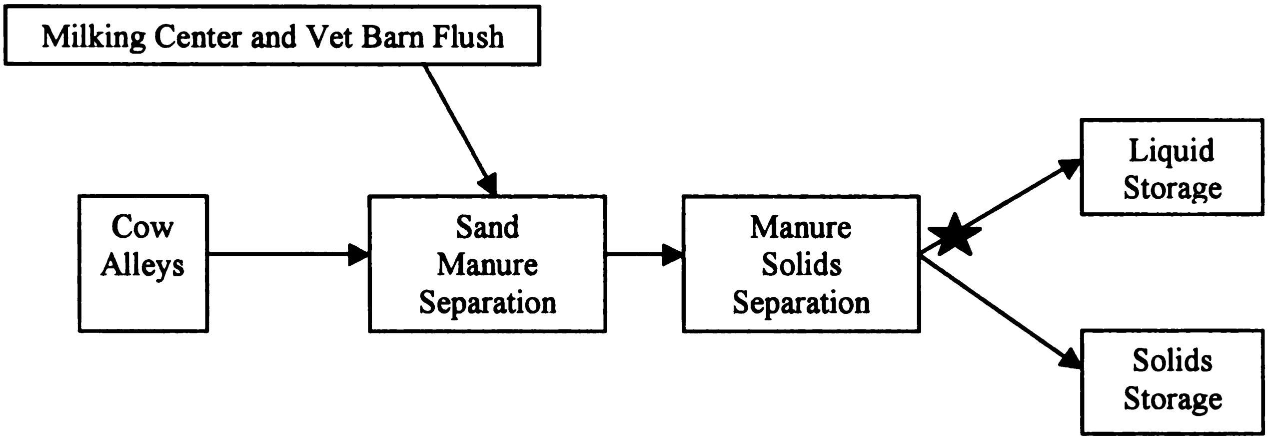
The temperature and pH of the manure samples were measured prior to and following the addition of a chemical coagulant in the laboratory tests. Pilot unit samples were subject to pH measurements in the laboratory during the analysis for the other characteristics listed in this chapter. Temperature was not measured on pilot unit samples.

3.2.10 Manure Sampling

Manure samples for both laboratory and pilot unit tests were collected at Green Meadow Farms in Elsie, Michigan. Figure 3.1, a manure system flow diagram for Green

Meadow Farms, gives an overall view of the system. The red star indicates the location in the system where manure samples were drawn.

FIGURE 3.1 : Manure System Flow Diagram for Green Meadow Farms



Manure scraped from the cow alleys is collected in reception pits located at the end of the freestall barns. Manure from the reception pits is then metered into sand manure separators. Screened flush water from the milking center and treatment barn serves as the dilution water for the sand manure separators. Each freestall barn is equipped with a reception pit and sand separator. Effluent from the sand separators is the pumped to a rotating drum separator (Manure Solids Separation). The drum separator removes larger solids from the manure stream. Effluent from the drum separator is stored in earthen basins (liquid storage), while the solids are deposited onto a stacking/drying pad (solids storage).

3.2.10.1 Materials

10 L Polypropylene container

50 ml Whirlpak

3.2.10.2 Methodology

Samples for analysis and treatment are collected from the effluent of the solid/liquid separator before it reaches the earthen basins. A valve installed in the effluent pipe allowed for sample collection. Laboratory samples were collected in a 10 L polypropylene container and cooled for transport to the lab. All samples were refrigerated (4 to 6°C) until use, manure samples were tested within 48 hours of collection. The pilot system was stored in a building adjacent to the solids separator. Manure for pilot tests was piped directly from the drum separator to the pilot unit. In order to establish a daily phosphorus concentration, a separate individual sample was collected in a whirlpak. This individual sample served as the control and was analyzed for TP, SP, TS, VS, COD, and pH.

3.2.11 Jar Test Procedure

Jar testing is a quick method for comparing the effectiveness of various coagulants and flocculants for wastewater treatment. Laboratory jar tests should imitate the actual mixing conditions in wastewater treatment plants. Variable speed jar tests can simulate rapid mix chambers or flocculation basins. Gang stirrers allow different chemicals or dosages to be compared in side by side tests which simulate the actual mixing conditions anticipated in the field. Prior to testing, the wastewater was characterized for pH and the target property for removal, in this case phosphorus. By characterizing the wastewater, the type of coagulants or flocculants and their dosage range can be narrowed to those which are known to work best on similar waste streams.

3.2.11.1 Materials

The equipment used in the jar tests was:

Phipps and Bird Jar Test Apparatus, 6 jar, variable speed
2000ml beakers
50ml Beakers
10 ml Pipette and Pipette Filler

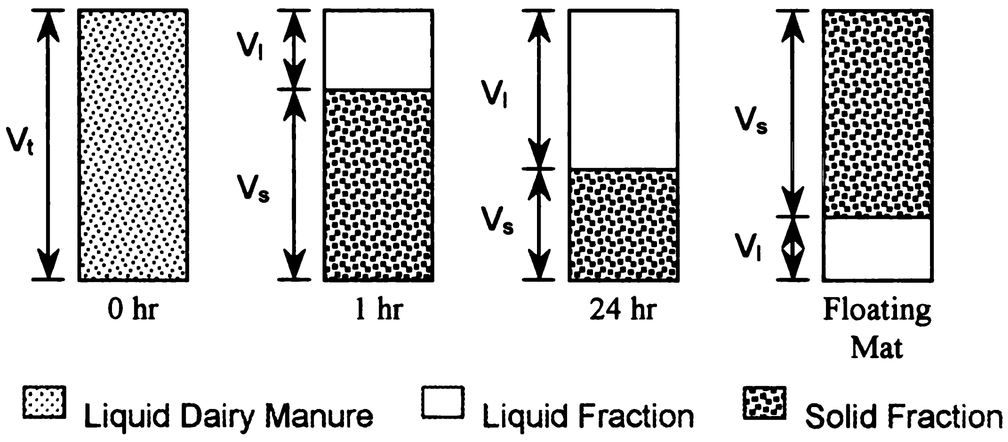
3.2.11.2 Methodology

No standard for jar testing was found in published standards for wastewater. However, the suppliers of coagulants and equipment have published basic guidelines for jar tests that are accepted by the industry. The procedure used for jar testing followed this routine:

- 1000 ml of well mixed dairy wastewater was measured into 6 - 2 liter beakers.
- 25 ml of sample was measured and set aside for later testing, this sample received no treatment or mixing and served as the control sample.
- The jar test apparatus was then turned on and the speed set to 100 rpm.
- Samples were mixed for ten minutes prior to coagulant addition, during this time pH was measured.
- Chemical were added.

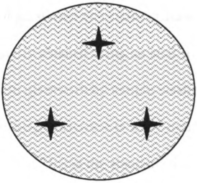
- Following additions, mixing continued for a 5 minute period during which time pH was again measured.
- After mixing was completed the paddles were removed and the contents were allowed to settle for a period of sixty minutes.
- Three 10 ml samples were drawn from each jar using the pipette, the samples were pulled from the liquid layer and deposited into the 50 ml beaker. Figure 3.2 presents the general settling pattern for the coagulated dairy manure during jar tests. The sampling pattern occurred in a triangular pattern in the horizontal plane similar to that shown in Figure 3.3.

FIGURE 3.2: Typical Settling Patterns for Jar



- After thorough mixing, a 2 ml sub-sample was drawn from the 30 ml sample; this sub-sample was used in the 200 to 1 dilution for analysis.
- Shortly after the sample was taken, the sludge and liquid height are measured using a meter stick. The liquid-sludge line was determined by visual observation.

FIGURE 3.3: Jar Test Sampling Pattern, Top View



- The jar test beakers were then allowed to set for twenty-four hours at which time they were sampled following steps 8 and 9. The sludge and liquid height was again measured and recorded after twenty-four hours.

3.2.12 Glassware Preparation

To assure accurate results glassware was cleaned prior to use. Generally, this wais done by simply washing glassware with a non-phosphorus based detergent. However, periodically washing glassware in a acid solution to remove film and residue left by normal cleaning was necessary. Acid washing of glassware was essential to remove residue and contaminants left from other laboratory projects.

3.2.12.1 Materials

To clean glassware the following was needed:

Polypropylene tub

3.2.12.2 Methodology

Continuous use of glassware can cause cross contamination and inaccurate results if glassware is not regularly cleaned using an acid solution. Acid washing breaks down the residue and film left on glassware by simple washing with soap and water. Acid washing was carried out by soaking glassware in a 1N solution of Hydrochloric Acid followed by a deinonized water rinse. This is the standard procedure accepted by the AWWA. After rinsing, glassware was allowed to dry prior to use.

3.3 Pilot Unit

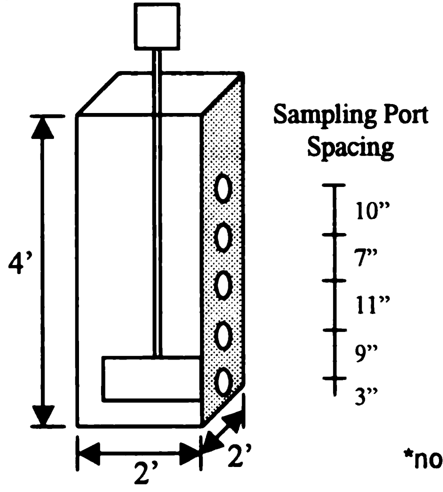
3.3.1 Pilot Tests

Pilot tests were conducted in a 100-gallon tank built from Plexiglas. Pilot testing allowed the laboratory findings to be applied in actual field conditions on a much larger scale. The pilot unit was not an actual scale up of the jar tests, though velocity gradients and mixer clearances were maintained. Pilot tests were conducted at Green Meadow Farms in Elsie, Michigan. The 100 gallon capacity of the pilot unit was approximately 1/1000th of the total daily manure stream of Green Meadow Farms.

The tank of the pilot unit was a two foot by two foot square box, four feet tall, with ½" thick Plexiglas sidewalls. A square tank was selected over a round tank due to cost. Five ½" National Pipe Thread (NPT) sampling ports were located down the side (a second set was added in the field). The sampling ports were ½" ball valves with 1 ½" long nipples protruding into the tank. The nipples were installed to assure that samples were drawn from the inner portion of the tank. A measuring tape attached to the tank allowed for sludge height measurements.

A schematic of the mixing tank is shown in Figure 3.4. The tank and paddle were built in the prototype laboratory shop in Farrall Hall. The mixing paddle is made of stainless steel. The motor is mounted on a steel frame that sets on top of the tank, the frame has legs which hook into the corners preventing the frame and motor from twisting. The tank is top filled with liquid dairy manure, and emptied through a 2" ball valve located near the bottom of the tank. Once assembled, the tank was filled with water and the mixer speed was calibrated with a hand held tachometer.

FIGURE 3.4: Pilot Unit*



*not drawn to

3.3.1.1 Materials

The following is a list of materials used in pilot testing:

2' * 2' * 4' Plexiglas tank and stand
½ Horsepower variable speed drive (Range 64 to 364 rpm)
Paddle, flat face, 5" * 14", elevated 10" from the bottom
Polypropylene tub
Hose and scrub brush.

3.3.1.2 Methodology

The pilot unit tests were conducted in a similar fashion to the jar test described in an earlier section. The process was as follows:

- The mixing tank was filled with 100 gallons of effluent from the drum separator.
- Control samples were drawn at the onset of filling and at the cessation of filling. (The two samples were then mixed and sub-sampled. The sub-sample served as the control.)
- Premixing was initiated, premixing lasted for ten minutes at 100 rpm.
- Chemical coagulants were added at the ten-minute mark.
- Mixing at 100 rpm continued for 5 minutes after the chemical addition.
- Following the cessation of mixing, settling began. (The timer was started as soon as the mixer was shut off.)
- Sludge settling was monitored by visually observing the height of the sludge line at the measuring tape attached to the tank. (Sludge height measurements were taken after 30 minutes, 1 hour, 24 hours, and 48 hours of settling.)
- Manure samples were drawn from the five sampling ports at 1 hour, 24 hours, and 48 hours. (Samples were collected in whirlpaks after allowing the sampling ports to clear, approximately two seconds after opening the valve.)
- Samples were transported to the Environmental Teaching Laboratory for analysis.
- Pilot unit analysis was carried following the same procedures discussed for the jar test.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General Comments

The results of characterizing the waste stream at Green Meadow Farms (GMF) are imparted in Chapter 4. In addition, the findings from laboratory tests using various chemical coagulants for phosphorus reduction in the liquid dairy manure are presented. Testing of coagulants in the 100-gallon rapid mix chamber (the pilot test unit) is discussed in the later portion of the chapter.

4.2 Manure Stream Characterization

The physical characteristics of dairy manure are influenced by numerous variables, both environmental and physiological. Examples of factors include: 1) growth or lactation stage of the animals, 2) manure age, 3) climatic conditions, 4) ration fed, 5) bedding material, and 6) the manure handling system. A 640 kg (1400 lb) lactating dairy cow will produce 67 kg (148 lb) of manure per day with a moisture content of 88% and a density of 993 kg/m^3 (62 lb/ft^3) (MWPS, 2000). A further look at the composition of the manure reveals that the total solids (TS) content of manure as excreted is 9.5% with a volatile solids (VS) of 8.0%. The daily production of phosphorus in the manure as excreted is 0.2 kg (0.42 lb) of P_2O_5. In addition, MWPS (2000) estimates manure lagoon concentrations of P_2O_5 to be 19 lbs/1000 gal. It is important to remember that the published book values can vary by as much as ±30% from field measurements.

Liquid manure samples were collected over a 14 month period from various points in the manure handling system at Green Meadow Farms. Following the installation of a rotary drum separator in July of 2001, 33 manure samples were drawn at approximately the same time of the day from the effluent of the separator for analysis. The manure stream at Green Meadows is diluted by several different sources including: 1) the purging of the cattle waterer's (dumping the contents of tip-tanks), 2) dilution water added in the sand manure separation system, and 3) the cleaning of the floors of the milking parlor, holding area, and special needs barn by flushing with fresh water. The daily volumes of dilution water and manure produced by the 3,600 lactating cows housed at GMF are presented in Table 4.1. The volumetric ratio of dilution water to manure is approximately 1.7 to 1.

TABLE 4.1: GMF Manure Stream and Dilution Water Volumes for 3,600 Cows

Component	Quantity
	(gal/d)
Manure[1]	**35,400**
Special Needs Barn Flush[2]	6,000
Parlor Flush[2]	18,000
Tip Tank Waters[2]	2,000
Sand Separators[2]	35,400
Total Dilution Water	**61,400**
Water to Manure Ratio	**1.7 to 1**

[1] MWPS-18 (2000), Section 1, Table 6
[2] Information provided by GMF

The 33 manure samples were analyzed for TS and VS on a wet basis as described in Chapter 3, Method and Materials. Results and analyses of the liquid manure stream characterization at GMF are listed in Table 4.2. For the 33 samples tested, TS averaged 2.79% with a standard deviation of 0.86%. Similarly, the liquid manure stream had an average VS of 1.97% with a standard deviation of 0.44%. The TS and VS coefficients of variance for the 33 samples were found to be 30.8% and 22.2%, respectively. This range of variation is common for biological material like manure. Table A1, found in the appendix, contains the raw data for the liquid manure stream characterization at GMF.

TABLE 4.2: Liquid Manure Stream Characterization Summary (n=33 from GMF)

Characteristic	Mean	Standard Deviation	Range	Units	Coefficient of Variance
Total Solids (TS)	2.85%	0.85%	1.33 - 5.02	%	29.97%
Volatile Solids (VS)	2.00%	0.45%	1.05 - 3.00	%	22.46%
COD	37,154	10,013	14,700 - 53,600	mg / L	26.95%
Soluble Phosphorus (SP)	196	36	108 - 278	mg / L	18.21%
Total Phosphorus (TP)	2,831	548	1,780 - 3,745	mg / L	19.34%
pH	8.47	0.27	7.84 - 8.89		3.19%

Throughout the study, samples were split and a side-by-side analysis was run to assure that laboratory testing procedures were accurate. Split samples analysis for TS revealed a coefficient of variance (the ratio of the standard deviation to the mean) of 9.01%. The coefficient of variance for the VS analysis of the liquid dairy manure was 4.47%. Table 4.3 contains the results of the split sample analysis. TS and VS, like the other parameters characterized, had relatively low coefficients of variance, generally less than 10%. A coefficient of variance of 10% or less for a spilt analysis of manure is considered an acceptable error attributed to sampling (Overcash et al., 1974).

TABLE 4.3: Split Sample Analysis and Average Coefficient of Variance

Characteristic	Mean	Standard Deviation	Coefficient of Variance	Average C. V.*
SP (ppm)	163	9	5.55%	6.59%
TP (ppm)	2620	122	4.66%	6.15%
COD (ppm)	39,500	11,078	28.04%	18.38%
TS (%)	2.44	0.22	9.01%	9.01%
VS (%)	1.95	0.09	4.47%	4.47%

*The average coefficient of variance for multiple split samples.

The 33 liquid manure stream samples were also tested for SP, TP, COD, and pH as discussed in Chapter 3. The samples were found to have an average SP of 196 mg/L with a standard deviation of 36 mg/L. The overall variance of the 33 samples was 18%. The mean TP of the liquid dairy manure was 2,831 mg/L with a standard deviation of 548 mg/L. TP varied by 19% for the 33 samples.

Again, the split samples were tested simultaneously to check for errors in laboratory procedures and testing accuracy. The coefficients of variance for SP and TP were 6.59% and 6.15%, respectfully. Overcash et al. (1974) reported that a coefficient of variance of 10% is typical for total phosphorus measurements in the same phosphorus range as this study.

COD analysis of the manure samples found a mean of 37,154 mg/L with a standard deviation of 10,013 mg/L. Split sample testing found a coefficient of variance of 18.38% for COD, the highest coefficient of variance for all the parameters evaluated. pH averaged 8.47 with a range of 7.84 to 8.89.

Preliminary data revealed that turbidity measurements provided little insight into predicting phosphorus or solids removal. One issue that made turbidity measurements difficult is the sensitivity of the turbidity machine. Calibration is an ongoing process while measurements are taking place. In addition, moisture and dust accumulation on the bulb caused difficulties with maintaining a consistent source of light. Furthermore, the dilution rate used for phosphorus analysis did not produce significant differences in turbidity measurements. The range used for turbidity measurements was 0 to 100 Nephelometric Turbidity Units (NTU). The range of turbidity measurements for untreated samples was 17 to 28 NTU, while the range of turbidity for various treated samples was 15 to 30 NTU. This being understood, turbidity analysis was not continued beyond the preliminary tests.

4.3 Laboratory Testing of Coagulants and Liquid Dairy Manure

Laboratory tests were conducted using several chemical coagulants to evaluate their usefulness in reducing phosphorus concentrations in the liquid fraction of the dairy manure stream from GMF. The chemicals used to treat the dairy manure included hydrated lime, 40% Alum solution, and 40% Ferric Chloride. Laboratory analyses were conducted using a six slot jar test apparatus and followed the jar test procedure outlined in Chapter 3. Samples were collected after 1 and 24 hours of settling from the liquid layer. Figures 3.2 and 3.3 show the sampling points for the jar tests. The liquid layer was determined by visual observation and generally occupied the upper portion of the beaker. The liquid dairy manure was collected from GMF as discussed in Chapter 3 and transported to the lab for same day testing.

The goal of the lab tests was to reduce SP and TP in the effluent (liquid layer) by 80% using chemical additions. The level of phosphorus concentration reduction desired will be farm specific, depending on several factors including land base, soil phosphorus test levels, field distance from livestock, compost market, fertilizer prices, and livestock management goals. With this in mind, treatments were set up to demonstrate that effluent phosphorus concentration can be managed to meet the needs of the dairy operation.

The phosphorus reductions discussed in this chapter are strictly reductions of the phosphorus concentration in the liquid fraction (the upper portion of the jars) and concentrations of phosphorus in the sludge. Phosphorus was not removed from the system, only transformed and concentrated. Through further processing with readily available technology, the phosphorus-rich sludge could have been removed. Processing options to recover the sludge include filter bags, filter presses, clarifiers, and centrifuges.

4.3.1 Settling with No Chemical Addition

Each set of jar test experiments included a control jar. The control jar received no treatment other than mixing. The control jar was subjected to the same mixing conditions as the treatment jars. SP and TP were measured in the liquid layer 60 minutes and 24 hours after the cessation of mixing. The liquid layer was determined by visual observation. Each experiment with a chemical coagulant also had a control jar, Table 4.4 presents the average phosphorus reduction in the control jar for each coagulant tested (lime, alum, and ferric chloride). Additionally, Table 4.4 contains the average reduction of SP and TP and their standard deviations for all control jars. Overall, the SP and TP in liquid fraction of the control jar was reduced by 22.82% and 24.03%, respectively, after 1 hour of settling. At 24 hours of settling, SP and TP reductions in the liquid portion increased to 71.5% and 60.0%, respectively. All the results had a standard deviation of less than 5.10%.

TABLE 4.4: Control Jar – Phosphorus Reduction

	Phosphorus Reduction (%)			
Experiments	**1 Hour**		**24 Hour**	
	SP	TP	SP	TP
Lime	23.92	29.74	73.53	57.92
Alum	17.28	20.53	70.79	65.50
Ferric	27.26	21.82	70.23	56.51
Average:	**22.82%**	**24.03%**	**71.52%**	**59.97%**
Standard Deviation:	**5.08%**	**4.98%**	**1.77%**	**4.83%**

The natural settling that occurs appears to be Type 3 or zone settling because the mass of manure solids and nutrients (phosphorus) settle as a unit. The settling types are defined in Chapter 2. The agitation of the contents of the control jar may enhance the normal settling process by utilizing natural polymers in the dairy manure as flocculating agents. Similar to flocculation using synthetic polymers, the natural polymers may bridge phosphorus ions, trapping and precipitating the phosphorus when agitation ceases. The unaided settling of phosphorus after 1 hour in this trial is less than reported in other studies discussed in the literature review. However, the phosphorus reductions for 24 hours agree with results reported in Chapter 2.

4.3.2 Lime Additions

Lime, in the form of a 5% lime solution, was added to the liquid dairy manure for the purpose of phosphorus coagulation. Table 4.5 contains the mean results found in jar test experiments where lime was added as the coagulant. Five treatments levels - 1.32, 2.64, 3.97, 5.29, and 6.61 g of lime/L wastewater - were selected for testing based on earlier experiments. Estimated chemical costs for the five treatments are $0.50, $1.00, $1.50, $2.00, and $2.50 / 1000 gal of liquid dairy manure from GMF, respectively. The chemical costs are based on the December 2000 issue of the Chemical Market Reporter in which hydrated lime is listed at $70/ton.

Coagulating of phosphorus in the liquid manure stream with lime proved to be a useful method for reducing the phosphorus concentration in the liquid portion. SP concentration reductions in the liquid fraction ranged from 30 to 79% after 1 hour of settling. Similarly, 1 hour of settling reduced the concentration of TP in the liquid

TABLE 4.5 Phosphorus Concentration Reduction Using Lime

	Treatment	Phosphorus Reduction (%)			
Dosage	Cost	1 Hour		24 Hour	
(g/L)	($/1000 gal)	SP	TP	SP	TP
0.00	0.00	23.92	29.74	73.53	57.92
1.32	0.50	39.18	42.43	77.91	69.92
2.64	1.00	40.49	39.43	82.04	66.76
3.97	1.50	62.04	53.17	82.49	67.50
5.29	2.00	77.80	62.67	83.75	74.17
6.61	2.50	78.70	67.90	81.70	66.90

fraction by 42 to 68%. One hour of settling in the control jar decreased the SP and TP concentrations by 24% and 30%, respectively. Lime as a coagulant increased the minimum SP reduction by 6% and the minimum TP reduction by 12% over that achieved in the control jar, for all treatment levels. Figure 4.1 presents the average phosphorus reduction versus the lime treatment dose. Table A2 in the appendix, contains the raw data for the laboratory jar tests using lime as the coagulant. Allowing settling to continue for 24 hours improved both SP and TP reductions markedly in the lower doses (1.32, 2.64, and 3.97 g/L). The highest lime doses (5.29 and 6.61 g/L) saw much smaller increases in the phosphorus reduction. A slight reduction in the efficiency from 1 hour to 24 hours for the TP was seen at the 6.61 g/L dose.

The lime dose that most closely meets the goal set for the laboratory tests was determined to be 5.29 g/L. This level of treatment achieved an average decrease in SP of 78% and TP of 63% after 60 minutes of settling. At 24 hours of settling, SP and TP were reduced in the liquid fraction by 84% and 74%, respectively. The range of the standard deviation for the results from the 5.29 g/L treatment was 2.2 to 5.5% with an average deviation of 3.8%. The next higher lime dose (6.61 g/L) produced only marginal increases in phosphorus reductions with no change in the standard deviation. Lower

FIGURE 4.1: Average Phosphorus Concentration Reduction Using Lime as the Coagulant, Lab Tests

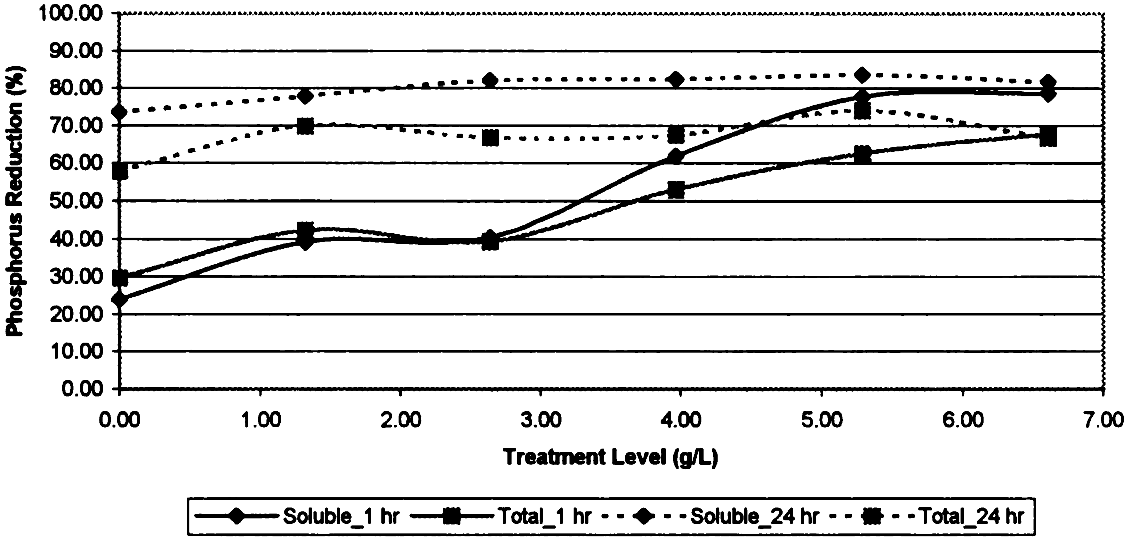
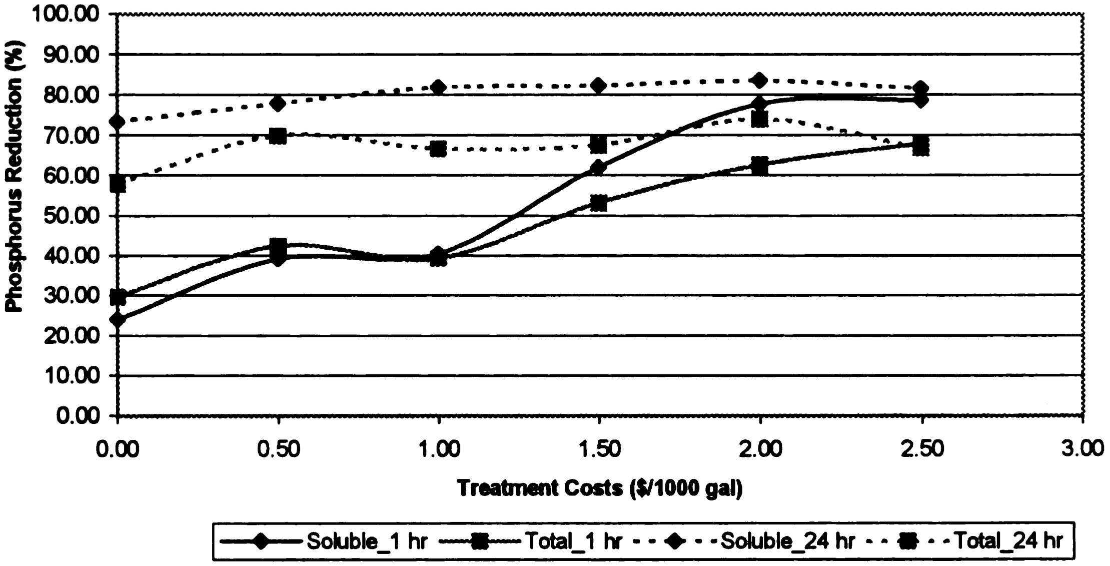


FIGURE 4.2: Lime Treatment Costs Vs Phosphorus Reduction Lab Tests



treatment levels were much less predictable and had a much larger deviation from the mean. Treating the liquid dairy manure from GMF for the desired phosphorus reduction using lime would cost approximately $2.00 per 1000 gallons of liquid dairy manure. Figure 4.2 is a graph of the chemical (lime) cost versus the percent reduction in phosphorus in the liquid fraction.

The benefits of using lime as a coagulant over settling alone to separate phosphorus include increased removal rates after 1 hour and 24 hours. Additionally, the sludge formed from the calcium phosphorus and manure solids appears to be more stable than the nutrient-rich sludge produced by natural settling. The addition of lime as a coagulant did not increase the volume of sludge produced. Naturally settled sludge and sludge coagulated with lime occupied approximately one third of the volume of the 1000 mL sample, the other two thirds of the volume was occupied by the liquid fraction. If the stability is actually increased, further processing options that cannot be used on a less stable sludge become available.

4.3.3 Alum Additions

Alum, as a 40% solution in water, was also used as a coagulant for phosphorus removal. The alum was purchased as a solution from Chemco Products Inc. in Howell, Michigan. The dosages of alum used were 0.8, 2.0, 4.0, 6.0, and 8.0 g/L of liquid dairy manrue. A summary of the experimental results is contained in Table 4.6. The chemical cost of alum for the respective treatments is $2.12, $5.29, $10.58, $15.88, and $21.17 per 1000 gallons of liquid manure from GMF. The treatments costs are based on an aluminum sulfate price of $281 per ton (Chemical Market Reporter, 2000). Table A3 in the appendix, contains the raw data from the laboratory experiments where alum was used as the coagulant.

TABLE 4.6: Phosphorus Concentration Reduction Using Alum

	Treatment	Phosphorus Reduction (%)			
Dosage	Cost	1 Hour		24 Hour	
(g/L)	($/1000 gal)	SP	TP	SP	TP
0.00	0.00	31.96	40.64	66.28	66.80
0.80	1.41	41.45	16.47	79.74	75.50
2.00	3.53	72.58	38.27	88.91	85.40
4.00	7.06	92.75	48.16	103.80	89.70
6.00	10.58	95.57	69.98	104.31	88.02
8.00	14.11	101.80	82.29	107.74	100.79

Alum proved to be extremely useful in coagulating and settling phosphorus under laboratory conditions. The range of SP decrease in the effluent was 41 to 100% after 1 hour of settling. During that same period, the TP concentration was reduced in the liquid by 16 to 82% for the various treatment levels. After 24 hours of settling, the minimal SP concentration reduction increased to 80% and the range of TP reductions was 76 to 100%. The control jar produced a decrease in the concentration of SP by 32% and TP by 40% after 60 minutes of settling. A more detailed summary of the results for phosphorus reduction using alum as the coagulant can be seen in Table 4.6.

The reductions in TP for the two treatment levels of 0.8 and 2.0 g/L after 1 hour of settling were actually lower than for the control jar. This can be attributed to incomplete flocculation due to an insufficient dose of alum. Flocculation was observed in the jars for both treatments, but the size of the coagulated particles was observed to be smaller than for the three higher doses (4.0, 6.0, and 8.0 g/L). Smaller particles translate into lower molecular weight of the individual particles, hence the slower settling with some alum treatments.

Unlike with lime, the determination of the desired dose is much more difficult with alum. The 8 g/L dose achieved the set goal of 80% reductions in the concentrations of both SP and TP in the liquid fractions, after only one hour of settling. The standard deviation for this treatment level is 21%, much higher then the standard deviation for the lime treatments. However, the average deviation for all alum treatments is 22%. The problem with this level of alum treatment (8 g/L) is the cost, 8 g/L of alum is estimated to cost $14.11 per 1000 gallons of liquid manure. If settling were to continue for 24 hours, the 4 g/L treatment level achieved a 100% reduction in SP and a 90% decrease in TP, well above the goal of 80% phosphorus reduction. The standard deviation for the 4 g/L treatment level was 22%, this standard deviation is nearly identical to that of the 8 g/L dose of alum. The chemical cost for 4 g/L of alum is $7.06 per 1000 gal of liquid dairy manure, half the cost of the 8 g/L dose. The percent reduction in the phosphorus concentration versus the treatment dose and cost is displayed in Figures 4.3 and 4.4.

The floc produced using alum was a visibly larger aggregate than produced by the lime addition. The sludge production in the alum treated jars occupied approximately 50% of the total manure volume. The other 50% was occupied by the liquid fraction (Figure 3.2). The increased volume of the sludge is attributed to the dissolved particulates that react with the alum to form the floc. The flocs are large "fluffy" molecules that contain both dissolved and suspended particulate. Compression settling did not occur in the 24 hour settling period. In some instances, the solid fraction formed a floating mat of sludge rather than a settled sludge.

FIGURE 4.3: Average Phosphorus Concentration Reduction Using Alum as the Coagulant, Lab Test

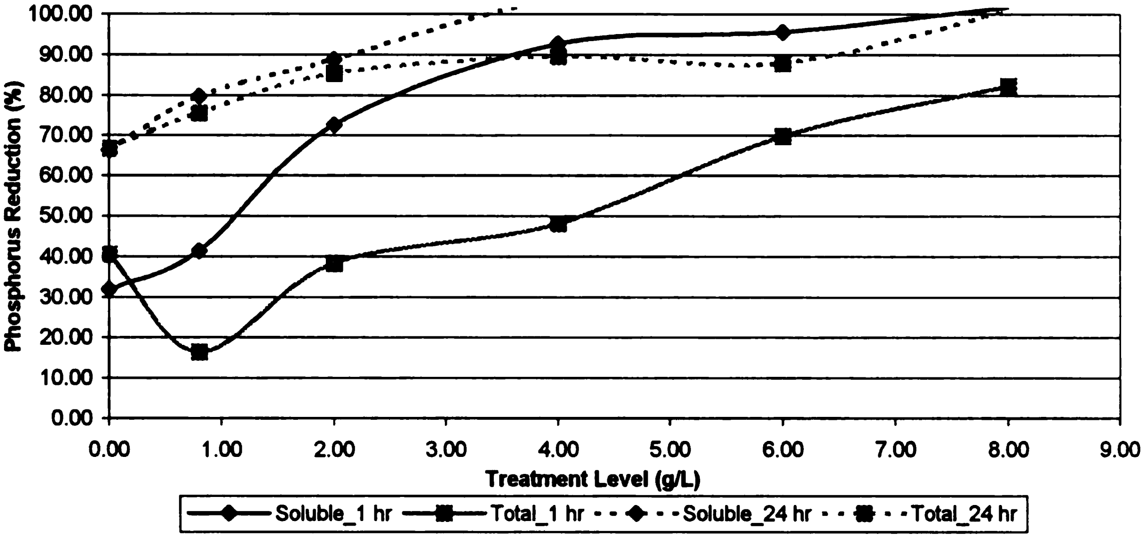
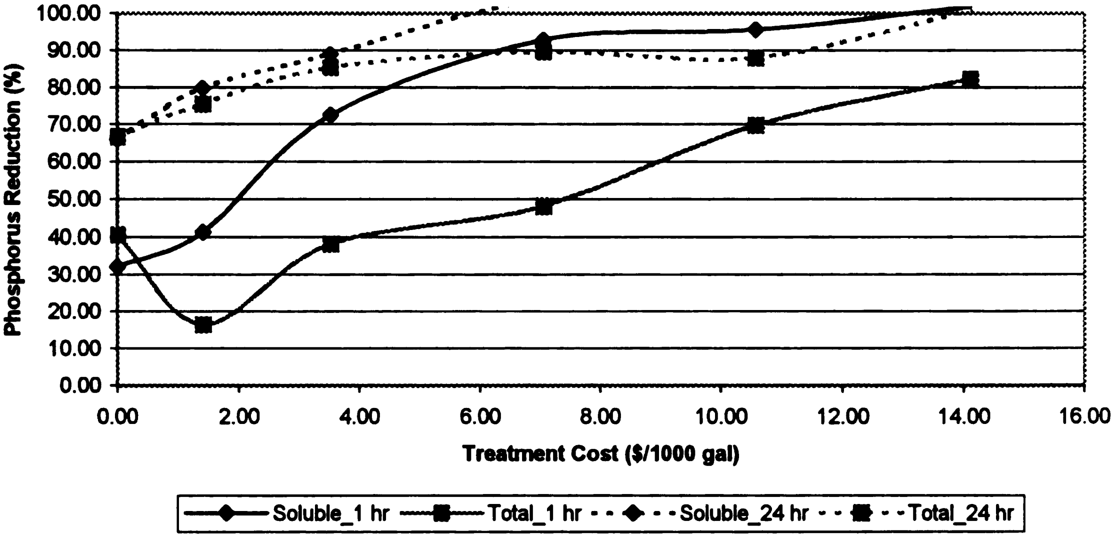


FIGURE 4.4: Alum Treatment Cost Vs Average Phosphorus Reduction Lab Tests



4.3.4 Ferric Chloride Additions

The last of the chemical coagulants tested in the laboratory was ferric chloride ($FeCl_3$). A 40% solution of ferric chloride purchased from Chemco Products Inc., was used in both laboratory and pilot unit tests. The $FeCl_3$ treatment levels selected for testing were 0.8, 2.0, 4.0, 6.0, and 8.0 g/L. Estimated treatment costs ($/1000 gal of liquid dairy manure) for the respective treatments are $2.42, $6.05, $12.10, $18.14, and $24.19. The chemical costs are based on purchasing $FeCl_3$ in bulk at $315/ton. A summary of the average concentration reductions of SP and TP for the various treatment levels of $FeCl_3$ is found in Table 4.7. Table A3 in the appendix contains the raw experimental data from laboratory tests using $FeCl_3$ as the coagulant.

TABLE 4.7 Phosphorus Concentration Reduction Using $FeCl_3$

	Treatment	Phosphorus Reduction (%)			
Dosage	Cost	1 Hour		24 Hour	
(g/L)	($/1000 gal)	SP	TP	SP	TP
0.00	0.00	27.26	21.82	70.23	56.51
0.80	2.42	42.54	32.60	78.72	56.45
2.00	6.05	52.68	25.23	79.13	56.79
4.00	12.10	65.55	31.89	81.32	62.31
6.00	18.14	101.82	65.93	99.03	76.25
8.00	24.19	104.51	73.92	103.77	82.52

Using $FeCl_3$ as a phosphorus coagulant produced mixed results in the laboratory. The goals of 80% reduction in SP and TP were achieved by two treatments, 6 and 8 g/L, after 1 hour of settling. The 4 g/L dose after 24 hours of settling produced a decrease in SP of 81%, slightly above the goal. All treatment levels showed an increase in the reduction of SP when compared to the control jar results. The SP concentration in the liquid fraction of the control was reduced by 27% after 60 minutes of settling, while the

range for SP reduction using various treatment levels of $FeCl_3$ was 43% to 100%. Likewise, TP reductions benefited from the addition of $FeCl_3$, the TP of the control was decreased by 22% after 1 hour of settling. The 1 hour settling range for TP reductions with $FeCl_3$ was 25% to 74%. Figure 4.5 presents a graphic view of the treatment level versus the percent reduction in the phosphorus concentration of the liquid fraction.

Allowing the settling to continue for 24 hours produced very different results from those recorded after only 1 hour of settling. The range for SP reductions after 24 hours was 79 to 100% with the control reduction at 70%. The TP reduction range for 24 hours was 56 to 83%, the control jar produced a reduction in TP of 57%. The three low doses of $FeCl_3$ (0.8, 2, and 4 g/L), in addition to the control, showed almost identical results in TP reduction. The 8 g/L treatment level achieved the goals of 80% reductions in both SP and TP after 24 hours. However, the 6 g/L dose of $FeCl_3$ appears to be the optimum treatment level for ferric chloride. After 24 hours of settling, the liquid fraction SP level was decreased by 99% with the TP level dropping by 76%. The 8 g/L treatment produced identical SP results with an increased reduction of 6% for TP. Increasing from 6 g/L to 8 g/L increases chemical costs by \$6.05 per 1000 gal of liquid dairy manure. The increase in chemical dosage translates into a daily increase of \$605 if a dairy were treating 100,000 gallons of liquid dairy manure. Figure 4.6 presents the chemical cost versus the phosphorus reduction for ferric chloride.

Liquid dairy manure treated with ferric chloride did not produce the distinct liquid-solid interface experienced as with other chemical coagulants. The low pH of the $FeCl_3$ and the buffering capacity of the dairy manure caused a reaction resulting in a large

FIGURE 4.5: Average Phosphorus Concentration Reduction Using $FeCl_3$ as the Coagulant, Lab Tests

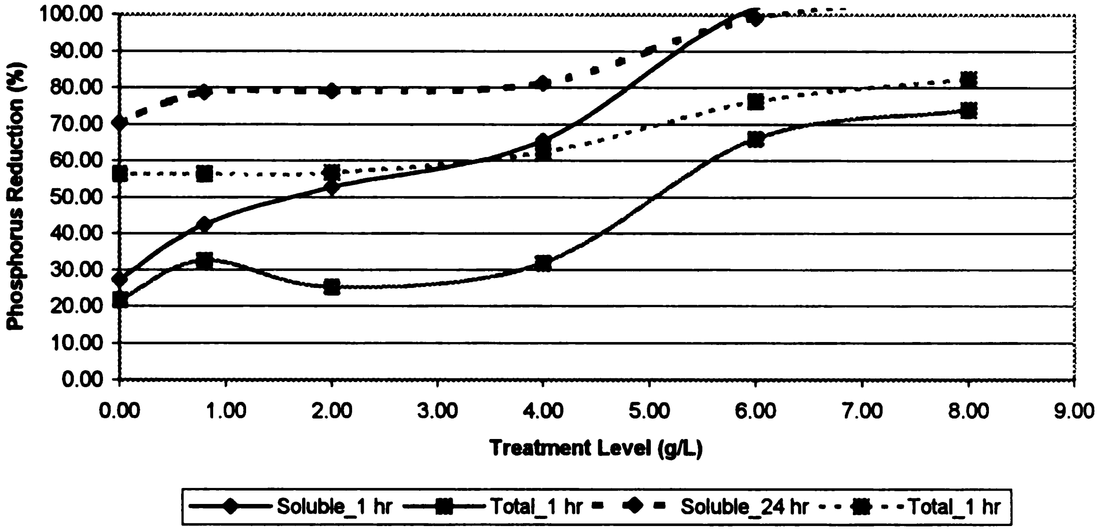
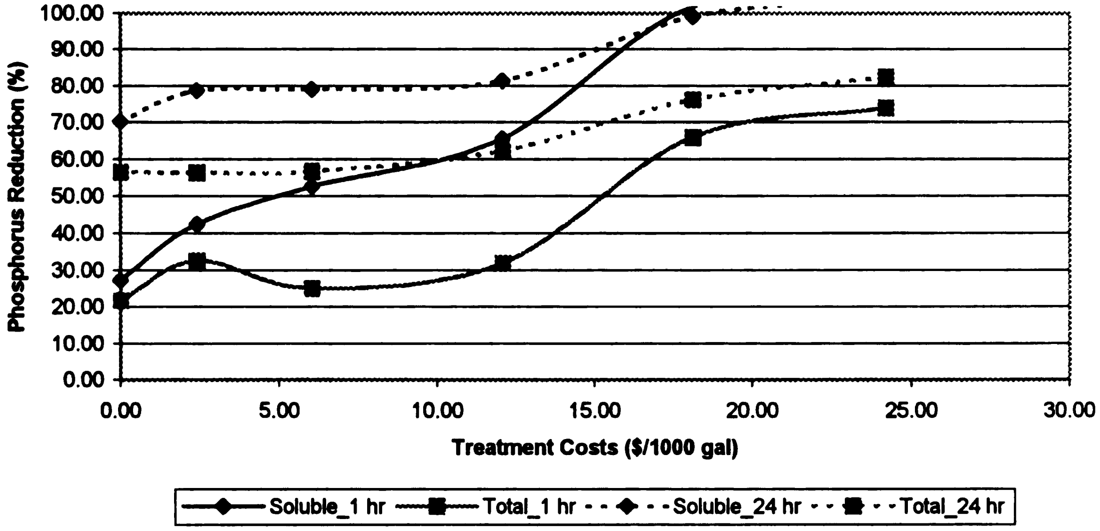


FIGURE 4.6: $FeCl_3$ Treatment Costs Vs Phosphorus Reduction Lab Tests



release of CO_2. This reaction occurred in the treatment levels 4, 6, and 8 g/L. The release of CO_2 caused a floating mat to form. The floating mat contained the sludge that would normally be expected to settle. Distinct settling seldom occurred when $FeCl_3$ was used as the coagulant. The two low level treatments (0.8 and 2 g/L) resulted in good flocculation with very little settling, but no foam formation. In the cases of foam formation, sampling was difficult because settling did not occur. On the highest treatment levels (6 and 8 g/L) small pockets of free water were mixed into the foam or located at the bottom of the jar.

4.3.5 Chemical Treatment Cost Analysis

Table 4.8 summarizes the treatment levels for the various coagulants which best met the goals of 80% reduction in SP and TP. Not all coagulants achieved the goal of 80% reductions of SP and TP in the liquid fraction. The last column of Table 4.8 shows the daily treatment costs for the selected treatment level of the three coagulants. Equipment costs are not accounted for in the values.

TABLE 4.8: Chemical Doses for Desired Reduction in Phosphorus Concentration

		Chemical	Phosphorus Reduction (%)				GMF
	Dosage	Costs	1 Hour		24 Hour		Daily
	(g/L)	($/1000 gal)	SP	TP	SP	TP	Costs*
5% Lime Solution	5.29	$2.00	78	63	84	74	$239.73
40% Alum Solution	4.00	$7.06	93	48	100	90	$846.72
40% $FeCl_3$ Solution	6.00	$18.14	100	66	99	76	$2,177.28

*Assuming 120,000 gal/d of liquid dairy manure

Table 4.9 presents market values for the two most common phosphate fertilizers used in agriculture. Triple superphosphate (TSP) and Diammonium phosphate (DAP) contain 45% and 46% actual P_2O_5 and have an average cost of $138 and $148 per ton respectively (Fertilizer Market Bulletin, 2000). The actual cost per pound of phosphorus in TSP and DAP is $0.35 and $0.37, respectively.

TABLE 4.9: Common Phosphate Fertilizers and Prices

Fertilizer Type	P_2O_5	Actual P_2O_5	Actual P	Price*	Price
	(%)	(lb/ton)	(lb/ton)	($/ton)	($/lb of P)
Triple Superphosphate	45	900	444	$137.50	$0.35
Diammonium Phosphate	46	920	453	$148.00	$0.37

*Fertilizer Market Bulletin, 2000

Table 4.10 presents the value of the phosphorus concentrated in the sludge from the liquid dairy manure stream. The value of the TP recovered is based on the assumption that elemental phosphorus has a value of $0.35 per pound and the average daily concentration of TP in the liquid manure stream is 2,734 mg/L. Infrastructure and labor costs are not taken into account in this cost analysis.

TABLE 4.10: Comparison of Chemical Costs Vs Value of TP Recovered

Settle			Treatment	TP	Value of
Time	Treatment	Dosage	Costs	Concentrated[1]	Recovered TP[2]
(hr)		(g/L)	($/d)	(lb/d)	($/d)
1	5% Lime Solution	5.29	$239.73	1,716	$600.60
1	40% Alum Solution	4.00	$846.72	1,319	$461.50
1	40% $FeCl_3$ Solution	6.00	$2,177.28	1,805	$631.81
24	5% Lime Solution	5.29	$239.73	2,031	$710.78
24	40% Alum Solution	4.00	$846.72	2,456	$859.56
24	40% $FeCl_3$ Solution	6.00	$2,177.28	2,088	$730.71

*Assumes 120,000 gal/d of liquid manure

[1] Calculated using phosphorus reductions found in laboratory tests multiplied by average TP in the manure stream

[2] Assumes that phosphorus reductions in effluent can be recovered in the sludge

The data presented in Table 4.10 makes it clear that, if the assumptions are correct, phosphorus removal via chemical additions is a viable option for liquid dairy manure. Treating 120,000 gal/d of liquid dairy manure with lime could concentrate 1,716 lb/d of phosphorus in the sludge after 1 hour with a fertilizer value of $600. The daily chemical cost for the 5.29 g/L of lime is $240. This yields a potential profit of $360. From Table 4.10, it is apparent that alum and ferric chloride are not economically viable after 1 hour settling period. However, after 24 hours of settling, the fertilizer value of the phosphorus reduction is $860 with a treatment cost of $847. This implies that, after 24 hours of settling with a treatment of 4 g/L of alum, enough phosphorus would be contained in the sludge to yield a $13 profit. Additionally, alum eliminated 100% of the SP in the liquid fraction after 24 hours of settling, lime reduced the SP concentration by 84% in the effluent. After 24 hours settling, the chemical cost of ferric chloride versus the value of the recovered phosphorus proved uneconomical for treating this type of liquid dairy manure. In line with the goals of the project, alum and lime are the recommended chemical treatment options for reducing the phosphorus concentration in the liquid manure stream.

4.4 Pilot Unit Results

In the fall of 2001, a pilot unit was constructed. A schematic diagram is found in Chapter 3, Figure 3.4. The pilot unit has a capacity of 100 gallons. The pilot unit was designed to mimic the jar test apparatus. The velocity gradient and mixing regime were maintained. However, the pilot unit is a rectangular chamber, while the jar tests were completed in circular beakers. The rectangular design was selected due to construction costs and practicality of future scale-ups. The pilot unit, in addition, was equipped with five sampling ports spaced vertically to allow for profile sampling. A second set of sampling ports was installed later to allow for horizontal profile sampling.

4.4.1 Velocity Gradient Calculations

The velocity gradient (G) or mixing intensity is a critical element in wastewater coagulation. The G-value is a function of the mixer power (W), chamber volume (m^3), and the absolute viscosity ($N \cdot s \cdot m^{-2}$). The velocity gradient is calculated using Equation 2.1. As discussed in Chapter 2, Sievers (1989) found the optimum velocity gradient for liquid dairy manure coagulation with iron to be 22.3 s^{-1}. The G-values achieved in the jar test were found to be approximately 50 s^{-1}, based on Figure 4.7, which contains G-Curves supplied by the Phipps and Bird Company. The curves in Figure 4.7 were created using water. The mixing apparatus for the pilot unit was designed based on the optimum value for the velocity gradient from the literature (22.3 s^{-1}) and the actual velocity gradient achieved in lab tests (determined to be 50 s^{-1} from Figure 4.7). The calculated G-value for the pilot unit using Equation 2.1 is 33.77 s^{-1}, assuming that manure has a dynamic viscosity similar to water.

4.4.2 Pilot Unit Tests

The pilot unit tests focused primarily on coagulation with lime as a coagulant with alum and ferric chloride used to a lesser extent. Each pilot test was conducted over a 48 hour period. The procedure was to fill and chemically treat the tank of liquid dairy on the morning of day one. Operating procedures for the pilot unit are found in Chapter 3. The first samples were drawn after 1 hour settling. Samples were then collected on the next 2 consecutive mornings at approximately the same time. Sample analysis was completed in the afternoon of collection. Pilot unit tests were completed during the fall of 2001 and the winter of 2002. The goal of the pilot unit tests was to compare laboratory findings with a larger scale treatment operation under actual field conditions.

FIGURE 4.7: G Curves for Phipps and Bird Jar Test Apparatus
See Michigan State University, Department of Agricultural Engineering Library

4.4.2.1 Pilot Unit Sampling

As discussed in Chapter 3, the pilot unit was equipped with 5 primary sampling ports oriented in the vertical plane. A secondary set of sampling ports was installed on the adjacent face (at a 90° angle to the primary set) to test the uniformity of the horizontal plane. The full data set used for analyzing the uniformity of the horizontal plane is located in Table A5 in the appendix. Table 4.11 presents a condensed summary of the results.

Table 4.11: Horizontal Plane Differences in the Pilot Unit*

	Mean		Standard Deviation		Coefficient of Variance	
Depth (cm)	SP (mg/L)	TP (mg/L)	SP (mg/L)	TP (mg/L)	SP (%)	TP (%)
96.5	208	2,525	5	91	2.54%	3.59%
76	208	2,657	7	233	3.39%	8.78%
58.5	205	2,342	2	212	1.20%	9.04%
30.5	213	2,589	8	251	3.64%	9.68%
7.5	217	2,275	3	393	1.46%	17.28%
Averages	210	2,478	5	236	2.45%	9.68%

*Standard deviation and coefficient of variance for mean values of SP and TP at various depths in the pilot unit.

The concentration of SP varied little from one horizontal plane to another. TP concentrations showed a slight increase in variation with tank depth. The deepest ports, located 3 inches off the floor of the tank, had the largest standard deviation for TP at 393 mg/L. Sampling and lab error can sighted for differences in the standard deviation. The results of sampling the horizontal plane show clearly that liquid manure in the plane is uniform and that one set of sampling ports was sufficient for further experiments.

4.4.2.2 Phosphorus Reduction without Chemical Addition

Several experiments were carried out to characterize the reduction of the phosphorus concentration in the liquid fraction with no chemical treatment. The experiments with no chemical additions are broken into two categories, mixing and no-mixing. The mixing experiments utilized the same mixing schedule as if a chemical coagulant were being added, the procedure is described in Chapter 3. The no-mixing experiments involved simply filling the chamber with effluent from the solid separator (liquid dairy manure) followed by undisturbed settling.

Phosphorus settling with no mixing produced similar results to those observed in the laboratory tests. Figures 4.8 and 4.9 present the average reductions in the concentrations of SP and TP in the pilot unit with no mixing. The raw data for the no-mixing and mixing experiments are found in Table A6 in the appendix. Figures 4.8 and 4.9 demonstrate that both SP and TP are reduced in the upper two sampling ports after 24 hours. Allowing settling to continue to 48 hours further reduced the TP concentration in ports 1 and 2, the concentration of SP did not change. Additionally, the sludge layer (solids fraction) occupied 55% of the chamber volume after 48 hours. As discussed earlier, the settling that is observed is believed to be of the type 3 nature or hindered settling.

The data set used to create Figures 4.8 and 4.9 is presented again in Figures 4.10 and 4.11. The axis orientation in Figures 4.10 and 4.11 is such that the sampling height is presented on the x axis and the percent phosphorus reduction is presented on the y axis. The bold lines running perpendicular to the x axis represent the liquid/solid interface depth at the sampling time (the line color and dash spacing corresponds with the legend).

The bold lines running perpendicular to the x axis represent the liquid/solid interface depth at the sampling time (the line color and dash spacing corresponds with the legend).

FIGURE 4.8: SP Reductions with No Mixing or Chemical Treatment

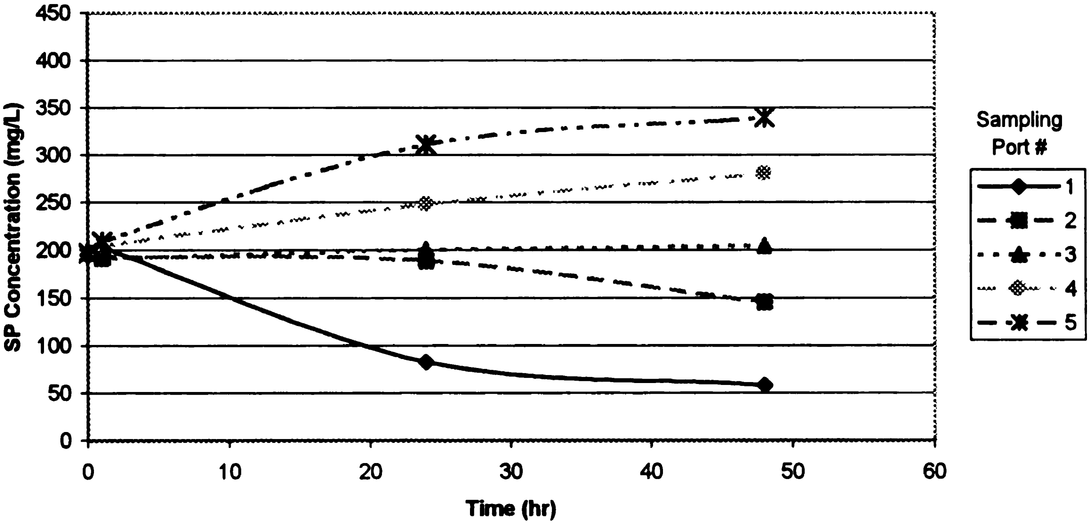


FIGURE 4.9: TP Reductions with No Mixing or Chemical Treatment

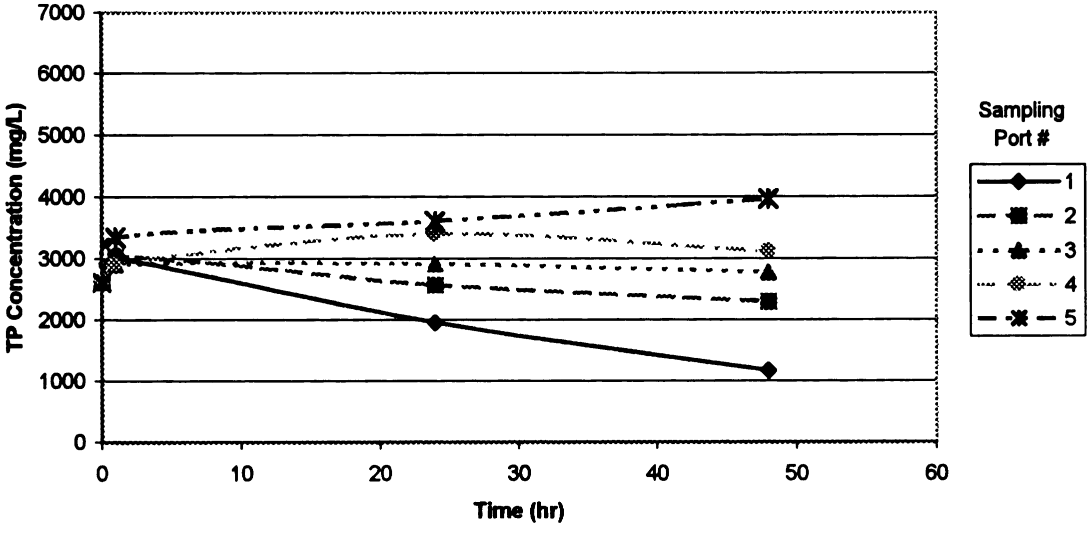


FIGURE 4.10: Pilot Unit SP Reduction (or Concentration) with No Treatment

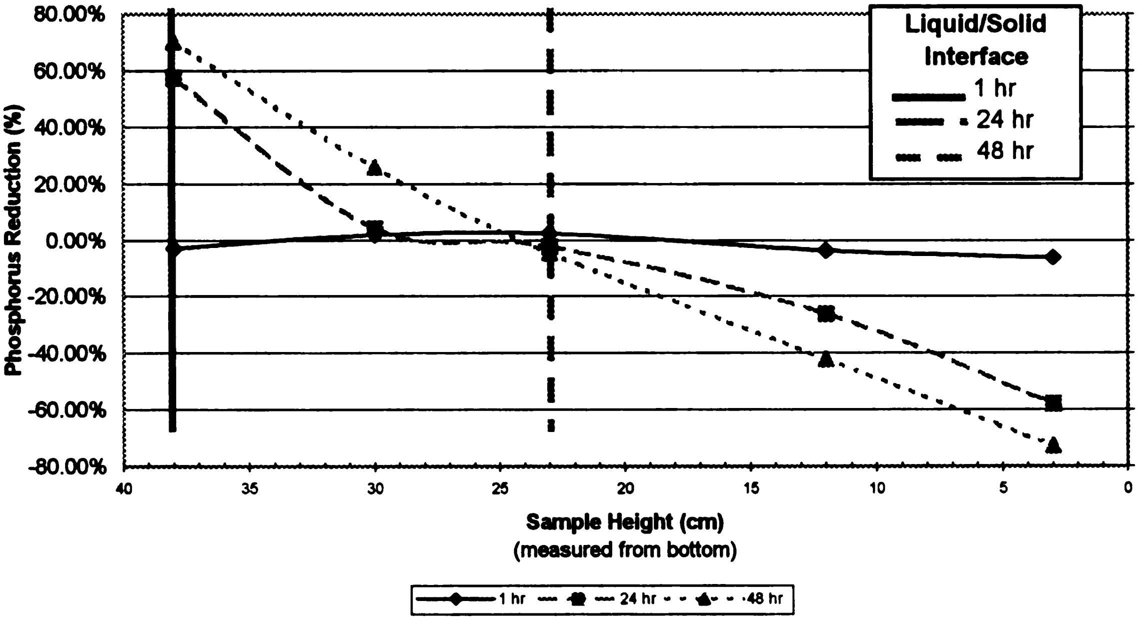
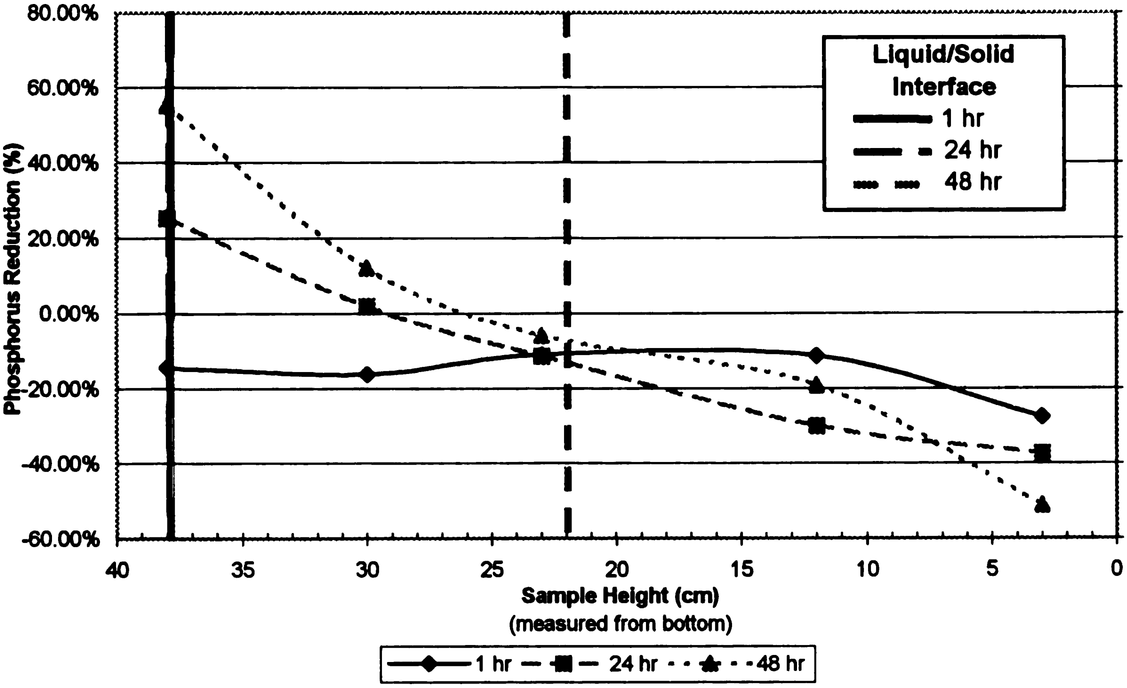


FIGURE 4.11: Pilot Unit TP Reduction (or Concentration) with No Treatment



For the sample taken at 48 hours, Figures 4.10 and 4.11 show that the liquid/solid interface corresponds with the change from phosphorus reduction to phosphorus concentration.

Figures 4.12 and 4.13 show the average SP and TP concentration reductions for the second experiment with no chemical coagulant. In this experiment, the pilot unit contents were mixed in the same manner as if a coagulant were to be added, however no chemical coagulant was added. In comparison with the no mixing results, it appears that mixing enhances separation by increasing the phosphorus concentration reduction depth and decreasing the volume of the sludge. Table A6 in the appendix contains the raw data used to generate Figures 4.12 and 4.13. Similar to the control jar, mixing may enhance phosphorus adsorption to the naturally occurring polymers excreted in the feces. The larger particles created by the adsorption are denser, thus settling is improved.

Figures 4.12 and 4.13 are created from the same data set as Figures 4.14 and 4.15. A described previously, the figures have different axis configurations. The bold lines rising from the x axis represent the depth of the liquid/solid interface. Samples collected after 24 and 48 hours with the mixing only treatment show a distinct pattern at the liquid/solid interface. Both SP and TP reductions switch to concentrations near the interface. The liquid/solid interface generally moved the most (settling) in the first 24 hours after undisturbed settling began.

FIGURE 4.12: SP Reductions with Mixing, but No Chemical Coagulant

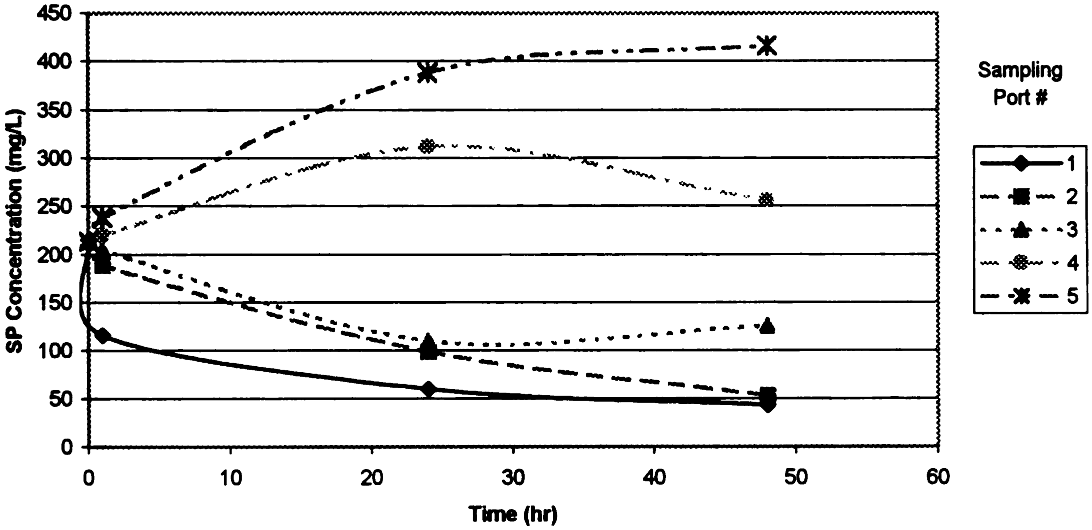


FIGURE 4.13: TP Reductions with Mixing, but No Chemical Addition

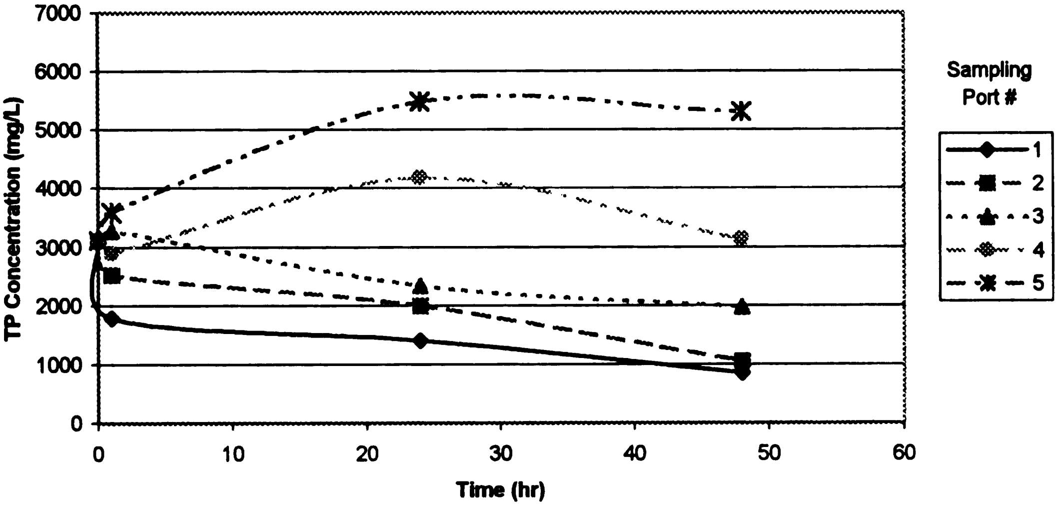


FIGURE 4.14: Pilot Unit SP Reduction (or Concentration) with only Mixing

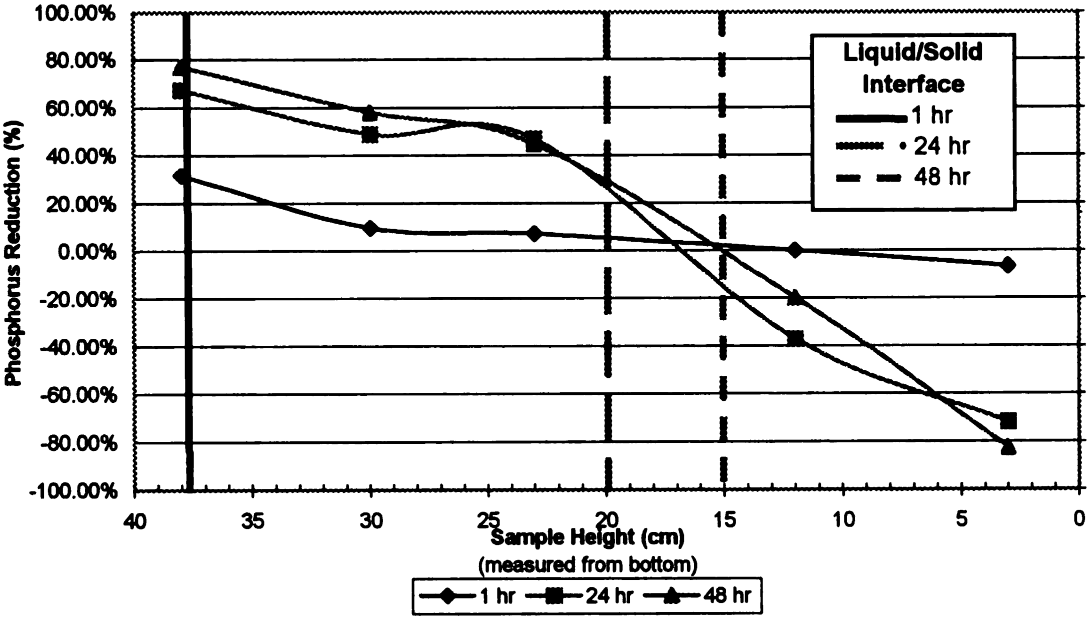
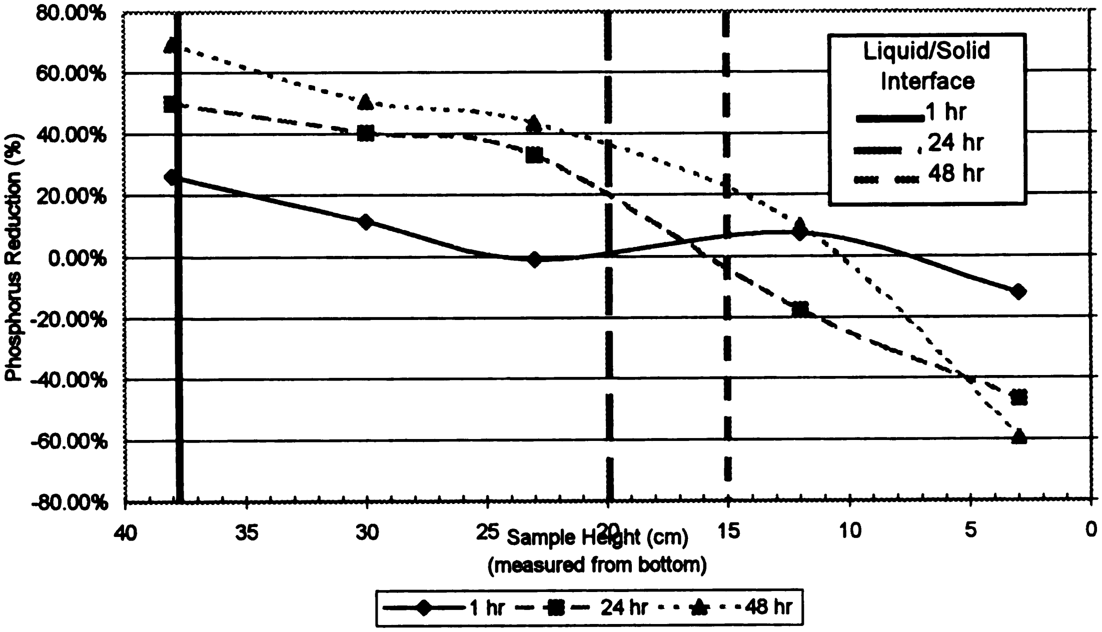


FIGURE 4.15: Pilot Unit TP Reductions (or Concentrations) with only Mixing



4.4.2.3 Chemical Coagulation with Lime Additions

Coagulation using lime was the primary focus of the pilot unit tests. Similar to laboratory analysis, five treatment levels were used in the field tests. The five lime treatment levels tested in the pilot unit were 0.66, 1.32, 2.64, 3.96, and 5.28 g/L. Table 4.12 contains the averaged phosphorus reductions at sampling port 2 in the pilot unit for each of the lime treatment levels. The highest treatment level for the pilot test coincides with the laboratory treatment level that produced results closest to the project objective. Figures 4.16 and 4.17 present the SP and TP concentration reductions using 5.28 g/L of lime at each sampling port with respect to time. The phosphorus concentrations (SP and TP) were significantly reduced in sampling port 1 after 24 hours. After 48 hours, the SP and TP concentrations in the effluent drawn from ports 1 and 2 were reduced by 66% of the initial sample. The effluent sampled from port (5) saw a sharp increase in SP and TP concentrations from 1 to 24 hours of settling. Phosphorus concentrations in the slurry sampled from port 5 did not change significantly from 24 to 48 hours.

Table 4.12: Averaged Phosphorus Reduction at Sampling Port 2 in the Pilot Unit

Sample Location (Port #)	Treatment (Lime) (g/L)	1 Hour		24 Hour		48 Hour	
		Soluble (ppm)	Total (ppm)	Soluble (ppm)	Total (ppm)	Soluble (ppm)	Total (ppm)
2	0.66	96%	86%	43%	49%	30%	38%
2	1.32	51%	73%	40%	48%	28%	41%
2	2.64	70%	78%	32%	38%	32%	37%
2	3.96	73%	85%	34%	38%	25%	34%
2	5.28	65%	89%	57%	70%	27%	40%

FIGURE 4.16: SP Reductions with 5.28 g/L of Lime as the Chemical Coagulant

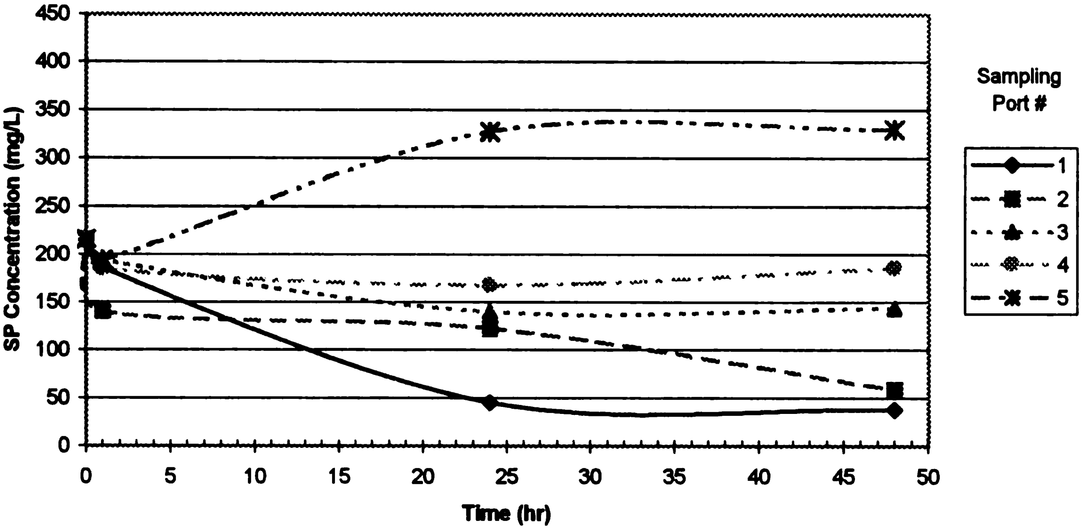
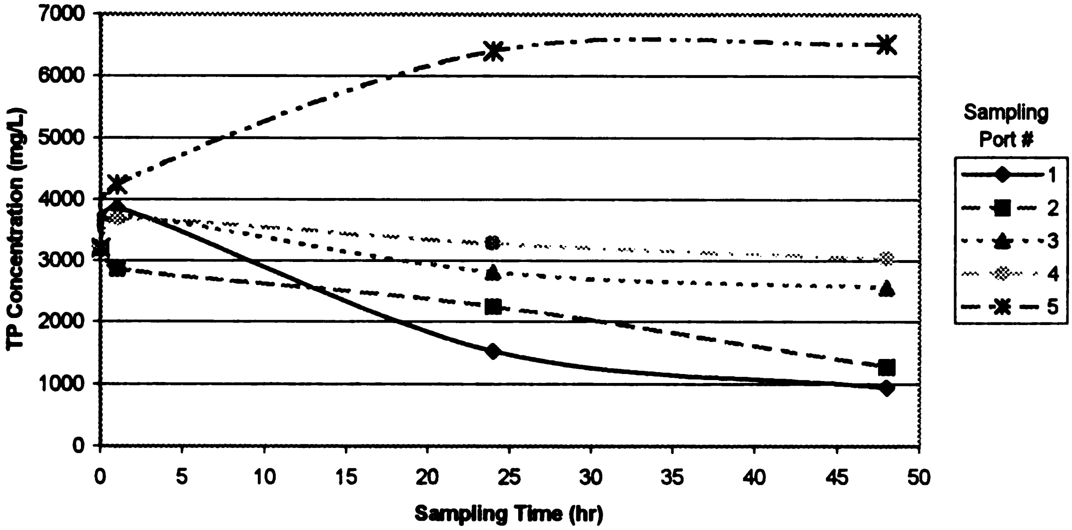


FIGURE 4.17: TP Reductions with 5.28 g/L of Lime as the Chemical Coagulant



The results from pilot unit experiments where lime was used as the coagulant differed from the laboratory results. Laboratory tests using lime to coagulate phosphorus resulted in a treatment level of 5.29 g/L to meet the goals of the project. However, in the pilot unit, much lower treatment levels (0.66 and 1.32 g/L of actual lime) produced results similar to the optimum treatment from the laboratory experiments. Note that the best phosphorus concentration reductions in the pilot unit occurred at 48 hours, laboratory measurements ceased after 24 hours. The 0.66 and 1.32 g/L of lime treatment levels produced the least amount of sludge and showed the largest reductions in SP and TP at sampling points 3 and 4. The higher lime doses, 2.64, 3.96, and 5.28 g/L of actual lime, produced no additional benefit when compared to the averaged phosphorus reductions (Table 4.12) using 0.66 and 1.32 g/L of lime.

4.4.2.4 Chemical Coagulation with Metal Salts (Alum and $FeCl_3$)

The two metal salts used in the chemical coagulation were alum and ferric chloride ($FeCl_3$). Due the constraints of time and inclement weather, only a few trials using metal salts were completed. Several trials were scrapped due to frozen valves or hindered settling.

A discussed in section 4.3.3, the laboratory results using 4 g/L of alum met the goal set forth at the beginning of the project, 80% reduction of SP and TP. A similar dose of alum (3.17 g/L) was applied to liquid dairy manure in the pilot unit. Figure 4.18 shows the SP concentration reductions using 3.17 g/L of alum. Concentrations of SP in liquid manure at the five sampling levels were lower after 1 hour. The initial reduction in the SP (1 hour) is due to the binding of the SP with the cationic metal salt (alum). The

FIGURE 4.18: SP Reductions with 3.17 g/L Alum as the Chemical Coagulant

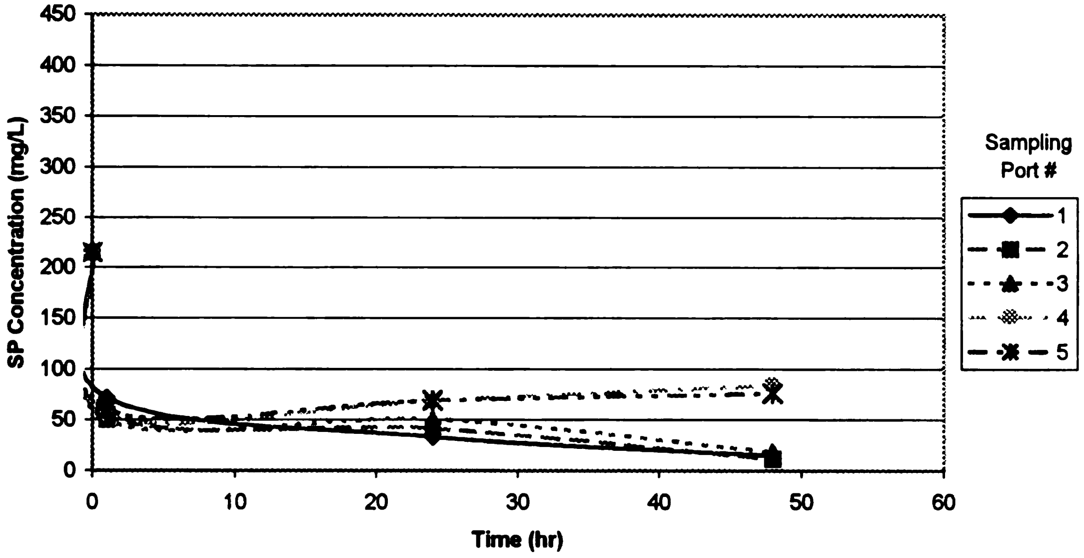


FIGURE 4.19: TP Reductions with 3.17 g/L of Alum as the Chemical Coagulant

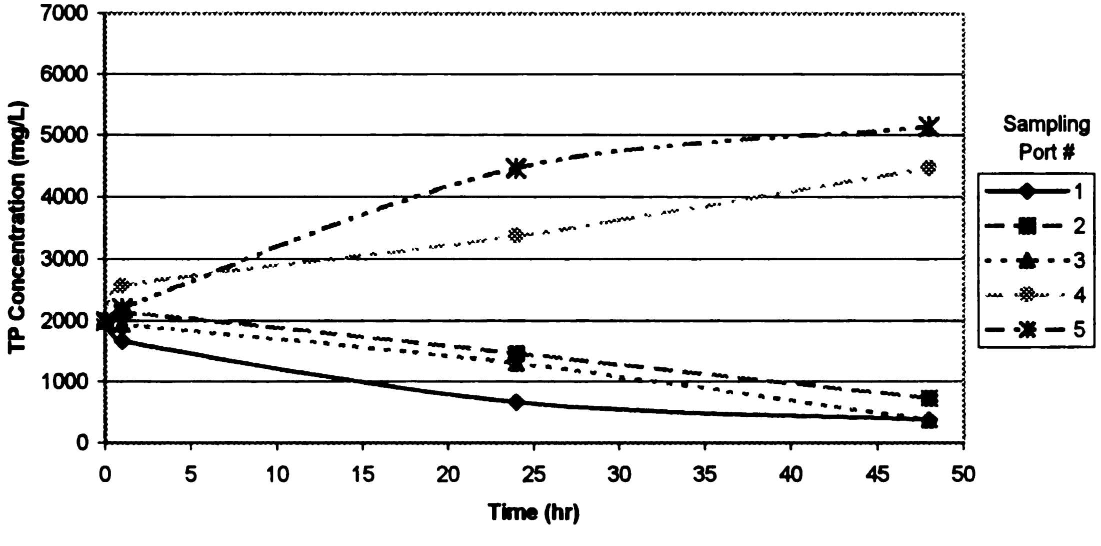


FIGURE 4.20: SP Mass Balance, Treatment 3.17g/L of Alum, Pilot Unit

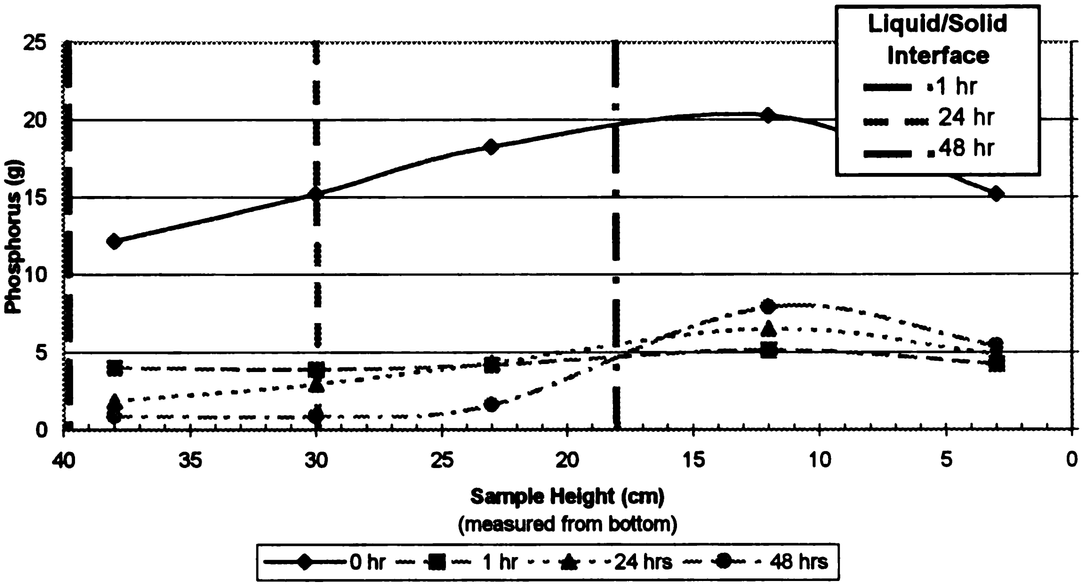
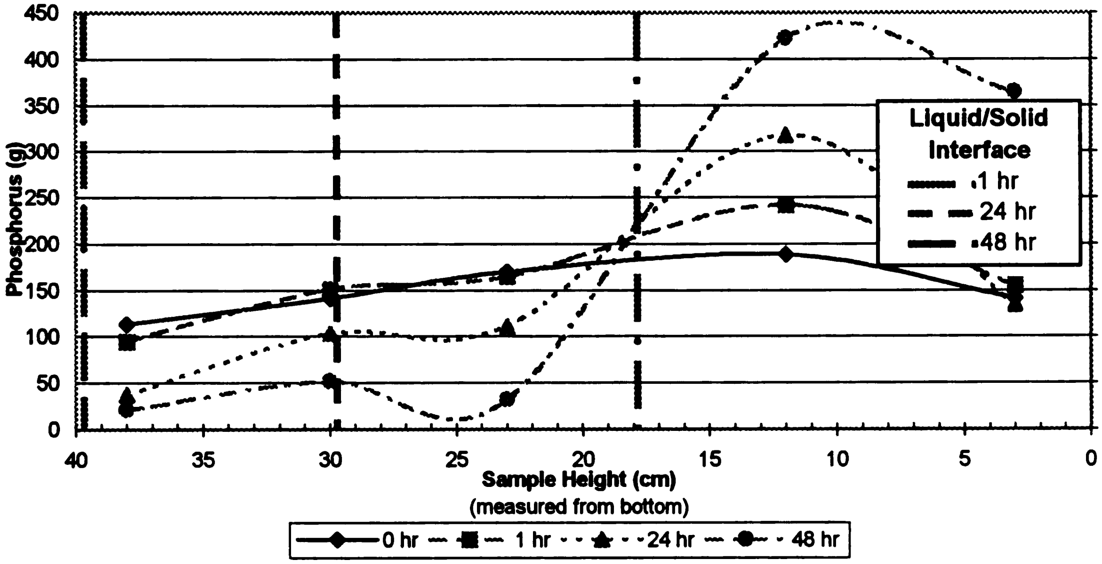


FIGURE 4.21: TP Mass Balance, Treatment 3.17 g/L of Alum, Pilot Unit



coagulation reactions with alum (Al^{+3}) and $FeCl_3$ (Fe^{+3}) occur faster than with lime (Ca^{+2}). Section 2.5.1 in Chapter 2 offers more discussion of the reaction speed. After 24 hours, samples from ports 1, 2, and 3 showed 80% reductions in SP in the effluent. At 48 hours, the SP in the effluent at points 1, 2, and 3 was reduced by 90% or more. After 48 hours, samples from the deep sampling points (4 and 5) were slightly higher in SP than the 24 hours samples. This is due to the settling of the non-coagulated phosphorus. The raw data for the pilot unit experiments using metal salts as the coagulant is found in Table A8 in the appendix. The graph of the TP reduction using the 3.17g/L of alum is presented in figure 4.18.

Figures 4.19 and 4.20 display the same data as in Figures 4.17 and 4.18 with the x axis acting as the sampling depth and the y axis as the phosphorus mass. The phosphorus mass was calculated by assuming horizontal layering around the sampling ports with the distance between ports split equally. Figure 4.20 shows a trend of increased phosphorus concentration below the liquid/solid interface.

As discussed earlier, $FeCl_3$ was also used to coagulate phosphorus in the liquid dairy manure at GMF using the pilot unit. The raw data for the experiment are found in the appendix Table A9. Figure 4.21 is the graph of the SP reduction at each sampling port with respect to time. Similar to alum, $FeCl_3$ is very aggressive at coagulating and settling SP, hence the large reductions in SP. The treatment level for Figures 4.21 and 4.22 was 1.06 g/L of $FeCl_3$. Figure 4.22 illustrates a difficulty when sampling a non-homogeneous biological material like liquid dairy manure. Samples taken at Port 2 were found to have less TP than samples at Port 1 at 24 hours and more TP than Port 3 after 48 hours. Table 4.11 demonstrates that there are differences in the horizontal plane of the

FIGURE 4.22: SP Reductions with 1.06 g/L of $FeCl_3$ as the Chemical Coagulant

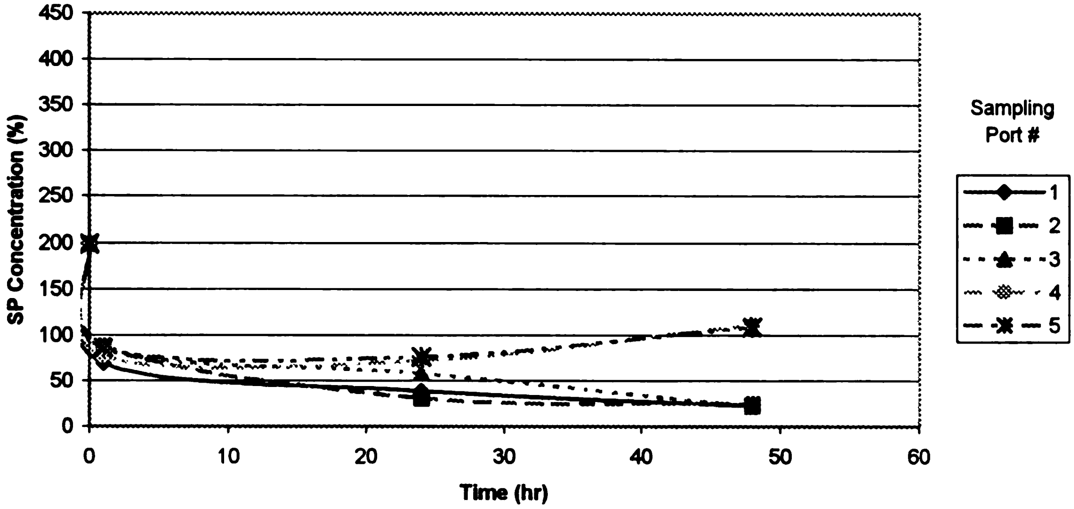
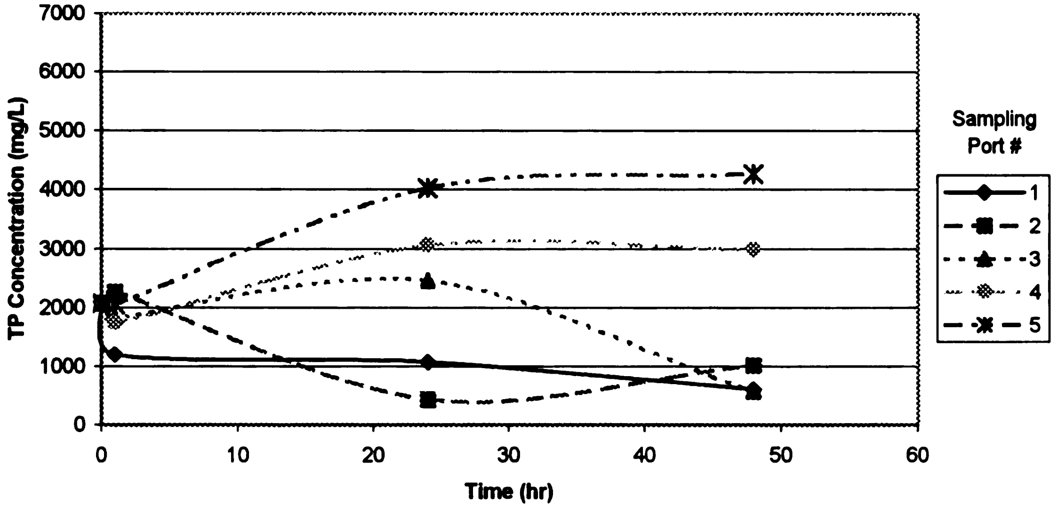


FIGURE 4.23: TP Reductions with 1.06 g/L $FeCl_3$ as the Chemical Coagulant



pilot unit, the coefficient of variance calculated in Table 4.11 was just under 10%. Accepted book values can vary by as much as 30%. The $FeCl_3$ did not produce an observable solid / liquid settling interface. Results varied and no observable settling occurred.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary

The goal of the project was to develop a strategy for managing the liquid manure stream prior to storage and application to lessen the threat of environmental degradation. For this project, chemical coagulation was selected as the method for separating phosphorus from the liquid fraction of the manure stream. A variety of chemical coagulants known to bind and coagulate phosphorus in wastewater treatment were tested. The three that performed the best in the preliminary research were lime, alum, and ferric chloride. Laboratory and pilot unit test demonstrated the usefulness of these coagulants for concentrating the phosphorus in the sludge, while leaving a liquid fraction with little or no phosphorus.

Based on the laboratory results, a pilot unit was developed to evaluate the laboratory results on a larger scale and under real conditions. The pilot unit was a combination of rapid mix chamber and settling tank. Similar reductions in the concentration of both SP and TP in the liquid fraction were found in laboratory and pilot unit tests.

5.2 Conclusions

5.2.1 Laboratory Experiments

- The characterization of the liquid dairy manure stream at Green Meadow Farms was completed for soluble phosphorus (SP), total phosphorus (TP), chemical oxygen demand (COD), total solids (TS), volatile solids (VS), and pH. The range found for each characteristic evaluated was within the expected ±30% range accepted for book values.

- The Stannous Chloride Method for analyzing phosphorus concentration is accurate and repeatable. The laboratory error resulting from the sampling and analysis is well within the acceptable limits for biological materials.
- Turbidity at the dilutions used in the laboratory (1/200) is not a useful measurement for predicting SP or TP concentration. At lower dilutions turbidity may be useful for predicting TP or TS.
- Alum and ferric chloride achieved the goals of 80% reduction in both SP and TP in the liquid fraction. Lime did not achieve the 80% goal for TP, but did reduce SP by 80% after 24 hours of settling.
- An economic analysis of the laboratory results showed that treating liquid dairy manure for phosphorus reduction with lime is economical after 1 and 24 hours of settling. Alum was not economically viable after 1 hour of settling, but after 24 hours of settling was economical. Ferric chloride in the project proved to not be an economical option.
- Polymers alone could not economically achieve the goal of 80% reduction in phosphorus concentration set for this project.

5.2.2 Pilot Unit Experiments

- Results of field trials with lime and ferric chloride in the 100 gallon pilot unit were more positive than results of laboratory tests. However, alum did not perform as well in the field experiments.
- The differing results using similar treatments in both the laboratory and pilot unit experiments may be attributed to variations in the day-to-day characteristics (SP, TP, COD, TS, and VS) of the manure stream.
- Daily temperature fluctuations seemed to play a role in the rate and amount of settling occurring, however daily temperatures were not recorded

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TABLE A1: Manure Stream Characterization, Green Meadow Farms

Date	SP	TP	COD	TS	VS
	(ppm)	(ppm)	(g/L)	(%)	(%)
7/31/01	221	2,316	39,700	3.63	2.37
8/20/01	108	1,881	14,700	2.02	1.58
9/5/01	225	2,801	25,600	2.92	1.99
9/6/01	245	2,529	26,850	2.05	1.26
9/20/01	215	1,999	25,100	1.33	1.05
9/26/01	121	2,130	35,100		
10/1/01	202	2,957	32,850	3.25	2.45
10/9/01	211	2,981	18,850	2.14	1.45
10/11/01	180	3,410	29,350	2.28	1.84
10/15/01	145	1,780	18,100	2.06	1.34
10/25/01	156	2,533	31,667	2.60	2.01
10/25/01	169	2,706	47,333	2.29	1.88
10/29/01	176	2,788	26,350	2.82	2.08
10/31/01	278	3,701	47,333	2.43	1.98
11/5/01	0	199	47,333	2.45	1.69
11/11/01	189	3,161	37,350	1.99	1.62
11/14/01	208	3,273	47,600	2.62	1.94
11/20/01	178	3,061	39,350	2.89	1.86
11/26/01	221	3,433	43,100	2.82	2.08
11/28/01	157	2,380	39,600	3.19	2.08
12/5/01	187	3,051	43,850		
12/11/01	210	2,754	46,100	5.02	2.33
12/12/01	208	3,411	39,100	3.82	2.79
12/19/01	203	3,745	43,600	3.19	2.17
12/20/01	242	3,486	43,500	5.39	2.58
12/27/01	196	3,530	44,350	2.86	2.15
1/2/02	199	3,114	43,100	2.98	2.24
1/2/02	197	2,624	53,600	3.40	3.00
1/3/02	245	3,221	42,100	2.92	2.17
1/28/02	180	2,338		2.25	1.76
2/19/02	208	2,605	42,100	3.02	2.23
3/5/02	69	1,104	27,100	1.66	1.43
3/6/02	108	1,362	26,850	2.20	1.71
Average	184	2,678	36,518	2.79	1.97
Standard Deviation	55	785	10,003	0.86	0.44

TABLE A2: LABORATORY RESULTS USING LIME AS THE COAGULANT

Date:	12/12/2001						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Actual Lime	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		208	3,411	208	3,411	TS (%)	5.02%
1	0.00	121	1,808	68	1,587	VS (%)	2.33%
2	1.32	73	1,511	50	1,044	COD (ppm)	-
3	2.64	60	1,479	45	1,139		
4	3.97	50	1,347	38	1,025		
5	5.29	41	1,170	37	1,012		
6	6.61	42	1,038	37	1,353		

Date:	12/19/2001						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Actual Lime	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		203	3,745	203	3,745	TS (%)	3.82%
1	0.00	190	3,278	41	1,410	VS (%)	2.79%
2	1.32	175	2,653	40	1,107	COD (ppm)	39,100
3	2.64	183	2,912	29	1,240		
4	3.97	106	2,028	34	1,309		
5	5.29	50	1,511	30	823		
6	6.61	46	1,265	38	993		

Date:	2/19/2002						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Actual Lime	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		208	2,605	208	2,605	TS (%)	3.02%
1	0.00	183	2,555	49	1,026	VS (%)	2.23%
2	1.32	148	1,960	41	1,048	COD (ppm)	42,100
3	2.64	63	1,310	39	1,026		
4	3.97	53	993	36	871		
5	5.29	45	937	38	948		
6	6.61	35	937	44	837		

TABLE A3: LABORATORY RESULTS USING ALUM AS THE COAGULANT

Date:	12/19/2001						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Alum	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		203	3,745	203	3,745	TS (%)	3.82%
1	0.00	198	5,209	62	1,303	VS (%)	2.79%
2	0.80	69	2,849	31	1,151	COD (ppm)	39,100
3	2.00	57	3,057	30	1,170		
4	4.00	23	2,969	10	1,927		
5	6.00	21	2,653	3	1,751		
6	8.00	-3	406	-8	381		

Date:	12/27/2001						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Alum	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		196	3,530	196	3,530	TS (%)	5.39%
1	0.00	124	2,349	59	1,388	VS (%)	2.58%
2	0.80	178	3,211	44	1,144	COD (ppm)	43,500
3	2.00	107	2,844	23	966		
4	4.00	20	2,691	5	526		
5	6.00	6	526	-2	550		
6	8.00	-7	415	-9	293		

Date:	3/5/2002						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	Alum	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		69	1,104	69	1,104	TS (%)	1.66%
1	0.00	30	576	28	281	VS (%)	1.43%
2	0.80	35	1,276	16	115	COD (ppm)	27,100
3	2.00	0	253	4	-163		
4	4.00	0	0	-13	-391		
5	6.00	0	48	-9	-291		
6	8.00	0	337	-10	-230		

TABLE A4: LABORATORY RESULTS USING FERRIC CHLORIDE AS THE COAGULANT

Date:	12/27/2001						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	$FeCl_3$	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		196	3,530	196	3,530	TS (%)	5.39%
1	0.00	107	2,135	57	1,462	VS (%)	2.58%
2	0.80	106	1,963	47	1,480	COD (ppm)	43,350
3	2.00	148	2,636	50	1,504		
4	4.00	104	2,520	48	1,358		
5	6.00	-2	1,664	1	1,199		
6	8.00	-9	1,523	-5	825		

Date:	1/2/2002						
	Treatment	1 Hour		24 Hour		Characterization	
Jar	$FeCl_3$	SP	TP	SP	TP	Parameters	Results
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
Sample		199	3,114	199	3,114	TS (%)	2.86%
1	0.00	181	2,985	61	1,419	VS (%)	2.15%
2	0.80	121	2,465	37	1,407	COD (ppm)	44,350
3	2.00	38	2,330	33	1,364		
4	4.00	31	2,018	26	1,150		
5	6.00	-5	654	3	422		
6	8.00	-9	281	-10	360		

TABLE A5: Horizontal Layer Sampling, Pilot Unit

Sampling Ports		SP	TP
Set	Port #	(mg/L)	(mg/L)
1	1	211	2,461
1	2	203	2,492
1	3	203	2,492
1	4	207	2,412
1	5	219	1,997
2	1	204	2,589
2	2	213	2,822
2	3	206	2,192
2	4	218	2,767
2	5	214	2,553

TABLE A6: Pilot Unit Phosphorus Reductions with No Chemical Additions

1/2/2002								
TS	2.98%		VS	2.24%		COD	43,100	ppm
		Sampling	1 Hour		24 Hour		48 Hour	
Treatment	Sampling	Depth	Soluble	Total	Soluble	Total	Soluble	Total
	Location	(cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
None	Sample		197	2,624	197	2,624	197	2,624
	1	38	203	3,003	83	1,957	58	1,174
	2	30	193	3,052	189	2,575	146	2,306
	3	23	192	2,912	201	2,924	205	2,777
	4	12	204	2,924	248	3,413	280	3,126
	5	3	209	3,346	311	3,603	340	3,964
Sludge Line (cm)			40		40		22	

10/31/2001								
TS	2.43%		VS	1.98%		COD	47,333	ppm
		Sampling	1 Hour		24 Hour		48 Hour	
Treatment	Sampling	Depth	Soluble	Total	Soluble	Total	Soluble	Total
	Location	(cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Mixing Only	Sample		278	3,701	278	3,701	278	3,701
	1	38	115	1,768	85	1,832	32	704
	2	30	210	2,470	77	1,429	57	877
	3	23	227	3,246	81	1,682	82	1,285
	4	12	250	3,166	331	3,729	87	1,193
	5	3	285	3,793	449	4,908	449	6,133
Sludge Line (cm)			35		12		10	

11/14/2001								
TS	2.62%		VS	1.94%		COD	47,600	ppm
		Sampling	1 Hour		24 Hour		48 Hour	
Treatment	Sampling	Depth	Soluble	Total	Soluble	Total	Soluble	Total
	Location	(cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Mixing Only	Sample		208	3,273	208	3,273	208	3,273
	1	38	127	1,948	51	852	58	908
	2	30	203	2,701	62	1,375	65	1,194
	3	23	206	3,404	58	1,450	65	952
	4	12	221	2,651	346	3,977	385	3,877
	5	3	230	3,479	408	5,570	445	5,271
Sludge Line (cm)			38		18		14	

TABLE A6, continued

11/28/2001								
TS	3.19%		VS	2.08%		COD	39,600	ppm
		Sampling	1 Hour		24 Hour		48 Hour	
Treatment	Sampling	Depth	Soluble	Total	Soluble	Total	Soluble	Total
	Location	(cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Mixing Only	Sample		157	2,380	157	2,380	157	2,380
	1	38	107	1,661	45	1,527	38	942
	2	30	155	2,406	158	3,196	37	1,096
	3	23	183	3,176	192	3,863	232	3,690
	4	12	189	2,875	259	4,820	297	4,338
	5	3	198	3,491	307	5,975	353	4,537
Sludge Line (cm)			41		30		22	

TABLE A7: PILOT RESULTS USING LIME AS THE COAGULANT

10/9/01								
TS	3.25%		VS	2.45%		COD	32,850	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	5.28		211	2,981	211	2,981	211	2,981
1	5.28	38						
2	5.28	30	100	1,892	87	1,314	81	1,451
3	5.28	23	175	3,356	87	1,761	57	1,433
4	5.28	12	175	3,594	76	1,743	75	1,719
5	5.28	3	176	4,410	347	6,838	307	8,505
Sludge Line (cm)			27		10		8	

10/11/01								
TS	2.28%		VS	1.84%		COD	29,350	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	2.64		180	3,410	180	3,410	180	3,410
1	2.64	38						
2	2.64	30	81	2,154	60	1,267	55	1,225
3	2.64	23	143	2,975	58	1,082	62	1,112
4	2.64	12	156	3,642	59	874	62	1,457
5	2.64	3	202	3,511	368	5,683	426	8,207
Sludge Line (cm)			27		9		8	

10/15/01								
TS	2.07%		VS	1.34%		COD	18,100	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	1.32		145	1,780	145	1,780	145	1,780
1	1.32	38	72	1,584	63	1,406	39	1,027
2	1.32	30	79	1,475	69	1,280	48	986
3	1.32	23	104	1,745	56	986	59	1,274
4	1.32	12	184	2,573	68	1,308	56	1,015
5	1.32	3	237	3,672	436	7,053	454	7,053
Sludge Line (cm)			20		7		7	

TABLE A7, continued

10/25/01								
TS	2.60%		VS	20.10%		COD	39,500	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	0.66		163	2,619	163	2,620	163	2,620
1	0.66	38	73	1,343	63	1,406	39	1,027
2	0.66	30	157	2,240	69	1,280	48	986
3	0.66	23	159	2,631	56	986	59	1,274
4	0.66	12	172	2,430	68	1,308	56	1,015
5	0.66	3	253	3,867	436	7,053	454	7,053
Sludge Line (cm)			30		12		10	

10/29/01								
TS	2.82%		VS	2.08%		COD	26,350	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	1.32		176	2,788	176	2,788	176	2,788
1	1.32	38	89	1,879	52	877	33	877
2	1.32	30	86	1,854	59	896	43	896
3	1.32	23	185	3,111	66	1,014	32	1,014
4	1.32	12	199	3,690	83	1,394	51	1,394
5	1.32	3	243	4,885	459	7,574	385	7,574
Sludge Line (cm)			35		24			

11/11/01								
TS	1.99%		VS	1.62%		COD	37,350	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	2.64		189	3,161	176	3,161	176	3,161
1	2.64	38	96	1,835	67	1,250	62	1,773
2	2.64	30	161	2,277	67	1,163	63	1,437
3	2.64	23	145	2,545	62	1,207	67	1,717
4	2.64	12	149	2,290	289	4,020	381	5,284
5	2.64	3	179	3,273	291	4,462	331	6,006
Sludge Line (cm)			36				12	

TABLE A7, continued

11/20/01								
TS	2.89%		VS	1.86%		COD	39,350	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	3.96		178	3,061	178	3,061	178	3,061
1	3.96	38	90	2,008	58	1,315	35	1,019
2	3.96	30	129	2,611	61	1,173	45	1,039
3	3.96	23	146	2,637	59	1,090	34	1,161
4	3.96	12	143	2,785	289	4,236	52	1,552
5	3.96	3	178	3,305	322	4,845	380	7,927
	Sludge Line (cm)		39		14		12	

11/26/01								
TS	2.82%		VS	2.08%		COD	43,100	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	5.28		221	3,433	221	3,433	221	3,433
1	5.28	38	186	3,863	45	1,527	38	942
2	5.28	30	181	3,838	158	3,196	37	1,096
3	5.28	23	213	4,139	192	3,863	232	3,690
4	5.28	12	194	3,773	259	4,820	297	4,338
5	5.28	3	211	4,069	307	5,975	353	4,537
	Sludge Line (cm)		41		30		22	

12/6/01								
TS			VS			COD	43,850	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Sample	2.64		187	3,051	187	3,051	187	3,051
1	2.64	38	97	1,883	46	1,296	54	918
2	2.64	30	150	3,032	46	1,265	57	855
3	2.64	23	152	3,057	44	930	99	722
4	2.64	12	153	3,171	304	4,319	202	1,763
5	2.64	3	192	3,329	472	5,960	477	5,506
	Sludge Line (cm)		39		17		12.5	

TABLE A8: PILOT RESULTS USING ALUM AS THE COAGULANT

9/20/01								
TS	1.33%		VS 1.05%			COD	25,100	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
		40	215	1,999	215	1,999	215	1,999
1	3.17	38	72	1,671	33	665	15	374
2	3.17	30	55	2,136	42	1,469	12	731
3	3.17	23	50	1,939	51	1,308	19	374
4	3.17	12	55	2,558	69	3,362	84	4,469
5	3.17	3	60	2,195	69	1,910	76	5,148
Sludge Line (cm)			40		30		18	

01/29/02								
TS	2.92%		VS	2.17%		COD	42,100	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
		40	180	2,338	180	2,338	180	2,338
1	1.59	38	103	2,305	85	2,049	48	926
2	1.59	30	106	2,394	80	2,316	88	2,371
3	1.59	23	102	2,327	81	2,616	86	2,583
4	1.59	12	106	2,516	76	2,560	94	2,388
5	1.59	3	130	2,572	85	2,883	90	2,244
Sludge Line (cm)								

TABLE A9: PILOT RESULTS USING FERRIC CHLORIDE AS THE COAGULANT

11/05/01								
TS	2.45%		VS	1.69%		COD	47,333	ppm
	Treatment	Depth	1 Hour		24 Hour		48 Hour	
	(g/L)	(cm)	Soluble	Total	Soluble	Total	Soluble	Total
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
		40	199	2,073	199	2,073	199	2,073
1	1.06	38	69	1,199	39	1,073	23	607
2	1.06	30	89	2,274	31	428	25	1,015
3	1.06	23	85	1,837	68	2,470	22	578
4	1.06	12	77	1,745	72	3,062	111	2,982
5	1.06	3	86	2,056	76	4,028	109	4,264
Sludge Line (cm)			40		24		22	