

# **Reclaiming Phosphorus as Struvite from Hog Manure**

by

Joe Nelson Ackerman

A Thesis submitted to the Faculty of Graduate Studies at the

University of Manitoba

in partial fulfilment of the degree of

**DOCTOR OF PHILOSOPHY**

Department of Biosystems Engineering

University of Manitoba

Winnipeg, Canada

Copyright © 2012 by Joe N. Ackerman

## **Abstract**

The over application of manure phosphorus (P) to farmlands can lead to P build up in the soil and eventual runoff to surface waters causing eutrophication. Reducing P in manure by precipitation of struvite enables P capture and reuse as a fertilizer in the agricultural supply stream. Struvite precipitation is dictated by levels of soluble P which can be highly variable according to manure treatment and management. This research studied P forms in liquid pig manure, ways of increasing P-PO<sub>4</sub> levels in manure from strategic storage conditions, novel struvite reactors, and the effectiveness of struvite as a fertilizer. Studies that monitored soluble nutrients during manure storage revealed that P-PO<sub>4</sub> concentration was sensitive to pH and time. Anaerobic fermentation of manure increased P-PO<sub>4</sub> by 2.5 fold with 12 days of storage, provided the buffering by alkalinity was low. Two different struvite reactors were operated, a batch-type system for processing lagoon supernatant and an upflow air sparged reactor that used supernatant from a rotary press solids separator. They achieved 75% and 31% total P removal, respectively. The upflow reactor operated without chemical addition at pH 6.8 to produce high purity struvite free of calcium phosphates. Costs of both reactors were comparable (\$0.0139 and \$0.0167/kg live pig wt) and similar to other pilot struvite reactors. Manure derived struvite was compared with pure struvite and commercial fertilizer for agronomic value in canola production. Results of a greenhouse pot experiment showed no significant difference between the two struvites despite impurities in the manure precipitate.

## **Aknowledgments**

In recognition of things that made this a wonderful graduate experience, I would like to extend my warmest thanks to my advisor, Nazim Cicek for the encouragement and inspiration over the last several years. I also thank the staff and technicians in numerous departments for their patient guidance on the use of equipment and analysis techniques. As well, fellow graduate students Umesh Ramachandran, Francesco Zurzolo and good friend Sara Nasr have made coming in to work a dynamic and pleasant experience. The organizations that made this research possible by their generous funding were: National Science and Engineering Research Committee, Agricultural and Rural Development Initiative, Manitoba Livestock Manure Management Initiative and the University of Manitoba. I thank each of them for their support.

## Table of Contents

<b>Abstract</b> .....	<b>ii</b>
<b>Aknowledgments</b> .....	<b>iii</b>
<b>List of Tables</b> .....	<b>vii</b>
<b>List of Figures</b> .....	<b>ix</b>
<b>1 Introduction</b> .....	<b>1</b>
1.1 A systems approach to P reclamation .....	3
1.2 Research objectives .....	6
<b>2 Literature Review</b> .....	<b>8</b>
2.1 Introduction .....	8
2.2 Struvite Formation.....	8
2.3 Factors Affecting Struvite Formation .....	11
2.4 Methods of Precipitation .....	32
2.5 Fine Tuning Precipitation.....	38
2.6 Pilot Scale Reactors and Hog Manure.....	41
2.7 Hog manure solids as a source of dissolved P .....	43
2.8 Struvite as a fertilizer .....	49
2.9 Literature Review Summary .....	51
<b>3 Manure: Lagoons, P-PO<sub>4</sub>, and storage</b> .....	<b>53</b>
3.1 Introduction .....	53
3.2 Lagoon Survey .....	54
3.3 The effect of acidifying lagoon supernatant on P-PO <sub>4</sub> .....	60
3.4 Nutrient monitoring in lagoon supernatant over time .....	61

3.5	General Discussion.....	67
<b>4</b>	<b>Batch struvite reactor and elutriation of manure solids .....</b>	<b>70</b>
4.1	Introduction .....	70
4.2	Objective 1) Pilot scale batch reactor design, operation, and performance .....	70
4.3	Solids Analysis.....	77
4.4	Results and Discussion.....	78
4.5	Conclusions .....	88
4.6	Objective 2) Elutriation of Manure Solids with Struvite Reactor Effluent.....	89
<b>5</b>	<b>Anaerobic fermentation of manure to increase P-PO<sub>4</sub>.....</b>	<b>95</b>
5.1	Section 1: Anaerobic fermentation of hog manure to lower pH and increase P-PO <sub>4</sub>	95
5.2	Methods.....	97
5.3	Results .....	100
5.4	Discussion .....	107
5.5	Section 2: Anaerobic fermentation of commercial manure.....	110
5.6	Methods.....	111
5.7	Results and discussion.....	112
5.8	General discussion.....	119
<b>6</b>	<b>Pilot scale struvite reactor using fermented manure liquid and no chemical additions.....</b>	<b>121</b>
6.1	Introduction .....	121
6.2	Methods.....	122
6.3	Results and Discussion.....	125

6.4	Solids analysis .....	128
6.5	General Conclusion .....	132
<b>7</b>	<b>Comparing reclaimed struvite with pure struvite and commercial fertilizer for growing canola .....</b>	<b>134</b>
7.1	Introduction .....	134
7.2	Methods .....	136
7.3	Results .....	140
7.4	Discussion .....	146
<b>8</b>	<b>Engineering significance.....</b>	<b>149</b>
8.1	Manure storage.....	149
8.2	Use of existing infrastructure .....	150
8.3	Batch reactor .....	150
8.4	Crystaphos™ up-flow reactor .....	150
8.5	Costs.....	151
<b>9</b>	<b>Conclusions.....</b>	<b>156</b>
9.1	Contributions to the field.....	159
<b>10</b>	<b>References.....</b>	<b>160</b>
<b>11</b>	<b>Appendix A.....</b>	<b>169</b>
<b>12</b>	<b>Appendix B.....</b>	<b>172</b>
<b>13</b>	<b>Appendix C.....</b>	<b>178</b>

## List of Tables

Table 2.1	Equilibrium and precipitation software used to model struvite precipitation..	10
Table 2.2	Struvite solubility product values found in literature (compiled by .....	14
Table 2.3	Optimum Mg:P ratios with experimental pH levels and phosphate .....	21
Table 2.4	Solubility product of common calcium phosphate compounds. ....	27
Table 2.5	Phosphate removal achieved under different pH conditions. ....	38
Table 2.6	Quantitative and X-ray diffraction analysis of reclaimed precipitate from .....	39
Table 2.7	Pilot scale struvite reactors using hog manure and potato wastes. Initial and ..	42
Table 3.1	Changes in P-PO <sub>4</sub> concentration in four lagoon supernatants .....	61
Table 4.1	Nutrient removal in the struvite reactor as determined by total digestion of...	81
Table 4.2	Phosphorus forms present in reactor influent and effluent. ....	81
Table 4.3	Elemental analysis of air-dried reactor solids and percent soluble.....	84
Table 4.4	Dissolved nutrient concentrations in supernatant. ....	91
Table 4.5	Nutrients in manure solids and those recovered by elutriation.....	93
Table 5.1	Characteristics of manure solids collected at Glenlea research farm .....	97
Table 5.2	Dissolved nutrients measured in influent manure and reactor effluent .....	103
Table 5.3	Dissolved nutrient concentration of manure slurry as a percentage .....	104
Table 5.4	Chemical characteristics of manure slurries used.....	112
Table 5.5	Ranking of manure according to alkalinity/grams of volatile solids.....	117

Table 6.1 Reactor influent and effluent composition as a mean of 7 trials (SD).....	126
Table 6.2 Reactor trials using rotary press manure liquid. ....	127
Table 7.1 Nutrient solution source added to all treatments and controls. Rates are .....	138
Table 7.2 Phosphorus amendments and nutrient content.....	140
Table 7.3 Comparison of means for biomass production and P uptake.....	142
Table 7.4 Literature comparing struvite to commercial P fertilizer.....	148
Table 8.1 Costs of installing and operating a batch reactor .....	153
Table 8.2 Costs of installing and operating a Crystaphos™ upflow reactor .....	154
Table 12.1 Analysis of variance of sampling means between 3 manures in 3 reactors.	172
Table 12.4 Total solids (means of 3 samples from 3 replicate reactors.....	177
Table 12.5 Volatile solids (means of 3 samples from 3 replicate reactors .....	177
Table 13.1 Mass Balance of Niverville Reactor using Rotary Press Liquid.....	179

## List of Figures

Figure 1.1 Three scenarios of hog manure management .....	4
Figure 2.1 Equilibrium of phosphorus species at a range of pH values.....	13
Figure 2.2 Nucleation pathways of struvite formation (Wu and Bishop 2004).....	18
Figure 2.3 Anaerobically digested hog manure with different Mg:P ratios and pH.....	19
Figure 2.4 Initial liquor and effluent PO <sub>4</sub> concentrations before and after struvite.....	20
Figure 2.5 Struvite (MAP) reactor placement at an enhanced biological phosphorus ....	31
Figure 3.1 Total (A) and soluble phosphorus (B) at commercial hog lagoons in.....	57
Figure 3.2 Lagoon pH (C) and total solids (D). Sampling locations are as described in .	58
Figure 3.3 Alkalinity at primary and secondary lagoons.....	59
Figure 3.4 Experimental results from Trial 1 stored manure (6% TS), .....	64
Figure 3.5 Soluble P, Mg and Ca from Trial 1 of stored manure supernatant.....	65
Figure 3.6 Trial 2 supernatant pH and alkalinity. ....	66
Figure 3.7 Trial 2 supernatant soluble nutrients P, Mg, and Ca. ....	66
Figure 4.1 Schematic of the gravity-settling batch reactor. ....	74
Figure 4.2 Determination of P forms in manure slurry.....	76
Figure 4.3 Reactor performance during (a) July and (b) August processing liquid hog..	79
Figure 4.4 Forms of calcium present in reactor influent and effluent.....	83
Figure 4.5 Total solids and inorganic solids contained in reactor supernatant.....	83

Figure 4.6 Dried solids analyzed with XRD indicating struvite and sylvite .....	85
Figure 5.1 Fermentation reactor.....	98
Figure 5.2 The pH change from anaerobic conditions of fresh manure .....	101
Figure 5.3 Phosphorus forms in mixed manure from stirred reactors. ....	105
Figure 5.4 P forms in the stirred reactor supernatant after 1 hr settling. ....	106
Figure 5.5 Total solids in effluent supernatant of manure settled.....	106
Figure 5.6 DMS pH and P-PO <sub>4</sub> concentration during 12 days of anaerobic .....	113
Figure 5.7 Manure 2 pH and P-PO <sub>4</sub> concentration during 12 days of anaerobic .....	114
Figure 5.8 Manure 3 pH and P-PO <sub>4</sub> concentration during 12 days.....	114
Figure 5.9 Manure 4 pH and P-PO <sub>4</sub> concentration during 12 days.....	115
Figure 5.10 The change in three commercial manures and DMS.....	116
Figure 5.11 Relationship between initial alkalinity/VS .....	119
Figure 6.1 Schematic diagram and photo of 130 L struvite reactor.....	123
Figure 6.2 Increase in pH and decrease in P-PO <sub>4</sub> concentration .....	128
Figure 6.3 Reactor settled solids showing struvite crystals of different size. ....	129
Figure 6.4 Analysis of collected solids by X ray diffraction .....	130
Figure 6.5 Dissolved nutrients removed from manure liquid during reactor .....	131
Figure 7.1 Biomass production for each P amendment. ....	143
Figure 7.2 P uptake response to P fertilizer amendments at different rates.....	144

Figure 7.3 P recovery efficiency for struvite and commercial fertilizer amendments...	145
Figure 8.1 Process diagram of the batch reactor processing liquid .....	151
Figure 8.2 Process diagram of the Crystaphos upflow reactor operating .....	152
Figure 11.1 Concentration of P-PO <sub>4</sub> in wash medium.....	169
Figure 11.2 Concentration of P-PO <sub>4</sub> in wash medium.....	170
Figure 11.3 Concentration of P-PO <sub>4</sub> in wash medium.....	170
Figure 11.4 Magnesium in wash medium (reactor effluent at pH 8). .....	171
Figure 11.5 Magnesium in wash medium (reactor effluent at pH 7).....	171
Figure 12.1 Daily sampling (in duplicate) of nutrients .....	173
Figure 12.2 Comparison of Mg in filtered samples .....	174
Figure 12.3 Comparison of Ca in filtered samples .....	174
Figure 12.4 Comparison of NH <sub>4</sub> in filtered samples .....	175
Figure 12.5 Comparison of total alkalinity as CaCO <sub>3</sub> .....	175
Figure 12.6 Comparison of VFA in filtered samples.....	176
Figure 12.7 Change in pH for each of the manures stored under anaerobic conditions.	176
Figure 13.1 Influent and effluent phosphorus concentrations.....	179

## 1 Introduction

Phosphorus availability in our environment poses an interesting dichotomy: on one hand it is a limited natural agricultural resource that needs to be preserved and on the other hand it is a pollutant from the municipal/agricultural sector that needs to be eliminated (Elser and Bennett 2011). Depending on the context, phosphorus (P) is one of the fundamental nutrients in the formation of life and from a global supply perspective, it is the most scarce of all non gaseous nutrients, thus is the “bottleneck”, or rate limiting element for life on earth (Asimov 1974). Because life has evolved from low background levels of P, the effect of increased P on simple life forms like algae is dramatic, and a small increase in P concentration can result in the eutrophication of entire water bodies (Schindler 1976a). This effect is from microbial recycling of P from wastes back into life formation, and by some estimations, a single P atom is reused 1500 times in an aquatic ecosystem before it is retired to the sediment (Schindler et al. 1976b). Global scarcity and increasing agricultural demand however, makes P a non-renewable resource and reduced P fertilizer availability threatens industrial agriculture just as our economy is threatened by reduced fossil fuel supply (Cordell et al. 2009; Viccari 2009).

In our present environment, phosphorus use has increased due to inexpensive mined phosphate rock fertilizer and economic pressure on farmers to maximize yields. In Manitoba, the problems of excess P are most apparent in the eutrophication of Lake Winnipeg. High P levels in the Red River watershed may be in part due to the recent expansion and geographical concentration of the hog industry in southern Manitoba (MB). Farms have increased in size and are now located close to each other, resulting in

the over application of P to adjacent fields. Hog manure spread on farm fields is generally applied according to crop needs for nitrogen, however, at this loading rate, P is often in excess of the annual plant usage (Bowers and Westerman 2005; Shepherd et al. 2009) and results in P build-up in the soil. Excess P can be lost to rivers, lakes and oceans where it increases background P, seriously disturbing the ecological nutrient balance and causing eutrophication, producing toxic blue green algae, fish kills and lower overall water quality.

In order to ensure a viable agriculture industry into the future, we must begin to recycle phosphorus from waste streams back into the supply stream. Recovery of P by precipitation reactors to form struvite is a way to accomplish P reclamation for reuse (Jaffer et al. 2002; Durrant et al. 1999; de-Bashan and Bashan 2004). In Manitoba, hog manure is potentially a good waste stream to reclaim P. Animal wastes are diluted 10-20 fold with wash water and pumped into earth-bermed lagoons, where heavier solids settle, leaving a surface liquid portion holding the majority of the soluble P at concentrations between 40 and 250 mg/L. Soluble P is the P form most likely to be washed out of the soil and into waterways and is the target for struvite precipitation. Struvite, or magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ ), has good qualities as a fertilizer because both nitrogen and phosphate are present, and due to low solubility, can be applied at a heavier rate in a single application, releasing nutrients gradually to crops throughout the growing season (Bridger et al. 1962). Struvite can be precipitated out of wastewater when the three components are present in concentrations greater than ~1 mM (30 mg P- $\text{PO}_4$  /L, 24 mg Mg/L, 14 mg  $\text{NH}_4$ -N/L) by raising pH. However, to solve the problem of over application of P to land, the levels of TP contained in the manure solids

need to be reduced substantially. How to accomplish this aim, or if it is possible to perform this task at a typical MB hog farm is not known.

To remove surplus P from manure as struvite, it is necessary to first understand the formation requirements of struvite and the chemical and physical characteristics of manure, and then to determine at which stage of a typical hog operation struvite precipitation should be considered. Struvite precipitates from saturated solutions of  $\text{PO}_4^{-3}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{+2}$  by increasing pH, which can happen naturally under normal storage conditions. Hog operations can have up to three storage lagoons and the forms and concentration of P in each lagoon is different and changes over time.

Additionally, to reclaim more than half of manure total P (TP) through struvite precipitation requires conversion of TP to soluble P, an approach not addressed in the scientific literature except for the conversion of TP to soluble P accomplished by anaerobic digestion (Harris et al. 2008). Other methods of conversion such as acidification of manure by natural fermentation may lead to manure management practices aimed specifically at P reclamation.

## **1.1 A systems approach to P reclamation**

Reclaiming P from hog manure before its application to land requires an approach to manure management in which the fate and forms of P are considered. This research project looks at several process scenarios (Fig. 1.1) on hog farms and this section explains how the research projects fit into each scenario. The research investigates key aspects of each scenario, leading to a manure management system in which surplus P can re-enter the supply stream at reasonable cost and minor changes to typical hog operations.

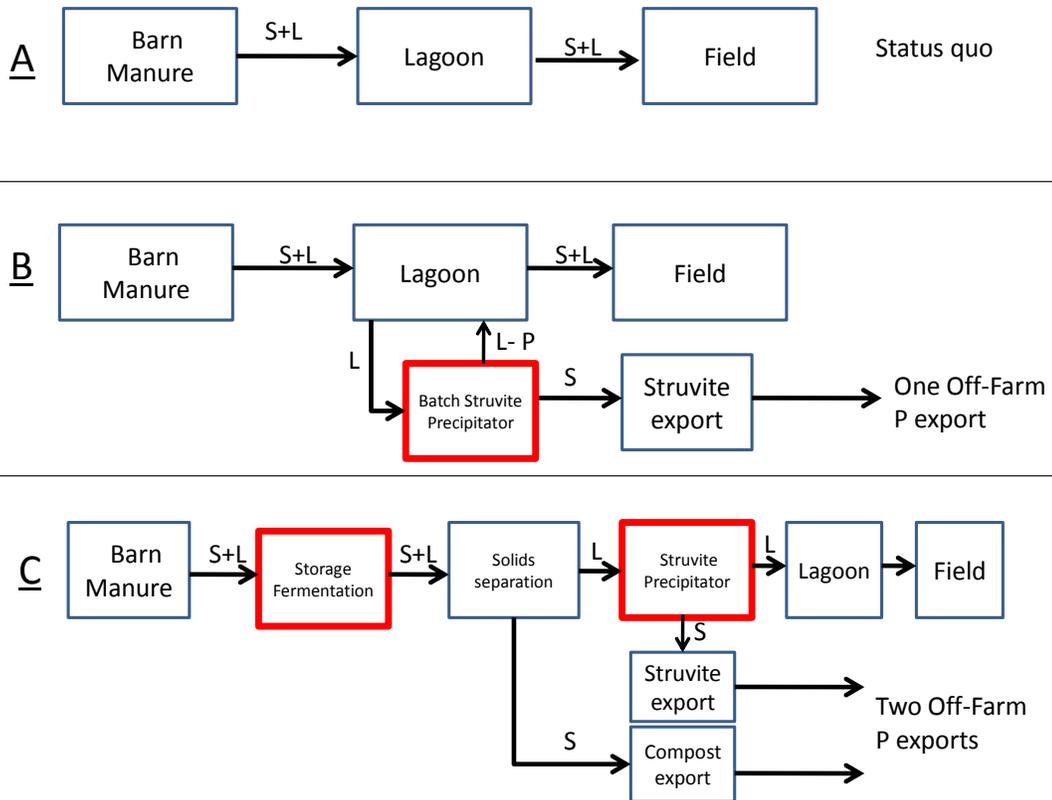


Figure 1.1 Three scenarios of hog manure management. Solids (S) and liquids (L) are separated in scenario C.

Understanding struvite formation and current manure management practices (Fig 1.1 A) help to identify advantageous manure pre-treatment goals and the placement of a pilot batch reactor to produce an exportable high P product (Fig. 1.1 B). Scenario B also allows investigation into the process of elutriation of reactor effluent back through manure solids to remove additional soluble P. Maximizing P removal by struvite precipitation depends on manure slurry soluble P concentration. Storing manure anaerobically can increase these P levels significantly via acid fermentation. Variations in manure chemical composition, length of fermentation and mixing requirements are investigated for different manure types to provide an understanding of P release.

Ultimately, they form a basis of optimum manure storage conditions for P recovery by struvite precipitation (Fig. 1.1 C).

Manure solids contain the majority of total P whereas manure liquid contains most of the total nitrogen (N). Manure from a typical hog lagoon contains TP concentration in excess of crop demand when applied at correct N rates. Removal of excess P by separation of manure solids for export off the farm is enabled by several technologies such as centrifugation or filter pressing. The separated liquid stream from these operations contains ample ammonium, magnesium and P-PO<sub>4</sub> for struvite precipitation. Using this liquid in a continuous feed up-flow reactor enables production of struvite and further TP removal from manure (Fig. 1.1 C). Aspects of the thesis research that is encompassed by this particular scenario are the character of the reactor influent and struvite precipitation requirements, pre-treatment of the manure by anaerobic storage to increase P-PO<sub>4</sub> concentration, and novel reactor design with no chemical addition. In this scheme, P is exported from the farm, both as separated manure solids and as struvite.

Struvite produced from hog manure must be comparable to commercial P fertilizer for this project to have the desired impact on manure management. This research project used manure struvite from the batch reactor (Fig. 1.1 B) to grow canola in a typical growth trial. Manure derived struvite is compared with pure struvite as a P source to evaluate any agronomic differences in struvite purity. In addition, the struvites are compared with mono-ammonium phosphate fertilizer for an indication of its agronomic and economic value.

## 1.2 Research objectives

To address specific aspects of the broad area of P recovery from hog manure, this research follows a number of investigative paths. These studies investigate P characteristics in manure, determine the forms and fate of P over time, design, build and operate struvite reactors, determine the agronomic value of reclaimed struvite and perform economic evaluation of installing and operating these struvite reactors. The research sets out the following objectives:

1. To investigate current Manitoba hog manure practices and the characterization of manure qualities most conducive to P reclamation within the context of typical farm infrastructure.
2. To understanding struvite precipitation requirements with laboratory chemicals and with the chemically complex manure supernatants.
3. To investigate the varied parameters affecting anaerobic fermentation of manure as a means of increasing soluble P concentrations in manure.
4. To determine the viability of elutriation as a means of increasing P recovery from manure solids.
5. To design, operate, and evaluate a pilot scale batch struvite reactor using manure liquid directly from a commercial hog lagoon without pre treatment.
6. To install, operate, and evaluate a novel up-flow continuous-feed pilot struvite reactor operating without chemical additions at a commercial hog farm.

7. To determine through growth trials of canola the agronomic difference between reclaimed manure struvite with pure struvite and commercial P fertilizer.

This thesis project investigates aspects of what is required to successfully reclaim P from manure in a feasible way, that is cost effective and without major changes to the current methods of raising pigs.

## **2 Literature Review**

### **2.1 Introduction**

This literature review identifies the scientific literature needed to solve the problems in developing a viable process of struvite recovery from hog manure. The review defines chemical parameters of struvite formation and the state of current knowledge in struvite precipitation. Methods of recovery developed over the last 20 years are evaluated as to their applicability to struvite precipitation from hog lagoons in terms of ease of operation and net yield. Methods available for nutrient dissolution from manure solids and changes in manure composition over time are investigated. Finally, effectiveness of struvite as a fertilizer is reviewed.

### **2.2 Struvite Formation**

#### **2.2.1 Background**

Struvite is a compound of magnesium, ammonium and phosphate that is found in many places in the human and natural environment. Struvite precipitates out of an aqueous solution forming a hydrated compound,  $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$  with low solubility in basic conditions. Due to the biological origin of ammonium, struvite formation in nature is linked to biological activity, usually waste accumulation, hence it is found in bat guano, livestock manure piles, soil, as well as within human bodies, where it forms kidney and urinary tract stones. It is a potentially valuable crop fertilizer due to the

presence of two macronutrients:  $\text{NH}_4$  and  $\text{PO}_4$ . It has lower solubility than conventional fertilizers, which can be an advantage when slow release of nutrients is desired.

Struvite can precipitate at low concentrations (1 mM of the constituents Mg,  $\text{NH}_4$  and  $\text{PO}_4$ ), making it a nuisance precipitate in municipal wastewater treatment plants (MWWTP). This can be an acute problem when digester centrate is returned to the wastewater headworks, sometimes clogging pipes and valves. This is especially true in biological nutrient removal (BNR) processes that concentrate nutrients in the sludge. Digestion of the sludge releases cell-bound P and magnesium (Mg) into the supernatant and subsequent changes to aerobic conditions allows  $\text{CO}_2$  release, pH increase and struvite precipitation in pipes and equipment that carry the centrate. This wastewater sidestream is often targeted in commercial struvite systems (Munch and Barr 2001; Britton et al. 2005) and reclaiming P from this sludge dewatering liquor reduces TP within the entire wastewater system by 25% or more (Jaffer et al. 2002).

Scientific research to understand the causes of struvite formation in MWWTP has been used to find optimum conditions for intentional struvite recovery. Recent reviews have dealt with fundamental struvite chemistry (Doyle et al. 2000; Valsami-Jones 2001; Bhuiyan et al. 2007), recovery methods (de-Bashan and Bashan 2004), and manure wastewaters (Suzuki et al. 2007). In MWWTP, prediction of infrastructure struvite precipitation locations and physio-chemical requirements have led to the use of chemical equilibrium and reaction kinetics modelling software. These models rely on input nutrient concentration, temperature, pH and equilibrium values for precipitate compounds. Many

authors have modelled optimum struvite precipitation conditions with this same equilibrium software (Table 2.1).

Table 2.1 Equilibrium and precipitation software used to model struvite precipitation.

<b>Model software (version)</b>	<b>Tested medium</b>	<b>Reference</b>
Struvite (3.1)	Municipal centrate	Jaffer et al. 2002
MINTEQA2	Municipal centrate	Munch and Barr 2001
MINTEQA2	Swine lagoon liquor	Nelson et al. 2003
Mineql+	Dairy manure	Gungor and Karthikeyan 2005
Visual Minteq (2.23)	Swine lagoon liquor	Celen et al. 2007
CHARON	Swine and poultry	Bril and Salomons 1990
PHREEQC (2.11)	None	Wang et al. 2006
ORIGIN PRO (6.1)	Synthetic	Matynia et al. 2006
MINEQL+ (4.5)	Synthetic	Wang et al. 2005

The software enables fairly accurate predictions of mineral precipitations at specified temperatures, pH, and ion concentrations. Other aids, such as fuzzy logic algorithms have been used for the non-linear and time variant response of pH during precipitation (Pastor et al. 2008).

Modeled outcomes are usually verified with real or synthetic liquors at a bench scale to test predicted results. Modelling has helped to predict struvite yields under varying ion concentrations, pH conditions and temperatures. There is general agreement in the literature that modelling is a good tool but results need to be verified with real

wastewater because mathematical assumptions of steady state equilibrium and thorough mixing are not always met in waste streams.

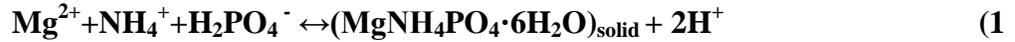
Some researchers have used struvite precipitation as a means of reducing or recovering ammonia levels in effluent (Maekawa et al. 1995, Kim et al. 2004, El Diwani et al. 2007). In most wastewaters, ammonium concentration is much in excess of P, so significant reduction requires addition of Mg and P, often resulting in higher effluent P than when P removal is the goal. This review will focus on methods of using struvite only for P removal and reclamation.

### **2.3 Factors Affecting Struvite Formation**

Precipitation of struvite from aqueous solutions is dependent on several factors, some of which are interdependent. Component ion concentrations ( $Mg^{2+}$ ,  $NH_4^+$ ,  $PO_4^{3-}$ ) and the presence of competing ions and pH level are all individually important, but must also be considered together. For instance 1:1:1 stoichiometric component concentrations produce different precipitate yield rates at different pH conditions. Calcium competes with Mg reducing net struvite yield and purity. Temperature and nucleation induction times also play a part in crystal size and growth rate. These parameters are introduced in this section.

### 2.3.1 Solubility Product and Kinetics

The solubility product determines the concentration needed for struvite to precipitate and the kinetics govern the speed of the precipitation reaction. The chemical reaction of struvite formation has been found in the literature as



but some equations in the literature use  $\text{HPO}_4^{2-}$  or  $\text{PO}_4^{3-}$ , indicating that there is some ambiguity about the form of P involved. Some authors found declining pH with struvite formation with synthetic mediums (Stratful et al. 2001), suggesting  $\text{H}^+$  is produced as a result of a protonated phosphate species in the reaction.

The precipitation of struvite is governed by its solubility product ( $K_{\text{sp}}$ ), as well as the kinetics of formation, pH, and ion activities (Doyle et al. 2000). For purposes of predictive calculations,  $K_{\text{sp}}$  is most often used. Solubility product is a measure of the moles of each constituent ion in 1 litre of pure water at equilibrium:

$$K_{\text{sp}} = k_1[\text{Mg}^{2+}] k_2[\text{NH}_4^+] k_3[\text{PO}_4^{3-}] \quad (2)$$

where brackets indicate concentration and  $k_1, k_2, k_3$  are the activities for each ion.

Measurement of ion activities is difficult in practice due to the competing equilibrium reactions. When only ion concentrations are measured, the conditional solubility product is found ( $K_{\text{co}}$ ), producing a value of higher solubility than  $K_{\text{sp}}$  and dependent on pH conditions.

$$K_{\text{co}} = [\text{Mg}^{2+}] [\text{NH}_4^+] [\text{PO}_4^{3-}] \quad (3)$$

Because the formation of struvite affects pH by releasing protons into solution (Equation 1), to fully consider struvite component species' concentration, other chemical species affected by pH change must be calculated. These additional species include  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{NH}_3^-$ ,  $\text{H}^+$ , as well as magnesium hydroxides and magnesium phosphates. As a solution pH changes, the relative abundance of P species change dramatically (Fig. 2.1). Similarly, ammonium is in equilibrium with ammonia at pH 9.3 and volatilization of ammonia to the atmosphere means steady state (equilibrium) is never reached in open tank conditions.

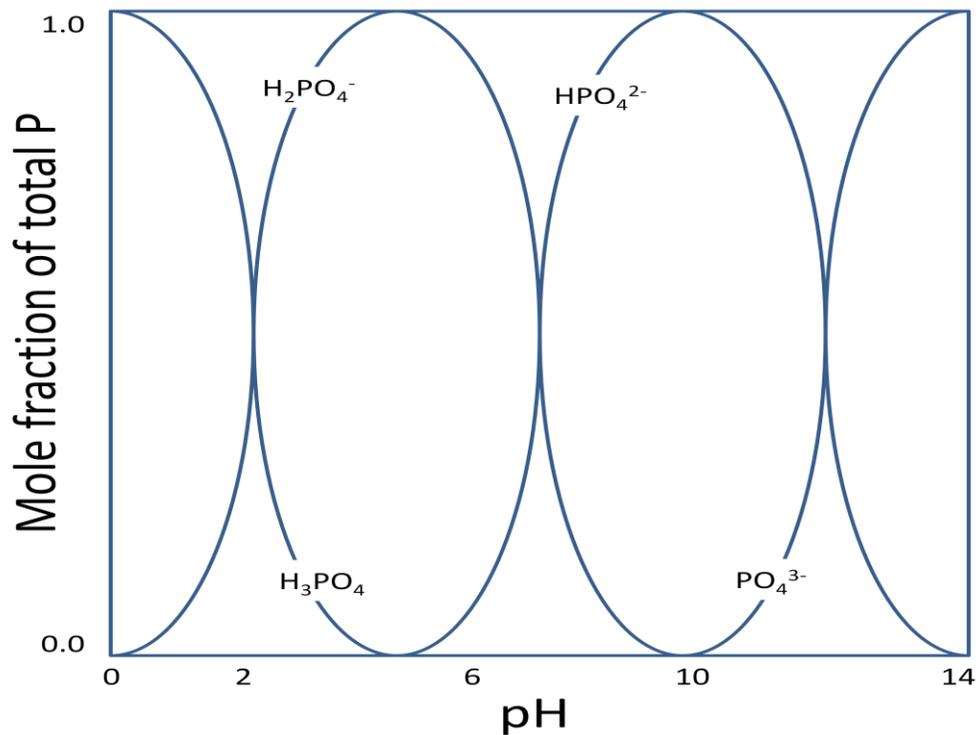


Figure 2.1 Equilibrium of phosphorus species at a range of pH values

At equilibrium, precipitation and dissolution are equivalent, so  $K_{sp}$  is a measure of maximum concentration. Struvite is a relatively insolvent compound with literature  $K_{sp}$

values indicating a wide range (Table 2.2) from  $3.89 \times 10^{-10}$  to  $4.37 \times 10^{-14}$  moles/L, but the most common figure used in engineering studies is  $2.51 \times 10^{-13}$ . For sparingly soluble compounds  $K_{sp}$  is often converted to  $pK_{sp}$  by taking the negative log of  $K_{sp}$ .

Table 2.2 Struvite solubility product values found in literature (compiled by Bhuiyan et al. 2007).

<b>pK<sub>sp</sub></b>	<b>K<sub>sp</sub> (mol/L)</b>	<b>Origin</b>
9.41	$3.89 \times 10^{-10}$	Wastewater
9.94	$1.15 \times 10^{-10}$	Aqueous solution
11.84	$1.14 \times 10^{-12}$	Aqueous solution
12.36	$4.36 \times 10^{-13}$	Simulation
12.6	$2.51 \times 10^{-13}$	Water
12.6	$2.51 \times 10^{-13}$	Simulation
12.76	$1.74 \times 10^{-13}$	Water
12.93	$1.17 \times 10^{-13}$	Aqueous solution
13.12	$7.58 \times 10^{-14}$	Water
13.15	$7.08 \times 10^{-14}$	Aqueous solution
13.27	$5.37 \times 10^{-14}$	Synthetic supernatant
13.36	$4.37 \times 10^{-14}$	Aqueous solution

The variance in  $K_{sp}$  values is likely due to differences in experimental parameters (e.g., temperature, synthetic or real wastewaters, ion activities etc). Bhuiyan (2007) reports that ionic strength is often ignored, electro neutrality equations are not used and values at experimental temperatures are not extrapolated for zero ionic strength. Recent

tests found that struvite was soluble in deionized water at a minimum of 169 mg/L at 25 °C and a maximum of 212 mg/L at 35 °C (Bhuiyan et al. 2007). This converts to a  $K_{sp}$  of  $3.3 - 6.5 \times 10^{-10}$  with dissolved P levels of 21 to 27 mg/L in pure water at neutral pH. Phosphorus levels in struvite reactor effluent can be similar, depending on pH. It is for this reason wastewaters with P concentrations below 30 mg/L are not targeted for struvite recovery.

In a complex ion matrix such as wastewater, thermodynamics and kinetics also affect precipitation. The thermodynamic state of the precipitate and is as important as the solubility product in predicting formation (Doyle et al. 2000). Kinetics describe the rate at which a reaction takes place and reflects the energy consumed by the reaction. Within thermodynamic constraints, the rate of struvite crystal formation depends on the kind of nucleation taking place. Different Mg sources affect the time of struvite reaction completion, ranging from a few minutes (Stratful et al. 2001) using  $MgCl_2$ , to 20 minutes and significantly longer with  $Mg(OH)_2$  and waste Mg such as bittern (Nelson et al. 2003). High pH or high component ion concentration completes the reaction faster.

Due to problems when using struvite  $K_{sp}$  calculations in non-equilibrium high nutrient and poorly mixed mediums like wastewater, some authors have come up with more accurate ways of predicting an influent's struvite potential (Britton et al. 2005). One system used a pre-test of the liquor's conditional solubility curve to give a super saturation ratio (SSR). Essentially, SSR measures the potential precipitate in a sample if it were dosed with Mg, the pH raised to a specific point and then allowed to equilibrate. Component ion concentrations (moles) are determined of initial and equilibrated liquor:

$$P_s = [Mg^{2+}]_{total}[NH_4^+]_{total}[PO_4^{3-}]_{total} \quad 4)$$

where the brackets indicate concentration in moles per litre. The same liquor is dosed with Mg at a specific pH and concentrations are measured again, establishing the concentration that remains. The super saturation ratio of these is an indication of the ion concentrations that are removable:

$$SSR = P_{sample} / P_{equilibrium} \quad 5)$$

Unlike a  $K_{sp}$  value, SSR is solution and pH specific. This calculation enables plotting pPs against pH to find a curve for the pre-test liquor at various pH levels. A polynomial curve is then generated with x being pH. Variable influent concentrations of  $PO_4^{3-}$ ,  $Mg^{2+}$  and  $NH_4^+$  can then be accounted for only adjusting pH and still reaching maximum struvite precipitation.

This method has been used for pilot scale fluidized bed reactors for MWWTP (Adnan et al. 2003; Britton et al. 2005; Mavinic et al. 2007). Recycled effluent serves to reduce SSR by diluting influent concentrations allowing slower crystal growth and thus larger aggregated pellets. Use of this pH adjustment method in conjunction with a fluidized bed can result in high P removal 90-95% (Britton et al. 2005). The operational pH range was below 8, significantly lower than in most precipitation studies, for savings on NaOH and producing a better struvite pellet (Adnan et al. 2003; Britton et al. 2005).

### 2.3.2 Nucleation and crystal growth

Nucleation is the evolution of aqueous ionic forms into a solid matrix and occurs when the component ions are present at a molar ratio of 1:1:1 at supersaturated

concentration (i.e., above equilibrium  $K_{sp}$ ). Ions in solution go through a process of desolvation, ion-pair formation and complex formation, leading to molecular aggregates that form either discrete crystals or grow existing crystals (Wu and Bishop 2004). In more dilute solutions or at lower pH, the process takes the less energetic pathway, participating in crystal growth or finding favourable sites on existing surfaces. Higher ion densities are needed to form new crystals spontaneously in a process called homogeneous nucleation (Fig. 2.2).

Solution pH is a key driver of nucleation because fewer protons (higher pH) drive Equation 1 to the right, thus at higher pH, lower molar concentrations of the constituents will precipitate. For example, at pH 7.5 a solution of 1 mM of  $PO_4^{3-}$ ,  $Mg^{2+}$  and  $NH_4^+$  will not precipitate as struvite, but at a pH of 9.5, most of the molar mass will precipitate. As the pH increases, two distinct zones of nucleation are encountered, first, the metastable zone, where crystals will grow on other crystals or particles (heterogeneous), and then at high pH, the unstable zone, where spontaneous nucleation takes place (Adnan et al. 2003). Similar observations can be made with high concentrations of the constituents (Stratful et al. 2001; Ali and Schneider 2008).

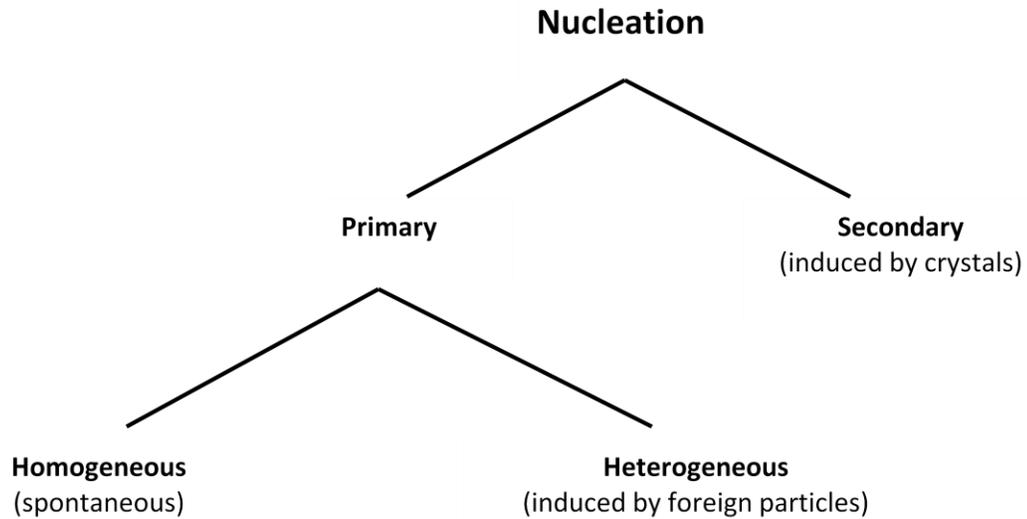


Figure 2.2 Nucleation pathways of struvite formation (Wu and Bishop 2004).

A good example of precipitation zones can be seen in solubility curves in relation to pH (Fig. 2.3) for anaerobically digested manure (Jordaan et al. 2010). For each Mg:P ratio curve, the area under the curve is unsaturated, while areas above the curve are supersaturated leading to instant nucleation and homogeneous nucleation. The curve itself falls within the metastable zone. Homogeneous nucleation produces very fine crystals (5-30  $\mu\text{m}$ ) that settle with difficulty and are often lost in effluent. Heterogeneous nucleation tends to increase existing crystal size. High dosing of  $\text{MgCl}_2$  extends the metastable zone and precipitates more  $\text{PO}_4$  out of solution (Nelson et al 2003). Equilibrium dynamics indicate there will always be residual constituent ions in the solution after precipitation (Fig. 2.4), with final concentration depending on ion activity and pH. Final P- $\text{PO}_4$  concentrations are not consistent in Fig. 2.4 because experimental pH varied, mediums were chemically different and Mg addition was inconsistent. Due to the particular

chemical nature of wastewaters and different experimental aims, the optimum pH for struvite formation will vary.

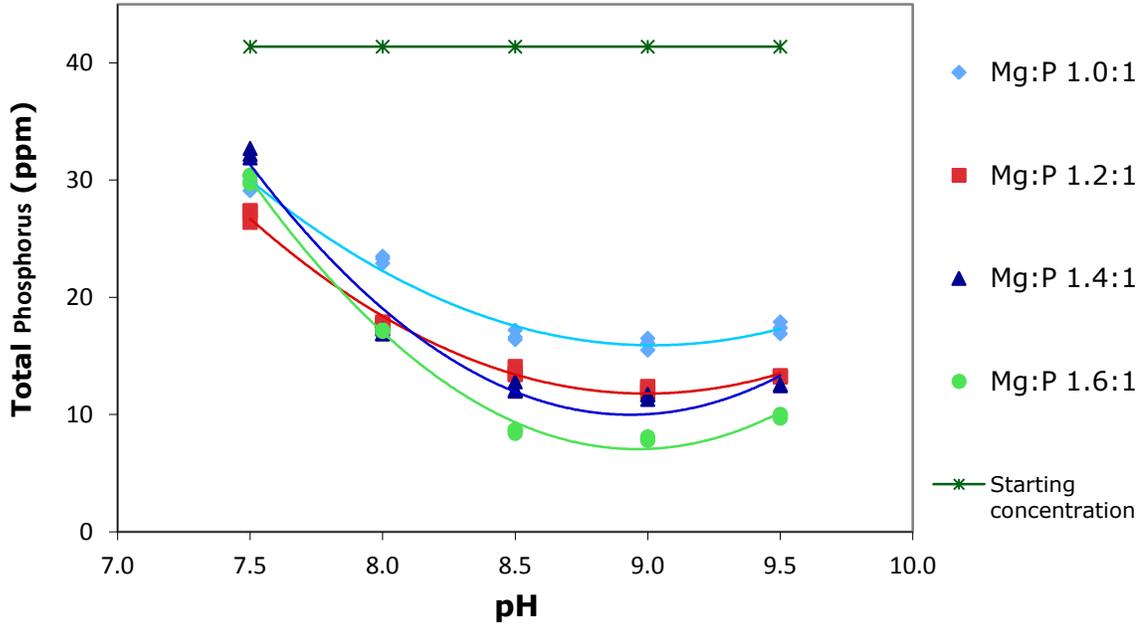


Figure 2.3 Anaerobically digested hog manure with different Mg:P ratios and pH values (Jordaan et al. 2010).

This direct relationship between struvite constituent concentration and pH is important in hog manure analysis because high concentrations of P-PO<sub>4</sub>, NH<sub>4</sub> and Mg can be found in manure liquor leading to struvite formation even at pH levels of 6 (Sommer and Husted 1995).

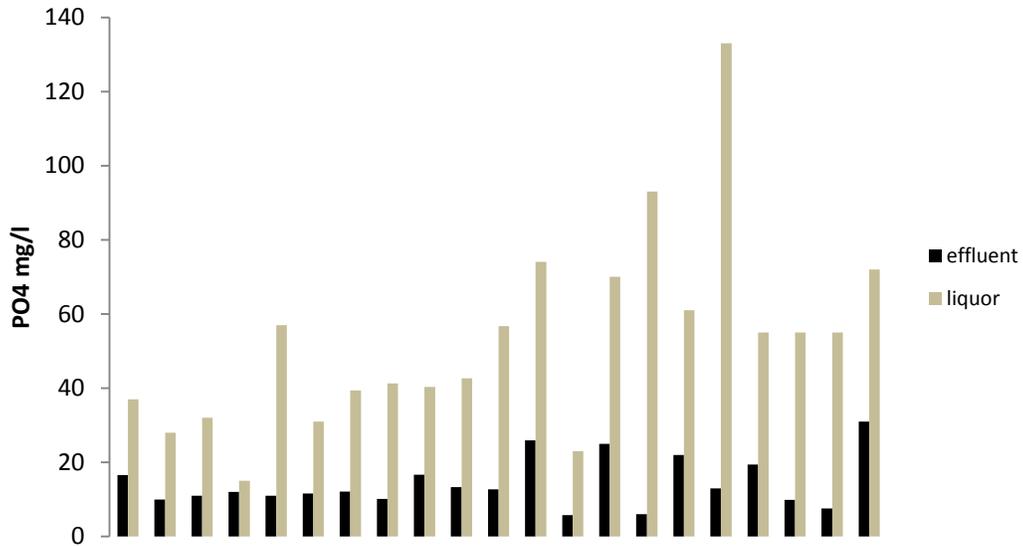


Figure 2.4 Initial liquor and effluent PO<sub>4</sub> concentrations before and after struvite precipitation. Compiled data from 21 literature sources using wastewater and manure slurries.

### 2.3.3 Concentration

Phosphate and Mg concentrations determine the maximum struvite mass that can be removed, whereas ammonium is usually in excess in wastewaters. As an example, wastewater with 100 mg P-PO<sub>4</sub> l<sup>-1</sup> (~3 mM) can have 500 to 2000 mg NH<sub>4</sub> l<sup>-1</sup> (35-130 mM) and Mg is often present in the 10-50 mg l<sup>-1</sup> range (0.5-2 mM). Mg must be added to at least match the molar concentration of PO<sub>4</sub>, but researchers commonly use Mg in excess to drive the reaction and safeguard against fluctuating P levels. Optimum ratios of Mg:P have been recorded at below 1 and as high as 3.46 (Table 2.3). Generally, a lower precipitation pH requires a higher Mg:P ratio to remove the same amount of P than if pH were adjusted to a higher level (Mavinic et al. 2007). Burns et al. (2003) tested swine

manure slurry at a ratio of 1.6 achieving 98% P removal. Nelson et al. (2003) and Jordaan et al. (2010) dosed swine lagoon liquid with MgCl<sub>2</sub> at ratios from 1.0 to 1.6 and achieved the lowest effluent P at 1.6. Several studies report that the quality of crystal changes at higher Mg:P ratios, becoming more brittle (Matynia et al. 2006), or struvite pellets with reduced strength (Adnan et al. 2003; Britton et al. 2005).

Table 2.3 Optimum Mg:P ratios with experimental pH levels and phosphate removal efficiencies.

Ref	Medium	Initial PO <sub>4</sub> conc (mg/L)	Optimum Mg:P ratio	P removed %	pH
Nelson et al. 2003	Swine manure	55	0.8	85	9.0
Jordaan et al. 2010	Digested swine manure centrate	42	1.6	81	9.0
Burns et al. 2003	Swine manure	590	1.6	98	8.5
Mavinic et al. 2007	WWTP Centrate	133	2.5-3.6	93-98	7.8-8.0
Jaffer et al. 2002	WWTP Centrate	95	3.46	97	9.0
Song et al. 2007	Synthetic	80	2	97	9.5-10.5
Celen et al. 2007	Synthetic	524	2	98	8.5
Quintana et al. 2004	Synthetic	55	2.5	96	8.5
Pastor et al. 2010	Synthetic	77	1.1	70.3	8.7

#### 2.3.4 pH

Most research on pH is concerned with finding an optimum level for P removal. Studies can be grouped into work with synthetic liquors, real liquors at a bench scale and pilot plants with large flows. Consequently, pH recommendations from each study reflect specific aims and physical conditions of the medium tested. Those working with synthetic substrates often find high optimum pH with P removal increasing as pH increases (e.g., pH increase from 8.2 to 9.5 in an upflow reactor increased P removal from 40 to 80%, Pastor et al. 2008). Studies with synthetic solutions have achieved 97% P removal (pH 9.5, Song et al. 2007) and lower effluent P concentration as pH increased (e.g., 30 mg/L

at pH 8; 15 mg/L pH 8.5; 10 mg/L pH 9 and 5 mg/L pH 9.5), the results verifying the nucleation curve in Fig. 3. Synthetic liquors are more stable and predictable than anaerobic digester supernatant due to dissolved CO<sub>2</sub> and the influence of microbial communities on supernatant chemistry.

Depending on the substrate being used, liquors can have very different responses to pH adjustment and significant P removal has been demonstrated with pH increase and no addition of Mg. Raising the pH of high P wastewater (524 to 234 mg/L) from 6.8 to 8.5 led to 55% P removal (Celen et al. 2007). Others (Battistoni et al. 2000) used only air stripping (no chemical pH adjustment or Mg addition) of anaerobic supernatants to raise pH from 7.6 to 8.6 and removed 80% of the soluble P. Battistoni et al. (2000) found pH change, P removal and precipitate composition in a fluidized bed with a 2-3 hr hydraulic retention time (HRT) mirrored natural aging of the same supernatants over 2-8 days. Air stripping has been shown to raise pH of centrate by 1 unit (Suzuki et al. 2007; Battistoni et al. 2000; Battistoni et al. 2002), half a unit at a bench scale (Shepherd et al. 2009) and 0.24 units at pilot scale (Shepherd et al. 2009). Air stripping will have little or no effect on pH when CO<sub>2</sub> is at equilibrium with the atmosphere, thus anaerobic manure sources will tend to show greater pH change at the same air flow rate than aerobic ones.

As mentioned in the nucleation section, high pH will cause instant nucleation of struvite sometimes causing scaling problems with reactors. Working on a bench scale fluidized bed reactor with synthetic wastewater, Adnan et al. (2003) developed a term of maximum pH working limit, pH<sub>lim</sub>, above which many fines are produced which clog ports and surfaces and do not form struvite aggregates. Reactor operation below this point

produced good aggregates minimal clogging, but also achieved lower P removal. These results verify the nucleation theory.

When pH is too high, both  $\text{NH}_4^+$  and Mg can be lost from solution, decreasing struvite yield.  $\text{NH}_4^+$  and  $\text{NH}_3$  are at equilibrium at pH 9.27, resulting in loss to the atmosphere of volatile  $\text{NH}_3$ . In systems open to the air or receiving aeration, large losses of  $\text{NH}_3$  occur as pH approaches 9.3. At pH 10.7 Mg is removed from solution to form  $\text{Mg}(\text{OH})_2$ , making Mg unavailable for struvite (Wang et al. 2005; Ali and Schneider 2008).

Optimum pH for struvite recovery depends to some degree on the chemical characteristics of the liquor and on the recovery method. P precipitation from solution is high at pH 9-10, but this is by homogeneous nucleation, resulting in fine crystals that can be lost with effluent in a flow-through system. This is well demonstrated in experiments on hog manure that used bench and pilot scale reactors that very effectively reduced soluble P by 90% but failed to lower total P, meaning the reactor precipitated P but as crystals too fine to settle (Shepherd et al. 2009). Lower pH appears to be better for building crystal size in a fluidized bed reactor. In such a reactor, Mavinic (2007) demonstrated precipitation can be controlled by either pH adjustment or Mg concentration. A pH of 7.2 in synthetic wastewater achieved >80% P removal when Mg:P ratio was increased to 3. Due to the production of  $\text{H}^+$  during precipitation (Equation 1), pH control is important in any struvite precipitation system.

### 2.3.5 Ion competition

In real wastewaters the presence of competing ions can affect optimum precipitation pH and produce other precipitates than struvite, reducing the purity and potential value of the precipitate. To illustrate, Nelson et al. (2003) compared two hog lagoons, dosing with different ratios of Mg:P at a pH between 7.75 and 9.75. The lagoons had quite different optimum struvite precipitation pH of 9.5 (Fig. 2.3) for the first and between 8.5 and 9 for the second. The authors concluded this was due to higher (2X) ion concentrations of  $\text{NH}_4^+$ ,  $\text{K}^-$ , and  $\text{CO}_3^{2-}$  in the second lagoon.  $\text{CO}_3^{2-}$  can also be associated with problems of struvite purity, because it precipitates with Mg above pH 9.5. Starting at pH 8, calcium (Ca) will form  $\text{CaCO}_3$  and precipitation rates increase with increasing pH (Le Corre et al. 2005; Jordaan et al. 2010). Interactions between  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ , and P have not been clearly discerned and research is often performed with synthetic liquor with an incomplete suite of the ions found in wastewater. For example, Song et al. (2007) found  $\text{CO}_3^{2-}$  at ratios of 0.5-2  $\text{CO}_3$ :Mg had very minor effect on P and Mg removal or struvite purity (2-8% less). Le Corre et al. (2005) however, used different ratios of Mg,  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  and found non-struvite compounds formed at ratios of 1:1:1 and greater (i.e. 1:2:2). Energy dispersive spectrometry indicated the precipitate was amorphous calcium phosphate or calcium carbonate but not struvite. There is evidence that  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  may interfere with nucleation of struvite and that once  $\text{CaPO}_4/\text{CaCO}_3$  precipitation begins, it advances quickly (Le Corre et al. 2005). Struvite nucleation induction times slowed from 2 min to >3 min when a 0:1 ratio of Ca:Mg was increased to 1:2. Even higher ratios of 1:1 and 2:1 produced higher turbidity and instant nucleation, precipitate analysis showed it was a mixture of  $\text{CaCO}_3$ ,  $\text{CaPO}_4$  and struvite. X-ray diffraction

analysis (XRD) showed increased amounts of amorphous calcium phosphate at higher ratios. The exact role of  $\text{CO}_3^{2-}$  on struvite purity was not determined, but precipitation with  $\text{Ca}^{2+}$  may act to interfere with struvite nucleation or crystal growth. Synthetic wastewater experiments need to be verified with tests on real wastewaters. Some calcium phosphate compounds are less soluble than struvite (Table 2.4) and do not contain  $\text{NH}_4^+$ , reducing the fertilizer value of recovered struvite.

Presence of high  $\text{Ca}^{2+}$  concentration in solution tends to produce a range of calcium phosphates and hydroxyapatites (Table 2.4). Calcium can out-compete Mg when the Ca:Mg ratio is above 1. Research on synthetic wastewaters kept P concentration steady (e.g., 86 mg/L, Song et al. 2007) and tests ion concentration of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$  and  $\text{Mg}^{2+}$  as the Ca:Mg ratio is increased. Song et al. (2007) found P removal was constant; Mg removal dropped and  $\text{Ca}^{2+}$  removal increased, indicating calcium phosphate formation. Wang et al. (2005) observed Ca in ratios of 0.5:2:1 (Ca:Mg:P) produced 85% pure struvite, 1:2:1 produced 61% pure struvite and 2:2:1 produced 38%. They also noted precipitation reactions at pH higher than 8.7 produces many other compounds than struvite. This result agreed with Song et al. (2007) who noted that above pH 9.5 calcium phosphates and  $\text{MgHCO}_3$  readily form, reducing Mg ion strength and struvite formation. Fewer struvite crystals were observed in XRD analysis as the Ca: Mg ratio increases above 1 (Le Corre et al. 2005).

Equilibrium modelling was used to predict  $\text{Ca}^{2+}$  interferences with struvite. (Pastor et al. 2008) used MINTEQA2 to model Ca:Mg ratios of 0.1, 0.6, 1.0, 1.8 and found % struvite purity in precipitate to be 93, 62, 39, and 12% respectively. It was

concluded that increasing Ca:Mg ratios produced mostly amorphous calcium phosphate and not struvite. Bench trials proved that P removal increased with  $\text{Ca}^{2+}$ . High Ca (172 mg/L) produced effluent with 5.3 mg/L  $\text{PO}_4\text{-P}$  and low  $\text{Ca}^{2+}$  (3.6 mg/L) yielded 23 mg/L effluent P. Analysis of the solids produced revealed struvite in the second case and none in the first.

These results are the same as observed in a full scale struvite reactor in Europe processing anaerobically digested potato wastes (Moerman et al. 2009). No struvite was produced when Ca:P ratio was high (2.36), but did form when P levels increased to make a ratio of 1.26. It was suspected that excess  $\text{Ca}^{2+}$  formed a calcium phosphate floc that was too fine to be retained by the reactor leading to very low TP removal. Municipal sludge dewatering liquor is usually low in divalent ions so high  $\text{Ca}^{2+}$  concentrations are not usually a problem in struvite production. Calcium concentrations in animal wastewater, however, are often high due to  $\text{Ca}^{2+}$  in animal feed and the dilution of manure with farm well water, which is often  $\text{Ca}^{2+}$  rich. In addition,  $\text{Ca}^{2+}$  may increase disproportionately with dilution.

Table 2.4 Solubility product of common calcium phosphate compounds (Valsami-Jones 2001).

Name	Formula	Molar Ratio Ca:P	pK <sub>sp</sub> Solubility Product (mol L <sup>-1</sup> )
Struvite	MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O		10.48
Brushite	CaHPO <sub>4</sub> ·2H <sub>2</sub> O	1.0	7.60
Monetite	CaHPO <sub>4</sub>	1.0	7.90
Octacalcium phosphate	Ca <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub> ·2.5 H <sub>2</sub> O	1.33	47.90
Tricalcium phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.5	29.92
Hydroxylapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	1.67	59.33
Amorphous Ca phosphate	Ca <sub>3</sub> (HPO <sub>4</sub> ) <sub>2</sub>	~1.5	Variable, more soluble than crystalline forms

Dilution of animal slurry reduced all ion concentrations proportionally except Ca<sup>2+</sup> and Mg<sup>2+</sup> (van der Stelt et al. 2005). These ion concentrations remained high in spite of dilution due to equilibration from calcium compounds and struvite contained in the slurry. This finding suggests Ca<sup>2+</sup> and Mg<sup>2+</sup> are supersaturated in most animal slurries in normal dilution ranges.

Few studies have addressed practical remediation for high Ca<sup>2+</sup> concentration. One study found storage of sludge dewatering liquor (pH adjusted to 9) removed 77% of the Ca<sup>2+</sup>, eliminating it as a competing ion (lowered to 6 mg Ca /L). Only 7% of the PO<sub>4</sub><sup>3-</sup> was removed with Ca<sup>2+</sup> (Jaffer et al. 2002). This observation is in direct contradiction with tests by Bastioni (2000) who found PO<sub>4</sub><sup>3-</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> were removed during natural aging of sludge dewatering liquor. In an effort to reduce calcium phosphate

formation in a cone struvite reactor accepting dairy manure, (Shen et al. 2011) acidified manure to pH 4.5 and then added EDTA and oxalate to bind  $\text{Ca}^{2+}$  ions. Total P removal was >90% but the forms of precipitate not did include struvite.

Competing ions, especially  $\text{Ca}^{2+}$ , present a serious challenge in the production of pure struvite from hog manure diluted with hard water common on the Canadian Prairies.

### **2.3.6 Turbulence**

Turbulence is thought to contribute to the formation of struvite crystals but whether this is from more favourable nucleation conditions or physical aggregation of already formed crystals has not been clearly determined. Struvite forms in municipal water treatment pipes and appears to be related to changes in pressure and release of  $\text{CO}_2$  (Valsami-Jones 2001). Bench scale synthetic struvite precipitation found fouling occurred in zones of high supersaturation in the vicinity of receptive metal surfaces and in areas of low flow rates but tests of different mixing speeds does not support faster nucleation theories. Total suspended crystals mass in mixed and unmixed reactors were equal but low velocity mixing had smaller crystal size than those formed at high velocity (Suzuki et al. 2002).

### **2.3.7 Temperature**

Solubility increases with higher solution temperature, with maximum solubility reported at 35° C (Bhuiyan et al. 2007). Increased precipitation at lower temperatures has been recorded but this has not been extensively tested because most bench work is carried out at room temperatures. In a pilot reactor, greater precipitation was recorded operating

at 15 C versus 25 C (Adnan et al. 2003) and researchers found 72% more aggregates were formed of a larger size at the lower temperature. Total P removed from the influent increased from 27.1% at 25 C to 37.8% at 15 C.

### **2.3.8 Wastewater/Lagoon water challenges**

Struvite precipitation from wastewater or animal manure slurries is much less predictable than from synthetic mediums. Real liquors are chemically complex, containing compounds buffering pH change, making targeted pH levels difficult to maintain. Struvite precipitation is driven by  $\text{PO}_4\text{-P}$  concentration, which can vary, so addition of alkali and Mg must be adjusted constantly. In addition, P is actively scavenged by microbes living in the medium, so changes in growth conditions may lead to changes in P levels (Battistoni et al. 2000). Changing conditions from aerobic to anaerobic will cause release of P from these organisms as well as potential dissolution of solid forms of inorganic P such as struvite and calcium phosphates. The variable chemical parameters of wastewater is important to note in bench scale experiments because stored liquor can change significantly over time (Jaffer et al. 2002).

### **2.3.9 Process Placement**

Placement of a struvite precipitation reactor within a wastewater or manure slurry operation should be based on maximum P and Mg concentration, but since analysis has only been undertaken for MWWTPs the guiding parameters must be transferred to hog farms. In MWWTP, a reactor most commonly treats liquid (centrate) from centrifuged anaerobic digester sludge because centrate is free from suspended solids, high in ammonium and P. Induced struvite precipitation at this stage reduces clogging of pipes

and significantly reduces P re-entering the wastewater headworks, lowering total P to be removed by the biological nutrient reactor (BNR). Jaffer et al. (2002) estimate elimination of the internal P recycle would reduce 26% of total P load in a typical BNR plant.

Optimal reactor placement within a manure system should be based on the same criteria of high P-PO<sub>4</sub> concentration, but hog operations differ from one another and TP and P-PO<sub>4</sub> levels depend on the manure management system used. Under a hog pen, long-term holding tanks may be anaerobic, and thus would promote higher P-PO<sub>4</sub> levels as would covered primary lagoons. In the open lagoon storage systems common to MB there is a likely evolution of P from soluble to insoluble forms, but a systematic analysis of the highest P-PO<sub>4</sub> areas or conditions is lacking in the literature. P-PO<sub>4</sub> levels of 1000 mg/L have been reported from in-barn holding pits and concrete storage tanks (Burns et al. 2001; Moody et al. 2009) as compared with levels of 50-200 mg/L found in many uncovered primary lagoons (Wang et al. 2006).

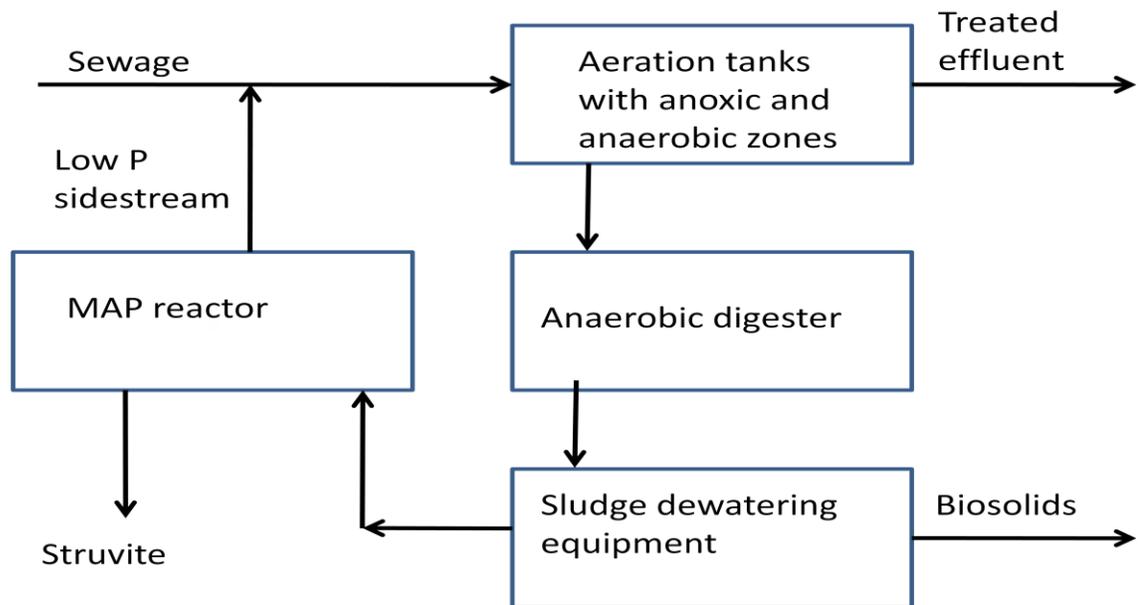


Figure 2.5 Struvite (MAP) reactor placement at an enhanced biological phosphorus removal facility (Jaffer et al. 2002).

Extensive holding time in an open lagoon likely lowers P-PO<sub>4</sub> concentration in a similar way to the processes observed by Battistoni et al. (2000) with municipal wastewater. Bacterial scavenging and mineral precipitation were thought to account for the large percentage of the soluble P removed from centrate during “natural aging” time of 2-8 days (Battistoni et al. 2000). P-PO<sub>4</sub> spiked digester liquors (initial dosed concentrations of 10-160 mg/L P-PO<sub>4</sub>) were noted to have a final P-PO<sub>4</sub> concentration of 7-20 mg/L in 4 days. A concurrent rise in pH from 7.6 to 8.3 was also observed and Mg<sup>2+</sup> and Ca<sup>2+</sup> concentrations indicated struvite and hydroxyapatite formed and settled out of the liquid. The liquors were high in Ca<sup>2+</sup> (184 to 456 mg/L). Similar processes of mineral precipitation likely occur in hog lagoons where the slurry is saturated with Ca<sup>2+</sup>, Mg<sup>2+</sup>, and PO<sub>4</sub>. Bril and Salomon (1990) studied swine and poultry manure examining mineral

equilibriums and concluded that volatile fatty acids (VFA) complexed  $Mg^{2+}$  and  $Ca^{2+}$ , holding them out of free association and interaction with  $HPO_4^{-2}$ . It may be that as fatty acids are degraded over time, the cations are released and precipitates are formed, lowering nutrient concentrations. One study was found tracking changes in manure  $NH_4^+$  and P- $PO_4$  over 34 days of manure from 3 hog operations. Researchers found no change in  $NH_4^+$  and two manure sources showed increase in P- $PO_4$  and the third showed a decrease (Christensen et al. 2009) but no conclusions were drawn by the authors as to the reasons for this. Others have noted significant changes in manure nutrients between initial and subsequent tests (Shepherd et al. 2009). Optimum placement of a struvite reactor within a manure management system needs to acknowledge the evolution of P between solid and soluble states as governed by time and natural processes. Understanding these process would enable manipulation of them for increased P removal.

## **2.4 Methods of Precipitation**

Successful reclamation of P requires efficient precipitation of struvite crystals in a form that can be utilized. Applied research in this area has led to several innovations and techniques, the most common of which are listed in this section.

Under normal conditions the nutrient concentration of wastewater and hog lagoon liquor is adequate in terms of  $NH_4^+$  (20-100 mM) and P- $PO_4$  (1-4 mM), but is often Mg limited (0.5-3 mM). Simple dosing with Mg and NaOH creates fine crystals in the 15 to 40  $\mu m$  size range. The viscosity of the wastewater inhibits good settling of precipitate, making recovery of the product difficult. Faster settling requires either larger particle size, less distance to settle, or reduced liquor viscosity. Most research has focused on

increasing the particle size, either by avoiding spontaneous nucleation by supplying a crystal seed; maintaining the reaction within the metastable zone by recycling of effluent; or by aggregating the crystals on a steel mesh.

#### **2.4.1 Seeding**

Seeding a struvite reactor is the addition of an aggregate to promote crystal growth. It has been found to speed up the rate of crystal growth due to the lower energy required compared with nucleation of new crystals. Homogeneous nucleation occurs at higher P concentrations or high pH, producing very fine crystals, prone to washing out with reactor effluent. Longer contact time at lower concentrations with a seed starter tends to produce larger crystals. Seeds also give a designated surface, enabling larger crystals to form and keep scale from forming on reactor surfaces. Common seed substrates are silica sand and large struvite crystals, although research has been conducted on a wide range of possible seed types including phosphate rock, bone char, magnesia clinker, zirconium hydroxide (Kaneko and Nakajima 1988) and magnesium oxide (Harris et al. 2008). To illustrate the value of seeding, Burns et al. (2003) added Mg to raw swine liquor with treatments of added struvite seeds, sand and no seeds. No seeds produced crystals (16-30  $\mu\text{m}$ ), sand produced sets of larger crystals (16-40 and 47-78  $\mu\text{m}$ ) as did struvite (16-47 and 63-110  $\mu\text{m}$ ). Allowing for the size of the seeds themselves, the authors concluded that seeds increased crystal size by 2-3 fold. Wide experimentation of seed types is seen in bench trials but pilot scale operations use almost exclusively struvite (Munch and Barr 2001; Britton et al. 2005; Bowers and Westerman 2005), or sand (Battistoni et al. 2000).

### **2.4.2 Mixing tank**

Simple tank mixing is common in many bench-scale experiments where wastewater is mixed and dosed with Mg and NaOH. This batch method requires settling time and decanting, making it impractical for larger scale continuous operations. Jaffer et al. (2002) used a bench scale unit flow-through reactor (3.6 liter tank, flow rate 20ml/min HRT 3 hr, 220 ml/min aeration), achieving a 95% P removal rate at pH 9.0. On a larger scale (420 L/hr influent, with air flow 7 L/min), Munch and Barr (2001) used centrate dosed with  $\text{Mg}(\text{OH})_2$  and produced a sludge (16% solids) that settled to the bottom of the tank. This reactor successfully removed P (influent ~ 60 mg/L, effluent ~ 5 mg/L), the sludge was >90% struvite by weight and struvite crystals of 110  $\mu\text{m}$  median size. Aeration of a funnel shaped tank has been employed to increase the pH without alkali addition. Adequate air flow rate can also be used to keep struvite crystals in suspension. Process adjustments such as crystal suspension with aeration and flow-through design bring tank mixing much closer to a fluidized bed model.

### **2.4.3 Fluidized Bed**

A fluidized bed reactor is a common pilot scale reactor that uses influent upflow to keep crystals in suspension and within the reaction zone (Britton et al. 2005). Mg,  $\text{OH}^-$  and sometimes air are added at the reactor base along with influent feed to create a reaction zone (Britton et al. 2005, Suzuki et al. 2007). Recirculation of the tank effluent back into the system allows more contact time with the forming crystal aggregates and moderates the effect of dosing, keeping instant nucleation to a minimum and maximizing slow crystal growth. The Ostara design implements these aspects in a series of concentric

pipes of increasing diameter with height (Manivic et al. 2007). A steady input rate is slowed progressively as influent rises in the reactor, allowing fine particles to settle back down into the reaction zone and grow in size. As struvite particles grow they are harvested and dried. Using this design on MWW, Adnan et al. (2003) reported P reduction from 45 to 28 mg/L (at pH 8.2) and further reduction to 13.7 mg/L at higher pH (8.8). A larger reactor (19 L) with constant pH monitoring and more frequent P sampling have allowed a lower operating pH with high P removal and struvite recovery. This reactor was fed centrate for 3 months and produced 11.62 kg of struvite (7.82 kg harvested plus 3.80 kg left in reactor).

The theoretical yield over that time was 13.54 kg for a 86% recovery of struvite at a pH of 8.5. A second reactor ran at a pH of 7.6-8.0 with >50% recovery. Crystals grew steadily throughout the experiment by 0.016 mm/d and longer retention times producing stronger denser pellets of increasing size (mean size of 0.7 mm at the beginning and 1.3 mm by the end). Struvite produced in the Ostara reactor has been verified as pathogen free, making handling and marketing easier. This is because upflow movement tends to take bacteria to the surface out of the reaction zone and dried struvite acts as a desiccant, effectively killing any remaining bacteria. To date, no tests of the Ostara reactor have been conducted on animal manure slurries.

Bowers and Westerman (2005) treated swine lagoon supernatant with a cone shaped reactor with only 1.5 minute HRT, raised the pH only 0.5 units and were able to achieve a 60% TP reduction in their reactor. This was accomplished with a much simpler

system than the Ostara reactor, using a deep fluidized bed of struvite (Bowers and Westerman 2005) and no effluent recirculation.

#### **2.4.4 Metal Mesh Surface Crystallization**

Metal mesh crystallization was developed in Japan (Suzuki et al. 2002) with additional research recently taking place in England (Le Corre et al. 2007b). The original rationale was to reduce soluble P of hog manure at the farm treatment facility headworks to eliminate problems of scale and clogging of downstream pipes. If P-PO<sub>4</sub> concentration can be lowered to 50 mg/L, scale problems are much reduced (Suzuki et al. 2006). To accomplish this, a manure holding tank was aerated (12-16 m<sup>3</sup>/hr with hydraulic flow rate of 4-5.3 m<sup>3</sup>/d) and oil added to reduce foaming. A stainless steel screen was suspended in the aeration zone, providing a surface for struvite precipitation and agglomeration. This action alone reduced PO<sub>4</sub> from 72 to 34 mg/L by raising the pH from 7 to 8.5. Further reduction to 19 mg/L was achieved when bittern (a waste produced from desalination plants, high in Mg) was added (30% MgCl<sub>2</sub>, at rate of 4.1 L/d). Considering the simplicity of this apparatus, it achieved good TP reduction (67%) but the majority of struvite was retained in the bottom sludge (73%), and would require further processing to produce a useable fertilizer. No mention was made to the composition of the sludge or what processes might be required to stabilize it.

At a bench scale, Le Corre et al. (2007b) used a stainless steel mesh as substitute seed material with synthetic wastewater. From earlier studies (Le Corre et al. 2007a), it was determined that struvite adhesion to metal was superior to other seed materials. Stainless steel wire mesh was placed at the top of a fluidized bed with enough aeration to

keep particles in suspension. Mesh removed 96% of particles from suspension in 2 hrs of reaction. The screen collected struvite at a rate of  $7.6 \text{ g m}^{-2} \text{ h}^{-1}$ . The authors believed the mesh provided a surface for crystals already in suspension to adhere to.

## **2.4.5 Other P removal methods**

### ***2.4.5.1 Sludge Crystallization***

Reduction of TP from swine slurry has been accomplished with the addition of polymers producing low P concentration in dewatered supernatant and a P fortified sludge (Szogi et al. 2006). Unfortunately, this technique does not yield a product with any greater value than dewatered unstabilized biosolids.

### ***2.4.5.2 Flocculants to increase struvite crystal size***

Cationic polymers and flocculants ( $\text{FeCl}_3$ ,  $\text{CaCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ) had the effect of increased struvite crystal size (500-1000  $\mu\text{m}$ ) and removed fines from effluent (Le Corre et al. 2007a). The precipitate produced is a matrix of P and the flocculant (or polymer complex) but no research has been found on plant availability or biodegradability of the precipitate.

### ***2.4.5.3 Electro chemical precipitation***

Passing a mild charge through a water stream causes reduction of water at the cathode and elevated pH (Moussa et al. 2006). Tests found localized pH of 10 was attained in the absence of carbonate and 9 when carbonate was dissolved in the wastewater. A typical wastewater solution will precipitate struvite onto the cathode with no addition of alkali. This technique has been used for water softening without the

addition of salts and may have application for struvite in specific conditions. Drawbacks in the technique is the difficulty in reclaiming struvite scale from the cathode surface.

## 2.5 Fine Tuning Precipitation

### 2.5.1 Recovery Rates

Struvite recovery yield from a liquor can be different than  $\text{PO}_4^{3-}$  removal rates because nucleated fine crystals may be lost in reactor effluent. Depending on the type of system, improved recovery can be achieved from increased settling times (for mixed tanks), effluent settling tanks, seeding, lowering the saturation ratio, or lowering reaction temperature. Many of these improvements involve slowing the system performance in some manner, so an oversized reactor will allow for system adjustments to achieve higher recovery rates. Examples of recovery rates from reactors operating for extended periods are scarce in the literature. Mavinic (2007) reported that recovery efficiency over 3 months was 86 and 82% of theoretical values for two reactors at two sites (Table 2.5). Actual recovery was 93.8 and 89.1% when equipment downtime, surface deposits, losses during drying and handling are included.

Table 2.5 Phosphate removal achieved under different pH conditions in each reactor. Data from Mavinic (2007).

	Synthetic supernatant		Annacis Supernatant		Lulu Supernatant	
	Reactor A	Reactor B	Reactor A	Reactor B	Reactor A	Reactor B
<b>pH range</b>	7.1-7.4	7.4-7.6	7.8-8.0	8.2-8.3	7.7-7.8	7.6-8.4
<b>Phosphate removal</b>	68-96	74-93	93-98	88-97	90-96	88-96

The quality of recovered struvite is also important for assessing system efficiency and marketability of final product. Analysis of collected precipitate from both pilot and bench scale experiments show a wide range of constituent components (Table 2.6). Variation from pure struvite indicates impurities.

Table 2.6 Quantitative and X-ray diffraction analysis of reclaimed precipitate from various struvite bench scale and pilot plant operations.

Author	Mg (g/kg)	NH <sub>4</sub> -N g/kg	PO <sub>4</sub> -P g/kg	Ca	CO <sub>3</sub> <sup>2-</sup>	XRD analysis
Quintana et al. 2004	99	57	126	0	-	Pure struvite
Burns et al. 2003	34	18	431	-	-	Struvite, brushite
Munch & Barr 2001	91	51	124	-	-	Struvite, quartz
Britton et al. 2005	99	56	128	-	-	Struvite
Mavinic et al. 2006	97	49	115	12	38	-
Suzuki et al. 2006	97	74	366	0.2	-	-
Quintana et al. 2004	148	33	98	25	-	-

### 2.5.2 pH Adjustment

Raising pH of wastewater solutions is the key control component in struvite precipitation. Upward pH adjustment is achieved through either addition of alkali or air stripping of dissolved CO<sub>2</sub>, but the use of NaOH is the most common in the literature. Sodium hydroxide is preferred over Mg(OH)<sub>2</sub> because of faster disassociation and thus shortened reaction time (Munch and Barr 2001; Wu and Bishop 2004). Mg(OH)<sub>2</sub> addition

satisfies both Mg addition and  $H^+$  suppression and is therefore a cheaper amendment but its use limits independent control over Mg and pH. Several data sets show lower P removal with  $Mg(OH)_2$  when compared with NaOH (e.g., final endpoint of residual  $PO_4$  was 10 mg/L vs. 4 mg/L for  $MgCl_2$ , Wu and Bishop 2004).

Some authors have increased P- $PO_4$  concentration of influent by lowering pH with acid. Acidification of MWWTP anaerobic centrate from 7.7 to 6.2 pH increased  $PO_4$  by 37% from 68 to 93 mg/L (Wu and Bishop 2004). After dosing for struvite precipitation, solution  $PO_4$  concentration was 10 mg/L after 40 min. vs 80 min for non-acidified centrate indicating the rate of precipitation was improved with acidified liquor. After 90 minutes of mixing however, both samples had concentration of 5 mg/L. This suggests acidified centrate forms  $H_2PO_4^-$  and that this species has faster kinetics in struvite formation (Equation 1).

### **2.5.3 Magnesium Addition**

Most experiments use  $MgCl_2$  for Mg addition although researchers have used alternative forms such as  $Mg(OH)_2$  and waste Mg such as MgO or bittern (a by-product from the desalinization process). Pure MgO and a waste by-product from MgO production were used to precipitate struvite at different Mg:P ratios with a mixing time of 240 minutes (Quintana et al. 2004). Increased ratios increased P removal significantly with the waste MgO but total removal rates were about one half that of pure MgO. The waste product contained several compounds that may interfere with struvite formation including Fe, Al, Ca and  $CO_3$ .

Several studies used bittern to make struvite, for example, El Diwani et al. (2007) added it to synthetic and industrial wastewater at various pH levels. He found that pH 9.6 in synthetic medium produced precipitate with least Ca, and the most Mg and NH<sub>4</sub>. Chromatogram XRD analysis however, indicated formation of additional compounds than struvite when using bittern (Zeng and Li 2006).

## **2.6 Pilot Scale Reactors and Hog Manure**

Processing hog manure through a struvite reactor offers several challenges in chemistry, process placement and reactor design. Six researchers have worked with pilot scale systems using hog manure and in one case, digested food processing supernatant (Table 2.7). The reactors were continuous flow systems or batch reactors, or both (Song et al. 2011), but only Bowers and Westerman (2005) has a fluidized bed seeded with struvite. Feedstock total solids (TS) ranged from 0.5 to 2.2 % in some cases from anaerobically digested sources. Laridi et al. (2005) used manure that had been flocculated with FeCl<sub>3</sub> and then passed through a peat trickle filter that halved total suspended solids (TSS) and produced struvite of greater purity. For some reactors, pH adjustment was solely by air sparging (Suzuki et al. 2007; Shepherd et al. 2009; Song et al 2011), and others augmented this with alkali (Laridi et al. 2005; Moerman et al. 2009).

Table 2.7 Pilot scale struvite reactors using hog manure and potato wastes. Initial and final adjusted pH is noted as pH<sub>i</sub> and pH<sub>f</sub>. Units are in mg/L unless otherwise noted.

Source	Reactor Volume (L)	Liquor	% TS	TP	P-PO <sub>4</sub>	Mg	N-NH <sub>4</sub>	Ca	pH <sub>i</sub> , pH <sub>f</sub>	Removal (%) TP PO <sub>4</sub>	
<b>Bowers and Westerman (2005)</b>											
	25	Hog	0.5	88	41	62	184 <sup>[a]</sup>	NA	7.7, 8.2	59-70	61-82
<b>Shepherd et al. (2009)</b>											
	3785	Hog <sup>[b]</sup>	2.2	800	22	NA	3200	NA	7.83, 7.93	9-14	14-91
	3785	Hog <sup>[c]</sup>	2.1	420	130	NA	NA	NA	7.04, 7.3	18	92
<b>Laridi et al. (2005)</b>											
	15	Hog <sup>[d]</sup>	1.1	NA	159	362	2282	260	6.3, 8.5	NA	90
<b>Suzuki et al. (2007)</b>											
	3720	Hog	0.4	138	70	46	532	80	7.4, 8.0	73	63
<b>Moerman et al. (2009)</b>											
	200	Potato waste <sup>[e]</sup>	NA	64	60	NA	110	140	7.1, 8.5	78	85
<b>Song et al. (2011)</b>											
	1000	Hog	NA	NA	40	60	760	124	7.0, 8.5	86-89	88-95
<sup>[a]</sup> Bowers and Westerman (2005) measured total ammonia nitrogen, i.e., combined NH <sub>4</sub> and NH <sub>3</sub> . <sup>[b]</sup> Deep pit storage, not agitated before extraction. <sup>[c]</sup> Concrete storage, agitated before extraction. <sup>[d]</sup> Manure was flocculated and then run through peat trickle filter to lower TSS. <sup>[e]</sup> Anaerobically digested potato wastes.											

Reduction in P-PO<sub>4</sub> but no reduction in TP indicates precipitation of P-PO<sub>4</sub> has occurred but the precipitates are not retained by the reactor. In Shepherd's reactor (2009), the use of a hydrocyclone located after the reactor did not retain these fines, whereas the fluidized bed of struvite particles (Bowers and Westerman 2005) recovered most of the P-PO<sub>4</sub> precipitated. Some researchers did not measure TP (Laridi et al. 2005), so the true effectiveness of the reactor is not known. Moerman et al. (2009) had a high Ca:PO<sub>4</sub> ratio (2.7) as previously mentioned, and no struvite was produced in the reactor until this was changed to 1.36.

The varying success of pilot scale reactors appears to be related to the presence of a seed substrate (Bowers and Westerman 2005; Moerman et al. 2009), and possibly low Ca: PO<sub>4</sub> ratios, although this data is not supplied in many papers.

## **2.7 Hog manure solids as a source of dissolved P**

Hog manure is ideal for struvite recovery because it is high in P and in most cases, already in liquid form, with total solids ranging from 10 to 50 g/L as it leaves the barn. The total P level ranges from 800 to 3000 mg/L with lagoon solids commonly holding from 80% to 90% of TP (Christensen et al. 2009; (Bicudo et al. 1999). The variation may be much wider depending on the storage time and storage conditions. Efficient PO<sub>4</sub> removal (80-90% from supernatant) via struvite production can at best recover only 8-25 % of TP, making only a small difference in N:P ratios. If a greater percentage of TP can be converted to PO<sub>4</sub>, it is then available for struvite reclamation, bringing greater reactor efficiency and removing P from the system. If ammonium losses are limited to

stoichiometric struvite removal and not lost to volatilization during the reaction process, the N:P ratio of field applied manure will improve. This section explores literature relating nutrient release from the solid manure fraction to the supernatant through anaerobic digestion, fermentation, and lowering pH.

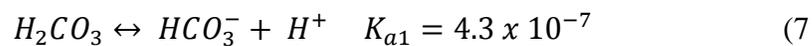
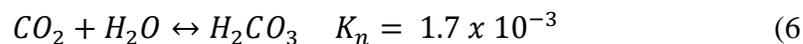
### **2.7.1 Fermentation**

The working hypothesis of this section is that acidic conditions arising from two processes of natural acid production from fermentation can dissolve P from the solid phase. Municipal wastewater sludge and manure are similar in many respects and the fundamental biological and chemical processes taking place in wastewater can be applied to manure with reasonable confidence. Under anaerobic conditions complex organics in municipal sludge are hydrolyzed by enzymes to produce sugars, amino acids and fatty acids. These compounds are converted by acidogenic bacteria to produce VFA and further degraded by acetogenic bacteria to produce acetate, CO<sub>2</sub> and hydrogen. Within several days methanogenic bacteria become established, and the acids are consumed to produce methane (Zoetemeyer et al. 1982; Harper and Pohland 1986). Reactor pH can be a good indicator of these processes and there are many examples of initial pH suppression during the acidogenic period and pH stabilization and increase as methane is produced. The pH dropped from 7.3 to 6.4 in 5 days (Yuan et al. 2009) in a bench scale reactor using waste activated sludge (WAS). The pH also fell in acidogenic reactors processing dairy manure (Yilmaz and Demirer 2008), with lower values reached as organic loading rate (OLR) increased. A pH of 6.55, 6.43 and 6.23 was observed at OLR of 5, 10, and 15 g volatile solids (VS)/L, respectively at 2 day solids retention time (SRT). The extent of

acidification varies considerably depending on storage conditions and the characteristics of the feedstock.

VFA has been found to increase with VS content as well as SRT under anaerobic conditions and a negative correlation was found between VFA levels and lower pH (Yilmaz and Demirer 2008). Others also observed that pig manure high in TS is correspondingly high in VFA concentration (Zhu et al. 2005). SRTs of four days increased VFA production as well as methane output, but did not produce lower pH (Zhu et al. 2005). It is likely communities of methanogenic microbes developed that consumed VFA and stabilized pH. Therefore, the SRT of manure through an anaerobic chamber may impact the level of acidification possible, with stable or decreasing acidity at longer SRTs.

The second process is carbonic acid production from CO<sub>2</sub> build-up. If manure is kept in a covered tank, CO<sub>2</sub> produced from microbial respiration can increase in concentration in the solution, leading to an increase in carbonic acid and adding to the acidity of the manure (equations 6, 7, Christian 1994). However, measurement of carbonic acid and dissolved CO<sub>2</sub> in a manure fermenter has not been described in the literature.



Depending on the levels of carbonates and other natural buffers in manure, the processes of acidification may lower manure pH. Carbonates, phosphorus, VFA, ammonia and other buffering compounds reduce the impact of increasing acidity by scavenging  $H^+$  protons. High concentrations of buffers increases the buffering capacity of the solution and will neutralize the manure, minimizing the effect of VS acidogenesis. In a poorly buffered manure however, acidic conditions are likely to result in the dissolution of some portion of the mineral P forms present in manure solids. Struvite makes up the majority of the P solids in pig manure (Bril and Salomons 1990) which has greater solubility at low pH, thus providing a source of P- $PO_4$ . Research into the composition of pig manure found that lowering swine manure pH to 5.5 solubilised 70% of TP (Christensen et al 2009). However, dissolution of Ca present in manure as calcite and calcium phosphates (Sommer and Husted 1995; Bril & Salomons 1990) may be counter-productive for P recovery via struvite formation due to ion competition with Mg.

Once nutrients ( $PO_4$ , Mg,  $NH_4$  and Ca) are in solution several factors determine whether they precipitate out of solution or remain aqueous. The acidic environment may work in two ways to keep nutrient concentrations high. Firstly, the major forms of phosphate precipitates, struvite and calcium phosphates, have higher solubility at low pH. Secondly, the presence of VFA may hold these cations out of free association with phosphate. Research on the chemical composition of pig and poultry manure showed that 10% of dissolved Mg and Ca in pig manure slurry are associated with carbonate ligands, 10% is freely associated and 80% is associated with VFA ligands (Bril and Salomons 1990). It stands to reason that over time as VFA are degraded these cations are liberated and can then form precipitates of struvite and calcium phosphate and settle out of

solution, however this has not been shown in the literature. Manure nutrient concentrations change with time, but no studies have been found specifically devoted to quantifying this, only references to preliminary nutrient analysis being very different from subsequent testing (Shepherd et al. 2009) and different manure sources increasing or decreasing in P concentrations over 34 days of storage (Christensen et al. 2009).

Increasing available nutrient content by anaerobic digestion has been tested for several struvite constituents with the most dramatic increase found in Mg, usually the limiting component of struvite production (Moody et al. 2009). After 36 days of anaerobic digestion Mg increased from 88 to 313 mg/L, PO<sub>4</sub> increased from 1256 to 1591 mg/L and NH<sub>4</sub> decreased 3240 to 2360 mg/L. The reported values for PO<sub>4</sub> in this study are very high, likely due to analysis of unfiltered samples. If so, this results in a PO<sub>4</sub> value closer to TP than a filtered (0.45µm) sample. Lowering pH to 4 and 5 has been shown to increase PO<sub>4</sub> (50 to 250 mg/L) and NH<sub>4</sub> (10 to 400 mg/L) in waste activated sludge after 20 days of anaerobic digestion (Chen et al. 2007). Whether this increase was from liberation of nutrients from organic matter breakdown or from dissolution of particulate phosphate compounds was not certain.

### **2.7.2 Mineral P in Manure**

Researchers have reported high mineral P forms in manure solids and that the majority of this was in the form of struvite (Bril and Salomons 1990) and others found only struvite and calcite by X ray diffraction (Sommer and Husted 1995). Careful acid titration of manure stored for 3 days revealed equal molar mass of Mg<sup>2+</sup> and PO<sub>4</sub> entering solution between pH 5.5 and 6.3 (Christensen et al. 2009). Authors stated that 70% of TP

dissolved by lowering the pH to 5.5. This finding has two significant implications for struvite production. One is that if manure pH can be lowered sufficiently, the majority of P can first be dissolved and later converted to struvite in a reactor. The other is that if supernatant holds particulate struvite, and that agglomeration of the crystals may be possible by mixing action. Larger crystals are easier to separate and remove from supernatant. Agglomeration of this kind may account for actual reactor yield to be higher than theoretical yield as reported in some reactors (Bowers and Westerman 2005).

### **2.7.3 Manure pH reduction**

Manure pH can be lowered either by inducing suitable anaerobic conditions or by the addition of acids. Naturally induced acid production is preferable due to cost savings but requires process monitoring. Manure chemical oxygen demand (COD) is the source of all acid production and SRT limits the potential consumption of VFA by other microbes. Two stage anaerobic systems rely on a fairly short acid generation step with maximum acidification of dairy manure of 2 days HRT and 15 g VS/L (Yilmaz and Demirer 2008) and 3 days for municipal sludge with COD of 10 g/L in a thermophilic system (Puchajda and Oleszkiewicz 2006). The pH attained in these experiments was 6.3 and 6.3-7.1 respectively. A higher VS loading may result in greater acid production.

### **2.7.4 Elutriation**

Elutriation is a technique of removing substances of interest from a complex and usually heavier solid matrix by passing dilute carrier liquid through or over the solids. It has been developed as a method to remove VFA produced in fermented primary sludge and transport them to the BNR process (Bouzas et al. 2007). This process relies on the

transport of VFA from an area of concentration by more dilute supernatant. The elutriating liquid is passed over or through the fermented sludge removing the solutes. This process may be adapted to remove P from manure solids by passing struvite reactor effluent (low in P-PO<sub>4</sub>) through manure solids (high in P solids) and dissolve a portion of P solids. A pH adjustment may need to be made to the effluent to facilitate dissolution of mineral P in the solids. If particulate P exists as solid struvite in manure, pH adjustment to 6.0 or below would serve to dissolve a portion of this into the elutriation stream, facilitating a stripping of P from solids into the liquid portion. No research has been found that investigates this technique as far as manure nutrient elutriation or phase change from solid to liquid by elutriation.

## **2.8 Struvite as a fertilizer**

The end use of struvite is to replace commercial inorganic phosphorus fertilizer, so it is important to know if manure-derived struvite is comparable to commercial P fertilizer for agronomic uses. Several studies have investigated this question as well as questions of soil pH, and struvite solubility in soil. Depending on the recovery process, reclaimed P in agronomic studies can be in the form of WWTP sludges (Plaza et al. 2007; Ponce and De Sa 2007), bone and sewage ash (Cabeza et al. 2011), or struvites and other P precipitates (Johnston and Richards 2003; Cabeza et al. 2011). Only one study has used precipitate reclaimed from hog manure (Liu et al. 2011).

Several authors compared different P sources as fertilizers and showed struvite is not significantly different (Johnston and Richards 2003; Plaza et al. 2007; Ponce and De

Sa 2007; Massey et al. 2009; Cabeza et al. 2011) and sometimes superior (Gonzalez-Ponce et al. 2009; Liu et al. 2011) to commercial phosphate fertilizers when measuring biomass and P uptake. These studies used a variety of agricultural crops such as ryegrass, maize, lupin, and lettuce grown in a variety of soils. Struvite is more soluble in acid than alkaline solutions, raising the question of its effectiveness in neutral or alkaline soils. Studies have tested struvite's effectiveness in acid versus neutral and found crops grown in neutral soil with a struvite fertilizer had better P uptake (Johnston and Richards 2003; Massey et al. 2009) compared to acid soils. Johnston et al. (2003) compared struvite in two soils and found 5 harvests of biomass removed 6-17% of available P in the acid soil (pH 6.6) whereas 13-24% of P was removed in a neutral soil (pH 7.1), suggesting P was more available in neutral soil. Massey et al. (2009) also found a significantly greater biomass and P uptake response using struvite in a limed soil (pH 7.6) than the same unlimed soil (pH 6.5). This finding is surprising because struvite is less soluble in alkaline solutions but the limed soil had higher background P and N than the same soil at its natural pH, indicating liming influenced nutrient solubility.

Other research has shown that P solubility of different phosphorus precipitates in water and this poorly correlate with soil solution P (Cabeza et al. 2011) when it has been used as a fertilizer. Authors compared different reclaimed P products (calcium phosphates, struvites from WWTPs, ash, and commercial fertilizer) and concluded that there is not a good correlation between solubility in water and soil porewater concentrations, probably due to the complexity of soil chemistry P interactions.

## 2.9 Literature Review Summary

The field of struvite production from municipal and animal wastewaters has quickly developed in the last 15 years. Out of this literature, many important findings can be used to guide this research project.

- Solution pH and Mg:P ratios can be increased (e.g., pH 9) to maximize P removal if that is the desired outcome. However, as pH nears 9.27 equilibrium of  $\text{NH}_4^+$  and  $\text{NH}_3$  causes significant loss of  $\text{NH}_3$  to the atmosphere. Lower precipitation pH (e.g. pH 8), produce better conditions for crystal growth and pellet formation. There is little investigative research regarding precipitation at levels below pH 7.8.
- Under most circumstances, supersaturated conditions in manure exist for struvite and calcium phosphate precipitation.
- Calcium to P ratios (Ca:P) in wastewater above 2 have been shown to reduce struvite purity and can reduce struvite recovery to zero in some reactors. To what extent this affects struvite precipitation in hog manure has not been determined.
- Struvite seeded upflow reactors appears to be the most successful pilot scale reactor to produce struvite from animal manure.
- A small pH increase can be the best for struvite crystal growth, and for some supernatants, this can be achieved by air stripping, removing the need for alkali addition.

- There is good indication that a high percentage of P in manure solids is in the form of struvite or calcium phosphate. A portion of this may be available for dissolution by acidic conditions, but no studies have explored this potential.
- Agronomic studies have shown struvite performs as well or better than commercial fertilizer in terms of biomass production and plant P uptake, but no studies have compared manure derived-struvites of different purity.

### 3 Manure: Lagoons, P-PO<sub>4</sub>, and storage

#### 3.1 Introduction

Removal and recovery of P from hog manure requires background information on the character and fate of manure P in the current manure management system of a typical MB hog farm. Manure is generally considered to be uniform in nutrients throughout production and storage, with little data existing on forms of P appropriate for struvite precipitation. Information on P-PO<sub>4</sub> concentration and TS can inform appropriate placement of a struvite reactor within the manure handling system on a commercial farm. Pilot struvite reactors have achieved highest P removal efficiencies with low TS supernatant (e.g. 5 g/L TS and 59-70% TP removal, Bowers and Westerman 2005) and high P-PO<sub>4</sub> concentrations. In MB, manure is stored in a series of lagoons with only surface liquid filling the secondary cell. This low TS supernatant may be a good feedstock for struvite reactors. However, soluble P as a percentage of TP can be variable in manure and is reported as ranging from 3% (Shepherd et al. 2009) to 30% (Christensen et al. 2009). Burns et al. (2003) reported an order of magnitude variation in P-PO<sub>4</sub> for hog manures with similar TP. Determination of the levels of P-PO<sub>4</sub> in functioning primary and secondary lagoons is imperative to assess the feasibility of P recovery and reactor placement at commercial farms in Manitoba. What changes take place over the storage time is important to note as well as the effect of manipulation of manure to increase P-PO<sub>4</sub> concentrations. Artificial manipulation of manure pH by acidification has increased soluble P levels in hog manure slurry (226 to 821 mg/L, Daumer et al. 2004) and lagoon supernatant may have a similar response.

The objective of this work was to determine whether or not manure handling practices in Manitoba produce appropriate supernatants for struvite recovery, and what changes, if any, could increase P-PO<sub>4</sub> content. Fulfilling this objective was comprised of several aspects that are presented in the following sections:

**I.** A survey of local hog farms with physical and chemical analysis of storage lagoon manure was conducted to collect data addressing feasibility of struvite reactors in MB.

**II.** An experiment using supernatant from primary and secondary lagoons was performed to test increased P-PO<sub>4</sub> concentration by acidification with HCl.

**III.** Stored manure in a simulated storage lagoon was monitored over 66 days to determine nutrient fate.

**IV.** A general discussion brings together important findings that have guided subsequent experiments in the overall research project.

### **3.2 Lagoon Survey**

Manure management in commercial hog barns in Manitoba is a pull-pit system, where holding pits directly under animal stalls collect feces, urine, spilled feed, and drinking water. The plugs of these pits are “pulled” once or twice weekly and the manure is flushed into a wet well and from there pumped directly into a primary storage lagoon. Farms differ in their lagoon configuration, with one, two and sometimes three lagoons in sequence, with overflowing liquid from the first slowly filling the second and so on.

In assessing a farm for optimum struvite reactor placement, access to manure at all stages of handling would be beneficial, but due to biohazard restrictions and H<sub>2</sub>S danger, no farm allowed access to barns or the wet well to sample manure. Lagoons provided the safest sampling access and the survey addressed questions of horizontal and vertical nutrient stratification within primary and secondary lagoons. Primary lagoons are nutrient rich but secondary lagoons are much lower in total solids and thus be superior in a struvite reactor.

### **3.2.1 Methods**

Four commercial barns with primary and secondary lagoons were selected for sampling. Primary lagoons were small and often had manure inflow pipes located below the surface, providing some mixing activity to the lagoons and no expected stratification of nutrient concentration. A single sample point was chosen in the primary lagoon. In the secondary lagoons, samples were taken near the inlet from the primary cell, mid way along the lagoon and at the end. These sampling locations are identified numerically from 1 to 4 respectively. Surface sampling was conducted using a 12 ft. extension pole with a ½ L plastic bottle at the end. Samples from 1m depth were taken with the same apparatus but with the empty bottle inverted to 1 m at which point it was then turned upward to allow material from that depth to fill the bottle. A Students T-test for significance was performed on data taken from surface and 0.5 m depth.

Supernatant pH was measured in the field before samples were transported to the lab and stored at 4° C. TS and alkalinity were measured by Standard Methods (Clesceri et al. 1998) and filtered samples tested for P-PO<sub>4</sub> by the ascorbic acid method (Murphy and

Riley 1962) using a UV/Vis spectrometer (Ultrospec 4300 Pro, GE Healthcare, Piscataway NJ). Total P was measured by wet digestion of each slurry using a Hach Digestahl (430° C, 4 ml conc. sulphuric acid and 50% hydrogen peroxide). Processed samples were measured for P-PO<sub>4</sub> as described above.

### **3.2.2 Results & Discussion**

The survey gave an indication of the range of chemical values in the lagoon storage systems, with variation probably due to differences in lagoon management at different farms. A wide variation was found for TP, which ranged from 18 to 175 mg/L in primary lagoons and 14 to 92 mg/L in secondary lagoons (Fig. 3.1).

P-PO<sub>4</sub> was considerably lower in secondary lagoons and ranged from 4 to 29 mg/L versus 23 to 66 mg/L in primary lagoons. Primary lagoon pH ranged between 6.9 and 7.8 (Fig. 3.2 C), whereas secondary lagoons were higher in pH (7.6 to 8.1). It is interesting to note that supernatant pH was moderate to high in all lagoons except Site 1 (primary), which had TP 200% greater than the mean of the other two primary lagoons. Secondary cells were lower in TS (4.8 to 7.5 versus 6.3 to 12.3 g/L in primary lagoons), except for site 2 and 4, where overflow and intermixing rendered them identical to the primary lagoon (Fig. 3.2 D). The wide variation in secondary lagoon characteristics and the similarity of some secondary lagoons to primary lagoons resulted from one of two reasons. Either the secondary lagoon was at capacity and manure was circulating between both lagoons (e.g. Site 2) or the primary lagoon was undersized for the manure inflow volume and solids directly entered the secondary lagoon (e.g. Site 4). Site 4 had a thick

crust of solids on the surface of the primary cell that spilled into the second cell and prevented sampling in the primary.

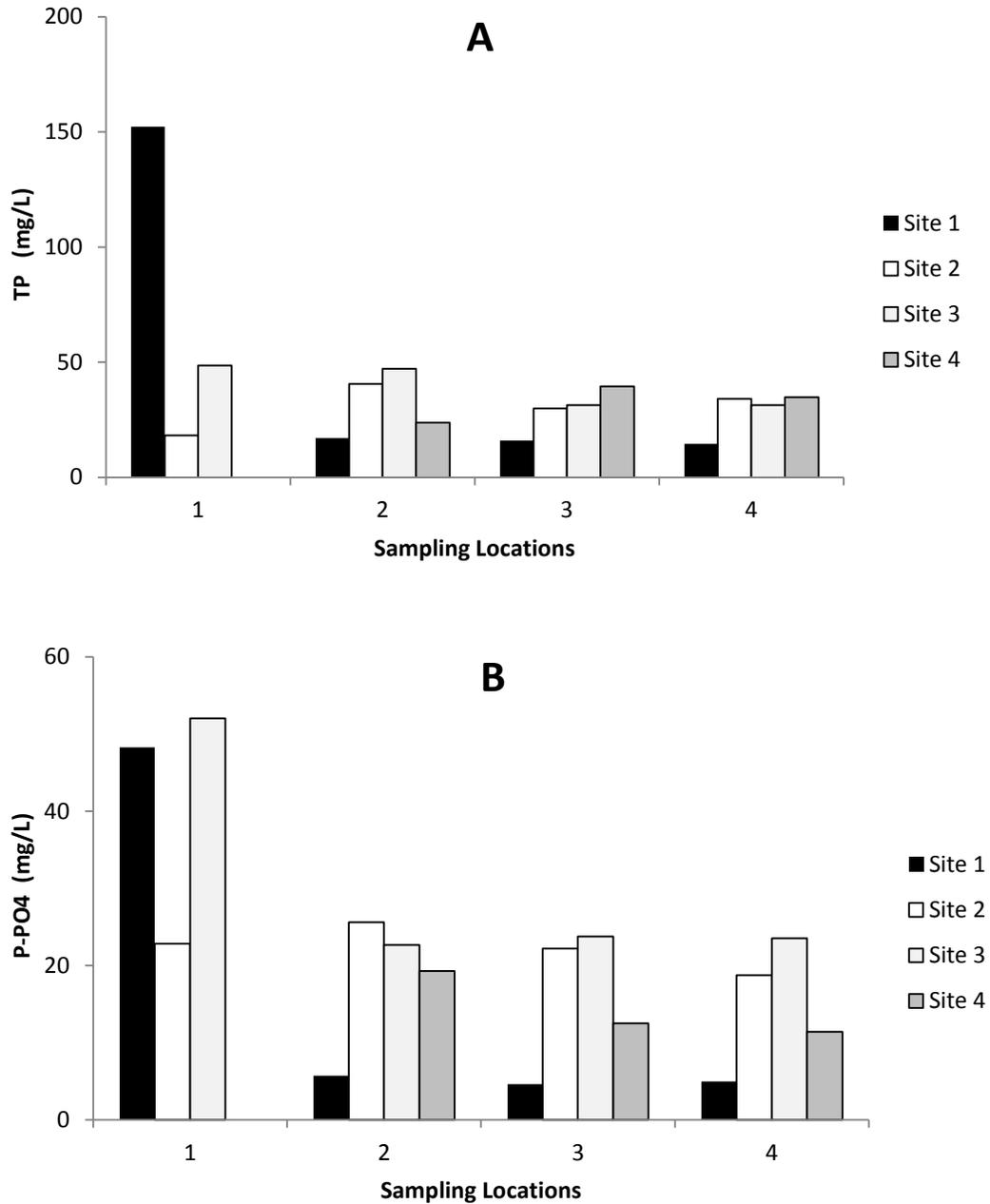


Figure 3.1 Total (A) and soluble phosphorus (B) at commercial hog lagoons in Manitoba. Sampling locations are: primary cell (1), secondary cell inlet (2); mid way (3), and at the end of the lagoon (4).

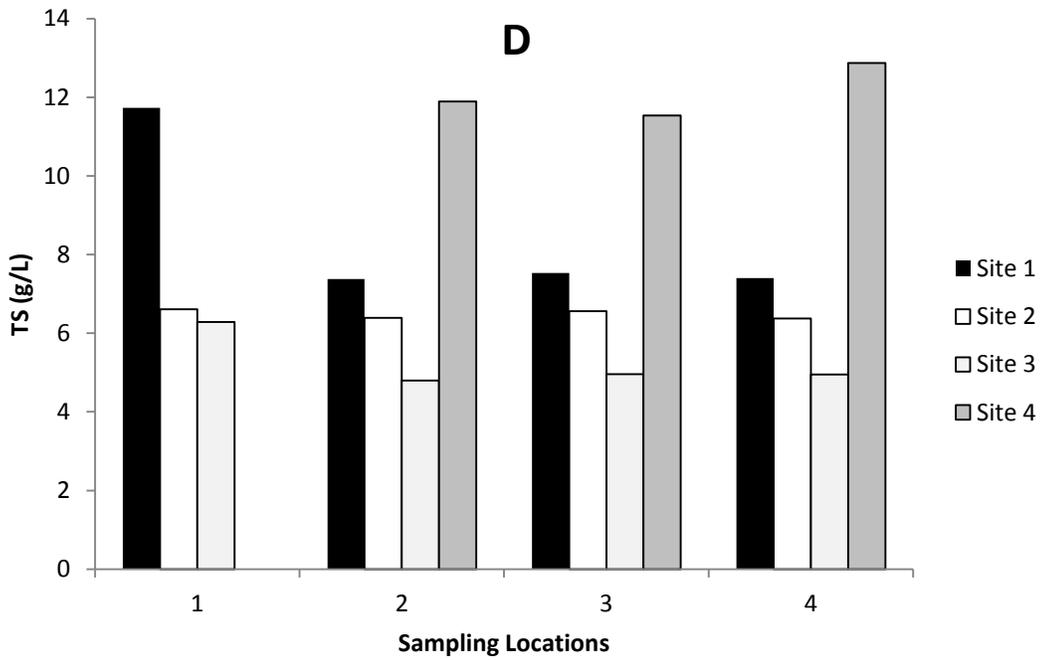
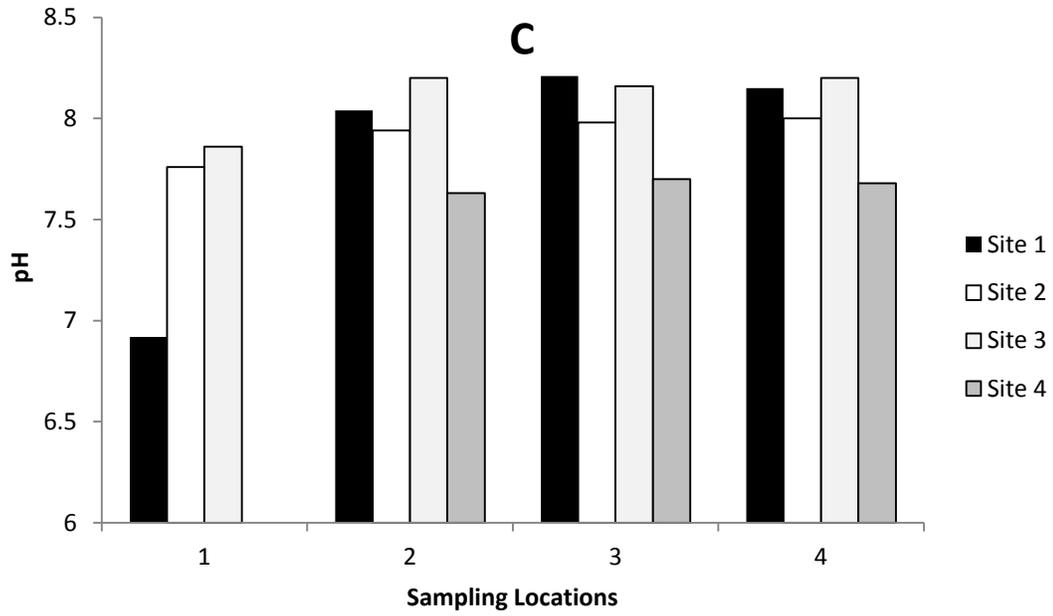


Figure 3.2 Lagoon pH (C) and total solids (D). Sampling locations are as described in Fig. 3.1.

When a lagoon system is functioning as intended, solids settled in the primary cell and only supernatant flowed to the second. This resulted in lower TS and alkalinity (Fig.

3.3), as well as lower TP and P-PO<sub>4</sub> (e.g., Sites 1 and 3). A larger survey sample would be needed to properly establish typical characteristics of primary and secondary lagoons in Manitoba, enabling exclusion of any sites that were not functioning properly.

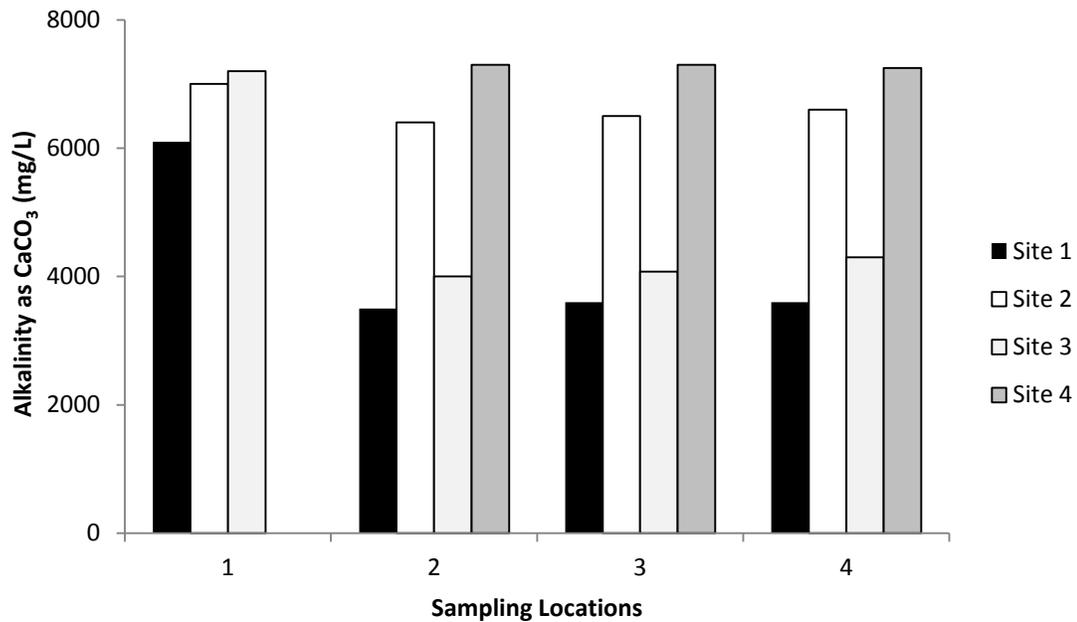


Figure 3.3 Alkalinity at primary and secondary lagoons.

A longer residence time in the lagoon would theoretically have allowed for more decomposition of suspended and dissolved solids. This has been found to affect ion precipitation result in pH increase. These parameters were not measured in this survey but low nutrient concentrations and high pH were observed at Site 1 and 3 secondary lagoons.

T-tests of sample results taken at 0.5 to 1m depth indicated they were not significantly different from surface samples in both primary and secondary lagoons. As well, samples taken from the secondary lagoons showed that nutrients and

physical/chemical characteristics were not horizontally stratified for most parameters (data not shown). It was expected that nutrients in the secondary lagoon would be progressively less concentrated as distance from the primary lagoon inlet increased. Absence of any nutrient gradient may be from the effects of wind mixing, since all lagoons are exposed to open prairie weather conditions.

### **3.3 The effect of acidifying lagoon supernatant on P-PO<sub>4</sub>**

The lagoon survey showed lagoon supernatants were higher in TP than P-PO<sub>4</sub>, indicating a portion (20-70%) of P was associated with suspended particulates, some of which may be soluble at a lower pH.

#### **3.3.1 Methods**

Acidification of lagoon samples with HCl was conducted to determine how much of this suspended particulate P was soluble in the pH 6 to 7 range. Stored supernatants from two primary and two secondary lagoons were acidified with concentrated HCl from their original pH levels incrementally to pH 6.1. Aliquots of acidified supernatant were sampled and filtered as the pH decreased. The filtered samples were analyzed for P-PO<sub>4</sub>

#### **3.3.2 Results & Discussion**

Primary lagoons had the highest initial P-PO<sub>4</sub> concentration and the greatest increase due to acidification to pH 6.1, increasing by 360% and 65% of original lagoon PO<sub>4</sub> levels (Table 3.1). Secondary lagoons had lower initial PO<sub>4</sub> concentrations and acidification to 6.1 produced marginal increases that may have only been within the

sampling error of the experiment. This finding suggests that there is insufficient amounts of particulate P in secondary lagoon supernatant that can be converted to P-PO<sub>4</sub> by acidification, whereas P-PO<sub>4</sub> concentration can be increased 2 to 4 fold in primary lagoons.

Table 3.1 Changes in P-PO<sub>4</sub> concentration in four lagoon supernatants from acidification. The first row gives starting pH and P-PO<sub>4</sub> levels.

Site	1		1		3		3	
Lagoon type	Primary		Secondary		Primary		Secondary	
	pH	PO <sub>4</sub> mg/L	pH	PO <sub>4</sub> mg/L	pH	PO <sub>4</sub> mg/L	pH	PO <sub>4</sub> mg/L
Original measurement	6.8	45	7.9	9	8.0	43	8.2	33
Adjusted pH	6.6	84	7.1	12	7.1	60	7.1	36
Adjusted pH	6.3	143	6.6	13	6.6	67	6.6	35
Adjusted pH	6.1	207	6.1	12	6.1	71	6.1	37

### 3.4 Nutrient monitoring in lagoon supernatant over time

Results from the lagoon survey showed a change in nutrient concentrations with retention time and PO<sub>4</sub> concentrations during refrigerated storage suggested manure nutrient levels can change over time. For example, Site 1 had P-PO<sub>4</sub> levels of 48 mg/L in the primary lagoon but only 5 mg/L in the secondary lagoon (TP of 152 and 17 mg/L respectively), indicating P had changed form over time, likely precipitated from the supernatant and settled on the bottom. The pH was 6.75 in the primary lagoon and 8.15 in

the secondary, suggesting a possible relationship between pH and P loss. Another example is 27 of 30 manure samples from survey sites stored at 4° C had a decrease in pH within 48 hrs by an average of 0.10 pH point. PO<sub>4</sub> measurements of random samples showed a 10-20% increase in samples with high original TP and no increase in low TP samples. This suggests the pH and PO<sub>4</sub> concentrations may have been the result capping the samples and creation of anaerobic conditions within the storage bottles. Researchers have reported a significant decrease in P-PO<sub>4</sub> and rise in pH in anaerobically digested municipal biosolids centrate during 8 day storage of the effluent (Battistoni et al. 2000). Some researchers have made reference to decreases in manure P-PO<sub>4</sub> during storage (Shepherd et al. 2009) but data that tracks P change and pH in manure supernatant under natural or covered refrigerated storage conditions has not been found.

### **3.4.1 Methods**

To further understand the processes involved in manure storage and P fate, an experimental small scale “lagoon” was installed in a fume hood in the lab. Fresh manure solids from the Glenlea Research Farm were diluted with farm tap water to a slurry of 6% TS and placed in a 20 litre plastic pail open to the air. The tap water was same source as is used to wash pig pens and is the dilution water in liquid manure slurry. Soluble P, Mg, Ca, pH and alkalinity were measured on a regular basis from the surface supernatant without mixing. Due to evaporation in the fume hood, distilled water was added from time to time to keep the liquid levels constant.

The experiment was monitored for 66 days and is reported as Trial 1. Trial 2 was a repeat of the experiment with more frequent sampling during the first 30 days. Trial 2

required a second batch of manure from the research farm. This manure was diluted to 6% as with Trial 1.

Nutrients were measured from centrifuged and filtered samples as follows: P-PO<sub>4</sub> with the ascorbic acid method using a UV/Vis spectrometer (Ultrospec 4300 Pro, GE Healthcare, Piscataway NJ) and elemental Mg, Ca, K, and P using an ICP-OES (Varian 700 Series, Agilent Technologies Inc., Santa Clara, CA).

### **3.4.2 Results & Discussion**

Over the course of 66 days in the fume hood, the pH of Trial 1 manure increased at a steady rate, rising from 6.97 to 8.30 by the end of the experiment. At the same time, alkalinity decreased from 7880 to 3200 mg/L CaCO<sub>3</sub> equivalent (Fig. 3.4). Soluble nutrients also changed during storage, soluble Ca decreased from 164 mg/L to 52 mg/L from day 6 to day 66. The P-PO<sub>4</sub> on the other hand increased from 37 to over 100 mg/L by day 18 and slowly decreasing back to 37 by day 66. No significant trends were found in soluble Mg (Fig. 3.5).

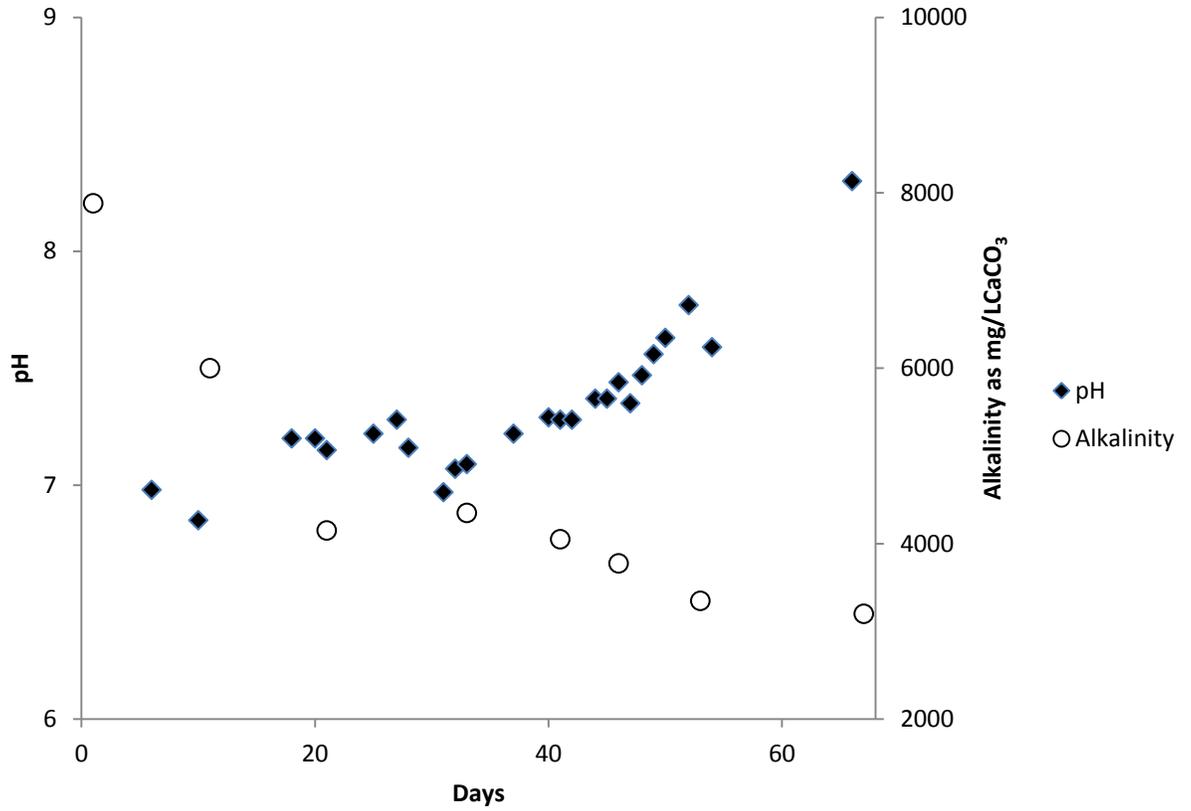


Figure 3.4 Experimental results from Trial 1 stored manure (6% TS), sampled for pH and alkalinity.

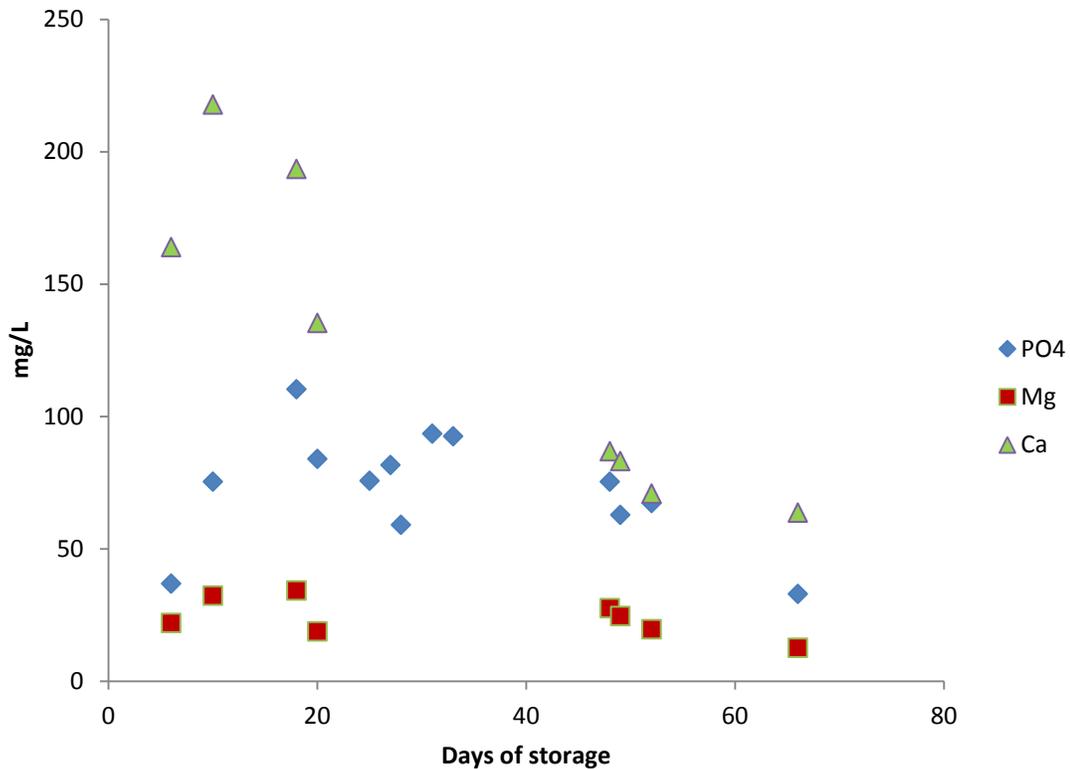


Figure 3.5 Soluble P, Mg and Ca from Trial 1 of stored manure supernatant.

Trial 2 gave different results, possibly due to the character of the manure, which was collected from the research farm a month after manure for Trial 1. It was diluted to the same TS% as Trial 1 but other measured parameters differed, such as alkalinity and Ca concentration. Initial supernatant alkalinity was 2300 mg/L and rose to 3000 mg/L over the 30 day storage period. The initial pH was 7.4 and dropped to a low of 6.42 on day 19 before rising to 6.86 by day 30 (Fig. 3.6). Soluble nutrients all increased in concentration from initial levels and then decreased by the end of the experiment. Mg and Ca were 51 and 93 mg/L on day 1 of storage and peaked at 195 and 163 mg/L on day 18, respectively (Fig. 3.7).

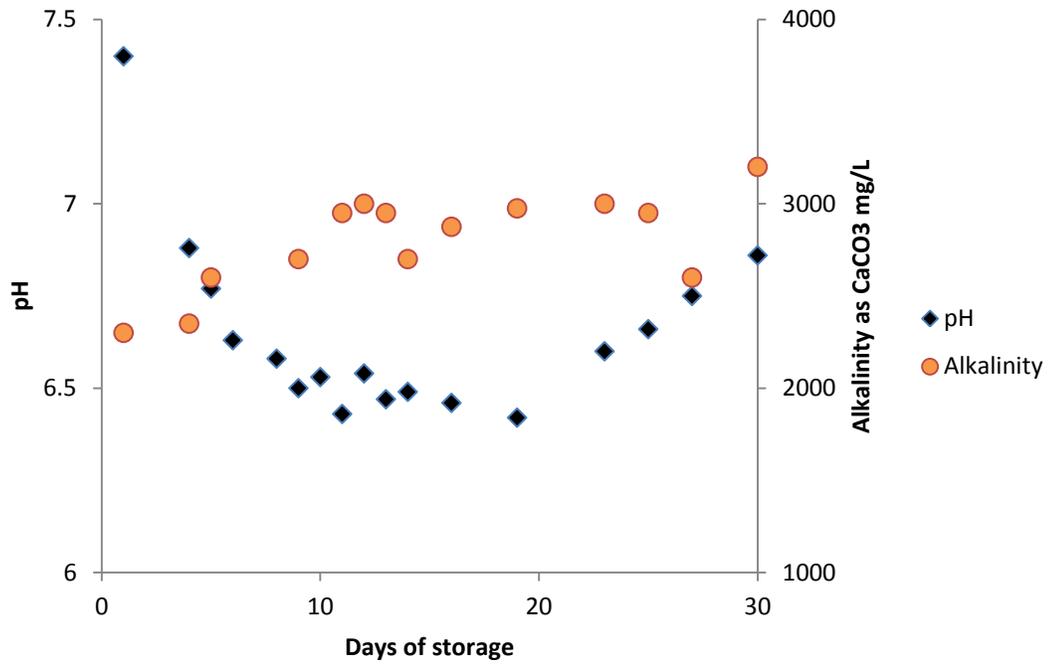


Figure 3.6 Trial 2 supernatant pH and alkalinity.

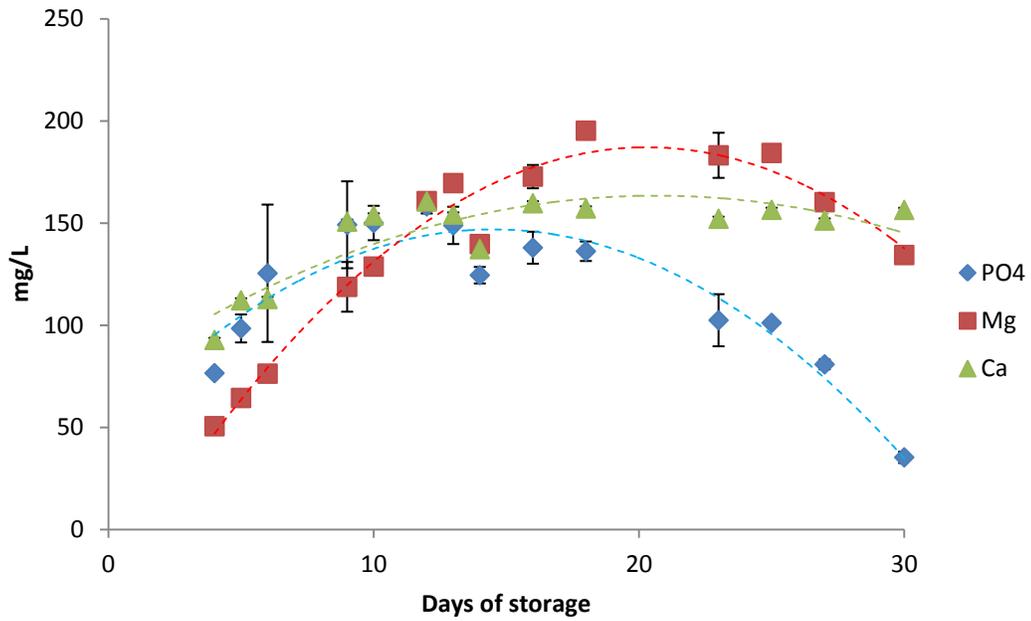


Figure 3.7 Trial 2 supernatant soluble nutrients P, Mg, and Ca.

Both Mg and Ca decreased somewhat by day 30 but remained at a higher level than initial concentrations. Soluble P also increased from its original concentration of 76 mg/L but after a high of 138 on day 16, it decreased to 35 mg/L by day 30. Comparing the results from Trial 1 and Trial 2 it is evident that pH and alkalinity followed very different trends over the first 30 days. Dissolved P exhibited some of the same trend in both trials but Mg and Ca cannot be compared for lack of data points over the first 30 days of Trial 1. The likely explanation for the variation in results between trials is the different manures used in each trial. For example, the high alkalinity in Trial 1 may have had a buffering effect on pH resulting in less dissolution of P and Mg. Similar variability of nutrient change during storage between manures has been reported by others (Christensen et al. 2009). They reported that the P-PO<sub>4</sub> levels of three manures monitored over 33 days of storage increased for one manure (200 to 260 mg/L), increased and subsequently decreased in another (100 to 140 and then to 90 mg/L), and was unchanged in a third (a range between 50 and 70 mg/L). Nutrient concentration in manure following storage is influenced by factors of original manure chemistry not understood at the present time.

### **3.5 General Discussion**

Chemical aspects of manure, physical characteristics and storage time were found to impact pH and soluble struvite constituents. P-PO<sub>4</sub> concentrations were different between hog farms using similar management practices, likely due to physical effects of dilution, storage conditions, and duration of storage. In addition, differences in animal age, diet, wash water usage, and well water chemistry all affect manure characteristics as

it enters the lagoon. Once in the lagoon, lagoons size, mixing, settling and retention time further affect important features such as TS, TP, pH and P-PO<sub>4</sub>.

Measurements made at lagoons and experimental results shown that manure pH and soluble P concentration are interrelated. Lagoons with low pH had very high TP and P-PO<sub>4</sub>, whereas high pH often (but not always) occurred with low or very low P-PO<sub>4</sub>. Studies using liquid hog manure has shown that VFA and other soluble organic compounds with multi charged sites adsorb NH<sub>4</sub>, Mg, Ca, keeping them separate from anions in solution (Bril and Salomons 1990). When these organic compounds are consumed by bacteria these cations are free to form precipitates and fall out of solution. These dissolved organic ligands are the major controlling factor in determining the composition of inorganic solids, such as struvite and calcium phosphate (Bril and Solomons 1990). These may be the same chemical interaction behind P loss from aging of wastewater supernatants observed by Battistoni et al. (2000). Two of the farm lagoon systems sampled had secondary lagoons lower in P and higher pH than the primary lagoon, possibly a function of retention time.

Acidification of manure supernatant increased P-PO<sub>4</sub> in manures with initial high P levels. This was likely due to the dissolution of suspended particles, either struvite or calcium phosphate. It has been reported that struvite is the most abundant form of mineral P in fully mixed hog manure (Bril and Salomons 1990) and it has been demonstrated by others that 70 % of TP can be dissolved by lowering the pH to 5.5 (Christensen et al. 2009), in which newly dissolved P and Mg were in a 1:1 molar ratio, indicating struvite was the source. The results of our experiments confirmed that manure supernatant can

have significant acid soluble particulate P. This P is a potential source for struvite precipitation if it can be dissolved by lowering pH, either by natural or artificial means. Storage of manure can provide a natural acidification for some manures, as seen in the manure storage experiment. The pH and P-PO<sub>4</sub> were negatively correlated for Trial 1 (-0.48) and Trial 2 (-0.930). A strong negative correlation would be expected between the two as P dissolved at lower pH and P precipitated as pH increased.

This work suggests that handling and storing manure for the optimum time can increase P-PO<sub>4</sub> concentration, which in turn would increase the recoverable P in a struvite reactor. There is also a link between pH and maximum P-PO<sub>4</sub> concentration, thus driving pH lower should result in higher P-PO<sub>4</sub> levels. These experiments on manure storage have indicated P levels fluctuate over time, reaching a maximum at 10- 20 days and decreasing slowly after that. In maximizing soluble P using an optimum manure storage time, it may be possible to remove more than the P held in a hog lagoon as P-PO<sub>4</sub>. The novel aspect to this work is the concept of engineering the processes of manure storage and handling for the greatest P availability and thus the highest struvite recovery.

## **4 Batch struvite reactor and elutriation of manure solids**

### **4.1 Introduction**

This chapter addresses two experiments, one on the construction and operation of a pilot scale struvite reactor (Ackerman and Cicek 2011) and the second on the feasibility of extracting P-PO<sub>4</sub> from manure solids by elutriation. Most struvite reactors are up-flow or through-flow reactors requiring constant energy input for pumps and intensive operational management. A low energy reactor that is simple to operate may be more appropriate for the current MB hog manure management system. Manure typically has over 70% of TP associated with the solids and a portion of this is soluble by elutriation, a process in which struvite reactor effluent (depleted in P) was recycled back through manure solids to dissolve P into the liquid phase. This P enriched supernatant could potentially be run through the reactor for additional P removal.

#### **4.1.1 Objectives of this chapter**

1. Assess the operational feasibility and precipitate quality of a simple pilot scale struvite batch reactor processing primary lagoon supernatant at a commercial hog farm.
2. Evaluate elutriation of manure solids as a means to remove P from manure solids and into a soluble form that can be removed by struvite precipitation.

#### **4.2 Objective 1) Pilot scale batch reactor design, operation, and performance**

Several researchers have targeted hog wastewater for struvite precipitation (Burns et al. 2003; Bowers and Westerman 2005; Jordaan et al. 2010; Laridi et al. 2005; Suzuki

et al. 2006) leading to published accounts of six pilot-scale struvite reactors (Table 2.6). The most successful of these reactors used hog waste supernatant of <5 g/L TS to produce high-purity struvite. Researchers utilized supernatants with upstream processes that settled TSS in an anaerobic lagoon (Bowers and Westerman, 2005); digesters (Song et al. 2011); digested TSS in a trickling filter (Laridi et al., 2005); or used a suspended metal surface for struvite crystallization (Suzuki et al. 2006). Utilizing primary lagoon supernatant would presumably require TS reduction unless the reactor was designed to accommodate TS of over 10 g/L.

Calcium is an important factor in the viability of using hog waste to make struvite because Ca is an inhibitor of struvite formation in wastewater supernatants (Moerman et al. 2009) and in synthetic supernatants at high concentrations (> 100 mg Ca/L, Le Corre et al., 2005). Hog farms use high calcium feed, and in some MB locations, dilute manure with groundwater that is naturally high in Ca. Before P can be reclaimed from these kinds of farms at an economical scale, it must be determined if supernatants high in Ca impedes P recovery.

In theory, a nutrient-rich supernatant in a simple batch reactor needs only alkali pH adjustment and adequate settling time for a low energy, low capital, reactor system. This approach was taken with lagoon supernatants in test beakers at a bench scale and pilot scale system in the field.

High concentrations of Ca have been reported to compete with Mg to form calcium phosphates (see section 2.3.5), lengthening crystal induction time and growth rate of struvite (Le Corre et al., 2005). As a precipitate, calcium phosphate has less value

as a fertilizer than struvite because of the lack of  $\text{NH}_4$  and the low solubility of some species. Particle size analysis and x-ray diffraction (XRD) showed that struvite crystals in the range of 13.4 to 15.1  $\mu\text{m}$  formed in the absence of Ca, while particles of 2.7, 3.1, and 4.5  $\mu\text{m}$  sizes formed at Mg:Ca ratios of 2:1, 1:1, and 1:2, respectively (Le Corre et al., 2005). Since standard TSS measurement records all particles larger than 10  $\mu\text{m}$ , the presence of Ca may produce particles that are not recorded, and TSS of this size would be lost to effluent in most upflow struvite reactors, leading to lower TP removal. A recent study found that dairy manure with high Ca (480 to 1040  $\text{mg L}^{-1}$  range) and an Mg:Ca ratio of 1:2 removed only 1% to 13% of TP in an upflow struvite reactor (Zhang et al. 2010). Similar Ca effects were found in a commercial struvite reactor processing anaerobically digested potato wastewater. Ca:P ratios of 2.7:1 resulted in 70% to 75%  $\text{P-PO}_4$  reduction, but no struvite was produced, and flocculent matter was evident (Moerman et al., 2009). This material may have been calcium phosphate but the author did not collect it for analysis.

In this research, Ca concentration in primary lagoon supernatant was 467  $\text{mg/L}$ , giving a Ca:P ratio of 1.67 and Ca:Mg ratio of 2. Both of these metrics indicate that P will precipitate primarily as calcium phosphate rather than struvite. Using this kind of supernatant in upflow reactors (Bowers and Westerman, 2005) or flow through tanks (Laridi et al., 2005; Moerman et al., 2009; Shepherd et al., 2009) would likely result in little precipitate retention because of the small floc size of calcium phosphate.

For phosphorus reclamation from liquid manure to be adopted on a wide scale, the process of P reclamation must be simple and inexpensive so that average farmers can

install a system with a minimum of capital expenditure. This study took a low capital, low energy input approach to precipitation of P from lagoon supernatant and used a gravity settling system that removed the majority of TP and produced settled solids to be processed into dry fertilizer. The term “settled solids” is used to include precipitates and flocs resulting from alkali addition as well as organic solids that settle out of the supernatant. The focus was on the function of the system and the precipitated product in terms of nutrient content and struvite purity.

#### **4.2.1 Methods**

A commercial feeder barn in southern Manitoba with a primary and secondary lagoon system was selected for installation of the reactor. Two 410 L cone-bottomed plastic tanks equipped with two-way drain valves were installed adjacent to a full-scale primary lagoon. The tanks were filled from the top with a hand-operated diaphragm pump, dosed with KOH (5M solution) to reach pH 8.5, and allowed to settle for 24 h. This pH level was selected because there is indication that pH adjustment above 8.5 precipitates Ca as calcite (Jordaan et al. 2010). No Mg was added because laboratory tests showed no increase in P removal with Mg ion addition. Liquid samples were taken from the top of the reactor before alkali dosing and again after 24 h of settling. Settled solids were drained into separate containers, and the remainder of the effluent was released to the secondary storage (Fig. 4.1). It was found that an additional 24 h of settling further stratified this sludge. The collected sludge was stored in the lab at 4°C and later dried in the sun in flat shallow trays and then pulverized in a ball bearing mill to produce the final product.

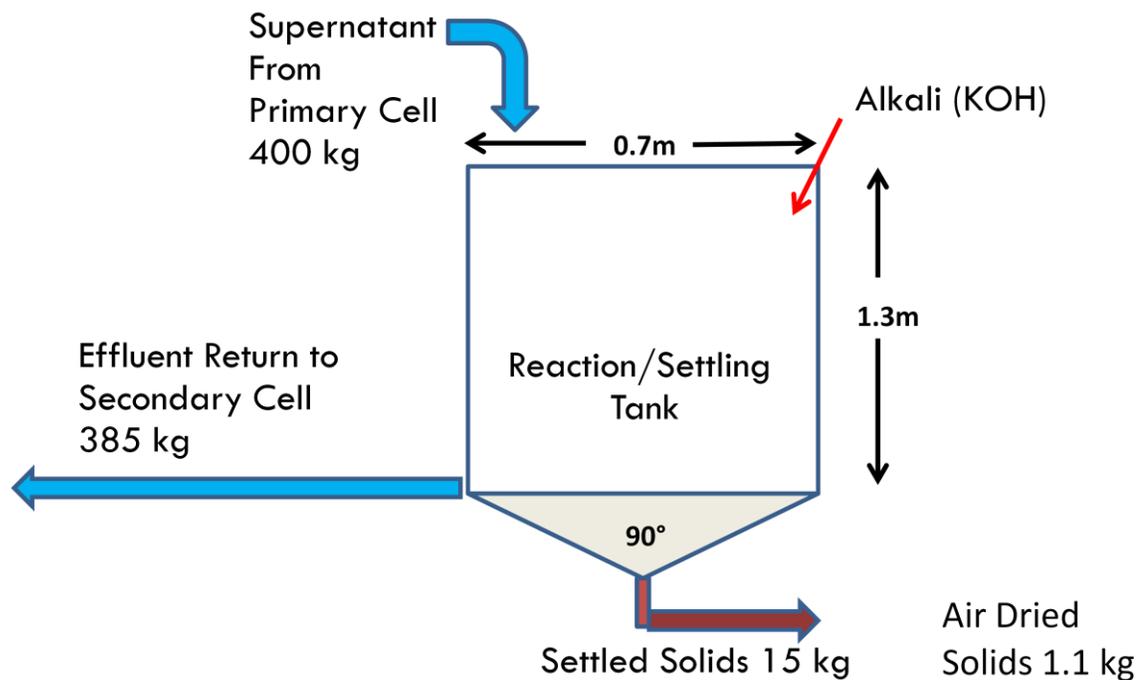


Figure 4.1 Schematic of the gravity-settling batch reactor.

Many researchers conducted analysis of manure only measuring P-PO<sub>4</sub> and TP, which were measured by centrifuge and filtered slurry (0.45 µm filter), and by complete digestion. Measurement of particulate mineral and organic P forms was of interest in this study to find the forms of P removed from the manure, but quantitative determination represents a challenge due to the complexity of the manure matrix. In other research, filtered and unfiltered manure slurry were diluted using 0.5 M perchloric acid (Daumer et al. 2004), the difference being particulates soluble in acid and representing mineral P particulates. This approach was first used by (Appeldoorn et al. 1992) for determining mineral P forms in wastewater sludge, and a similar system was used recently for wastewater P analysis (Scherrenberg et al. 2008). The method used in this study varied

slightly from these, as nitric acid was used to dissolve mineral P from unfiltered samples and determining organic particulate P by subtraction of mineral P from total particulate P (Fig. 4.2). With this analysis, measured P parameters can be used to find unmeasured ones: Total P – filtered P = total particulate P, Total acid dissolved P-filtered P= mineral particulate P. Total particulate P-mineral particulate P=organic particulate P.

This scheme has several advantages over others by resolving both analysis and storage problems. The nitric acid dilution medium was the same concentration as required by ICP-OES, enabling companion analysis without other adjustments. In addition, the acid inhibits bacterial communities that would otherwise consume P-PO<sub>4</sub> during sample storage.

When values are derived from adding or subtracting measured values, the standard deviation of the new value must be calculated using the following equation:

$$s_3 = \sqrt{(s_1)^2 + (s_2)^2} \quad (8)$$

where  $s$  is the standard deviation, subscripts 1 and 2 denote measured values, and subscript 3 is the calculated value (Utts and Heckard 2010).

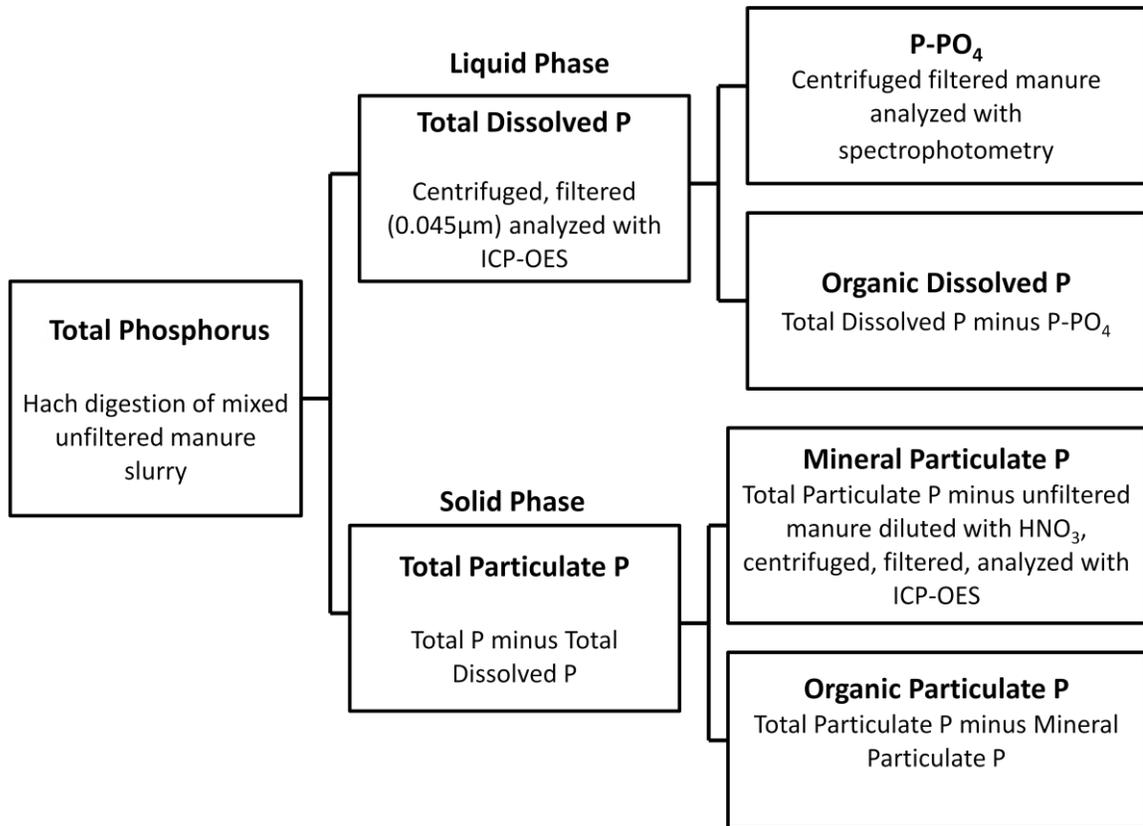


Figure 4.2 Determination of P forms in manure slurry.

The system was operated for one week in July and one week in August 2009, and included three tank filling, dosing, and settling events in July and four in August. Single influent samples were taken for each event, and single effluent samples from each tank were taken in July. No significant difference (at  $p \geq 0.05$ ) was found between tank effluents, so a pooled effluent was sampled in triplicate for the August events. In July, reactor sampling was limited to unfiltered supernatant, but in August sampling included filtered and unfiltered samples as well as digested sample analysis.

Samples of influent and effluent were measured for TS, TSS, and alkalinity according to Standard Methods (Clesceri et al., 1998). Triplicate filtered (0.45 µm) and

unfiltered manure samples were diluted 8.3 fold with acid ( $\text{HNO}_3$  0.5%) allowing for dissolution of P, Mg and Ca present in particulate mineral form. These and the filtered samples were analyzed on the spectrophotometer for P- $\text{PO}_4$  and by inductively coupled plasma emission spectroscopy ICP-OES (Varian 700-ES Agilent Technologies Inc., Santa Clara, CA) for P, Mg Ca, K and Na.  $\text{NH}_4$  concentration was determined in a flow injection analyser (LaChat QuikChem 8500 LaChat Instruments, Hach Co., Loveland, Colo) and after sample digestion in the Hach Digestal, TP, Mg, Ca, K and Na were determined by ICP-OES as previously described.

### **4.3 Solids Analysis**

Three representative samples of the dried, ground solids were mixed and further ground in a mortar and pestle. Total digestion of triplicate 0.5 g portions was processed with the Digesdahl hydrogen peroxide method. Struvite and calcium phosphates were dissolved in 1 g portions of dried sludge added to a weak  $\text{HNO}_3$  solution (0.5% vol/vol) and adjusted several times over 24 h to a final pH of 1.5. These solutions were analyzed for Mg, Ca, P, K and  $\text{NH}_4$  as described above. Organic carbon in the sludge was removed by loss on ignition at  $550^\circ\text{C}$  for 2 h using replicate 10 g samples. Analysis of crystalline mineral forms in the precipitate was conducted by XRD with a reflection diffractometer (Phillips PW 1710, Amsterdam, The Netherlands). Determination of the purity of struvite formed in the reactor is difficult and can only be approximated by measuring the concentration of struvite constituents. To accomplish this, acid-soluble nutrients were compared with nutrients measured by total digestion. It was found that all

Mg dissolved at pH 1.5, suggesting that no Mg was associated with organic particulate forms, as in the case of P and NH<sub>4</sub>. For these reasons, Mg was taken as the indicator of struvite, and total struvite content was calculated according to the Mg concentration. Statistical tests of significance were conducted with Prism 4.0 (GraphPad Software Inc., San Diego, CA).

#### **4.4 Results and Discussion**

Lagoon nutrient levels fluctuated considerably over the four-week period that elapsed between the two reactor operation events in July and August 2009 (Fig. 4.3). During this time, concentrations of P, Mg, and Ca in unfiltered reactor influent increased by 281%, 278%, and 299% of July levels. Reactor performance was very similar, however, removing  $80.1 \pm 1.8\%$  of P in July and  $83.8 \pm 0.8\%$  in August on a batch-in/batch-out basis. On the same basis, removal of Mg was  $70.1 \pm 1.3\%$  vs.  $81.7 \pm 1.3\%$  and removal of calcium was  $35.1 \pm 0.9\%$  vs.  $67.3 \pm 1.1\%$  in July and August, respectively.

There are several possible causes of the summer nutrient increase. The diet and age of the pigs producing the waste was not considered in our study, but manure nutrient content increases with pig age (Westerman et al. 2010). High P levels in the August sampling period may have been due to the straw cover placed over the lagoon by the farmer (after the July experiment) to reduce odours. The straw moved over the surface of the lagoon according to the wind direction, and small daily changes in nutrient content (and pH) appeared to correspond with the extent of straw cover at the reactor intake

pump. When straw covered the intake area, pH was 0.1 to 0.3 units lower than when the area was free of straw.

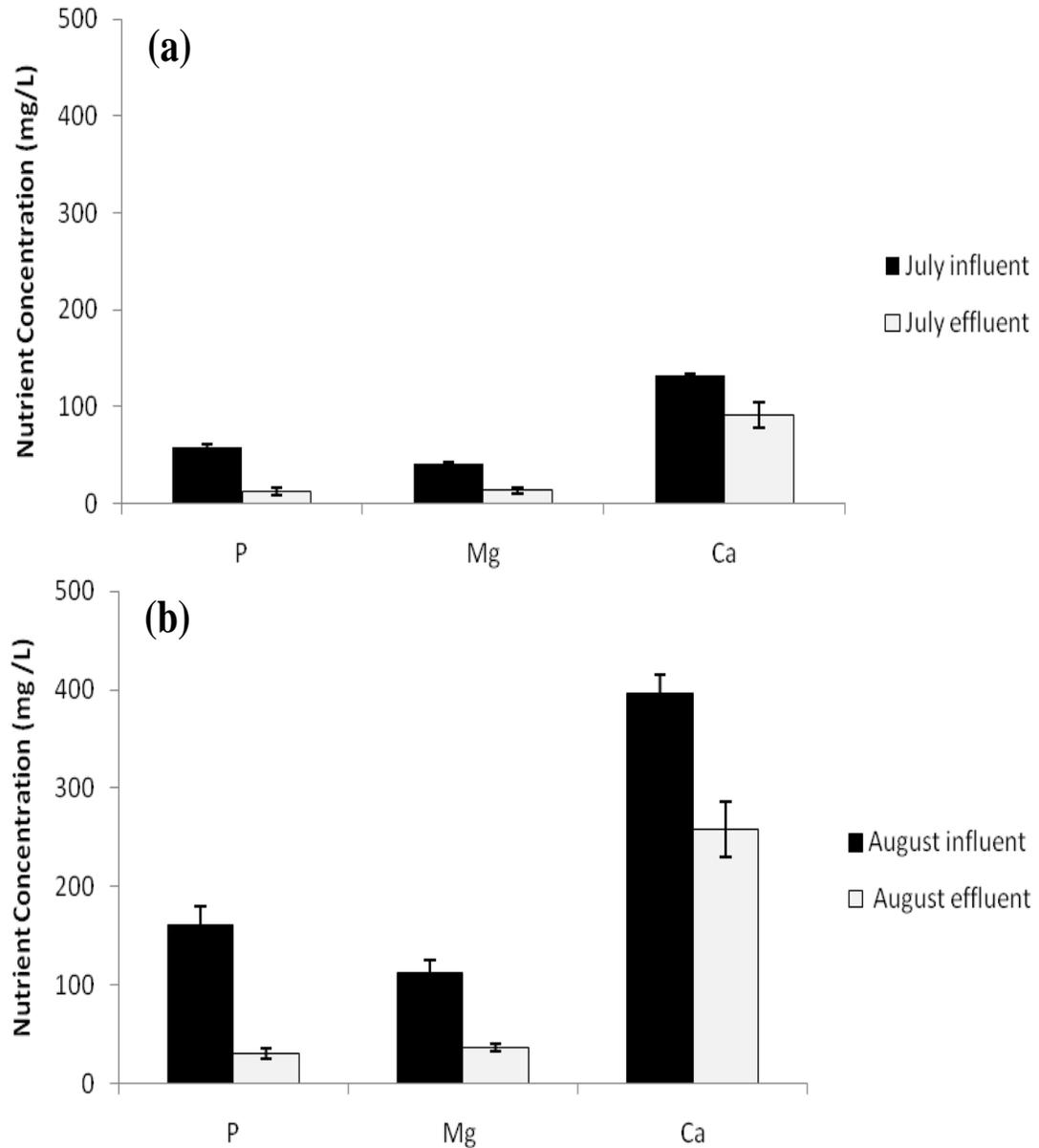


Figure 4.3 Reactor performance during (a) July and (b) August processing liquid hog manure from a primary storage lagoon.

A covered lagoon may cause buildup of acids that lower pH. For example, pig manure in a geotextile-covered lagoon has been observed to have lower pH than similar open

lagoons (pH of 6.3 to 6.6 for covered lagoons vs. 6.8 to 7.4 for open lagoons; personal observations). In addition, an increase in ambient summer temperature between the two periods may have favourably promoted biotic activity. Bubbling anaerobic gases from the solids on the lagoon bottom may re-suspend solids and brought high-nutrient solids to the surface. This process may have changed the nutrient content in the surface supernatant from the previous month.

Reactor operation removed the majority of supernatant TP at the lower and higher TP levels, which was significantly reduced by 79% in July and 82% in August (as grouped influent and effluent unfiltered samples,  $p \leq 0.05$ ). No significant difference was found in performance of the two reactors ( $p \leq 0.05$ ), although variation was high, with post-reaction P levels of  $11.5 \pm 2.4$  and  $13.2 \pm 3.8$  mg L<sup>-1</sup> for reactors I and II in July, possibly due to slight differences in alkali dosing and final pH.

Total P removal was determined by complete digestion of supernatant of influent and effluent (Table 4.1). This was performed once in August in conjunction with determination of P forms (Table 4.2). The precipitation reaction reduced all P forms to some extent, but the greatest reduction was found in P-PO<sub>4</sub> (92%) and mineral particulate forms (68%). The dissolved P reduction made up 57% of TP precipitation and particulate mineral P settling was 37% of TP reduction. It is possible that mineral particles settled by flocculation along with newly formed precipitate or by solids settling. The common assumption is that only P-PO<sub>4</sub> can be removed from supernatant because it can precipitate, but these data indicate that other processes can play an important role in P removal.

Table 4.1 Nutrient removal in the struvite reactor as determined by total digestion of influent and effluent.

	<b>TP (mg L<sup>-1</sup>)</b>	<b>Mg (mg L<sup>-1</sup>)</b>	<b>Ca (mg L<sup>-1</sup>)</b>
<b>Influent</b>	216 (4)	142 (3)	467 (21)
<b>Effluent</b>	63.6 (12.3)	48.3 (8.6)	335 (117)
<b>Percent reduction (%)</b>	70.6	66.0	28.3
<b>Removed nutrients (mM L<sup>-1</sup>)</b>	4.9	3.9	3.3

Table 4.2 Phosphorus forms present in reactor influent and effluent.

<b>Phosphorus Species</b>	<b>Influent (mg L<sup>-1</sup>)</b>	<b>Effluent (mg L<sup>-1</sup>)</b>
<b>Dissolved reactive P</b>	94.5 (1.4)	8.0 (1.5)
<b>Dissolved organic P</b>	9.1 (1.9)	3.4 (2.1)
<b>Particulate mineral P</b>	82.5 (4.5)	25.9 (4.8)
<b>Particulate organic P</b>	29.8 (5.4)	26.3 (9.5)
<b>Total P</b>	215.9 (4.3)	63.6 (8.0)

The majority of P-PO<sub>4</sub> and mineral particulate P was removed in the reactor, whereas particulate organic P remained almost the same during the process. This is similar to the forms of Ca present in supernatant indicated by the same sampling process (Fig. 4.4). In the case of Ca, a decrease in the soluble form was accompanied by an increase in particulate mineral forms.

Total suspended solids were reduced by reactor operation. Typical influent TSS was  $4.9 \pm 0.4 \text{ g L}^{-1}$ , and effluent TSS was  $2.17 \pm 0.53 \text{ (} N = 3 \text{)}$ . Inorganic solids remained

about the same ( $0.6 \text{ g L}^{-1}$ ) in both influent and effluent, indicating that the loss to the precipitate fraction was mostly organic solids.

Supernatant total solids increased from  $18.05 \pm 1.7 \text{ g L}^{-1}$  in the influent to  $22.47 \pm 3.2 \text{ g L}^{-1}$  in the effluent (Fig. 4.5), but there was no significant difference ( $p \geq 0.05$ ). A significant increase in inorganic solids occurred in the effluent as determined from loss on ignition of dried solids at  $550^\circ \text{C}$ . Calcium phosphate floc formation may account for the anomaly in the lower TSS and yet higher TS of the reactor effluent. The TSS filter size was  $10 \mu\text{m}$ , allowing most newly formed flocs to pass through, yet organic solids had already settled with larger precipitate particles, yielding a lower effluent TSS while maintaining small mineral particulates in suspension.

Higher TS in the reactor effluent than in the influent, even with loss of organic carbon and struvite, may have been from an inverse stratification of lighter particles such as calcium phosphate flocs and calcium carbonate. This hypothesis was strengthened by the higher inorganic solids found in the effluent, but a larger sample group is needed to make definitive conclusions.

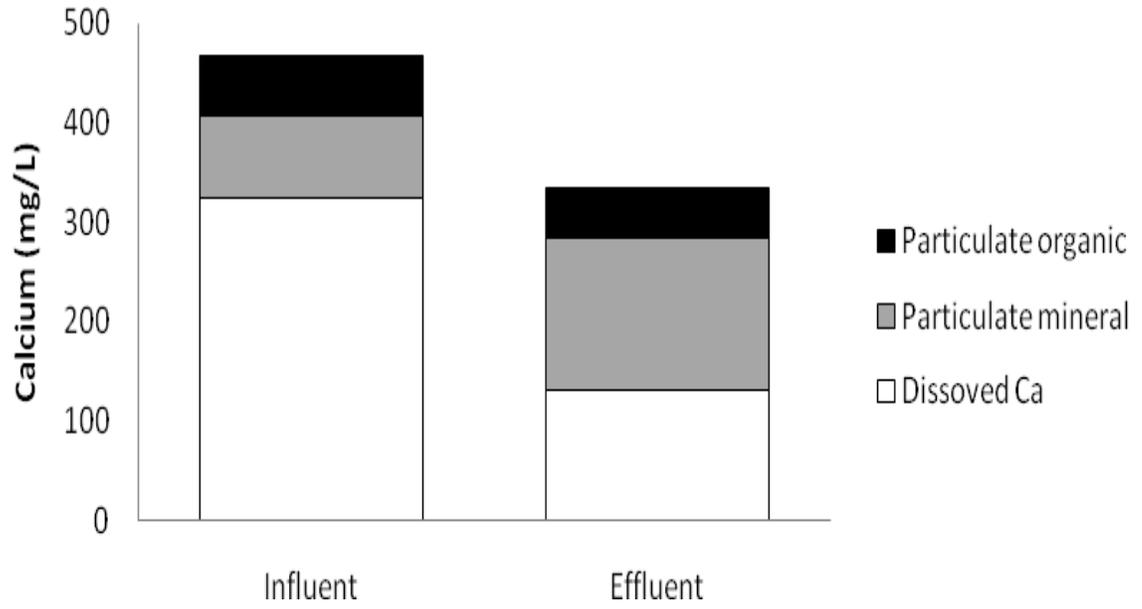


Figure 4.4 Forms of calcium present in reactor influent and effluent.

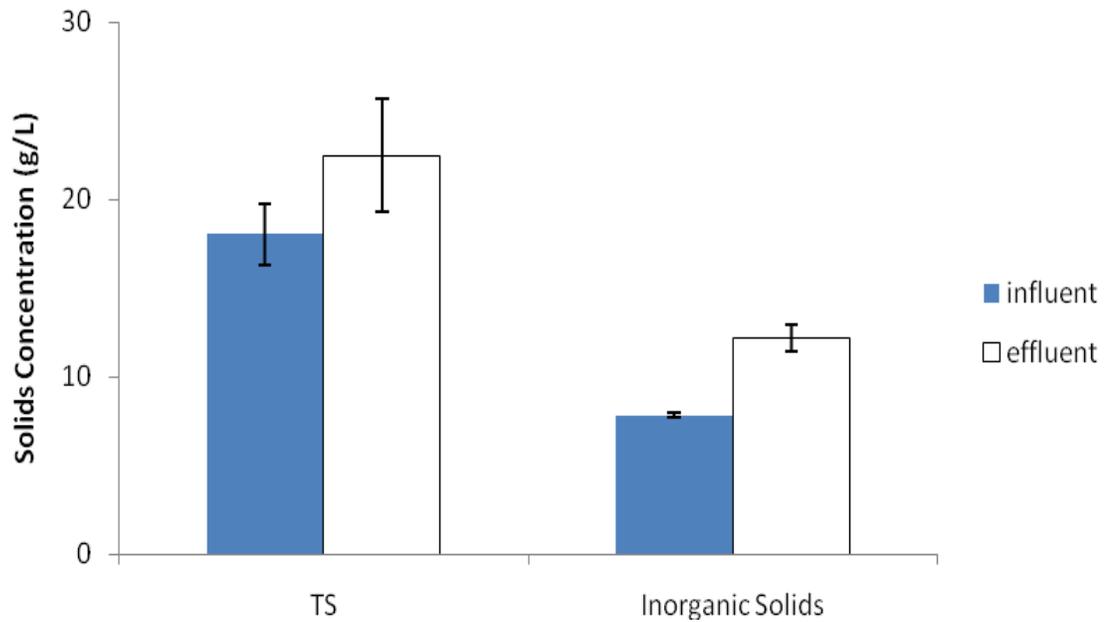


Figure 4.5 Total solids and inorganic solids contained in reactor supernatant before and after precipitation reaction.

#### 4.4.1 Batch reactor solids analysis

X ray diffraction indicated two crystalline compounds present in the dried solids (Fig. 4.6), struvite and sylvite (KCl). Analysis of the air-dried solids showed that the mass loss was  $65.9 \pm 0.14\%$  ( $N = 6$ ) by ignition at  $550^\circ\text{C}$ , this represents loss of organic matter, hydrates and other volatiles such as ammonium. For example, if all the water molecules and  $\text{NH}_4$  of pure struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) were volatilized at  $550^\circ\text{C}$ , then the mass would be reduced by 48.6%. If the struvite content could be estimated, then the carbon determination would be easier. ICP-OES analysis of the digested dried solids showed that the concentrations of K, P, and Mg were 3.8, 5.6 and 3.3% respectively (Table 4.3). All Mg in the precipitate was soluble at pH 1.5 and no crystalline forms of Mg were found using XRD. This suggests all Mg present is in the form of struvite.

Table 4.3 Elemental analysis of air-dried reactor solids and percent soluble at pH 1.5 to estimate struvite content.

	<b>P</b>	<b>Mg</b>	<b>Ca</b>	<b>TN</b>	<b>K</b>	<b>Na</b>
<b>Nutrients from total digestion (%)</b>	5.6 (0.1)	3.3 (0.1)	4.2 (0.3)	6.3 (0.2)	3.8 (0.0)	1.5 (0.0)
<b>Nutrients soluble at pH 1.5 (%)</b>	4.5 (0.1)	3.3 (0.1)	3.9 (0.2)	2.5 (0.1)	3.4 (0.0)	1.3 (0.0)
<b>Nutrients in 100 g (M)</b>	0.146	0.135	0.098	0.178	--	--
<b>Estimated struvite in 100 g (g)</b>	35.6	33.1	--	43.4	--	--

Note: Maximum struvite content (244 g per mole) is estimated as the mole fraction of the least abundant soluble element.

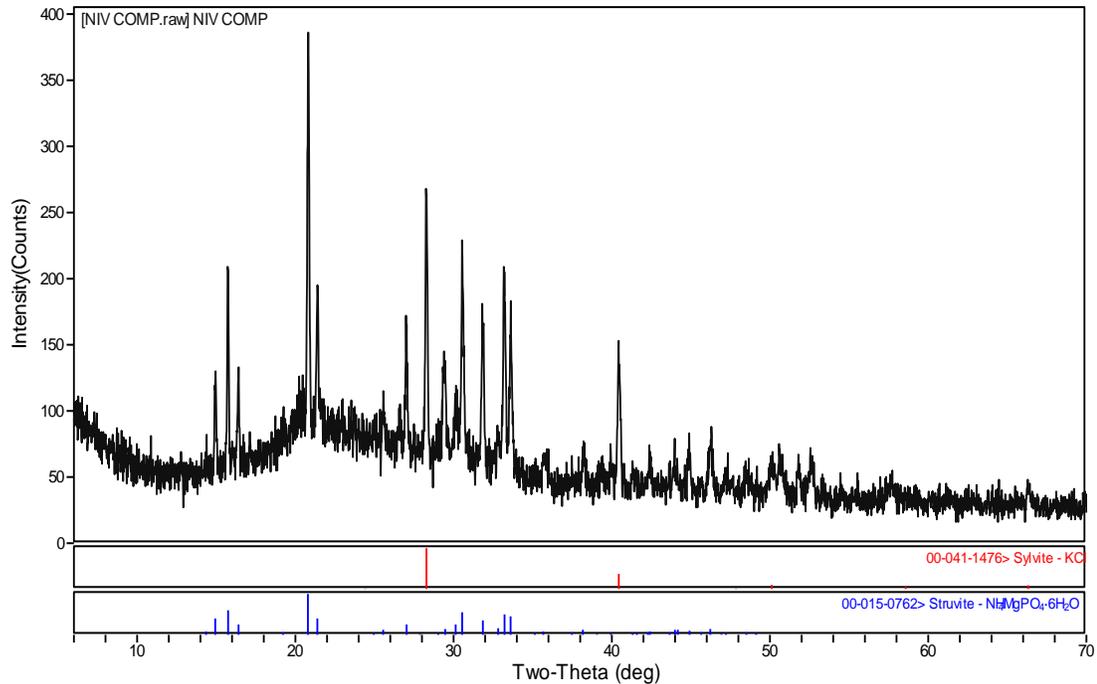


Figure 4.6 Dried solids analyzed with XRD indicating struvite and sylvite (KCl) presence.

Another method for identification of precipitate compounds was to infer by the molar mass of nutrients removed from the supernatant (Table 4.3). If only struvite were produced, then equal molar mass removal of P and Mg would be found. However, P was removed from the supernatant in excess of Mg by  $1 \text{ mM L}^{-1}$ , indicating that other phosphorus compounds were produced, the most likely being calcium phosphates. Calcium phosphates are a group of different compounds and do not have a specific Ca:P molar ratio, but an approximate ratio of 1.5:1 can be assumed (Valsami-Jones, 2001). Even so, 3.3 mM Ca was removed from the supernatant, indicating that Ca precipitated in

other forms as well. Another possible Ca precipitate is  $\text{CaCO}_3$ , but there was no evidence of this in the XRD analysis. Not all precipitated Ca settled, as can be seen from an increase in particulate calcium forms (Fig. 4.4). This was evidence of unsettled calcium phosphate flocs that precipitated but remained suspended due to the viscosity of the manure and the flocs' small particle size. The literature suggests that the low Mg:Ca ratio in this supernatant should produce less struvite than the theoretical yield (Le Corre et al., 2005; Zhang et al., 2010), but this experiment differed from other pilot reactors and allowed much more time for small precipitates to settle. More study is needed to provide certainty of the precipitates formed in this experiment.

Personal observations from laboratory work with high-calcium manure supernatants suggested that struvite and calcium phosphate precipitate in very different forms, affecting their ability to settle and be removed from the supernatant. This observation concurs with literature stating the size of amorphous calcium phosphate (3- to 100 nm) is dependent on Ca:P ratio, concentration and pH (Dorozhkin 2010). Struvite forms crystals that increase in size from agglomeration or crystal growth, potentially forming large particles (50 to 500  $\mu\text{m}$  size particles are common depending on the reactor configuration). Calcium phosphates precipitated as amorphous flocs of low density and little structural integrity. Flocs broke apart when the supernatant was stirred and then settled very slowly. Preliminary laboratory work with high-calcium lagoon supernatants showed reduced mixing time increased the volume of settled precipitate. Maximum precipitate settled with zero mixing time, whereas 10 min of mixing produced no settled precipitate at all in 4 h. This suggests that mixing destroys the floc structure, and the floc particles do not settle out. Other researchers have noted similar problems when the Ca:P

ratio was 2.67:1 (Moerman et al., 2009) or the Mg:Ca ratio was less than 1:1 (Le Corre et al., 2005; Zhang et al., 2010). In our experiment, the dissolved Ca:P ratio was 3.4:1 and the Mg:Ca ratio was 0.4:1, suggesting that Ca concentration was too high to produce struvite. Among researchers who investigated this subject, some recorded total Ca and Mg (soluble in acid at pH 1 to 2; Zhang et al., 2010), whereas others recorded dissolved forms (Le Corre et al., 2005; Moerman et al., 2009). Better comparison of the results and information of precipitate settleability could be made if dissolved and total forms were recorded in all studies. Problems of precipitate loss to effluent in upflow reactors were avoided in the experiment by minimal mixing of reactor contents after alkali addition. As well, a long settling time collects precipitate and suspended particulate P usually lost to effluent.

Composition of the settled solids was deduced to be no higher than 33% struvite if all Mg soluble at pH 1.5 is from struvite. There may be quantities of other Mg precipitates that are also present and soluble at pH 1.5, but no evidence of these were found with XRD analysis. Determination of the organic carbon content required an assumption that loss on ignition removed all carbon and that the mass loss of volatile hydrates and  $\text{NH}_4$  were only from struvite. Theoretical mass loss of 33 g of struvite (the assumed struvite content in 100 g of precipitate) from heating to 550° C would leave 16 g of inorganic solids and remove 17 g of volatiles. Total solids without struvite volatile loss would then be 51 g per 100 g of precipitate, yielding 49 g of organic solids. Therefore, assuming no other hydrated or volatile species, about half of the dried solids were organic carbon. When comparing the nutrient analysis with that of pure struvite, the solids contain 5.6% vs. 12.7% P, 6.3% vs. 5.7% N, and 3.8% vs. 0% K. The total N content of

the solids was not impaired due to calcium phosphate precipitation but was probably high due to the high organic solids content. Table 4 shows that 60% of the  $\text{NH}_4$  in the dry precipitate was not soluble at pH 1.5 and is thus assumed to be related to the organic fraction. The use of KOH instead of NaOH had a favorable effect on the total K content of the final product.

#### **4.5 Conclusions**

The gravity-settling batch reactor was very easy to operate and removed >76% of TP with a 24 h settling period. P was removed by precipitate formation and a long settling time, which indicated particulate forms as well as  $\text{P-PO}_4$  could be removed. The settled sludge was difficult to dry and was malodorous due to the high (~50%) organic solids content. More research is needed to determine optimum low-energy drying and grinding processes appropriate at a farm scale. The struvite purity was estimated to be 33%, assuming that all of the Mg content was attributable to struvite crystals. For total nutrient content, the precipitate contained 5.6% P, 6.3% N, and 3.8% K whereas pure struvite would have 12.7% P, 5.7% N, and 0% K. The high Ca concentration in the supernatant may have reduced struvite formation in favour of amorphous calcium phosphates, but these compounds settled to some extent, adding to total P removal. Since this method removes all settleable precipitates, high Ca content was not found to be a problem in achieving high TP removal. The low struvite content did not impair the N content of the product, and the use of KOH as an alkali contributed favourably to the product value as a fertilizer.

#### 4.6 Objective 2) Elutriation of Manure Solids with Struvite Reactor Effluent

Struvite precipitation requires P-PO<sub>4</sub> as a P source and after this is removed, additional P may be derived from particulate P that makes up the majority (70-90%) of TP in manure solids. The concept of elutriation is to re-circulate reactor effluent back through manure in a storage lagoon where equilibrium dynamics can dissolve a portion of the mineral P. The equilibrium equation for struvite is

$$K_{sp} = 2.51 \times 10^{-13} \text{ in moles/L} \quad \mathbf{9)}$$

$$K_{sp} = [Mg][NH_4][PO_4] \text{ in moles/L} \quad \mathbf{10)}$$

Using a K<sub>sp</sub> value of  $2.51 \times 10^{-13}$  gives a concentration of 15 mg/L PO<sub>4</sub>, but as other solubility products have been used (see page 14), this value may not be correct. A K<sub>sp</sub> of  $3.3 \times 10^{-10}$  indicates PO<sub>4</sub> would be 169 mg/L. This is important because 169 mg/L PO<sub>4</sub> is reasonable feedstock for a struvite reactor while 15 mg/L PO<sub>4</sub> is not.

An increase in concentration may warrant recycle back through the struvite reactor where this P could be reclaimed. No literature has been found investigating the concept of using P depleted reactor effluent to “wash” P rich manure solids and dissolve particulate P into P-PO<sub>4</sub>.

##### 4.6.1 Methods

Due to uncertainty in the K<sub>sp</sub> value and unknown ion activities in the supernatant determining the feasibility of elutriation was carried out in the lab experiment rather than by partition equilibration calculations. Particulate P solubility is dependent on both pH

and ion activity, so tests were conducted with pure water to find optimum elutriation potential as well as tests of real lagoon supernatant reactor effluent of different pH levels. Manure solids from a previous experiment were collected and dried. They were selected because a majority of P had precipitated from the supernatant into the solids, similar to what might be expected from a real lagoon. Approximately 2 g of dried manure was weighed into plastic 50 ml centrifuge tubes (four replicates) and 10 ml of a wash medium added. The wash mediums were deionized water (pH 7) and real lagoon supernatant that had been dosed with NaOH to pH 8 and allowed to settle for 2 hrs. The liquid collected from the surface after this reaction synthesized struvite reactor effluent (Table 4.4). A portion of this synthesized effluent was also pH adjusted to pH 7 with HCl. The tubes were shaken for 1 minute and then centrifuged (8000 RPM for 5 min), filtered (0.45 $\mu$ m syringe filter), diluted (0.5% HNO<sub>3</sub>) and analyzed for P-PO<sub>4</sub>, total dissolved P, Mg, Ca (ICP-OES), and NH<sub>4</sub> (FIA). All analysis techniques and analysis equipment used in this experiment have been described in sections 4.2 and 4.3 of this chapter. The washing process was repeated with the same dried manure sample and the wash medium for 10 or more consecutive washes. Care was taken to retain all manure particles in the decanting process and wash medium volume was calculated by weighing samples. This entire process was repeated with each wash medium: deionized water, effluent at pH 8 and effluent at pH 7. At the end of each trial the manure solids were dried, weighed and then ground and digested to determine TP, Ca, and Mg, as previously described. These results were compared against those of the original dried manure solids to form a mass balance of nutrients removed by elutriation.

A mass balance was conducted in which the exact weight of each wash cycle supernatant and the corresponding concentration were used to calculate total mass of nutrients collected during the run. The mass of effluent background nutrient concentration was subtracted from each wash cycle concentration, giving the net gain for each elutriation medium. These figures were used to calculate the mass of each nutrient removed from the total nutrients contained in the dry manure solids at the beginning of the experiment.

Table 4.4 Dissolved nutrient concentrations in supernatant used to elutriate manure solids. Total dissolved P (TDP) includes P-PO<sub>4</sub> and organic dissolved P. Standard deviations are in parentheses.

	TDP mg/L	P-PO <sub>4</sub> mg/L	Mg mg/L	Ca mg/L	NH <sub>4</sub> mg/L
<b>pH 8</b>	21.1 (0.9)	18.3 (1.2)	106.2 (1)	105.5 (0.7)	89.4 (0.5)
<b>pH 7</b>	64.2 (0.3)	59.0 (4.5)	144.7 (0.2)	117.7 (0.8)	96.5 (2.1)

#### 4.6.2 Results

Elutriation with deionized water dissolved >150 mg /L P from manure solids for the first two washes and less for each consecutive wash (data is displayed in Fig. 11.2 Appendix A). This test proved that enough P could be dissolved from manure solids by pure water to feed a struvite reactor (50 mg/L could be the minimum required).

Reactor effluent (pH 8) used as an elutriation medium removed >50 mg PO<sub>4</sub>/L for the first five wash cycles (Fig. 11.4). These values are presented as final wash P concentration minus initial effluent P, which gives the net removal from each elutriation

wash. When the effluent pH was adjusted to 7, net P recovery from solids did not improve (Fig. 11.3), likely because the lower pH dissolved suspended P particulates in the effluent, increased P-PO<sub>4</sub> concentration and limited dissolution of additional P due to the common ion effect.

Magnesium dissolution from solids was most effective with deionized water and much less was recovered when reactor effluent was used. Acidification of effluent to pH 7 increased dissolved Mg in the supernatant and only produced enough net Mg for use in a struvite reactor in the first 2 wash cycles. Calcium removal was limited using deionized water and the net removal with effluent was negative, meaning Ca precipitated in the manure solids during the experiment. Reasons for the precipitation of soluble Ca in the solids was not clear, nor was it apparent what Ca precipitates formed at pH 8 and 7, as P was simultaneously dissolved from the solids. Mg was removed at a higher molar mass than P, suggesting precipitation of Ca with P, perhaps due to the formation of calcium phosphates.

Dried manure was digested before and after the elutriation process but sample variation and high standard deviation obscured any difference in nutrient concentration (Table 4.5). Addition of the nutrient mass removed from each wash cycle gave more accurate indication of effectiveness of elutriation (Table 4.5). Elutriation did not remove significant quantities of P from manure solids: data of nutrients recovered in the washing process indicated 8% TP recovery using deionized water and less with reactor effluent. Effluent at pH 7 captured 2.2% of TP and 3.7% at pH 8 (Table 4.5).

Table 4.5 Nutrients in manure solids and those recovered by elutriation.

<b>Digested dry manure solids</b>			
	<b>TP mg/dry g</b>	<b>Mg mg/dry g</b>	<b>Ca mg/dry g</b>
<b>Original manure solids</b>	68.7 (4.6)	19.9 (0.8)	110.7 (18.3)
<b>After elutriation pH 8</b>	62.1 (3.3)	18.1 (0.8)	95.9 (15.5)
<b>After elutriation pH 7</b>	66.7 (3.2)	19.4 (0.7)	97.3 (12.1)

<b>Recovered nutrients</b>			
(% changed from original manure: minus indicates removal)			
	<b>DTP</b>	<b>Mg</b>	<b>Ca</b>
<b>Deionized water</b>	-8.0	-14.3	-0.7
<b>Effluent pH 8</b>	-3.5	-9.5	1.7
<b>Effluent pH 7</b>	-2.1	-5.6	2.1

### 4.6.3 Conclusions

Elutriation provided a net removal of P-PO<sub>4</sub> in adequate concentration (>50 mg/L) to be considered a feedstock for a struvite reactor. These data indicated acidified manure wash medium did not improve elutriation compared to un-acidified effluent. This was a result of increased PO<sub>4</sub> concentration in the acidified supernatant due to dissolution of particulate forms of P already present in the effluent at the lower pH. At the higher

PO<sub>4</sub> concentration, less P was dissolved from P solids resulting in lower net removal.

Elutriation on a commercial scale might involve pumping reactor effluent through manure solids and then processing the liquid through the reactor again. The infrastructure and costs involved in performing this operation would not yield an appreciable net removal of P from the solids, ranging from 2 to 4% of TP with several cycles. The small change in net TP recovery leads to the conclusion that it is not a feasible method to remove P from manure solids.

## **5 Anaerobic fermentation of manure to increase P-PO<sub>4</sub>**

The working hypothesis for the experiments in this chapter was that natural acids produced during fermentation are adequate to lower manure pH and dissolve mineral P solids. The experiments are presented in two sections. Section 1 contains the experimental results of an investigation into P-PO<sub>4</sub> solubility from anaerobic fermentation of hog manure. The results of this experiment showed a significant drop in pH and an increase in P-PO<sub>4</sub>, however, the manure used in the experiment was very low in urine and not representative of commercial hog manure in MB. Section 2 contains the results from similar fermentation trials with three more manures, each from an operating commercial hog farm. From these additional trials, the chemical characteristics that governed pH change and subsequent P-PO<sub>4</sub> increase are discussed.

### **5.1 Section 1: Anaerobic fermentation of hog manure to lower pH and increase P-PO<sub>4</sub>**

#### **5.1.1 Introduction**

This experiment was designed from initial observations of P-PO<sub>4</sub> abundance in manure during aerobic storage (section 3.4) and anaerobic storage (manure kept in tightly sealed containers often resulted in lower pH and higher P-PO<sub>4</sub>, even when stored at 4 C).

Fresh hog manure typically holds from 10 to 25% of total phosphate (TP) as P-PO<sub>4</sub> (Christensen et al. 2009) the rest being associated with the manure solids, either bound in organic P as phytic acid (7-15% of TP, Baxter et al. 2003) or as mineral solids

such as struvite and calcium phosphate (50- 70% of TP, Christensen et al. 2009). A wide variation in reported soluble P content was found in the literature suggesting other factors contribute to its abundance, both as absolute amounts and as a proportion to TP. Research into the causes of high or low relative P-PO<sub>4</sub> in manure has not been found in the literature, yet this information is vital to P reclamation. Removal of TP by a precipitation reactor was limited by the abundance of P-PO<sub>4</sub>, so a reactor that reclaimed most of the P-PO<sub>4</sub> from supernatant may have left 80-90% of TP in the solids. In order to increase P recovery from manure, P from solids must be transferred to the liquid phase and the processes that enable this must be understood.

The working hypothesis of this research was that acidic conditions arising from two processes of natural acid production from fermentation can dissolve P from the solid phase to the dissolved form. The processes of VFA and CO<sub>2</sub> production responsible for acidification of manure are driven by manure TS and more specifically, VS. Acidogenic microbial communities create VFA (Ucisik and Henze 2008) and CO<sub>2</sub> (and carbonic acid due to equilibrium reaction), but when methanogenic bacteria become established, they consume VFA and CO<sub>2</sub>, stabilizing or raising manure pH. For this reason, manure HRT is important. All of these processes are described in detail in section 2.7.1 of the Literature Review.

The purpose of this experiment was to investigate the abundance of P-PO<sub>4</sub> and other struvite constituents during anaerobic fermentation. Varying HRTs were tested to find optimum conditions for acidification. To simulate on-farm conditions, where

manure may not be continuously stirred, an unstirred reactor was also tested for acid build-up and P-PO<sub>4</sub> concentration.

## 5.2 Methods

Manure was collected from stalls at the Glenlea University of Manitoba research farm, a conventional barn rearing two month old feeder pigs. The manure was collected from the slatted stalls and was comprised of mostly faeces. The manure solids were mixed with tap water into a slurry of 2.4% TS and a portion was used to fill the reactors, but the majority was frozen in one liter containers, making a uniform supply for the duration of the experiment. Physical and chemical characteristics of the diluted manure solids were measured and showed low concentrations of alkalinity and TN, due to a lack of urine in the manure (Table 5.1). For simplicity in language, this manure mixture will be called manure in this chapter, although it is fundamentally different due the low urine content.

Table 5.1 Characteristics of manure solids collected at Glenlea research farm and diluted to 24 g/L total solids.

TS (g/L)	VS (g/L)	Alkalinity mg/L as CaCO <sub>3</sub>	TP mg/L	P-PO <sub>4</sub> (mg/L)	NH <sub>4</sub> (mg/L)	TN (mg/L)	Mg <sub>diss</sub> (mg/L)	Ca <sub>diss</sub> (mg/L)	VFA (mg/L)	pH
23.9 (1.1)	18.3 (0.2)	1563 (247)	741 (95)	88 (8)	94 (8)	1041 (74)	67 (5)	51 (3)	391 (8)	7.46

Note: Values are the mean of triplicate samples of mixed manure slurry with standard deviation in parenthesis.

Two identical stirred reactors were used to verify manure response to anaerobic fermentation, and a single unstirred reactor was employed to compare the effects of stirring. Fresh diluted manure was poured into cylindrical 4 liter Plexiglas reactors fitted

with top mounted stirring paddles and small motors (Arrow 6600, Arrow Engineering, Hillside, NJ, USA), except for the unstirred reactor which had no mixing mechanism.

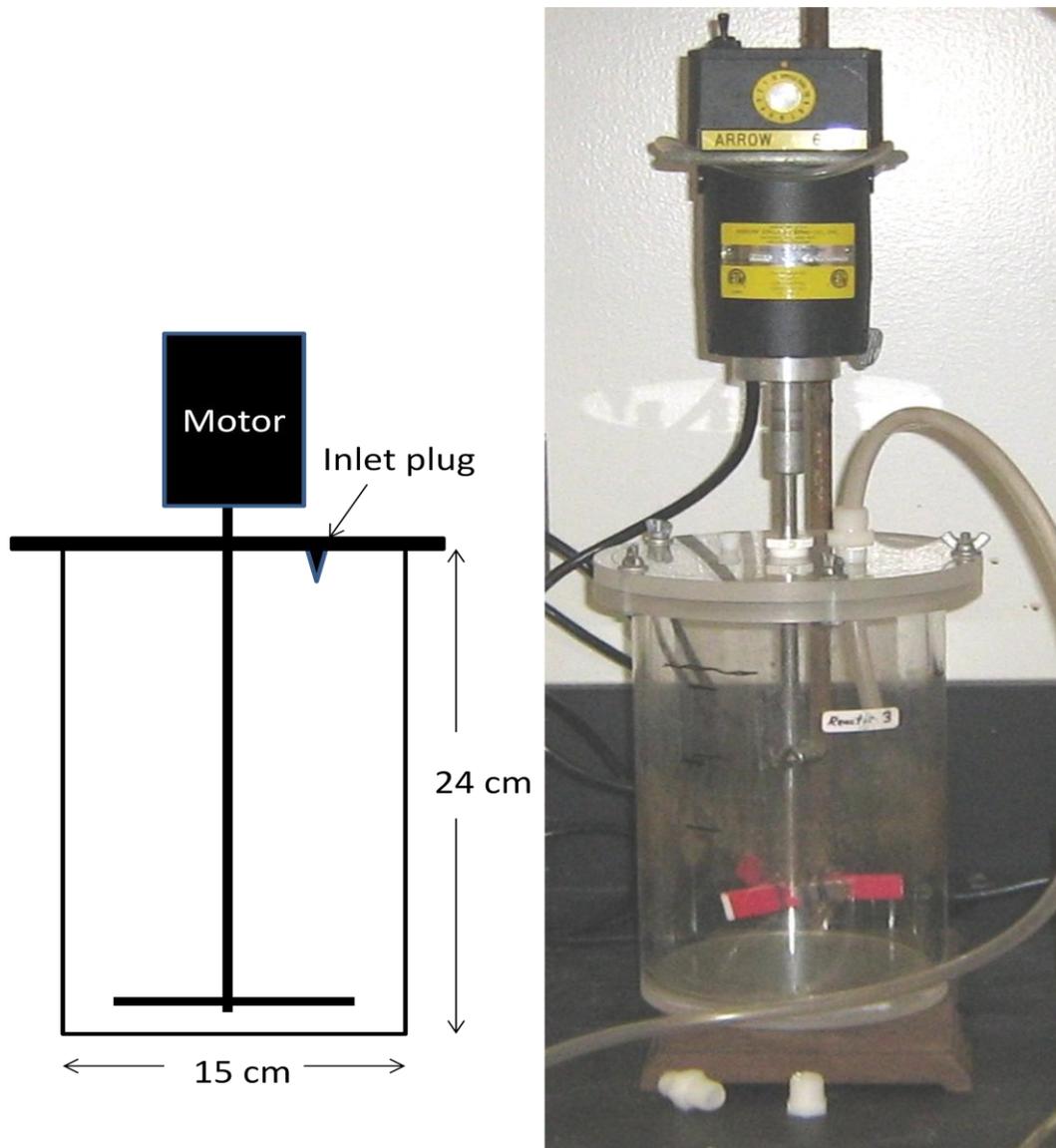


Figure 5.1 Fermentation reactor

Access ports (3/4") on the top of the reactor allowed pH measurement and manure addition and removal. The reactors were kept sealed except to take pH measurements

daily and oxidation reduction potential was measured at -180 to -200 mV (Accumet AP115, Fisher Scientific, Waltham Ma, USA) indicating anaerobic conditions. The extent of acidification was tested in a batch mode (no feedstock additions) at room temperature with two reactors stirred at 90 RPM and one unstirred reactor agitated by hand once a day. When reactor pH stabilized or began to increase, the reactors were taken from batch mode to flow through mode. This involved removing 1 liter of manure with a 3/8" hose and peristaltic pump on a daily basis and replacing it with manure kept from the original slurry, thus replacing the entire volume in 4 days and creating a 4 d HRT. An eight d HRT required one liter manure replacement on alternate days and the 12 d HRT required one litre of manure every third day. Approximately two cycles of each HRT elapsed before the effluent was sampled.

Reactor effluent was sampled as two slurries: the complete mixed slurry as it exited the reactor, and the liquid portion of the mixed slurry after it had settled for one hour. This provided opportunity to understand changes in total manure slurry characteristics and in the portion that would be processed through a struvite reactor. Sampling was conducted (in triplicate) on each of these fractions included TS, VS, and alkalinity (Clesceri et al. 1998). Centrifuged (8000 RPM 5 min) and filtered manure (0.2  $\mu\text{m}$  syringe filter) was tested for VFA concentration with headspace gas chromatography (CP 3800 GC, Varian, Middleburg, The Netherlands) and included acetic, propionic, butyric, valeric, and caproic acids. For nutrient analysis, filtered (0.45  $\mu\text{m}$ ) and unfiltered manure samples were diluted 8.3 fold with  $\text{HNO}_3$  (0.5% v/v). The acid dissolved P, Mg and Ca present in particulate mineral form in the unfiltered samples. Concentrations of P, Mg, Ca and N were measured by wet digestion of each slurry using a Hach Digestahl® as

previously described. Processed samples were measured for P-PO<sub>4</sub> by ascorbic acid method in a spectrophotometer, NH<sub>4</sub><sup>+</sup> in a flow injection analyser as previously described in section 4.2.1.

### **5.3 Results**

The two stirred reactors behaved comparatively during the experiment. The single unstirred reactor was only sampled for the liquid portion due to difficulty in getting a representative mixed sample with a peristaltic pump.

#### **5.3.1 pH**

Initial manure pH was 7.40 and decreased in all reactors over the batch mode period. Perhaps due to imperfect air sealing, the pH of the stirred reactors was not identical. On two occasions the ½ inch influent feed plug on the top of Reactor 2 was left open overnight and the subsequent pH reading was noticeably higher (e.g., Day 13 in Fig. 5.2). Reactor 1 reached a pH low of 5.61 after 12 days and Reactor 2 pH reached 5.75 after 15 days (Fig. 5.2). The unstirred reactor pH dropped to 5.84 in 19 days (data not shown).

After two HRT cycles of 4d, both stirred reactors had a pH of 6.33. The 8d HRT produced a pH of 5.84 and 6.08 in Reactors 1 and 2, while the 12 d HRT produced pH of 5.84 and 6.01 in Reactors 1 and 2 respectively. The TS of the stirred reactors remained consistent throughout the experiment whereas the unstirred reactor TS varied due to difficulty in removing a homogeneous portion of solids and liquid with the peristaltic pump and no mixing mechanism. Thus, measured parameters affected by TS were

variable in the unstirred reactor. In spite of this, nutrient measurements were not significantly different between reactors at 4d HRT ( $p=0.13$ ). At higher HRTs the stirred had significantly more dissolved nutrients than the unstirred reactor ( $p=0.001$ ,  $>p=0.001$ ).

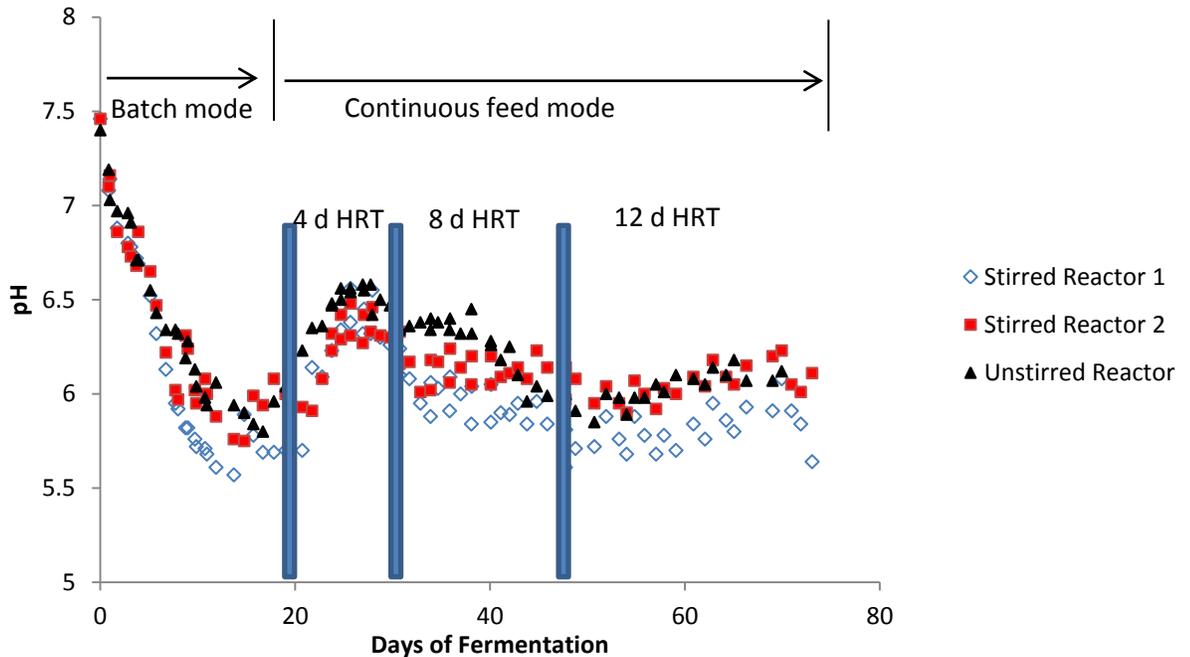


Figure 5.2 The pH change from anaerobic conditions of fresh manure in two stirred 4 litre reactors.

Alkalinity as  $\text{CaCO}_3$  increased from  $895 \pm 40$  mg/L in influent manure liquid (settled for 1 hr) to  $1351 \pm 7$  and  $1382 \pm 32$  mg/L in effluent liquid of the stirred reactors at 12d HRT, but alkalinity of complete mixed slurry showed no trends over time. The VFA concentration approximately doubled at 4 d HRT from influent levels and increased from  $391 \pm 8$  mg/L to  $816 \pm 49$  mg/L for both stirred and unstirred reactors. VFA data from 8 and 12 d HRT was lost due to malfunction of the headspace GC.

### 5.3.2 Dissolved Nutrients

There was no significant difference found in dissolved nutrients in the liquid fraction compared to those measured in the mixed manure slurry. Measurement of dissolved nutrients between the two stirred reactors was not significantly different for most nutrients (Table 5.2). The concentration of all tested nutrients increased with increasing HRT except  $\text{NH}_4$ , which had high initial response at 4 d HRT and then decreased somewhat. Dissolved P increased from 3.0 mM/L ( $92 \pm 5$  mg/L) in influent manure to 7.6 mM ( $231 \pm 13$  mg/L) at 12 day HRT. The molar ratio of struvite components is 1:1:1 for P, Mg and  $\text{NH}_4^+$  and the theoretical struvite formation potential was limited by the nutrient in lowest abundance. Struvite formation potential increased from 2.6 mM in influent manure (Mg limiting) to 7.4 mM at 12 day HRT, which was  $\text{NH}_4^+$  limited (Table 5.2). Fermentation had little effect on the dissolved Ca:Mg ratios, which were near 0.5. Using the data from total digestion of the manure, the portion of nutrients soluble at different HRTs revealed that on a concentration basis, dissolved P increased from 10% of TP in influent manure to 27% at 12 d HRT. At 12 d HRT almost all Mg (80%) was converted to soluble form, whereas only 18% of Ca was dissolved (Table 5.3).

One difference between the stirred and unstirred reactor effluent was the level of TP in the supernatant portion (due to mechanical breakdown of solids) but the concentration of P- $\text{PO}_4$  was similar in both reactor types. In the unstirred reactor, P- $\text{PO}_4$  concentration reached a maximum of 6.4 mM at 8 d HRT, compared with 7.6 and 7.0 mM in the stirred reactors at 12 d HRT.

Table 5.2 Dissolved nutrients measured in influent manure and reactor effluent at 4, 8, and 12 day hydraulic retention times (HRT) in stirred and unstirred reactors.

HRT	mM (stdev)				mg/L
	P-PO <sub>4</sub>	Mg	Ca	NH <sub>4</sub>	VFA
<b>Influent</b>	3.0 (0.02)	<b>2.6</b> (0.02)	1.1 (0.02)	4.7 (0.01)	338 (100)
<b>Stirred reactor 1</b>					
<b>4 day</b>	<b>5.5</b> (0.02)	6.1 (0.07)	3.0 (0.15)	11.5 (0.07)	776 (26)
<b>8 day</b>	<b>7.3</b> (0.08)	7.7 (0.07)	4.3 (0.05)	9.2 (0.06)	NA
<b>12 day</b>	7.6 (0.03)	9.0 (0.07)	4.9 (0.05)	<b>7.4</b> (0.07)	NA
<b>Stirred reactor 2</b>					
<b>4 day</b>	<b>5.8</b> (0.07)	6.3 (0.06)	3.0 (0.04)	11.4 (0.08)	856 (24)
<b>8 day</b>	<b>6.4</b> (0.06)	7.2 (0.07)	3.2 (0.03)	9.9 (0.07)	NA
<b>12 day</b>	<b>7.0</b> (0.04)	8.8 (0.09)	3.9 (0.04)	8.1 (0.03)	NA
<b>Unstirred reactor</b>					
<b>4 day</b>	<b>4.7</b> (0.06)	5.2 (0.15)	2.3 (0.17)	11.8 (0.02)	746 (139)
<b>8 day</b>	<b>6.4</b> (0.04)	6.5 (0.03)	3.3 (0.03)	10.7 (0.02)	NA
<b>12 day</b>	<b>6.0</b> (0.03)	8.2 (0.08)	3.3 (0.03)	8.8 (0.02)	NA

Notes:

Values are means of triplicate samples with standard deviation in parenthesis  
 Bold faced values indicate the limiting component for struvite formation  
 VFA data was lost for 8 and 12 d HRT due to instrument malfunction

Table 5.3 Dissolved nutrient concentration of manure slurry as a percentage of total manure nutrients under anaerobic conditions from pooled stirred reactor data.

	<b>P-PO<sub>4</sub> %</b>	<b>Mg %</b>	<b>Ca %</b>	<b>NH<sub>4</sub> %</b>
<b>Influent manure</b>	10 (1)	25 (1)	4 (0)	13 (0)
<b>4 day HRT</b>	19 (1)	55 (1)	9 (1)	43 (0)
<b>8 day HRT</b>	25 (2)	61 (2)	13 (2)	26 (1)
<b>12 day HRT</b>	27 (1)	80 (2)	18 (2)	23 (1)

Notes:

Values are derived from filtered nutrient concentration and digested manure nutrients, from pooled replicate stirred reactors. Standard deviations in parenthesis.

### 5.3.3 Phosphorus forms

Nutrient data from filtered, unfiltered and digested samples was used to determine P forms present in mixed manure slurry and in the liquid portion of settled slurry (Figs. 5.3 and 5.4). TP in mixed manure was consistent through all HRTs but in the settled liquid portion TP increased significantly, from 193 ( $\pm 4$ ) mg/L in fresh manure to 393 ( $\pm 19$ ) mg/L at 12 d HRT (Fig. 5.4). Unstirred settled liquid TP remained lower and ranged from 153 ( $\pm 10$ ) to 249 ( $\pm 5$ ) mg/L throughout all HRTs. Total solids and TP both increased in stirred reactor settled liquid (Fig 5.5). This TP increase was primarily from the increase in P-PO<sub>4</sub> but also from mineral particulate P and organic particulate P that increased on account of physical breakdown of solids from stirring. Due to the effect of additive standard deviation on calculated values, precision of organic particular P is low, but increasing trends are evident in P-PO<sub>4</sub> and a decreasing trend suggested for mineral

particulate P (Fig. 5.3). Organic dissolved P was very small and sometimes hidden in sample variance between the spectrophotometer and ICP analysis.

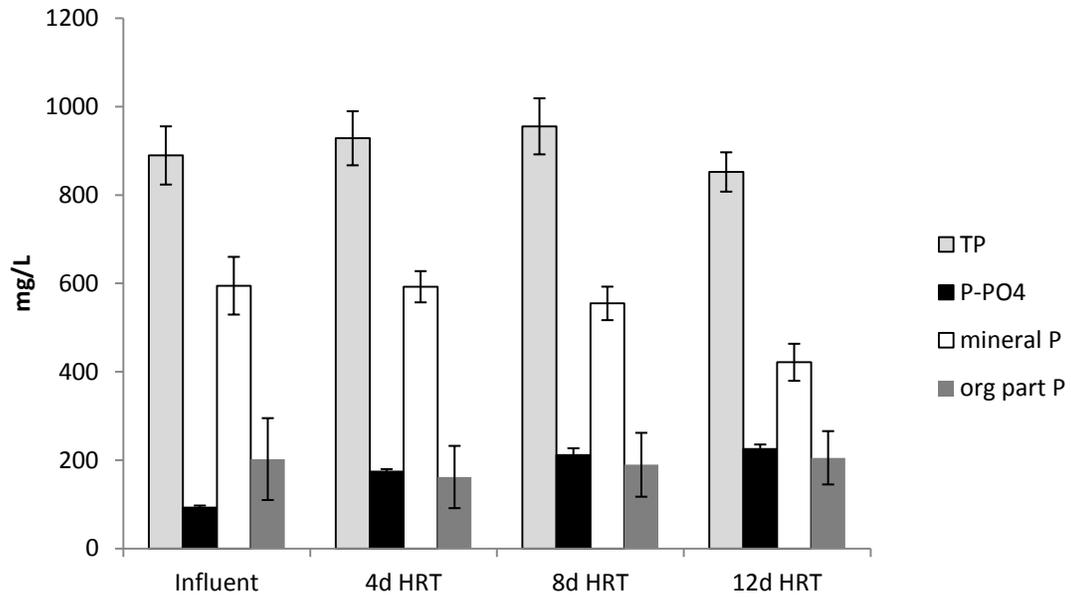


Figure 5.3 Phosphorus forms in mixed manure from stirred reactors.

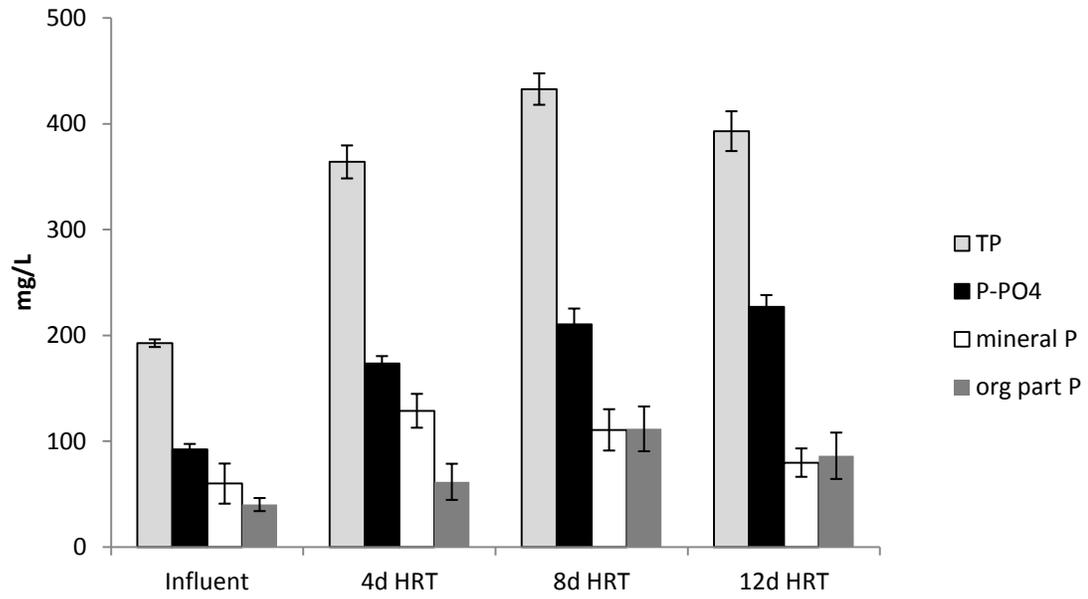


Figure 5.4 P forms in the stirred reactor supernatant after 1 hr settling.

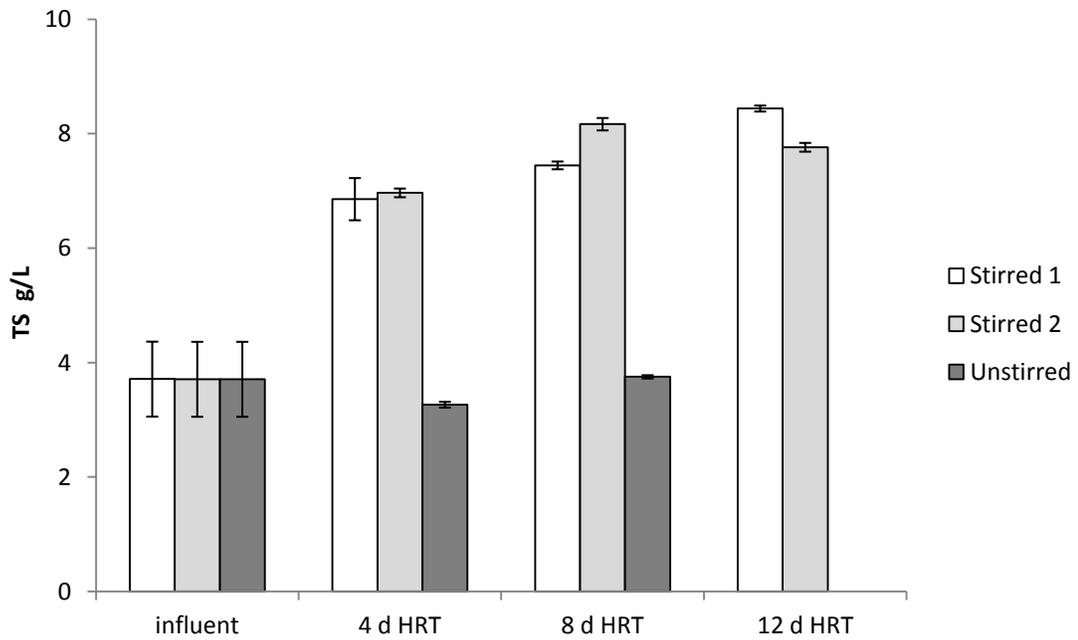


Figure 5.5 Total solids in effluent supernatant of manure settled for 1 h from stirred and unstirred reactors.

## 5.4 Discussion

Manure pH decreased in all reactors from the anaerobic conditions applied during the experiment. During the batch mode period, this trend extended with time until equilibrium was reached in 12 to 19 days, depending on the reactor. The procedural mistake of the ½ inch intake plug being left off overnight resulted in increased pH levels from which the reactor took several days to recover. This suggests that a portion of the pH decrease was from CO<sub>2</sub> accumulation in headspace which then increased the concentration of carbonic acid in the manure. By leaving the cap off, CO<sub>2</sub> could escape from the bioreactor, thereby reducing the concentration of HCO<sub>2</sub>. This adds to the evidence that carbonic acid accumulation contributed to the acidity of the manure.

Similar acidic conditions have been created in other studies operating pre-treatment reactors for municipal solids for the purpose of pathogen destruction (Puchajda and Oleszkiewicz 2006). These authors found pH decreased from 6.05 to 5.2 in 5 days and VFA increased from 2,000 to 10,000 mg/L over 9 days Yuan et al. (2009) noted that, after five days of anaerobic fermentation of waste activated sludge, the pH declined from 7.3 to 6.4 and not lower, even though VFA production continued to rise and precautions were taken to keep the reactor free of methanogens. Yuan et al. (2009) proposed that NH<sub>4</sub><sup>+</sup> and phosphate were liberated to solution from cell lysis, and that these buffers also contributed to pH stability. In this experiment, the pH decrease to anaerobic conditions was strongest in batch mode, after which pH increased even when HRT was maintained at 12 d (Fig. 5.2). Methanogenic communities became established over the length of the experiment and consumed some of the acids produced, raising pH increased as a result.

Stirred reactors had slightly lower pH than the unstirred reactor and reached maximum acidity faster, possibly due to a better microbial environment in the homogeneously mixed conditions. Dissolved P and Mg increased in the stirred and unstirred reactors indicating acidification and nutrient dissolution occurred without constant stirring. Maximum theoretical struvite potential increased by 2.5, 2.7 and 2.8 fold in the unstirred and stirred reactors 2 and 1, respectively. Stirring increased TS and TP in the settled supernatant, whereas TS of unstirred reactor liquid was low. The unstirred reactor results are positive because on-farm practices would not likely involve constant mixing of manure. These results show that unstirred manure during anaerobic fermentation produced similar acidic conditions and dissolved comparable quantities of struvite constituents as the energy-intensive stirred method. A low TS, high P-PO<sub>4</sub> feedstock produced in the unstirred reactor would be ideal for a fluidized bed struvite reactor.

The determination of different P forms gave values with high error and was useful only when a definite trend occurred, such as the P forms in the 1 hr settled supernatant at various HRTs (Fig. 5.4). In this case, the increase in TP was evident as well as P-PO<sub>4</sub>. Decreased abundance with each HRT of mineral P in the mixed manure (Fig. 5.3) suggests this was the source of increased P-PO<sub>4</sub> but the error in calculated P forms limits certainty. Even with very careful analytical techniques throughout the experiment, variance in some measurements was large, sometimes exceeding 5% between replicates. This was found with mixed manure sample digestions, whereas liquid manure fractions and filtered samples were more consistent between replicates. When data from the stirred reactors was combined, the standard deviation increased. A variance of 4% between

replicates from the two reactors would result in an 8% variance when reactors were combined. When these aggregate values were used in calculation of P forms such as subtracting one from another, the standard deviation increased while the calculated P form became smaller. This resulted in P form values with standard deviations too large to be useful (for example, organic particulate P in Fig. 5.3). Sampling changes to rectify this problem might involve homogenization of manure, weighing volumetric samples or possibly drying and grinding mixed manure to ensure homogenization.

While Ca was not at levels that would inhibit struvite production, some interesting observations can be made from nutrient solubility in the experiment. Soluble Mg increased from 25% of total Mg (influent manure) to 80% at 12 day HRT, suggesting Mg is almost exclusively associated with the acid soluble mineral fraction of swine manure. This was also found by Daumer et al. (2004) who determined 0% Mg was bound in organic particles in dairy manure while 4-5% of total Ca is bound by biomass. In this study, soluble Ca increased from 4% to 18% of total Ca at 12 d HRT. Over these HRTs pH did not steadily decrease: the pH at 8d HRT and 12 d HRT were almost identical. This indicates that under the same pH conditions, most of the Mg had been dissolved from solids whereas less soluble mineral Ca requires more time to bring Ca into solution. This suggests if Ca levels were a problem in struvite production, a shorter HRT would be advantageous.

#### **5.4.1 Conclusions**

Anaerobic fermentation was effective in decreasing the pH of fresh swine manure and this change caused a significant increase in soluble concentrations of P-PO<sub>4</sub>, Mg, and

N-NH<sub>4</sub>. The increase of each nutrient was stoichiometrically equivalent and theoretical struvite potential of 2.5 to 2.8 fold after 12 d of fermentation. The increase in acidity was attributed to the acidic products of solids decomposition CO<sub>2</sub> and VFA, of which VFA concentration had doubled in 4 days of fermentation. The forms of P present in the manure suggested mineral particulate forms dissolved during the experiment whereas organic particulate forms stayed constant. The overall fraction of soluble P-PO<sub>4</sub> increased from 10% of the total phosphorus to 27%. The increase in dissolved nutrients occurred in both stirred and unstirred reactors, indicating energy intensive stirring is not a requirement for P release.

## **5.5 Section 2: Anaerobic fermentation of commercial manure**

The manure used in the preceding experiment was from a research barn and different from manures at commercial hog operations. NH<sub>4</sub> levels were 5- 10% of many manures, indicating a low level of urine in the manure: making it atypical. In order to verify the results of the preceding experiments using commercial farm manures, the experiment was repeated with some changes:

- 1) A batch reactor system was used in order to eliminate the need to freeze manure. Freezing manure changes the composition of P forms, likely precipitating P-PO<sub>4</sub> out of solution. VFA loss due to sublimation while frozen is likely. Three 4 L reactors were filled once with commercial manure, continuously stirred and sampled in triplicate at 0, 4, 8, and 12 day HRT.

2) Previous experimental results concluded very little difference between stirred and unstirred reactors, resulting in using 3 stirred reactors for all manure trials.

## 5.6 Methods

Manure was collected on three separate occasions from different commercial MB hog operations. At each farm, manure had been stored in pull pits for less than one week. For comparative purposes, the manure fermentation trials are named Manure 1 (low urine manure slurry described and reported in Section 1 of this chapter), and Manure 2, 3, and 4 which were from commercial farms (Table 5.4). Manure 2 and 3 were taken from outside discharge pipes as it was being pumped into lagoons and Manure 4 was taken from under a stall grating inside a barn by farm staff. Manure 1 is very different from commercial manures in terms of VFA, alkalinity, P-PO<sub>4</sub>, and NH<sub>4</sub>, due to the low urine content. It will be labelled “diluted manure solids” (DMS) within this chapter. All manures were “fresh” and had been stored for less than one week at the time of collection. Manure was transported to the lab to fill three 4L anaerobic reactors fitted with a stirring motor and paddle. Manure characteristics of the fresh slurry were measured after 4, 8, and 12 d, except for pH, that was measured daily.

Manure TS, VS, alkalinity, VFA, dissolved and total nutrients P, Mg, Ca, NH<sub>4</sub>, were sampled as previously described in Section 1. During the Manure 4 trial, one reactor was sampled and analyzed daily for dissolved nutrients in addition to the HRT intervals. Analysis of variance was performed with SAS statistical software for tests of significance between reactor replicates, manure types and fermentation times.

Table 5.4 Chemical characteristics of manure slurries used in anaerobic fermentation. Parenthesis denote standard deviation.

<b>manure</b>	<b>TS</b>	<b>VS</b>	<b>VS</b>	<b>VFA</b>	<b>Alkalinity</b>	<b>P-PO<sub>4</sub></b>	<b>TP</b>	<b>NH<sub>4</sub></b>
	<b>g/L</b>	<b>g/L</b>	<b>%</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>
<b>DMS</b>	23.4	17.9	76.5	391	1312	91	890	75
	(4.1)	(0.4)	(2.1)	(8)	(71)	(6)	(20)	(13)
<b>2</b>	23.4	14.9	63.6	8419	7828	298	697	2213
	(0.1)	(0.04)	(0.2)	(630)	(211)	(7)	(8)	(171)
<b>3</b>	24.5	15.2	62.0	9536	7887	357	657	2095
	(0.2)	(0.1)	(0.5)	(516)	(40)	(3)	(17)	(23)
<b>4</b>	74.0	56.5	76.4	4611	10582	229	2518	1640
	(2.7)	(0.1)	(0.7)	(199)	(233)	(14)	(59)	(46)

## 5.7 Results and discussion

The manures tested in this experiment responded differently to anaerobic conditions than the manure tested in Section 1 in terms of pH change and P-PO<sub>4</sub> concentration. Data from Section 1 have been used appropriately here for comparative purposes. Manures 2 and 3 had virtually no change of pH or P-PO<sub>4</sub> in 12 days of storage, while the pH of DMS and Manure 4 decreased (Figs. 5.6-5.9) along with a concurrent increase in P-PO<sub>4</sub>. In a similar way, Mg and Ca did not increase in Manures 2 and 3, while Manure 4 Mg increased from 42 to 84 mg/L by the 4 day HRT with no further increase after that (TS, VS, Mg, Ca NH<sub>4</sub>, VFA, alkalinity and statistical data are in Appendix B). The dissolved nutrients of Manure 4 were sampled daily for and indicated

PO<sub>4</sub> increased steadily during the 12 day fermentation from 229± 14 to 349± 8 mg/L (Appendix B). NH<sub>4</sub> increased significantly in Manure 4 (41 ±4%), but less so in Manure 3 (21± 3%), and there was no change in Manure 2. VFA increased for each manure, although to a greater extent for Manure 4 (99% increase) than for Manures 2 and 3 (27 and 19% respectively). Total solids decreased over the 12 day HRT for all manures (Table 12.2 in Appendix B) and percentage VS decreased also, indicating the destruction of volatile solids during storage (Table 12.3 in Appendix B).

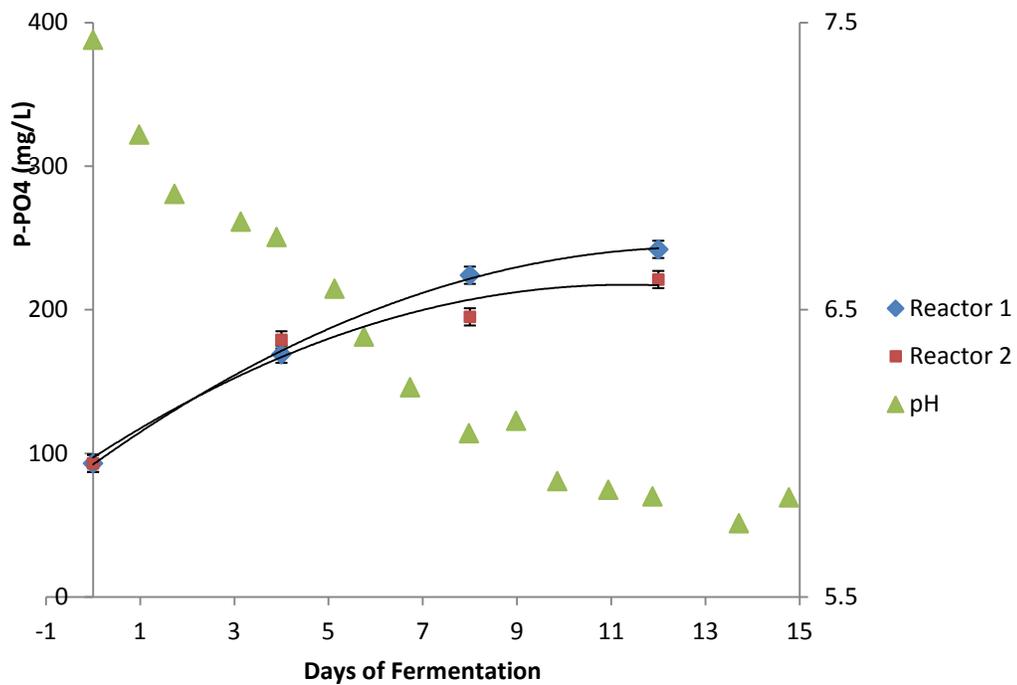


Figure 5.6 DMS pH and P-PO<sub>4</sub> concentration during 12 days of anaerobic fermentation.

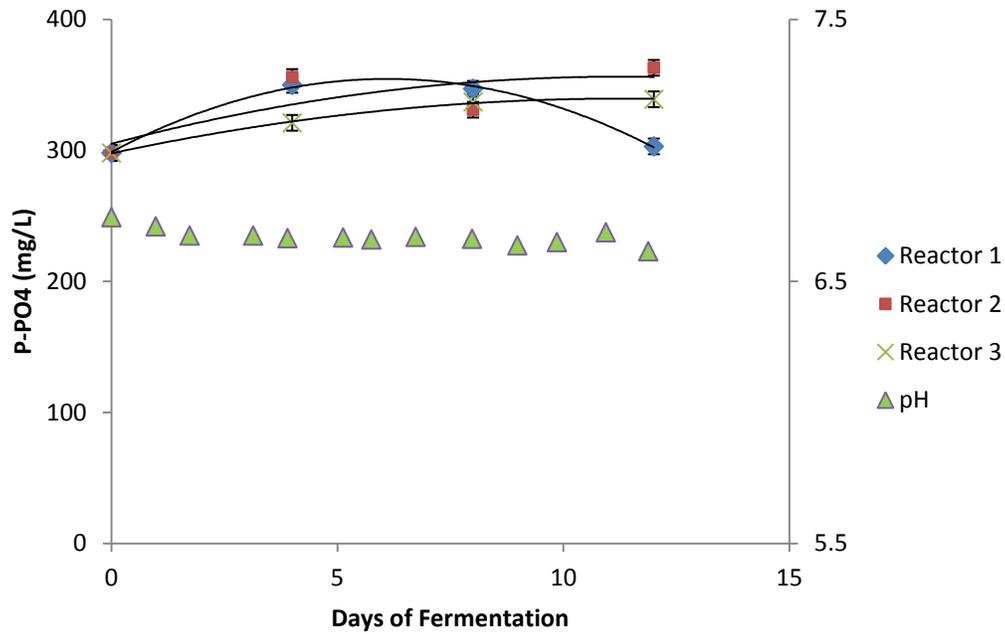


Figure 5.7 Manure 2 pH and P-PO4 concentration during 12 days of anaerobic fermentation.

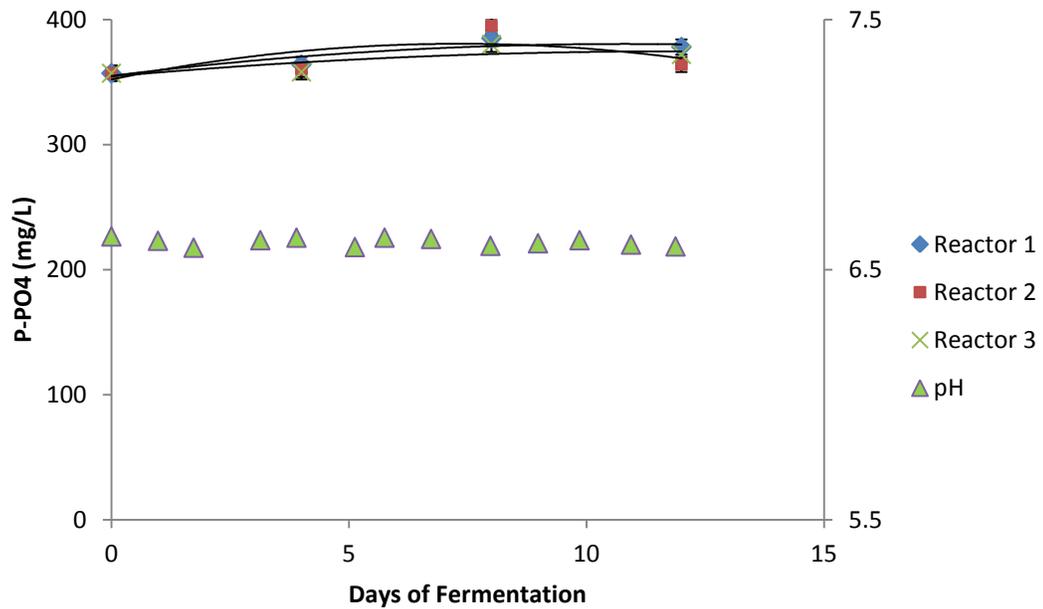


Figure 5.8 Manure 3 pH and P-PO4 concentration during 12 days of anaerobic fermentation

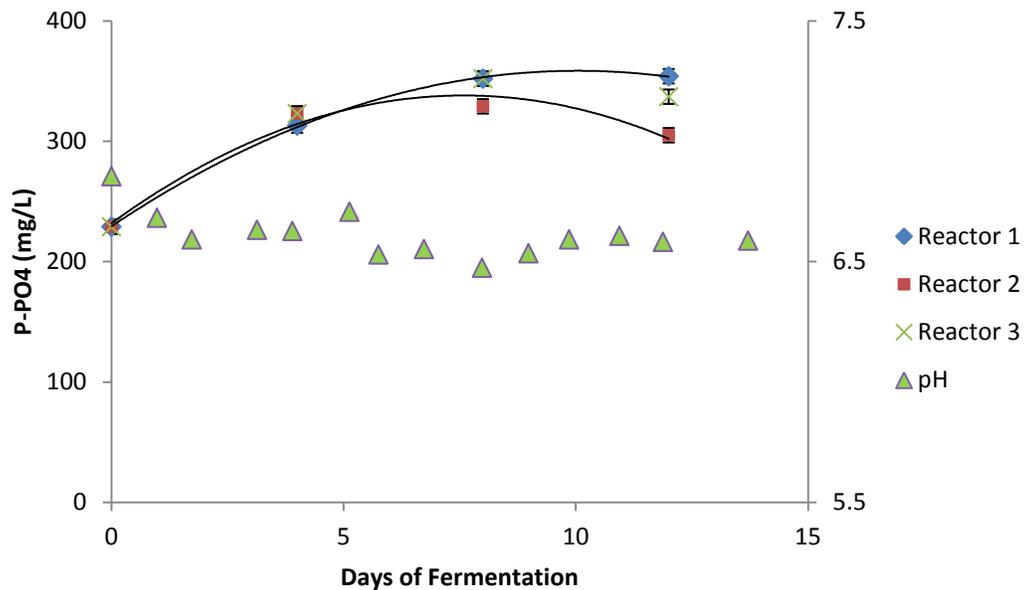


Figure 5.9 Manure 4 pH and P-PO<sub>4</sub> concentration during 12 days of anaerobic fermentation.

The four manures tested under the same conditions had quite different pH responses, with either gradual change, no change, and in the case of DMS, a large change. DMS displayed both a large decrease in pH also had large increases in P-PO<sub>4</sub> and Mg. These trends were present in Manure 4 to a lesser extent. A strong relationship between pH change and P-PO<sub>4</sub> increase in all manures (Fig 5.10). Change in P-PO<sub>4</sub> and pH were negatively correlated with values of -0.98, -0.88, -0.68, and -0.94 for DMS, Manures, 2, 3, and 4 respectively. A negative correlation (-0.93) was also found in the manure storage experiment in Chapter 3.

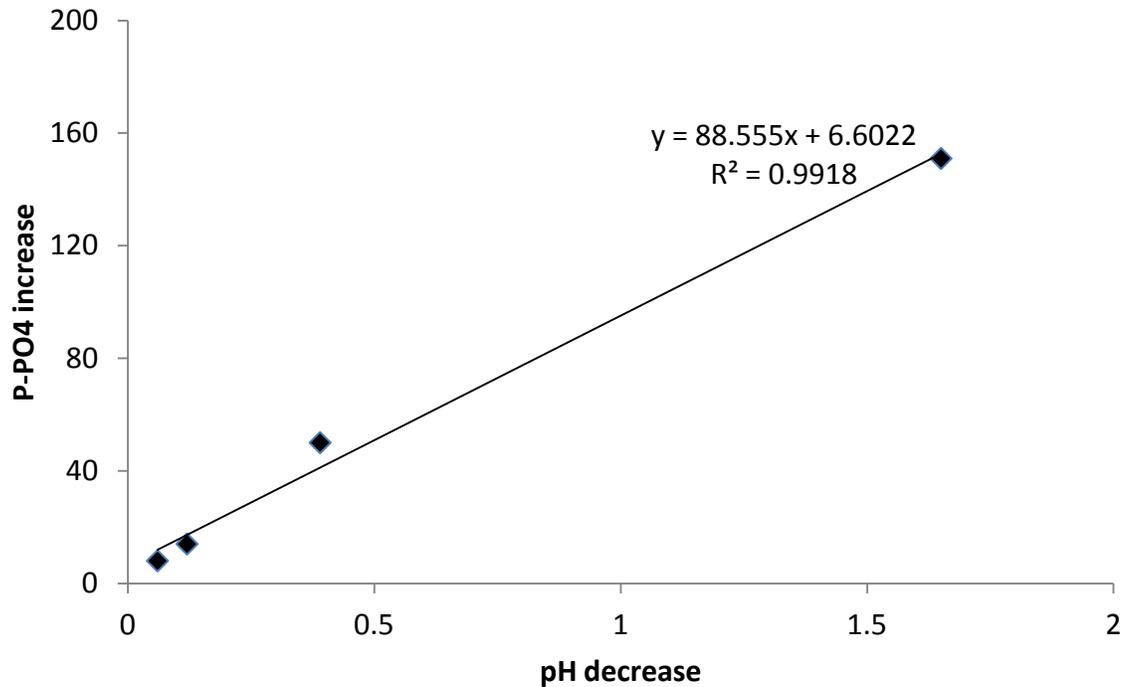


Figure 5.10 The change in three commercial manures and DMS as a result of 12 days of fermentation.

VFA concentration was not a driver in pH change, even though destruction of TS and reduction of VS indicates microbial activity. DMS had very low levels of VFA (~800 mg/L) and yet had a very large pH change while Manures 2 and 3 had very high VFA levels (~9,000 mg/L) but displayed virtually no change in pH and little change in soluble nutrients. In the course of the 12 day retention time methanogenic communities likely became established and consumed VFA, leading to no net increase in some manures. Alkalinity and the buffering capacity (presence of acid/base neutralizing compounds) of manure is likely the important chemical trait governing pH change.

Total alkalinity in manure is a measure of all compounds capable of accepting H<sup>+</sup> protons and includes PO<sub>4</sub> species, NH<sub>3</sub>/NH<sub>4</sub>, bicarbonate salts, VFA and other acids. However, it is not the buffering capacity alone that determines pH change. Alkalinity of Manures 2 and 3 was ~8,000 mg/L, and these manures had the least change in pH during anaerobic fermentation. Manure 4 however, had alkalinity of ~10,500 mg/L and had moderate pH decrease as well as an increase in P-PO<sub>4</sub>. If pH change came from the conversion of VS to acids, and alkalinity buffers acid effect on pH, then the ratio of available VS (in grams) to alkalinity (in mg) should be a predictor of pH change and consequent P dissolution. The ratio of total alkalinity to grams of VS gave low numbers for manures that had large changes in pH (labelled delta pH in Table 5.5) and greater percent increase in P-PO<sub>4</sub>. Ratios of alkalinity/g TS gave values that were similar.

Table 5.5 Ranking of manure according to alkalinity/grams of volatile solids (VS) for changes in pH (delta pH) and dissolved nutrients. Alkalinity and VS are values measured in original manure slurry.

<b>Manure</b>	<b>Alk/g VS</b>	<b>Alk/g TS</b>	<b>Delta pH</b>	<b>P-PO<sub>4</sub> increase %</b>	<b>Mg increase %</b>
<b>DMS</b>	73	56	1.65	151	239
<b>4</b>	187	143	0.39	50	98
<b>3</b>	520	322	0.06	8	-2
<b>2</b>	525	334	0.12	14	32

When manures were ranked using this ratio, other parameters such as pH change, P-PO<sub>4</sub>, and Mg increase generally corresponded. Thus, manures with low alkalinity/VS ratios

became acidic during anaerobic fermentation and consequently increase in P-PO<sub>4</sub> concentration. Manures 2 and 3 were very similar to each other in terms of alkalinity/g VS ratios and responded to anaerobic storage in the same way. The differences in the manures tested illustrate the variability that was found in manure chemistry and subsequent changes or lack of change during anaerobic storage, however a strong relationship was found between P-PO<sub>4</sub> increase and pH decrease (Fig. 5.10).

Accurate prediction of P-PO<sub>4</sub> release from manure solids is a necessary part of P reclamation from manure solids. Plotting the ratio against % P-PO<sub>4</sub> increase a logarithmic relationship can be seen (Fig 5.11). This is due to fact that high buffering capacity neutralizes all pH change even with high VS. In the case of a very low ratio, no buffering capacity allows a large pH change and consequent P-PO<sub>4</sub> increase. Using the ratio as a predictive measure of P-PO<sub>4</sub> solubility in manure would enable rapid assessment of a manure's suitability to anaerobic fermentation as a pre-treatment for struvite recovery. Alkalinity/g TS could also be used as a predictive ratio and has advantages of being simple tests that can be performed without a muffle furnace.

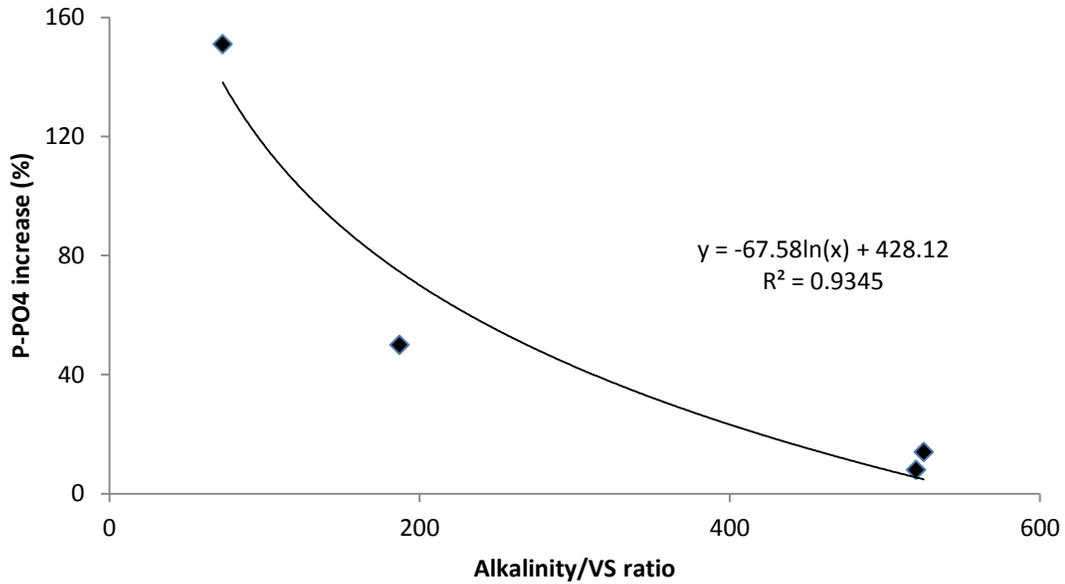


Figure 5.11 Relationship between initial alkalinity/VS (mg/L:g/L) and % increase in P-PO<sub>4</sub> after 12 day HRT for each manure.

## 5.8 General discussion

This research has practical application for designing liquid manure management systems for the removal of P. Section 1 tested a manure mixture with very low alkalinity that was optimum for P-PO<sub>4</sub> dissolution. A farm with urine/faeces separation technology would produce a manure similar to this and a process of batch fermentation could be implemented that would hold manure in anaerobic conditions for a period of days to acidify and dissolve P from the solids. The supernatant could then be processed through a struvite (or calcium phosphate) precipitation reactor, increasing the potential P removal two to three fold. Supernatant circulation through the reactor would need to be immediate, as some of the pH suppression depends on CO<sub>2</sub> supersaturation and would be lost to the atmosphere if stored in an open lagoon. This aspect however, suggests that pH

adjustment in the reactor could be performed by air sparging of CO<sub>2</sub> which can raise the pH by up to 1 unit (Suzuki et al. 2007; Shepherd et al. 2009).

Section 2 revealed an important aspect of manure chemistry as it related to pH change. Several manures were tested from different commercial operations, the limitations of highly buffered manure slurries was revealed and a simple test of alkalinity/g VS ratio was developed that predicted P solubility potential. A larger survey of hog barn effluents would indicate what operations could use fermentation as a means of increasing P-PO<sub>4</sub> and which farms would need to reduce manure alkalinity in order to do so. This may be accomplished by diet manipulation or manure handling systems that separate feces and urine to produce low alkalinity manure similar to Manure 1.

The concept of dissolving manure solids P by means of natural acidification during anaerobic fermentation is novel and has not been found in scientific literature. Using the alkalinity/g VS ratio as means of predicting pH and P-PO<sub>4</sub> response is an additional contribution this research has made to the technology of P recovery from manure.

## **6 Pilot scale struvite reactor using fermented manure liquid and no chemical additions.**

### **6.1 Introduction**

This chapter describes the operation of a reactor in a context that brings together many aspects of this research project of separating P from hog manure:

- Manure from a commercial barn that had been subjected to on-site anaerobic fermentation
- Commercial scale manure solids separation producing a liquid high in soluble P and low in TSS
- A pilot scale reactor using air stripping for pH increase

Previous work indicated that temporary storage of manure may increase the P-PO<sub>4</sub> concentration if acid build-up was not severely buffered by alkalinity. A commercial farm was located that used an in-ground concrete cistern to hold 1-2 weeks of manure before pumping it to a storage lagoon. This farm was also selected to test manure solids/liquid separation technologies by Prairie Agricultural Machinery Institute, thus providing a liquid stream low in TSS and high in P-PO<sub>4</sub>. An upflow struvite reactor was designed by an independent engineering firm (Prongineer) to process a portion of the separated manure liquid effluent. This continuous flow reactor was built and installed by staff and students of the Biosystems Engineering Department. The reactor was designed to increase pH by air stripping residual CO<sub>2</sub> from the manure, thereby reducing operating costs by eliminating the need for alkali addition. Most struvite reactors add MgCl<sub>2</sub> to ensure Mg is not stoichiometrically deficient and ensuring maximum P removal.

However, this reactor was designed for only partial reduction of manure TP, thus eliminating the need for Mg additions. This chapter describes the construction and operation of this reactor using anaerobically stored commercial barn manure liquid. Total P reduction was 30% and the precipitate harvested was found to be high purity struvite.

## **6.2 Methods**

### **6.2.1 Manure storage**

A commercial feeder hog barn near Niverville, MB used a covered concrete tank (10 m X 15 m X 10 m deep) to hold barn manure slurry before it was pumped to the outdoor lagoon. Farm staff estimated retention time to be 1-2 weeks. This is adequate time for potential acid build-up from fermentation as well as any related P-PO<sub>4</sub> increase. Manure from the tank had a pH of 6.50-6.60 and sample tests showed air stripping could raise the pH to 7.3 in 1.5 hrs (4L air/min and 1L sample) indicating a CO<sub>2</sub> build-up and potential success of pH increase in our reactor.

Manure solids separation was conducted first with an Alpha Laval centrifuge and then with a Fournier rotary press. Due to time for reactor set up and technical delays, only data from the rotary press liquid processed through the reactor is presented here.

### **6.2.2 Prongineer Ltd. reactor design**

The 130 L upflow reactor (Crystaphos® Struvite Recovery Process) was built in a tall funnel shape from clear plexiglass to enable inspection of precipitate build up. The steep smooth sides enabled precipitate to collect at the bottom where influent manure

liquid was injected by peristaltic pump, thereby encouraging crystal growth and agglomeration. Low pH reaction ensured metastable formation conditions and minimized spontaneous nucleation. Air sparging was introduced by two air pumps (totalling 85 L/min) through copper tubes with fine diffusion via 0.8 mm holes. A 100 L recycle tank collected outflow from the top of the reactor and a second peristaltic pump enabled controlled recirculation back through the bottom bracket (Fig. 6.1). Reactor effluent exited through the side of the recycle tank.

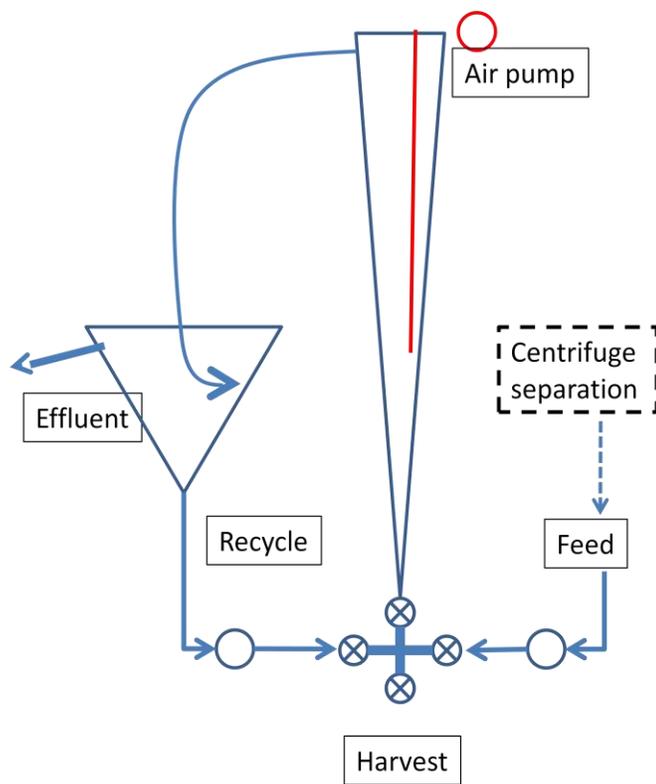


Figure 6.1 Schematic diagram and photo of 130 L struvite reactor with 100 L recycle tank. The system receives manure liquid from a rotary press or centrifuge.

### **6.2.3 Reactor operation**

The reactor was tested at 2 hr and 24 hr operational runs. Influent feed for both run times were set at 1.3 L/min due to influent storage limitations of 2400 L. Manure recycle for the reactor was set at 4 L/min, making a 1 hr retention time for the 230 L reactor system. Two 1200 L influent feed tanks were filled with manure liquid when the rotary press was in operation. Rotary press effluent may have contained residual polymer flocculant that could form solids in the feed tanks, so as a precaution, reactor feed was taken from the top of one tank by a floating hose to avoid any solids that may form and settle. The feed tanks were connected by a hose at the bottom, for passive equalization of the tanks. Effluent was collected by gravity into a similar 2400 L tank system.

Composite samples (in triplicate) of influent were taken from the top of the influent feed tank when they were filled, and again at the end of the run (usually 24 hrs later), and these values were averaged. Composite effluent samples (in triplicate) were taken at the end of the gravity drain hose from the recycle tank. Precipitate was collected by shutting down the air pump and peristaltic pumps and allowing the reactor to sit idle for 20 minutes. Precipitate could be seen settling and flowing down the sides of the cone. Precipitated solids settled in the bottom bracket of the reactor (1 L vol) and was isolated by closing the other valves and collected by opening the bottom valve.

### **6.2.4 Analysis**

Reactor influent and effluent was analyzed for TS, TSS, pH, and TP according to methods described in previous chapters. Samples were filtered through 0.45  $\mu\text{m}$  membrane and analyzed for P- $\text{PO}_4$ , Mg, and Ca as previously described. Precipitated

solids were analyzed for crystal size and TS and then digested for TP, Mg and Ca content. Dried solids were subjected to several tests for struvite purity including X ray diffraction as previously described in this thesis.

### **6.3 Results and Discussion**

The reactor was operated for ten successful runs, for either 2 hrs or overnight (22-26 hrs). The general effect on manure liquid through the reactor was a small increase in pH, and decreased P-PO<sub>4</sub>, TP and Mg (Table 6.1). True reduction in nutrients is greater than values in this Table suggest, due to the variance in influent feed as received from the rotary press (Table 6.2). Suspended solids as well as TS were reduced from reactor operation, while %VS increased, which indicated a change in effluent composition to lower TS but made up of more organic material, evidence of retention of mineral particulates in the reactor.

Problems were experienced in air pump operation, with burst hoses and plugged air diffusion holes. These problems were not immediately recognized, so some runs had full aeration and others had partial aeration. This appeared to affect TP reduction more than change in pH (Table 6.2), which was unexpected, as TP reduction should be directly linked with rise in pH, not aeration. Influent pH was within a narrow range of 6.55 to 6.63.

Table 6.1 Reactor influent and effluent composition as a mean of 7 trials (SD).

	pH	TS g/L	VS %	TSS g/L	P-PO <sub>4</sub> mg/L	TP mg/L	Mg mg/L	Ca mg/L	Alkalinity as CaCO <sub>3</sub> mg/L	VFA mg/L
<b>Influent</b>	6.57	9.3	50.7	1.5	202	336	174	217	5291	7939
<b>N=7</b>		(1.3)	(1.4)	(0.6)	(18)	(37)	(41)	(36)	(345)	(262)
<b>Effluent</b>	6.80	8.6	52.0	1.3	154	297	143	210	NA	NA
<b>N=7</b>		(0.2)	(0.9)	(0.2)	(31)	(36)	(17)	(30)		

Reactor operation resulted in a reduction in P-PO<sub>4</sub> and TP whether the reactor was run for 2 hrs or 22 hrs. The trials with full aeration (trials 1, 7, and 8) averaged 32% PO<sub>4</sub> and 31% TP removal. Air stripping did not increase pH as much as expected, with an average increase of only 0.25 pH units. This was attributed to the buffering effect of high VFA concentration. Even so, increase in pH and decrease in P-PO<sub>4</sub> concentration were related (Fig. 6.2). The TP was also reduced with a small pH increase at a pH below 7, which is novel in the literature of struvite reactors. Most pilot struvite reactors adjust pH to a much higher end point, from 8.2 (Bowers and Westerman 2005) to 9 (Burns et al. 2003; Song et al. 2011) with a few examples of low pH endpoints (e.g., reactor pH of 7.8 for 50% TP removal, Britton et al. 2005). This is likely because most pilot struvite reactors are operated for maximum TP reduction rather than minimal operating cost.

Table 6.2 Reactor trials using rotary press manure liquid.

<b>Trial</b>	<b>Hr of run</b>	<b>Aeration</b>	<b>Delta pH (increase)</b>	<b>P-PO<sub>4</sub> reduction (%)</b>	<b>TP reduction (%)</b>
<b>1</b>	22	Full/leak	0.08	21	30.1
<b>2</b>	2	0.2	0.29	NA	2.3
<b>3</b>	23	0.2	0.24	0.8	-8.8
<b>4</b>	26	Full/partially plugged?	0.19	12.8	9.4
<b>5</b>	2	Full/partially plugged?	0.22	27	2.3
<b>6</b>	22	Plugged	0.07	9.2	11.3
<b>7</b>	2	Full	0.29	31.5	36.7
<b>8</b>	23	Full	0.61	44.3	27.4
<b>9</b>	22	Full/no effluent	0.94	40.7	52.8
<b>10</b>	22	0	0.13	14.7	1.7

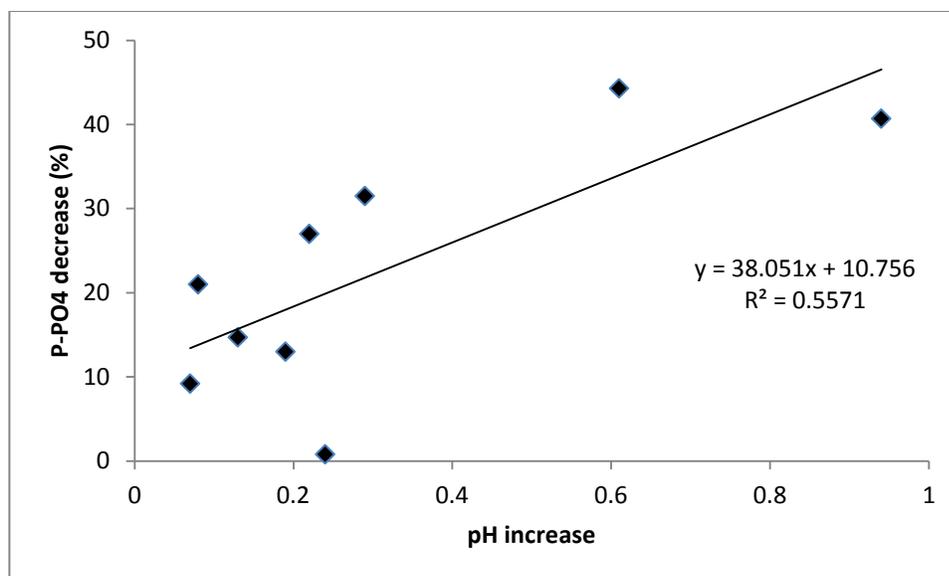


Figure 6.2 Increase in pH and decrease in P-PO<sub>4</sub> concentration of manure liquid processed through air sparged upflow reactor.

#### 6.4 Solids analysis

Settled solids harvested out of the bottom of the reactor were wet-sieved in an effort to determine any agglomeration or increase in crystal size with run duration or over the course of entire reactor operation. It was thought that crystals not collected in the bottom bracket and residing in the reactor would increase in size with successive trials. No large crystals or aggregated precipitates were found, and crystals did not increase in size with duration of trial or throughout the experiment. Photos of wet solids showed distinct singular crystals to a maximum of 200  $\mu\text{m}$  in length (Fig. 6. 3), with no agglomeration. The majority of organic particles were easily separated from inorganic solids and this technique could be integrated into the operation to improve struvite purity. For mass balance purposes the organics were added back to the mineral solids.

Settled solids were analyzed by ICP-OES, X ray diffraction, and assessed by molar mass ratio to determine struvite purity. Analysis by digestion and ICP-OES indicated struvite of high purity formed in the reactor. Companion analysis of pure lab-synthesized struvite indicated P and Mg to be 128.4 ( $\pm 1.8$ ) and 106.6 ( $\pm 4.8$ ) mg/g respectively, and as a benchmark, the solids collected from reactor runs varied in purity between 61.7% and 99.9% with a mean of 84.0%. Dried powdered solids were analyzed with X ray diffraction and samples from each run were found to contain only struvite crystals (Fig. 6.4).

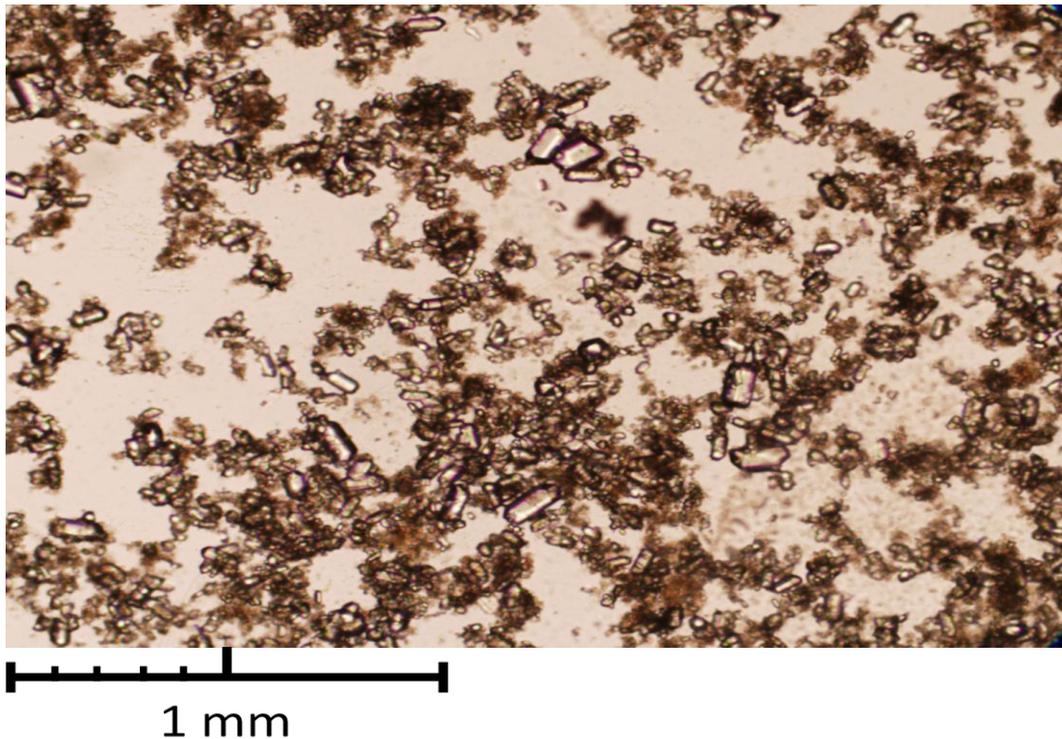


Figure 6.3 Reactor settled solids showing struvite crystals of different size.

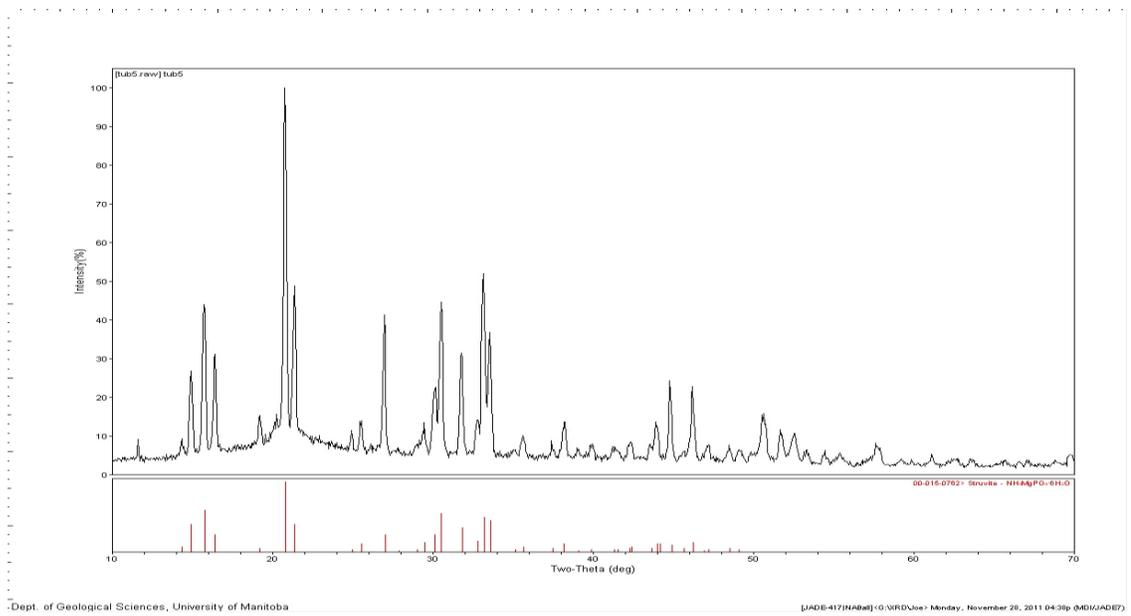


Figure 6.4 Analysis of collected solids by X ray diffraction. The reference chromatogram (lower part of figure) and the sample output match, indicating the only crystalline structure was struvite.

Struvite purity was also assessed by calculating soluble P and Mg removed from influent during reactor operation. These values, when expressed as mM/L, showed similar amounts were precipitated from solution (Fig. 6.5) and indicated P and Mg were removed at a 1:1 ratio as required by struvite formation.

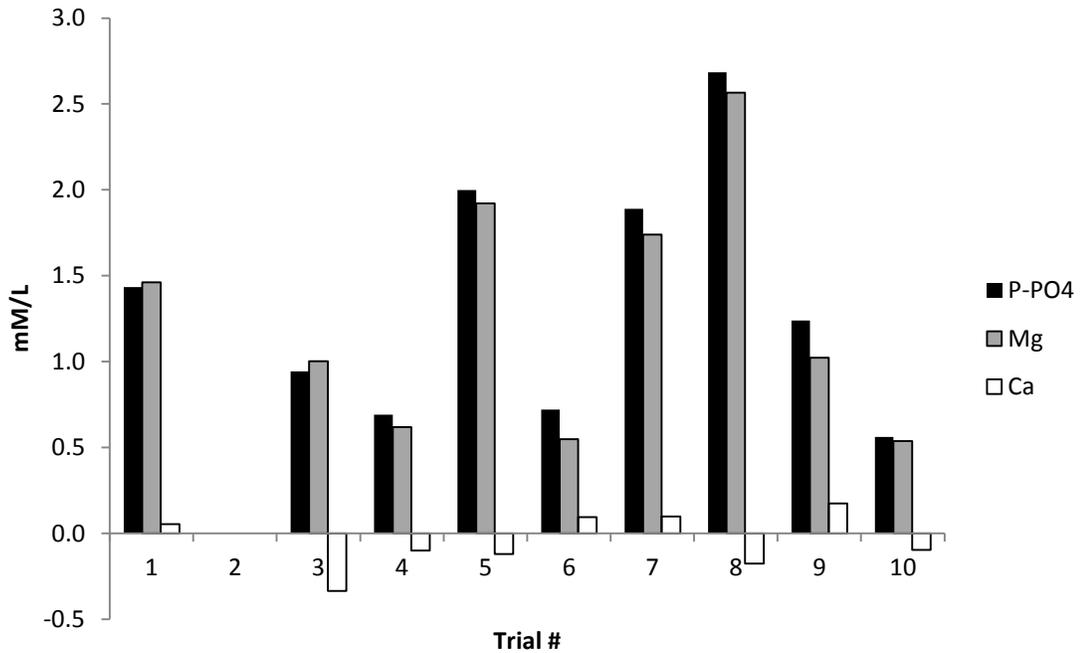


Figure 6.5 Dissolved nutrients removed from manure liquid during reactor operation. Near identical molar ratios of P and Mg indicate struvite precipitation.

Calcium was not removed from the supernatant even though it was present in high concentrations and could potentially form calcium phosphates. Average Ca:Mg ratios were 0.76, and according to other research, levels that impede struvite formation begin at 0.25 (Wang et al. 2005) and 0.5 (Le Corre et al. 2005). Calcium precipitates more readily

at high pH (Wang et al. 2005; Jordaan et al. 2010) and the reactor operated at pH 6.8 which eliminated Ca precipitation in the reactor.

A mass balance of TP through the reactor showed 13000 L of manure liquid were processed removing 740 g of elemental P, while recovery of settled solids reclaimed 120 g (Appendix C). It is estimated that the remainder (approximately 19 L of precipitate solids) was retained in the reactor in areas that could not be accessed by the collection means used in the experiment.

## **6.5 General Conclusion**

This experimental trial offers a good example of what can be achieved in struvite recovery from a few extra steps in manure management. The concrete storage cistern contained manure with high soluble P and enough CO<sub>2</sub> that aeration could raise the pH. The exact effect of storage on the manure cannot be determined because the barn had no provision to sample manure as it entered the cistern, but manure from the cistern had low pH and high P-PO<sub>4</sub>, both qualities that result from fermentation. Solids separation technologies supplied supernatant to the reactor low in TSS, an ideal feed substrate for an air-sparged upflow reactor. Together, these manure characteristics and the unique reactor achieved a moderate TP reduction with no chemical additions.

The Prongineer reactor design and the choice of fermented manure eliminated the need for alkali addition but TP reduction was moderate. The NH<sub>4</sub>/NH<sub>3</sub> equilibrium of pH 9.3 is important for total N retention in reactor effluent and reactors raising manure to

high pH levels will likely lose nitrogen to the atmosphere. Reactor effluents with near neutral pH could be stored with minimal loss of  $\text{NH}_3$ .

The novel aspect of this experiment is the removal of 31% TP, producing high purity struvite with a very small increase in pH. Reactor operation at low pH prevented Ca precipitation, a key part of the struvite purity. Recovery rates could be improved by installing a settling basin with a 1 hr retention time. A spot test was conducted, collecting twelve litres of reactor effluent that produced 60 ml of sludge in 1 hr of settling. This sludge was 18% TS and was identical to sludge collected from the bottom bracket (i.e., high purity struvite). The spot test showed settling boosts P recovery by 106 mg/L and if this representative of an improved settling system, TP removal can be increased by at least two- fold. This change would bring TP removal from this reactor and manure handling system in line with high recovery pilot struvite reactors. Additional improvements would include changes to the aeration system to prevent clogging.

## **7 Comparing reclaimed struvite with pure struvite and commercial fertilizer for growing canola**

### **7.1 Introduction**

Struvite is a compound that will likely increase in importance over the next few years as an agricultural fertilizer. Concerns of phosphorus (P) contribution to eutrophication of water bodies is now resulting in stricter regulations of P use and release to the environment (Carey and Migliaccio 2009) and removal from waste water. The limited global P resources favour policies for the recovery of P for reuse and recovery of P by precipitation of struvite is perhaps the best way to accomplish P removal in a form easy to reuse. These factors will translate into increased amounts of struvite of various qualities coming back into the agricultural supply chain, the sector that presently consumes the majority of mined phosphorus (Vaccari 2009).

Estimations of struvite value, both economic and agronomic are important in reactor design and overall feasibility of P reclamation systems. Designers need to know if the product sale value is equal to the equivalent mass of  $P_2O_5$  in the product, or if impurities affect agronomic effectiveness and corresponding sale value. Presently, many kinds of struvite reactors have been built and they produce varying purities of struvite (Gaterell et al. 2000). Deriving a pure struvite product from manure is difficult, but increased cost and effort in reactor design can increase struvite purity, so it needs to be determined if these efforts are worthwhile when considering nutrient availability to the plant and biomass yield.

The central question of this research is if manure derived struvite is comparable to commercial P fertilizer for agronomic uses, and if the purity of struvite has any effect on plant growth. Previous agronomic studies have compared P sources and showed struvite is not significantly different and sometimes superior to commercial fertilizer when measuring biomass and P uptake (see section 2.8). In these studies struvite is most often obtained from WWTPs, with only one author testing struvite derived from hog manure. Comparison of struvite reactor product with pure struvite has not been conducted.

This study used the dried settled solids precipitated from a hog lagoon (described in section 4.4.1) and pure struvite made from chemical reagents in the lab. The recovered material provided P potentially less soluble than pure struvite or struvite coming from WWTPs. Comparing these two struvites for growing agricultural crops provides an indication of the necessity of a pure struvite product and can help determine reactor design and process.

Low solubility of struvite provides “slow release” attributes which may be advantageous compared to commercial fertilizers when the slow release of nutrients is beneficial to a crop’s success (i.e., non-burning of plant roots when over applied, single application for an entire growing season, Bridger et al. 1962). A slow release P source may also be less prone to runoff and leaching in field conditions, but no studies have been conducted that explore this. This “slow release” quality has been applied to commercial fertilizer in the development of a polymer coated mono ammonium phosphate that releases nutrients over a period of time. Comparison of these two kinds of fertilizer helps to determine if release time is a factor in P utilization by a plant.

The purpose of this study was to determine if an agricultural crop (canola) responds differently to fertilizer P supplied by manure derived struvite or pure struvite. P uptake and biomass response to these alternative fertilizers is compared against standard mono ammonium phosphate as well as a “slow release” coated mono ammonium phosphate over 5 different rates in a P deficient soil.

## **7.2 Methods**

### **7.2.1 Phosphorus sources**

Manure derived struvite was obtained from a pilot scale reactor that processed hog lagoon supernatant with KOH to precipitate solids. The solids had been dried and finely ground and contained 5.6 % elemental P and 6.3 % TN along with approximately 50% organic matter. Previous analysis indicated the product contained a minimum of 33% struvite with remaining P likely as calcium phosphates. Pure struvite was synthesized in the lab by making a solution of analytical grade base chemicals ( $\text{KHPO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$  and deionized water) and precipitating it with NaOH at pH 9. The precipitate was dried and powdered, with the final product containing  $12.84 \pm 1.8\%$  P and 5.5% TN.

Mono ammonium phosphate and coated mono ammonium phosphate were obtained from Agrium Incorporated. Both had a nutrient analysis of 12% N and 22% P (51%  $\text{P}_2\text{O}_5$ ).

### **7.2.2 Soil description**

The soil used in this experiment was a loamy Indian Head soil with available N, P, and K of 12, 12 and 258 ppm respectively. The soil was alkaline with a pH of 7.7, 3318 ppm Ca and 332 ppm Mg. Organic matter was 2.9% and it had a low EC of 0.63 dS/m. Two kg soil (air dried wt) were mixed and placed into plastic pots without drainage holes. Field capacity of three 200 g soil samples was  $25 \pm 1.3\%$  (wt/wt). The soil was wetted to one half of its field capacity and left covered for 5 days before planting canola. This allowed the soil ecology to become established and reduced any flux of P from initial wetting of dry soil.

### **7.2.3 Experimental setup**

Four P treatments were used: manure derived struvite (MDS), pure struvite (PS), mono ammonium phosphate (MoAP) and coated mono ammonium phosphate (CMoAP). Five rates of application were 12.5, 25, 37.5, 50 and 62.5 kg  $P_2O_5$ /ha, calculated on an area basis of the pots rather than soil wt. All treatments and rates were replicated (3X) along with three controls with no added P fertilizer but receiving other nutrient additions equally to the other pots. The purpose of the study was to examine plant response to different forms of P, so efforts were made to ensure all other nutrients were available equally to canola. A solution of nutrients (Table 7.1) was added to each pot with macro nutrients (N, K and S) mixed separately and adjusted for struvite contribution of N for each treatment and rate.

Table 7.1 Nutrient solution source added to all treatments and controls. Rates are calculated as the required elemental amount of nutrient of the larger compound (e.g., 100 mg N/kg soil as  $\text{NH}_4\text{NO}_3$  is 35 mg N/kg).

<b>Nutrient</b>	<b>Source</b>	<b>Rate (mg/kg soil)</b>
<b>N</b>	$\text{NH}_4\text{NO}_3$	100
<b>K</b>	KCl	100
<b>S</b>	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20
<b>Zn</b>	$\text{ZnCl}_2$	4.0
<b>Mn</b>	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	2.0
<b>Mo</b>	$\text{NaMoO}_4 \cdot 5\text{H}_2\text{O}$	0.4
<b>B</b>	$\text{H}_3\text{BO}_3$	1.0
<b>Cu</b>	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.0
<b>Fe</b>	Fe·EDTA	4.0

Planting was designed to mimic field sowing with a shallow (1/2 inch) furrow made in the centre of each pot for 8-9 fungus-treated canola seeds and adjacent furrows (one inch away) made for the P fertilizer treatment, normalized for equal TP to each pot (Table 7.2). Aliquots of the nutrient solutions and water were added to attain 75% of field capacity. The pots were placed in a growth room maintained under a temperature regime of 22/15°C (day/night) at a photon flux density of  $250 \mu\text{mol m}^{-2} \text{s}^{-1}$  and a 16-h photoperiod, with relative humidity set at ~60%. The pots were weighed once every day or two and any lost moisture replenished with reverse osmosis water to maintain soil

moisture content at approximately 75% of container capacity. Plants were thinned to 3 per pot one week after emergence.

Fifty six days from planting, when flowering had commenced in most pots, the above ground biomass was cut at the soil surface, placed in separate paper bags and dried in an oven at 45° C for 3 days. These samples were then weighed and ground in a 0.5 mm mill and digested on a block digester. Samples were analyzed for P concentrations with a flow injection analyzer.

#### **7.2.4 P uptake and P efficiency**

Biomass (dry wt) and tissue P concentration were combined to derive P uptake by the plants in each pot.

$$PU_{\text{uptake}} = (DW \times P_{\text{conc}}) \quad (11)$$

Measured units are in g/pot and mg/g, giving P uptake in mg/pot. P uptake efficiency is a measure of effectiveness of the plant to benefit from increased P rate for each amendment. This is derived from amendment P uptake minus P uptake from the controls, divided by the rate.

$$PUE = \left( \frac{PU_{\text{amend}} - PU_{\text{control}}}{\text{amendment rate}} \right) \times 100 \quad (12)$$

P uptake efficiency can give a good indication of the most efficient use of added P by the plant and is useful in determining at what rate an amendment is best utilized.

Table 7.2 Phosphorus amendments and nutrient content.

<b>Amendment</b>	<b>Code</b>	<b>TP %</b>	<b>TN %</b>
<b>Manure derived struvite</b>	MDS	5.6	6.3
<b>Pure struvite</b>	PS	12.7	5.5
<b>Mono ammonium phosphate</b>	MoAP	22.4	12.0
<b>Coated mono ammonium phosphate</b>	CMoAP	22.4	12.0

### 7.2.5 Statistical analysis

The study followed a randomized block design repeated in triplicate plus three controls. Biomass and P uptake were analyzed using SAS software for tests of normal distribution and analysis of variance (ANOVA) for significance between means of biomass and P uptake. These tests indicate significant differences among P amendments ( $p < 0.05$ ) and further tests group amendments and rates of application with letter grades, so it is evident which aspects are similar (same letter groups) and which are significantly different.

## 7.3 Results

### 7.3.1 Biomass

Dried above ground biomass was normally distributed (Shapiro-Wilk = 0.972) and no data transformation was needed to perform ANOVA. Tests of fixed effects with the controls showed a significant difference between amendments, rates and controls.

There were also significant differences between amendments and rates excluding controls (Table 7.3).

Biomass produced from each pot indicated MDS was not significantly different from PS, with biomass production for each amendment rate virtually identical. Both struvites had an initial increase of biomass in pots with rates of 12.5 to 37.5 kg/ha and no increase at rates from 50 to 62.5 kg/ha (Fig. 7.1). The struvites had a significantly smaller biomass response to P fertilization than the mono ammonium phosphates which both displayed steeper curves. CMoAP had a near linear response (linear model  $r^2 = 0.9858$ , 2<sup>nd</sup> order polynomial model  $r^2=0.9944$ ). Statistical analysis confirmed an identical biomass response to P rate with struvites (letter group A for both struvites at all P rates, data not shown), whereas response to mono ammonium phosphates was greater and spanned more letter groups. Curve models that best fit the data were all 2<sup>nd</sup> order polynomial (MDR  $r^2 = 0.9936$ , PS  $r^2= 0.9883$  MoAP  $r^2=.9985$ , CMoAP  $r^2=0.9962$ ).

Table 7.3 Comparison of means for biomass production and P uptake of amendments and rates of application. Letter grouping defines significant differences among groups and experimental standard error (SE) was calculated.

<b>Effect</b>	<b>Biomass (g/pot)</b>	<b>Letter</b>	<b>P uptake (mg/pot)</b>	<b>Letter</b>
	<b>SE 0.16</b>	<b>Group</b>	<b>SE 0.47</b>	<b>Group</b>
<b>Amendment</b>				
<b>Control</b>	5.38	A	6.05	A
<b>MDS</b>	7.54	B	13.61	B
<b>PS</b>	7.55	B	14.70	BC
<b>MoAP</b>	9.22	C	16.0	C
<b>CMoAP</b>	9.45	C	14.74	BC
<b>Rate (kg P<sub>2</sub>O<sub>5</sub>/ha)</b>				
	<b>SE 0.18</b>		<b>SE 0.45</b>	
<b>Control</b>	5.38	A	6.05	A
<b>12.5</b>	6.85	B	8.52	A
<b>25</b>	7.85	C	11.8	B
<b>37.5</b>	8.57	CD	15.5	C
<b>50</b>	9.29	DE	18.5	D
<b>62.5</b>	9.64	F	19.5	D
<b>P value</b>				
<b>Amendment</b>	<.0001		<.0001	
<b>Rate</b>	<.0001		<.0001	
<b>Amendment*rate</b>	<.0001		<.0001	

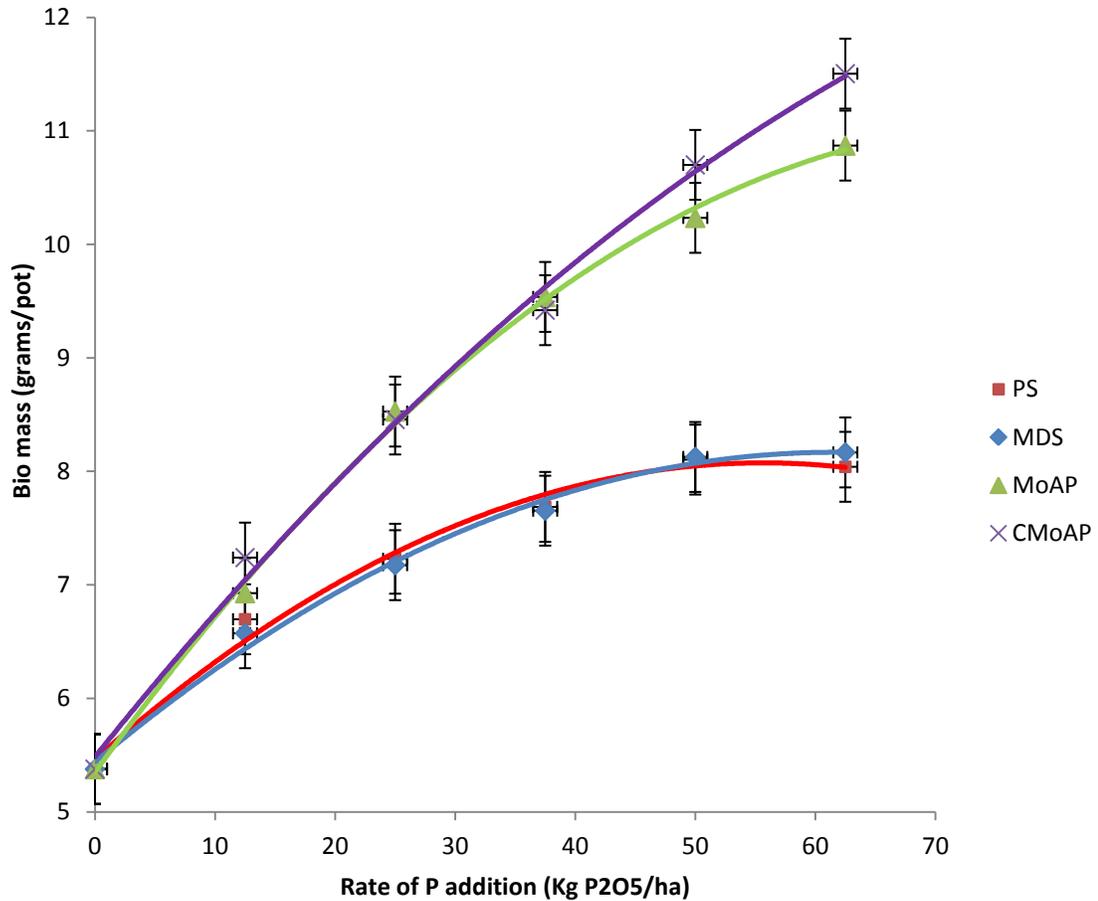


Figure 7.1 Biomass production for each P amendment.

### 7.3.2 P uptake

Analysis of P concentration in dried biomass was used to derive total P incorporated into plant tissue per pot. Amendments, rates, and the compounded effect of rates x amendments were significantly different from controls (Table 7.3). Excluding controls, these same aspects were significantly different from each other. Comparison of amendments (Tukey-Kramer  $P < .05$ ) gave letter groupings that indicated MoAP and manure struvite were significantly different but pure struvite and coated MoAP were not.

P uptake from manure struvite increased to  $16.4 \pm 1.1$  mg P/pot at the 37.5 kg/ha rate but did not increase further at higher application rates. Pure struvite P uptake increased in a linear fashion ( $r^2=0.974$ ) with application rate to 20.6 mg P/pot at 50 kg P/ha, but decreased to 16.2 mg P/ha at 62.5 kg P/ha (Fig. 7.1). Both commercial fertilizers exhibited linear increase of P uptake as rates increased, even at 62.5 kgP/ha.

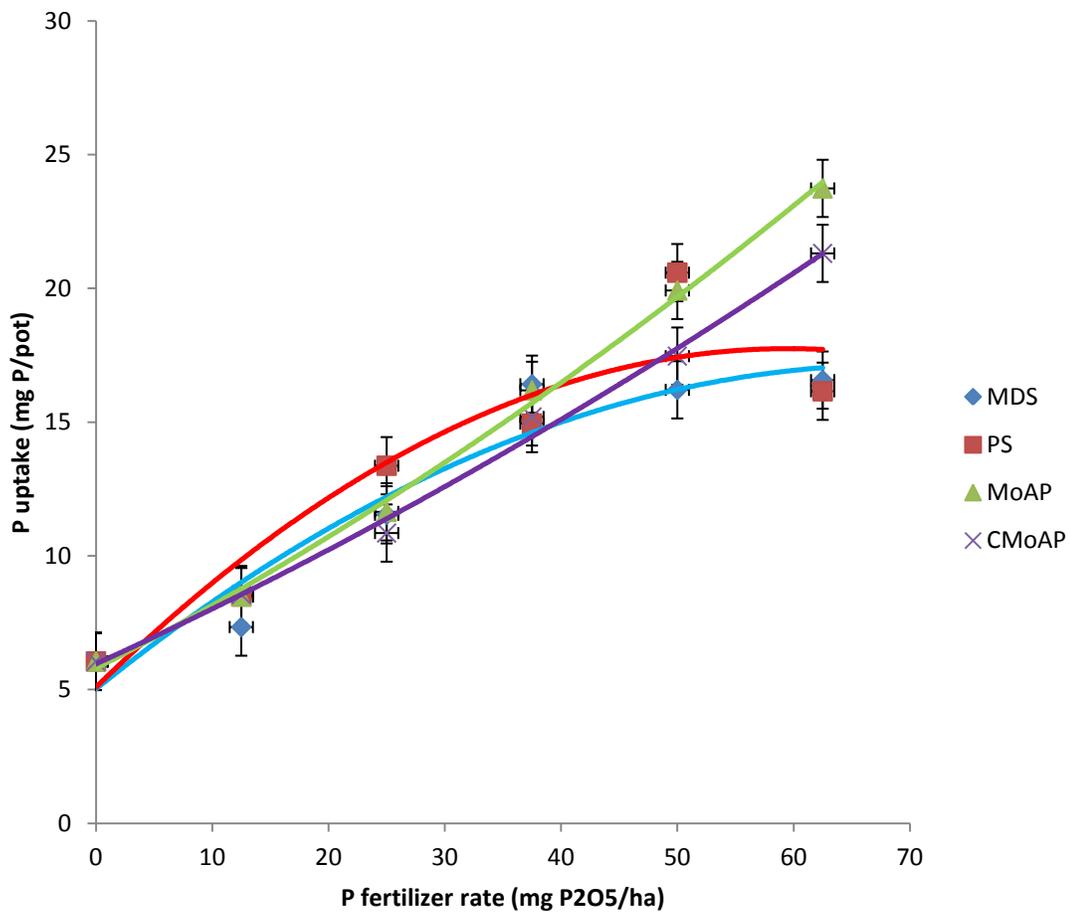


Figure 7.2 P uptake response to P fertilizer amendments at different rates of application.

### 7.3.3 P Recovery Efficiency

Phosphorus recovery efficiency identifies the optimum rate of fertilizer application by indicating the percentage of fertilizer incorporated into the plant. Manure struvite had an efficiency rate of 63% at 37.5 kg/ha (Fig. 7.3) at higher application rates the efficiency declined. Pure struvite did not have a clear maximum efficiency but peaked at 66% at both 25 and 50 kg/ha, which suggests the 37.5 kg/ha data point was in error. Commercial fertilizers also had good efficiency at 37.5 kg/ha with 61% and 55% efficiency for MoAP and CMoAP. Increased rates did not significantly change efficiency with these two fertilizers. On the basis of this data, the optimum rate of P application for three of the fertilizer types is 37.5 kg/ha, and was undetermined for PS.

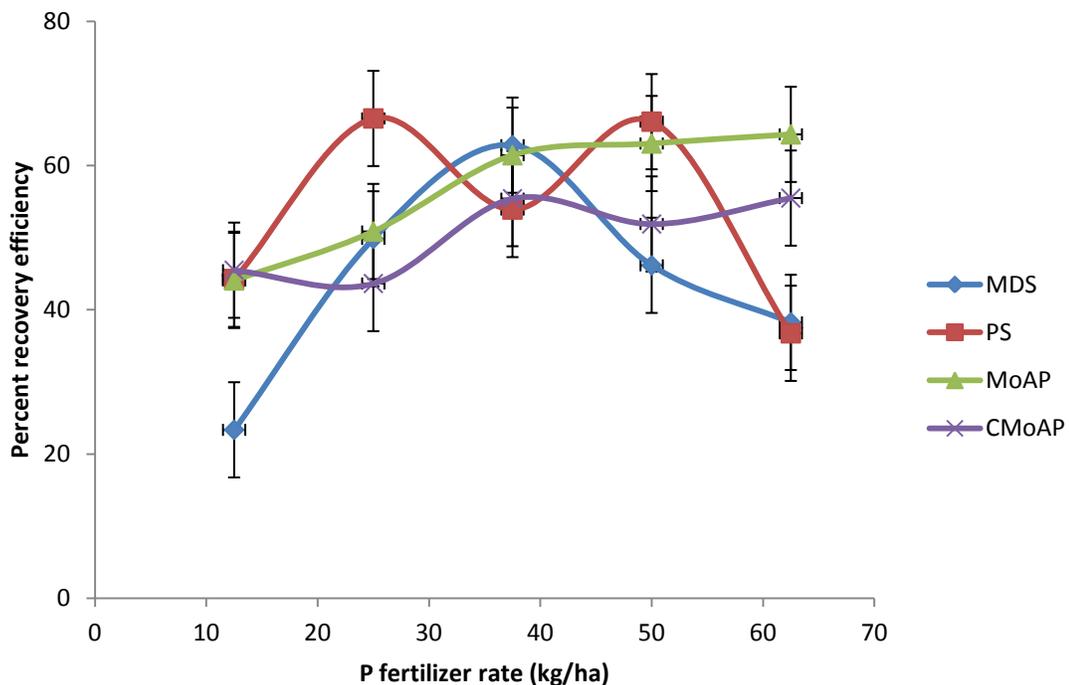


Figure 7.3 P recovery efficiency for struvite and commercial fertilizer amendments.

## 7.4 Discussion

Manure derived struvite and pure struvite applied at the same phosphorus application rates produced canola plants with identical biomass production and very similar phosphorus uptake. This indicated that canola utilized pure struvite and a reclaimed manure product (with a mixture of struvite and the less soluble calcium phosphate) in a very similar way. From the perspective of phosphorus reclamation technology development, this is an important finding. It suggests that producing a purer struvite product is not necessarily agronomically advantageous, and increased processing costs to this end will not be recovered by higher product value since higher purity does not increase biomass yield in the plant.

Comparing struvites with commercial fertilizer gave unexpected results. Biomass yields indicate significantly greater yield with commercial fertilizer, which is different from findings in other studies (Section 2.8). Other research has indicated struvite is either not significantly different to commercial fertilizer, or that struvite produced significantly more biomass and plants had greater P uptake (Table 7.4). Differences between this study and other studies may account for the discrepancy. Other studies used acidic or neutral soils ranging in pH from 4.7 to 7.1. Only one soil had similar pH as a result of lime addition to an acidic soil. However, the data obtained in this way may not be reliable. Liming increased available P in this soil by 50% and  $\text{NO}_3$  by 200%, suggesting a lime-induced increase of soil nutrients the skewed plant response. In other studies, experimental procedures used very high rates of P application, presumably leading to complete P saturation, perhaps masking the effects of fertilizer type. Additionally, each soil is unique, and soil response to P fertilization can vary widely: the soil in the current

study was more alkaline (pH 7.7) than any other in struvite fertilizer research. High soil pH and common ion effect from high soil Ca and Mg levels may have inhibited solubility of the struvites, whereas fast dissolving MoAP and the polymer coated mono ammonium phosphate were not affected. The differences in plant response may be based on P source solubility in the soil matrix. The soil used in this study was P deficient, so these effects became more pronounced as the rates of fertilizer were increased. P uptake sample means from the different amendments are ranked as follows: MoAp > CMoAp > PS > MDS. This ranking follows the expected solubility of each of these fertilizers, leading to the conclusion P uptake in high Ca alkaline soils is governed by P source solubility. Finally, some experiments did not state if N addition had been adjusted for struvite's N contribution (Table 7.4), so the results may have been dictated by differences in N rather than source of P.

The slow release qualities of struvite and CMoAP were not clearly advantageous for canola growth in this study. Pots with no drainage holes were used and the fast dissolving MoAP was contained in the pot, unlike horticulture pot drainage or field conditions where runoff is possible. Consequently, this experiment was unable to properly compare fertilizers in this respect. The use of CMoAP in this experiment was intended to replicate struvite's slow release qualities but plant growth was not impaired at high fertilizer rates with MoAP, ruling out root damage at the rates used in this experiment. The alkaline soil may have inhibited solubility of struvite more than the polymer coating of CMoAP, and this may have accounted for the superior results of commercial fertilizers at higher rates of application. Further study of agronomic uses of struvite would establish solubility ranking among the fertilizers along with a pot design

that would better mimic both drainage and runoff tendencies found in normal field conditions.

Table 7.4 Literature comparing struvite to commercial P fertilizer in terms of biomass production and P uptake.

Study	Struvite source	Rate	Soil avail P	Soil pH	Soil Ca, Mg content mg/kg	Biomass struvite vs comm. fert	P uptake struvite vs comm. fert
<b>This study</b>	Swine	12, 25, 37, 50 62 kg/ha	12	7.7	3318, 332	Significantly less	Mixed response
<b>Cabeza et al. 2011</b>	WWTP	60 mg/kg	21, 24**	6.6, 4.7	NA	NSD	NSD
<b>Johnston and Richards 2003</b>	WWTP + pure struvite	100,150, 200,250, 300 mg/kg	28, 11**	6.6, 7.1	NA, 155;59	NSD	NSD
<b>Liu et al. 2011</b>	Swine	30, 40 kg/ha	12*	6.0	NA	Significantly greater	ND
<b>Massey et al. 2009</b>	WWTP	45, 90 kg/ha	31, limed 44**	6.5, limed 7.6	NA	NSD nor from control	NSD nor from control
<b>Plaza et al. 2007</b>	WWTP	60, 120, 180, 240,300 kg/ha	12*	5.7	NA	NSD	NSD
<b>Gonzalez-Ponce et al. 2009</b>	WWTP	4, 8, 12, 16, 20 mg/kg	19.6*	5.9	204, 6	Significantly greater	Significantly greater
<b>Ponce and De Sa 2007</b>	WWTP	6, 12, 18, 24, 30 mg/kg	11**		NA	NSD	NSD
<b>Ponce and De Sa 2008</b>	WWTP	6, 12, 18, 24, 30 mg/kg	11*	5.7	NA, 6	NSD	NSD

WWTP = Waste Water Treatment Plant

\*=N adjusted for struvite N content

\*\*= no N adjustment

NSD= no significant difference (p<.05), NA= data not available

## **8 Engineering significance**

The research completed in this thesis gives practical direction to changes in manure management to better facilitate removal and reclamation of P. This chapter looks at applicability of this research to commercial hog farms and conducts a preliminary costing of each pilot reactor on a small farm.

### **8.1 Manure storage**

Through observations and experimentation this project has determined that soluble forms of P can be increased by short term anaerobic manure storage, serving as a simple but effective pre-treatment before manure supernatant is processed through a struvite recovery reactor. Manure stored in anaerobic conditions for a period of 4 to 12 days allowed natural acidification to take place and dissolved P from manures with low alkalinity/VS ratios. This pre treatment could be accomplished on existing hog farms by a short or no retention time under the stalls and manure conveyance to covered holding tanks with manure capacity of approximately one week. A batch type system would be required to reduce buildup of methanogenic bacteria and their detrimental effects on manure pH and hazardous gas production. The settled manure supernatant would then be processed through a struvite reactor directly, or the mixed slurry first processed with a rotary press or centrifuge for solids/liquids separation and then the liquid stream fed through a struvite reactor. The size of the P-PO<sub>4</sub> increase was related to the buffering capacity of the manure and volatile solids, thus reduction of total alkalinity may be required for highly buffered manures. This may be accomplished through diet alteration or by separation of urine from solids in the barn.

## **8.2 Use of existing infrastructure**

Both pilot struvite reactors used in this research have a small footprint and could be placed in existing farms with a minimum of infrastructure changes. Recovered solids from the struvite reactors require drying before they can be integrated into the fertilizer supply chain. Existing barn heat and exhaust blowers could be adapted to dry this material with little additional operational cost.

## **8.3 Batch reactor**

The batch reactor is advantageous due to its simplicity of operation, requiring only filling, dosing, settling and emptying. It requires no change in current manure infrastructure as it uses supernatant from the surface of a primary lagoon. It is well suited as a sidestream process, utilizing a portion of total lagoon supernatant. Loss of nitrogen to the atmosphere may also occur from reactor effluent due to its pH (8.5), although secondary lagoon pH has been measured as high as 8.3, so loss may be no more than that occurring naturally.

## **8.4 Crystaphos™ up-flow reactor**

The up flow reactor produces high purity struvite product with no alkali costs for pH adjustment. It would be ideal on a farm with manure solids separation technology in place because the reactor utilizes the low TSS and high P-PO<sub>4</sub> manure liquid. The reactor enables a reduction in manure TP in addition to that removed by solids separation, and when coupled with pre-treatment fermentation, can be operated without chemical additions. In our experiments, the reactor did not elevate pH to levels where ammonia

loss to the atmosphere was a concern and in practical application this would enable storage time before field application with little or no loss of TN. A farm with soils over-saturated with P may want to remove the majority of P from manure before field application. In such a case, solids separation and subsequent P removal from the liquid stream would result in low P liquid fertilizer yet maintain the majority of TN.

## 8.5 Costs

An annual cost estimate was prepared for installing and operating the batch reactor and the Crystaphos™ upflow reactor as described in Chapters 4 and 6 respectively. A farm of 10000 pigs/yr was chosen because liquid manure production of 30000 L d<sup>-1</sup> could be handled with only minor changes to the pilot reactors described, but economies of scale could likely be achieved on a larger farm.

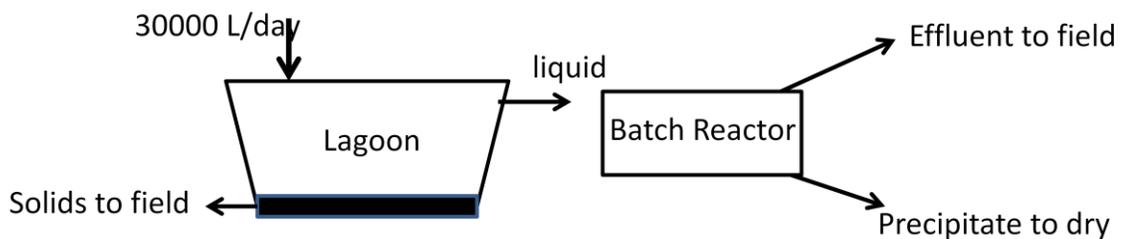


Figure 8.1 Process diagram of the batch reactor processing liquid from the lagoon surface of a 10,000 pig farm.

The estimate includes 60% volume over capacity (ten tanks of 5000 L) for the batch reactor (Fig.8.1) and three settling tanks to accompany the ten Crystaphos reactors as described in Chapter 6 (Fig. 8.2). No increase to precipitate yield has been made with the addition of settling tanks although TP recovery of 30% would likely increase.

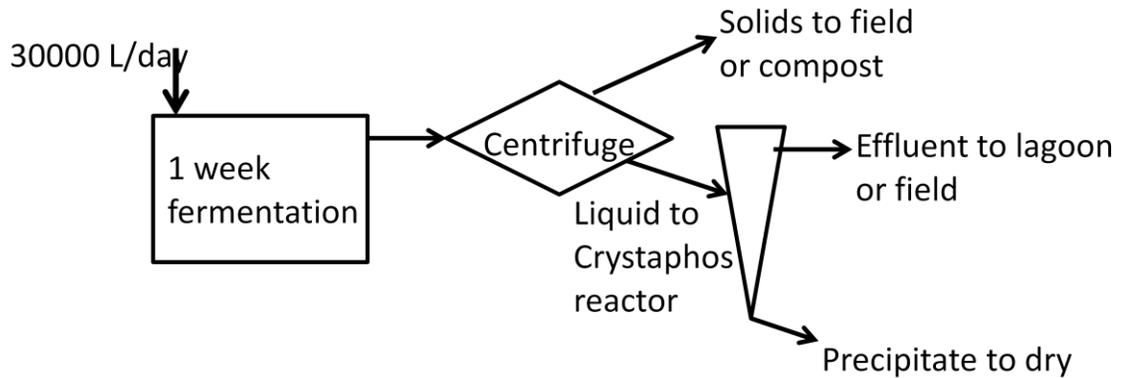


Figure 8.2 Process diagram of the Crystaphos upflow reactor operating with fermented manure from a 10,000 pig farm.

A seven-year amortization at 6% of the capital costs was used, amounting to 18% for annual costs. Costs associated with processing the precipitate sludge have not been completed in either cost projection due to lack of data on energy expenses for drying and grinding. Both systems would require drying and grinding of the precipitated solids, but this unknown cost would be similar for both. Drying could potentially be integrated into the larger farm energy system, for example, by using waste heat from barn ventilation or a greenhouse-type enclosure. Value of the dried product was estimated to be equal to its nutrient content (N,P, and K) and the comparative value as commercial fertilizer.

Table 8.1 Costs of installing and operating a batch reactor on a 10,000 pigs/yr farm.

	Units	Quantity	Price	Annual Amount
<b>Capital cost</b>				
Capital Equipment cost	\$	26,400	18%	\$4752
Installation	\$	9,000	18%	\$1620
<b>Subtotal</b>	<b>\$</b>	<b>35,400</b>		<b>\$6372</b>
<b>Operating cost</b>				
KOH (45%)	L	40,000	\$0.65	\$26,000
Electricity	kWh	30420	\$0.06	\$1825
Labor	h	550	\$12	\$6570
Maintenance (5% of capital cost)	\$	35400	5%	\$1770
<b>Subtotal</b>				<b>\$36,165</b>
<b>Total costs</b>	<b>\$</b>			<b>\$42,505</b>
<b>Revenue</b>				
Dry precipitate N, P value	kg	35040 kg	\$210 per tonne	\$7365
Offset K <sub>2</sub> O value	\$	15203 kg	\$700 per tonne	\$17,737
<b>Revenue with K offset</b>				<b>\$25,088</b>
<b>Net cost</b>				<b>\$17,403</b>
<b>Cost per kg live weight</b>	<b>\$</b>			<b>\$0.0139</b>

**Assumptions:**

- 10,000 finish pigs per year at market weight of 125 kg.
- 30,000 L d<sup>-1</sup> manure produced with supernatant of 216 mg L<sup>-1</sup> TP and 76% removal.
- 4% of manure volume collected as precipitate sludge at 8% TS.
- No costs are included for precipitate drying and grinding.
- K addition will offset K<sub>2</sub>O fertilizer purchase in both precipitate and effluent liquid.
- Value of dried precipitate is equal to the fertilizer value of N, P, and K.
- Without K offset cost per kg live wt is \$0.028

Table 8.2 Costs of installing and operating a Crystaphos™ upflow reactor on a 10,000 pig farm.

	Units	Quantity	Price	Annual Amount
<b>Capital cost</b>				
Capital Equipment cost	\$	40,450	18%	\$7281
Installation	\$	10,000	18%	\$1800
<b>Subtotal</b>	<b>\$</b>	<b>50,450</b>		<b>\$9081</b>
<b>Operating cost</b>				
Electricity	kWh	82200	\$0.06	\$4932
Labor	h	730	\$12	\$8760
Maintenance (5% of capital cost)	\$	50,450	5%	\$2522
<b>Subtotal</b>				<b>\$16,214</b>
<b>Total costs</b>	<b>\$</b>			<b>\$25,295</b>
<b>Revenue</b>				
P value as P <sub>2</sub> O <sub>5</sub>	kg	5,202 kg	\$730 per tonne	\$4365
<b>Net cost</b>	<b>\$</b>			<b>\$20,930</b>
<b>Cost per kg live wt at 30%</b>	<b>\$</b>			<b>\$0.0167</b>
<b>TP removal</b>				

**Assumptions:**

- 10000 finish pigs per year at market weight of 125 kg.
- 30000 L d<sup>-1</sup> manure with rotary press solids separation
- Supernatant of 336 mg L<sup>-1</sup> TP and 31% removal.
- No costs are included for precipitate drying and grinding.
- Value of dried precipitate is equal to commercial fertilizer value of N, P, K (12-45-0)

Manure TP content was different for each costing analysis as it reflected experimental data. The batch manure supply was direct from a lagoon surface and had lower TP than the manure feed for the upflow reactor, which had higher P-PO<sub>4</sub> levels due to the fermentation step before the rotary press. The net cost of either system after product sales was very similar, 1.39 and 1.67 cents per kg live weight produced for the batch and upflow reactor respectively. The batch reactor attained such low costs due to the assumed value of potassium as a fertilizer. If this value was excluded the cost per kg live weight would double to 2.81 cents. Both systems reduced supernatant TP (76 and 30%), although these calculations do not account for P in solids in lagoon sediments or separated with the rotary press. The cost for struvite systems developed here compares favourably with other schemes found in the literature, which range from 1.5 cents (Westerman et al. 2010) to 7.1 cents/kg live wt (Shepherd et al. 2009). Westerman's cost projection used a farm twice as large, so further economies of scale and process improvement would likely improve the cost estimation of this scheme. The projected phosphorus recovery costs of \$1.75 to \$2.08 per pig would be a disincentive in the current market, especially if they were incurred by some farmers and not by others. Regulations requiring P recovery may be a method of equal distribution of additional costs.

## 9 Conclusions

The results from the experiments conducted in this research project were informative about the P forms in hog manure; efficient reactor designs for reclaiming P as struvite; and the agronomic value of reclaimed struvite. These findings can be applied to developing manure management methods where P reclamation is a priority.

Hog manure, which is often considered to be a static medium, undergoes constant modification by the microbial and physical agents that act on it during storage. In the course of this research it was observed that manure liquid held in primary and secondary lagoons have different characteristics: the pH increased with retention time of several months and P-PO<sub>4</sub> and TP decreased. This trend was verified in controlled laboratory conditions over 70 days, providing good evidence of loss of P and Mg over time and the relationship between pH decrease and P-PO<sub>4</sub> concentration increase as well as pH increase accompanied by P-PO<sub>4</sub> decrease. This was found in both aerobic and anaerobic conditions and indicated precipitation of P-PO<sub>4</sub> as pH increased and dissolution when pH decreased. However contrary to the general trend identified, it was noted that during the first 10-20 days of storage nutrient concentration increased compared to original manure levels. This aspect was explored with anaerobic fermentation experiments which determined P-PO<sub>4</sub> increase was concurrent with acid build-up, caused by the increase in VFA and CO<sub>2</sub> concentration in manure, both of which resulted from decomposition of VS by acidogenic bacteria. Natural acidification of manure does not occur when VS is low and alkalinity is high, due to the buffering response to increased acids. Trials with

four separate manures led to the conclusion that a low ratio of alkalinity (mg/L)/VS (g/L) will lead to acid buildup and P-PO<sub>4</sub> concentration increase in manure.

Two precipitation reactors were constructed and operated, one very “low tech” and capable of reclaiming P from any typical commercial hog lagoon in MB and the other was an upflow system designed for manure handling systems equipped with a centrifuge or rotary press for solids separation. The reactors removed 75% and 31% of TP respectively, with further improvements on these systems enabling increased recovery. Both of these reactors demonstrated that TP removal from manure supernatant can be accomplished by consideration of the precipitation dynamics of P-PO<sub>4</sub> under different conditions. Both manures had high levels of Ca which would pose a problem in precipitate recovery in normal upflow reactors due to the formation of poorly settling calcium phosphate and subsequent loss in the effluent. This problem was addressed by a long retention time (24 hr) for the batch reactor, allowing calcium phosphate flocs adequate time to settle, and in the upflow reactor by precipitation in a low pH environment (pH 6.8) in which no calcium phosphates are formed. High TSS was avoided in the batch reactor because of a long settling time, and because of rotary press pre-treatment for the upflow reactor. Presence of CO<sub>2</sub> in manure used in the second reactor enabled air stripping as a means of pH adjustment, which saved chemical costs.

These adaptations to the manure characteristics enabled good P removal and recovery from two very different manure supernatants. The forms of P as well as Ca, TSS, Mg, CO<sub>2</sub> and pH levels were all important in maximizing P precipitation.

Consideration of these parameters helped to create and improve reactor design, leading to higher TP removal and recoveries.

The investigation into elutriation as a means of increasing P removal from manure solids revealed this process did not dissolve adequate amounts of TP to warrant the effort. Cycling reactor effluent back through manure solids reclaimed only 2-3% of TP present in solids, likely due to the low solubility of struvite and the high ion activity in the effluent.

The commercial value of struvite as a fertilizer is based on nutrient availability to a plant and this aspect may assign a better sale price to pure struvite than one with calcium phosphate impurities. Is a precipitation process that produces pure struvite worth the investment compared to one that produces struvite with impurities? This question was addressed by an agronomic study on canola and determined there is no significant difference in biomass yield in plants fertilized with pure struvite and those fertilized with struvite produced from lower purity struvite. The study found that in a P deficient soil, a canola plant will extract P it needs from struvite of high and low purity on an equal basis. The study also found struvite did not perform as well as commercial P fertilizer, which was contrary to the findings by other researchers. Struvite is less soluble in alkaline soils than neutral or acidic soils and our study used a soil more alkaline than any other agronomic struvite study found in the literature. It is clear that more research is needed to determine optimum soil types for struvite fertilization and its eventual fate in alkaline soils.

## 9.1 Contributions to the field

The work completed in this research project has made several contributions to the science of P removal and recovery from the waste stream. There have been five distinct contributions to the science of P removal and recovery during the course of this research.

- Development of a sampling technique to determine four forms of P in manure: soluble organic, soluble inorganic, particulate mineral and particulate organic. This technique has been published in an engineering journal (Ackerman and Cicek 2011).
- Development of manure storage conditions that can increase P-PO<sub>4</sub> concentrations significantly by acidification during natural fermentation. Discovery that the total alkalinity/g VS ratio is a predictive measure for the acidification of manure. (In press, Biological Engineering Transactions).
- Determination that struvite with impurities and pure struvite have the same value as fertilizer on an agronomic basis for canola plants. No significant difference was found in biomass yield using pure struvite versus precipitated manure solids with only 33% pure struvite. (Submitted to peer reviewed journal).
- Significant TP removal is possible in an upflow reactor from manure supernatant with a very small pH change and a reaction level below pH 7. Precipitation at this pH also prevented calcium phosphate floc formation which normally inhibits P removal and reduces recovery (paper in progress).
- Collected evidence of the inverse relationship between pH and P-PO<sub>4</sub> concentration under both aerobic and anaerobic storage conditions.

## 10 References

- Ackerman, J. N. and N. Cicek (2011). Phosphorus Removal and Recovery from Hog Lagoon Supernatant Using a Gravity-Settled Batch Reactor and Increased pH. *Biological Engineering Transactions* 4(4): 207-218.
- Adnan, A., D. S. Mavinic and F. A. Koch (2003). Pilot-scale study of phosphorus recovery through struvite crystallization - examining the process feasibility. *Journal of Environmental Engineering and Science* 2(5): 315-324.
- Ali, M. I. and P. A. Schneider (2008). An approach of estimating struvite growth kinetic incorporating thermodynamic and solution chemistry, kinetic and process description. *Chemical Engineering Science* 63(13): 3514-3525.
- Appeldoorn, K. J., A. J. Boom, G. J. J. Kortstee and A. J. B. Zehnder (1992). Contribution of precipitated phosphates and acid-soluble polyphosphate to enhanced biological phosphate removal. *Water Research* 26(7): 937-943.
- Asimov, I. (1974). Life's bottleneck. Asimov on Chemistry. Garden City, New York, Double Day and Company Inc.
- Battistoni, P., A. De Angelis, M. Prisciandaro, R. Boccadoro and D. Bolzonella (2002). P removal from anaerobic supernatants by struvite crystallization: long term validation and process modelling. *Water Research* 36(8): 1927-1938.
- Battistoni, P., P. Pavan, M. Prisciandaro and F. Cecchi (2000). Struvite crystallization: A feasible and reliable way to fix phosphorus in anaerobic supernatants. *Water Research* 34(11): 3033-3041.
- Baxter, C. A., B. C. Joern, D. Ragland, J. S. Sands and O. Adeola (2003). Phytase, high-available-phosphorus corn, and storage effects on phosphorus levels in pig excreta. *Journal of Environmental Quality* 32(4): 1481-1489.
- Bhuiyan, M. I. H., D. S. Mavinic and R. D. Beckie (2007). A solubility and thermodynamic study of struvite. *Environmental Technology* 28(9): 1015-1026.
- Bicudo, J. R., L. M. Safley and P. W. Westerman (1999). Nutrient content and sludge volumes in single-cell recycle anaerobic swine lagoons in North Carolina. *Transactions of the Asae* 42(4): 1087-1093.
- Bouzas, A., J. Ribes, J. Ferrer and A. Seco (2007). Fermentation and elutriation of primary sludge: Effect of SRT on process performance. *Water Research* 41(4): 747-756.

- Bowers, K. E. and P. W. Westerman (2005). Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. *Transactions of the Asae* 48(3): 1227-1234.
- Bridger, G. L., R. W. Starostka and M. L. Salutsky (1962). Micronutrient sources – metal ammonium phosphates as fertilizers. *Journal of Agricultural and Food Chemistry* 10(3): 181-195.
- Bril, J. and W. Salomons (1990). Chemical-Composition of Animal Manure - a Modeling Approach. *Netherlands Journal of Agricultural Science* 38(3): 333-351.
- Britton, A., F. A. Koch, D. S. Mavinic, A. Adnan, W. K. Oldham and B. Udala (2005). Pilot-scale struvite recovery from anaerobic digester supernatant at an enhanced biological phosphorus removal wastewater treatment plant. *Journal of Environmental Engineering and Science* 4(4): 265-277.
- Burns, R. T., L. B. Moody, I. Celen and J. R. Buchanan (2003). Optimization of phosphorus precipitation from swine manure slurries to enhance recovery. *Water Science and Technology* 48(1): 139-146.
- Burns, R. T., L. B. Moody, F. R. Walker and D. R. Raman (2001). Laboratory and in-situ reductions of soluble phosphorus in swine waste slurries. *Environmental Technology* 22(11): 1273-1278.
- Cabeza, R., B. Steingrobe, W. Roemer and N. Claassen (2011). Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. *Nutrient Cycling in Agroecosystems* 91(2): 173-184.
- Carey, R. O. and K. W. Migliaccio (2009). Contribution of Wastewater Treatment Plant Effluents to Nutrient Dynamics in Aquatic Systems: A Review. *Environmental Management* 44(2): 205-217.
- Celen, I., J. R. Buchanan, R. T. Burns, R. B. Robinson and D. R. Raman (2007). Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research* 41(8): 1689-1696.
- Chen, Y. G., S. Jiang, H. Y. Yuan, Q. Zhou and G. W. Gu (2007). Hydrolysis and acidification of waste activated sludge at different pHs. *Water Research* 41(3): 683-689.
- Christensen, M. L., M. Hjorth and K. Keiding (2009). Characterization of pig slurry with reference to flocculation and separation. *Water Research* 43(3): 773-783.
- Christian, G. D. (1994). Analytical Chemistry. New York, John Wiley & Sons Inc.

Clesceri, L. S., A. E. Greenberg and A. D. Eaton, Eds. (1998). *Standard Methods for the Examination of Water and Wastewater*. Washington D.C., American Public Health Assn., American Water Works Assn., Water Environment Federation.

Cordell, D., J. O. Drangert and S. White (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change-Human and Policy Dimensions* 19(2): 292-305.

Daumer, M. L., F. Beline and M. Sperandio (2004). The effect of phytase in pig diet and solid/liquid separation of pig slurry on phosphorus, calcium, and magnesium fractionation. *Transactions of the Asae* 47(4): 1247-1253.

de-Bashan, L. E. and Y. Bashan (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research* 38(19): 4222-4246.

Dorozhkin, S.V. (2010). Amorphous calcium (ortho)phosphates. *Acta Biomaterialia* 6:4457-4475

Doyle, J. D., R. Philp, J. Churchley and S. A. Parsons (2000). Analysis of struvite precipitation in real and synthetic liquors. *Process Safety and Environmental Protection* 78(B6): 480-488.

Durrant, A. E., M. D. Scrimshaw, I. Stratful and J. N. Lester (1999). Review of the feasibility of recovering phosphate from wastewater for use as a raw material by the phosphate industry. *Environmental Technology* 20(7): 749-758.

El Diwani, G., S. El Rafie, N. N. El Ibiari and H. I. El-Aila (2007). Recovery of ammonia nitrogen from industrial wastewater treatment as Struvite slow releasing fertilizer. *Desalination* 214(1-3): 200-214.

Elser, J. and E. Bennett (2011). A broken biogeochemical cycle. *Nature* 478(7367): 29-31.

Gaterell, M. R., R. Gay, R. Wilson, R. J. Gochin and J. N. Lester (2000). An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environmental Technology* 21(9): 1067-1084.

Gonzalez-Ponce, R., E. G. Lopez-de-Sa and C. Plaza (2009). Lettuce Response to Phosphorus Fertilization with Struvite Recovered from Municipal Wastewater. *Hortscience* 44(2): 426-430.

- Gungor, K. and K. G. Karthikeyan (2005). Probable phosphorus solid phases and their stability in anaerobically digested dairy manure. *Transactions of the Asae* 48(4): 1509-1520.
- Harper, S. R. and F. G. Pohland (1986). Recent developments in hydrogen management during anaerobic biological waste water treatment. *Biotechnology and Bioengineering* 28(4): 585-602.
- Harris, W. G., A. C. Wilkie, X. Cao and R. Sirengo (2008). Bench-scale recovery of phosphorus from flushed dairy manure wastewater. *Bioresource Technology* 99(8): 3036-3043.
- Jaffer, Y., T. A. Clark, P. Pearce and S. A. Parsons (2002). Potential phosphorus recovery by struvite formation. *Water Research* 36(7): 1834-1842.
- Johnston, A. E. and I. R. Richards (2003). Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use and Management* 19(1): 45-49.
- Jordaan, E. M., J. Ackerman and N. Cicek (2010). Phosphorus removal from anaerobically digested swine wastewater through struvite precipitation. *Water Science and Technology* 61(12): 3228-3234.
- Kaneko, S. and K. Nakajima (1988). Phosphorus Removal by Crystallization Using a Granular Activated Magnesia Clinker. *Journal Water Pollution Control Federation* 60(7): 1239-1244.
- Kim, B. U., W. H. Lee, H. J. Lee and J. M. Rim (2004). Ammonium nitrogen removal from slurry-type swine wastewater by pretreatment using struvite crystallization for nitrogen control of anaerobic digestion. *Water Science and Technology* 49(5-6): 215-222.
- Laridi, R., J. C. Auclair and H. Benmoussa (2005). Laboratory and pilot-scale phosphate and ammonium removal by controlled struvite precipitation following coagulation and flocculation of swine wastewater. *Environmental Technology* 26(5): 525-536.
- Le Corre, K. S., E. Valsami-Jones, P. Hobbs, B. Jefferson and S. A. Parsons (2007a). Agglomeration of struvite crystals. *Water Research* 41(2): 419-425.
- Le Corre, K. S., E. Valsami-Jones, P. Hobbs, B. Jefferson and S. A. Parsons (2007b). Struvite crystallization and recovery using a stainless steel structure as a seed material. *Water Research* 41: 2449-2456.
- Le Corre, K. S., E. Valsami-Jones, P. Hobbs and S. A. Parsons (2007c). Kinetics of struvite precipitation: Effect of the magnesium dose on induction times and precipitation rates. *Environmental Technology* 28(12): 1317-1324.

- Le Corre, K. S., E. Valsami-Jones, P. Hobbs and S. A. Parsons (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* 283(3-4): 514-522.
- Liu, Y., M. M. Rahman, J.-H. Kwag, J.-H. Kim and C. Ra (2011). Eco-friendly Production of Maize Using Struvite Recovered from Swine Wastewater as a Sustainable Fertilizer Source. *Asian-Australasian Journal of Animal Sciences* 24(12): 1699-1705.
- Maekawa, T., C. M. Liao and X. D. Feng (1995). Nitrogen and Phosphorus Removal for Swine Waste-Water Using Intermittent Aeration Batch Reactor Followed by Ammonium Crystallization Process. *Water Research* 29(12): 2643-2650.
- Massey, M. S., J. G. Davis, J. A. Ippolito and R. E. Sheffield (2009). Effectiveness of Recovered Magnesium Phosphates as Fertilizers in Neutral and Slightly Alkaline Soils. *Agronomy Journal* 101(2): 323-329.
- Matynia, A., J. Koralewska, B. Wierzbowska and K. Piotrowski (2006). The influence of process parameters on struvite continuous crystallization kinetics. *Chemical Engineering Communications* 193(2): 160-176.
- Mavinic, D. S., F. A. Koch, H. Huang and K. V. Lo (2007). Phosphorus recovery from anaerobic digester supernatants using a pilot-scale struvite crystallization process. *Journal of Environmental Engineering and Science* 6(5): 561-571.
- Moerman, W., M. Carballa, A. Vandekerckhove, D. Derycke and W. Verstraete (2009). Phosphate removal in agro-industry: Pilot- and full-scale operational considerations of struvite crystallization. *Water Research* 43(7): 1887-1892.
- Moody, L. B., R. T. Burns and K. J. Stalder (2009). Effect of anaerobic digestion on manure characteristics for phosphorus precipitation from swine waste. *Applied Engineering in Agriculture* 25(1): 97-102.
- Moussa, S. B., G. Maurin, C. Gabrielli and M. B. Amor (2006). Electrochemical precipitation of struvite. *Electrochemical and Solid-State Letters* 9(6): C97-C101.
- Munch, E. V. and K. Barr (2001). Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research* 35(1): 151-159.
- Murphy, J. and J. P. Riley (1962). A modified single solution method for determination of phosphate in natural waters *Analytica Chimica Acta* 26(1): 31-37.
- Nelson, N. O., R. L. Mikkelsen and D. L. Hesterberg (2003). Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg : P ratio and determination of rate constant. *Bioresource Technology* 89(3): 229-236.

- Pastor, L., D. Mangin, R. Barat and A. Seco (2008). A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process. *Bioresource Technology* 99(14): 6285-6291.
- Pastor, L., D. Mangin, J. Ferrer and A. Seco (2010). Struvite formation from the supernatants of an anaerobic digestion pilot plant. *Bioresource Technology* 101(1): 118-125.
- Pastor, L., N. Marti, A. Bouzas and A. Seco (2008). Sewage sludge management for phosphorus recovery as struvite in EBPR wastewater treatment plants. *Bioresource Technology* 99(11): 4817-4824.
- Plaza, C., R. Sanz, C. Clemente, J. M. Fernandez, R. Gonzalez, A. Polo and M. F. Colmenarejo (2007). Greenhouse evaluation of struvite and sludges from municipal wastewater treatment works as phosphorus sources for plants. *Journal of Agricultural and Food Chemistry* 55(20): 8206-8212.
- Ponce, R. G. and M. De Sa (2007). Evaluation of struvite as a fertilizer: a comparison with traditional P sources. *Agrochimica* 51(6): 301-308.
- Ponce, R. G. and M. De Sa (2008). Efficacy of magnesium ammonium phosphate recovered from wastewater on white lupin plant. A greenhouse experiment. *Agrochimica* 52(6): 352-359.
- Puchajda, B. and J. Oleszkiewicz (2006). Extended acid digestion for inactivation of fecal coliforms. *Water Environment Research* 78(12): 2389-2396.
- Puchajda, B. and J. Oleszkiewicz (2006). Thermophilic anaerobic acid digestion of biosolids: hydrolysis, acidification, and optimization of retention time of acid digestion. *Journal of Environmental Engineering and Science* 5(3): 187-195.
- Quintana, M., M. F. Colmenarejo, J. Barrera, G. Garcia, E. Garcia and A. Bustos (2004). Use of a byproduct of magnesium oxide production to precipitate phosphorus and nitrogen as struvite from wastewater treatment liquors. *Journal of Agricultural and Food Chemistry* 52(2): 294-299.
- Scherrenberg, S. M., A. F. van Nieuwenhuijzen, H. W. H. Menkveld, J. J. M. den Elzen and J. van der Graaf (2008). Innovative phosphorus distribution method to achieve advanced chemical phosphorus removal. *Water Science and Technology* 58(9): 1727-1733.
- Shen, Y., J. A. Ogejo and K. E. Bowers (2011). Abating the effects of calcium on struvite precipitation in liquid dairy manure. *Transactions of the Asabe* 54(1): 325-336.

- Shepherd, T. A., R. T. Burns, L. B. Moody, D. R. Raman and K. J. Stalder (2009). Development of a bench-scale air sparged continuous flow reactor for struvite precipitation from two different liquid swine manure storage systems. *Applied Engineering in Agriculture* 25(3): 425-430.
- Schindler, D. W. (1976a). Biogeochemical evolution of phosphorus limitation in nutrient-enriched lakes of the Precambrian Shield. Environmental Biogeochemistry. J. O. Nriagu. Ann Arbor, Mich., Ann Arbor Science Publishers Inc.
- Schindler, D. W., R. W. Newbury, K. G. Beaty and P. Campbell (1976b). Natural water and chemical budgets for a small Precambrian lake basin in Central Canada. *Journal of Fisheries Research Board of Canada* 33: 2526-2543.
- Sommer, S. G. and S. Husted (1995). The chemical buffer system in raw and digested animal slurry. *Journal of Agricultural Science* 124: 45-53.
- Song, Y. H., G. L. Qiu, P. Yuan, X. Y. Cui, J. F. Peng, P. Zeng, L. Duan, L. C. Xiang and F. Qian (2011). Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions. *Journal of Hazardous Materials* 190(1-3): 140-149.
- Song, Y. H., P. Yuan, B. H. Zheng, H. F. Peng, F. Yuan and Y. Gao (2007). Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater. *Chemosphere* 69(2): 319-324.
- Stratful, I., M. D. Scrimshaw and J. N. Lester (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Research* 35(17): 4191-4199.
- Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto and T. Yasuda (2006). The technology of phosphorus removal and recovery from swine wastewater by struvite crystallization reaction. *JARQ* 40(4): 341-349.
- Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto, T. Yasuda and M. Waki (2007). Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology* 98(8): 1573-1578.
- Suzuki, K., Y. Tanaka, T. Osada and M. Waki (2002). Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Research* 36(12): 2991-2998.
- Szogi, A. A., M. B. Vanotti and P. G. Hunt (2006). Dewatering of phosphorus extracted from liquid swine waste. *Bioresource Technology* 97(1): 183-190.

- Ucisik, A. S. and M. Henze (2008). Biological hydrolysis and acidification of sludge under anaerobic conditions: The effect of sludge type and origin on the production and composition of volatile fatty acids. *Water Research* 42(14): 3729-3738.
- Utts, J. M. and R. F. Heckard (2010). *Mind on Statistics*. Boston, Mass., Brooks Cole Cengage Learning.
- Vaccari, D. A. (2009). Phosphorus: A Looming Crisis. *Scientific American* 300(6): 54-59.
- Valsami-Jones, E. (2001). Mineralogical controls on phosphorus recovery from wastewaters. *Mineralogical Magazine* 65(5): 611-620.
- van der Stelt, B., E. J. M. Temminghoff and W. H. van Riemsdijk (2005). Measurement of ion speciation in animal slurries using the Donnan Membrane Technique. *Analytica Chimica Acta* 552(1-2): 135-140.
- Wang, J., J. G. Burken and X. Q. Zhang (2006). Effect of seeding materials and mixing strength on struvite precipitation. *Water Environment Research* 78(2): 125-132.
- Wang, J., J. G. Burken, X. Q. Zhang and R. Surampalli (2005). Engineered struvite precipitation: Impacts of component-ion molar ratios and pH. *Journal of Environmental Engineering-Asce* 131(10): 1433-1440.
- Westerman, P. W., K. E. Bowers and K. D. Zering (2010). Phosphorus recovery from covered digester effluent with a continuous-flow struvite crystallizer. *Applied Engineering in Agriculture* 26(1): 153-161.
- Wu, Q. Z. and P. L. Bishop (2004). Enhancing struvite crystallization from anaerobic supernatant. *Journal of Environmental Engineering and Science* 3(1): 21-29.
- Yilmaz, V. and G. N. Demirer (2008). Improved anaerobic acidification of unscreened dairy manure. *Environmental Engineering Science* 25(3): 309-317.
- Yuan, Q., R. Sparling and J. A. Oleszkiewicz (2009). Waste activated sludge fermentation: Effect of solids retention time and biomass concentration. *Water Research* 43(20): 5180-5186.
- Zeng, L. and X. M. Li (2006). Nutrient removal from anaerobically digested cattle manure by struvite precipitation. *Journal of Environmental Engineering and Science* 5(4): 285-294.
- Zhang, T. X., K. E. Bowers, J. H. Harrison and S. L. Chen (2010). Releasing Phosphorus from Calcium for Struvite Fertilizer Production from Anaerobically Digested Dairy Effluent. *Water Environment Research* 82(1): 34-42.

Zhu, J., Z. Zhang and C. Miller (2005). Effect of pig slurry solids on aeration efficiency and odour generation. *Biosystems Engineering* 90(4): 443-450.

Zoetemeyer, R. J., J. C. Vandenhevel and A. Cohen (1982). pH influence on acidogenic dissimilation of glucose in an anaerobic digester. *Water Research* 16(3): 303-311.

## 11 Appendix A

Additional data from section 4.6

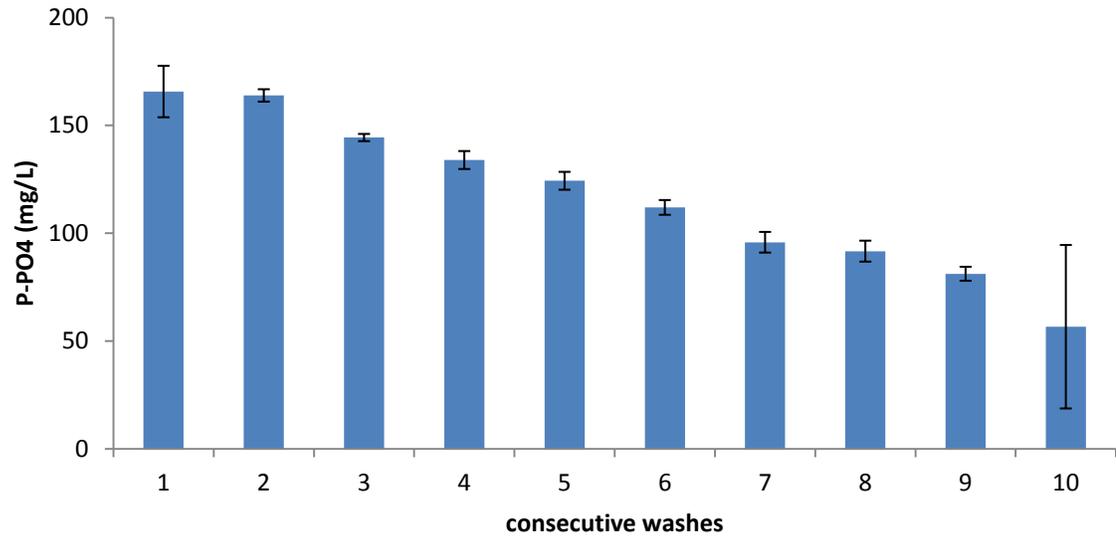


Figure 11.1 Concentration of P-PO<sub>4</sub> in wash medium (deionized water) used to elutriate dried manure solids.

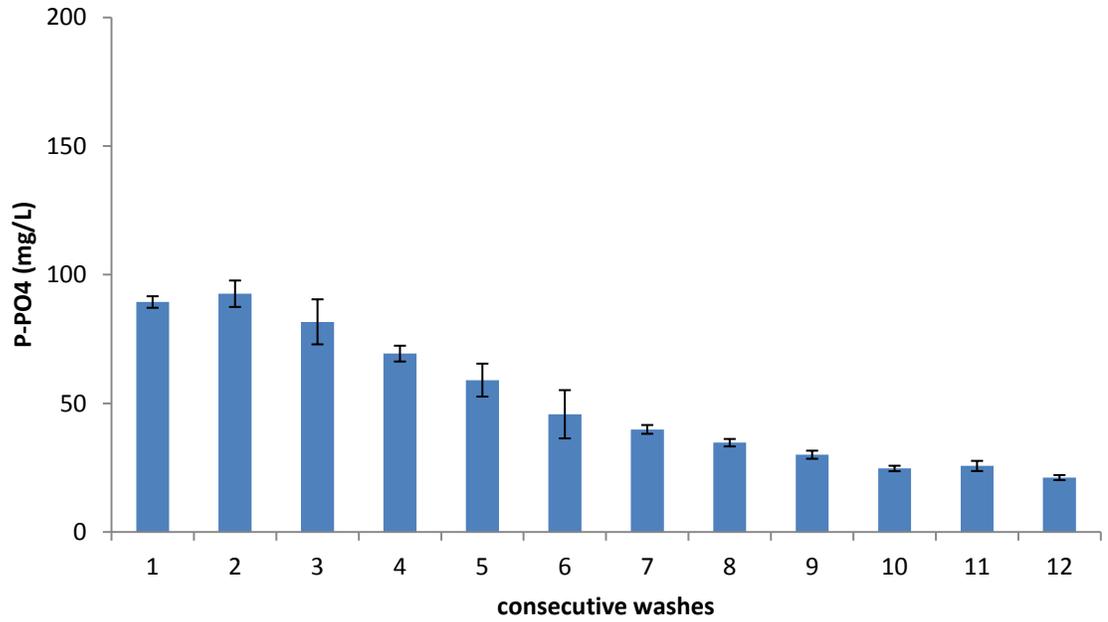


Figure 11.2 Concentration of P-PO<sub>4</sub> in wash medium (struvite reactor effluent at pH 8). This data is the net P removal after subtraction of effluent background P-PO<sub>4</sub> levels of 18 mg/L.

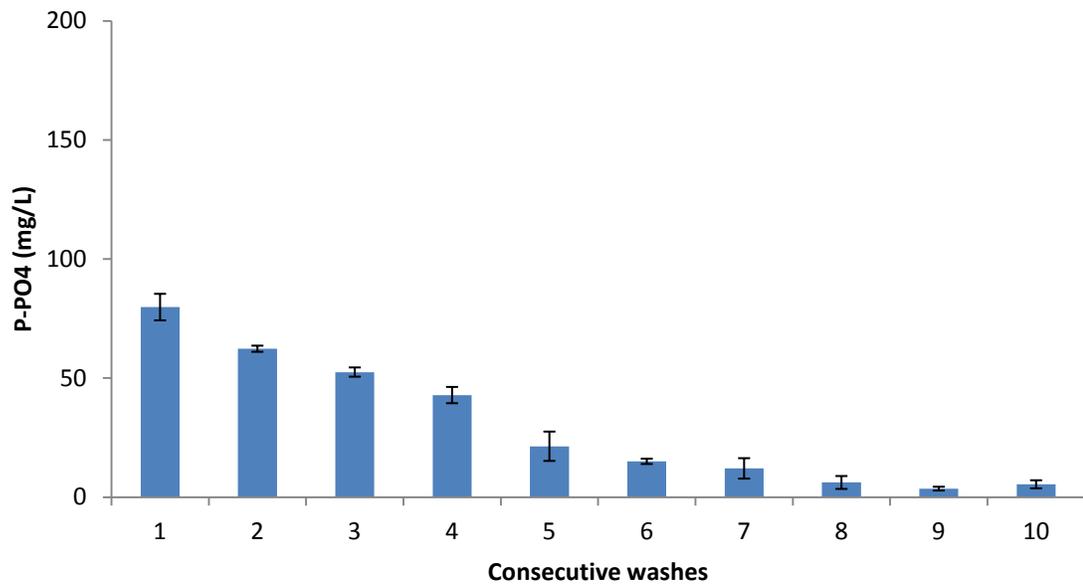


Figure 11.3 Concentration of P-PO<sub>4</sub> in wash medium (struvite reactor effluent at pH 7). This data is the net P removal after subtraction of effluent background P-PO<sub>4</sub> levels of 62 mg/L.

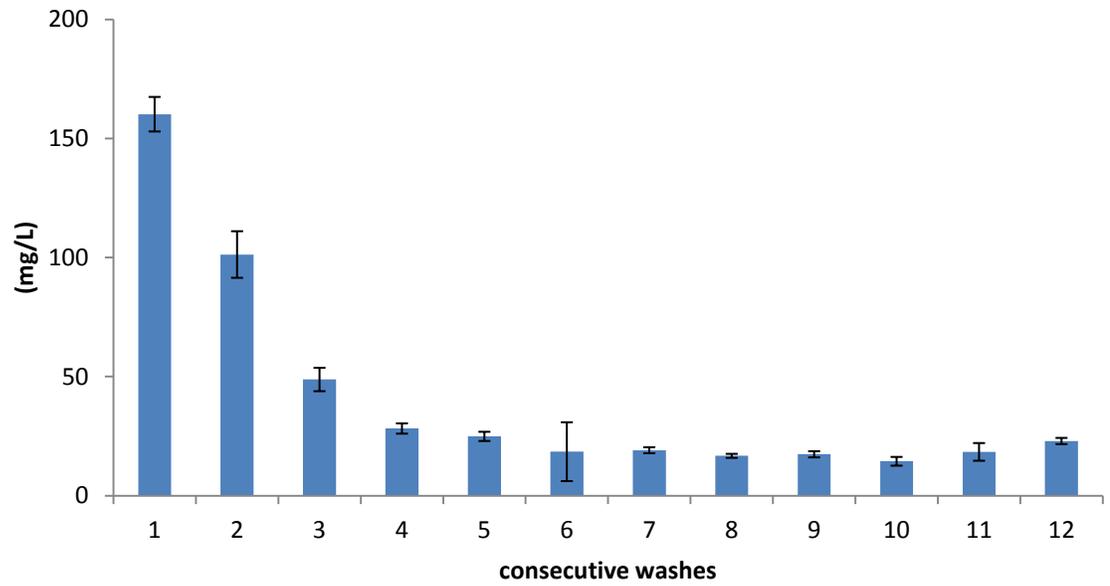


Figure 11.4 Magnesium in wash medium (reactor effluent at pH 8). Data is the net amount removed after subtracting background Mg present in effluent (106 mg/L).

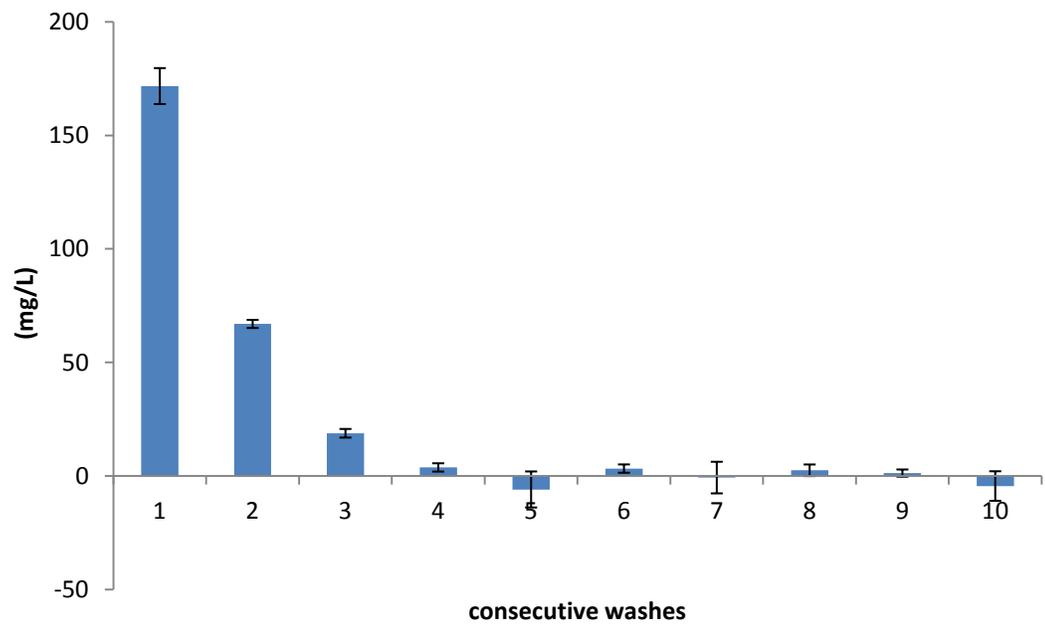


Figure 11.5 Magnesium in wash medium (reactor effluent at pH 7). Data is the net amount removed after subtracting background Mg (145 mg/L).

## 12 Appendix B

Additional data from section 5.7

Table 12.1 Analysis of variance of sampling means between 3 manures in 3 reactors replicates at 3 HRTs.

	<b>P-PO<sub>4</sub></b>	<b>Mg</b>	<b>NH<sub>4</sub></b>	<b>Ca</b>	<b>Alkalinity</b>	<b>VFA</b>
<b>Manure</b>	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
<b>Reactor</b>	0.5329	0.008	0.0501	0.7214	0.0267	<0.0001
<b>Manure * reactor</b>	<0.0001	<0.0001	0.0096	0.1514	0.0261	<0.0001
<b>Time</b>	<0.0001	<0.0001	<0.0001		<0.0001	<0.0001
<b>Manure * time</b>	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
<b>Reactor* time</b>	0.0391	0.0004	0.0113	0.1236	0.0358	0.9773
<b>Manure* reactor*time</b>	<0.0001	<0.0001	0.1802	0.2135	0.2557	

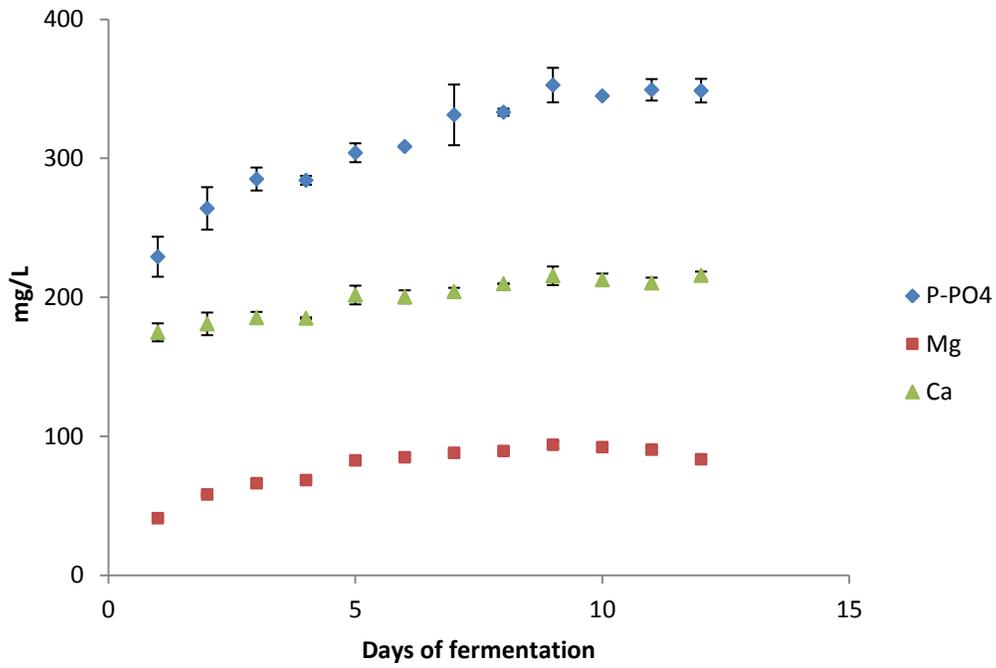


Figure 12.1 Daily sampling (in duplicate) of nutrients from a replicate reactor during fermentation of Manure 4.

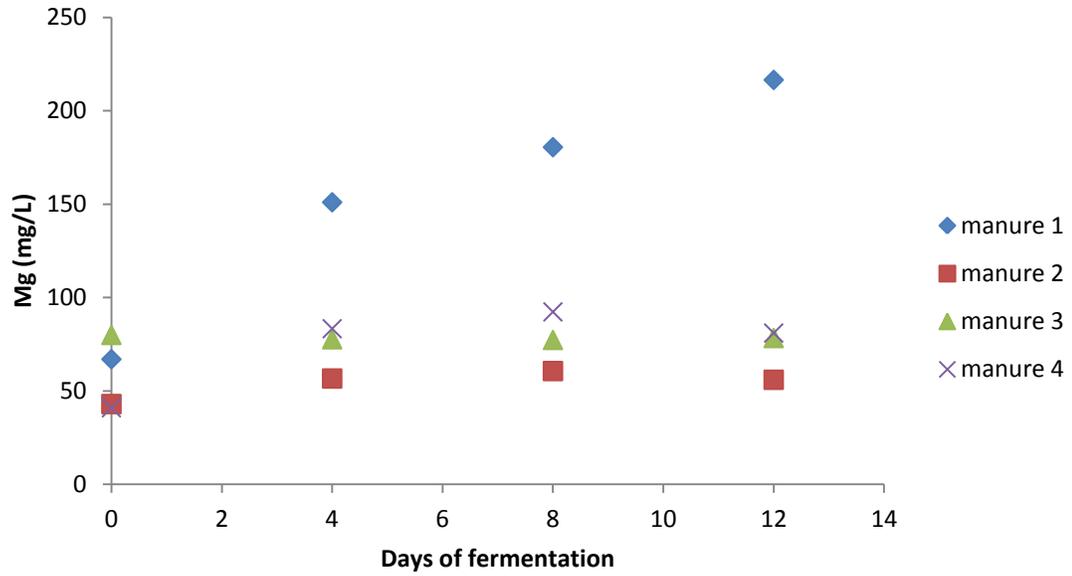


Figure 12.2 Comparison of Mg in filtered samples at 0, 4, 8, and 12 days of fermentation of four manures. Standard Error = 1.2.

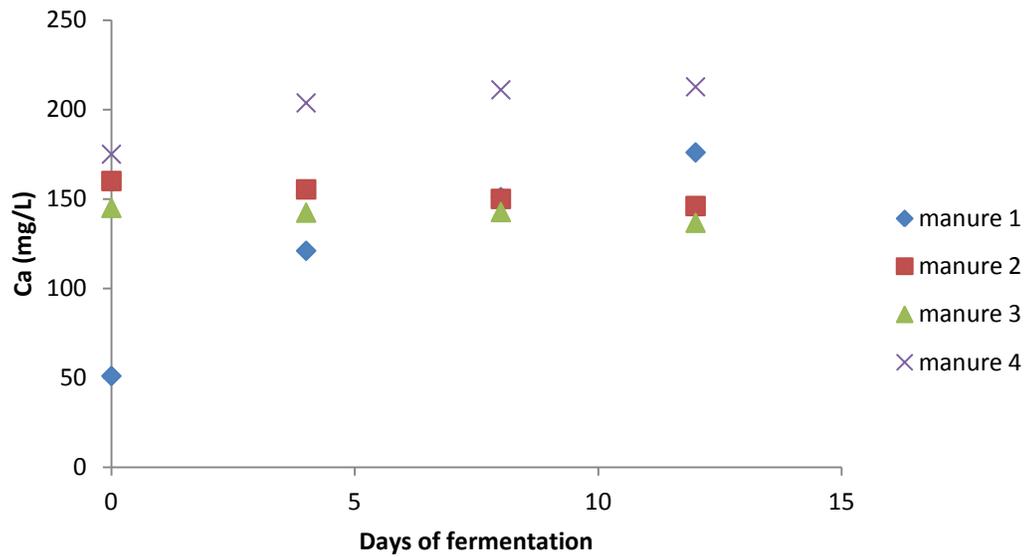


Figure 12.3 Comparison of Ca in filtered samples at 0, 4, 8, and 12 days of fermentation of four manures. Standard Error = 3.7.

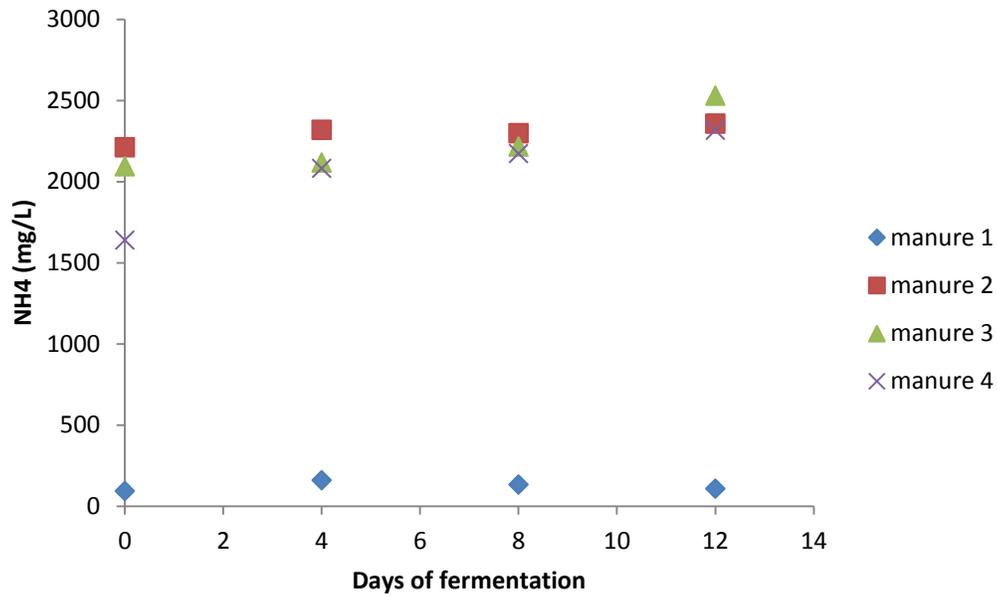


Figure 12.4 Comparison of NH<sub>4</sub> in filtered samples at 0, 4, 8, and 12 days of fermentation of four manures. Standard Error = 47.4

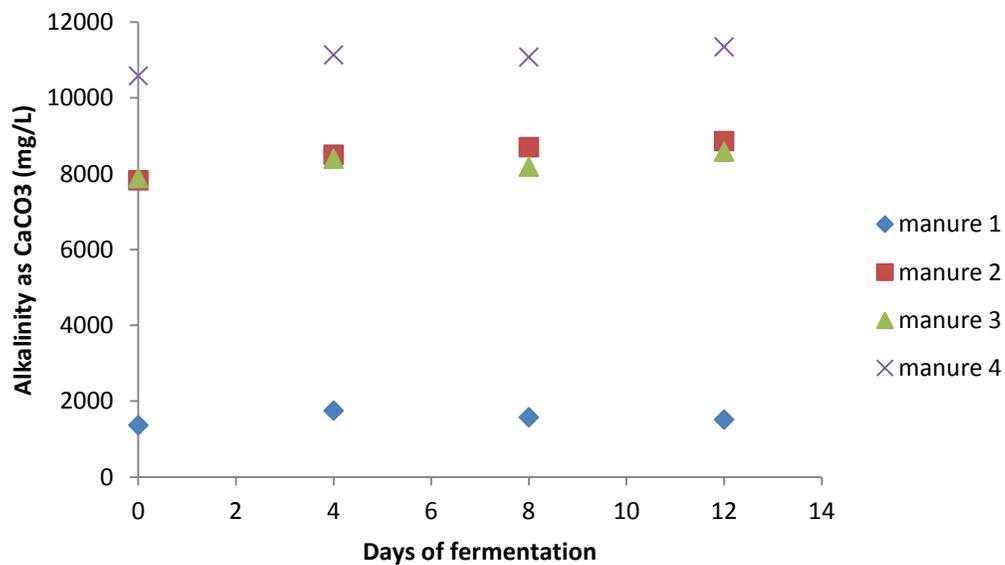


Figure 12.5 Comparison of total alkalinity as CaCO<sub>3</sub> in filtered samples at 0, 4, 8, and 12 days of fermentation of four manures. Standard Error = 104

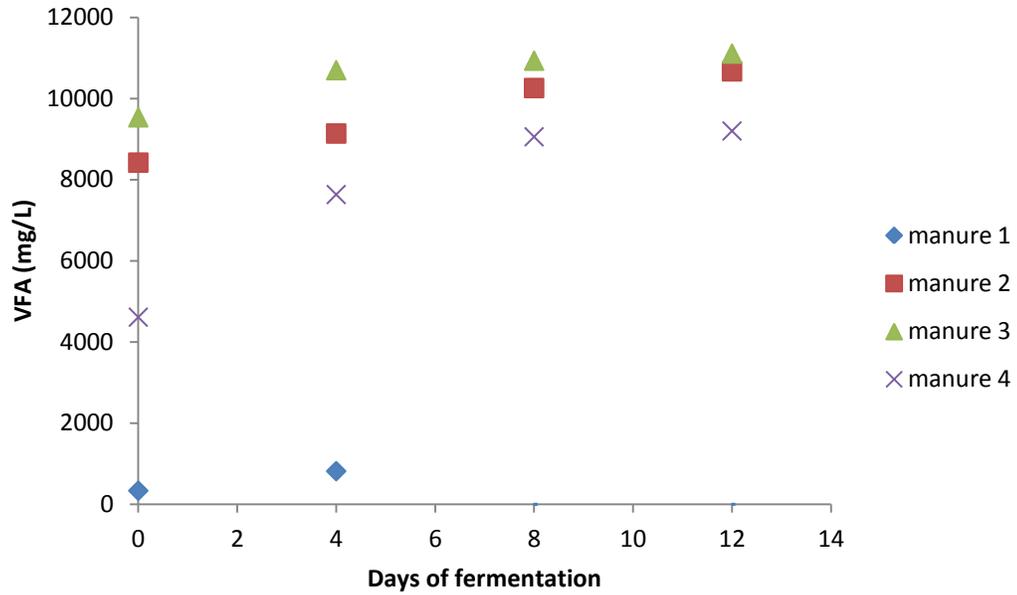


Figure 12.6 Comparison of VFA in filtered samples at 0, 4, 8, and 12 days of fermentation of four manures. Data for manure 1 for 8day and 12 HRT was lost due to instrument malfunction. Standard Error = 388 for Manure 2, 3, and 4.

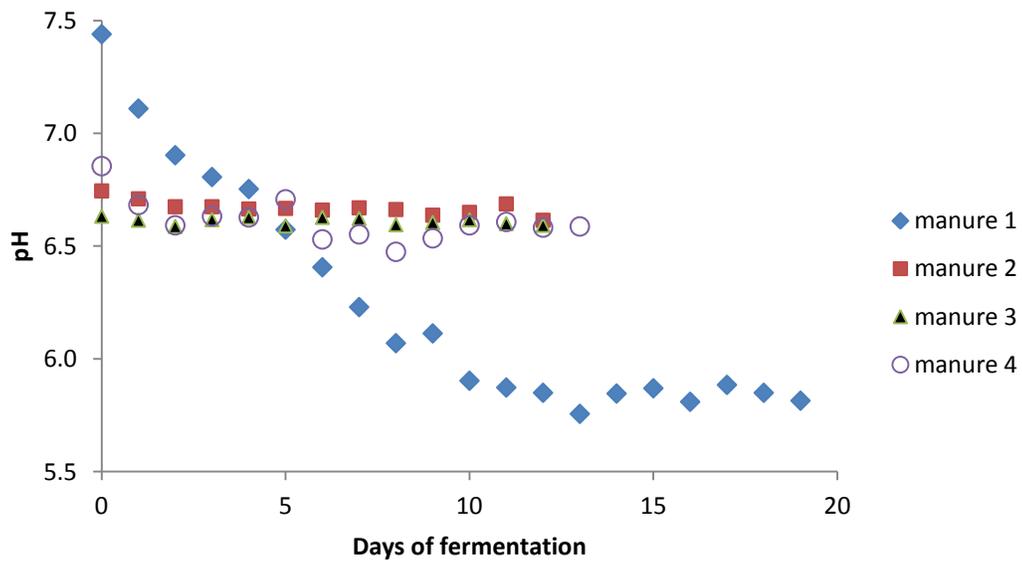


Figure 12.7 Change in pH for each of the manures stored under anaerobic conditions.

Table 12.2 Total solids (means of 3 samples from 3 replicate reactors with standard deviation) of the four manures at the start and at each HRT under anaerobic conditions.

<b>TS</b>				
<b>Manure</b>	<b>Influent</b>	<b>4D HRT</b>	<b>8D HRT</b>	<b>12D HRT</b>
<b>1</b>	2.39 (1.1)	2.73 (0.68)	2.64 (0.5)	2.67 (0.6)
<b>2</b>	2.34 (0)	2.24 (0.06)	2.12 (0.05)	2.07 (0.09)
<b>3</b>	2.45 (0)	2.33 (0.13)	2.27 (0.07)	2.28 (0.14)
<b>4</b>	7.41 (0.08)	6.20 (0.57)	6.19 (0.15)	5.51 (0.09)

Table 12.3 Volatile solids (means of 3 samples from 3 replicate reactors with standard deviation) of the four manures at the start and at each HRT under anaerobic conditions.

<b>VS</b>				
<b>Manure</b>	<b>Influent</b>	<b>4D HRT</b>	<b>8D HRT</b>	<b>12D HRT</b>
<b>1</b>	76.49 (2.12)	76.63 (0.39)	75.86 (0.85)	
<b>2</b>	63.60 (0)	61.87 (1.73)	59.17 (4.43)	59.50 (4.10)
<b>3</b>	61.97 (0)	58.96 (1.9)	61.05 (1.3)	60.16 (2.0)
<b>4</b>	76.39 (0.30)	74.42 (0.83)	74.03 (0.75)	72.05 (0.26)

### 13 Appendix C

Additional data from section 6.3.1

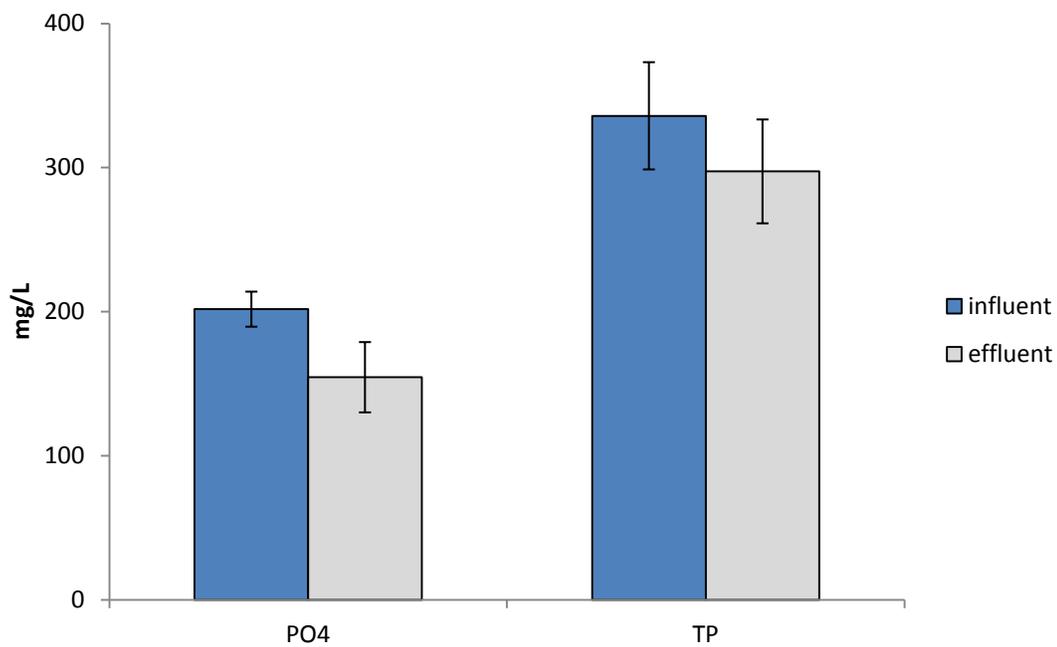


Figure 13.1 Influent and effluent phosphorus concentrations using the struvite reactor with rotary press liquid effluent. When all influents and all effluent concentrations are averaged, effluents were 22% and 17% lower than influents for P-PO<sub>4</sub> and TP respectively

Table 13.1 Mass Balance of Niverville Reactor using Rotary Press Liquid.

<b>Trial</b>	<b>Hrs</b>	<b>Total</b>	<b>TP</b>	<b>Mass</b>	<b>TP</b>	<b>Mass</b>	<b>Removed</b>	<b>Recovered</b>	<b>Recovered</b>
	<b>of</b>	<b>volume</b>	<b>Influent</b>	<b>P (g)</b>	<b>effluent</b>	<b>P (g)</b>	<b>P (g)</b>	<b>solids (dry</b>	<b>solids mass</b>
	<b>Op</b>	<b>(L)</b>	<b>(mg/L)</b>		<b>(mg/L)</b>			<b>g)</b>	<b>P (g)</b>
<b>1</b>	22.5	1755	357	626	249	437	189	90	7.4
<b>2</b>	2	156	308	48	301	47	1	0	0
<b>3</b>	23	1794	302	542	328	589	-47	115	13.7
<b>4</b>	26	2028	366	742	331	672	71	170	18.3
<b>5</b>	2	156	342	53	334	52	1	0	0
<b>6</b>	22.5	1755	288	506	256	448	57	160	15.6
<b>7</b>	1	78	480	37	304	24	14	0	0
<b>8</b>	23	1794	388	696	282	505	191	193	22.8
<b>9</b>	22	1716	282	483	133	228	255	161	20.2
<b>10</b>	23	1794	263	472	259	465	8	208	21.8
<b>total</b>		13026					<b>739</b>	<b>1097</b>	<b>120</b>