The Impact of Phosphorous Species on Dewaterability of Wastewater Solids

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by

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ABSTRACT
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Phosphorus regulations are causing Water Resource Recovery Facilities (WRRFs) to implement new technologies to remove phosphorus (P) before they discharge liquid effluent. Enhanced Biological Phosphorus Removal (EBPR) is often employed to remove P from water. However, sludges from EBPR plants have shown decreases in dewaterability soon after EBPR was initiated. This decline in dewaterability is not well understood, nor is the best way to improve the dewatering EBPR sludge. Specifically, the role of different P species on sludge dewaterability is not well understood. Several laboratory experiments were conducted at the Marquette University Water Quality Center with the following objectives: i) determine the impact of P speciation on dewaterability of various sludges, ii) determine an effective method for converting non-reactive P to reactive P in sludge, and iii) determine the impact of acid treatment and decanting on anaerobic digester dewaterability. P speciation and capillary suction time (a measurement of dewaterability) of sludge were the main characteristics measured in this research. A survey of various sludges from full-scale WRRFs was conducted and revealed that particulate P correlated to poor dewaterability in undigested sludges. Lab-scale anaerobic digesters were fed acid pretreated sludge to determine the impact of pretreatment and P species on the dewaterability of anaerobic digester biosolids. Acid pretreatment did not significantly affect dewaterability relative to control digesters that received untreated sludge. Centrate reactive P, which would contain orthophosphate, was correlated to poor dewaterability in anaerobic digester biosolids. It was suspected that orthophosphate reacted with divalent cations and increased the monovalent to divalent (M/D) cation ratio. The M/D ratio was previously suggested to correlate to dewaterability. Indeed, results from these lab-scale studied revealed that an increase in M/D ratio correlated with higher CST values, i.e. worse dewaterability.

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DEDICATION

I would like to dedicate this work to the wonderful God that created this Earth and to all of humanity that is making efforts to preserve it.

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1 INTRODUCTION

1.1 Motivation

Phosphorus (P) is a valuable commodity due to its need as a fertilizer, but an over-abundance of P in wastewater effluent can lead to eutrophication (Mayer et al. 2013). Stricter effluent limits on P are forcing water resource recovery facilities (WRRFs) to consider technologies to remove P from their effluent (Wisconsin DNR 2010). Enhanced biological phosphorous removal (EBPR) is one technology that can aid in reducing P from liquid effluent. The sludge generated from EBPR, also known as Bio-P solids, carry high amounts of P in their cell structure. It has been observed at full-scale WRRF facilities that, when EBPR is implemented, dewaterability of wastewater solids has decreased (Higgins et al. 2014). A decline in dewaterability is a major issue for WRRFs because polymer costs increase as dewaterability decreases.

Phosphorus-accumulating organisms (PAOs) are bacteria that perform EBPR. Soluble phosphate (PO_4^{3-}), is taken up into the organism and converted to polyphosphate, a form of P that is not as reactive as phosphate. Wastewater solids that contain these PAO organisms have high amounts of P. If the P in the wastewater solids could be converted to soluble phosphate and removed prior to anaerobic digestion, then P possibly could be recycled as a fertilizer and the dewaterability of the anaerobic digester effluent solids could potentially improve. While phosphate is suspected to negatively impact dewaterability (Higgins et al. 2014), it is possible that other P species, such as particulate P, could also impact dewaterability, but, to the author's knowledge, no research has been done to determine the impact of various P species on dewaterability. Research is required to better understand how altering and potentially removing P species could impact dewaterability and potentially reduce dewaterability costs.

1.2 Objectives

The goal of this research was to investigate the impact of P speciation in wastewater solids samples on dewaterability and to determine if an anaerobic digestion pretreatment method to reduce P content could improve dewaterability of digester effluent samples. It is not clearly understood why bio-P sludges have poorer dewaterability. The specific objectives of this research were to:

- Determine the impact of P speciation on dewaterability of available unthickened sludges from full-scale WRRFs specifically including sludge from the Bio-P process
- Determine the impact of acid pretreatment followed by replacement of centrate with de-ionized water on downstream anaerobic digester biosolids dewaterability
- Determine the impact of P speciation on anaerobic digester biosolids dewaterability
- Determine the impact of anaerobic digestion on P speciation

1.3 Approach

Primary sludge, waste activated sludge (WAS), and bio-P sludge were collected from four full-scale WRRFs. The sludge samples were characterized for four different P species as described in Section 3.1: i) centrate reactive P (cRP), ii) centrate non-reactive

P (cNRP), iii) particulate reactive P (pRP) and iv), particulate non-reactive P (pNRP). Volatile solids (VS), total solids (TS), monovalent cations, and divalent cations were also measured. In addition, dewaterability was quantified by capillary suction time (CST).

Lab-scale anaerobic digestion experiments were conducted to determine how P species and other sludge properties correlated to the dewaterability of anaerobic digester effluent biosolids. One set of digesters was fed primary sludge and another set was fed a sludge blend that contained Bio-P sludge. Each set included digesters fed acid pre-treated sludge for which feed sludge was mixed with acid to alter P speciation as well as control digesters fed conventional sludge that was not pretreated (Lhao, Mavinic, and Koch, 2003). Microsoft Excel and Graphpad Prism (Graphpad Software Inc., CA, USA) were used to conduct linear regressions and determine correlations between sludge characteristics, including P species, and dewaterability. Finally, the impact of anaerobic digestion on P speciation was determined.

1.4 Thesis Structure

A literature review on relevant sludge properties that affect dewaterability is presented in Chapter 2. The experimental approach and methods are presented in Chapter 3. The results and discussion are found in Chapter 4. Finally, the summary of key findings and recommendations for future work are shown in Chapter 5. Appendices are attached with supporting graphics and data. Appendix A contains a graphic explaining P speciation and appendices B-E contain supporting data and graphs for discussion in Chapter 4.

2 LITERATURE REVIEW

2.1 Goals of Biosolids Handling

Wastewater solids are a byproduct of wastewater treatment. The United States Environmental Protection Agency estimated that over 8 million dry tons of biosolids were produced in the US in 2000 (U.S. Environmental Protection Agency 1999). The handling of wastewater solids at a WRRF can range from 25%-50% of the operational cost (Batstone, Darvodelsky, and Keller 2014). At such a large portion of operating costs, there is a large financial incentive to reduce the costs associated with biosolids handling. Finding ways to reduce the volume of biosolids has been the main method to reduce solids handling costs (Tchobanoglous et al. 2003). Biosolids volume reduction can be achieved through anaerobic digestion as well as thickening and dewatering.

Anaerobic digestion is a solids handling process whereby sludges generated from primary and secondary treatment processes are placed in an anaerobic environment with microbes that convert a portion of the organic material to biogas. Anaerobic digestion has been reported to reduce total solids by as much as 50% to 60% (Appels et al. 2008). The effectiveness to stabilize sludge, reduce odor, and reduce sludge volume has made anaerobic digestion a common process in the United States, with over 1200 digesters operating at WRRFs across the country (Edwards, Othman, and Burn 2015). As an additional benefit, methane is created during the anaerobic digestion process which facilities can use for energy recovery, typically as electricity or heat (Batstone, Darvodelsky, and Keller 2014). While some solids are destroyed and converted to biogas during digestion, some undigested biosolids still remain that must be handled and transported off-site.

Thickening and dewatering are processes used to remove water from sludge. Thickening generally describes removing water from sludge with the product being a pumpable liquid. Thickening is often achieved using gravity thickeners, gravity belt thickeners or dissolved air flotation. Influent digester solids are typically thickened to be between four and six percent total solids. Dewatering generally describes the process of removing water from sludge with the product being a solid-like cake with final solids concentration of 15% or greater. Dewatering commonly occurs via belt filter presses or centrifuges (Tchobanoglous et al. 2003). Dewatering aids such as polymers are used with thickening and dewatering processes to alter the characteristics of the sludge to allow greater water removal (Reynolds and Richards 1996). Polymers can be very effective at increasing the amount of water removed, but some WRRFs spend hundreds of thousands of dollars a year to purchase the polymer (McNamara and Lawler 2008). Polymer demand is impacted by the sludge characteristics that affect dewaterability.

2.2 Wastewater Solids Characteristics that Affect Dewaterability

Many characteristics of wastewater solids affect dewaterability, and not one characteristic completely governs dewaterability. The monovalent to divalent (M/D) cation ratio, floc structure, particle size distribution, sludge type, and characteristics of extracellular polymeric substances (EPS) have all been investigated for their impacts on dewaterability (Neyens et al. 2004). Yet no consensus has been reached regarding the impacts of a given characteristic. Indeed sludge is a complex matrix, and in specific cases, certain factors are correlated to dewaterability for one type of sludge, but the correlation was not found when considering other sludge types (Poxon and Darby 1997). The following characteristics have been studied in the greatest detail with respect to their effects on dewaterability: cation ratio, floc structure, particle size distribution, and phosphorus.

2.2.1 Monovalent to Divalent (M/D) Cation Ratio

The M/D cation ratio was first used by Higgins and Novak (1997) to explain the impact of cations on sludge dewaterability. In their work, the M/D ratio was related to the divalent cation bridging theory which postulates that divalent cations can bridge together flocs (the connection of flocs is the goal of adding polymer) and improve dewaterability. Higgins and Novak (1997) suspected that monovalent cations would replace divalent cations in sludge flocs mimicking the ion-exchange reaction. This reaction would remove the bridging ability of the floc, thereby weakening the bonds between flocs. This weakened floc structure would then lead to worse dewaterability. Higgins and Novak (1997) added varying ratios of four common cations: sodium, potassium, magnesium, and calcium. They found that sludge with higher M/D ratios resulted in poorer dewaterability than sludge with lower M/D ratios. Thus, chemical or biological reactions in wastewater sludge that decrease the available magnesium or calcium content would likely hurt dewaterability.

2.2.2 Floc Structure

Extracellular polymeric substances (EPS) are the non-living organic materials that are found in flocs and can negatively or positively affect dewaterability. The structures that EPS forms between cells have the ability to hold water. EPS slime can bind cells together, creating flocs, and with more EPS, bigger flocs form, allowing for better dewaterability (Lima et al. 2005). Many of these bonds, however, can lead to bound water within the flocs and decrease dewaterability. Houghton, Quarmby, and Stephenson (2001) found that there is an amount of EPS that is beneficial to creating sludge flocs until a threshold is achieved where increased amounts of EPS becomes detrimental as more water is trapped inside the flocs.

Interestingly, there is not agreement in the literature for how to quantify EPS. Previously, classification of EPS was conducted by protein and polysaccharide measurement until Shao et al. (2009) created a method that defined EPS into categories of loosely bound EPS, tightly bound EPS and slime layer. Sometimes EPS can be found as a slime layer containing up to 99% water that covers bacteria (Costerton and Irvin 1981) suggesting an important role in dewaterability.

2.2.3 Particle Size Distribution

The particle size distribution of wastewater solids has commonly been investigated for its impact on dewaterability (Jin, Wilén, and Lant 2004; Filali et al. 2012; McNamara and Lawler 2008; Lawler et al. 1986; Higgins, Tom, and Sobeck 2004). Floc size has a significant correlation to CST and dewaterability, but also bound water. Usually larger floc size correlates to more free water and better overall dewaterability. However, flocs too large in size result in higher percentages of bound water in the sludge (Jin, Wilén, and Lant 2004).

2.2.4 Phosphorus

P can be found in different forms in a wastewater solids matrix, and certain forms of P can influence dewaterability more than others, with ortho-phosphate suspected to have the greatest impact on dewaterability. Struvite, which is a phosphate crystal bound with magnesium ($MgNH_4PO_4 \cdot 6H_2O$), has been observed to precipitate in digesters (Doyle and Parsons 2002; E. Neyens and Baeyens 2003). Struvite contains magnesium. Therefore, the formation of struvite can reduce the soluble divalent cation concentration in the wastewater solids; a drop in divalent cations can be linked to poor dewaterability (Higgins et al. 2014; Higgins and Novak 1997; Higgins, Tom, and Sobeck 2004). Soluble ortho-P could be related to floc structure and dewatering by reducing the available divalent cations, but there is a gap in knowledge of how other forms of P influence dewaterability.

2.3 P Species in Sludge

P can be found in many forms in sludge, yet only a few forms have been investigated in relation to dewaterability. Soluble ortho-phosphate and total P have been the prevailing forms of P measured in sludge (Novak et al. 2017; Popel and Jardin 1993; Barnard and Shimp 2013). Ortho-phosphate, also known as reactive P, is observed to create precipitates and influence dewaterability in sludge and biosolids (Popel and Jardin

1993; Doyle and Parsons 2002). Some researchers have begun to define and measure other forms of P, such as loosely-bound P, resin exchangeable P, and organic P (Huang, Chen, and Shenker 2006).

P classified as non-reactive P encompasses any form of P that is stable and does not react chemically in solution when measuring reactive P according to standard methods(Rice et al. 2012). Examples of non-reactive P are P bound to organic compounds or as phosphate bound to multiple phosphates in a chain called poly-phosphates.

Based on the literature reviewed, it is not known if soluble non-reactive P impacts dewaterability. Guibaud et al. (2005) stated in their study on the complexation potential of EPS that their measurement method of P did not determine the species of P but only total P, thus exposing the need for research in this area. Park et al (2007) found that total P influenced the hydrophobicity of EPS, which strongly correlated to bound water and poor dewaterability. No explanation for P speciation was given in this research so it was not determined if poor dewaterability was impacted by a specific P species or simply total P. The lack of reporting on specific P species highlights the lack of knowledge regarding the impacts of different P species on dewaterability.

2.4 Summary of Research Needs

Existing literature has several gaps in knowledge regarding how P speciation affects dewaterability in sludge and digested biosolids. A deeper understanding of P speciation and its effects on dewaterability could allow WRRFs to implement new technologies and processes to help reduce polymer costs and create new value-added products. In this study, the impact of P on sludge and biosolids dewaterability was evaluated through four research objectives.

Objective 1: Determine the impact of P speciation on dewaterability of WRRF sludges

Hypothesis: Higher soluble reactive P (most closely measured in this study as centrate reactive P (cRP)) decreases dewaterability

Objective 2: Determine the impact of acid treatment and replacement of supernatant on anaerobic digester biosolids dewaterability.

Hypothesis: Acid treatment will improve digester biosolids dewaterability.

Objective 3: Determine the impact of P speciation on anaerobic digester effluent sludge dewaterability.

Hypothesis: Higher cRP will decrease digester biosolids dewaterability

Objective 4: Determine the impact of anaerobic digestion on P speciation.

Hypothesis: Non-reactive P species will increase due to the formation of struvite.

3 METHODS

3.1 Phosphorus Species Characterization

3.1.1 Particulate and Centrate P

Four types of P are reported in this work: centrate reactive P (cRP), centrate non-reactive P (cNRP), particulate reactive P (pRP), and particulate non-reactive P (pNRP), and are further detailed in Table 3.1. P speciation in wastewater solids was defined and measured in these experiments to mimic a wastewater solids centrifuge system since centrifugation is used in full-scale systems (Dueñas et al. 2003), i.e, solids and liquids are commonly separated by a centrifuge and not a 0.45 micron filter in a full-scale system. Measuring P speciation in a sample of centrate can be helpful to WRRFs looking to design P recovery processes from the centrifuge effluent stream.

Centrate P was the P remaining in the centrate from a sludge sample that was centrifuged at 6000 rpm for 7 minutes. Rotation speed was the maximum speed of the existing equipment, and centrifuge time was determined experimentally to ensure all visible sludge particles were found in pellet form. To quantify particulate P, total phosphorus (TP) concentration was measured in a well-mixed (uncentrifuged) sludge sample and in a centrate sample; the difference in TP between the sludge sample and the centrate sample concentrations was calculated as the particulate P concentration. Determining particulate P by difference of two values followed the assumption, but not the process, laid out by standard methods, i.e., that all P not in centrate is assumed to be particulate (Rice et al. 2012).

3.1.2 Reactive P and Non-reactive P

Reactive P was measured according to standard methods (Rice et al. 2012). Briefly, a sample was diluted with DI water to be within the limits of the standard curve values. Then, 1.6 mL of a reagent containing potassium tartrate, ammonium molybdate, sulfuric acid, and ascorbic acid were added to 10 mL of sample. The sample was mixed and reacted for ten minutes. Then absorbance at 880 nm wavelength was measured on a spectrophotometer. A standard curve was made by adding dipotassium phosphate to de-ionized water at concentrations ranging from 0.12 to 3 mg/L as ortho-P.

TP was measured according to standard methods (Rice et al. 2012). Briefly, solids digestion was performed to break down organic matter and convert all phosphorus to ortho-P. Section B of method 4500-P was followed whereby persulfate and acid were added to a sample prior to autoclaving (Higgins et al. 2014; Britton et al. 2015). For the results reported, 0.5 grams of potassium persulfate and 1 mL of 30% sulfuric acid were used in each sample. Non-reactive P was calculated by subtracting the measured reactive P from the TP measurement (Table 3.1). In standard methods, the difference between total P and reactive P is defined as organic P, non-reactive P. However not all P converted in the digestion process is in organic form; there are inorganic polyphosphates converted as well (Moore 2010). Therefore, the term non-reactive was used to encompass all P species converted via persulfate digestion.

Table 3.1 P Species Calculation Explained.

*Four P species were analyzed in sludge samples (labeled with *). P species that were measured directly via a single lab method are indicated with the word "measured" below the name. P species that were calculated by the difference of other measured P values are indicated by "Calc" followed by the equation used to determine the value.*

	Total P	**Reactive P**	**Non-reactive P**
total P	total P (TP) *measured*	total reactive P (tRP) *measured*	total non-reactive P (tNRP) *Calc: TP-tRP*
centrate P	centrate total P (cTP) *measured*	*centrate reactive P (cRP) *measured*	* centrate non-reactive P (cNRP) *Calc: cTP-cRP*
particulate P	particulate total P (pTP) *Calc: TP-cTP*	* particulate reactive P (pRP) *Calc: tRP-cRP*	*particulate reactive P (pNRP) *Calc: pTP-pRP*

3.2 QA/QC

3.2.1 Impact of Solids on P Measurements

The solids present in wastewater could interfere with P measurements, ostensibly due to solids reacting with the oxidant. To test this effect, aliquots from the same batch of sludge were diluted to different ratios before being digested with the same amount of acid and oxidant. The TP values of the diluted samples were measured and normalized by the dilution factor so that, if solids had no impact on P measurements, then all reported TP values would be the same. Solids interference would result in lower TP measurements.

3.2.2 Reproducibility of P Species Measurements

P species were measured in triplicate in a subset of sludge samples to determine the reproducibility and variability of the P species measurements. Three aliquots were taken from the same sludge sample and all four P species (cRP, cNRP, pRP, pNRP) were measured for each aliquot resulting in three values for each P species. The average and standard deviation of the three values were determined, and the relative standard deviation (RSD) was calculated by dividing the standard deviation by the average. In total, 38 sludge aliquots were analyzed in triplicate. The average RSD value from the 38 samples was calculated to find the largest variability.

3.3 Dewaterability Characterization by Capillary Suction Time

CST was conducted to determine dewaterability of sludges (Higgins, Tom, and Sobeck 2004) . A multi-purpose CST apparatus (Triton Electronics Limited, Great Dunmow, Essex, England) measured the time for water to move across filter paper (GE Whatman, Grade 17 7x9cm) from an inner diameter near an input well to an outer diameter. The sludge solids remained in the well on top of the filter paper, and the water from the sludge flows out of the sludge and through the paper. The time for water to move from inner diameter to outer diameter was measured by electrodes and is typically called CST. A low CST value indicates good dewaterability, while a higher CST value indicates poorer dewaterability.

3.4 Full-scale Sludge Survey to Determine Links between P Species and Dewaterability

Sludge samples were collected from four different wastewater reclamation districts to test the hypothesis that cRP decreases dewaterability (CST). This survey was conducted to complete the following objective:

Objective 1: Determine the impact of P speciation on dewaterability of WRRF sludges

Hypothesis: Higher soluble reactive P (most closely measured in this study as centrate reactive P (cRP)) decreases dewaterability

Sludge samples were characterized by measuring P speciation (cRP, cNRP, pRP, pNRP), TP, TS, and VS). Dewaterability was characterized by measuring CST. Four sewerage districts in the midwest US contributed sludge; Milwaukee Metropolitan Sewerage District (MMSD), Green Bay Metropolitan Sewerage District, City of Fond du Lac Wastewater Treatment Division, and the Metropolitan Water Reclamation District of Greater Chicago (MWRD). Different types of sludges were surveyed. A thickened blend of primary and waste activate sludge (WAS) was analyzed from Green Bay, Fond du Lac, and MWRD. Unthickened primary sludge was analyzed from Green Bay, MMSD Jones Island plant, and MMSD South Shore plant. The WAS sample from Fond du Lac included bio-P sludge 80% of the time, according to the superintendent of the facility (A Fischer, Personal Communication, June 19, 2017). A thickened primary sludge sample was analyzed from Green Bay, as well as WAS samples from MMSD Jones Island plant and MMSD South Shore plant. All different types of samples from these locations were analyzed once with the exception of the blended sludge from Fond du Lac and the primary sludge from South Shore which were analyzed twice.

Table 3.2 Sludge Inventory from different WRRFs.

MMSD	Green Bay	Fond du Lac	MWRD
Unthickened primary, WAS	Thickened blend, Unthickened primary, thickened primary	Thickened blend, WAS	Thickened blend

Linear regressions between the sludge characteristics and CST values were plotted. Coefficient of determination (r^2) values and linear regression slope values were calculated. The slope of the linear regression trendline was used to determine the impact of the correlation. A low slope value indicated less of an impact of a parameter on CST than a higher slope value. GraphPad was used to determine if the mean slope from replicate analyses was statistically different from zero.

3.5 Lab-Scale Anaerobic Digestion Experiments to Test Impact of Acid Pretreatment on Dewaterability

3.5.1 Purpose of Experiments

Lab-scale anaerobic digesters were operated to meet the following research objectives and test the following hypotheses:

Objective 2: Determine the impact of acid treatment and replacement of supernatant on anaerobic digester biosolids dewaterability.

Hypothesis: Acid treatment will improve digester biosolids dewaterability.

Objective 3: Determine the impact of P speciation on anaerobic digester effluent sludge dewaterability.

Hypothesis: Higher cRP will decrease digester biosolids dewaterability

Objective 4: Determine the impact of anaerobic digestion on P speciation.

Hypothesis: Non-reactive P species will increase due to the formation of struvite.

3.5.2 Sample Procurement

Two sets of lab-scale digesters were operated. One digester set was fed screened primary sludge from the South Shore WRRF (Oak Creek, WI) and the other set was fed a blend of primary and WAS from the city of Fond du Lac WRRF. According to the wastewater superintendent, the activated sludge system at Fond du Lac was run intermittently as bio-P approximately 70-80% of the time. The sludge from Fond du Lac was shipped weekly on ice to the Water Quality Center lab. Primary sludge from the

South Shore facility was picked up from the facility on a weekly basis. Sludge fed to the digesters was stored in refrigerators at 2-5 °C for up to two weeks.

Primary sludge samples were also procured from Jones Island for pre-treatment tests described in the following section. This sludge was used for pre-treatment testing for two reasons: 1) Jones Island primary sludge is piped to the South Shore facility for anaerobic digestion and 2) Jones Island was more readily accessible for sample procurement. Primary sludge from South Shore was used for the lab-scale anaerobic digesters because it most closely represented the typical sludge fed to the anaerobic digesters at the South Shore facility. For the remainder of this thesis, the primary sludge from the South Shore facility will be referred to as South Shore sludge (SS), and the blended sludge from Fond du Lac will be referred to as Fond du Lac sludge (FDL).

3.5.3 Selection and Implementation of Acid Pretreatment Step

Various pre-treatment processes, which occur directly before the anaerobic digestion of sludge, were assessed to determine the impact of treatment on P-speciation in sludge samples. The goal was to determine which pretreatment was most effective at increasing cRP in sludge, because cRP is the form of P that is easiest to recover. These pretreatment tests were conducted to determine which pre-treatment step would be used to alter influent cRP levels for lab-scale digester experiments.

MMSD primary sludge from Jones Island WRRF was treated in the following ways: sulfuric acid treatment, sodium hydroxide treatment, calcium hydroxide treatment, mechanical lysis using a blender, and heat treatment using autoclave. The concentrations of chemical addition can be found in Appendix A. One experiment was performed for each method with a control for each due to the variability of the sludge used, as several sludge samples from Jones Island were used to conduct the experiments. All control samples underwent stirring and no pre-treatment for the same time the test sludge was stirred (30 minutes) with the exceptions of the heat treatment that was not stirred and blender treatment which was treated for 10 minutes. This step of stirring the control was done to account for any effects from stirring. From the multiple pre-treatment methods that were tested, acid pretreatment resulted in the largest increase in cRP (See Appendix B). Acid pretreatment converted the highest percentage of P to cRP and was selected as the process to increase the cRP content in sludge and subsequently remove it via centrifuging the sludge and decanting the supernatant.

The acid pre-treatment process follows the steps depicted in Figure 3.1. First, hydrochloric acid was used at a dosage of 180 meq/L. To treat the sludge, half of the volume fed to the digesters (150 mL) was treated with 3.1 mL of 6N acid to create the 180 meq/L dosage conditions and stirred in an open beaker for 30 minutes. After treatment, the sludge was centrifuged at 6000 rpm for 7 minutes in 50 mL centrifuge tubes. The centrate was discarded and DI water was added to reconstitute the sludge to the original solids concentration by matching the original volume. The reconstituted sludge was then mixed with the same volume of untreated sludge to increase the pH of the sludge and keep the digesters from becoming too acidic. This final mix was fed to the acid digesters. Control digesters received the same volume of sludge without any pre-treatment (Figure 3.1).

A
Add acid
Stir 30 minutes

B
Centrifuge 7 minutes

C
Decant centrate, fill to original volume with DI

D
Mix with non-treated half

Figure 3.1 Sludge pre-treatment process schematic. *A Step: Addition of 3.1 mL of 6N HCl into 150 mL of sludge and stirred for 30 minutes on a stir plate. B Step: Sludge placed in centrifuge tubes and ran in centrifuge. C Step: Centrate decanted from tubes, lost volume replaced with de-ionized water and remixed into sludge. D Step: 150 mL of reconstituted sludge was mixed with 150 mL of untreated sludge.*

3.5.4 Digester Set Up & Operation

Four sets of duplicate digesters were operated. The sets included: i) test digesters fed acid-treated primary sludge from SS (named SA1 and SA2), ii) control digesters fed primary sludge from SS (named SC1 and SC2,) iii) test digesters fed acid-treated, blended sludge from FDL (named FA1 and FA2), and iv) control digesters fed blend sludge from FDL (named FC1 and FC2). All digesters were operated in a temperature-controlled room at 35 °C on multi-position stir plates operated between 180 and 190 rpm. The stir plates ran on a timer for 6 hours a day and digesters were fed during the stirring hours. Intermittent stirring was conducted to match full scale digestion practices, as well as for concern of erosion of internal stir bars due to sediment buildup. Each digester was a cylinder of poly-carbonate with an acrylic lid and a ½" valve port on the lid and 1" from the bottom as the feed and effluent ports respectively. A volume (2.25 L) of digester effluent from full scale digesters at the South Shore WRRF were used to seed all digesters and the digesters were initially sparged with a 30% carbon dioxide and 70% nitrogen gas. One small port was installed on each lid of the digester cylinders to release the gas via Tygon tubing to a Tedlar bag which held the gas until analysis.

The digesters were operated on a 15-day solids retention time (SRT) for a total of 69 days, which was the amount of time needed to measure P speciation seven times each for all digesters during steady state conditions. Feeding required 150 mL of sludge to be removed and fed each day to the digesters. A funnel was placed in the top of the feed valve to aid in sludge feeding and care was taken to close the valve quickly after the sludge flowed into the digester. Original experimental planning estimated quasi-steady-state to be attained after digesters were operated for 3 SRT values (i.e., after 45 days), after which P measurements and CST measurements were taken to observe the effects of P speciation on CST. However, after operation and data analysis, it was determined that substantial variation in P speciation was still occurring after 45 days (see Appendix D). Quasi-steady-state was assumed to occur when the average total P effluent concentration was within 20% of the influent total P concentration. This definition resulted in n=4 steady state samples for the digesters fed SS sludge and n=6 steady state samples for the digesters fed FDL sludge.

Several sludge and biogas characteristics were measured during digester operation to monitor performance. The pH of the effluent sludge was measured every day after feeding. The biogas methane concentration as well as TS, VS, CST, cation concentrations and concentration of various P species were measured weekly in effluent from all digesters. Biogas volume was measured as needed as the Tedlar bags filled up.

3.5.5 Analytical Methods

Biogas methane concentration and gas production volume from the digesters were measured to determine overall digester function. Gas production was determined by attaching Tedlar bags to the digester and measuring the gas volume in the bag using a wet test meter (Precision Test Company, San Antonio, Texas, United States). Average daily gas production was determined by dividing the measured volume in the bag by the number of days gas was collected. Gas composition was determined by taking a well-mixed gas sample from Tedlar bags attached to the digester vessel and analyzing the sample using a gas chromatograph with a thermal conductivity detector (GC-TCD) as described elsewhere (Venkiteshwaran 2010).

4 RESULTS & DISCUSSION

4.1 QA/QC for P Measurements

4.1.1 Reproducibility of P Speciation Measurement

Reproducibility of P measurements was investigated to understand precision of the method. Triplicate P samples were taken from 38 samples and relative standard deviation was calculated. For each sample, three values for each P species concentration were generated and the average, standard deviation, and relative standard deviation (RSD) were calculated for every sample. The RSD values from all triplicate sample groups were averaged together for each species and the results are found in Table 4.1 (e.g., all cRP RSDs were averaged). TP and cRP were determined from direct measurements, cNRP and pRP were calculated by the difference of two measured values, and pNRP was derived by taking the difference twice (see Table 3.1 for description of measurements and calculations). The average RSD for TP was lowest which was expected because TP was determined directly and did not encompass taking the difference of multiple values determined in the lab. The pNRP, on the other hand, had the highest RSD value and encompassed multiple measurements in the lab and inherently contained more steps for variability. The determination of some P species concentrations by difference yielded some individual results that were negative (see Appendix B for a list of all data from these 38 triplicate measurements).

***Table 4.1** Average RSDs of P species for triplicate samples (n=38).*

cRP	cNRP	pRP	pNRP	TP
10%	10%	12%	23%	6%

4.1.2 Impact of Solids on P Measurements

Experiments were performed to determine how solids concentration impacted P measurements. Triplicate samples from the same sludge sample were diluted to different solids concentrations. TP was measured in all samples, and the dilution factors were used to determine original P concentrations. TP measurements fell within ten percent of the average for diluted samples with solids concentrations less than or equal to 225 mg/L (Figure 4.1). A variation of ten percent was deemed acceptable and was attributed to inherent measurement variability. At solids concentrations higher than 225 mg/L, the corrected TP values declined, indicating that solids were interfering with TP measurements. Therefore, the concentration of solids in diluted sludge samples for analysis in remaining experiments did not exceed 225 mg/L to minimize inhibition due to solids. To be conservative, a solids concentration of 45 mg/L was used as a target in diluted samples for P analysis.

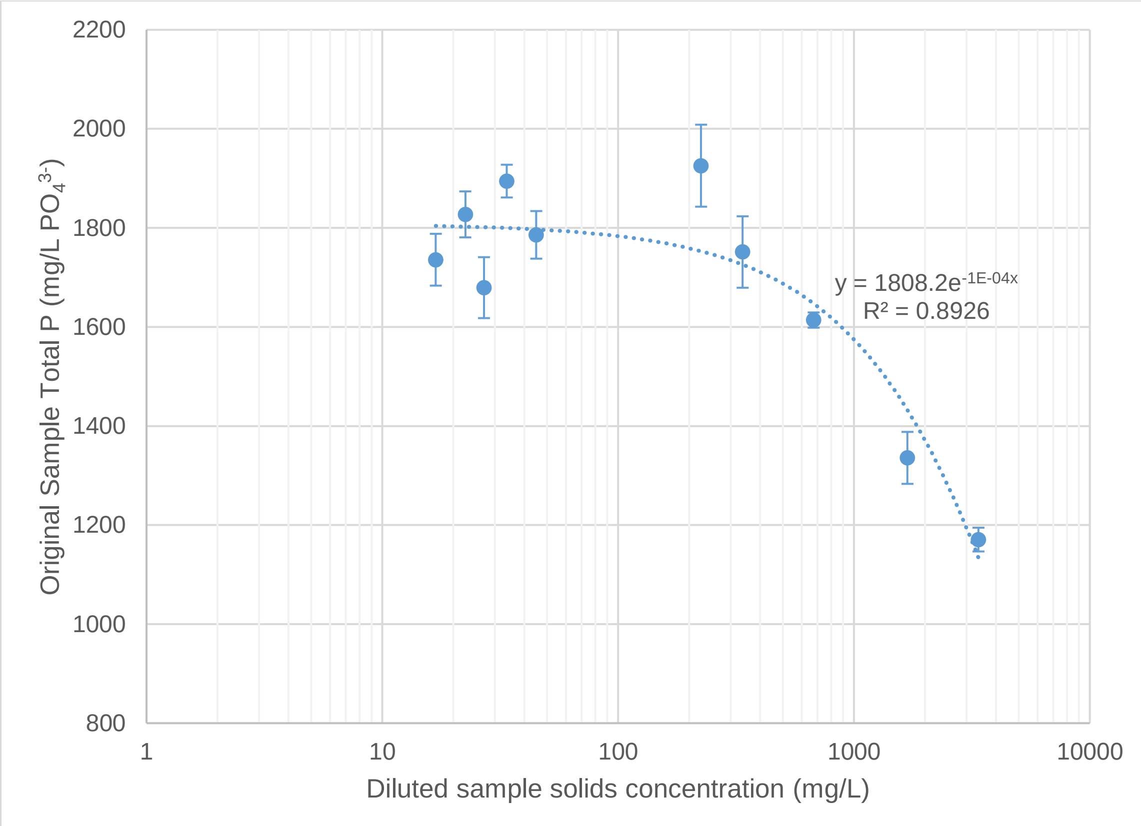

Figure 4.1 Solids concentration can affect P measurements*. A sludge sample was diluted and the total P was measured. Dilution factors were taken into account such that all samples should have the same total P values if solids were not inhibitory.*

4.2 Full-Scale Sludge Survey: Correlations Between Dewaterability and Sludge Characteristics

Analyses were performed to determine how P speciation in full-scale sludge samples correlated to dewaterability. The hypothesis stated that higher cRP concentrations would result in worse dewaterability. This hypothesis was rejected on the grounds of the low r^2 value between cRP and CST (r^2= 0.06, n=8, see Appendix C). However, pRP and pNRP concentrations were found to trend with CST with slopes of 1.80 and 1.13, respectively (Figure 4.2). Raw EBPR sludge has been reported to have between 3-6% P content by mass (Bi, Guo, and Chen 2013). If particulate P increases, ostensibly solids concentration increases as well.

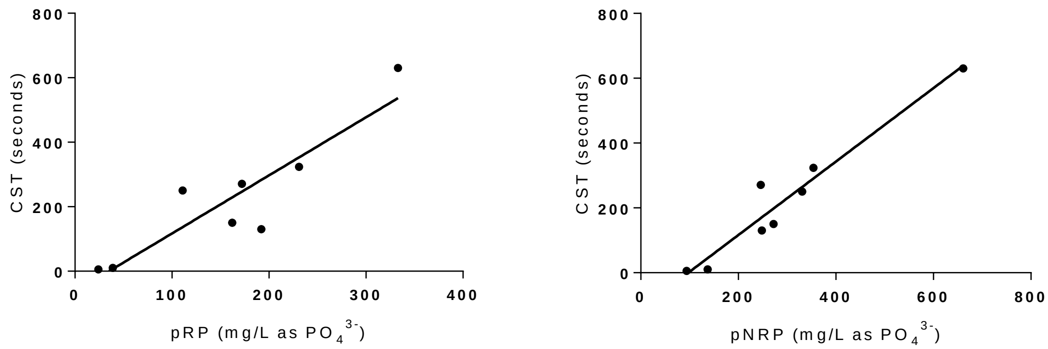

Figure 4.2 ***Dewaterability becomes worse as pRP and pNRP increase****. Data points represent CST measurements from sludge samples acquired from various municipal WRRFs. Trendline R^2 values are 0.81 and 0.94, respectively; n= 8.*

4.3 Bench Scale Digesters: Dewatering Performance

4.3.1 Impact of Acid Pretreatment Followed by Decanting of Centrate on Dewaterability

Experiments were executed to test the hypothesis that removing cRP would improve dewaterability. Influent sludge to the lab-scale anaerobic digesters was treated with acid, centrifuged, and the centrate was decanted and replaced with DI water. Pretreatment with acid followed by decanting of centrate did not impact dewaterability of biosolids from South Shore (SS) digesters (Figure 4.3). The average CST of effluent from steady state acid-treated digesters was lower but not significantly different from that of the control (t-test, p = 0.366). Centrate was decanted to mimic removal of soluble phosphates, which in this work was qualified as cRP. This step, however, would also remove other constituents such as soluble anions and cations like sodium and magnesium. Any effects on dewaterability would have to consider effects of removing chemical species beyond P. Nevertheless, this step had minimal impact on dewaterability.

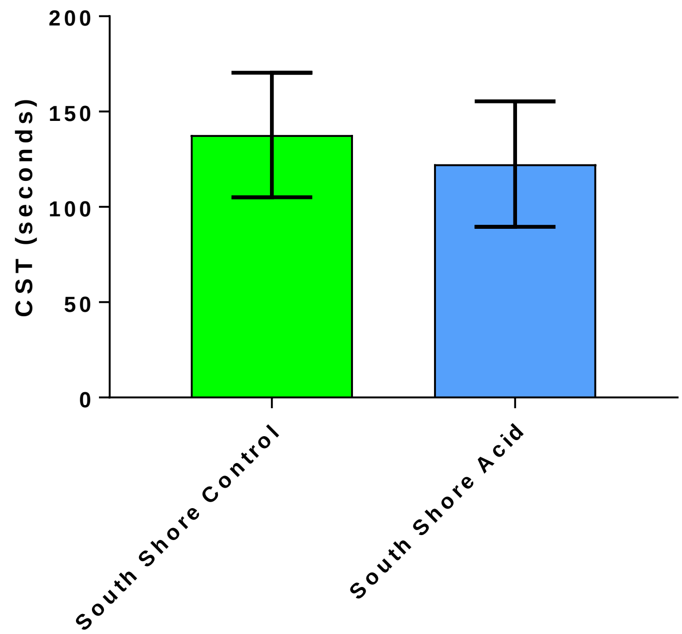

Figure 4.3 Acid pretreatment did not impact dewaterability. *Error bars represent average CST values of South Shore Digesters. Error bars represent ± 1 standard deviation; n=8*

Similarly, pretreatment with acid followed by decanting of centrate did not impact dewaterability of biosolids from Fond Du Lac (FDL) digesters (Figure 4.4). Again, average CST of effluent from acid-treated digesters was lower but not significantly different from that of the control (p = 0.456). This trend was observed in both SS and FDL digesters. Therefore, acid-pretreatment followed by decanting of centrate is not recommended as an approach to improve downstream dewaterability.

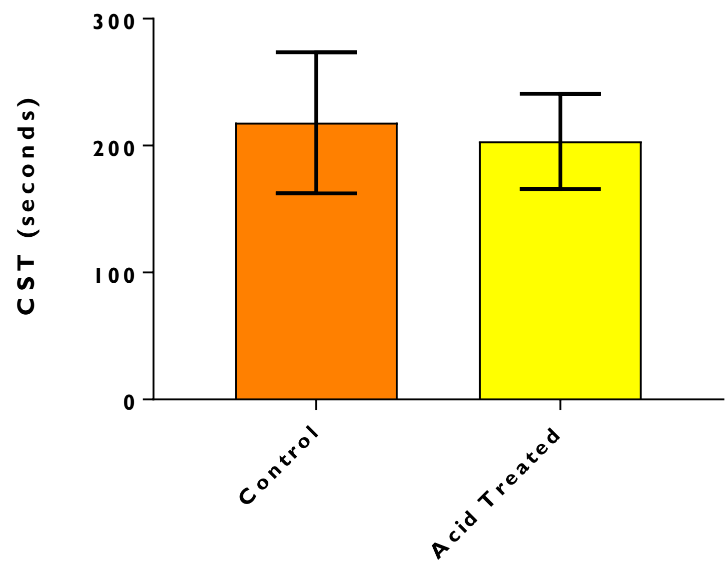

Figure 4.4 ***Acid pretreatment did not impact dewaterability.*** *Bars represent average CST values of Fond du Lac Digesters. Error bars represent ± 1 standard deviation; n=12*

Interestingly, feed sludge type did have an impact on biosolids dewaterability (Figure 4.5). The average CST values for digesters fed SS sludge were significantly lower than CST values for digesters fed FDL sludge ($p<0.001$) These findings are in line with previously reported results from literature indicating that bio-P sludge is more difficult to dewater (Roeleveld et al. 2004; Britton et al. 2015). These data indicate there are inherent characteristics of sludge that influence dewaterability, but the acid pretreatment applied in this work does not significantly impact dewaterability with the sludge tested.

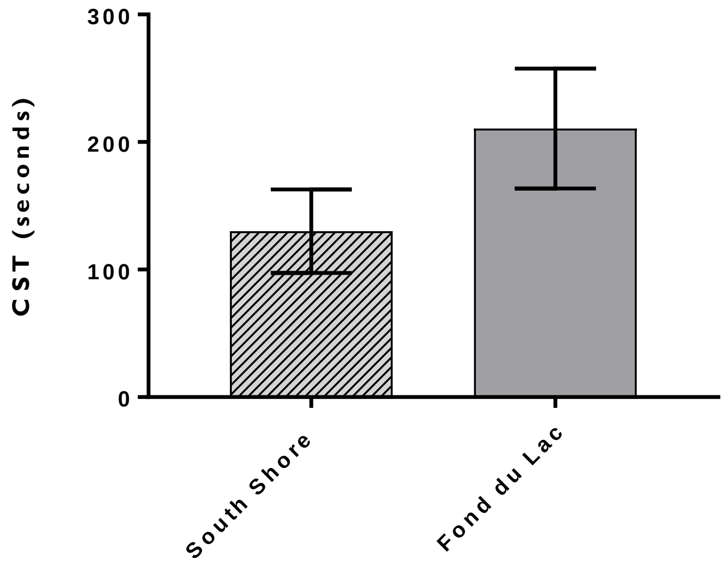

Figure 4.5 ***Digester effluent from Bio-P (Fond du Lac) fed digesters is statistically higher than primary (South Shore) fed digesters.*** *Error bars represent ± 1 standard deviation, n= 18 (SS), n=24 (FDL)*

4.3.2 Correlation between anaerobic digester effluent sludge characteristics and dewaterability.

Experiments were also executed to test the hypothesis that increasing cRP would make dewaterability worse. The dewaterability, as measured by CST, from the eight lab-scale anaerobic digesters was correlated to the cRP in effluent from the anaerobic digesters (Figure 4.6). The cRP species characterizes the liquid content in the sludge matrix more than the solid flocs in the sludge matrix. The cRP content potentially influences dewaterability in a manner described by the divalent cation bridging theory and the M/D ratio. This theory posits that divalent cations can connect or "bridge" flocs together thereby contributing towards better dewaterability (Britton et al. 2015; Roeleveld et al. 2004; Higgins and Novak 1997). Anions, such as ortho-phosphate (a reactive P species that would be measured as cRP in this work) can negatively impact divalent cation bridging by binding to divalent cations and neutralizing their ability to bridge flocs. The results in Figure 4.6 add evidence to support the M/D theory.

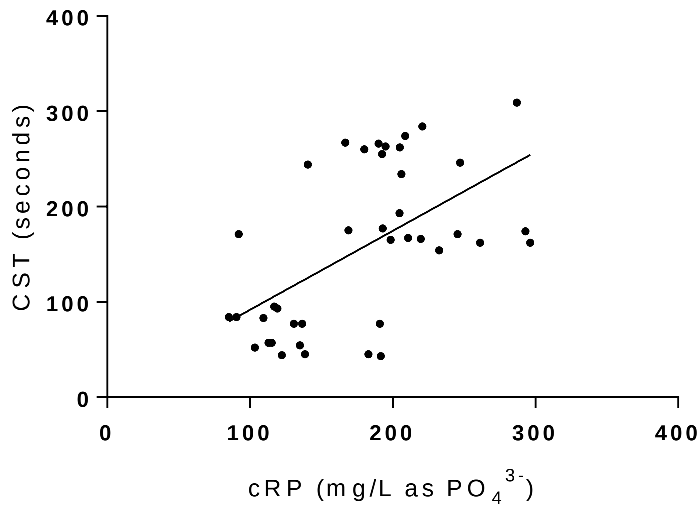

Figure 4.6 ***Dewaterability becomes worse as cRP concentration increases.*** *Data points represent effluent sludge measurements from all digesters during quasi-steady state. Trendline* r^2 *value is 0.32 and n= 40.*

The M/D ratio was also quantified in digester effluent, and the M/D ratio was compared with CST (Figure 4.7). The sum of the sodium and potassium concentrations was used for monovalent quantification, and the sum of magnesium and calcium concentrations was used for divalent quantification. A higher M/D ratio means there are more monovalent cations than divalent cations. As the M/D ratio increased, dewaterability became worse. The divalent cation bridging theory states that the divalent cations aid in flocculation, therefore a lower M/D ratio would be most beneficial for dewatering. Figure 4.7 supports this theory by presenting a correlation between lower M/D ratio to better dewaterability. The r^2 value was 0.26 meaning that 26% of the variation in CST (the y-variable) can be explained by M/D (the x-variable)(Stackexchange.com 2017). While M/D impacts dewaterability, this ratio is not the only factor that affects dewaterability (based on R^2 value less than 1).

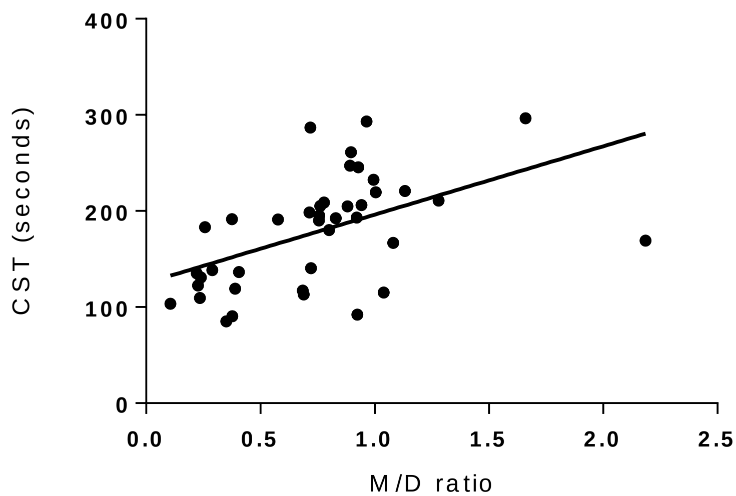

Figure 4.7 Monovalent to divalent (M/D) cation ratio plotted against CST*. r^2 value= 0.26 n=40. A higher M/D ratio indicates more monovalent cations to divalent cations. The positive correlation indicates that dewaterability decreases as more monovalent cations are present relative to divalent cations.*

The cNRP, pRP, and pNRP concentrations were not strongly correlated to dewaterability (Figure 4.8). cNRP line of best fit had a negative slope (-0.055, r^2=0.00), pRP had a r^2 value of 0.04, and pNRP had a positive slope with a slightly higher r^2 value (slope =0.118 r^2=0.10). Physical properties of the sludge as measured by these P species may not affect dewaterability, while other qualities such as particle size, sludge age, and EPS could impact dewaterability.

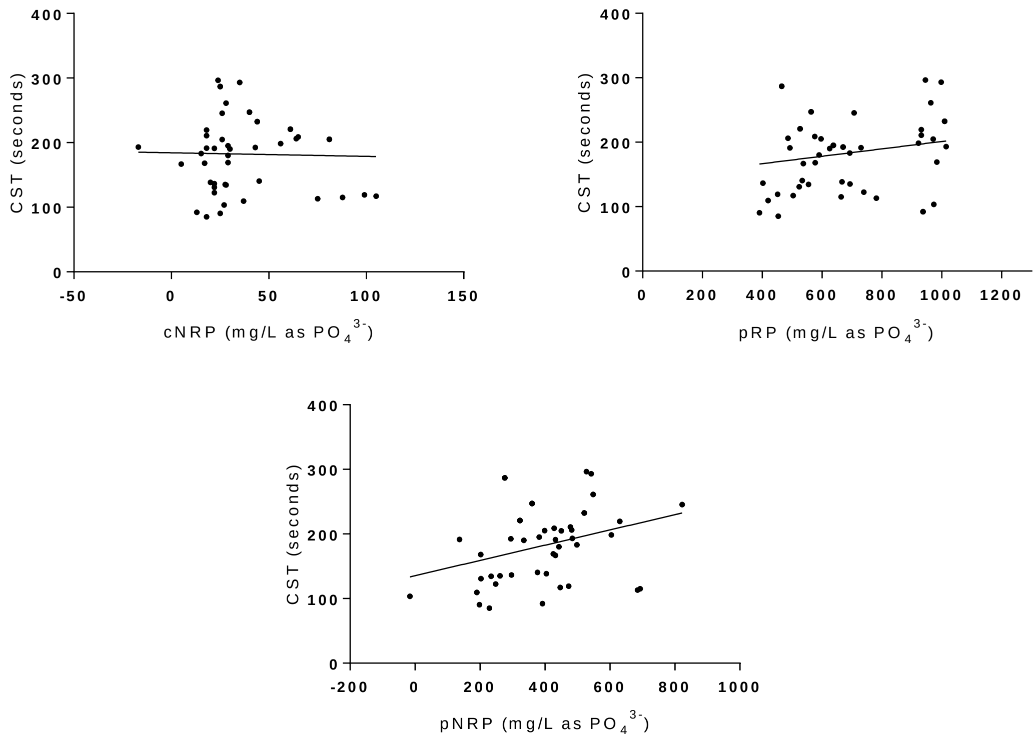

Figure 4.8 cNRP, pRP, and pNRP, plotted against CST. *Data points represent effluent sludge measurements from all digesters during quasi-steady state. Trendline* r^2 *values 0.00, 0.04, and 0.10 respectively. n= 40*

Interestingly, pNRP and pRP had higher r^2 values with CST of non-digested sludge samples in the full-scale survey (Section 4.2) than in the lab-scale anaerobic digester study. The major difference between the full-scale survey and the lab-scale digester experiments was the type of sludge analyzed, specifically related to if the sludge had undergone anaerobic digestion. The r^2 values from data in Figures 4.6-4.8 was comprised of only anaerobic digested biosolids samples. The full-scale survey was comprised of sludge samples such as primary or WAS that had not undergone digestion. These two sets of results reflect comparisons between sludge characteristics and dewaterability on different types of sludge. Therefore, sludge type, and characteristics not measured in this work that describes these sludge types such as floc structure could impact dewaterability.

VS concentrations were also measured to determine if organic solids content had an impact on dewaterability. VS content was not positively correlated to CST (Figure 4.9). The slope for the trendline was -0.009 and the R^2 value was 0.04. A positive trend would have indicated that higher VS content increased CST times, but this trend was not observed. Overall, VS can be considered a proxy for biomass, but the results suggest an increase in effluent biomass does not impact dewatering.

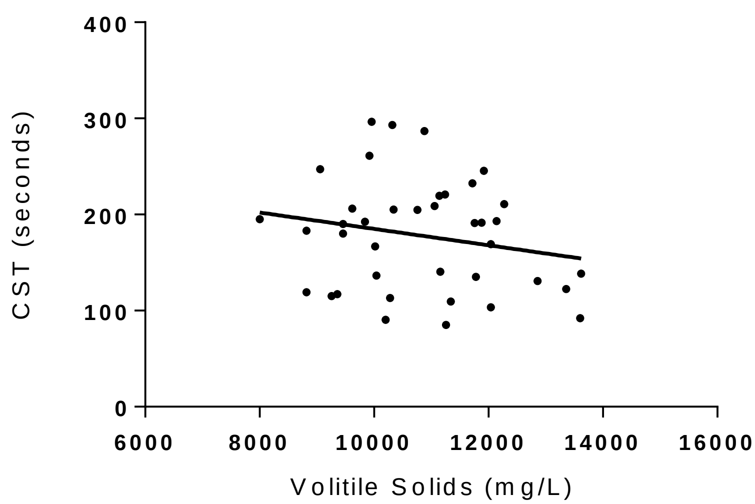

Figure 4.9 Volatile solids plotted against CST. *R^2 value= 0.04 n=40.*

4.3.3 Impact of Digestion on P Speciation

The third objective of these lab-scale anaerobic digestion experiments was to determine the effect of digestion on P speciation. Note that the sample size for the influent was less than the sample size for the effluent because the influent was characterized and fed to duplicate digesters. Therefore, both duplicates received the same influent sludge, but each produced independent effluent results.

The pRP species increased after digestion in both the SS fed control digesters and SS acid treated digesters (Figures 4.10 & 4.11, p-value for influent vs effluent in control and acid digesters = 0.001 and 0.001, respectively). P was ostensibly converted from pNRP to pRP. In other words, the P converted from a non-reactive form to a reactive form. Reactive forms of P are chemically reactive (ortho-phosphate) and can interact with cations. Non-reactive forms of P are P in forms that do not chemically react and need to be digested with acid and heat to be measured by the method employed herein. The increased pRP in effluent could be struvite, brushite, or could indicate biomass destruction in digester (Poxon and Darby 1997)

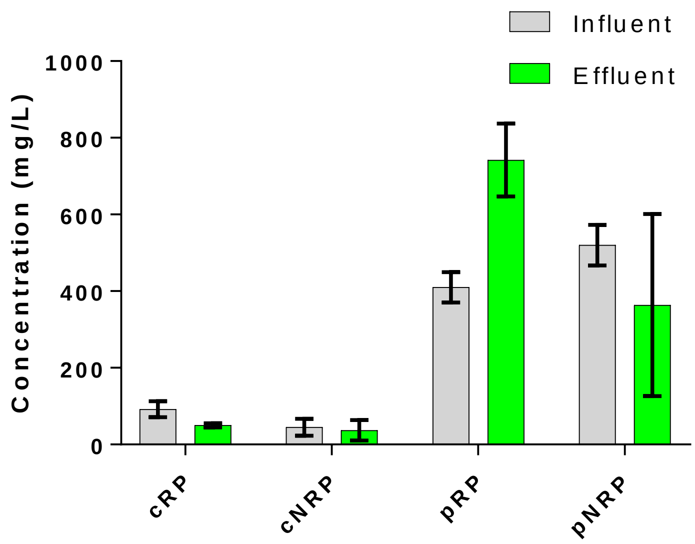

***Figure 4.10* Particulate reactive P increases in control digesters fed with primary sludge from South Shore treatment plant.** *Bars represent average values taken at quasi-steady state and error bars represent standard deviation. Influent n=4, effluent n=8*

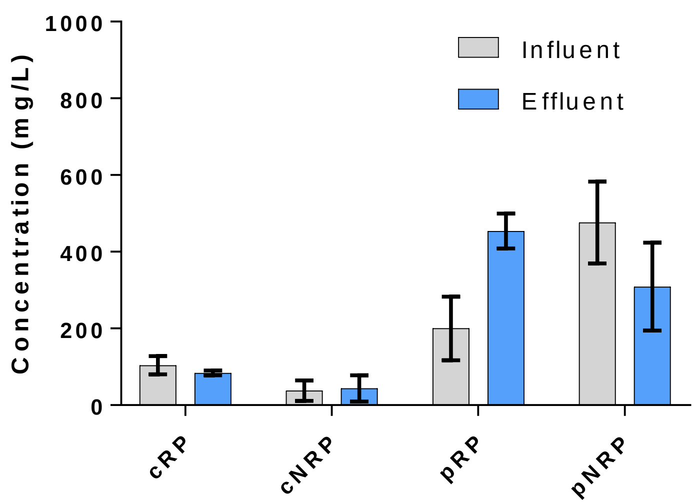

***Figure 4.11* Particulate reactive P increases in acid treated digesters fed with primary sludge from South Shore treatment plant.** *Bars represent average values taken at quasi-steady state and error bars represent standard deviation. Influent n=4, effluent n=8*

Unlike digesters fed SS sludge, the biggest change for the digesters fed FDL sludge for P speciation was from high cRP in the influent to high pRP in the effluent. In contrast to the primary-fed digesters, cRP decreased after digestion in the FDL fed control and acid digesters (Figures 4.12, 4.13. FC p=0.001, FA p=0.002). P was converted from a centrate form to a non-centrate form during digestion. It is possible that P was used for growth of anaerobic microbial biomass or used to create EPS by the microbes. Another possibility was that struvite or brushite was formed (Guibaud et al. 2005). Phosphorus accumulating organisms in Bio-P sludge accumulate high amounts of P as polyphosphate and release P as ortho-P, this behavior could explain the elevated cRP levels observed and the higher overall P levels in the FDL sludge(Bi, Guo, and Chen 2013).

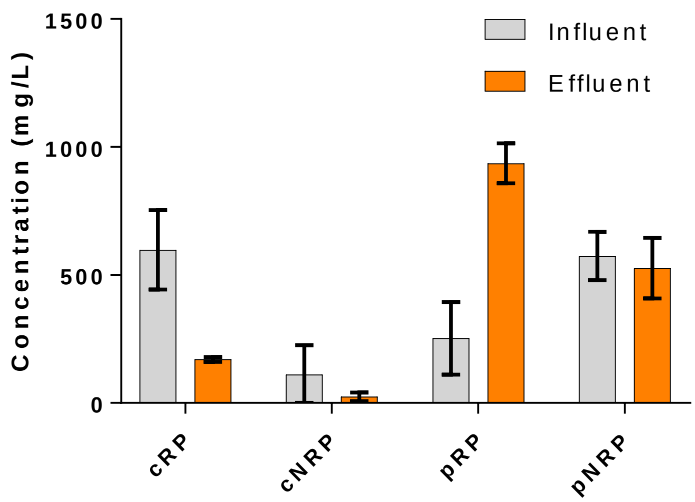

***Figure 4.12* Particulate reactive P increases in control digesters fed with Fond du Lac sludge.** *Bars represent average values taken at quasi-steady state and error bars represent standard deviation. Influent n=5, effluent n=12*

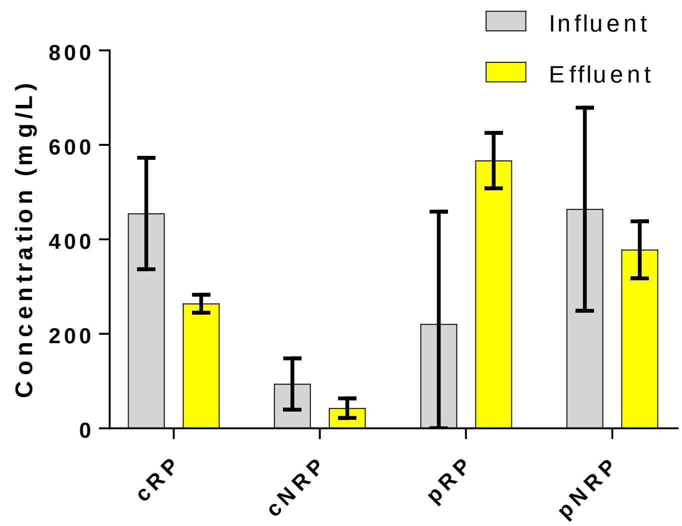

***Figure 4.13* Particulate reactive P increases in acid treated digesters fed with Fond du Lac sludge.** *Bars represent average values taken at quasi-steady state and error bars represent standard deviation. Influent n=5, effluent n=12*

5 CONCLUSIONS

The goal of this research was to investigate the impact of P speciation in various sludges on dewaterability and to determine if an anaerobic digestion pretreatment method to reduce P content could improve dewaterability. It is not clearly understood why bio-P sludges are observed to have poorer dewaterability. A more detailed understanding of the speciation of P in raw sludge is necessary to understand what pre-treatment technologies would be most effective at converting P to a recoverable form. These conclusions are based on the experiments performed at the Marquette University Water Quality Center:

1. Particulate P speciation had r^2 values of 0.81 and 0.94 for CST of raw wastewater sludges. These results imply that solids concentration is correlated

with poorer dewatering. Further work should be done to determine if other sludge characteristics correlate to dewaterability for these sludge types, or if particulate P is the dominant characteristic impacting dewaterability..

2. Acid pre-treatment of sludge was conducted in attempt to remove soluble reactive P. However, the method conducted for P removal allowed for cation removal as well. If future work were to be completed, development of a method to selectively remove P without affecting cations would provide a clearer understanding of the effects P has on dewaterability.

3. Acid pretreatment and decanting did not significantly influence the dewaterability of digested sludge. The sludge used for this experiment was a primary and WAS blend, and perhaps the effects of P removal could have been more pronounced if complete bio-P sludge with more total P was characterized and treated.

4. Anaerobic digestion resulted in the conversion of centrate P to particulate reactive phosphorus. Further work could be done to investigate the chemical nature of the particulate reactive P. Knowledge on whether struvite was formed would be helpful for solids handling design.

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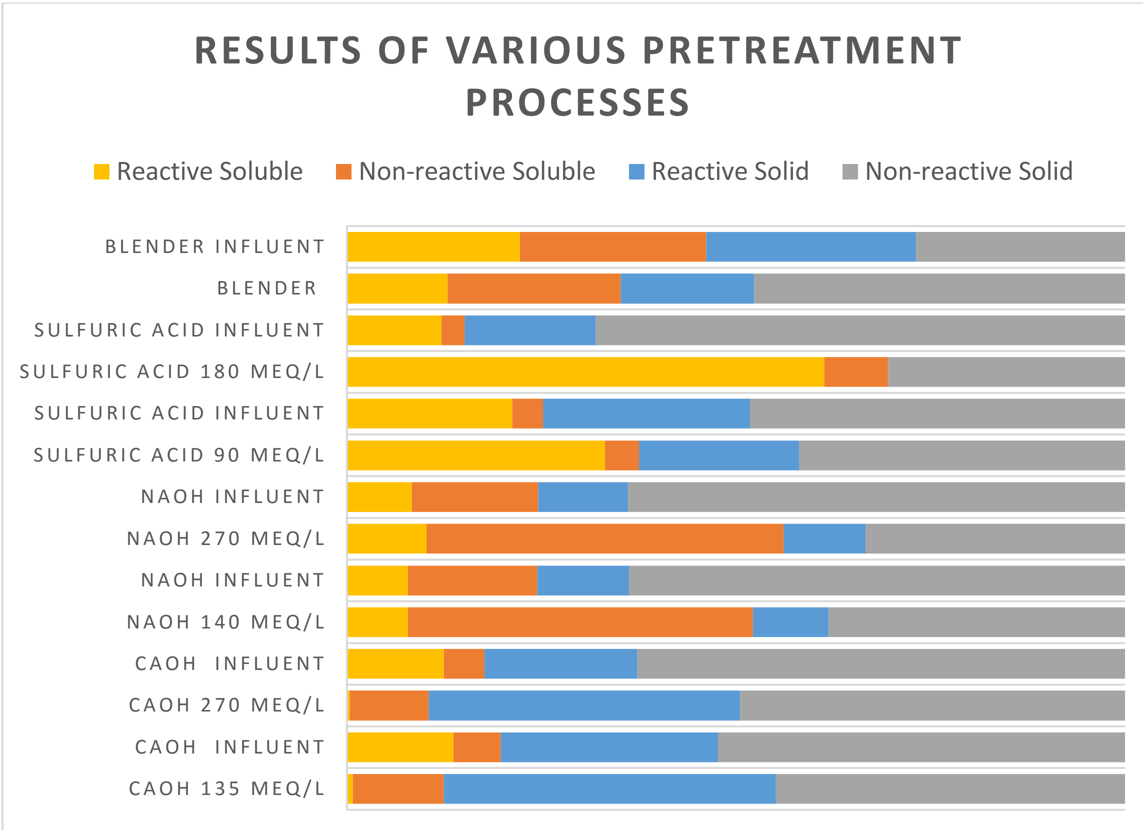
APPENDIX

A: Results from Pre-treatment testing



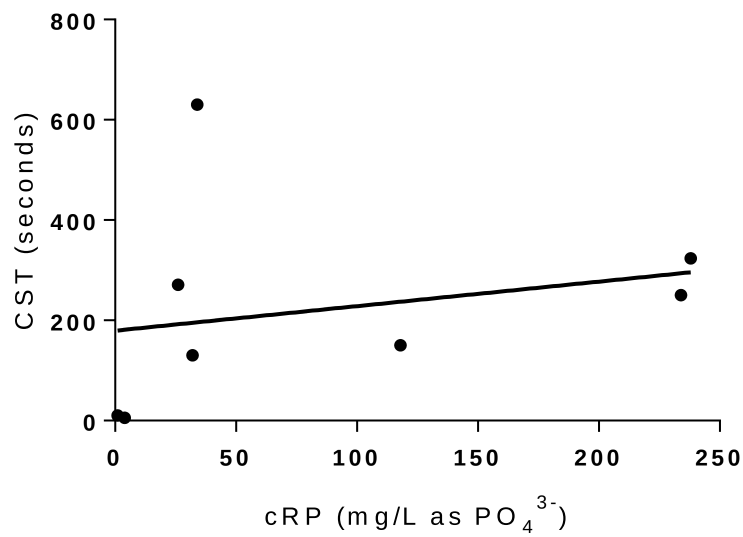
B: Average, Standard Deviation, and Relative Standard Deviation Data for P Species from Triplicate Tests on Sludge Samples from Full-Scale WRRFs

Code	Location
FC	Fond du Lac Bio-P and primary blend
FA	Fond du Lac acid treated Bio-P and primary blend
SC	South Shore Primary
SA	South Shore acid treated primary
FM	Fond du Lac mesophillic digester effluent
FT	Fond do Lac Thermophillic digester effluent
GB UTP	Green Bay unthickened primary sludge
GB TP	Green Bay thickened primary sludge
GB C	Green Bay combined WAS and primary
SW	South Shore WAS
CB	Chicago combined WAS and primary
--inf	indicates samples used as digester influent
--eff	indicates samples used as digester effluent

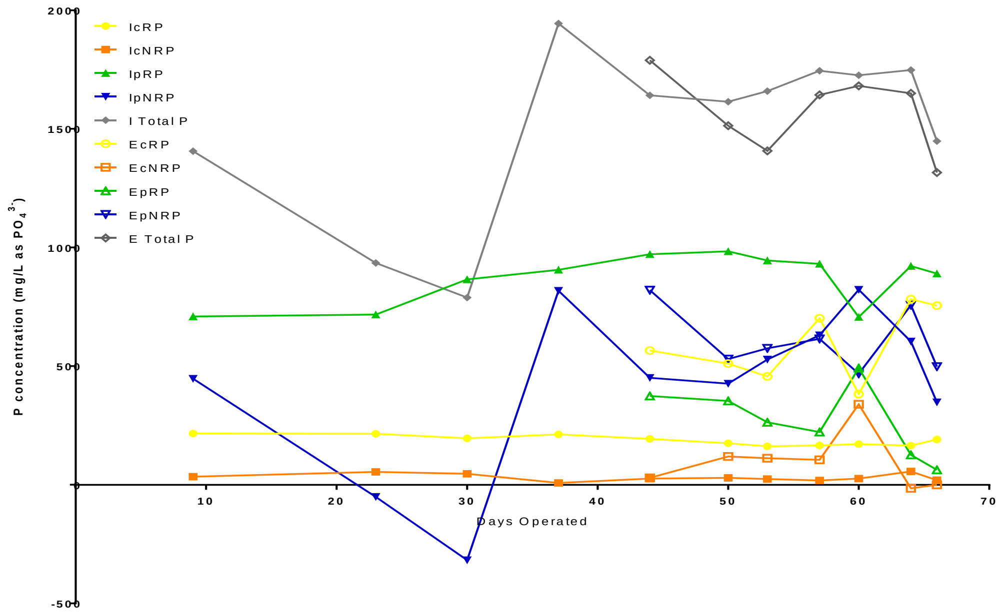
Average & standard Deviation					Relative Standard Deviation				
cRP	**cNRP**	**pRP**	**pNRP**	**Total**	**cRP**	**cNRP**	**pRP**	**pNRP**	**Total**
782 ± 2	-15 ± 19	126 ± 15	757 ± 70	1650 ± 77	0%	-128%	12%	9%	5%
557 ± 3	67 ± 6	31 ± 15	657 ± 41	1311 ± 33	0%	10%	48%	6%	3%
97 ± 0	39 ± 3	375 ± 12	482 ± 17	993 ± 9	0%	8%	3%	3%	1%
115 ± 0	15 ± 4	230 ± 9	372 ± 83	733 ± 82	0%	29%	4%	22%	11%
166 ± 2	18 ± 4	931 ± 7	630 ± 14	1745 ± 22	1%	24%	1%	2%	1%
162 ± 1	28 ± 5	963 ± 7	548 ± 46	1701 ± 52	1%	17%	1%	8%	3%
234 ± 3	64 ± 1	486 ± 54	482 ± 64	1265 ± 11	1%	1%	11%	13%	1%
246 ± 2	40 ± 5	563 ± 12	360 ± 23	1209 ± 9	1%	12%	2%	7%	1%
71 ± 1	26 ± 1	804 ± 75	386 ± 147	1287 ± 77	2%	4%	9%	38%	6%
64 ± 1	23 ± 4	619 ± 28	489 ± 32	1196 ± 2	2%	16%	4%	6%	0%
101 ± 2	30 ± 3	493 ± 17	292 ± 23	916 ± 8	2%	9%	4%	8%	1%
179 ± 2	-48 ± 1	444 ± 24	361 ± 27	936 ± 4	1%	-3%	5%	7%	0%
305 ± 264	264 ± 266	416 ± 254	423 ± 253	1407 ± 10	87%	101%	61%	60%	1%
76 ± 0	23 ± 2	238 ± 9	293 ± 54	630 ± 46	1%	7%	4%	19%	7%
52 ± 1	25 ± 1	165 ± 12	264 ± 11	506 ± 4	1%	5%	7%	4%	1%
511 ± 4	119 ± 8	353 ± 3	530 ± 17	1513 ± 16	1%	7%	1%	3%	1%
232 ± 12	168 ± 18	675 ± 6	53 ± 6	1129 ± 1	5%	11%	1%	11%	0%

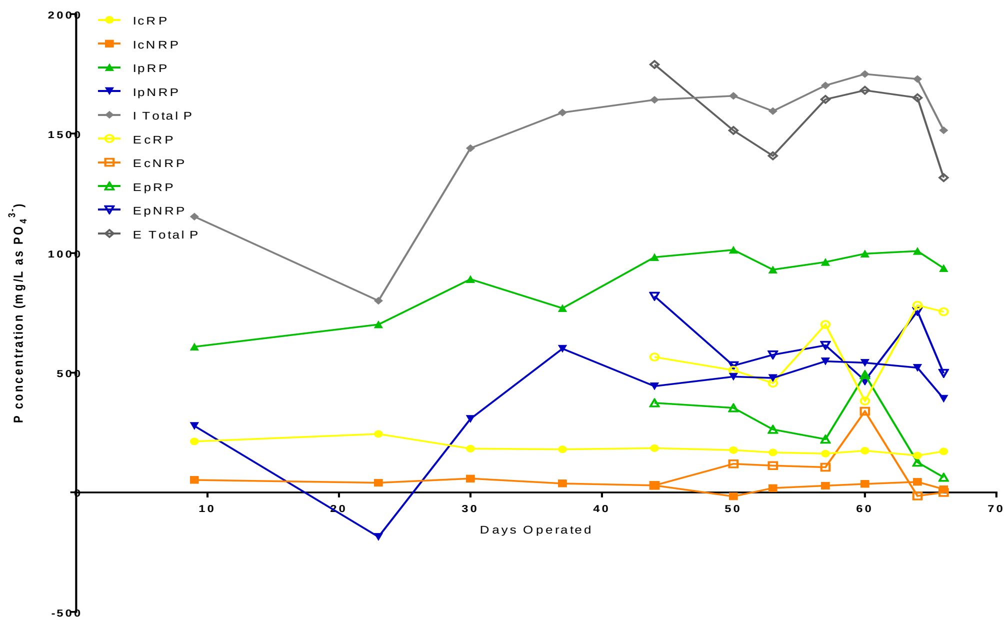
60 ± 1	17 ± 3	342 ± 37	665 ± 116	1084 ± 151	1%	17%	11%	17%	14%
65 ± 0	23 ± 2	161 ± 9	312 ± 17	560 ± 26	1%	8%	6%	5%	5%
566 ± 15	29 ± 10	374 ± 39	820 ± 61	1789 ± 94	3%	34%	11%	7%	5%
432 ± 20	20 ± 28	238 ± 39	465 ± 35	1155 ± 17	5%	139%	17%	7%	1%
96 ± 6	29 ± 7	269 ± 30	374 ± 20	767 ± 11	6%	24%	11%	5%	1%
125 ± 4	6 ± 5	200 ± 32	224 ± 25	556 ± 9	3%	85%	16%	11%	2%
508 ± 2	57 ± 8	254 ± 21	431 ± 37	1250 ± 41	0%	13%	8%	9%	3%
91 ± 2	23 ± 2	1028 ± 4	394 ± 12	1535 ± 9	2%	7%	0%	3%	1%
425 ± 547	-295 ± 548	666 ± 544	581 ± 535	1376 ± 15	129%	-186%	82%	92%	1%
897 ± 3	-32 ± 12	163 ± 31	1664 ± 55	2691 ± 28	0%	-38%	19%	3%	1%
1 ± 0	51 ± 1	544 ± 13	383 ± 9	979 ± 12	65%	3%	2%	2%	1%
850 ± 10	138 ± 19	99 ± 18	311 ± 1229	1398 ± 1211	1%	13%	18%	396%	87%
660 ± 9	111 ± 15	109 ± 18	716 ± 21	1596 ± 36	1%	14%	17%	3%	2%
2 ± 0	5 ± 1	17 ± 2	36 ± 4	59 ± 4	25%	23%	10%	11%	6%
12 ± 1	11 ± 1	72 ± 9	289 ± 38	383 ± 33	11%	10%	12%	13%	9%
105 ± 2	35 ± 2	1023 ± 57	2027 ± 71	3190 ± 125	2%	7%	6%	4%	4%
718 ± 33	59 ± 28	342 ± 49	1016 ± 37	2135 ± 29	5%	47%	14%	4%	1%
80 ± 0	38 ± 2	529 ± 56	755 ± 138	1402 ± 147	0%	6%	11%	18%	10%
4 ± 1	20 ± 1	120 ± 11	420 ± 20	565 ± 11	25%	3%	9%	5%	2%
730 ± 5	59 ± 7	708 ± 25	1086 ± 89	2583 ± 88	1%	11%	4%	8%	3%
362 ± 2	105 ± 7	498 ± 5	834 ± 145	1799 ± 138	1%	7%	1%	17%	8%

C: cRP vs CST scatter plot

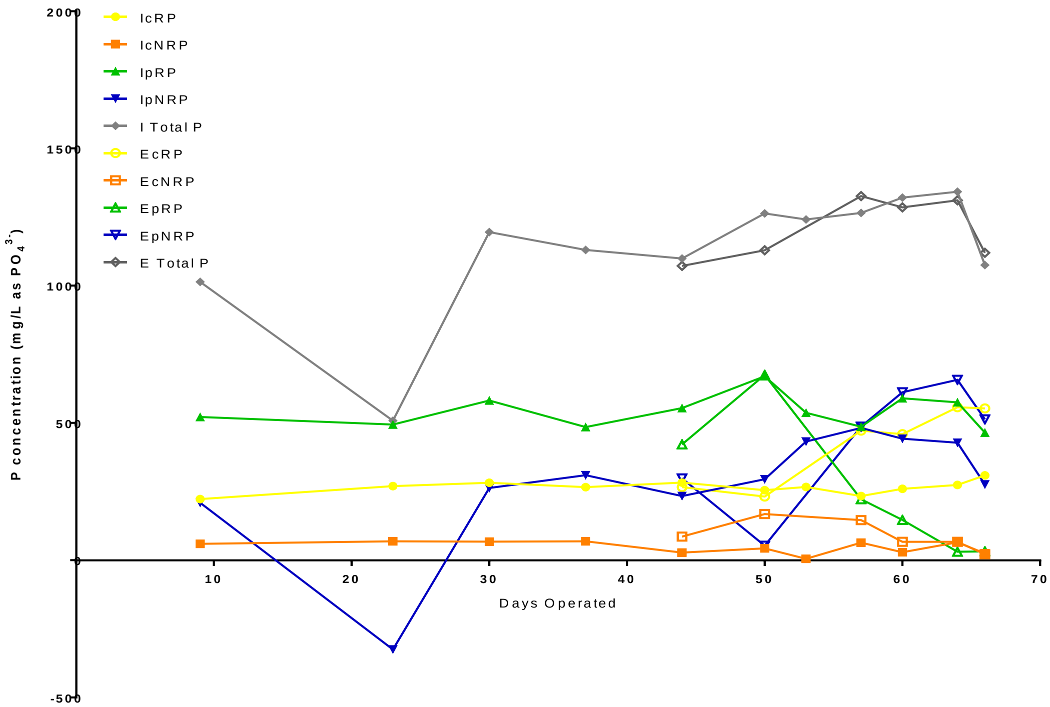


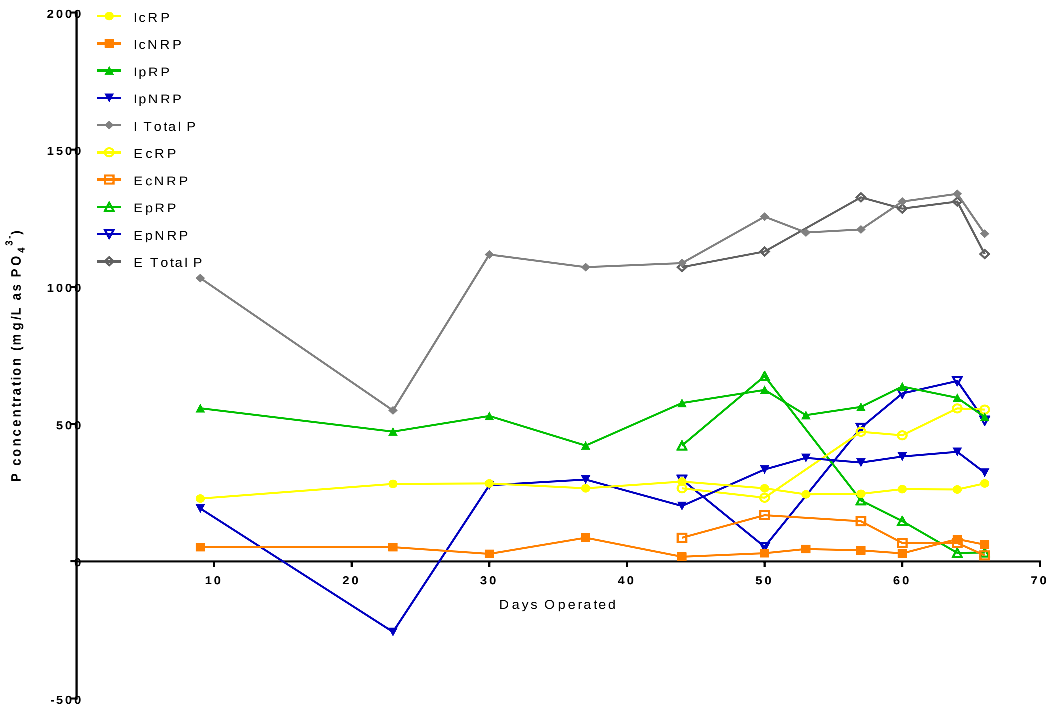
D: Time series of P Species for Every Digester



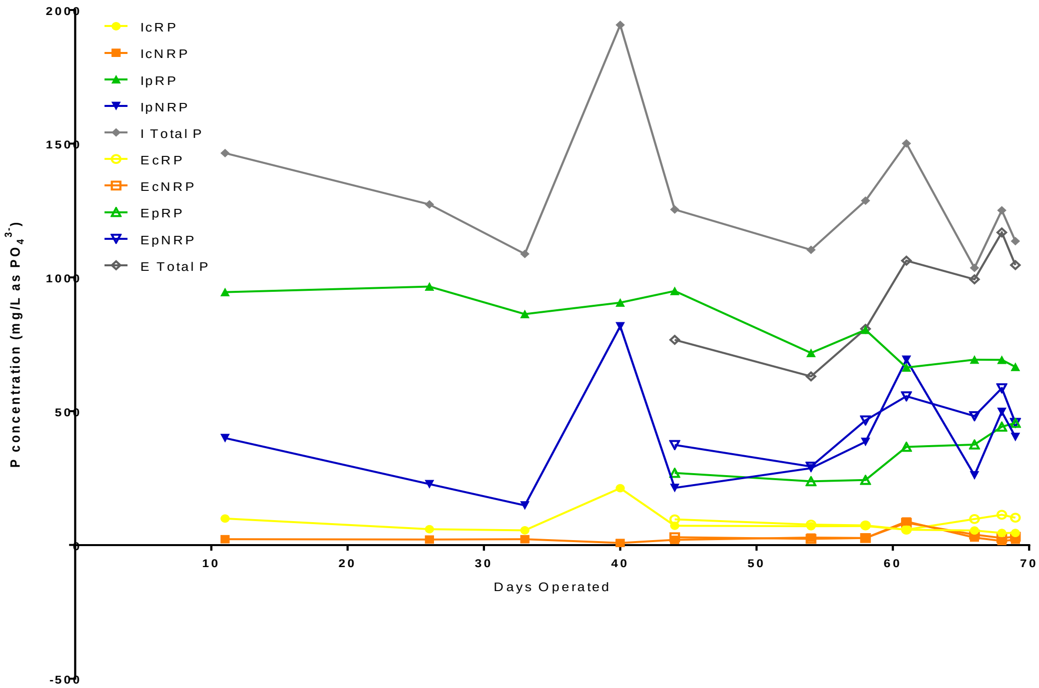


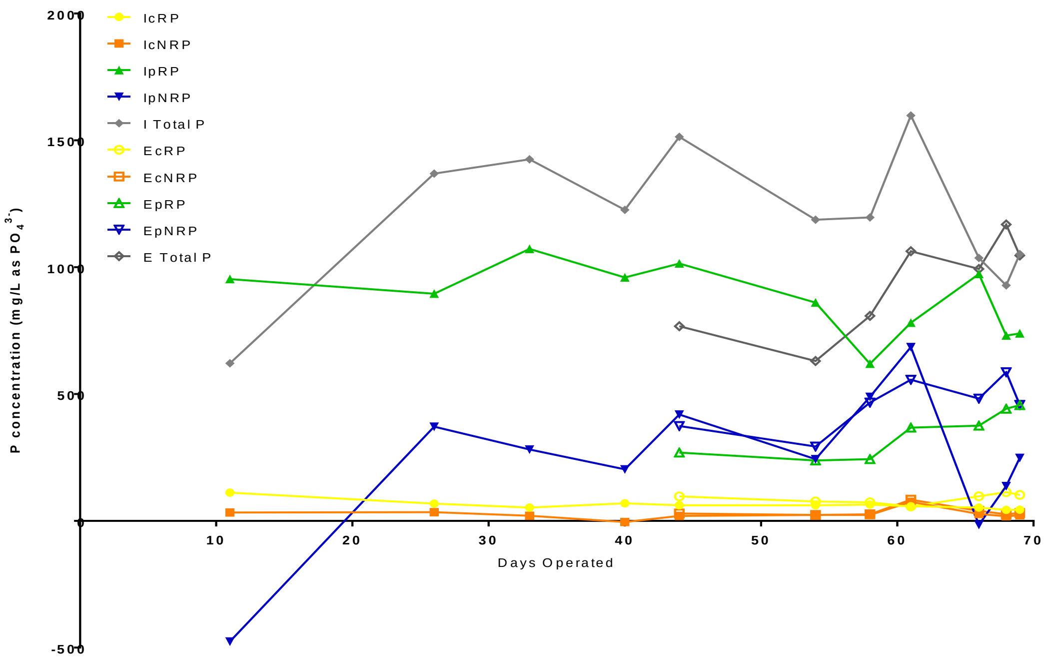
Digesters FC1 and FC2 (Top and bottom respectively), ExXX stands for effluent species, IxXX stands for influent species



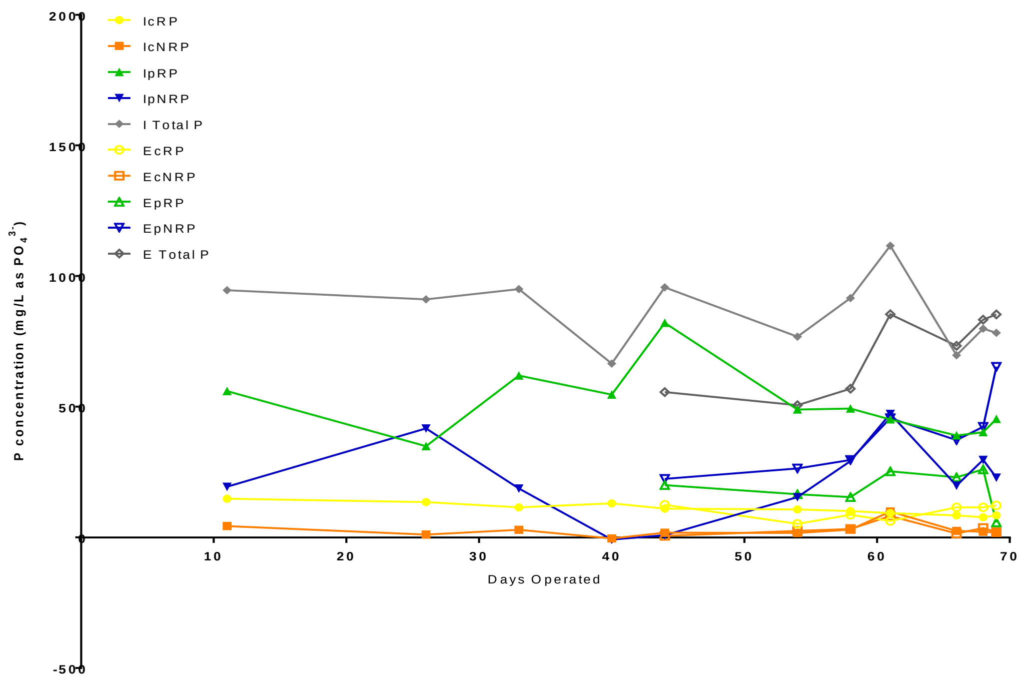


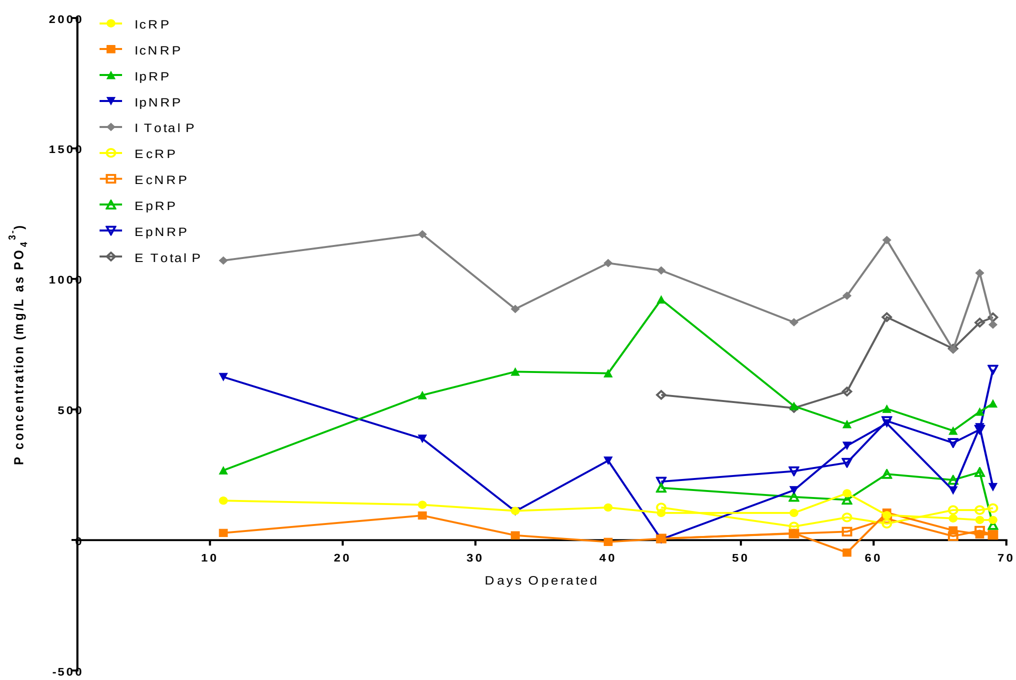
Digesters FA1 and FA2, ExXX stands for effluent species, IxXX stands for influent species





SC1 and SC2, ExXX stands for effluent species, IxXX stands for influent species





SA1 and SA2, ExXX stands for effluent species, IxXX stands for influent species