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PHOSPHORUS SPECIATION IN MUNICIPAL BIOSOLIDS FOR EFFICIENT PHOSPHORUS RECOVERY

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PHOSPHORUS SPECIATION IN MUNICIPAL BIOSOLIDS FOR EFFICIENT PHOSPHORUS RECOVERY

by

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Dedication

To my parents Julio and Yolanda and my fiancé Maria for their unconditional support

over these many years.

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Phosphorus speciation in municipal biosolids for efficient phosphorus recovery

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Phosphorus is a required element for industrialized crop production. Our ability to produce phosphorus fertilizers has allowed humanity to sustain its population. The current sources of phosphorus are apatite sedimentary deposits geographically concentrated in four countries (Vaccari 2009). Recent reports have suggested that these resources will be exhausted by the end of this century and that the limited geographical distribution of phosphorous deposits may prove to be a source of political conflict in the future (Smil 2000, Cordell et al. 2009, Vaccari 2009).

To avoid these conflicts, the potential for spent phosphorus recovery and reuse must be explored. One promising source stream for phosphorus recovery is from municipal wastewater biosolids. Current methods of phosphorus recovery from these solids only target 10% of the total phosphorus in the biosolids. To recover greater quantities of phosphorus from biosolids, we must understand the phosphorus speciation within, and be able to predict the most effective recovery method for biosolids generated from conventional activated sludge, chemical phosphorus removal or enhanced biological phosphorus removal (EBPR).

In order to understand the speciation of these three types of biosolids, nine municipal wastewater treatment plants were sampled. The results showed that in biosolids post-anaerobic digestion and gravity thickening a large portion of the phosphorus is present as particulate orthophosphate and polyphosphate and requires a process that targets these species.

Comparison of the speciation of conventional biosolids to the speciation of biosolids from chemical phosphorus removal and EBPR showed that energy intensive technologies such as the Stuttgart process and KREPRO can recover significant quantities of phosphorus from all types of biosolids. Commercial technologies (AIRPREX) only recovered significant quantities of phosphorus when used only with EBPR biosolids.

Finally, a life cycle impact assessment was performed to assess eutrophication and green-house gas potential under various scenarios of phosphorus recovery. The results showed that scenarios with chemical or biological phosphorus removal plants typically had a lower eutrophication potential than those with conventional activated sludge. Even though treatment plants with biological and chemical phosphorus removal require more energy and chemicals to operate, the global warming potentials were lower than for conventional activated sludge scenarios.

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Chapter 1: Introduction

MOTIVATION:

Phosphorus and nitrogen are two vital elements required for plant growth and food production. Our ability to recover these nutrients from natural sources and produce fertilizers has allowed us to sustain the current world's population. In 1913 Carl Bosch was able to scale to an industrial capacity a process developed a few years earlier by Fritz Haber to synthesize ammonia from nitrogen and hydrogen present in air (Haber-Bosch process)(Smil 1997). The ammonia produced by the Haber-Bosch process was used, among other purposes, for the manufacture of synthetic fertilizers (Erisman et al. 2008). After the invention of the Haber-Bosch process the population of the world exploded (Smil 1997, Smil 1999). Estimates suggests that the Haber-Bosch process is responsible for supporting 27% of the world's population over the past century (Erisman et al 2008). As a result, humanity over the past century became dependent on synthetic fertilizers containing nitrogen, phosphorus and potassium (Erisman et al. 2008, Cordell and White 2011).

Phosphorus, as opposed to nitrogen, is not present in air and to this day phosphate rock deposits are the only readily available source of primary phosphorus (Cordell et al. 2009, Cordell and White 2011). These deposits are the product of millions of years of mineralization and tectonic uplift which, by definition, makes phosphate rock a non-renewable resource (Smil 2000). The majority of phosphate rock deposits are located in Morocco, China, the US and South Africa (Fixen 2008, Cordell et al. 2009, Vaccari 2009). These countries control 45%, 21%, 7%, and 5%, respectively of the world's phosphorus

reserves (Fixen 2008, Vaccari 2009). Despite its control over 7% of the world's phosphate rock reserves, the US is still the largest individual importer of phosphate rock (Jasinski 1999, Cordell et al. 2009, Smit and Bindraban 2009, Vaccari 2009). Highly populated countries in Asia have to import large quantities of phosphorus and now account for about half of the consumption of phosphorus fertilizers (Schoumans et al. 2015). The high demand for phosphorus and the concentration of phosphate rock mines in a few geographic locations could prove to be a source of political conflict in the future as the availability of phosphate rock decreases. Some researchers estimate that, under current conditions, the world's phosphate production will peak in 2033 and will be exhausted by the end of the century (Smil 2000, Cordell et al. 2009, Cordell and White 2011).

After mining, the phosphate rock undergoes additional treatment to make it soluble and readily available for growing crops (Smit and Bindraban, 2009). The mined phosphorus then makes its way through the food chain and ultimately ends up in municipal sewer systems. According to different estimations, 20 -30% of mined phosphorus is wasted as sewage globally (Shimamura et al. 2003, Brunner 2010). Once in the wastewater treatment plant, phosphorus is removed from the liquid phase in the sedimentation and activated sludge processes. Dueñas et al. (2003) reported the removal of up to 70% phosphorus from influent wastewater in treatment plants without phosphorus removal processes and Barnard (1984) reported up to 99% phosphorus removal in plants with biological phosphorus removal processes. All the removed phosphorus is concentrated into the biosolids which are usually disposed via landfilling of dewatered or incinerated solids (Cornel and Schaum 2009, Hong et al. 2009, Blotcher et al. 2012).

There are many options available to reuse the phosphorus present in biosolids. The most successful options to date are direct land application, and recovery via inorganic precipitation (Coats et al. 2011). Land application is a method in which anaerobically digested biosolids are mixed with topsoil to replenish lost nutrients. Municipalities such as the City of Austin sell composted biosolids for fertilizing purposes. The major drawback of land application is the low nitrogen to phosphorus mass ratio ($N:P_2O_5$) in the biosolids. Usually plants need more nitrogen than phosphorus to grow. A mass $N: P_2O_5$ ratio between 3 and 5 is considered optimum for plant growth, but biosolids have a $N:P_2O_5$ ratio of approximately 1 (Yuan et al. 2012). Imbalanced biosolids can produce run-off with high concentrations of phosphorus that contribute to the eutrophication of natural water bodies (Maguire et al. 2000a & b, Schroder et al. 2008). Some states limit the amount of total phosphorus that can be applied to land and these regulations have made the application of biosolids unsustainable at some sites. Other drawbacks of reusing phosphorus by direct application of biosolids are the bulkiness of the product. Moreover, shipping biosolids from cities, where the sewage is produced and treated, to farms is a logistical challenge and a high energy burden.

The second option for recovery of phosphorus is via inorganic precipitation, most commonly as struvite. Struvite is a solid crystal that is produced when equal moles of magnesium (Mg^{2+}), ammonium (NH_4^+) and orthophosphate (PO_4^{3-}) are present under alkaline conditions (Liu et al. 2013). Municipal biosolids are ideal candidates for struvite formation since they are rich in both phosphate and ammonium. This technology utilizes either the liquid portion of the biosolids separated during thickening/dewatering (known as

supernatants or sidestreams) or the bulk pre-dewatering biosolids as a source of ammonium and phosphate. The supernatant or sludge is passed through a reactor in which pH is increased to 9 and the Mg^{2+} concentration is controlled to reach a molar $Mg^{2+}:PO_4$ ratio of 1.05:1 (Liu et al. 2013). Struvite crystals form in the reactor, precipitate and are collected (Battistoni et al. 2001, Shimamura et al. 2003, Liu et al. 2013, Maaβ et al. 2014). Struvite precipitation from biosolids has been extensively studied (Battistoni et al. 2001, Doyle and Parsons et al. 2002, Shimamura et al. 2003, Shimamura et al. 2008, Pastor et al. 2010), and different variations of the previously described technology are available in the market today (Liu et al. 2013, Cullen et al. 2013, Maaβ et al. 2014, Schoumans et al. 2015). Although this technology has been successfully implemented around the world, the major drawback is that only the dissolved orthophosphate present in the biosolids is targeted for recovery. The phosphorus present as particulate phosphates cannot be recovered.

Shortcomings of the current recovery technologies can be solved by targeting the appropriate species of phosphorus for a particular type of biosolids for recovery. Targeting a more abundant species of phosphorus in the biosolids will increase valuable inorganic phosphates recovery and in turn will promote a more balanced N: P2O5 ratio in the biosolids for direct land application. The knowledge of the speciation of phosphorus in liquid and solid fractions of municipal biosolids collected from various processes within a treatment plant will provide a rational approach for selection of appropriate target phosphorus species and technologies for its recovery. Moreover, phosphorus speciation and recovery data need to be incorporated into a life-cycle analysis to assess the potential

eutrophication and global warming benefits associated with replacing fertilizers sourced from phosphorus mines with phosphorus recovered from wastewater treatment plants.

APPROACH:

Phosphorus can be present as orthophosphates, polyphosphates or organic phosphates in wastewater: (Sawyer et al. 2003, Tchobanoglous et al. 2004), and all of these forms can be found either in the dissolved phase or in the particle phase. The goal of this dissertation research was to couple detailed measurements of phosphorous speciation in biosolids from conventional and advanced wastewater treatment plants in the US with P-recovery technology data and life cycle analyses to identify the most effective and least environmentally-harmful phosphorus recovery and reuse strategies for wastewater treatment plants in the U.S.

This research focused on achieving four objectives necessary to understand phosphorus speciation in typical wastewater treatment processes and to identify the most suitable technologies for phosphorus recovery and reuse. The first two of the four objectives address phosphorus speciation within conventional activated sludge wastewater treatments plants.

Objective 1. Determine the effect of anaerobic digestion on the speciation of phosphorus in biosolids generated from conventional activated sludge wastewater treatment plants.

There is a need to understand the effects of anaerobic digestion on phosphorus speciation in conventional biosolids. Optimizing anaerobic digestion for methane production has been well researched but its role in the speciation of phosphorus in the

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digested biosolids is still unknown. Several investigators have monitored the dissolved orthophosphate and total phosphorus concentrations in biosolids before and after digestion of enhanced biological phosphorus removal biosolids (EBPR). However, there is a need to understand how the particulate orthophosphates, polyphosphates and organic phosphates species change during anaerobic digestion as recovery of phosphorus from these biosolids depends on the speciation. Moreover, information about the speciation of conventional activated sludge biosolids before and after anaerobic digestion is lacking in the current published literature.

Objective 2. Understand the effect of gravity thickening on phosphorus speciation in biosolids generated from conventional activated sludge wastewater treatment plants.

A second question addressed in this research focuses on how gravity thickener operation affects the speciation of phosphorus in biosolids. The residence time of biosolids in gravity thickeners (1 day) is sufficiently long that it may affect phosphorous speciation. Two published studies suggest that gravity thickening of biosolids enhances the orthophosphate concentration in the liquid phase of thickened solids (Marti et al. 2008 a, b). However, only gravity thickening of EBPR biosolids was studied and the effects of gravity thickening on phosphorus speciation in conventional biosolids are still unknown.

Objective 3. Use the phosphorous speciation data collected in this study and phosphorus recovery technology performance data published in the literature to estimate phosphorus recovery and the $N:P_2O_5$ ratio in biosolids generated from conventional and advanced wastewater treatment plants.

Three different phosphorus recovery technologies were examined. The AIPREX technology developed in Berlin targets dissolved orthophosphates, and published recovery estimates were based on plants with EBPR. The Stuttgart technology targets both dissolved and particulate orthophosphates and was developed to recover phosphorus from chemically treated biosolids. Thirdly, the KREPRO process targets polyphosphates and orthophosphates and was also developed to treat chemically treated biosolids. Objective 3 will be accomplished by utilizing the results of previous research quantifying the estimated P recovery from these technologies in conjunction with the data collected in this dissertation on phosphorus speciation in biosolids. Specifically, the speciation of phosphorus in biosolids generated in conventional, EBPR and chemically-enhanced wastewater treatment plants was used to estimate the percentage of the total phosphorus that can be recovered and the $N:P_2O_5$ that will be achieved after P-recovery via the AIPREX, KREPRO and Stuttgart technologies.

Objective 4. Determine the life cycle and environmental (global warming and eutrophication) impacts from recovering phosphorous from wastewater treatment plant biosolids.

There is a need to quantify the environmental impact of recycling phosphorus from wastewater treatment plants as a function of the type of wastewater treatment plant and P-recovery technology employed. Three types of wastewater treatment plants were considered: (1) conventional activated sludge plants (2) treatment plants that incorporate enhanced biological phosphorous removal (EBPR) and (3) treatment plants that incorporate chemical P removal processes. For each of these types of WWTPs, three

phosphorus recovery technologies were considered (AIRPREX, Stuttgart Process and KREPRO). Phosphorus recovery technologies such as the Stuttgart and KREPRO processes can recover significantly more phosphorus than commercial technologies such as AIRPREX but they require more energy and chemicals. Recovering higher quantities of phosphorus from biosolids will generate biosolids with higher $N:P_2O_5$ ratios with less potential to leach phosphorus into receiving waters.

As discussed previously, the current scientific literature does not provide complete answers to the questions identified above. The objectives listed above have been designed to provide a more thorough understanding of phosphorus speciation in WWTP biosolids and to identify conditions for improved phosphorus recovery and reuse.

The first two objectives are addressed in Chapter 3, the third objective is discussed in Chapter 4 and the final objective is discussed in Chapter 5 of this dissertation.

Chapter 2: Literature Review

Optimization of phosphorus recovery from wastewater treatment plants requires an understanding of the distribution and speciation of phosphorus in the liquid and solid streams as well as an understanding of the capabilities of current technologies for recovery of each species. The following literature review begins by providing a summary of the phosphorus species present in municipal wastewater and biosolids. Wastewater and biosolids treatment processes that may have an impact on phosphorus speciation are discussed as it is expected that phosphorus will not only be transferred between liquid and solid phases but that speciation will change within each phase during treatment. Finally, current options for recovery and reuse of phosphorus from municipal biosolids are reviewed within the context of recovery of the various phosphorus species, potential for reuse and the associated environmental and technical challenges. Throughout the review, knowledge gaps that require further research are highlighted.

PHOSPHORUS SPECIES IN WASTEWATER

Phosphorus species within the biosolids can be difficult to quantify. That is why phosphorus species are typically measured by extraction techniques coupled with colorimetry. In wastewater systems, scientists usually extract phosphorus species using methods established by the American Public Health Association (APHA). The extracted phosphorus is grouped into orthophosphate, polyphosphates or organic phosphates and any of these can be present in the particulate or dissolved phase (Tomson and Vignona 1984, Parsons and Smith 2001, Tchobanoglous et al. 2004). This speciation method was selected

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to be used in the present study because it is largely utilized in the published literature to determine phosphorus in wastewater and wastewater biosolids (Munch and Barr 2001, Dueñas et al. 2003, Shimamura et al. 2008, Pastor et al. 2008, Zeng et al. 2010 and others). Also, the materials and equipment required for the extraction methods utilized in this study are portable. This is very necessary for plants with EBPR biosolids since polyphosphate hydrolysis occurs quickly after biosolids going anaerobic (Romanski et al.1997). Moreover, the extraction methods are similar to the phosphorus recovery technologies being studied (Hansen et al. 2000, Güney et al. 2008, Sartorius et al. 2012, Antakyali et al. 2013). Soil scientists on the other hand utilize a method established by Psenner et al. (1984) and group phosphorus into water soluble phosphorus (water extraction), phosphate bound to iron (Bicarbonate Dithionite extraction), phosphate bound to aluminum (NaOH extraction), phosphate bound to calcium carbonate, magnesium (e.g., apatite and struvite)(HCl extraction) and organic phosphates (persulfate digestion) (Uhlmann et al. 1990). Polyphosphates are grouped in this case with apatite and struvite phosphorus (Uhlmann et al. 1990). Only a few techniques such as X-ray absorption fine structure (XAFS) and X-ray absorption near-edge structure (XANES) have been used to determine specific concentrations of individual phosphorus species in biosolids and manures. However these measurements require sophisticated equipment that cannot be utilized on the field.

Dueñas et al (2003) investigated the removal of phosphorus in wastewater treatment plants (WWTPs) in Spain. As illustrated by Figure 1, most of the particulate phosphorus in the influent to WWTPs is removed by primary clarification (Dueñas et al 2003). A

portion of the dissolved phosphorus is then captured in the particulate phase during biological treatment or by chemical treatment and removed from the wastewater during secondary clarification (Dueñas et al 2003). Phosphorus in the biosolids is mostly in the particulate phase (Cullen et al. 2013) but some phosphorus is present in the liquid phase and can be separated from the biosolids by thickening and dewatering. Parsons and Smith (2001) and Dueñas et al (2003) reported that close to 50% of the total phosphorus found in the influent to typical domestic wastewater treatment plants is in the form of orthophosphate with the remainder as polyphosphates (35%) and organically bound phosphates (15%). However, the speciation of the dissolved and particulate phosphorus in the biosolids produced by primary and secondary clarification is still largely unknown.
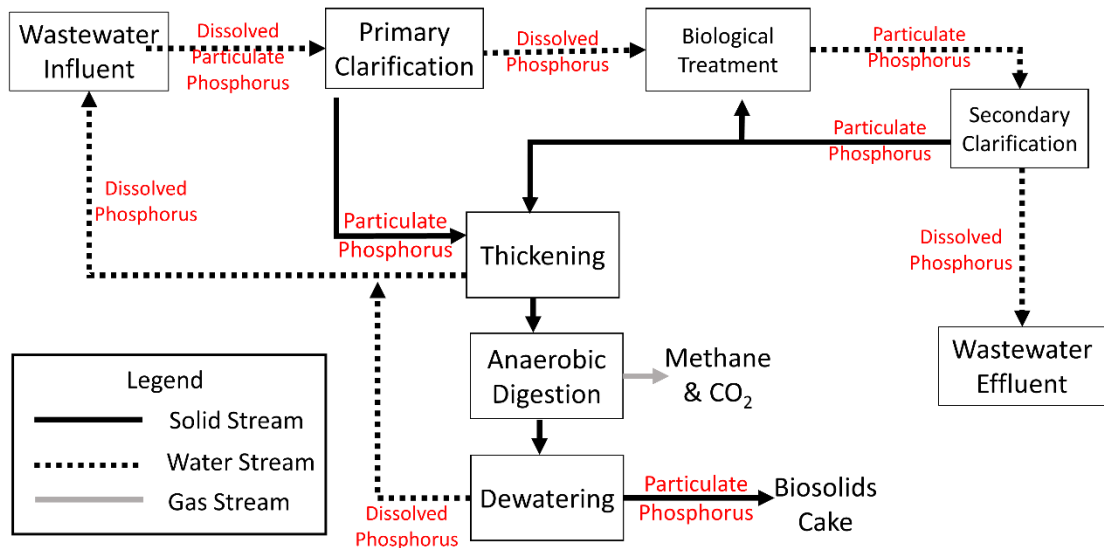
Figure 1. Fate of particulate and dissolved phosphorus in a wastewater treatment plant.

Orthophosphate

Orthophosphates are a group of phosphorus species that make up the phosphoric acid system and include H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. These species are the only bioavailable form of phosphorus and the only species that form solid minerals (Nriagu, 1984, Zeng et al. 2010, Doyle and Parsons 2002). Orthophosphates can form over 30 different compounds and their precipitation is governed by pH (Nriagu 1984, Stumm and Morgan, 1995). The most common solids that form in wastewater and wastewater biosolids are hydroxyapatite (HAP) $[Ca_{10}(PO_4)_6(OH)_2]$, brushite $[Ca(HPO_4) \cdot 2H_2O]$, strengtite $[FePO_4 \cdot 2H_2O]$, vivianite $[Fe_3(PO_4)_2 \cdot 8H_2O]$, variscite $[AlPO_4]$ and magnesium struvite $[MgNH_4PO_4]$ (Tomson and Vignona 1984, Wild et al. 1997, Marti et al. 2008a). The formation of potassium struvite has been reported in the literature but only under low

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ammonium concentrations which is not the case in typical municipal wastewaters (Marti et al. 2008a, Mehta and Batstone 2013). The occurrence of one phosphorus solid versus the other depends on the concentration of each individual ion as well as the pH and redox conditions of the solution (Wild et al. 1997, Mehta and Batstone 2013).

The production of phosphoric fertilizer involves the dissolution of sedimentary phosphate rock formed of particulate orthophosphates (Hydroxyapatite, fluoroapatite and chloroapatite) with sulfuric acid (Wood and Cowie 2004, Fixen 2008, Nieminen 2010). The reaction of sulfuric acid with phosphate rock produces orthophosphoric acid fertilizer that can be converted into polyphosphate fertilizer by heat treatment (Jensen 2007). It has been demonstrated that for farming applications there is no difference between using orthophosphate or polyphosphate fertilizer (Jensen 2007, Rhem 2013).

Polyphosphates

Polyphosphates are molecules formed by two or more phosphorus atoms sharing an oxygen atom (Tchobanoglous et al. 2004, Rao et al. 2009). In other words, polyphosphates are a combination of two or more orthophosphates. One of the most biologically important polyphosphates molecules is ATP, which serves as an energy source for microorganisms (Rao et al. 2009). Polyphosphates are very stable in drinking water over a range of pH levels and temperatures (Rao et al. 2009). Due to their stability, polyphosphates were used in synthetic detergents. Polyphosphates were later banned from their use in detergents to avoid excessive phosphorus discharges to natural streams.

Even though polyphosphates are stable in "clean" water, they are easily transformed to orthophosphates in the presence of bacterial enzymes (Snoeyink and Jenkins 1980, Kuroda et al. 2002); the widespread availability of these enzymes in soils is the reason that polyphosphates make excellent fertilizers. In EBPR plants, wastewater is alternated between anaerobic and aerobic conditions to stimulate bacteria into assimilating dissolved orthophosphate (liquid-phase) in large quantities and producing particulate polyphosphate within the cell (solid-phase) (Kuroda et al. 2002, Kodera et al. 2013). A detailed explanation of the EBPR process is provided later in this section.

Organic Phosphate

Organic phosphates are phosphorus molecules that have been incorporated into organic material including within microbial cells. Organic phosphates are present primarily in the cell membrane as phospholipids and in the DNA as the bond between base pairs (Madigan et al. 2009). Organic phosphates are not a significant fraction of the total phosphorus in domestic wastewater, but are significant in wastes rich in microorganisms such as wastewater biosolids and some industrial wastewaters (Tchobanoglous et al. 2004). Most organic phosphates are part of the bacterial cells (Shimamura et al. 2008) and thus it is likely that most will be in the solid phase of biosolids.

In the natural environment, the transformation among species of phosphorus sustains aquatic life. Orthophosphates in natural environments are utilized by algae and aquatic plants for their growth. The organic phosphates in the algal biomass is eventually

decomposed by microorganisms that store energy in the form of polyphosphates (Madigan et al. 2009). When microorganisms utilize the stored energy, orthophosphates are released to solution, replenishing the available orthophosphate pool for algae growth (Madigan et al. 2009, Sundby et al. 2012).

CONDITIONS THAT IMPACT PHOSPHORUS SPECIATION IN MUNICIPAL BIOSOLIDS

Municipal biosolids are formed during sedimentation of particles in wastewater treatment plants. Dueñas et al. (2003) reported that more than 90% of the particulate phosphorus in wastewater can be removed via sedimentation; the collected biosolids are then typically sent to solids processing facilities and ultimately to a landfill. In the last 50 years there has been an increasing interest in removing phosphorus from wastewater effluents to prevent algal blooms (Marti et al. 2008, Tchobanoglous et al. 2004). Future limitations on phosphorus discharges permitted for wastewater treatment plant effluents will increase the mass of phosphorus that is removed via the biosolids. In 1996, the USEPA established a recommended concentration limit of 0.05 mg/L for total phosphorus that enters lakes and 0.1 mg/L for total phosphorus that enters flowing waters (Litke 1999). Since this is just a recommended limit, states are free to choose their regulatory limits which can vary significantly (Litke 1999). For, example the Wisconsin Department of Natural Resources has established the limit for total phosphorus discharge at 1 mg/L for point sources and total phosphorus effluent limits; and, phosphorus limits for the Everglades area in Florida are as low as 0.01 mg/L (NR 217 2012, Mayer et al. 2013, Blair

et al. 2015). In contrast, states such as Iowa, Kansas and Nebraska (to name a few) have no phosphorus limits in place for discharges over 1 MGD (EPA 2016).

In this section the wastewater characteristics and treatment processes that may affect phosphorus speciation in municipal biosolids are reviewed.

Wastewater Treatment Plant Influent Effects

The principal wastewater influent characteristic that affects the removal of phosphorus in municipal biosolids is the concentration of cations, specifically the concentrations of Ca, Mg, Al and Fe. One of the principal cation sources in the wastewater treatment plant influent is rainfall runoff, especially in locations with soluble geology. The contribution of rainfall runoff also depends on the permeability of the sewer system. Older cities in the US (i.e., New York, Chicago, and Philadelphia) have combined sewers in which domestic and industrial discharges are mixed with rainfall runoff and treated before discharge (Burm and Vaughan 1966). In contrast, separate sewers carry only domestic and industrial discharges. However, separate sewers are not completely sealed and infiltration is possible (Tchobanoglous et al. 2004).

Alkalinity Source for Wastewater Treatment Effects

Another major source of cations in municipal biosolids are the salts used for supplemental alkalinity required to achieve the removal of organics and nutrients in the activated sludge process (Tomson and Vignona 1984, Droste 1997, Tchobanoglous et al. 2004). In some wastewater treatment plants, operators need to supply extra alkalinity in the form of $NaHCO_3$, $MgOH$, lime [$Ca(OH)_2$], or limestone [$CaCO_3$] (Tomson and Vignona

1984, Liu and Koenig 2002). The choice of additional alkalinity can have an impact on the phosphorus species found in biosolids because, as opposed to sodium, magnesium and calcium easily form precipitates with orthophosphates. Calcium ions alone, can significantly decrease the dissolved orthophosphate concentrations when present in the biosolids at concentrations above 100 mg/L (de-Bashan and Bashan 2004). The addition of sodium bicarbonate however, can produce minor inhibition of hydroxyapatite (HAP) formation at neutral pH, and produce major inhibition when coupled with Mg (Cao and Harris 2008).

Phosphorus Removal Processes Effects

Phosphorus removal processes in wastewater can be divided between chemical and biological processes. Chemical removal of phosphorus is still the most popular process due to its simple operation and effectiveness (Morse et al. 1998, de-Bashan and Bashan 2004). Chemical phosphorus removal consists of dosing wastewater with salts that react with orthophosphates and precipitate during sedimentation (Tomson and Vignona 1984). Iron salts and alum are the most commonly used reagents to chemically remove phosphorus from wastewater. Lime is also used when additional alkalinity is required (Tomson and Vignona 1984, Droste 1997). These salts can be added during primary, secondary, and even tertiary treatment (Tomson And Vignona 1984). The chemical dosage can significantly affect the speciation of phosphorus in the biosolids generated in each process. Studies suggest that utilizing biosolids generated from chemical phosphorus removal for recovery is challenging since the majority of the orthophosphates are bound to iron or aluminum as

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insoluble salts (de Bashan and Bashan 2004, Cornel and Schaum 2009). This matter will be further discussed later in this section and will be further studied in the light of phosphorus speciation in the subsequent chapters.

In addition to chemical precipitation approaches, a range of enhanced biological phosphorus removal (EBPR) treatment processes can also be employed at wastewater treatment plants to recover phosphorus. EBPR processes utilize a group of microorganisms known as phosphorus accumulating organisms (PAOs) that under alternating anaerobic and aerobic conditions store high quantities of phosphorus in the form of polyphosphate (Morse et al. 1998). PAOs such as *Acinetobacter spp.* can store polyphosphates at levels up to 30% of their dry weight (Parsons and Smith 2008). PAOs consume polyhydroxybutyrate (PHB) and orthophosphates under aerobic conditions to produce polyphosphates, which are stored inside their cell wall (de Bashan and Bashan 2004). Under anaerobic conditions PAOs utilize their stored polyphosphates as a source of energy to consume volatile fatty acids (VFAs), producing polyhydroxybutyrate (PHB) and orthophosphates (Fuhs, et al. 1975, Parsons and Smith 2008). When aerobic conditions are returned, these microorganisms consume more orthophosphates than they previously released. This process can achieve phosphorus removals from wastewater influents of greater than 90% (Morse et al. 1998, de Bashan and Bashan 2004). The phosphorus trapped in the solid phase of the biosolids can be released into the liquid phase as dissolved orthophosphate by allowing the biosolids to go anaerobic (Liao et al. 2003, de Bashan and Bashan 2004). This process is known in the literature as polyphosphate hydrolysis and will be discussed in this and the following chapters.

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EFFECT OF BIOSOLIDS TREATMENT PROCESSES ON PHOSPHORUS SPECIATION

As stated previously, biosolids accumulate during sedimentation of particles present in wastewater, and these biosolids usually require further treatment before final disposal. Some of the most common treatment processes are thickening, anaerobic digestion and dewatering. In this section the potential effects of these processes on phosphorous speciation will be reviewed in the light of the available literature.

Thickening

Thickening is a sedimentation process that increases the solids content of the biosolids obtained from primary or secondary clarifiers. Solids concentrations can be as high as 15%, depending on the thickening process; higher values would lead to issues with pumping the solids (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006, Sanin et al. 2011). This process is typically done to optimize the use of space in downstream anaerobic digesters (Tchobanoglous et al. 2004). The most common methods of thickening are gravity settling, air-flotation, centrifugation, belt thickening, and rotary drums (Droste 1997, Tchobanoglous et al. 2004). The effluents from thickening can be utilized for phosphorus recovery via struvite precipitation (Cullen et al. 2013).

Gravity thickeners

These thickeners are similar to clarifiers where larger particles are allowed to settle and water exits over weirs (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006, Sanin et al. 2011). Gravity thickeners have a higher bottom slope than clarifiers to avoid

anaerobic decomposition (Turovskiy and Mathai 2006). Gravity thickeners usually work best for primary biosolids since their high initial solids content [2-7%] require less thickening (Turovskiy and Mathai 2006, Droste, 1997). Although some authors report that this method is being used for secondary and mixed biosolids (Turovskiy and Mathai 2006, Pastor et al 2008), the low density of secondary sludge biosolids makes it difficult to effectively thicken them by gravity (Sanin et al. 2011)

The mixing of primary and secondary sludge can be a key factor that affects phosphorus speciation in the biosolids. Pastor et al. (2008) reported that mixing secondary and primary sludge for thickening promoted the hydrolysis of polyphosphates into orthophosphates due to the high concentration of VFAs in the primary sludge. Gravity thickeners are a good option when hydrolysis of polyphosphates is required due to the high retention time of these reactors (Turovskiy and Mathai 2006).

Dissolved air-flotation.

This method consists of introducing high pressure air into a tank containing biosolids in order to make particles float to the surface, from where they are removed by a skimmer (Turovskiy and Mathai 2006). This process works better for thickening secondary biosolids since particles in primary biosolids are too heavy to float (Tchobanoglous et al. 2004, Sanin et al. 2011). Hydraulic detention times in dissolved air-flotation thickeners are lower than in gravity thickeners (5-16 hours in gravity thickeners vs. 30 minutes in dissolved air-flotation)[Turovskiy and Mathai 2006, Sanin et al. 2011]. Lower retention

times than in gravity thickeners as well as the aeration process could prevent the hydrolysis of polyphosphates in the thickener.

Centrifugation.

Thickening by centrifugation is done by applying a centripetal force of 500 to 3000 times that of gravity to separate particles from liquid (Turovskiy and Mathai 2006). Since primary sludge contain heavy particles that can damage centrifugation systems, these are usually utilized only for secondary sludge (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006) However, several studies have reported centrifugation of primary and mixed sludge biosolids (Sanin et al. 2011). Centrifugation thickeners are very expensive to operate, maintain, and purchase but require less space than other systems (Turovskiy and Mathai 2006). Typically, centrifugation does not require biosolids conditioning, but sometimes inorganic polymer is used intermittently to improve performance (Tchobanoglous et al. 2004). Thickening by centrifugation is fast, thus hydrolysis of polyphosphates is not expected. Nevertheless, the addition of inorganic polymers may have an effect on the orthophosphate concentration in the biosolids supernatant.

Belt thickening

Belt thickeners consists of a large conveyor belt with a porous bottom that allows water to percolate through (Turovskiy and Mathai 2006, Sanin et al 2011). Belt thickening can be done on primary, secondary, and mixed biosolids (Turovskiy and Mathai 2006), and this choice can have an effect on the speciation of phosphorus in the biosolids. Belt

thickeners are not very energy intensive but require conditioning of the biosolids with a flocculant (Turovskiy and Mathai 2006, Sanin et al 2011).

Conditioning is a process to improve the separation of solid and liquid phases of the biosolids. Conditioning is typically done by the addition of organic or inorganic chemicals to the biosolids (Turovskiy and Mathai 2006, Sanin et al. 2011). Inorganic conditioning agents such as ferric chloride, ferrous sulfate, aluminum chloride, and lime can drastically change the phosphorus speciation in the biosolids. Organic polymers are long hydrophilic molecules that promote aggregation of particles in the biosolids and have become the conditioner of choice for belt and rotary thickeners (Turovskiy and Mathai 2006). Although there have been studies investigating the effect of organic conditioners on methane generation during anaerobic digestion (Gossett et al. 1978, Chu et al. 2003), their effect on the speciation of phosphorus in the biosolids has not been thoroughly studied.

Rotary drum

This system is similar to belt thickeners but instead of a conveyor belt, a circular rotating chamber with a permeable wall is utilized to improve the release of the water (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). Conditioned biosolids are required for this system as in the case of belt thickeners (Turovskiy and Mathai 2006).

Anaerobic Digestion

Anaerobic digestion is a biological process widely used to reduce the volume and stabilize biosolids. Anaerobic digestion is one of the oldest wastewater treatment processes, and it is utilized for streams with both high and low organic loading (Tchobanoglous et al.

2004, Turovskiy and Mathai 2006, Sanin et al. 2011). In anaerobic digestion, organic matter is decomposed by bacteria without the biomass increase observed in aerobic treatment (Droste, 1997, Tchobanoglous et al. 2004). Another important advantage of anaerobic digestion is that the production of useful methane gas usually makes anaerobic digestion an energy positive process (Turovskiy and Mathai 2006).

In the following subsection, the chemical and biological processes that occur during anaerobic digestion will be described and their potential effects on phosphorus speciation will be identified.

Steps in anaerobic digestion.

Anaerobic digestion is a processes with three identifiable steps that occur simultaneously. These steps are performed by a heterogeneous microbial community (Tchobanoglous et al 2004, Turovskiy and Mathai 2006). The first step of anaerobic digestion is hydrolysis. In this step large polymer molecules and particulate materials are solubilized by extracellular enzymes into smaller molecules that are more readily consumed (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). It has been reported that hydrolysis can become a rate limiting step in anaerobic digestion especially if the biosolids contain high portions of organic solids and extracellular polymeric substances (EPS) [Eastman and Ferguson 1981, Li and Noike 1992, Gavala et al. 2003, Appels et al. 2008, Carrere et al. 2010]. The biggest source of organic solids and EPS in municipal biosolids is the secondary biosolids from the waste activated sludge process (Li and Noike 1992). Muller (1999) and Carrere et al. (2010) showed that primary biosolids are easily

biodegradable compared to secondary biosolids due to EPS formed under long retention times. Digesting biosolids with low degradability means that some cells remain intact at the end of the process and the organic phosphates accumulated in these cells is not released.

The second step of anaerobic digestion is acidogenesis or fermentation. During this step the products of hydrolysis are transformed into volatile fatty acids, hydrogen and carbon dioxide by anaerobic and facultative bacteria (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006).

The third step of anaerobic digestion is methanogenesis. This step is carried out by obligate anaerobic archaea that utilize the volatile fatty acids produced during acidogenesis and generate methane (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). The methanogens and acidogens work symbiotically. The methanogens consume the products of fermentation while maintaining the partial pressure of H_2 low enough for acidogenesis to continue.

Solids and Hydraulic Retention Time

Solids retention time (SRT) is the average time that a solid particle spends in the reactor while the hydraulic retention time (HRT) is the volume of the reactor divided by the volume of biosolids removed per day (Droste 1997, Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). When the process does not employ a recycle flow, the SRT and HRT are equal.

Methanogens are slow growers and very sensitive to environmental conditions, especially pH (Turovskiy and Mathai 2006). If the SRT is not adequate, methanogens do

not grow in enough numbers to control the VFA concentration and the pH can decrease to inhibitory levels. Over accumulation of VFAs can affect phosphorus speciation in two different ways. First, low pH allows orthophosphates to stay in solution instead of precipitating. Secondly, as previously stated VFAs promote the hydrolysis of polyphosphates.

Temperature

Temperature is the parameter that determines the rate at which the microorganisms carry out the digestion steps. Anaerobic digestion can operate in mesophilic ranges (30-38 ºC) or thermophilic ranges (50-57 ºC) (Droste 1997, Tchobanoglous et al. 2004). Typically mesophilic digesters are preferred since the energy required to maintain a stable temperature is significantly lower (Tchobanoglous et al. 2004). However, better solids destruction and methane yields have been reported with thermophilic digesters (Angelidaki et al. 2003, Gavala et al. 2003, Climent et al. 2007). The increased performance reported in the literature suggests a higher conversion of organic phosphates into orthophosphates. Moreover, temperature increases the solubility of phosphate molecules (Stumm and Morgan 1995) and thus higher dissolved phosphates are expected in thermophilic digesters.

pH and Alkalinity

As discussed previously, methanogens are very sensitive to pH. The optimum pH is 7 and values below 6.8 have been reported to be difficult to correct (Tchobanoglous et al. 2004). In order to maintain an adequate pH, it is necessary to provide an alkalinity

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between 60 – 120 meq/L (Tchobanoglous et al. 2004). As discussed previously the choice of alkalinity can drastically affect the phosphorus speciation in the biosolids.

Dewatering

Dewatering is the process of removing most of the water from the biosolids to reduce the volume and decrease costs of disposal (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). The most common methods for dewatering are centrifugation, belt filter press dewatering and natural drying.

Centrifugation and belt filter press dewatering are similar to their thickening counterparts, but produce solids with over 15% solids content (Tchobanoglous et al. 2004, Turovskiy and Mathai 2006). Dewatering by natural drying is the use of sunlight, temperature, and drainage to remove water from biosolids (Turovskiy and Mathai 2006). Natural drying requires large land areas to deposit the biosolids and due to regulations it can only be applied using stabilized biosolids. Phosphorus does not volatize (Smil 2000), thus all of the phosphorus is likely to stay in the dewatered biosolids or the drained water. Although the drained water from the drying beds is not being considered for phosphorus recovery in the current literature, based on the performance of drying beds it likely that this is a stream rich in phosphorus (Uggetti et al. 2009, Vincent et al. 2011).

PHOSPHORUS RECOVERY ALTERNATIVES

Many researchers (Battistoni et al. 2001, Shimamura et al. 2003, Shimamura et al. 2008, Marti et al. 2008a, Marti et al. 2008b, Cordell et al. 2009, Bradford-Hartke et al. 2012) have proposed different alternatives to recover and reuse the phosphorus trapped

within the municipal biosolids. The most developed and prevalent alternatives in the literature are land application and inorganic precipitation. Both methods are described in the following subsections.

Land Application

Land application of human excreta has been utilized as a fertilizer for centuries (Cordell and White 2011), but the use of wastewater treatment plant generated biosolids for soil conditioning only dates back to 1927 (Epstein 2003). The modern definition of land application according to Tchobanoglous et al. (2004) is "the spreading of biosolids on or below the soil surface and this may be on agricultural land, forest land, disturbed land and dedicated disposal land."

As stated in previous sections, biosolids are rich in both nitrogen and phosphorus. When biosolids are applied to the soil, the phosphorus is solubilized by bacteria, thus making it readily available for plants (Yuan et al. 2012). The solubility of the phosphorus present in the biosolids is treatment process dependent as discussed in previous sections. Penn and Sims (2002) and Maguire et al. (2000 a & b) demonstrated that the phosphorus present in biosolids from EBPR processes are more soluble than the phosphorus present in biosolids from wastewater plants that incorporate chemical removal.

There are many limitations for reusing phosphorus present in biosolids via land application. The first limitation is the regulations imposed on land application practices. The utilization of biosolids in land application requires these to be classified as Class A or Class B biosolids (Tchobanoglous et al. 2004). Class A biosolids are those with a fecal

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coliform most probable numbers less than 1000/g of total solids. Class A biosolids have no restrictions over where they can be applied (Epstein 2003, Tchobanoglous et al. 2004). Class B biosolids are those with fecal coliform most probable numbers less than 2 million/g of total solids. These class B biosolids are limited as to the location and on what crops they can be applied (Epstein 2003, Tchobanoglous et al. 2004). Class B biosolids are also regulated for heavy metals for land application (Epstein, 2003). The majority of treatment plants in the US produce class B biosolids though anaerobic digestion (Viau and Peccia 2009) since class A biosolids require a composting process that some municipalities cannot afford.

Another limitation to the land application of biosolids is the imbalance of the nitrogen to phosphorus ratio ($N:P_2O_5$). In the agricultural literature this ratio is expressed as the mass of nitrogen as N to the mass of P as P_2O_5 (diphosphorus pentoxide). Plants usually require a $N:P_2O_5$ of 3-5 while municipal solids usually have a $N:P_2O_5$ close to 1 (Yuan et al. 2012). This imbalance leads to soils with excessive concentrations of phosphorus. This phosphorous excess can solubilize and contaminate bodies of water. Some states regulate the amount of phosphorus that can be applied to soils (Maguire et al 2000 a & b, Penn and Sims 2002) and the imbalance can lead to plots of land where biosolids application is banned (Schober and Sims 2003).

The final limitation to the reuse of phosphorus through land application is expensive transportation and risk management costs (Yuan et al. 2012). In large countries, like the US, farmlands are located far away from sewage treatment plants and in order to reuse the phosphorus trapped in the biosolids, the biosolids have to be transported

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considerable distances. These biosolids are bulky, produce strong odors and contain

pathogens and substances that need to be contained and managed (Yuan et al. 2012).

Despite these limitations, land application of biosolids cannot be avoided

completely and has to be a part of an integral solution to reuse phosphorus. However, the

quantities of phosphorus applied to the land have to be reduced for this practice to continue.

Inorganic precipitation

Phosphorus recovery via precipitation technologies has been extensively studied

especially in countries with little access to phosphate rock. The commercially available

technologies typically precipitate struvite. Struvite is a crystal that forms when equal molar

concentrations of ammonium, magnesium and phosphate (Equation 1) are present under

slightly alkaline conditions (Liu et al. 2013). In some wastewater treatment plants, struvite

is considered a nuisance as it clogs pipes and pump appurtenances (Marti et al. 2008b), but

over the past decade there has been renewed interest in struvite from the fertilizer industry.

Struvite has been identified to be present in the natural fertilizer guano and it can be

delivered to soils in high quantities without burning the roots of plants (Bridger et al., 1962;

Parsons and Smith, 2008). Struvite also has a low solubility which prevents it from washing

out as runoff (Bridger et al., 1962; Parsons and Smith, 2008).

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + OH^- + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \text{ (1)}$$
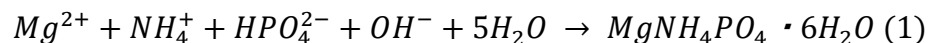
Many reactor configurations have been studied for struvite crystallization. Two of

the most developed at full-scale are the liquid fluidized bed reactor shown in Figure 1a

commercialized by OSTARA (Liu et al. 2013) and the AIRPREX[TM] sludge crystal

precipitation reactor (Figure 1b) developed by CNP (Maaβ 2014). The Ostara process utilizes the sidestream water separated from the biosolids by thickening/dewatering and supplies air to control pH by stripping the carbon dioxide. The AIRPREX ^{TM} system utilizes the bulk biosolids before dewatering as a phosphorus and ammonium source and also utilizes air to strip carbon dioxide and control pH. Both processes require chemicals to supply magnesium. Small struvite crystals or silica sand particles are sometimes added at the top of the reactor to promote nucleation (Battistoni et al. 2001). The optimal pH for struvite crystallization is between 8 and 9 (Shimamura et al. 2008; Iqbal et al. 2008, Pastor et al. 2010, Liu et al. 2013). When additional pH control is required NaOH, and $Ca(OH)_2$ can be utilized (Shimamura et al. 2003, Liu et al. 2013). Calcium hydroxide can reduce struvite yield but sodium hydroxide is more expensive. Since magnesium addition is usually required MgOH can be efficient as both pH control and Mg supply (Liu et al. 2013).
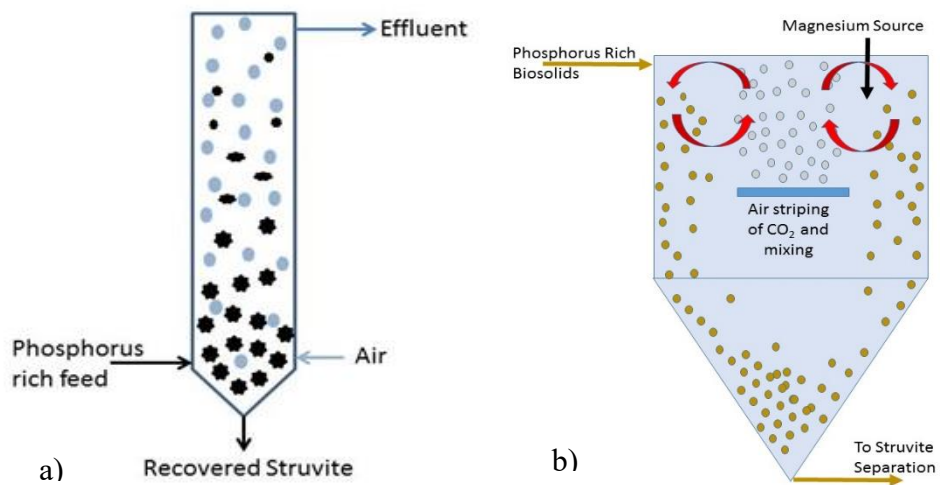
Figure 2. a) Fluidized bed reactor utilized to precipitate struvite crystals (adapted from: Parsons and Smith, 2008) b) Sludge crystal precipitation reactor (adapted from cnp-tech.com - Airprex ^{TM}).

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Phosphorus recovery through commercial struvite precipitation technologies can resolve many of the limitations of direct land application. Struvite has been proven to be an effective supply of phosphorus to agricultural fields without producing harmful runoff (Bridger et al. 1962, Parsons and Smith 2008, Liu et al. 2013). Also, since it is an inorganic crystal it can be washed and transported without the risk of exposing humans to harmful pathogens. Finally, struvite can be used as a phosphorus supply for applications other than agriculture.

Despite being a promising technology, commercial struvite recovery also has some limitations. The principal disadvantage of this product is that the main source of phosphorus for struvite precipitation is orthophosphate dissolved in the liquid fraction of the biosolids. That means that all the particulate phosphorus remaining in the solid's cake remains untouched. This is the reason why some authors claim that biosolids generated from chemical phosphorus removal plants are not suitable for recovery via struvite precipitation (de Bashan and Bashan 2004). Utilizing struvite precipitation to recover phosphorus from EBPR biosolids is more common since the phosphorus trapped in the solid phase of the biosolids can be effectively released into the liquid phase by allowing the biosolids to go anaerobic (Liao et al. 2003, de Bashan and Bashan 2004). The principal disadvantage of implementing EBPR processes in wastewater systems is the operational complexity involved and higher energy demand compared to chemical processes (Morse et al. 1998).

As reported by Cullen (2013) from a pilot study of the first struvite recovery plant in the US, most of the phosphorus in the biosolids produced by sedimentation is in the solid

phase and remains in the solid phase. To overcome this issue, we must understand the speciation of phosphorus in the biosolids.

To increase phosphorus recovery from municipal biosolids, some researchers have developed technologies that target more abundant species of phosphorus for precipitation. The Stuttgart process, developed in Germany, targets particulate and dissolved orthophosphate by decreasing the pH of the biosolids to 2 (Antakyali et al. 2013). At this pH over 98% of the orthophosphate is dissolved (Güney et al. 2008). The biosolids are then dosed with citric acid to complex mainly iron, aluminum and calcium to a lesser extent to inhibit precipitation. The solids are dewatered and the produced supernatants are used to precipitate struvite. (Antakyali et al. 2013).

The KREPRO process is another technology of recovery of phosphorus that targets particulate and dissolved species of phosphorus in the biosolids. In this case, KREPRO consists of acidifying biosolids to pH 2 and then heating to 140 ℃ for 30 minutes inside a pressurized vessel (Hansen et al. 2000). The biosolids are then dewatered and the phosphorus in the produced supernatants is precipitated as ferric phosphate. Hultman (1999) and Karlsson (2001) reported a recovery of 60 to 75% of the total phosphorus present in the biosolids. Hansen et al. (2000) showed that the recovered phosphorus is available for plant growth.

LIFE CYCLE IMPACT ASSESSMENT (LCIA)

Process based life cycle impact assessment is a method to account for the economic, energy, and environmental burden of a given process or product (Hong et al. 2009). To

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develop a LCA, a set of scenarios that will be compared against each other are first defined. Next, the energy, fuel and raw material requirements as well as harmful emissions for the scenarios are obtained either by experimentation, modeling or through literature research. These values are known as life cycle inventory (LCI). The LCI is then normalized by an arbitrary functional unit selected by the investigator. Once normalized, one can compare the environmental burden or energy requirements across scenarios.

Several researchers (Lundin et al. 2000, Hospido et al. 2005, Foley et al. 2007, Hong et al. 2009, Coats et al. 2011, Linderholm et al. 2012, Jossa and Remy 2015) have completed LCIA studies on methods for removing phosphorus from wastewater as well as technologies to recover the phosphorus from the biosolids produced. Foley et al. (2007) focused on the environmental burden that activated sludge processes have on the local and global environment. They analyzed eight different scenarios where activated sludge (AS) was utilized to treat different target chemicals (for COD, nitrogen or phosphorus removal). The functional unit utilized was the treatment of 10 million L/d of raw domestic wastewater. These scenarios were modeled using a biological simulation software package to obtain the life cycle inventory [LCI] (fuel, energy and chemical usage, atmospheric emissions and transportation costs). The impacts of these LCI were then divided into damage categories such as carcinogens, global warming potential (GWP), land occupation, ozone layer depletion, and mineral extraction as specified by the IMPACT 2002+ model (Joliet et al. 2003). The environmental burden index (EBI) was also calculated for each category. Foley et al. (2007) concluded that although biological phosphorus removal is beneficial for the local environment by reducing eutrophication of streams, it is detrimental

to the global environment because of its energy intensity. Coats et al. (2011) also compared different treatment processes for phosphorus removal (chemical and biological) but only compared the global warming impact of using one technology versus the other instead of calculating the EBI.

Hong et al. (2009) investigated the impacts of landfilling versus agricultural use of dewatered biosolids. They showed that anaerobic digestion, despite producing global warming gasses such as CO_2 and methane, is very effective at reducing the solid concentration in the biosolids. Less energy is then required to transport and land apply biosolids after anaerobic digestion.

Linderholm et al. (2012) investigated the global warming potential (GWP) generated by different alternatives to reuse phosphorus present in municipal biosolids for agricultural purposes in Sweden. Direct land application of biosolids as well as the use of precipitated struvite, and phosphorus from incinerated biosolids were studied and compared to commercial fertilizer triple superphosphate (TSP) in their investigation. The GWP generated per 1 kg of P delivered to farmlands was calculated for each scenario. Linderholm et al. (2012) concluded that direct land application of sewage sludge is the option with the least GWP followed by struvite precipitation. These results could be different in larger countries such as the United States where the distances of travel from treatment plant to farmlands are longer and phosphorus requirements are higher. It is important to note that Linderholm et al. (2012) recognized that the greatest drawback with large-scale struvite precipitation is the large percentage of phosphorus left in the biosolids. The alternatives considered in this study were not compared using eutrophication potential.

Linderholm et al. (2012) only stated that phosphorus emissions from wastewater treatment plants are likely to be larger than emissions from TSP production. They did not investigated the likelihood of TSP leaching higher quantities of phosphorus than struvite when used for agricultural purposes.

Lundin et al. (2004) and Jossa and Remy (2015) compared commercially available technologies (AIRPREX, Pearl, Struvia) with harsher technologies of phosphorus recovery (Stuttgart Process, KREPRO, Bio-con, Gifhorn Process). Lundin et al. (2004) came to the conclusion that the types of phosphorus present in the biosolids can significantly impact the feasibility of a particular recovery technology. For instance, they suggested that the KREPRO technology would be more effective at recovering phosphorus from biosolids generated in EBPR plants as compared to biosolids generated in plants employing chemical phosphorus removal. However, their study examined only the biosolids generated from chemical phosphorus removal methods. Jossa and Remy (2015) compared commercial phosphorus recovery technologies (AIRPREX, Struvia and Pearl Ostara) with acid leaching technologies (Stuttgart Process and Gifhorn Process) using EBPR-B or Chem-P-B as the phosphorus feed. Jossa and Remy (2015) found that the main factor that that affects GWP and eutrophication potential is the type of phosphorus removal employed at the wastewater treatment plant. Scenarios that represented the recovery of phosphorus from biosolids produced at plants employing chemical phosphorus removal had greater GWP and eutrophication potential than scenarios that represented the recovery of phosphorus from biosolids produced at EBPR plants. Jossa and Remy (2015) also concluded that

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wastewater effluents from treatment plants are reduced after phosphorus recovery starts their operation since phosphorus returns from dewatering are lower.

Despite the number of LCIA studies published to date, the previous studies have generally focused on the impacts of recovery phosphorus from biosolids generated at chemical phosphorus removal and EBPR treatment plants. A comprehensive analysis of the global warming and eutrophication impacts of phosphorus recovery that includes municipal biosolids generated from conventional activated sludge WWTP has not been performed. Conventional activated sludge (AS) is the most popular form of secondary treatment in the United States. According to the EPA only 3% of the wastewater discharges in the US are required to meet total phosphorus limits (EPA, 2016). In addition, the effects of nutrient runoff after farmland application of commercial fertilizers, struvite and dewatered biosolids have not yet been included in these previous analyses.

Chapter 3: Phosphorus speciation in thickened and anaerobically digested municipal biosolids

INTRODUCTION

Modern agriculture relies heavily on the manufacture of synthetic fertilizers from phosphorus and nitrogen. The ability to efficiently deliver nitrogen and phosphorus containing fertilizers to crops has allowed the world's population to increase steadily. In 1798 Thomas Malthus published, "Essay on the Principle of Population," in which he raised concerns about the ability for humankind to survive as food production grew arithmetically and human populations grew exponentially. In 1913, Carl Bosch changed these relationships by scaling an industrial process developed by Fritz Haber (Haber-Bosch process) to synthesize ammonia from nitrogen and hydrogen in air (Smil 1997). The ammonia produced by the Haber-Bosch process was used, among other purposes, for the manufacture of synthetic fertilizers (Erisman et al.2008). Since the invention of the Haber-Bosch process, food production has been able to match population growth (Smil 1997, Smil 1999). Estimates suggest that the Haber-Bosch process is responsible for supporting 27% of the world's population over the past century (Erisman et al 2008) as humanity has become dependent on synthetic fertilizers containing nitrogen, phosphorus and potassium (Erisman et al. 2008, Cordell and White 2011).

Phosphorus, as opposed to nitrogen, is not present in air. The current sources of phosphorus for fertilizer production are apatite sedimentary deposits (phosphate rock) (Cordell et al. 2009, Cordell and White 2011). These deposits are the product of thousands

of years of sedimentation and tectonic uplift, which makes phosphate rock a non-renewable resource by definition (Smil 2000). Moreover, some researchers estimate that these deposits are to be exhausted by the end of this century (Smil 2000, Cordell et al. 2009, Cordell and White 2011). These phosphate rock deposits are also geographically concentrated in Western Sahara/ Morocco, China, the US and South Africa. These countries control 45%, 21%, 7%, and 5%, respectively of the world's phosphorus reserves (Fixen 2008, Vaccari 2009). It has been suggested that this geographical concentration of such an important resource may prove to be a serious source of political conflict in the future, especially as countries without direct access to phosphate mines, such as India, increase in population. (Vaccari 2009).

After mining, phosphate rock is processed to produce commercial fertilizers. The production of phosphoric fertilizer involves dissolution of the phosphate rock with sulfuric acid to produce predominantly particulate orthophosphates (Hydroxyapatite, fluoroapatite and chloroapatite) (Wood and Cowie 2004, Fixen 2008, Nieminen 2010). The reaction of sulfuric acid with phosphate rock produces orthophosphoric acid (48% phosphorus as P_2O_5) that can be converted into orthophosphoric fertilizer or it can be heated to produce polyphosphate fertilizer (75% phosphorus as P_2O_5 with 1:1 ratio of orthophosphate to polyphosphate)(Jensen 2007). It has been demonstrated that for farming applications there is no difference between using orthophosphate or polyphosphate fertilizer (Jensen 2007, Rhem 2013). Polyphosphate hydrolyzes and readily forms available orthophosphate by soil enzymatic activity when water is applied (Jensen 2007).

After its manufacture, orthophosphate or polyphosphate-based fertilizers are applied to farmland soils where the phosphorus is absorbed by plants and subsequently makes its way up the food chain until it is consumed and excreted by humans. Some estimates suggest that between 20 to 30% of the total mined phosphorus ends up in municipal sewer systems as a mixture of particulate and dissolved phosphorus (Shimamura et al. 2003, Brunner 2010). The sewage is then conveyed to wastewater treatment plants where the wastewater and solids are treated via sedimentation and biological treatment processes.

Depending on the design of the wastewater treatment plant, from 70 to 99% of the phosphorus in the influent is removed from the liquid phase and concentrated in the biosolids (Barnard 1984, Dueñas et al. 2003). These biosolids are typically processed by anaerobic digestion followed by landfilling, incineration or direct land application of the remaining biosolids. Nearly half of the biosolids produced in the US are wasted by landfilling or incineration (Figure 3) (NEBRA, 2007) with the remainder discharged via direct land application. Biosolids for direct land application are first dewatered and then mixed with topsoil from agricultural fields to replenish lost nutrients. A major disadvantage of using direct land application for phosphorus reuse is the low concentration of nitrogen
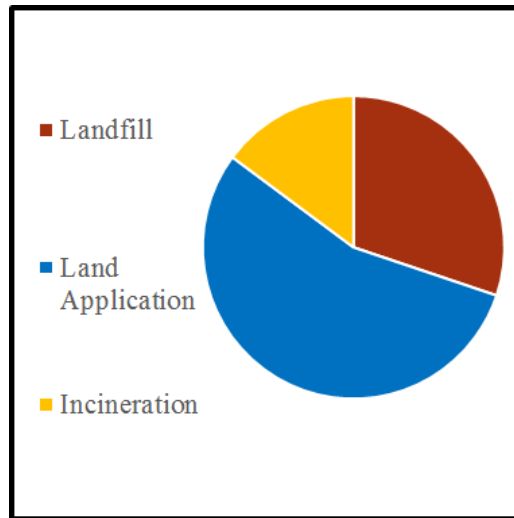
Figure 3. Disposal methods for biosolids produced in the
United States (NEBRA 2007)

relative to the phosphorus concentration (Korboulewsky et al. 1989, Yuan et al. 2012, Shaw et al. 2014). Phosphorus accumulation over time in the soil and treated fields prevents further amendment with wastewater biosolids (Maguire et al. 2000 a & b, Maguire et al. 2001).

To improve phosphorus reuse and reduce the quantities of biosolids that are used directly as soil amendments, many researchers (Shimamura et al. 2003, Berg et al. 2003, de-Bashan and Bashan 2004, Shimamura et al. 2008, Cordell et al. 2009, Mehta and Batstone 2013, Hultman et al. 2014 and others) have promoted the recovery of phosphorus in an inorganic form that can be readily stored and transported. The most common technology implemented to date involves the recovery of dissolved orthophosphate via struvite crystallization (Coats et al. 2011). Struvite crystallization is achieved by precipitating the orthophosphate (PO_4^{3-}) present in the liquid fraction of the biosolids

together with magnesium (Mg^{2+}) and ammonium (NH_4^+) under alkaline conditions (Liu et al. 2013). The struvite precipitant formed is an inorganic crystal with low water solubility that can be used as a slow release fertilizer. This technology has been extensively studied (Battistoni et al. 2001, Doyle and Parsons et al. 2002, Shimamura et al. 2003, Shimamura et al. 2008, Pastor et al. 2010) and commercially developed by Ostara and CNP Inc. among others companies. The major drawback associated with the current technology is that only the dissolved orthophosphate species is targeted for recovery and the phosphorus present in the particulate phase of the biosolids cannot be recovered.

For instance, application of the Ostara Pearl in 2011 to recover phosphorus from dewatering supernatants at the Durham advanced wastewater treatment plant was only minimally successful. 73% of the total phosphorus present in the municipal biosolids tested were not recovered by this process (Cullen et al. 2013). The Ostara Pearl process, which consists of increasing the pH of dewatering supernatants to a value close to 8 and dosing with magnesium to precipitate struvite, is not capable of extracting or dissolving phosphorus from many solids. The Durham plant utilized both biological and chemical phosphorus removal and it is likely that most of the phosphorus remained in the particulate solid phase after dewatering either bound to the chemicals used for phosphorus removal or within bacteria utilized for biological phosphorus removal. The low overall recovery at the Durham plant highlights one of the most significant criteria for evaluating P recovery technologies and is the focus of this research; selection of a P recovery technology should be based on matching the predominant P species in the biosolids of interest with phosphorus recovery technologies that target those phosphate species.

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Determining the particular phosphorus species in the water or solid phases of biosolids is challenging because most rapid and economically-feasible analytical techniques cannot differentiate between all the species potentially present (i.e., ferric phosphates, apatite, aluminum phosphates, pyrophosphates, metaphosphates, ADPs, ATPs etc.). As a result, phosphorus speciation is typically defined operationally by the technique used to extract and analyze the phosphorus. One of the most common and standardized phosphorus speciation techniques (Standard Method 4500-P) separates and quantifies the orthophosphate, polyphosphate and organic phosphate constituents in a sample (APHA, 2012). These three phosphate fractions can be found in the dissolved and particulate phases throughout wastewater treatment plants (Sawyer et al. 2003, Tchobanoglous et al. 2004). This method of phosphorus speciation is utilized by most environmental regulatory agencies, treatment plant operators as well as by researchers investigating phosphorus recovery technologies.

The concentration of each phosphorous species in the biosolids is affected by the presence or absence of a phosphorus removal process (e.g., enhanced biological phosphorus removal or chemically enhanced phosphorus removal) at wastewater treatment plants as well as the particular biosolids process employed (e.g., dissolved air flotation vs gravity thickening). For example, it has been established that anaerobic digestion of biosolids produced exclusively by enhanced biological phosphorus removal increases the dissolved orthophosphate concentration in the biosolids via polyphosphate hydrolysis (Latimer et al. 2012). While transformation of phosphorus species within gravity thickeners

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has not been investigated, gravity thickeners do operate under anaerobic conditions (Marti et al. 2008a, Pastor et al. 2008) that could promote hydrolysis of polyphosphates for EBPR or even conventional activated sludge biosolids (where no targeted phosphorus removal process is included). The vast majority of the studies that have investigated the recovery of phosphorus from wastewater biosolids (Hansen et al. 2000, Kuroda et al. 2002, Liao et el. 2003, Güney et al. 2008, Petzet and Cornel 2009, Marti et al. 2010, Rittmann et al. 2011, Cullen et al. 2013 and many others) have focused on biosolids generated from plants that incorporate either biological (EBPR) or chemical phosphorus removal (Chem-P). Indeed, studies investigating P recovery in biosolids generated in conventional activated sludge (AS) plants is absent from the published literature.

Conventional AS is the most common form of secondary treatment in the United States since only about 3% of wastewater treatment plant discharge permits include phosphorus limits (EPA, 2016). However, there are no published studies identifying the optimal location for phosphorus recovery (i.e., waste activated sludge [WAS], thickened sludge or digested sludge) or the appropriate phosphorus species that should be targeted to achieve maximum recovery. It has been suggested in the literature that the best location in a treatment plant to recover phosphorus via commercial technologies (i.e., AIRPREX, Ostara Pearl) is after anaerobic digestion because polyphosphate accumulated by bacteria hydrolyzes under anaerobic conditions, thereby increasing dissolved orthophosphate concentrations (Petzet and Cornel 2009, Marti et al. 2008, Marti et al. 2010). However, anaerobic digestion experiments with conventional AS biosolids performed by the author

(Fig 4.) showed that the recoverable phosphorus species (dissolved orthophosphate) for struvite precipitation actually decreases after anaerobic digestion.
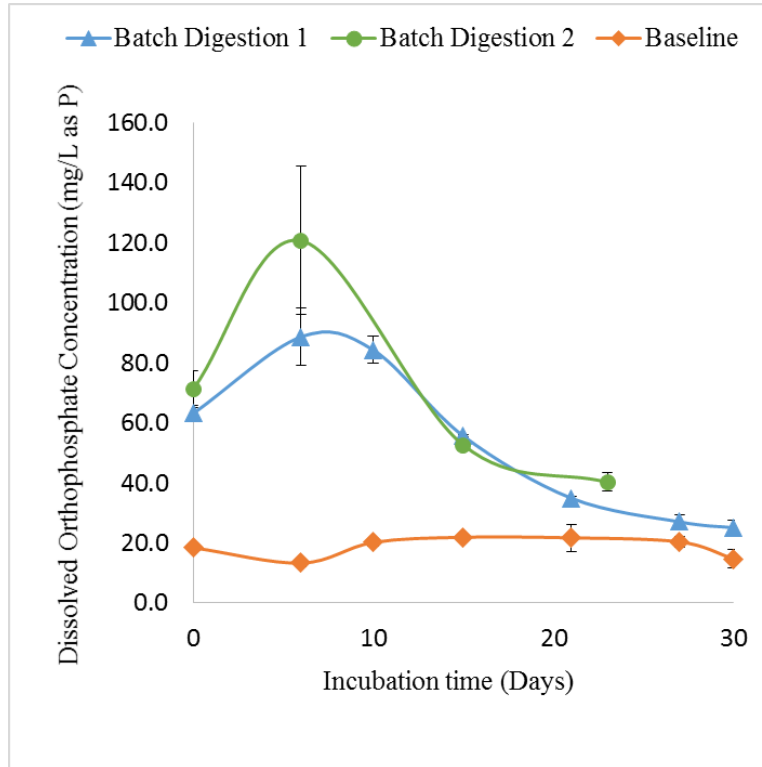
Figure 4.   Dissolved orthophosphate concentrations in conventional activated sludge biosolids undergoing anaerobic digestion in laboratory scale batch reactors. Thickened biosolids were obtained from Hornsby Bend Biosolids Treatment plant, Austin, Tx and incubated under anaerobic conditions at 35 ℃. The baseline sample consisted of anaerobically digested biosolids obtained from the same wastewater treatment plant.

OBJECTIVES

The overall hypothesis driving this research is that the most suitable location for collecting biosolids for P recovery (WAS, thickened sludge or digested sludge) is the one that maximizes the concentration of the target phosphorus species for a particular

phosphorus recovery technology. Assessment of this location for biosolids generated in conventional AS wastewater treatment plants requires an understanding of how the speciation of phosphorus changes within different wastewater treatment processes, particularly those where anaerobic conditions are favored (i.e., gravity thickening and anaerobic digestion). The specific objectives of the current research study are to: (1) determine if the hydrolysis of polyphosphates observed in anaerobic digestion of biosolids generated in EBPR wastewater treatment plants also occurs in biosolids generated in conventional activated sludge plants, and (2) if the hydrolysis of polyphosphates also occurs during gravity/dissolved air flotation thickening of conventional activated sludge. To this end, biosolids from five conventional activated sludge treatment plants in Texas were analyzed to determine the phosphorus speciation before and after anaerobic digestion and thickening. In addition, two treatment plants with EBPR served as a basis for comparison of polyphosphate hydrolysis during thickening and digestion.

MATERIALS AND METHODS

Facilities sampled:

Biosolids and water samples were collected from seven different municipal wastewater/biosolids treatment facilities identified in Table 1. Five of these facilities were conventional activated sludge plants and two utilized EBPR.

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Table 1. Characteristics of the wastewater treatment plants sampled.

Code	Phosphorus Removal	Thickening	Digestion	Digester HRT (days)	Average flow (MGD)[a]
AS1	No Removal	Gravity (Separate)	No	-	54
AS2	No Removal	DAF (Separate)	Anaerobic	23	100
AS3	No Removal	Gravity (Separate)	No	-	5.8
AS4	No Removal	Gravity (Comingled)	Anaerobic	45	1.25
AS5	No Removal	Belt (Comingled)	Anaerobic	48	16
EBPR1	Biological Removal	Rotary Press (Comingled)	Anaerobic	-	37
EBPR2	Biological Removal	Rotary Press (Comingled)	No	-	1.5

[a] MGD: Million gallons per day

The first four conventional activated sludge treatment plants (AS-1 to AS-4) employed configurations shown in Figure 5(a-d). The waste activated sludge (WAS) or comingled biosolids (primary biosolids + WAS) were thickened by gravity (AS1-Fig5a, AS3-Fig5c and AS4-Fig5d) or via DAF (AS2-Fig 5b). Two of these facilities (AS2-Fig 5b and AS4-Fig5d) anaerobically digested their thickened biosolids. AS5 (Fig 5e) is a biosolids processing facility. It receives conventional AS biosolids from AS1 and another wastewater treatment plant that employs the same treatment processes as AS1. The influents are mixed, thickened by belt filter press, anaerobically digested and dewatered.

EBPR1 (Fig 6a) is a treatment plant that utilizes an anaerobic and anoxic process prior to the aerobic activated sludge tank for the removal of nitrogen and phosphorus (A2O process). Both primary and WAS biosolids are mixed, dewatered and anaerobically

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digested. EBPR 2 (Fig 6b) is a 1.5 million gallon per day plant that operates an A2O process for removal of nitrogen and phosphorus. EBPR2 only produces WAS biosolids that are thickened and stored in a steel container before disposal. The treatment plant operators estimate that the biosolids are stored for 1 day on average before they are discarded.
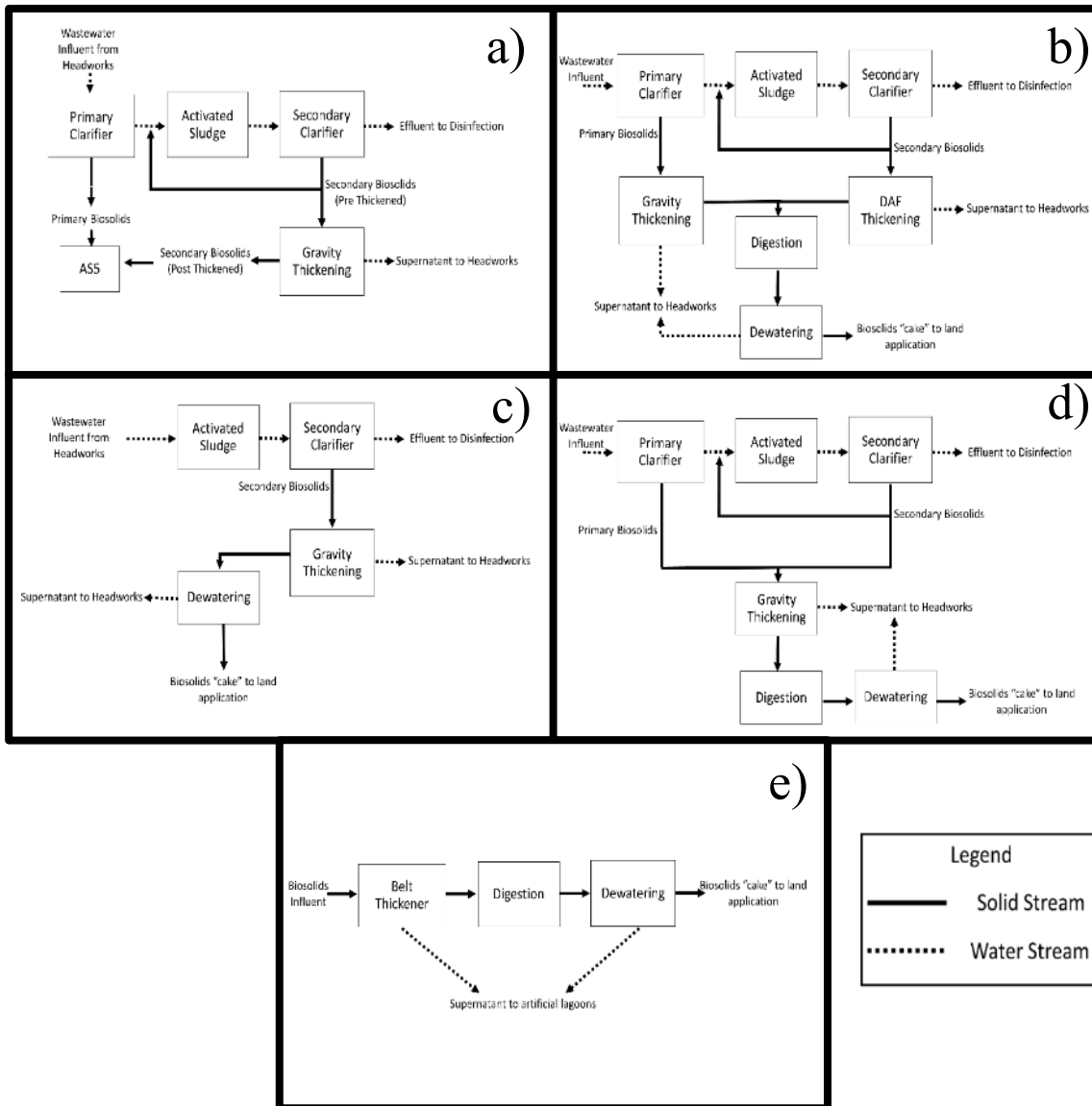
Figure 5. Flow diagrams for the conventional activated sludge wastewater treatment plants sampled. a) AS1, b)AS2, c)AS3, d)AS4 and e)AS5
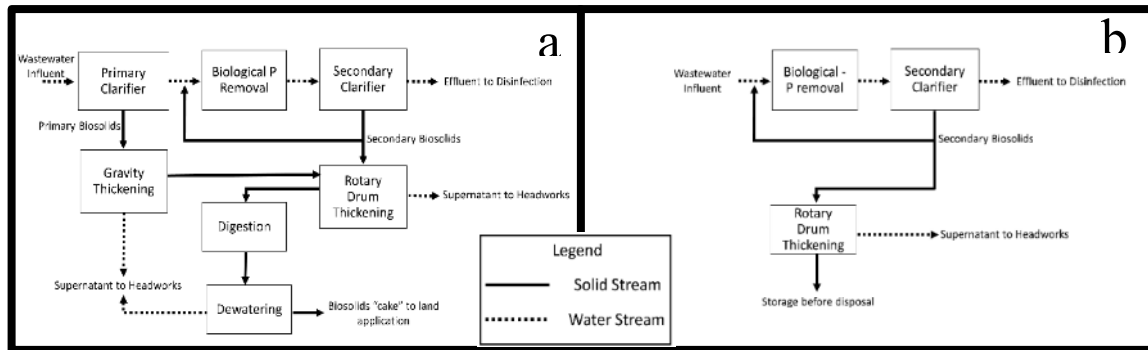
Figure 6. Flow diagram of the wastewater treatment plants with enhanced biological phosphorus removal. a) EBPR1 and b) EBPR2

Since biosolids produced at EBPR wastewater treatment plants are known to undergo polyphosphate hydrolysis during anaerobic digestion, changes in speciation after thickening and anaerobic digestion of conventional activated sludge biosolids will be compared to changes occurring in an EPBR biosolids. Consequently, it will be possible to assess the likelihood that polyphosphate hydrolysis also occurs for conventional AS plants.

Sampling regime:

Wastewater and biosolid samples were obtained from the influent and effluents of each of the processes shown in Figures 5 and 6. The samples were collected in 250 mL acid washed HDPE bottles on three different days. Whenever the samples were collected with a "dipping cup", the cup was rinsed three times with the stream of interest. If the

sample was taken from a pump, the sampling pipe line was flushed before collecting the sample.

AS1 and AS5 were sampled in the months of February, April and May of 2015 (average maximum ambient temperature of 79º F and average minimum temperature of 59 ºF) and AS2, AS3, AS4, EBPR1, EBPR2, were collected in the months of October, November and December of 2015 (76 ºF Average max ambient temperature and 55 ºF Average min average temperature). The samples were immediately refrigerated after collection.

Phosphorus Analysis:

Before analysis, a small fraction of each sample was filtered through 0.45 micron filter paper (reinforced cellulose Millipore RW03, Millipore Corp., Billerica, MA). The original sample was used to measure the total concentrations of each species and the filtrate was used to measure the dissolved concentrations of each species. The particulate fraction was calculated from the difference between the total and the dissolved fractions.

Dissolved orthophosphates were measured by the ascorbic acid method (Standard Methods 4500-P 2012). Total orthophosphates (dissolved + particulate) were measured using the same method, but the particulate orthophosphates were dissolved by acidifying the sample to pH 2 prior to analysis. Experiments by Güney et al. (2008), Zoppoth (1999), Hansen et al. 2000, Antakyali et al. 2013 reported that at pH 2, 98% to 99% of the total orthophosphate in municipal biosolids dissolves. Tests in our laboratory using a synthetic solution simulating concentrations of phosphorus, carbonate, iron, magnesium, ammonia

and calcium similar to those in the municipal biosolids at the local wastewater treatment plant confirmed the dissolution of all the particulate orthophosphate into dissolved orthophosphate at pH 2 (Table 2). Three 10 mL aliquots from the synthetic solution were centrifuged and the supernatant analyzed for dissolved orthophosphate. Subsequently, three more aliquots from the synthetic solution were acidified from pH 7 to pH 2 with 11N H_2SO_4. After acidification the aliquots were centrifuged and the supernatant was analyzed for dissolved orthophosphate.

Table 2. Results from orthophosphate dissolution of a synthetic wastewater solution.

Sample	P Concentration in centrifuge supernatant (mmol/L)	Standard Deviation	% Recovery
Raw Sample Orthophosphate	0.01	0.005	0.04%
Acidified Sample Orthophosphate	27.1	0.3	100%
Theoretical Orthophosphate	27.0	-	-

When the treatment plant of interest was located further than 30 miles from the authors' laboratory at the University of Texas campus (plants AS2, AS3, AS4, EBPR1 and EBPR2), total and dissolved orthophosphate were measured using the Hach PO-19 orthophosphate test kit and a portable spectrometer. Reagents used in the Hach test kit are chemically identical to those used in the laboratory (Hach, 2015) but a separate calibration curve was obtained for the portable spectrophotometer.

In order to measure organic and polyphosphates, the acid hydrolyzable phosphates (polyphosphates + orthophosphates) and total phosphorus (organic phosphates + polyphosphates + orthophosphates) were determined. Acid hydrolyzable phosphates were converted into orthophosphates by adding 11 M H_2SO_4 to a sample and heating to 120 ℃ for 30 minutes (Standard Methods 4500-P 2012). Total phosphorus was determined by converting all phosphorus into orthophosphates by adding potassium persulfate and 11 M H_2SO_4 to a sample and heating to 120 ℃ for 30 minutes (Standard Methods 4500-P 2012). After the samples were cooled at room temperature, they were neutralized with NaOH and measured for orthophosphates by the ascorbic acid method (Standard Methods 4500-P 2012).

The method detection limits (MDL) were 0.05, 0.05 and 0.06 mg/L as P for the orthophosphate, acid-hydrolyzable phosphorus and total phosphorus methods respectively obtained from measuring 7 replicates of a phosphate standard (0.2 mg/L) (USGS, 2016). A standard sample and a blank sample were run with each sample measurement.

Due to the time involved in processing (filtering, acidification, neutralization, and analysis) and measurement of each species of phosphorus, a single measurement was performed for each sample. However, for quality control purposes, triplicate extractions and analyses as well as spiked recoveries were conducted for selected samples. The relative standard deviation (RSD) obtained from triplicate orthophosphate analyses for each extraction method is reported in Table 3. Also, the average spiked recovery for each extraction method is reported in Table 3.

Table 3. Relative standard deviation obtained from triplicate measurements and results from spiked recovery tests.

Measurement	RSD (%)	Spiked Recovery (%)
Dissolved Orthophosphate	3	102 ± 7
Total Orthophosphate	5	100 ± 9
Total Acid Hydrolyzable	5	98 ± 6
Total Phosphorus	4	93 ± 11

Cations:

The dissolved concentrations of calcium, magnesium and potassium were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian 710-ES, USA) as described by EPA method 6010B (EPA, 1996). Samples were first filtered through a 0.45 micron filter paper. MDLs for calcium, magnesium and potassium were 0.005, 0.005 and 0.1 mg/L respectively. These MDLs were determined from measuring 7 replicates of a calcium magnesium and potassium standard solution (0.01, 0.01 and 0.5 mg/L respectively)(USGS, 2016).

pH, total and volatile solids analysis

The pH for each sample was measured with a Cole-Parmer double junction electrode and an Orion920A pH meter. The meter was calibrated before each use with three buffers (pH 4.0, 7.0 and 10.0). When the sampling site was located more than 30 miles away from the laboratory at The University of Texas campus, the pH was measured on site.

Total and volatile solids were measured gravimetrically using an adapted form of Standard Methods 2540 B and 2540 E (Standard Methods, 2012).

Statistical Analysis

The average concentration and standard deviations of each phosphorus species measured over three days before and after anaerobic digestion and thickening were computed. These average concentrations were compared using the one-sided Student's t-test with a significance level of $\alpha = 0.05$ (Helsel and Hirsh 1994). A null-hypothesis is considered to be rejected if the p-value is lower than or equal to the significance level (0.05).

The Student's t-test can only be used if the sampled data is normally distributed. To assume normality for our data, historical total phosphorus data from The City of Austin (Appendix A) as well as published data in Takiguchi et al. (2003) were tested using the D'agostino-Pearson normality test. The results showed the total phosphorus concentrations in both wastewater influents (City of Austin) and EBPR waste activated sludge (Takiguchi et al. 2003) are normally distributed. Thus, it is reasonable to assume normality for our collected data.

The data collected in the current study exhibited the same level of variability observed in other published studies based on comparisons of relative standard deviations (Lawler and Singer 1984, Takiguchi et al. 2003, Dueñas et al. 2003, and Danesh et al. 2008). This comparison was done to ensure that the variability observed in the phosphorous data in this study is in line with the variability observed in previously published studies conducted over extended periods of time (2 weeks to a 1 year). The relative standard

deviations (RSD) of the measured phosphorus (orthophosphate, polyphosphate and organic phosphorus) data in this study ranged from 10% to 57% and the RSDs for data published in the literature ranged from 11% to 82% (see Table 26, Appendix A).

RESULTS & DISCUSSION

The results from this research focus on characterizing the speciation of phosphorus in the four anaerobic digestion systems sampled and the six thickeners. The data were used to test hypotheses addressing differences between pre- and post- digested and thickened biosolids. The null hypothesis in each case was that the means were equal (i.e., there was no difference between pre- and post- samples in a particular phosphorus biosolids fraction).

Anaerobic Digestion:

Many researchers have reported increases in dissolved orthophosphate in EBPR biosolids after anaerobic digestion (Takiguchi et al. 2003, Marti et al. 2008, Mehta and Batstone 2013). The increase in dissolved orthophosphate is attributed to polyphosphate hydrolysis by phosphate accumulating bacteria (*Accumulibacter* and *Acinetobacter*) in the biosolids (Hrenovic et al. 2009, Yuan et al. 2012, Kodera et al. 2013). Figure 7 provides a comparison of dissolved (Figure 7a) and particulate (Figure 7b) orthophosphate levels in samples from EBPR1 and each of the conventional treatment plant anaerobic digestion systems normalized by the grams of dry solids fed to their corresponding digester. As expected, there was a significant increase ($p < 0.01$ from Table 3) in both dissolved and particulate orthophosphate for EPBR1 following digestion. In addition, there was a decrease in both

the polyphosphate concentration (p = 0.03) and in the organic phosphorus after anaerobic

digestion (p = 0.03).
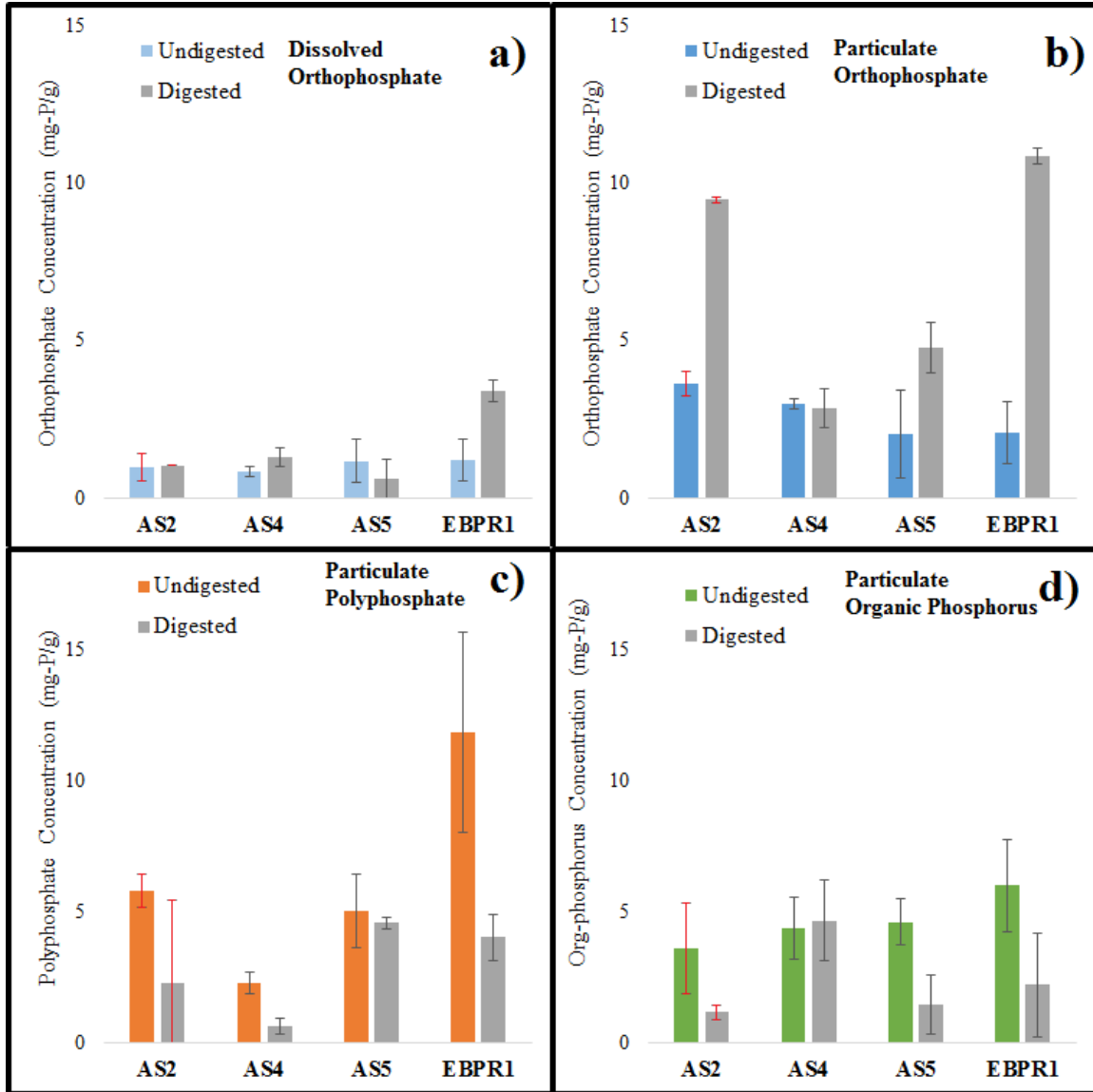
Figure 7.   Phosphorus speciation before and after anaerobic digestion at the different treatment plants sampled. a) Dissolved orthophosphate, b) particulate orthophosphate, c) polyphosphate and d) organic phosphorus. Concentrations expressed as mg P per g dry solids fed to anaerobic digester. The red error bars represent a range and the black error bars represent standard deviations.

Table 3. Student's t-test for the comparison of phosphorus concentrations before and after anaerobic digestion.

	Dissolved Orthophosphate ^		Particulate Orthophosphate ^		Polyphosphate ^^		Organic Phosphorus ^^	
	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?
AS4	**0.05**	**Yes**	0.38	No	**<0.01**	**Yes**	0.41	No
AS5	0.17	No	**0.03**	**Yes**	0.31	No	**0.01**	**Yes**
EBPR1	**<0.01**	**Yes**	**<0.01**	**Yes**	**0.03**	**Yes**	**0.03**	**Yes**

AS2 t-test was not computed due to the small sample size. ^ The hypothesis tested in these cases was that concentrations increase after digestion. ^^ The hypothesis tested in these cases was that concentrations decrease after digestion.

Conventional AS biosolids are also likely to contain phosphate accumulating bacteria, but at lower concentrations. Thus, the hydrolysis of polyphosphates may occur, but if so, to a lower extent, and the dissolved concentrations of orthophosphate should remain the same or increase slightly after digestion. Indeed, the concentration of polyphosphate prior to digestion and dissolved orthophosphate concentration after digestion in EPBR1 are significantly higher than the corresponding concentrations from the conventional AS systems. Comparison of the pre- and post- digestion orthophosphate concentrations showed varying trends among the three conventional AS plants. Only in plant AS4 was there a significant increase in the average dissolved orthophosphate concentration (Fig 7a) following anaerobic digestion (p=0.05). In contrast, increases in particulate orthophosphate pre- and post-digestion were observed for all digesters except for AS4. Thus, it is possible that higher quantities of phosphorus could be recovered by targeting total orthophosphates.

Since dissolved orthophosphate concentrations remain relatively constant before and after digestion, an increase in particulate orthophosphate could result from hydrolysis of polyphosphate or from degradation of organic phosphorus into dissolved orthophosphate and subsequent precipitation to a particulate orthophosphate phase. Figure 7c shows a decrease in polyphosphate concentrations after anaerobic digestion at plants AS4 (p=0.01). However, for AS2 and AS5 the polyphosphate concentrations remain statistically the same. Organic phosphorus concentrations on the other hand, showed a significant decrease for AS2 and AS5. This suggests that for AS2 and AS5 the increase in orthophosphate concentration is due to organic phosphorus degradation, and for AS4 the increase is due to polyphosphate hydrolysis.

In order to further confirm that polyphosphate hydrolysis indeed occurs in AS4, the concentration of dissolved potassium before and after digestion was examined (Figure 8). Potassium is a counter-ion for polyphosphate hydrolysis. This means that potassium is released from phosphorus accumulating bacteria to the solution together with orthophosphate during polyphosphate hydrolysis (Jardin and Popel 1994, Marti et al. 2008b, Pastor et al. 2008). Figure 8 shows that for anaerobic digestion where polyphosphate hydrolysis was statistically confirmed (AS4 and EBPR2) the dissolved potassium concentration increases the most after anaerobic digestion which is an indication of polyphosphate hydrolysis. For AS2 and AS5 the potassium concentration only increases slightly which suggests that some polyphosphate hydrolysis occurs, but the levels are not enough to be statistically confirmed.

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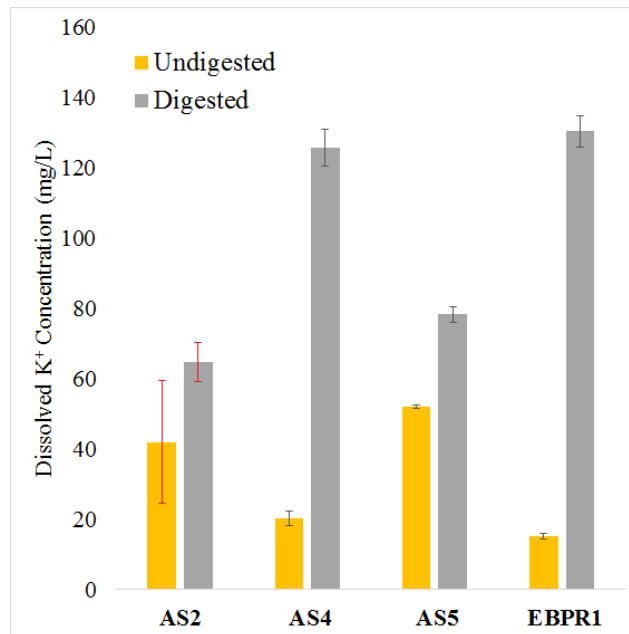
Figure 8. Dissolved potassium concentrations before and after anaerobic digestion. Red error bars represent ranges and not standard deviations.

The literature addressing phosphorus recovery technologies typically focus on recovery of dissolved orthophosphate after anaerobic digestion (Shimamura et al. 2003, Shimamura et al. 2008, Rittmann et al. 2011, Sartorius et al. 2012, Mehta and Batstone 2013). However, these results suggest that there is no benefit in performing anaerobic digestion for the recovery of dissolved phosphorus because most of the orthophosphate is in the particulate fraction after digestion. These results also suggest that in order to recover greater quantities of phosphorus from anaerobically digested conventional AS biosolids, the use of a technology that targets particulate orthophosphate is most appropriate.

Thickening:

Experiments by Marti et al. (2008) showed that during gravity thickening of EBPR biosolids, there is an increase in dissolved orthophosphate due to polyphosphate hydrolysis. It was hypothesized that the anaerobic conditions that occur during gravity thickening will promote the same hydrolysis in AS biosolids. In addition, due to the lower pH (Table 4) in gravity thickeners than in anaerobic digesters, it was hypothesized that the phosphorus would not form particulate orthophosphates and would remain dissolved. To investigate these hypotheses, the speciation of phosphorus before and after gravity thickening was determined and compared to the phosphorus speciation in EBPR biosolids and AS biosolids thickened by dissolved-air flotation (DAF) and belt presses. DAF thickeners utilize high pressure air bubbles to remove particles for suspension (Turovskiy and Mathai 2006) and in doing so maintain aerobic conditions. Thus, no hydrolysis of polyphosphates is expected in these thickeners. Belt thickeners have a solids loading rate (SLR) between 700 and 1100 kg of dry solids/m^2-h whereas DAF and gravity thickeners have a SLR between 2-200 kg of dry solids/m^2-h (Turovskiy and Mathai 2006). Having a higher SLR means belt thickening is a faster process and the biosolids have less opportunity to become anaerobic and release phosphorus. Thus, hydrolysis is not expected to occur in the belt thickener. The storage tank in the EBPR2 wastewater treatment plant was used as a proxy for gravity thickening, since it is estimated that sludge remains inside the steel tank for about a day. These conditions are suitable to develop anaerobic conditions and hydrolysis is expected to occur.

Table 4. Summary of pH measurements pre- and post- anaerobic digestion and gravity thickening.

Plant	pH		
	Pre-Thickening	Post-Thickening	Digested
AS1	6.71 ± 0.17	6.47 ± 0.14	-
AS2	6.75 ± 0.04	6.54 ± 0.05	7.23 ± 0.03
AS3	6.87 ± 0.07	6.29 ± 0.27	-
AS4	6.77 ± 0.11	6.35 ± 0.21	6.74 ± 0.01
AS5	5.9 ± 0.1	6.0 ± 0.5	7.79 ± 0.06

Red values represent ranges and not standard deviations

Figure 9a summarizes the dissolved orthophosphate concentrations pre- and post-thickening at each of the five conventional AS treatment plants investigated in this study normalized by gram of dry solids. The EBPR2 WAS biosolids stored in the steel tank, released significant quantities of dissolved orthophosphate as expected (p =0.04). In addition, a decrease in polyphosphates was observed for EBPR2, however, the standard deviations pre- and post- storage prevented statistical confirmation of the results (p=0.1) (Table 5). In contrast, the hydrolysis would not be expected across the DAF thickener as it should be an aerobic system. No apparent difference in polyphosphate concentrations was observed; however, it appears that orthophosphate increase while organic phosphorus may have decreased. This is consistent with potential biochemical oxidation of the organic matter within the biosolids. Experiments by Butler et al. (1997) showed a significant reduction of COD and BOD across DAF thickeners. There were only two samples to this system and results cannot be statistically validated.
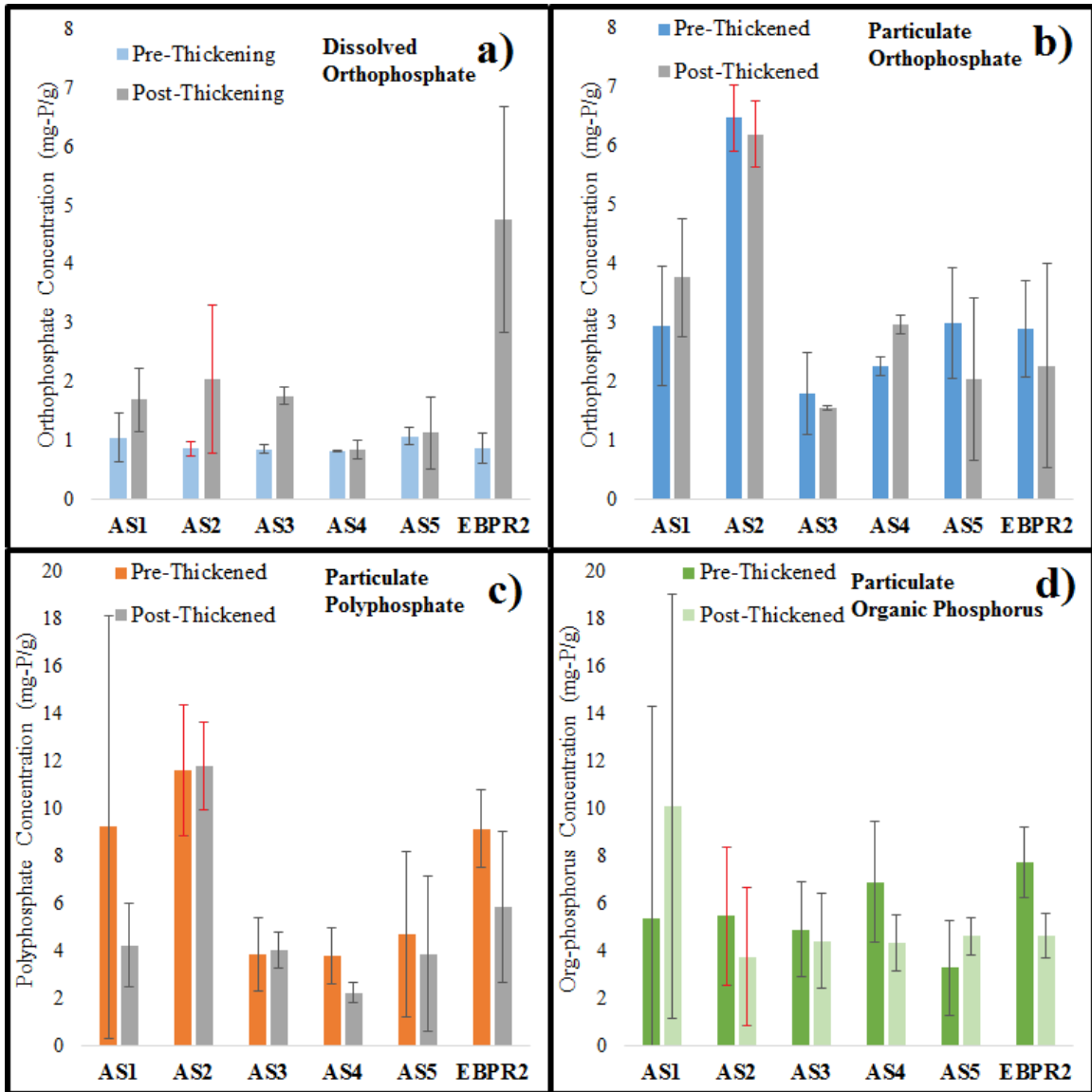
Figure 9. Phosphorus speciation pre- and post- thickening of the biosolids collected from five conventional AS wastewater treatment plants and one EBPR wastewater treatment: a) Dissolved orthophosphate, b) particulate orthophosphate, c) total polyphosphate and d) total organic phosphates. Concentrations expressed as mg P per g dry solids. Red error bars are range, the rest are standard deviations.

Table 5. Student's t-test for the comparison of phosphorus concentrations before and after thickening.

	Orthophosphate ^		Particulate Ortho Phosphorus ^		Particulate Polyphosphate ^^		Particulate Organic Phosphorus ^^	
	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?	p value	Reject null-hypothesis with 0.05 significance level?
AS1	0.09	No	0.15	No	0.22	No	0.23	No
AS3	**<0.01**	**Yes**	0.29	No	0.44	No	0.39	No
AS4	0.4	No	**0.01**	**Yes**	0.07	No	0.11	No
AS5	0.45	No	0.20	No	0.39	No	0.19	No
EBPR2	**0.04**	**Yes**	0.31	No	0.10	No	**0.02**	**Yes**

AS2 t-test was not computed due to the small sample size. ^ The hypothesis tested in these cases was that concentrations increase after thickening. ^^ The hypothesis tested in these cases was that concentrations decrease after thickening.

Gravity thickeners that only treat WAS (AS1 and AS3) yielded increased dissolved orthophosphate concentrations (Figure 9a). However, the statistical tests were only able to confirm this result for AS3 ($p<0.01$). For the AS4 gravity thickener, the concentration of dissolved orthophosphate remains the same after thickening (Figure 9a).

The particulate orthophosphate concentrations (Figure 9b) are the same before and after thickening for all treatment plants except for AS4 where it increases significantly ($p=0.01$). At AS4, both primary and secondary sludge are mixed before gravity thickening. Experiments by Pastor et al. (2008) suggest that the volatile fatty acids (VFA) of primary sludge promotes faster hydrolysis of polyphosphates, and also faster precipitation of orthophosphate. Primary biosolids contain higher concentrations of dissolved calcium than secondary biosolids (Figure S3 – Appendix B) which promotes precipitation of the released

orthophosphate. Effectively, in Figure 9c it appears that for AS4 there is a decrease in polyphosphate similar to the decrease in EBPR2. This further suggests hydrolysis of polyphosphates in gravity thickener AS4. However, these results were not supported by the statistical tests (p=0.07). In thickener AS1, there is also a decrease in average polyphosphate concentration but the standard deviation before thickening is too large to draw an accurate conclusion. To further examine the possible link between anaerobic conditions and differences in phosphorus speciation in thickeners it is necessary to consider variations in hydraulic residence times (HRTs) (Table 6).

Table 6. Hydraulic residence time for the gravity thickeners sampled.

	HRT (days)
AS1	1
AS2	0.6
AS3	0.3
AS4	0.9
AS5	Minutes
EBRP2	1 *

*Estimate by operators

AS4 and AS1 have the longest HRT. Thus, we can hypothesize that the longer HRTs in gravity thickeners of conventional activated sludge biosolids can decrease polyphosphate concentrations due to anaerobic conditions discussed previously.

Finally, the organic phosphorus remains the same after gravity thickening (Figure 9d). There is an observable decrease in organic phosphorus for AS2, AS4, and EBPR2; and, only in EBPR2 was there a statistical reduction (p=0.02) after thickening. This would indicate some degradation of the organic matter inside the steel storage tank. As expected,

for the belt thickener at AS5 there were no significant increases or decrease on any of the phosphorus species.

These results however, do not mean that pre-thickened biosolids are as suitable for recovery of phosphorus via technologies that target dissolved orthophosphate as post-thickened biosolids. It is important to consider the concentration of phosphorus per liter of solution shown in Figure 10. Commercial recovery technologies require a minimum concentration of 10 mg/L as P to operate and a threshold for economic feasibility between 20 and 30 mg/L as P (OSTARA 2009, Nieminen 2010). Without thickening, only AS5 biosolids would be over the 10 mg/L concentration suitable for phosphorus recovery and all of the pre-thickened biosolids would be under the 20 mg/L feasibility threshold. After thickening, all of the biosolids are over the 10 mg/L limit and only AS4 is under the feasibility threshold. Thickeners, are thus effective at removing water from the biosolids and therefore increasing the dissolved orthophosphate concentration on a per liter basis. '
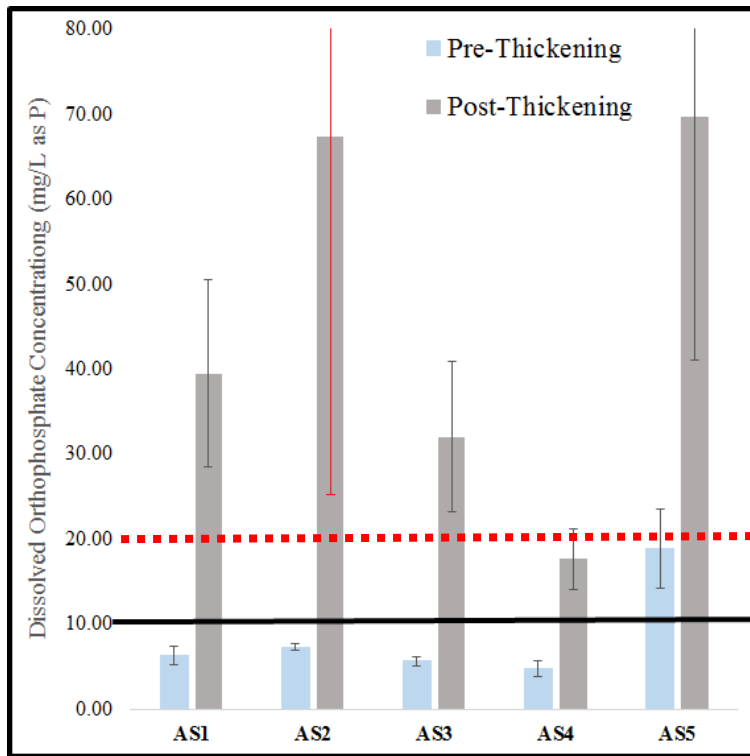
Figure 10. Dissolved orthophosphate concentrations before and after thickening in mg/L as P. Red error bar is a range, the rest are standard deviations.

CONCLUSIONS

After sampling five wastewater treatment plants with varied characteristics and operations, it is possible to state the following conclusions regarding the effect of anaerobic digestion and thickening on phosphorus speciation.

- Anaerobic digestion is not as effective at increasing the dissolved orthophosphate concentrations of conventional AS biosolids compared to EBPR biosolids. Recovery technologies that target dissolved orthophosphate would work as well on undigested as digested AS biosolids.

- Particulate orthophosphate concentrations do increase in AS biosolids after anaerobic digestion just as they do for EBPR biosolids. Technologies that target total orthophosphate for recovery would be more appropriate for conventional AS treatment plants than those that target dissolved orthophosphate.

- Polyphosphate hydrolysis was observed only in one of the conventional activated sludge digesters sampled (AS4). Dissolved potassium, however, would indicate some polyphosphate hydrolysis occurred in all conventional activated sludge digesters although to a lesser extent for AS2 and AS5 than for AS4.

- Gravity thickeners that only treat WAS increase the dissolved orthophosphate concentrations slightly. The gravity thickener that treats comingled primary and secondary sludge (AS4) appears to promote faster polyphosphate hydrolysis and precipitation of orthophosphate.

- Statistically there should not be any difference in the dissolved orthophosphate concentration between pre-thickened and post-thickened conventional activated sludge biosolids. However, thickening is necessary to achieve a per liter basis concentration for precipitation to occur and for economic feasibility of technologies that target dissolved orthophosphate for recovery.

Chapter 4: Using phosphorus speciation in municipal biosolids to select a phosphorus recovery technology

INTRODUCTION

Sedimentary apatite rock, known as phosphate rock, is the main source of phosphorus supplying the world's fertilizer industry. Phosphate rocks are obtained from massive deposits formed by thousands of years of oceanic sedimentation and tectonic uplift (Smil 2000). This makes phosphate rock a non-renewable resource by definition (Smil 2000). Recent estimates suggest that these deposits will be exhausted by the end of the century (Smil 2000, Cordell et al. 2009, Cordell and White 2011). Moreover, the geographic concentration of these deposits (78% of the deposits are located in just 4 countries) indicates that phosphorus may become limiting in some regions of the world and a significant political issue in the near future. Therefore, it is important to investigate and develop renewable sources of phosphorus.

Wastewater treatment plant biosolids are a promising source for phosphorus recovery because they contain high concentrations of phosphorus. After mining, phosphate rock is incorporated into commercial fertilizers that are spread onto farmlands. The phosphorus in the crops moves up the food chain, is consumed by humans and ultimately excreted into our sewer systems. It is estimated that between 20-30% of the phosphorus mined annually ends up in sewage (Shimamura et al. 2003, Brunner 2010). Sewage is then conveyed into wastewater treatment plants where between 70 -99% of the phosphorus is removed and incorporated into the biosolids (Barnard 1984, Dueñas et al. 2003). These

estimates suggest that if 100% of the phosphorus in the biosolids could be recovered, then between 14% - 30% of the total phosphorus mined annually could be reused. These percentages correspond to approximately 2.1 to 4.5 million metric tons of phosphorus reused a year (Cordell et al. 2009).

Unfortunately, current technologies for phosphorus recovery are far from achieving 100% efficient recovery or reuse. In the US, slightly less than 50% of the phosphorus contained within in biosolids is wasted to landfills or as incineration ash (NEBRA 2007). The remaining 50% is reused through land application as shown in Figure 11. In direct land application, biosolids are dewatered, transported to agricultural lands and mixed with topsoil to replenish lost nutrients.
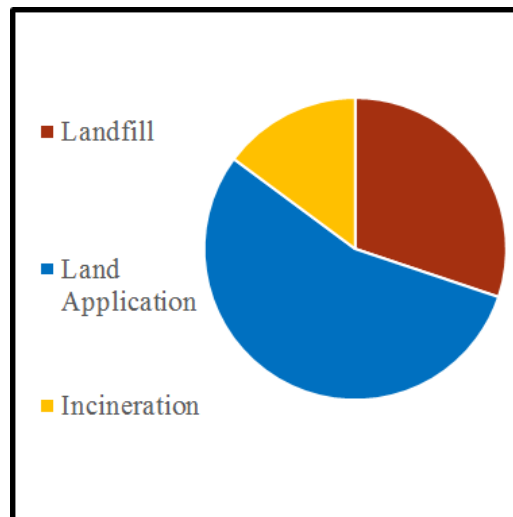
Figure 11. Disposal methods for biosolids produced in the
US. (NEBRA 2007)

A major disadvantage of direct farmland application of biosolids is the low nitrogen to phosphorus ratio present in the biosolids (Korboulewsky et al. 1989, Yuan et al. 2012,

Shaw et al. 2014). The ideal $N:P_2O_5$ (mass basis) ratio for plant growth should be between 3 and 5, but biosolids have a $N:P_2O_5$ closer to 1 or less (Maguire et al. 2001, Elliot et al. 2002, Chinault and O'Connor 2008, Yuan et al. 2012). The application of excessive phosphorus in biosolids can lead to an over accumulation of phosphorus in the soil. Some states limit the amount of phosphorus that can be present in the soil. In such cases, direct land application can become unsustainable for some sites (Maguire et al. 2001). Another shortcoming of direct land application is the bulkiness of the material which creates logistical issues for transporting dewatered biosolids from cities to farmlands.

Many researchers (Shimamura et al. 2003, Berg et al. 2003, de-Bashan and Bashan 2004, Shimamura et al. 2008, Cordell et al. 2009, Mehta and Batstone 2013, Hultman et al. 2014 and others) have investigated the use of biosolids for inorganic precipitation of struvite, calcium phosphates or ferric phosphates. The only commercially available process for inorganic recovery of phosphorus to date is struvite crystallization from dewatering supernatants or post-digestion bulk biosolids (Coats et al. 2011, Sartorius et al. 2012).

Struvite crystallization consists of precipitating orthophosphate (PO_4^{3-}) present in the liquid portion of the biosolids together with magnesium (Mg^{2+}) and ammonium (NH_4^+) under alkaline conditions (Liu et al. 2013). The struvite precipitate is recommended for use whenever a slow-release fertilizer is required (Table 7). This technology has been studied extensively (Battistoni et al. 2001, Doyle and Parsons et al. 2002, Shimamura et al. 2003, Shimamura et al. 2008, Pastor et al. 2010), but its major drawback is that only the dissolved orthophosphate species can be recovered from the waste stream. The phosphorus present in the particulate phase of the biosolids cannot be recovered. Cullen et al. 2013 reported

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that over 73% of the total phosphorus in the biosolids cannot be recovered using struvite precipitation technology.

Table 7. Solubility and $N:P_2O_5$ ratio of struvite, ferric phosphate and triple superphosphate (a commercial fertilizer).

	Water Soluble (% of TP)	Citrate soluble (% of TP)	Mass Ratio $N:P_2O_5$	Reference
Struvite	0.23	45	0.1 – 0.2	Cabeza et al. 2011, Li and Zhao et al. 2003
Ferric Phosphate	0	100	0 : 1	ECCO 2001, Odegaard et al. 2002
Triple Superphosphate	18	100	0 : 1	Cabeza et al. 2011 O'Connor et al. 2004

To overcome the limitations associated with struvite recovery, investigators are developing technologies to recover other phosphorus species present in the biosolids. Phosphorus species are typically defined in these applications by the technique used to extract and analyze the phosphorus. One of the most common and standardized phosphorus speciation techniques (Standard Method 4500-P) separates and quantifies the orthophosphate, polyphosphate and organic phosphates constituents in a solid or liquid phase sample (APHA, 2012). These three phosphate fractions are found in the dissolved and particulate phases throughout wastewater treatment plants (Sawyer et al. 2003, Tchobanoglous et al. 2004). In addition, this method of phosphorus speciation is utilized

by most environmental regulatory agencies, treatment plant operators as well as by researchers investigating phosphorus recovery technologies for biosolid streams.

Technologies such as the Stuttgart Process target total orthophosphate species by decreasing the pH in the sludge with sulfuric acid, prior to dewatering. At pH 2, virtually all the particulate orthophosphate is dissolved into the liquid phase (Güney et al. 2008, Antakyali et al. 2013). The supernatants from the dewatering process are pumped into a stirred tank where citric acid is added to prevent iron and aluminum phosphate precipitation. The pH is then increased to 8.5 with magnesium hydroxide and sodium hydroxide in order to precipitate struvite. (Antakyali et al. 2013). Long term laboratory experiments indicate that 60% of the total phosphorus in the biosolids could be recovered as struvite through the Stuttgart Process (Antakyali et al. 2013,). Despite successful trials, there is only one published report that describes a full scale implementation of the Stuttgart process (Jossa and Remy 2015).

Another potential phosphorus recovery technology is the KREPRO process developed in Sweden. This technology targets total polyphosphate as well as total orthophosphate (acid hydrolyzable phosphorus). The technology consists of acidification of biosolids to pH 2 followed by heating to over 100 ºC inside a pressurized vessel for 30 minutes. The particulate polyphosphate and particulate orthophosphate are dissolved into the liquid phase of the biosolids to form dissolved orthophosphate. The sludge is then dewatered and the supernatant moved into a stirred tank where iron is added for precipitation. The pH is increased to 3 to allow ferric phosphate precipitation while preventing precipitation of calcium or magnesium phosphates. Investigators have reported

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that between 60 to 75% of the total phosphorus present in the biosolids can be recovered with this technology (Hultman 1999, Karlsson 2001).

The phosphorus recovery results presented in the published literature usually report percentages of dissolved phosphorus recovered and in some cases percentages of total phosphorus recovered (see Table 8). The percent recovery values shown in Table 8 are likely to vary from plant to plant depending on whether a wastewater treatment plant incorporates chemical phosphorus recovery (e.g., ferric chloride addition) or enhanced biological phosphorus recovery. The efficacy of the phosphorus recovery technologies described above (e.g., AIRPREX, Stuttgart process and KREPRO) for conventional activated sludge biosolids has not been evaluated.

Table 8. Phosphorus recovery estimates reported in the published literature for the AIRPREX, Stuttgart and KREPRO technologies.

P recovery Technology	Recovery from biosolids (%)	Type of P removal at WWTP	Reference
AIRPREX	86 - 98 % DOP	EBPR	Stumpf et al. 2009, Nieminen 2010
Stuttgart Process	60-67% TP	Chem-P Removal	Güney et al. 2008, Antakyali et al. 2013
KREPRO	60-75% TP	EBPR with Chem-P Removal	Karlsson 2001, Hultman 1999

DOP= Dissolved orthophosphate, TP= total phosphate

As evident in Table 8, the quantity of phosphorus that can be recovered from municipal biosolids varies substantially. The recoverability of phosphorus from biosolids appears to depend on the phosphorus removal process employed at the treatment plant

(Jossa and Remy 2015, Lundin et al. 2004) as well as on the speciation of the phosphorus present in the biosolids.

To date, the effect of phosphorus speciation present in the biosolids and supernatants generated from a range of wastewater treatment plants has not been evaluated. Furthermore, the research on phosphorus recovery has focused mainly on biosolids from wastewater treatment facilities with enhanced biological phosphorus removal (EBPR) or chemical phosphorus removal (e.g., Chem-P). Plants with conventional activated sludge (AS) are the most common in the US and thus must be considered in the analysis in order to identify the most suitable phosphorus recovery technology for the range of wastewater treatment plants now in use. Moreover, a potential improvement in the suitability of dewatered biosolids (after phosphorus recovery) for farmland application (measured by $N:P_2O_5$ ratio) has not been researched. Therefore, the objective of this study is to evaluate the potential phosphorus recovery achievable via three commercially available technologies (AIRPREX, Stuttgart Process and KREPRO) as a function of the type of wastewater treatment plant being considered (e.g., AS, EBPR or Chem-P). To this end, the phosphorus speciation present in biosolids and dewatering supernatants collected from nine wastewater treatment plants were determined. The measured speciation data was then used to estimate the potential recovery of phosphorus via the AIRPREX, Stuttgart and KREPRO technologies. In addition, the $N:P_2O_5$ ratio of the treated biosolids was predicted for each type of wastewater treatment plant and phosphorus recovery technology examined.

MATERIALS AND METHODS

Wastewater treatment plants sampled:

Primary, secondary, thickened, digested and dewatered biosolids as well as thickener and dewatering supernatants were collected from nine wastewater treatment plants in Texas. A summary of the unit processes sampled at each treatment plant is presented in Table 9. Treatment plants are given a code to maintain anonymity and are grouped by the type of phosphorus removal incorporated into each wastewater treatment plant (e.g., no additional removal in conventional activated sludge plants (AS), chemical P removal via aluminum or ferric precipitation (Chem-P) or enhanced biological phosphorus removal (EBPR)).

The flow diagrams for the first five wastewater treatment plants are shown in Figure 12. AS1 thru 4 (Figure 12 a-d) do not have any type of phosphorus removal in place. AS1 treats about 54 million gallon per day (MGD) and does not process the biosolids on site. Instead, gravity thickened waste activated biosolids and primary biosolids are pumped to plant AS5. At Plant AS5 (16 MGD) (Figure 12e), the biosolids are mixed with biosolids from another conventional municipal wastewater treatment plant which does not incorporate phosphorus removal into the process. The solids are then thickened, anaerobically digested (48 day HRT), dewatered and land applied. The supernatants from thickening and dewatering are sent into an artificial aerated lagoon for final treatment. Plant AS2 (Figure 12b) treats approximately 100 MGD and operates two different types of thickeners - dissolved air flotation (DAF) for secondary biosolids and gravity thickeners

for primary biosolids. The supernatants from both thickeners are returned to the headworks. The thickened biosolids are anaerobically digested and then dewatered. The supernatant from dewatering is pumped back to the headworks whereas the dewatered cake is used for direct land application.

Table 9. Description of the wastewater treatment plants sampled.

Code	Phosphorus Removal	Primary Clarification	Thickening	Digestion	Dewatering
AS1	No Removal (Conventional AS)	Yes	Gravity (WAS only)	No	No
AS2	No Removal	Yes	DAF (WAS only)/ Gravity (Primary Sludge)	Anaerobic	Belt Filter Press
AS3	No Removal	No	Gravity (WAS only)	No	Belt Filter Press
AS4	No Removal	Yes	Gravity (Comingled)	Anaerobic	Belt Filter Press
AS5	No Removal	No	Belt (Comingled)	Anaerobic	Belt Filter Press
Chem1	$FeCl_3$	Yes	Belt (WAS only)	No	Belt Filter Press
Chem2	$Al_2(SO_4)_3 + FeCl_3$	No	No Thickening	No	Belt Filter Press
EBPR1	Biological Removal	Yes	Rotary Drum (Comingled)	Anaerobic	Belt Filter Press
EBPR2	Biological Removal	No	Rotary Drum (Comingled)	No	No

DAF= Dissolved Air Flotation, WAS = Waste Activated Sludge, Comingled = Primary biosolids + Secondary Biosolids
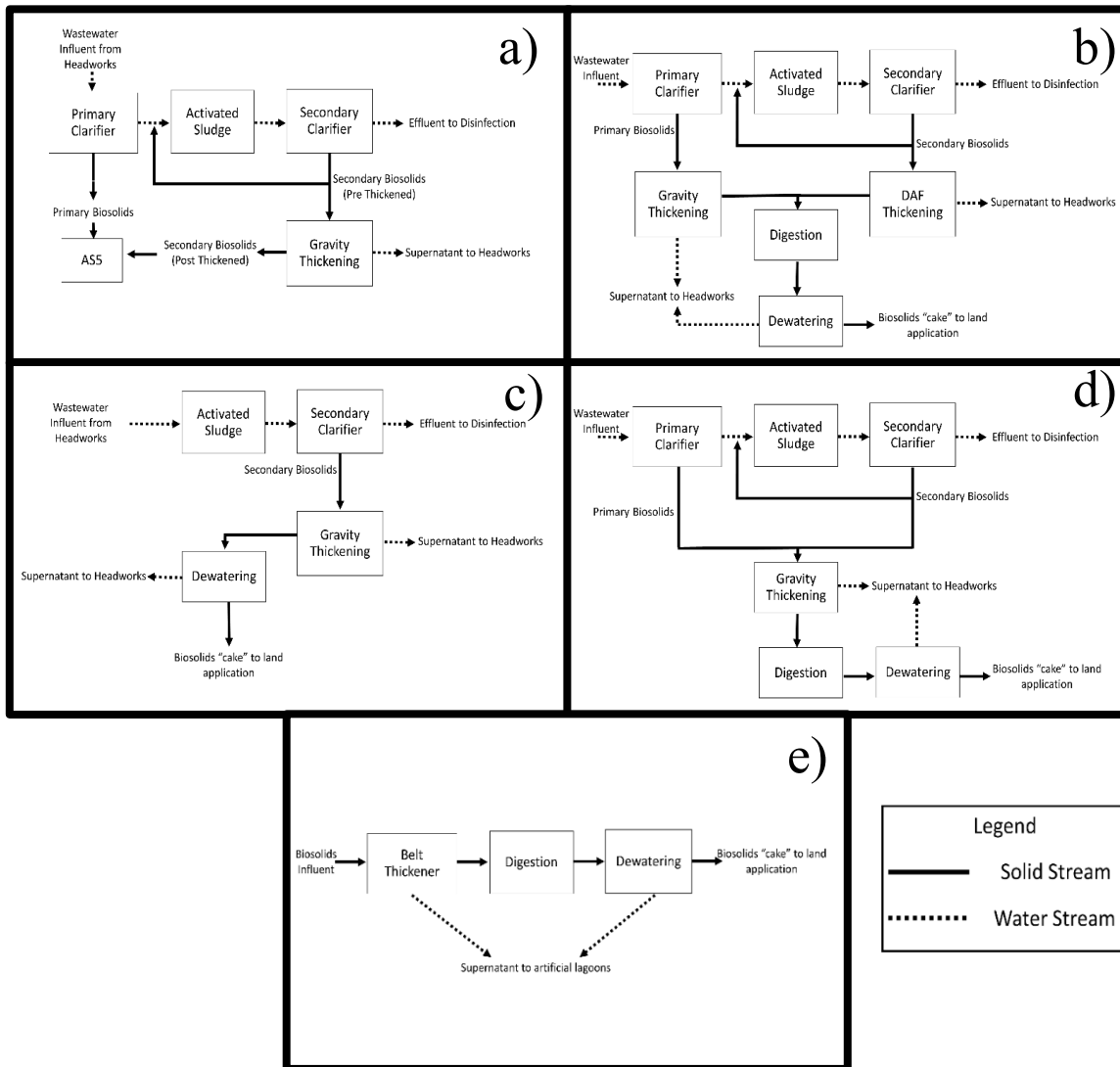
Figure 12. Flow diagrams for the conventional activated sludge wastewater treatment plants sampled in this study: a) AS1, b) AS2, c) AS3, d) AS4, e) AS5

Wastewater treatment plant AS3 (Figure 12c) is significantly smaller in capacity (5.8 MGD) than the other three plants. AS3 does not have primary clarifiers and thus their biosolids are composed of waste activated sludge (WAS) only. The WAS is thickened by gravity and then dewatered for direct land application. The supernatants from thickening and dewatering are pumped back to the headworks. AS4 (Figure 12d) treats 1.25 MGD and

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operates with primary and secondary clarifiers. AS4 mixes both primary and secondary biosolids before gravity thickening. The thickened solids are anaerobically digested and then dewatered for direct land application. The supernatants from both thickening and dewatering are pumped back to headworks.

Treatment plant Chem1 (Figure 13a) treats 48 MGD and produces primary biosolids and secondary biosolids from biological nitrogen removal and chemical phosphorus removal (precipitation via ferric chloride). The secondary biosolids are belt thickened and subsequently mixed with the primary solids for dewatering. The biosolids cake is trucked out to a landfill whereas the supernatants from belt thickening and dewatering are pumped to the headworks. Chem2 (Figure 13b) treats 2.5 MGD and only produces secondary biosolids from biological nitrogen removal and chemical phosphorus removal. Chem2 uses both ferric chloride and aluminum sulfate for phosphorus precipitation. The waste secondary biosolids are dewatered by a belt filter press and trucked to a landfill. The supernatants are pumped to the headworks.

EBPR1 with an average flowrate of 37 MGD, produces biosolids from primary clarification and biosolids from enhanced biological phosphorus removal. The primary biosolids are thickened by gravity and then mixed with the EBPR secondary biosolids for thickening via rotary drum. The thickened solids are then anaerobically digested and subsequently dewatered for land application. The supernatants from thickening and dewatering are sent back to the headworks.

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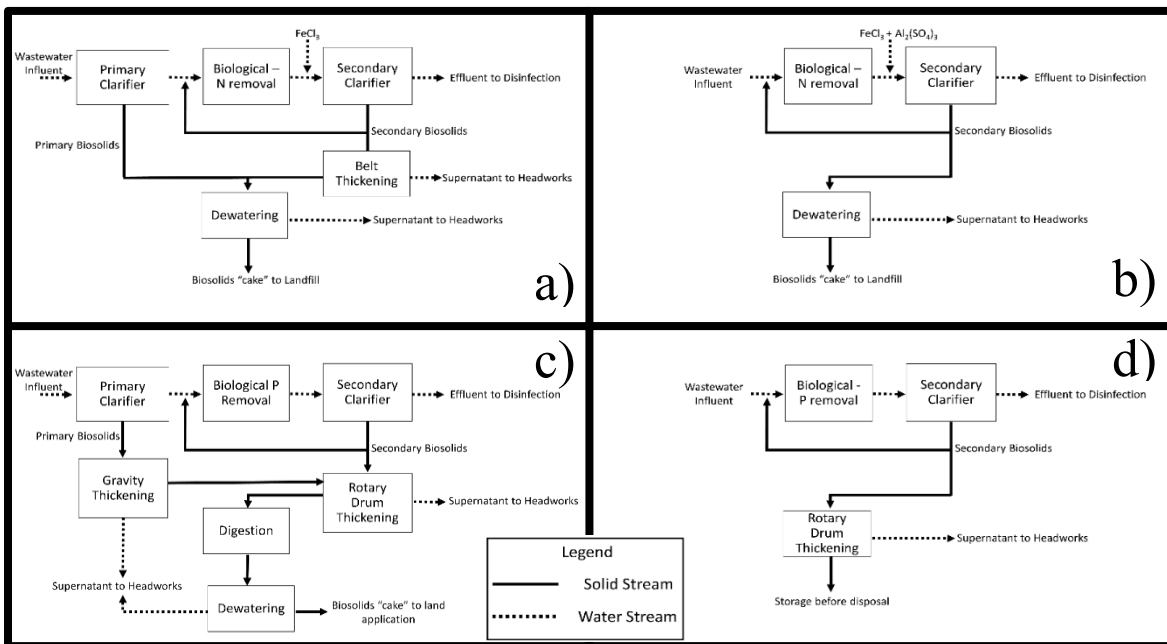
Figure 13. Flow diagrams for the wastewater treatment plants with chemical (a Chem-P1 & b Chem-P2) and biological phosphorus removal (c & d)

Finally, EBPR2 treats about 1.5 MGD and only produces secondary biosolids from biological phosphorus removal. The wasted solids are thickened by rotary drum thickening and then stored inside a steel container. Every day the container is emptied into a cistern truck and the solids are hauled to a solid's processing facility. The supernatants from thickening are pumped to the headworks.

Sampling regime:

Influents and effluent samples were collected from each unit process shown in Figures 10 and 11 on three different days. AS1 and AS5 were sampled in February, April and May of 2015 (average maximum ambient temperature of 79 °F and average minimum

temperature of 59 ºF) and AS2, AS3, AS4, EBPR1, EBPR2, Chem1 and Chem2 were sampled in October, November and December 2015 (average maximum ambient temperature of 76 ºF and average minimum temperature of 55 ºF). Due to a mild winter season, there was little variation in ambient temperatures in Texas for the year 2015. The samples were collected in 250 mL acid-washed HDPE bottles. The samples were immediately refrigerated after collection.

Phosphorus analysis:

Prior to analysis, samples were filtered through 0.45 micron filter paper (reinforced cellulose Millipore RW03, Millipore Corp., Billerica, MA). The filtrate was used to determine the dissolved phosphorus species present in the liquid phase and the unfiltered sample was used for determining total phosphorus species in the liquid and solid phases. The particulate concentrations were determined indirectly by calculating the difference between the measured total and dissolved concentrations of each phosphorus species.

Orthophosphate was measured by colorimetry using the ascorbic acid method (Standard Methods 4500-P 2012). Biosolid samples were acidified to pH 2 prior to determination of total orthophosphate (dissolved + particulate) in order to dissolve all the particulate orthophosphates (Hultman 1999, Hansen et al. 2000, Antakyali et al. 2013). Experiments by Zoppoth (1999) and Güney et al. (2008) reported that at pH 2, >98% of the total orthophosphate in the municipal biosolids is dissolved. In order to confirm these reported results, tests were conducted in the current study using a solution that simulates the phosphate, calcium, iron, magnesium, ammonia, and carbonate ion concentrations

present in municipal wastewater biosolids. Three 10 mL aliquots from the synthetic solution were centrifuged and the supernatant analyzed for dissolved orthophosphate. Subsequently, three additional aliquots from the synthetic solution were acidified from pH 7 to pH 2 with 11N H_2SO_4. After acidification the aliquots were centrifuged and the supernatant was analyzed for dissolved orthophosphate. The tests confirmed the dissolution of all the particulate orthophosphate present in the synthetic solution (Table 10).

Table 10. Results from orthophosphate dissolution experiments with a synthetic wastewater solution.

Sample	P Concentration in centrifuged supernatant (mmol/L)	Standard Deviation	% Recovery
Raw Sample Orthophosphate	0.01	0.005	0.04%
Acidified Sample Orthophosphate	27.1	0.3	100%
Theoretical Orthophosphate	27.0	-	-

Dissolved and total orthophosphate concentrations were measured within 2 hours of sample collection except when the treatment plant being sampled was located more than 30 miles from the analytical laboratory. For these samples, the total and dissolved orthophosphates as well as pH were measured on site. Orthophosphate on site was measured with a Hach PO-19 test kit. The reagents used for orthophosphate determination via the Hach kit are identical to those used in the laboratory (Hach, 2015).

To measure poly and organic phosphates, acid hydrolyzable (ortho + poly phosphorus) and total (organic + poly + ortho phosphorus) phosphorus species had to be converted into orthophosphate. Acid hydrolyzable phosphorus was converted to orthophosphate by acid digestion. The sample was acidified with 11 M sulfuric acid and then heated to 120 ℃ for 30 minutes (Standard Methods 4500-P 1998). Total phosphorus was converted to orthophosphate by persulfate digestion. The sample was acidified with 11 M sulfuric acid, then 0.6 g of potassium persulfate was added. The sample was then heated to 120 ℃ for 30 minutes (Standard Methods 4500-P 1998). After heating, the samples were allowed to cool to room temperature and neutralized with NaOH. Orthophosphate was then determined by the ascorbic acid method.

The method detection limits (MDL) for orthophosphate, acid-hydrolyzable and total phosphorus were 0.05, 0.05, 0.06 mg/L as P respectively. MDLs were obtained from measuring 7 replicates of a phosphate standard (0.2 mg/L) (USGS, 2016).

This speciation method was selected for use in the present study because it is a standard procedure to determine phosphorus in wastewater and wastewater biosolids (Munch and Barr 2001, Dueñas et al. 2003, Shimamura et al. 2008, Pastor et al. 2008, Zeng et al. 2010 and others). Moreover, the extraction methods are similar to the phosphorus recovery technologies being studied (Hansen et al. 2000, Güney et al. 2008, Sartorius et al. 2012, Antakyali et al. 2013).

pH, total and volatile solids:

pH was determined using a double junction Cole-Parmer pH probe and an ORION 920A pH meter. Total and volatile solids were measured gravimetrically using a modified Standard Method 2540 B and 2540 E (Standard Methods, 1998).

RESULTS AND DISCUSSION

Previous research (Chapter 3) examined speciation within the five conventional activated sludge plants and two EBPR plants to assess the impact of anaerobic digestion and thickening on speciation in conventional activated sludge systems relative to EPBR systems. This study expands the evaluation of phosphorus speciation in wastewater treatment operations to two additional treatment plants utilizing chemical phosphorus removal and the dewatering side streams from the nine treatment plants listed in Table 9. Based on the measured phosphorus speciation in this work and technology performance data from published literature for three phosphorus recovery technologies (AIRPREX, Stuttgart Process and KREPRO), phosphorus recovery was estimated based on the speciation. Finally, increases in the N: P_2O_5 biosolids ratio were also estimated in order to assess whether the phosphorus recovery technologies studied would be expected to improve the suitability of dewatered biosolids for farmland application.

Phosphorus speciation of undigested and digested biosolids

Figure 14 summarizes the phosphorus speciation within thickened biosolids (Figure 14a) and digested biosolids (Figure 14b) collected from the sampled WWTPs. Substantial variability was observed in the P measurements even at plants of similar design (e.g., conventional activated sludge systems). This result reflects the inherent differences in the design and operation of different wastewater treatment plants, an outcome that is not surprising given the variability in biosolids handling practices observed for plants AS1 through AS4 (Figures 12 and 13). This variability has also been observed and reported by other authors measuring phosphorus at full scale wastewater treatment plants (Lawler and Singer 1984, Szpyrkowicz 1995, Dueñas et al. 2003, Danesh et al. 2008). Despite this inherent variability, however, significant differences were observed in the phosphorus speciation of municipal biosolids produced at the different types of wastewater treatment plants (AS, Chem-P and EBPR). The total phosphorus concentrations present in undigested EBPR (30 mg/g $\pm$ 12) and Chem-P biosolids (29 mg/g $\pm$ 5) were on average twice the levels measured in undigested conventional activated sludge biosolids (15 mg/g $\pm$ 6). A two-sided Student's t-test with a significance level of $\alpha = 0.05$ was performed to assess the significance of the observed differences and the results are presented in Table 11. Indeed, the difference in total phosphorus concentrations between AS and EBPR (p=0.03) and between AS and Chem-P-B (p<0.01) are statistically significant. Also, undigested conventional activated sludge biosolids contain slightly higher concentrations of dissolved orthophosphates compared to EBPR (p<0.01) and Chem-P (p<0.01) undigested biosolids. EBPR plants and chemical phosphorus removal plants are designed to incorporate the

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dissolved phosphorus present in raw wastewater into the particulate phase to be removed via sedimentation (Tchobanoglous et al. 2004). Therefore, higher total phosphorus concentrations and lower dissolved orthophosphate concentrations are expected in undigested biosolids from EBPR and Chem-P plants relative to the undigested biosolids generated at AS plants.
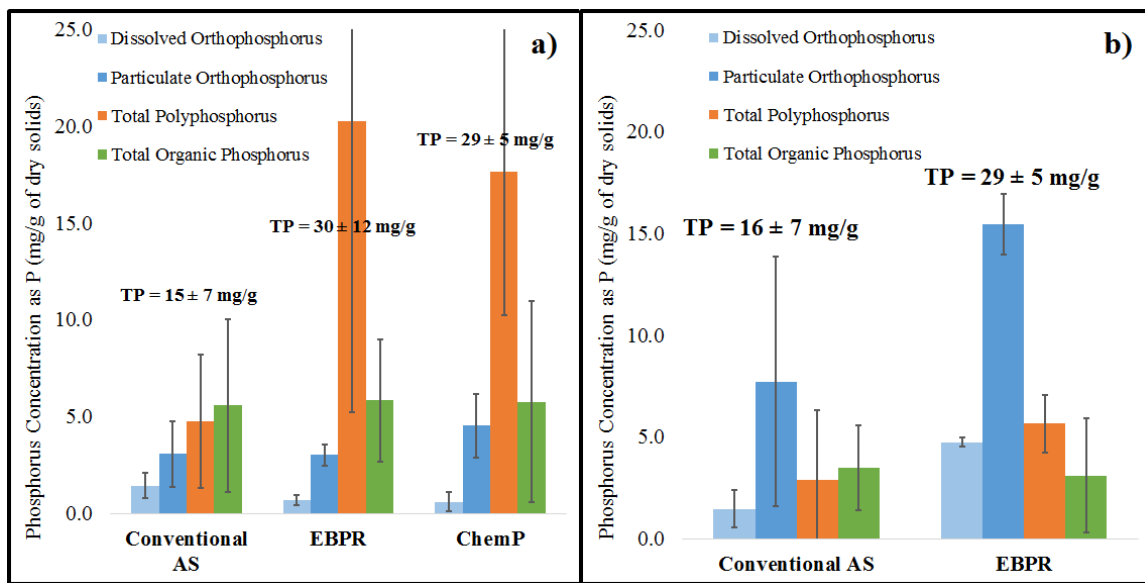
Figure 14. Phosphorus speciation for a) undigested biosolids and b) digested biosolids in three different wastewater treatment plant types

Table 11. Results of hypothesis testing of mean phosphorus concentrations from different types of wastewater treatment plants.

Reject Ho?/ p value	Ortho Phosphorus	Particulate ortho phosphorus	Poly Phosphorus	Organic phosphates	Total
Undigested EBPR Biosolids vs Undigested AS biosolids	**Yes / p<0.01**	No / p = 0.9	**Yes / p=0.05**	No / p=0.9	**Yes / p<0.03**
Undigested AS biosolids vs Undigested Chem biosolids	**Yes / p<0.01**	No/ p=0.1	**Yes/ p<0.01**	No / p=0.9	**Yes/ p<0.01**
Undigested EBPR biosolids vs Undigested Chem biosolids	No / p=0.7	No / p=0.07	No/ p=0.7	No / p=1	No / p=0.8
Digested EBPR biosolids vs Digested AS biosolids	**Yes / p<0.01**	**No / p<0.01**	No/ p=0.09	No / p=0.8	**Yes / p=0.01**
Undigested AS vs Digested AS	No/ p=0.9	No/ p=0.07	No/ p = 0.24	**Yes/ p<0.01**	No/ p=0.8
Undigested EBPR vs Digested EBPR	**Yes/ p<0.01**	**Yes/ p<0.01**	**Yes/ p<0.03**	**Yes/ p<0.01**	No/ p=0.88

Testing was performed on the hypothesis that the means are equivalent using a Student's t-test at a significance level with $\alpha = 0.05$.

With respect to the particulate phase, undigested biosolids derived from wastewater plants with chemical phosphorus removal had a higher particulate orthophosphate concentration compared to both EBPR (p=0.07) and AS (p=0.1) treatment plants, although

their differences were not statistically significant. This is not surprising given that aluminum or iron phosphate precipitation captures orthophosphate. However, the difference in the average concentration of particulate orthophosphate compared to AS and EBPR was not as high as expected. It appears that orthophosphate precipitation is not the primary mechanism for P removal in the Chem-P plants studied. Figure 14(a) shows that a significant portion of the phosphorus is also removed biologically and stored as polyphosphates which may be an unintended consequence of incorporating biological nitrogen removal processes at these plants. Nitrogen removal in the Chem-P plants studied was achieved using a modified Ludzack-Ettinger process. This process consists of an anoxic zone before the aerobic reactor (Tchobanoglous et al. 2004). The anoxic zone in both plants consisted of a series of three completely mixed reactors. It is likely that some fraction of these reactors operate under anaerobic (absence of oxygen & nitrate) instead of anoxic (absence of oxygen only) conditions. Phosphate accumulating bacteria (PAO) (*Accumulibacter, Acinetobacter* and others) when exposed to alternating anaerobic and aerobic conditions, can assimilate significant quantities of dissolved phosphorus as polyphosphate (Tchobanoglous et al. 2004, Hrenovic et al. 2009, Yuan et al. 2012,). Hence the significant quantities of polyphosphates observed in Figure 14a for the Chem-P biosolids as well as for the EBPR biosolids.

These polyphosphates in the biosolids can hydrolyze and form dissolved and particulate orthophosphate in anaerobic digestion (Liao et al. 2005, Marti et al. 2008a). EBPR biosolids contain significantly greater concentrations of polyphosphate than AS biosolids (p=0.05) and, as a result, the dissolved orthophosphate concentration increases

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significantly for EBPR biosolids (p<0.01) after digestion, but it remains approximately the same for conventional AS (p=0.9). An increase in particulate orthophosphate as well as a significant decrease in organic phosphorus was observed for both the EBPR (p<0.01) and AS biosolids (p<0.01) after anaerobic digestion. It is likely that the degradation of organic phosphorus is the source for the increase in particulate orthophosphate after anaerobic digestion of AS municipal biosolids whereas for EBPR biosolids the increase in orthophosphate is a combination of a decrease in both polyphosphates and organic phosphates. There are no anaerobic digesters in the chemical removal treatment plants sampled; therefore, the possibility of polyphosphate hydrolysis for this type of biosolids could not be examined.

Phosphorus speciation in thickening and dewatering sidestreams

Several authors suggest the use of thickening and dewatering sidestreams for phosphorus recovery (Baur et al. 2011, Cullen et al. 2013, Sharp et al. 2013) as opposed to using the bulk biosolids (liquid + solids). Figure 15a shows the phosphorus speciation in thickening sidestreams and Figure 15b shows the speciation in dewatering sidestreams sampled for this study. Supernatants from the sampled AS sand EBPR thickeners have concentrations lower than 20 mg/L which according to Ostara (2009) and Nieminen (2010) is the minimum required concentration for struvite recovery to be economically feasible. The supernatants from the belt thickener in plant Chem1 is the only one that meets these minimum requirements.
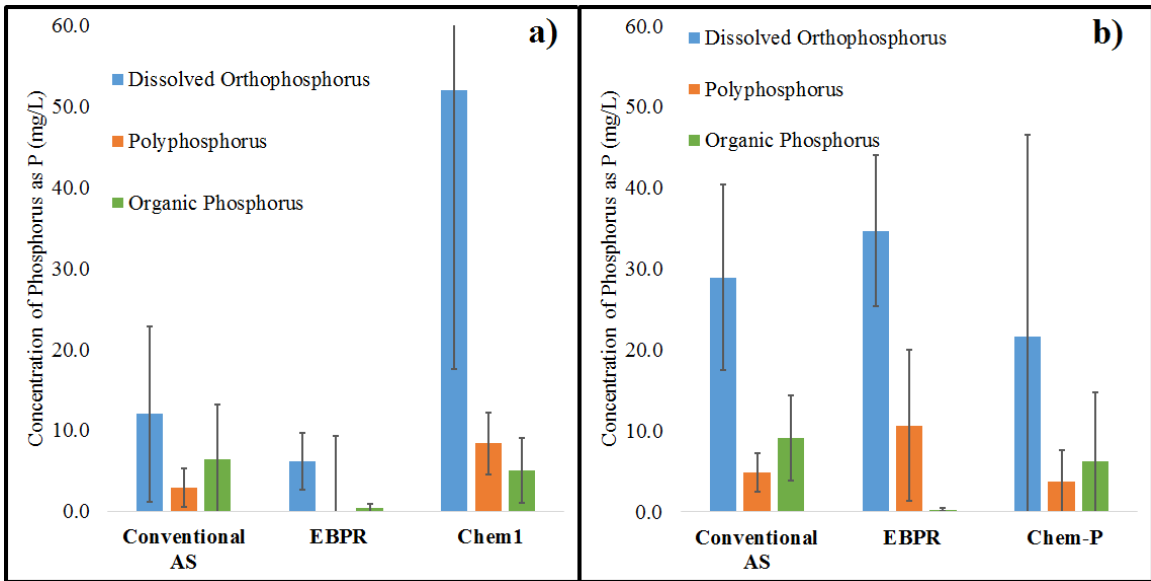
Figure 15. Phosphorus speciation in a) thickening and b) dewatering supernatants

Sidestreams from dewatering of AS and EBPR biosolids have greater concentrations of dissolved orthophosphate than their corresponding thickening sidestreams. This is likely because these biosolids have been through anaerobic digestion and the phosphorus stored as polyphosphate and the organic phosphorus have been released. Also, dewatering usually achieves greater water removal from the biosolids by using flocculation polyelectrolytes. These polymers can be cationic, anionic or nonionic. Depending on the electrolyte they can neutralize the charge or bridge particles to increase dewatering (Sanin et al. 2011). These electrostatic interactions might have an impact on the orthophosphate concentrations in the sidestreams. It has been observed (Nieminen 2010, Petzet and Cornel 2012, Shaw et al. 2014) that high concentrations of dissolved orthophosphate within the biosolids decrease dewaterability of biosolids; although, a mechanism to support phosphate induced water retention has not been well established (Bergmans 2011). Treatment plants usually compensate by dosing higher quantities of

polyelectrolyte (Nieminen 2010, Petzet and Cornel 2012, Shaw et al. 2014). Therefore, we can hypothesize that high concentrations of polyelectrolytes used for dewatering inhibit phosphate-induced water retention, and thus produce higher concentrations of phosphorus in the liquid sidestreams. Testing this hypothesis will require further observation and experimentation.

Considerable variability was observed in the sidestream phosphorus concentrations measured at the plants that have incorporated chemical phosphorus removal. The standard deviations are greater than the average values (Figure 15b). However, if we separate data from plants Chem1 and Chem2 (Figure 16), the variability decreases. Dewatering supernatants from plant Chem1 have high concentrations of dissolved orthophosphate while concentrations in supernatants from Chem2 are significantly lower. Chem2 plant treated their wastewater to a lower effluent concentration than Chem1 (<0.05 mg/L P for Chem2 vs 0.12 ± 0.03 mg/L P for Chem1). This indicates that Chem2 adds greater quantities of ferric and aluminum for phosphorus removal than Chem1, and these chemicals are more successful at creating stable particulate phases that do not dissolve during dewatering.
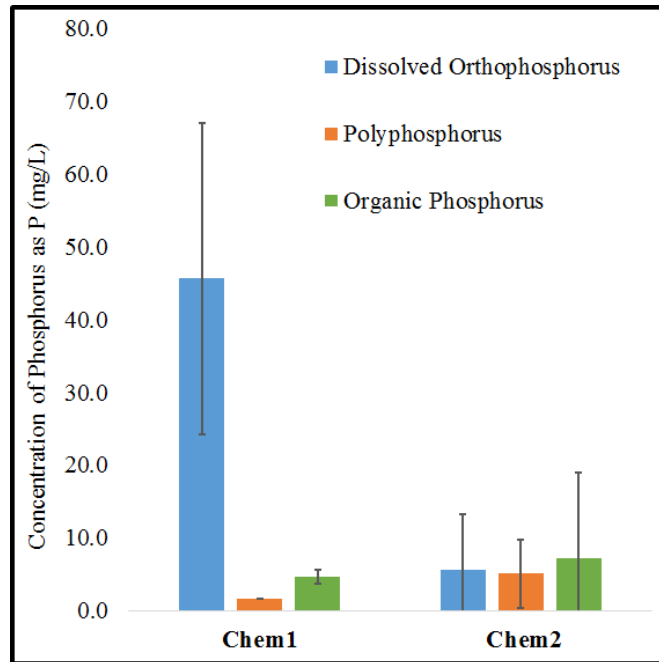
Figure 16. Phosphorus speciation of the dewatering sidestreams for the two chemical phosphorus removal wastewater treatment plants investigated

Relating phosphorus speciation with phosphorus recovery

Using the biosolids phosphorus speciation data collected in this study and the phosphorus recovery efficiencies reported in the literature for the AIRPREX, Stuttgart process and KREPRO technologies, it is possible to estimate the phosphorus recovery potentially achievable for each biosolid examined in this study (sample calculations in Appendix B). The AIRPREX recovery technology consists of a large batch reactor where sludge is aerated to strip CO_2 and increase the pH to over 8 (Stumpf et al. 2009). Magnesium chloride is supplied to maintain a molar $Mg:PO_4$ ratio of 1.05:1 and precipitate struvite (Stumpf et al. 2009, Uysal, 2010, P-Rex 2015). Stumpf et al. (2009) and Nieminen (2013) reported a 90% to 98% recovery of the dissolved orthophosphate present in the

biosolids. Thus, for our calculations, it was assumed that the AIRPREX technology would recover 90% of the dissolved orthophosphate species (target species for AIRPREX) present in each of the sampled biosolids (Table 12). No other species of phosphorus are expected to be recovered by the AIRPREX technology. Thus, in order to obtain an estimate of the potential recovery, the possible recovery from the target species (Table 11) was multiplied by the concentration of the target species within the biosolids of interest (Figure 14).

Table 12. Possible recovery from the target species.

Recovery Technology	Target P Species	Possible recovery from the target species (%)	Reference
AIRPREX	Dissolved Orthophosphate	90	Stumpf et al. 2009
Stuttgart	Total Orthophosphate	98	Güney et al. 2008
KREPRO	Polyphosphate + Orthophosphate	90	Karlsson (2001)

The Stuttgart recovery technology consists of several batch steps. First, the pH in the biosolids is decreased to pH 2 with sulfuric acid. At this pH, all of the phosphorus bound to calcium, magnesium, aluminum, and iron is dissolved into the liquid phase (Güney et al. 2008). The biosolids are then dewatered and the liquid portion (sidestream) is transferred into a stirred batch reactor where citric acid is added as a complexing agent to prevent precipitation of phosphorus with aluminum and iron. Subsequently, magnesium hydroxide and sodium hydroxide are added to increase the pH and supply magnesium for

struvite precipitation (Antakyali et al. 2013). It has been demonstrated that 98% of the phosphorus dissolved (at pH 2) can be recovered through the Stuttgart process (Güney et al. 2008, Antakyali et al. 2013). This phosphorus recovery technology is identical to our method for determination of total orthophosphate (dissolved + particulate orthophosphate) in which we achieved 100% dissolution of particulate orthophosphates. Thus, we assumed that 98% of the total orthophosphate species (target species for Stuttgart) measured in each of the sampled biosolid can be recovered though the Stuttgart process (Table 12). This estimate was used to calculate a potential recovery as described previously for the AIRPREX process.

Finally, the KREPRO technology also consists of a series of batch processes in which the biosolids are first acidified to pH 2 with sulfuric acid. The biosolids are then heated to just over 100 ºC at a pressure of 3.6 bar for 30 minutes to hydrolyze the polyphosphates into orthophosphates (Hansen et al. 2000). The biosolids are then cooled and dewatered. The sidestream from dewatering (liquid portion) is utilized for ferric phosphate precipitation at pH 2.8. Hansen et al. (2000) estimated that 90% of the phosphorus dissolved in the dewatering supernatant can be recovered by ferric phosphate precipitation. Also, Karlsson (2001) demonstrated that the KREPRO technology could recover 60 to 75% of the total phosphorus present in digested and undigested biosolids generated at plants with enhanced chemical phosphorus removal. This recovery technology is similar to our method for determination of acid hydrolyzable phosphorus (Orthophosphates + Polyphosphates) described previously. Moreover, the phosphorus speciation data collected in the current study indicates that acid hydrolyzable phosphorus

accounts for 60 to 80% of the total phosphorus before digestion and between 78 and 89% of the total phosphorus after digestion (Figure 14). This range falls within the recovery reported by Karlsson (2001). Therefore, it was assumed that 90% of the acid hydrolyzable phosphorus (target species for KREPRO) present in the sampled biosolids can be recovered via the KREPRO process (Table 12). The assumption was then used to calculate the potential for phosphorus recovery as described previously.

Predicted phosphorus recovery & N:P_2O_5 ratios:

To obtain a representative estimate of the N:P_2O_5 ratios before phosphorus recovery, the pertinent published literature was consulted since total nitrogen was not measured in the collected samples. Eighteen different references provided the data necessary to obtain N:P_2O_5 ratios of biosolids from conventional AS, EBPR and chemically enhanced phosphorus removal treatment plants (Maguire et al. 2001, Tchobanoglous et al. 2004, US EPA 1979, Penn and Sims 2002, Wang et al. 2010, Chinnault and O'Connor 2008, Vincent et al. 2011, Schroder et al. 2008, Uysal et al. 2010, Kroiss et al. 2008, Debosz et al. 2002, Bolzonella et al. 2012, Salsabil et al. 2009, Sarkar et al. 2005, Batziaka et al. 2008, Liao et al. 2005, Elliot et al. 2002 and Chinault 2007). Based on the potential recovery of phosphorus achievable (described previously) for each P recovery technology, the moles of phosphorus recovered via the AIRPREX, Stuttgart and KREPRO technologies as well as the nitrogen recovered via AIRPREX and Stuttgart technologies were subtracted from the concentrations reported in the previously mentioned studies and a new N:P_2O_5 ratio was obtained (sample calculations in Appendix B). Since

N:P_2O_5 before phosphorus recovery was obtained from the literature, we limit our discussion to the statistical significance of differences in ratios and not the absolute N:P_2O_5 values. The significance of the increase in N:P_2O_5 after phosphorus recovery was tested by a one-sided Student's t-test with a critical α of 0.05. The resulting predictions of potential phosphorus recovery for AIRPREX, Stuttgart and KREPRO and the predicted N:P_2O_5 of the biosolids generated are presented in Tables 14 – 16, respectively.

As shown in Table 13, it is estimated that approximately 15% of the total phosphorus present in the digested EBPR biosolids can be recovered via the AIRPREX technology. Only 5% of the phosphorus can be recovered when utilizing undigested EBPR biosolids. In contrast, using undigested conventional activated sludge (AS - 9.5% of TP) appears to improve recovery of phosphorus via the AIRPREX technology compared to using digested AS (7.8% of TP). The explanation for this difference in conventional AS processes is the high fraction of the P in the orthophosphate particulate phase. Although some organic phosphorus is converted into orthophosphate after anaerobic digestion, the majority of orthophosphates are present in the particulate phase which cannot be recovered via the AIRPREX technology (Figure 14). The biosolids from chemical phosphorus removal have very low predicted recovery through the AIRPREX technology which is expected since iron phosphate solids are relatively stable.

Table 13. Predicted phosphorus recovery and N: P_2O_5 ratios present in biosolids treated with the AIRPREX phosphorus recovery technology.

| | AIRPREX (Struvite) | | | | |
| | AS | | EBPR | | Chem |
	Undigested Biosolids	Digested Biosolids	Undigested Biosolids	Digested Biosolids	Undigested Biosolids
Predicted TP recovered (%)	9.5 ± 4.6	7.8 ± 5.3	5.1 ± 2.6	15 ± 2.4	2.0 ± 1.6
Kg of P recovered per metric ton of Dry Solids	1.3 ± 0.6	1.2 ± 0.1	1.0 ± 0.6	4.3 ± 0.2	0.5 ± 0.5
N/P_2O_5 Ratio Before Recovery	1.3 ± 0.4 [a]	1.1 ± 0.6[b]	0.94 ± 0.46[c]	0.78 ± 0.28[c]	1.0 ± 0.4[d]
N/P_2O_5 Ratio After Recovery	1.5 ± 0.2	1.1 ± 0.6	0.98 ± 0.02	0.88 ± 0.02	1.0 ± 0.01
Is N: P_2O_5 increase significant? (t-test)	No/ p = 0.1	No/ p=1	No/ p=0.8	No/ p=0.6	No/ p=1

[a]Maguire et al. 2001, Chinault 2007; [b] Penn and Sims 2002, Chinault and O'Connor 2008, Schroder et al. 2008, Uysal et al. 2010, Batziaka et al. 2008, Elliot et al. 2002; [c] Wang et al. 2010, Salsabil et al. 2009, Chinault 2007; [d] Maguire et al. 2001, Penn and Sims 2002, Debosz et al. 2002.

Recovery via AIRPREX technology does not increase the N:P_2O_5 ratio significantly in the spent biosolids. Struvite also removes nitrogen and thus prevents the N:P_2O_5 ratios from increasing significantly with the AIRPREX technology.

Data presented in Table 14 shows that the Stuttgart process significantly improves the predicted potential for P recovery from all types of biosolids compared to the recovery with the AIRPREX technology. With the Stuttgart recovery technology, the predicted recovery from digested AS biosolids is now greater than the recovery from undigested biosolids because this technology captures the particulate orthophosphate formed during anaerobic digestion. For the chemical phosphorus removal biosolids, there is also improvement when compared to the performance with the AIRPREX technology since the

orthophosphate that was bound to aluminum and iron during chemically enhanced phosphorus removal is released at pH 2.

Table 14. Predicted phosphorus recovery and N: P_2O_5 ratios present in biosolids treated with the Stuttgart Process phosphorus recovery technology.

| | Stuttgart Process (Struvite) | | | | |
| | AS | | EBPR | | Chem |
	Undigested Biosolids	Digested Biosolids	Undigested Biosolids	Digested Biosolids	Undigested Biosolids
Predicted TP recovered (%)	31 ± 11	50 ± 20	24 ± 14.5	69 ± 11	19 ± 8.8
Kg of P recovered per metric ton of Dry Solids	4.5 ± 2.0	8.8 ± 6.3	4.6 ± 3.1	19.7 ± 1.1	5.1 ± 2.0
N/P_2O_5 Ratio Before	1.3 ± 0.4 [a]	1.1 ± 0.6 [b]	0.94 ± 0.46 [c]	0.78 ± 0.28 [c]	1.0 ± 0.4 [d]
N/P_2O_5 Ratio After	2.0 ± 0.4	2.8 ± 2.6	1.2 ± 0.3	2.3 ± 0.9	1.2 ± 0.1
Is N: P_2O_5 increase significant? (t-test)	**Yes/ p<0.01**	**Yes/ p<0.01**	No/ p=0.3	**Yes/ p<0.01**	No/ p=0.5

[a] Maguire et al. 2001, Chinault 2007; [b] Penn and Sims 2002, Chinault and O'Connor 2008, Schroder et al. 2008, Uysal et al. 2010, Batziaka et al. 2008, Elliot et al. 2002; [c] Wang et al. 2010, Salsabil et al. 2009, Chinault 2007; [d] Maguire et al. 2001, Penn and Sims 2002, Debosz et al. 2002.

The N: P_2O_5 ratios increase significantly after the recovery of phosphorus with the Stuttgart technology except for undigested EBPR biosolids and undigested Chem-P biosolids. High quantities of phosphorus are present in the polyphosphate form for these two biosolids and thus they cannot be recovered by the Stuttgart technology.

Finally, using the KREPRO technology, over 50% of the phosphorus could be recovered for all types of biosolids (see Table 15). This process targets polyphosphates as well as orthophosphates present in the biosolids. For EBPR there is greater recovery with digested biosolids than with undigested biosolids since part of the organic phosphorus

degrades during anaerobic digestion and forms orthophosphate. For the same reason, digested AS biosolids achieves greater recovery than undigested AS biosolids with the KREPRO technology. It is predicted that over 70% of the total phosphorus present can be recovered from Chem-P WWTPs biosolids utilizing the KREPRO technology. This technology takes advantage of the phosphorus bound as polyphosphate in the biosolids which are a significant fraction of the phosphorus in biosolids from sampled plants with chemical phosphorus removal.

Table 15. Predicted phosphorus recovery and N: P_2O_5 ratios present in biosolids treated with the KREPRO phosphorus recovery technology.

	KREPRO (Ferric Phosphate)				
	AS		EBPR		Chem
	Undigested Biosolids	Digested Biosolids	Undigested Biosolids	Digested Biosolids	Undigested Biosolids
Predicted TP recovered (%)	55 ± 12	61 ± 18	62 ± 7.4	81 ± 8	72 ± 18
Kg of P recovered per metric ton of Dry Solids	8.4 ± 4.5	11 ± 7.2	12 ± 3.5	23 ± 2.0	21 ± 5.8
N/P_2O_5 Ratio Before	1.3 ± 0.4 [a]	1.1 ± 0.6[b]	0.94 ± 0.46[c]	0.78 ± 0.28[c]	1.0 ± 0.4[d]
N/P_2O_5 Ratio After	3.4 ± 1.5	3.5 ± 1.9	2.6 ± 0.6	4.8 ± 2.6	5.2 ± 3.4
Is N: P_2O_5 increase significant? (t-test)	**Yes/ p<0.01**	**Yes/ p<0.01**	**Yes/ p<0.01**	**Yes/ p<0.01**	**Yes/ p<0.01**

[a]Maguire et al. 2001, Chinault 2007; [b] Penn and Sims 2002, Chinault and O'Connor 2008, Schroder et al. 2008, Uysal et al. 2010, Batziaka et al. 2008, Elliot et al. 2002; [c] Wang et al. 2010, Salsabil et al. 2009, Chinault 2007; [d] Maguire et al. 2001, Penn and Sims 2002, Debosz et al. 2002.

With the KREPRO technology, the predicted N: P_2O_5 ratios of the spent biosolids increases significantly regardless of the phosphorus removal processes employed at the wastewater treatment plant. This is important if the spent biosolids are to be utilized for

farmland application. However, additional research is required to determine the effects that spent biosolids generated from the KREPRO phosphorus recovery technology will have on crops following land application of the treated biosolids.

CONCLUSIONS:

The phosphorus speciation of municipal biosolids determined in this study was utilized to compute estimated phosphorus recoveries from different types of biosolids. This same approach can be followed in the future to obtain estimates for phosphorus recovery for a given treatment plant in lieu of expensive pilot tests. The most significant findings of this work include the following:

- Biosolids from wastewater treatment plants that incorporate chemical phosphorus removal and enhanced biological phosphorus removal contain greater quantities of phosphorus than biosolids from conventional activated sludge plants.

- The dominant species observed in biosolids collected from plants with chemical phosphorus removal were polyphosphates, and not particulate phosphorus as intuition would suggest. This is presumably due to anaerobic zones (absence of oxygen & nitrate) within the reactors intended for anoxic (absence of oxygen only) operation.

- After digestion, the highest concentration (mg-P/g of dry solids) of phosphorus was present as particulate orthophosphate in biosolids generated at EBPR plants and conventional AS treatment plants.

- Sidestreams from the sampled thickeners were determined to be unsuitable for phosphorus recovery via struvite precipitation, except for thickening sidestreams from

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chemical phosphorus removal plant #1 (Chem1), based on the low orthophosphate concentrations. All sidestreams from dewatering are suitable for phosphorus recovery via struvite precipitation, except for dewatering sidestreams from chemical phosphorus removal plant #2 (Chem2).

- Using the AIRPREX phosphorus recovery technology, there is a potential to recover between 2% to 15% of the total phosphorus depending on the type of phosphorus removal used at the wastewater treatment. However, there was no significant change in $N:P_2O_5$ ratio of the spent biosolids after phosphorus recovery (Table14).

- The P recovery predicted for the Stuttgart phosphorus recovery technology appears to be higher than that for the AIRPREX technology. Also, it is predicted that the Stuttgart technology will increase the $N:P_2O_5$ ratio of undigested and digested AS biosolids as well as digested EBPR biosolids.

- With the KREPRO technology, the recovery potential is predicted to be greater than 50% for all types of biosolids. Also, the $N:P_2O_5$ ratio is predicted to increase for biosolids generated by AS, EBPR and chemical phosphorus removal treated with this technology.

Although technologies such as Stuttgart and KREPRO are predicted to be more effective at recovering phosphorus than the commercially available AIRPREX, the economic and environmental feasibility of these approaches needs to be examined further since factors such as the chemical demand (acids, magnesium, ferric) and energy requirements may limit their full-scale application.

Chapter 5: Life cycle impact assessment of phosphorus recovery technologies from conventional and phosphorus removal wastewater treatment plants

Acronym definition

AS-B = Biosolids generated in conventional activated sludge wastewater plant

EBPR-B = Biosolids generated in enhanced biological phosphorus removal plant

Chem-P-B = Biosolids generated in plant incorporating chemical phosphorus removal

FLA = Farmland application

L = Landfill disposal

C = Compost

A = AIRPREX phosphorus recovery technology

SP = Stuttgart phosphorus recovery technology

K = KREPRO phosphorus recovery technology

TSP = triple superphosphate

A2O = Anaerobic-Anoxic-Oxic phosphorus removal

INTRODUCTION:

The management, recycle and reuse of phosphorus is becoming a necessity as the world's population grows and high quality phosphorus mines are being depleted (Cordell et al. 2009, Cordell et al. 2011). Several researchers (Hansen et al. 2000, Donnert et al. 2002, Takiguchi et al. 2004, de-Bashan and Bashan 2004, Cordell et al. 2009, Bradford et al. 2012 and others) have investigated a variety of technologies for the recovery and reuse

of phosphorus from wastewater biosolids. The oldest and most common technology of phosphorus reuse is direct land application of dewatered or composted biosolids. Direct land application recycles all the phosphorus present in the dewatered biosolids, although there is a debate about how much of the phosphorus can actually be used by plants (Lu et al. 2012). This largely depends on the type of phosphorus species of phosphorus present in the biosolids ultimately determined by the type of removal process at the treatment plant (Lu et al. 2012). Recently developed technologies for phosphorus recovery target a particular species of dissolved or particulate phosphorus with the objective of separating the phosphorus present in the biosolids into an inorganic stream (Sartorius et al. 2012, Atienza-Martinez et al. 2014). These inorganic products are available for plant uptake (indicated by citrate solubility) (Hansen et al. 2000, Cabeza et al. 2011, Talboys et al. 2015), but their percent water solubility is less than commercial fertilizers [See Table 16]. A low percent water solubility yields a slow release of nutrients which can deter farmers from using these types of fertilizers; however, a lower water solubility also lowers the potential for phosphorus to leach into surface waters (Chinault & O'Connor 2008, Rahman et al. 2011, Cabeza et al. 2011). Most commercially-available technologies (i.e., Ostara Pearl, Struvia, AIRPREX) for inorganic P recovery target dissolved orthophosphates present in the dewatering supernatant or within the bulk biosolid phase with the objective of precipitating struvite. Harsher technologies such as the "Stuttgart Process" and KREPRO utilize strong acids and thermal hydrolysis, respectively, to solubilize particulate forms of phosphorus and thus achieve a much greater recovery (Sartorius et al. 2012). These harsh technologies however, have high energy and chemical demands that have

generally limited their utilization to pilot scale tests (Hansen et al. 2000, Sartorius et al. 2012).

Table 16. Phosphorus solubility of inorganic phosphates species as compared to commercial fertilizer (e.g., triple superphosphate (TSP)).

	Water Soluble (% of TP)	Citrate soluble (% of TP)	Reference
Struvite	1	45	Cabeza et al. 2011,
Ferric Phosphate	0	100	ECCO 2001, Odegaard et al. 2002
$Ca(H_2PO_4)$ [Triple Superphosphate]	90	100	Cabeza et al. 2011 O'Connor et al. 2004

Beyond the direct environmental implications of phosphorous recovery, numerous studies (Lundin et al. 2004, Hospido et al. 2005, Murray et al. 2008, Hong et al. 2009, Linderholm et al. 2012, Jossa and Remy 2015) have applied life cycle analysis to assess indirect environmental impacts. Hong et al. 2009 and Murray et al. 2008 focused their studies on the global warming potential and energy use of landfilling versus agricultural use of dewatered, composted, dried or incinerated conventional biosolids. Despite the high global warming potential associated with methane generation and heating requirements, Hong et al. 2009 showed that anaerobic digestion of biosolids is very effective in lowering overall environmental impacts by reducing the mass of solids that need to be discarded.

Linderholm et al. (2012) performed a life cycle intensity analysis (LCIA) to compare options for supplying phosphorus to Swedish farms. They investigated the use of mined phosphorus for commercial fertilizer (as triple superphosphate (TSP)), direct

farmland application of biosolids, struvite phosphorus from wastewater biosolids and ash from incinerated biosolids. Linderholm et al. (2012) concluded that direct farmland application of dewatered and anaerobically digested biosolids had a lower global warming potential (GWP) than the other options because less energy is consumed in the process. The study also found that the energy demand required to supply 1 kg of P from commercial fertilizers to farms in Sweden is much lower than that the required to supply 1 kg of P from recovered struvite. The eutrophication potential of the different options was not considered and Linderholm et al. (2012) only noted that phosphorus discharges from wastewater treatment plants are likely to be larger than the discharges associated with TSP production. They did not investigate the likelihood of TSP leaching higher quantities of phosphorus than struvite when used for agricultural purposes. In some parts of the US (the Great Lakes, Chesapeake Bay, the Everglades and others) (Maguire et al. 2001, Schober and Sims 2003), the eutrophication effects are a pressing concern and thus these effects were considered in the present LCIA study.

LCIA studies by Lundin et al. (2004) and Jossa and Remy (2015) compared commercially available technologies (AIRPREX, Pearl, Struvia) for phosphorus recovery with harsher technologies of phosphorus recovery (Stuttgart Process, KREPRO, Bio-con, Gifhorn Process). Lundin et al. (2004) concluded that the speciation of phosphorus in the biosolids can affect the feasibility of a given recovery process. For instance, the authors suggested that switching from biosolids generated in a wastewater plant that incorporates chemical phosphorus removal (Chem-P-B) to biosolids generated in an enhanced biological phosphorus plant (EBPR-B) would enhance the feasibility of technologies such

as acid thermal hydrolysis (KREPRO). Jossa and Remy (2015) compared commercial phosphorus recovery technologies (AIRPREX, Struvia and Pearl Ostara) with acid leaching technologies (Stuttgart Process and Gifhorn Process) using EBPR-B or Chem-P-B as the phosphorus feed. Scenarios that used Chem-P-B for phosphorus recovery had greater global warming and eutrophication potentials than did the scenarios involving EBPR-B. However, the energy required for the wastewater treatment operations were not considered. EBPR operations are more energy intensive than chemical phosphorus removal operations and this could possibly change the GWP results. Jossa and Remy (2015) also found that recovering phosphorus from municipal biosolids decreased the phosphorous concentrations in wastewater effluents from EBPR plants but not Chem-P plants and thus decreased the eutrophication potential for scenarios involving EBPR-B only.

While research to date has investigated the GWP and eutrophication effects of utilizing harsher technologies of phosphorus recovery for EBPR and Chem-P generated biosolids, missing in these previous analyses is an investigation of the LCIA impacts associated with recovering phosphorous from biosolids generated at conventional activated sludge wastewater treatment plants. As opposed to European countries, conventional activated sludge (AS) is the most popular form of secondary treatment in many states within the United States including Texas. According to the USEPA, only 1% of wastewater dischargers in Texas have total phosphorus discharge limits and are required to meet phosphorous removal limits (EPA, 2016). Activated sludge biosolids (AS-B) contain less total phosphorus than EBPR-B and Chem-P-B, but as noted by Lundin et al. (2004) and Jossa and Remy (2015), the phosphorous speciation may be more important than the total

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quantity of phosphorus present. The present study will fill this void and compare the GWP and eutrophication impacts of fertilizing Texas farmlands with commercially available fertilizer to the impacts associated with recovering phosphorus from AS-B, EBPR-B and Chem-P-B via three P recovery technologies: (1) struvite precipitation (AIRPREX), (2) acid leaching/struvite precipitation (Stuttgart process) and (3) acid thermal hydrolysis/ferric phosphate precipitation (KREPRO). To provide a basis for comparison, direct farm land application of dewatered biosolids as well composted biosolids followed by farm land application will be considered.

SCOPE AND METHODOLOGY:

This study estimates the life cycle impacts of producing and spreading 1 kilogram of phosphorus as P on agricultural farmland (LCA functional unit). The study area selected for this analysis is Texas, U.S. This selection influences the required travel distances from phosphorus mining grounds to fertilizer manufacture plants as well as distances from fertilizer manufacture and wastewater treatment plants to farmlands. Other geographical assumptions such as electricity mix, fuel mix, means of transport for materials are representative of the whole US. Our system boundary (Figure 16) includes the mining and manufacture of phosphorus fertilizer, wastewater treatment of sewage, composting, three phosphorus recovery technologies, farm land fertilization and landfill discard of spent biosolids. The packaging of fertilizers, capital infrastructure, wastewater collection

systems and production of food, beverages and other human consumption products are excluded.
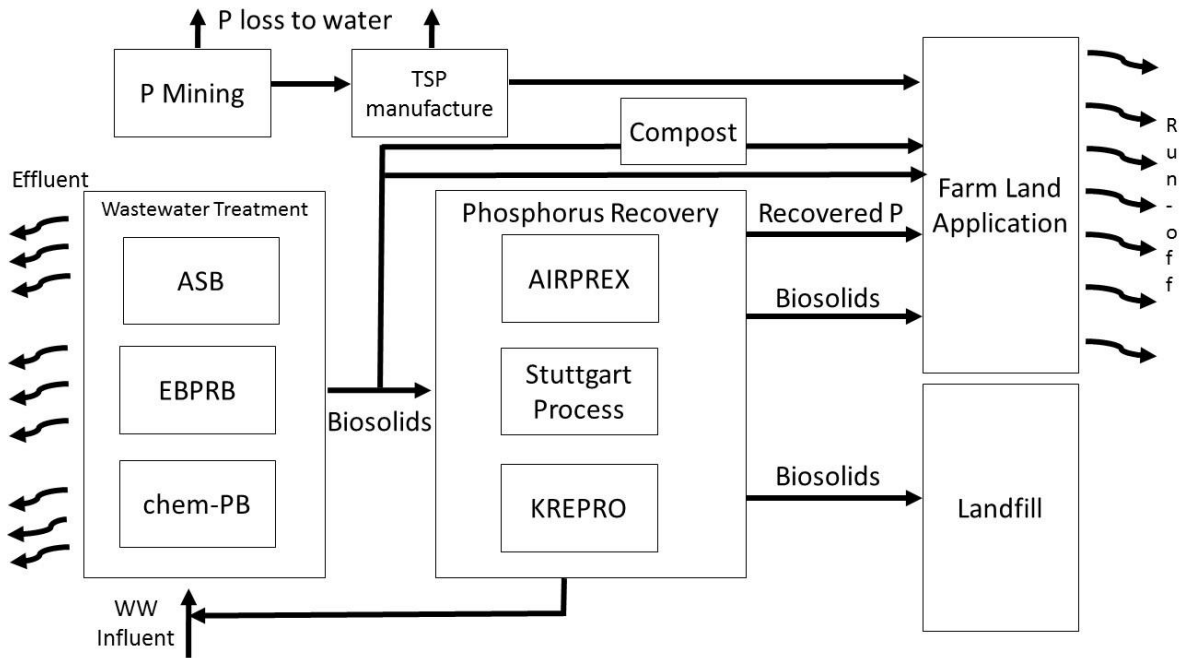
Figure 16. Processes involved in the supply of phosphorus for farm applications considered in this study.

We model structural uncertainty in phosphorous removal, recovery, and fate by defining 24 LCI scenarios that consist of all combinations of biosolids P source (i.e., biosolids from activated sludge plants (AS-B), as well as biosolids from plants that incorporate chemically enhanced P removal (Chem-P-B) and enhanced biological phosphorous phosphorus removal, EPBR-B), P-recovery technology (AIREPEX, Stuttgart Process, KREPRO, composting or none of these), and fate (farm land application or landfill).

The LCIA of each of the phosphorous recovery options from wastewater treatment plants were compared to a final scenario that represents the current baseline conditions for phosphorus supply to farmlands: the mining of virgin phosphorus to manufacture commercial triple superphosphate (TSP) fertilizer followed by farmland application. A summary of the scenarios considered for this study is presented in Table 17.

Table 17. Twenty-five phosphorus recovery scenarios considered in this study.

	Source of Phosphorus			
	AS-B	Chem-PB	EBPR-B	Mining
Dewatered Biosolids Direct Farm Land Application	(1) AS-B/FLA	(2) Chem-P-B/FLA	(3) EBPR-B/FLA	(25) TSP/FLA
Compost + Farm Land Application	(4) AS-B/C/FLA	(5) Chem-P-B/C/FLA	(6) EBPR-B/C/FLA	-
AIRPREX recovery + Farm Land Application	(7) AS-B/A/FLA	(8) Chem-P-B/A/FLA	(9) EBPR-B/A/FLA	-
AIRPREX recovery + Landfill	(10) AS-B/A/L	(11) Chem-P-B/A/L	(12) EBPR-B/A/L	-
Stuttgart Process Recovery + Farm Land Application	(13) AS-B/SP/FLA	(14) Chem-P-B/SP/FLA	(15) EBPRB/SP/FLA	-
Stuttgart Process Recovery + Landfill	(16) AS-B/SP/L	(17) Chem-P-B/SP/L	(18) EBPR-B/SP/L	-
KREPRO + Farm Land Application	(19) AS-B/K/FLA	(20) Chem-P-B/K/FLA	(21) EBPR-B/K/FLA	-
KREPRO + Landfill	(22) AS-B/K/L	(23) Chem-P-B/K/L	(24) EBPR-B/K/L	-

FLA= farm land application, C= Compost, A=AIRPREX, SP=Stuttgart Process, K=KREPRO, L = Landfill

Phosphorus Recovery Description and Assumptions:

The AIRPREX technology consists of a large batch reactor where sludge is aerated to strip CO_2 and increase the pH to over 8 (Stumpf et al. 2009). Magnesium chloride is supplied to maintain a molar $Mg:PO_4$ ratio slightly over 1:1 and precipitate struvite (Stumpf

et al. 2009, Uysal, 2010). Particles in the reactor are not removed until they reach a certain size, thus ensuring that phosphorus recovered is crystallized struvite and no other type of particles (Stumpf et al. 2009)

The Stuttgart technology consists of several batch steps. First the pH in the biosolids is decreased to pH 2 with sulfuric acid. At this pH all of the phosphorus bound to calcium, magnesium, aluminum and iron are dissolved in to the liquid phase (Güney et al. 2008). The biosolids are then dewatered and the liquid portion (sidestream) is transferred into a stirred batch reactor where citric acid is added to prevent precipitation of phosphorus with aluminum and iron. Subsequently, magnesium hydroxide and sodium hydroxide is added to increase the pH and supply magnesium for struvite precipitation (Antakyali et al. 2013).

Finally, the KREPRO technology, is another series of batch processes in which the biosolids are first acidified to pH 2 with sulfuric acid. Then the biosolids are heated to over just over 100 ℃ and at a pressure of 3.6 bar for 30 minutes (Hansen et al. 2000). The biosolids are then cooled and dewatered. The sidestream from dewatering (liquid portion) is utilized for ferric phosphate precipitation at pH 2.8.

Inventory.

The inventory is a list of materials, known as inputs, which are required to operate a certain process or to manufacture an item (i.e., electricity, heat, fuel, raw materials, etc.). It also lists the emissions and co-products, known as outputs of the process (i.e., CO_2, phosphorus, nitrogen, struvite, biosolids, etc.). The inventory lists the amount of each

material needed for the process and the emitted by the process divided by 1 kg of phosphorus, the chosen functional unit.

On average, most U.S. land-applied triple superphosphate (TSP) product is manufactured with a mixture of 56% domestic ore and 44% imported ore from Morocco (Mullins and Evans 1990, Vaccari, 2009). Transportation distances to Texas from Morocco (ocean freight) and Tampa, FL (rail / truck) are summarized in Table 18. Other life cycle inventory data summarized in Table 18 were obtained from Nemecek and Kagi (2007) and Linderholm et al. (2012).

Table 18. Inventory data for the production of commercial triple superphosphate (TSP). Values are normalized per kg of P produced.

	Amount	Reference
Input:		
Phosphorus Ore at Fertilizer Plant (kg)	3.4	Nemecek and Kagi 2007
Phosphoric Acid 70% (kg)	2.2	Nemecek and Kagi 2007
Natural Gas (m^3)	0.086	Nemecek and Kagi 2007
Electricity (MJ)	30	Linderholm et al. 2012
Transport ocean (km)	8600	Estimate/Sea-Distances.org
Transport Rail (km)	1500	Estimate/Google Maps
Transport truck (km)	80	Estimate/Google Maps
Outputs:		
Hydrogen Fluoride (kg)	0.00024	Nemecek and Kagi 2007
Heat (MJ)	6.2	Nemecek and Kagi 2007
Carbon Dioxide (kg)	1.5	Linderholm et al. 2012
Phosphorus (kg)	0.010	Nemecek and Kagi 2007

GPS-X (Hydromantis, Version 6.4), a wastewater process simulation, optimization and management tool, was used to simulate phosphorous removal from municipal wastewater and obtain energy requirements for the operation of wastewater treatment

plants as well as nitrogen and phosphorus releases into the environment. Concentrations of the influent wastewater constituents such as phosphorus, nitrogen, pH, BOD and others were obtained from historical data (City of Austin, 2016) from the Walnut Creek and South Austin Regional wastewater treatment plant located in Austin, TX (Appendix A).

Separate GPS-X simulations were performed assuming either conventional activated sludge, EBPR, or Chem-P removal in order to treat 13 million gallons a day of raw sewage (MGD). The average flowrate was selected to mimic the average flowrate of a single treatment "train" at Walnut Creek wastewater treatment plant in Austin, Tx (Paul, 2015). The conventional activated sludge plant was designed to meet the 1 day average of BOD (10 mg/L), TSS (15 mg/L) and NH_4 (2 mg/L as N) limits set for the local utility (City of Austin, 2016). The design consisted of a pumping station, aerated grit chambers, primary clarification, activated sludge, secondary clarification with waste and return sludge pumps, sand filter, chlorination/de-chlorination, gravity thickener, anaerobic digester and dewatering as displayed in Figure 17. The supernatant water from thickening and dewatering processes was returned to the primary clarifier and the methane produced by digestion was burned for electricity generation.
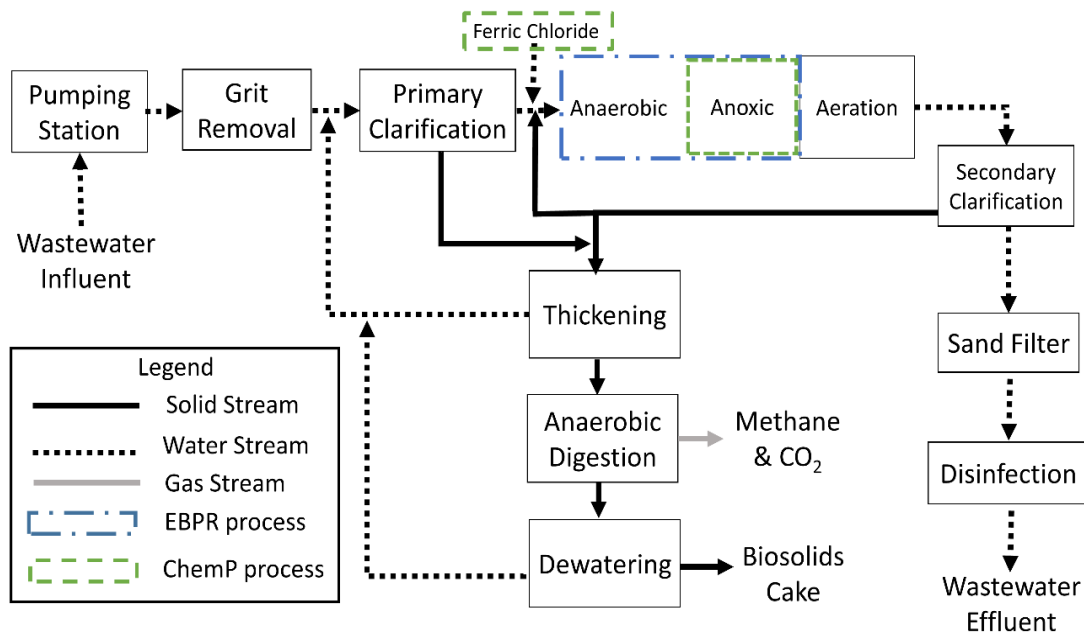
Figure 17. Flow diagram of the 13 MGD wastewater treatment plants modeled in GPS-X. The treatment processes highlighted in blue and green are exclusive to the EBPR and Chem P plants respectively.

The wastewater treatment plants with enhanced biological phosphorus removal (EBPR) and chemical (ferric chloride) phosphorus removal were designed to achieve daily average wastewater effluent concentrations of < 1, 2, and 20 mg/L of total phosphorus, ammonia and total nitrogen, respectively (TCEQ 2005, WMARSS 2008, TCEQ 2012, City of Austin 2016). These requirements were selected by reviewing permits for treatment plants with nitrogen limits as well as recommendations by the Texas Commission on Environmental Quality (TCEQ).

The wastewater treatment plant with chemical phosphorus removal was designed with the same unit processes as the conventional activated sludge plant but with slight modifications as shown in Figure 17. Phosphorus was removed from the effluent by

precipitation via ferric chloride addition before secondary clarification. Nitrogen limits were achieved by adding an anoxic completely mixed reactor after primary clarification and increasing the length of the activated sludge process. Pumping rates of return activated sludge were also increased. The nitrification process to remove ammonia consumed natural alkalinity in wastewater and soda ash was required to maintain an adequate pH in the anaerobic digester.

Biological removal of phosphorus was achieved via the anoxic-anaerobic-oxic (A2O) process (Tchobanoglous et al. 2004), which was implemented by adding anaerobic and anoxic completely mixed reactors after primary clarification. Higher pumping rates of return activated sludge were required to achieve the selected limits. Similarly as in chemical phosphorus removal, soda ash was required before anaerobic digestion. Other miscellaneous energy requirements to operate the treatment plants such as lighting, chlorine mixers, heating of anaerobic digesters, bar screens, and filtering were calculated according to a study by Burton (1996). The life cycle inventories for phosphorous removal in wastewater treatment plants are shown in Table 19.

Table 19. Inventory data for the treatment of wastewater and production of biosolids for all recovery technologies (land application, composting, AIRPREX etc.). Values are normalized by kg of P in the digested sludge.

	Amount per biosolid source		
	AS-B	Chem-P-B	EBPR-B
Input:			
Electricity (kw-h)	61	36	23
Electricity Generated (kw-h)	-4.8	-1.7	-1.0
Chlorine Gas (kg)	1.7	0.80	0.47
Soda Ash (kg)	-	7.3	4.4
Sulfur Dioxide (kg)	0.30	0.10	0.085
Ferric Chloride (kg)	-	6.1	-
Output:			
CO_2 (kg)	49	17	11
BOD (kg)	0.53	0.30	0.22
Phosphorus	1.2	0.0069	0.043
Ammonia (kg)	0.32	0.029	0.028
Nitrite (kg)	6.55	0.20	0.19
Nitrate (kg)	0	1.0	0.57

The inventory for the phosphorus recovery technology operations (AIRPREX, Stuttgart process and KREPRO), direct land application, composting and landfill disposal (shown in Table 20) was obtained from the published literature and the technology vendor manuals (Hansen et al. 2000, Suh and Rosseaux 2001, Linderholm et al. 2012, Jossa and Remy 2015, P-Rex 2015). The inventory published was modified to match the functional unit selected using unit conversions, data from GPS-X modeling or actual data shown in Chapter 3 and Chapter 4. For estimates of phosphorus runoff from soils after land application, the formula that relates water soluble phosphorus in dewatered biosolids with phosphorus leaching developed by Alleoni et al. 2008 was used. This inventory does not include long-life capital infrastructure requirements such as land use, additional reactor

construction, pump purchases etc. The application of struvite, compost and dewatered biosolids to farmlands displaces the use of some nitrogen fertilizer. Thus, the GWP and eutrophication potential required for nitrogen fertilizer manufacture was subtracted from scenarios that included farmland application of biosolids, compost farm land application or struvite land application.

After building the inventory, the 25 scenarios identified in Table 17 were coded in SimaPro (PRé sustainability, Version 7) and compared used the TRACI 2.1 method. This method was developed by the US Environmental Protection Agency (US EPA) and uses life cycle inventories coded into SimaPro (for example an X amount of phosphorus discharged by a wastewater treatment plant) to compute a life cycle impact which in this case is the eutrophication potential in kg of N equivalents (kg of N/ kg of P) and global warming potential in kg of CO_2 equivalents (kg of CO_2/kg of P). This computation is necessary in order to accurately compare the impact of ammonia releases versus those of phosphorus, or nitrates.

Table 20. Inventory data for the phosphorus recovery technologies studied. [a] The values are normalized by 1 kg of P recovered. [b] The values are normalized by 1 kg of P land applied.

	AS-B	CHEM-P-B	EBPR-B	Reference
Inputs:				
AIRPREX[a]				
Electricity (kw-h)	10	10	10	CNP 2015
$MgCl_2$ (kg)	15	15	15	CNP 2015
Stuttgart Process[a]				
Electricity (kw-h)	17	14	2.4	Jossa and Remy 2015

Table 20. Continued.

	AS-B	CHEM-P-B	EBPR-B	Reference
Sulfuric Acid 78% (kg)	32	26	4.4	Jossa and Remy 2015
Citric Acid 50% (kg)	17	18	3.1	Jossa and Remy 2015
$Mg(OH)_2$ (kg)	3.7	5.2	0.9	Jossa and Remy 2015
NaOH 50% (kg)	11	10	1.7	Jossa and Remy 2015
KREPRO[a]				
Electricity (kw-h)	48	22	11	Hansen et al. 2000
Sulfuric Acid 78% (kg)	21	9.5	5.0	Hansen et al. 2000
$Mg(OH)_2$ (kg)	1.2	0.6	0.3	Hansen et al. 2000
Ferric Chloride (kg)	40	19	10	Hansen et al. 2000
Compost[a]				
Electricity (kw-h)	3.0	1.2	1.3	Suh & Rosseaux 2001
Diesel (kg)	0.83	0.34	0.35	Suh & Rosseaux 2001
Land Application[b]				
Electricity (kg)	5.8	2.3	2.5	Hospido et al. 2005
Diesel (kg)	0.072	0.029	0.031	Hospido et al. 2005
Landfill[a] Transport (t-km) [AIRPREX]	160	340	27	Linderholm et al. 2012
Landfill[a] Transport (t-km) [Stuttgart Process]	26	36	6	Linderholm et al. 2012
Transport (t-km) [KREPRO]	21	9.5	5.0	Linderholm et al. 2012
Output: Struvite [AIRPREX & Stuttgart] [b]				
N fertilizer displaced (kg)	0.18	0.18	0.18	Linderholm et al. 2012

Table 20. Continued.

	AS-B	CHEM-P-B	EBPR-B	Reference
P (kg) [runoff]	0.010	0.010	0.010	Alleoni et al. 2008
N (kg) [runoff]	0.0087	0.0087	0.0087	Rahman et al. 2011
Ferric Phosphate [KREPRO][b]				
N fertilizer displaced (kg)	0	0	0	
P (kg) [runoff]	0	0	0	Estimate
N (kg) [runoff]	0	0	0	
Land Application [Composted Solids][b]				
N fertilizer displaced (kg)	1	0.30	0.40	Linderholm et al. 2012
P (kg) [runoff]	0.011	0.011	0.026	Brandt et al. 2004 and Chinault & Alleoni et al. 2008
N (kg) [runoff]	0.17	0.056	0.071	Knowles et al. 2011
Methane (kg)	0.320	0.130	0.130	Hospido et al. 2005
Land Application [Dewatered Solids][b]				
N fertilizer displaced (kg)	1.0	0.30	0.40	Linderholm et al. 2012
P (kg) [runoff]	0.013	0.012	0.10	Alleoni et al. 2008
N (kg) [runoff]	0.17	0.056	0.071	Knowles et al. 2011
Methane (kg)	0.32	0.13	0.13	Hospido et al. 2005
Landfill[b]				
Methane (kg) [AIRPREX]	2.6	5.5	0.4	Hong et al. 2009
Methane (kg)[Stuttgart Process]	0.41	0.58	0.09	Hong et al. 2009
Methane (kg) [KREPRO]	0.33	0.15	0.08	Hong et al. 2009

All phosphorus recovery technologies decrease the phosphorus concentrations in dewatering sidestreams that are ultimately returned to the headworks (Jossa and Remy 2015). The phosphorus and nitrogen concentrations in these sidestream were manually decreased in the GPS-X model to account for this effect. It is possible that decreasing the phosphorous concentrations of the sidestream returned to the headworks will, in turn, reduce the phosphorus recovered in the sewage biosolids. However, this possibility was not considered in the current analysis.

RESULTS AND DISCUSSION:

Eutrophication potential and global warming potential of each of the constructed scenarios were evaluated separately and measured in terms of equivalent kg of N and equivalent kg of CO_2 respectively. Contributions from each individual process (i.e., treatment plant operation effluents, run-off from farmland application, electricity for wastewater treatment, chemical supply etc.) were separated in order to identify the largest contributor. The eutrophication potential (Figure 18a) from conventional fertilizer triple superphosphate + farmland application (TSP/FLA) of 4 kg of N equivalents per kg of P is provided as a baseline for comparison of the other scenarios. 99% of the eutrophication potential of the TSP/FLA scenario is associated with run-off from farmlands.

The most noticeable observation from the results presented in Figure 18 is that phosphorous recovery from biosolids generated in a conventional activated sludge wastewater treatment plant are significantly greater than wastewater plants with EBPR or chemical phosphorous removal, regardless of the recovery technology, but for several of

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the scenarios, lower eutrophication potentials are predicted for conventional activated sludge compared to the baseline TSP case. Conventional activated sludge has a much larger contribution to eutrophication from the AS wastewater effluents than either EPBR or CHEM-P. These values reflect the difference in the ability to capture P within the wastewater treatment plants; AS treatment simulation effluents achieved a 4 mg/L P daily average effluent versus the 0.6 and 0.06 mg/L achieved by EBPR and Chem-P plants respectively.
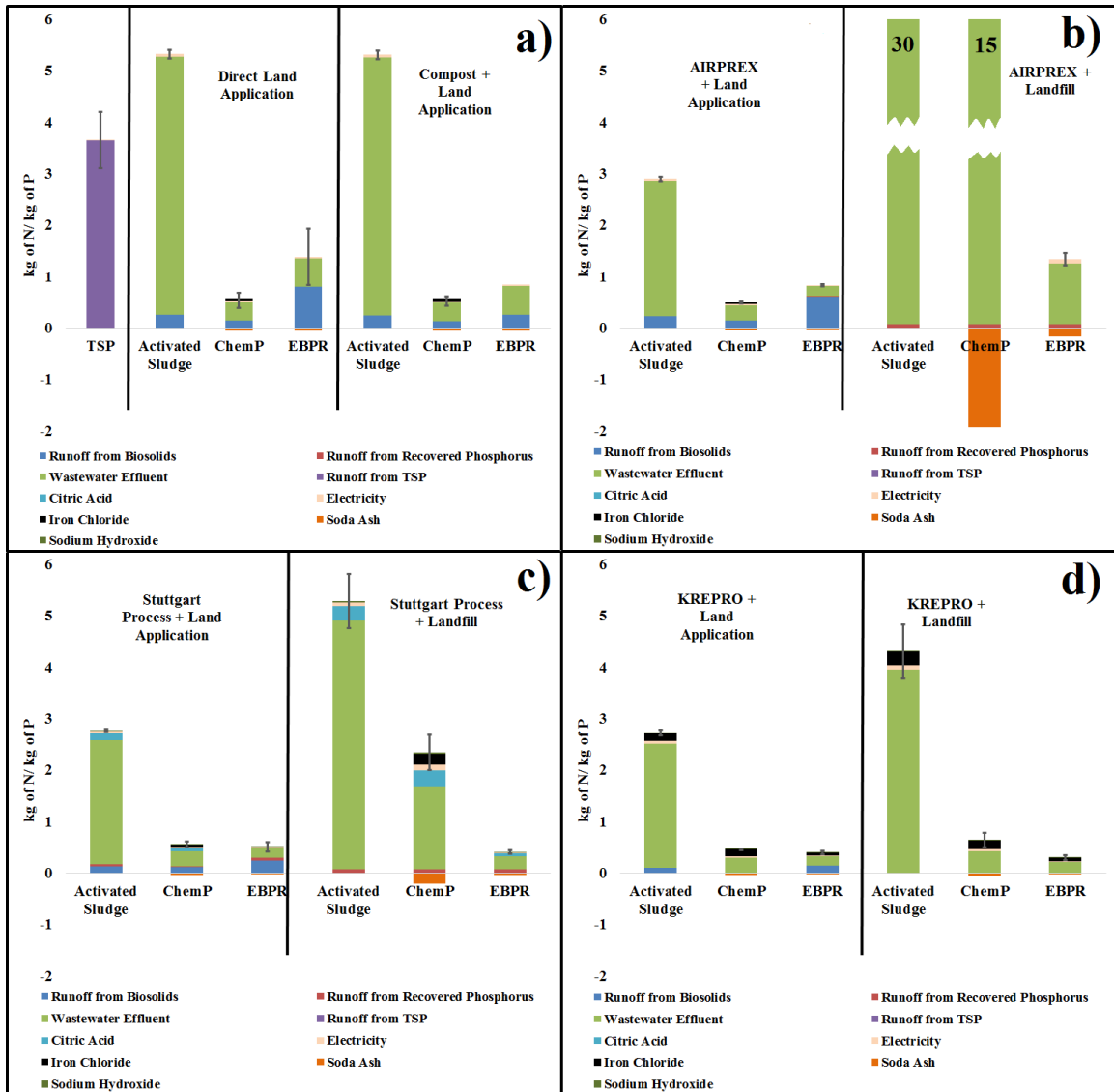
Figure 18. Eutrophication potential (measured as equivalent kg of N) for each of the 25 modeled scenarios. a) Commercial fertilizer scenario, direct land application or compost + land application scenarios (No phosphorus recovery) b) AIPREX phosphorus recovery scenarios, c) Stuttgart phosphorus recovery scenarios d) KREPRO phosphorus recovery scenarios.

Another important factor influencing the eutrophication potentials is the amount of phosphorus originally captured in the digested biosolids that is ultimately delivered to farmland soils via each scenario (the efficiency of recovery of each process). Table 21

summarizes the amount of phosphorus present in the digested biosolids that is delivered to farmlands in an inorganic form or in biosolids form via each of the modeled scenarios. The greater the amount of phosphorus that ultimately is delivered to farmlands, the lower the eutrophication potential. For example, scenario (7) AS-B/AIRPREX/Farmland Application produces an eutrophication potential of 2.9 kg of N equivalents and scenario (10) AS-B/AIRPREX/Landfill produces an eutrophication potential of 30 kg of N equivalents. In both scenarios, the same amount of phosphorus is contained within the digested biosolids after wastewater treatment (TP = 16 mg as P/g of dry solids). After recovery of phosphorus via AIRPREX, 7.8% of the TP is in struvite form while 64% of the TP is still within the biosolids. However, in scenario (7) AS-B/A/FLA both struvite (7.8% of TP = 1.3 mg/g) and biosolids (64% of TP = 10 mg/g) are delivered to farmlands, on the other hand, in scenario (10) AS-B/A/L only struvite is delivered to farmlands (7.8% of TP = 1.3 mg/g).

Another way to think about this would be in terms of phosphorus demand. For instance, if a hypothetical farm requires 1 kg of phosphorus to fertilize their crops (regardless if it is contained in biosolids or struvite). In scenario (7) AS-B/AIRPREX/Farmland Application, 90 kg of digested biosolids would be necessary to supply this demand. Conversely, for scenario (10)AS-B/A/L, 800 kg of digested sludge would be required to supply this demand since only struvite is used for agricultural purposes and the phosphorus contained in the biosolids are wasted to the landfill. Producing 10 times more digested sludge in turn increases eutrophication potential.

Table 21. The percentage of total phosphorus present in digested biosolids that is delivered to Texas farmlands in an inorganic form (struvite or ferric phosphate) or as biosolids.

Scenario	Recovery Technology	Disposal of spent biosolids	Total P in Digested Biosolids (mg/g)	Percentage of total P delivered to farmland	
				Inorganic (%)	Biosolids (%)
(1)AS-B/FLA	None	Land Application	16 ± 7	0	64
(2)Chem-P-B/FLA	None	Land Application	29 ± 5	0	48
(3)EBPR-B/FLA	None	Land Application	29 ± 5	0	86
(4)AS-B/C/FLA	None	Land Application	16 ± 7	0	64
(5)Chem-P-B/C/FLA	None	Land Application	29 ± 5	0	48
(6)EBPR-B/C/FLA	None	Land Application	29 ± 5	0	86
(7)AS-B/A/FLA	AIRPREX	Land Application	16 ± 7	7.8	64
(8)Chem-P- B/A/FLA	AIRPREX	Land Application	29 ± 5	2.0	48
(9)EBPRB/A/FLA	AIRPREX	Land Application	29 ± 5	15	86
(10)AS-B/A/L	AIRPREX	Landfill	16 ± 7	7.8	0
(11)Chem-P-B/A/L	AIRPREX	Landfill	29 ± 5	2.0	0
(12)EBPR-B/A/L	AIRPREX	Landfill	29 ± 5	15	0
(13)ASB/SP/FLA	Stuttgart	Land Application	16 ± 7	50	50
(14)Chem-P-B/SP/FLA	Stuttgart	Land Application	29 ± 5	19	81
(15)EBPR-B/SP/FLA	Stuttgart	Land Application	29 ± 5	69	31
(16)AS-B/SP/L	Stuttgart	Landfill	16 ± 7	50	0
(17)Chem-P-B/SP/L	Stuttgart	Landfill	29 ± 5	19	0
(18)EBPR-B/SP/L	Stuttgart	Landfill	29 ± 5	69	0
(19)AS-B/K/FLA	KREPRO	Land Application	16 ± 7	61	39
(20)Chem-P-B/K/FLA	KREPRO	Land Application	29 ± 5	72	28
(21)EBPR-B/K/FLA	KREPRO	Land Application	29 ± 5	81	19
(22)AS-B/K/L	KREPRO	Landfill	16 ± 7	61	0
(23)Chem-P-B/K/L	KREPRO	Landfill	29 ± 5	72	0
(24)EBPR-B/K/L	KREPRO	Landfill	29 ± 5	81	0

FLA= farm land application, C= Compost, A=AIRPREX, SP=Stuttgart Process, K=KREPRO, L = Landfill

Scenarios ASB/A/L and Chem-PB/A/L, which have the lowest amount of total phosphorus in digested biosolids delivered to farmlands (Table 21), also have the highest eutrophication potential per kg P delivered (Figure 18b). For the same reason, other

scenarios that utilize landfilling as the final disposal option have higher eutrophication potentials than those with farm land application as the final destination. The only exceptions to this trend are scenarios that utilize EBPR-B because high quantities of phosphorus are recovered in the biosolids using any of the three P recovery technologies (e.g., AIRPREX, Stuttgart Process or KREPRO) and thus the majority of this phosphorus is delivered to the farmland.

The direct application of biosolids or composted biosolids to farmlands (Figure 18a) represents the current operation of over half the treatment plants in the US (NEBRA, 2007). The model results indicate that with the exception of the EBPR plants, eutrophication impacts of the P released via wastewater effluents are greater than the impacts of the runoff containing phosphorus and nitrogen that are generated from the land applied biosolids. The Chem-P-B scenarios summarized in Figure 18a have lower eutrophication impacts than the other two P-removal alternatives because the phosphorus present in these biosolids is tightly bound by the iron and will not leach into streams when applied to farmlands (Soon and Bates 1982, Maguire et al. 2001, O'Connor et al. 2004, Rittman et al. 2011). Finally, it is important to note that in Figure 18a only the scenarios utilizing AS-B have higher predicted eutrophication potentials than the commercial triple superphosphate (TSP) scenario.

P Recovery Scenarios Coupled to Farmland Application (FIG 18 b, c, d left-half):

An examination of the combination of AIRPREX with direct land application of spent biosolids (Figure 18b left-half), reveals a eutrophication benefit of using AIRPREX

relative to the P-recovery options in Figure 18a (direct land application or composting followed by land application). The reason for this result is that dewatered supernatants contain dissolved phosphorus (Chapter 4, GPS-X simulation – Appendix B). By utilizing the AIRPREX process before dewatering, dissolved phosphorus is removed and less phosphorus is returned to the headworks of the treatment plant which decreases the phosphorous concentration in the wastewater effluent. However, for the Chem-P-B biosolids (Figure 18b – left-half), the eutrophication potential after the AIRPREX process remains almost the same relative to direct land application of Chem-P-B. A very small amount of the total phosphorus is actually recovered from the Chem-P-B sludge by AIRPREX (2.0%, Chapter 4) so there is no eutrophication benefit of using AIRPREX on biosolids produced at WWTPs that incorporate chemical phosphorus removal. A similar trend is observed when the Stuttgart process is coupled with farm land application (Figure 18c – left-half). The eutrophication potential is reduced relative to the scenarios in Figures 3a except for scenario Chem-PP-B/SP/FLA.

For scenarios with KREPRO paired with farmland application of spent biosolids (Figure 18d – left) the decrease in eutrophication potential is minimal and the advantage of these scenarios over the Stuttgart Process scenarios (Figure 18c) will depend on the GWP and economics of recovering greater quantities of phosphorus. All scenarios coupled with farmland application produced lower eutrophication potentials than the conventional fertilizer TSP scenario (TSP/FLA – Figure 18d).

As noted above, the effects of decreasing phosphorus and nitrogen concentrations in dewatering sidestreams are complex. Return flows can be a significant portion of the

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influent nutrient load to a wastewater treatment plant (Lawler and Singer 1985). Thus, decreasing nutrient concentrations in sidestreams can also decrease the total phosphorus concentration in the biosolids and this in turn decrease efficiency of recovery. This complexity was not incorporated in the LCIA model for this study but should be considered for future studies.

P Recovery Scenarios Coupled with Landfill Disposal (FIG 18 b, c, d right-half):

Switching from farmland application to landfill disposal increases the eutrophication potential of the scenarios ASB/SP/L and Chem-P/SP/L greatly because 50% and 81% of the total biosolids phosphorus contained in the biosolids produced in the wastewater treatment plant is wasted to the landfill respectively. Thus, more struvite has to be produced to cover a hypothetical demand of phosphorus. The one exception is EBPRB/SP/L because almost 70% of the phosphorus is recovered via the Stuttgart technology when EBPR-B is used.

The eutrophication potential for scenario Chem-P-B/K/L (Figure 18d – right-half) improves significantly from scenario Chem-P-B/SP/L (Figure 18c – right-half). The reason for this result is that for Chem-P-B, the P recovery quadruples when switching from the Stuttgart process to KREPRO (P-recovery increases from 19% to 72%, Chapter 4) thus, less digested biosolids are required to meet a 1kg demand.

The majority of scenarios modeled in this LCIA have a lower eutrophication potential than using TSP as a source for phosphorus in farmlands. The exceptions are

typically scenarios that involve conventional activated sludge wastewater treatment plants that discharge higher concentrations of phosphorus in their effluents.

It is important to note that all the costs of recovering phosphorus (energy, chemicals, manpower) are generally assumed by the wastewater treatment plant, and reducing the eutrophication potential may not be of direct benefit to the utility in terms of economic compensation. This however, may not be true in some areas of the US where eutrophication problems are of significant concern (e.g., Chesapeake Bay, Tar-Pamlico river basin, Mississippi basin at the Gulf of Mexico). Amendments to the Clean Water Act in 1987 allow States to design nutrient management plans on a "watershed-by-watershed basis" instead of a "discharger-by-discharger" basis (Letson 1992). In other words, the sum of all the nutrient discharges per day within a particular watershed has to be lower than the maximum amount a water body can receive and still maintain water quality standards (i.e., the total maximum daily load or TMDL). TMDLs have to be met regardless of whether if discharges occur at point sources or non-point sources. States allocate portions of the TMDL to point sources and non-point sources within a given watershed, but they are allowed to trade amongst each other their "unused" portion of the TMDL (Sadler et al. 2014). This means that if a treatment plant invests energy and chemicals in recovering phosphorus from wastewater biosolids, it can recover the investment by trading the nutrient discharge it reduced with other discharge sources in the watershed. For example, nutrient recovery scenario 19 (AS-B/K/FLA in Table 17) requires economic investment to cover the cost of chemicals for phosphorus precipitation, energy for thermal hydrolysis and acids for pH control. However, the eutrophication potential is reduced compared to Scenario 1

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(AS-B/FLA). The nutrient reduction can then be sold to farmers with nutrient rich runoff and, in this way, the economic feasibility of phosphorus recovery can be improved. Although nutrient trading can make phosphorus recovery more attractive to some utilities, the GWP of these technologies would still need to be addressed.

Global Warming Potential

The results presented in Figure 19 show that even though the manufacture of triple superphosphate requires mining and transport of raw materials across the Atlantic, this process has less of a predicted GWP than all the other scenarios examined. The reason for this result is that the raw material, in this case phosphate rock, is a more concentrated source of orthophosphate than wastewater biosolids. Phosphate rock has a 30% P_2O_5 concentration of orthophosphate (Villalba et al. 2008), whereas AS-B, Chem-PB and EBRPR-B have concentrations of 2.1, 1.2, 4.6 % P_2O_5 respectively (Chapter 4). Thus, minimum processing (energy + chemicals) is required to release phosphorus from phosphate rock and produce fertilizers (i.e., greater quantities of commercial fertilizer per unit energy input). It is important to note that the GWP does not address the fact that as phosphate rock reserves deplete they also decrease in quality (Cornell and White 2011) and thus more energy and chemicals will be required to produce the same amount of phosphorus in the future.
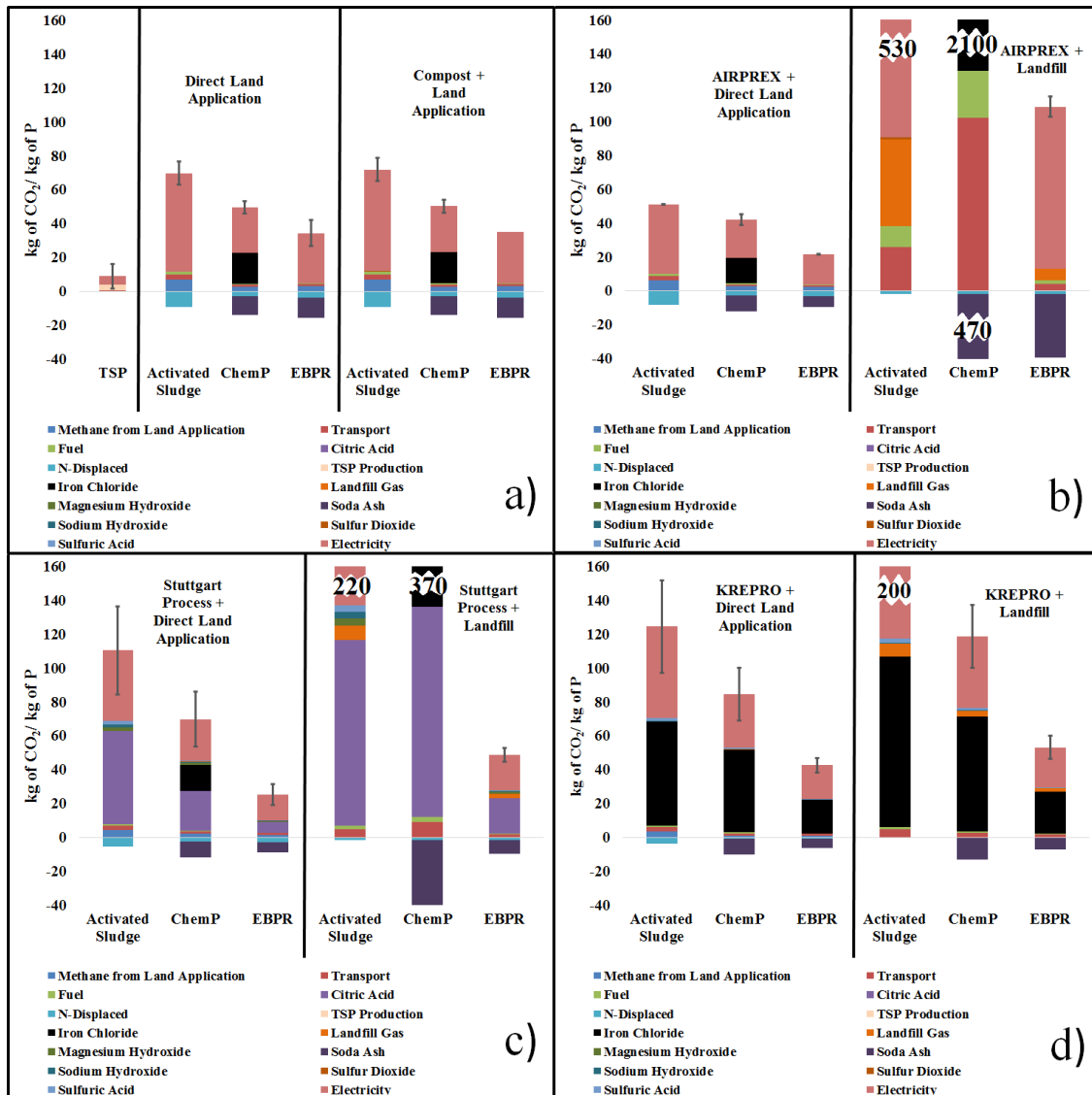
Figure 19. Global warming impact results (measured as equivalent kg of CO_2) for the 25 scenarios examined in this study. a) Commercial fertilizer, direct land application or compost + land application scenarios (No phosphorus recovery) b) AIPREX phosphorus recovery scenarios, c) Stuttgart phosphorus recovery scenarios d) KREPRO phosphorus recovery scenarios.

The global warming impact of electricity generation is the process that contributes the most to the overall GWP predicted for the direct and compost land application scenarios

(Figure 19a). This impact decreases when Chem-P-B and EBPR-B are used as the wastewater treatment process instead of AS-B. Similarly, as observed for the eutrophication impacts for each scenarios, the main factor that controls the global warming results is the amount of total phosphorus originally present in the digested biosolids that are delivered to farmlands (Table 21).

P Recovery Scenarios Coupled with farmland application (FIG 19 b, c, d left-half)

Scenarios that combine AIRPREX and farm land application of the spent biosolids (Figure 19b – left-half) seem to decrease global warming potential (GWP) relative to the direct land application (or composting followed by land application) scenarios presented in Figure 19a. The AIRPREX process takes advantage of the dissolved orthophosphate that otherwise would be returned to the wastewater treatment without using high quantities of chemicals or energy. In addition, the phosphorus remaining inside the spent biosolids can be utilized for farm land application.

The results from scenarios employing the Stuttgart Process (Figure 19c – left-half) show that the GWP increases, when compared to the direct land application and compost land application scenarios depicted in Figure 19a. The exception is EBPR-B/SP/FLA where the GWP is predicted to decrease slightly. The main contribution to the GWP in these scenarios is the electricity required for wastewater treatment and the material requirements for citric acid production (needed in the Stuttgart process). This means that in order to recover greater quantities of P in the inorganic form through the Stuttgart process, it is necessary to increase the GWP impact over that generated by the currently

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available methods of direct farmland application and composting. It is important to note that the LCI of citric acid required for the Stuttgart process was based on pilot tests recovering phosphorus from Chem-PB (Antakyali et al. 2013). It is likely that AS-B and EBPR-B will have a much lower citric acid LCI than what it was used in this study, but the current LCI gives us a good starting point for comparison.

Similar results as those described for the Stuttgart Process can be observed for the KREPRO scenarios (Figure 19d – left-side). The difference is that the production of Iron (III) chloride used for precipitation of phosphorus replaces the citric acid GWP observed with the Stuttgart technology. Again, it should be noted that the LCI were obtained from pilot tests of phosphorus recovered from Chem-PB (Hansen et al. 2000) and they will possibly be slightly lower for AS-B and EBPR. These results suggests that to reduce the GWP of the Stuttgart and KREPRO technologies , it would be worthwhile to develop sustainable chelating sources (for example *Aspergillus Niger* derived citric acid, Dhillon et al. 2011) and precipitation chemicals (for example Tobermorite from wastes generated in the construction industry, Berg et al. 2003).

P Recovery scenarios coupled with landfill disposal (FIG 19 b, c, d right-half):

For scenarios that dispose biosolids to a landfill (Figure 19 b, c, d – right-half), the GWP increases significantly due to the low quantities of phosphorus recovered from digested biosolids (struvite and ferric phosphate) that are ultimately delivered to farmlands (Table 21). Scenarios with AIRPREX recovery + landfill disposal produce the highest GWP from all landfill scenarios. As P-recovery is increased by advanced recovery

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technologies, such as the Stuttgart and KREPRO technologies, the GWPs decrease significantly. These results suggest that for treatment in municipalities where landfill disposal is the only option, the recovery technologies with the highest phosphorus recovery would be more appropriate for taking advantage of the energy imputed during wastewater treatment. Indeed, none of the scenarios with landfill disposal produce GWPs lower than direct farmland application or compost + farmland application scenarios shown in Figure 19a.

Additional research is still required to confirm that land application is still possible after harsh technologies such as the Stuttgart Process and KREPRO. The biosolids will have a more balanced $N:P_2O_5$ ratio as shown in Chapter 4, but the impact of citric acid, sulfuric acid and other chemicals on plant uptake requires further research.

CONCLUSIONS:

The study presented in this paper performed a comprehensive life cycle assessment of the current state of phosphorus recovery (direct farmland application, compost + land application and AIRPREX) as well as more advanced recovery technologies still under development (KREPRO and Stuttgart Process). The recovery of phosphorus from conventional activated sludge was considered for the first time in an LCIA. Also for the first time, eutrophication potential due to phosphorus run-off from applied biosolids to farmlands was considered. After completing the impact assessment of the 25 constructed scenarios, the following conclusions can be drawn:

- The wastewater effluent is the biggest source of eutrophication potential for all scenarios except for commercial fertilizers + land application (TSP/FLA) where runoff from farmlands is the greatest source.

- The energy used for wastewater treatment and recovery processes as well as the chemicals associated with the recovery technologies were the largest source of global warming potential (GWP) in all scenarios.

- When using conventional activated sludge biosolids (AS-B) as a source of phosphorus for recovery, all three phosphorus recovery technologies (AIRPREX, Stuttgart process and KREPRO) coupled with land application have lower eutrophication potentials than direct or compost farmland application scenarios. However, AIRPREX + land application is the only option that decreases GWP from compost and direct land application.

- If EBPR-B is the source of phosphorus, the best option is to use the Stuttgart process with land application. Even though the KREPRO process can recover over 80% of the total phosphorus versus the 70% recovered by the Stuttgart technology (Chapter 4), the energy requirements and use of ferric chloride to precipitate phosphorus yield slightly higher GWPs. These results might vary if a better estimation for the LCI of citric acid is obtained.

- The use of landfills for disposing spent biosolids after phosphorus recovery is not a viable option for reducing GWP or eutrophication potential.

- The TSP/FLA scenario had a very high impact on eutrophication due to its water solubility which means a large portion of the phosphorus manufactured is lost to

runoff. However, its solubility is precisely the reason why it is preferred for high yield farming. More research is required to find a balanced wastewater derived product that has lower water solubility than TSP but high plant uptake. TSP production has the lowest GWP because the source of phosphorus is highly concentrated. Still, the results in this study do not address the issue of depleting a non-renewable resource or reflect the impact of a change in phosphorus rock quality and economic dynamics of one commodity (phosphorus) versus the other (energy). These questions should be answered in future studies employing a different inventory.

Chapter 6: Conclusions

The main goal of this research was to determine and understand phosphorus speciation in different types of municipal wastewater treatment biosolids in order to evaluate recovery and reuse strategies. To this end, nine wastewater treatment plants were sampled and the speciation within the biosolids was determined using a speciation protocol that distinguishes orthophosphate, polyphosphate and organic phosphorus in liquid and solid phases. The effects of thickening and anaerobic digestion on the speciation of phosphorus within biosolids generated at conventional activated sludge was examined in Chapter 3. By employing the data collected on phosphorus speciation in both biosolids and sidestreams from a range of wastewater treatment plants and technology performance information from published literature, phosphorus recovery and N: P_2O_5 biosolids ratios were estimated for three different recovery technologies in Chapter 4. Finally in Chapter 5, a life-cycle analysis was performed to determine the environmental impact of 25 different combinations of wastewater treatment, process recovery technology and end use or disposal option.

The main conclusions from Chapters 3 and 4 address phosphorus speciation of biosolids and sidestreams for a range of treatment plant configurations, P recovery from application of different technologies to these biosolids, and suitability for land application:

- Biosolids generated from wastewater treatment plants that incorporate chemical phosphorus removal (Chem) or enhanced biological phosphorus removal (EBPR) contain greater quantities of phosphorus (per gram of dry solids) than biosolids generated from conventional activated sludge plants (AS).

- The dominant phosphorus species in the biosolids generated from plants with chemical phosphorus removal were polyphosphates and not particulate phosphorus as intuition would suggest.

- After digestion, the highest concentration of phosphorus was in the particulate orthophosphate species for biosolids generated from EBPR plants as well as for biosolids generated from conventional AS treatment plants.

- Despite substantial variability observed in the orthophosphate concentration of thickening sidestreams, it is possible to conclude that sidestreams from the thickeners are not suitable for recovery of phosphorus. They do not exceed the required dissolved concentration for economic feasibility (20 mg/L). The exception were sidestreams from plant chemical phosphorus removal plant #1.

- Using the AIRPREX phosphorus recovery technology, there is a potential to recover between 2% and 15% of the total P present in the biosolids, although the level of P recovery possible will depend on the type of phosphorus removal processes used at the wastewater treatment plant. However, regardless of the type of wastewater treatment plant, there is no significant change in the $N:P_2O_5$ ratio of the spent biosolids after phosphorus recovery.

- The recovery potential using the Stuttgart phosphorus recovery technology is higher than for the AIRPREX technology. There were significant increases in the $N:P_2O_5$ ratio of undigested and digested AS biosolids as well as digested EBPR biosolids for the Stuttgart technology which enhances its suitability for land application.

- With the KREPRO technology, the recovery potential is greater than with the other two technologies (50% for all types of biosolids). Also, there is a significant increase of the N:P$_2$O$_5$ ratio for all spent biosolids.

Technologies such as Stuttgart and KREPRO are in theory better alternatives than the commercially available AIRPREX; however, the environmental feasibility of these approaches may limit their application. The life cycle impact assessment performed in Chapter 5 compared the global warming potential (GWP) and eutrophication impacts of fertilizing Texas farmlands with commercially available fertilizer (baseline case) to the impacts associated with recovering phosphorus from selected wastewater biosolids and the three P recovery technologies described above. To provide a basis for comparison, direct farm land application of dewatered biosolids as well composted biosolids followed by farm land application was considered. The LCIA analysis in Chapter 5 produced the following conclusions:

- Wastewater effluents discharges to water bodies are the largest source of eutrophication potential of all the processes studied.

- The energy used for wastewater treatment and recovery processes as well as the chemicals associated with the recovery technologies were the largest sources of GWP in all scenarios.

- All three recovery technologies (AIRPREX, Stuttgart process and KREPRO) coupled with land application have lower eutrophication potentials than direct (or compost) farmland application when utilizing AS-B as a phosphorus source.

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- If EBPR biosolids are available for phosphorus recovery, the best overall option in terms of both GWP and eutrophication potential is to use the Stuttgart process and dispose of the biosolids via land application. Even if the KREPRO can recover higher quantities of phosphorus, the energy requirements of thermal hydrolysis and the manufacture of ferric chloride make this process less desirable in terms of its impact on global warming potential.

- Land application of both ferric phosphate and struvite produce less eutrophication than application of commercial triple super phosphate (TSP). TSP is more water soluble than struvite and ferric phosphate which increases its eutrophication potential.

- Production of TSP has a very low global warming potential since the source of phosphorus (phosphate rock) is highly concentrated.

Results from this doctoral work serve as a starting point for employing phosphorus speciation to select phosphorus recovery technologies that are matched to specific wastewater and biosolids treatment processes. The research also provides a LCIA tool that can be used to quantify the impacts of global warming and eutrophication for different wastewater treatment, P recovery and disposal or reuse scenarios. As phosphorus sources are depleted, the footprint of various scenarios are likely to change, especially with respect to energy utilization and global warming potential.

RECOMMENDATIONS FOR FUTURE WORK

The work presented in this dissertation provides a framework for further research utilizing phosphorus speciation for process and technology selection. The findings of this research highlight a number of avenues for future research that could be combined with the results presented here to validate the conclusions and refine the LCIA. As more data are available on speciation of P within different thickening processes and varying digester operating parameters, statistical analysis of these larger data sets can be used to corroborate or invalidate the findings from this work. Future research should also verify the assumptions made regarding the P recovery technologies, especially for the technologies that have not been applied at field scale. In addition, other novel technologies should be compared within the LCIA framework.

Several specific recommendations for selecting additional treatment options to study include plants employing chemical phosphorus removal without biological nitrogen removal, different EBPR configurations and thermal hydrolysis. It is possible that higher concentrations of particulate orthophosphate and lower concentrations of polyphosphates will be observed in the absence of nitrogen removal so including plants without nitrogen removal is a high priority.

The effects of polyelectrolytes on the phosphorus speciation of dewatering & thickening sidestreams also requires further study. CNP-tech (Hamburg, Germany) the company in charge of the commercialization of the AIRPREX process claim a reduction of dewatering polyelectrolyte when using their technology of phosphorus recovery (CNP,

2016). However, no published literature is available to date that explains the mechanism by which dissolved orthophosphate inhibits sludge dewatering.

Finally, the effects of spent biosolids from the KREPRO and Stuttgart technologies on crop growth needs to be evaluated. Both the KREPRO and Stuttgart technologies utilize strong acids and chemicals for the recovery of phosphorus. These may have an impact on plant uptake of phosphorus within the spent biosolids.

Appendix A

Table 22. Summary of phosphorus concentrations before and after anaerobic digestion of the sampled treatment plants.

	Day 1		Day 2		Day 3	
	Undigested	Digested	Undigested	Digested	Undigested	Digested
	Dissolve Orthophosphate (mg/g)					
AS2	1.28	1.03	0.67	1.03	-	-
AS4	0.97	1.19	0.67	1.07	0.89	1.64
AS5	1.94	1.28	0.82	0.12	0.74	0.36
EBPR1	0.6	3.01	1.11	3.48	1.89	3.68
	Particulate Orthophosphate (mg/g)					
AS2	3.9	9.42	3.34	9.53	-	-
AS4	2.78	3.22	3.07	3.16	3.05	2.14
AS5	2.49	5.13	0.47	3.83	3.14	5.35
EBPR1	3.1	10.82	1.97	11.16	1.13	10.62
	Total Polyphosphate (mg/g)					
AS2	6.23	4.49	5.32	0	-	-
AS4	1.76	0.48	2.46	0.93	2.5	0.36
AS5	3.59	4.65	5.1	4.68	6.4	4.3
EBPR1	10.78	4.21	8.65	3.05	16.08	4.76
	Total Organic phosphates (mg/g)					
AS2	2.34	1.35	4.79	0.96	-	-
AS4	4.05	6.15	5.67	4.7	3.38	3.07
AS5	3.65	2.32	5.4	0.19	4.7	1.8
EBPR1	6.44	2.6	7.46	0	4.04	3.93

Table 23. Summary of the Potassium, Calcium and Magnesium concentrations before and after digestion.

	Day 1		Day 2		Day 3	
	Undigested	Digested	Undigested	Digested	Undigested	Digested
Dissolved Potassium (mg/L)						
AS2	54	69	30	61		
AS4	20	128	18	120	22	130
AS5			52	80	52	77
EBPR1	16	128	15	128	14	136
Dissolved Calcium (mg/L)						
AS2	78	104	66	104		
AS4	26	120	22	104	36	128
AS5			426	241	419	192
EBPR1	82	83	96	88	110	84
Dissolved Magnesium (mg/L)						
AS2	26	30	12	27		
AS4	4	25	3	30	6	24
AS5			96	78	105	76
EBPR1	6	42	6	40	5	99

Table 24. Summary of phosphorus concentrations before and after thickening for the sampled treatment plants.

	Day 1		Day 2		Day 3	
	Pre-Thickening	Post-Thickening	Pre-Thickening	Post-Thickening	Pre-Thickening	Post-Thickening
	Dissolved Orthophosphate (mg/g)					
AS1	0.67	1.18	1.49	1.63	0.97	2.26
AS2	0.94	2.93	0.78	1.15	-	-
AS3	0.9	1.69	0.76	1.67	0.89	1.92
AS4	0.8	0.97	0.83	0.67	0.81	0.89
AS5	0.92	1.83	1.15	0.82	1.16	0.74
EBPR2	0.90	6.88	0.60	4.21	1.10	3.16
	Particulate Orthophosphate (mg/g)					
AS1	3.07	3.04	2.3	3.34	3.43	4.91
AS2	5.68	6.59	7.26	5.79	-	-
AS3	1.4	1.49	2.6	1.56	1.39	1.57
AS4	2.06	2.78	2.21	3.07	2.5	3.05
AS5	4.0	2.5	2.2	0.5	2.7	3.1
EBPR2	3.6	0.3	3.1	3.2	2.0	3.4
	Total Polyphosphate (mg/g)					
AS1	19.48	6.27	3.78	3.13	4.43	3.36
AS2	13.57	13.1	9.69	10.48		
AS3	3.06	3.3	2.89	4.78	5.64	4.03
AS4	2.9	1.76	5.14	2.46	3.36	2.5
AS5	2.44	0.18	3.01	5.1	8.7	6.4
EBPR2	9.22	9.52	10.78	4.32	7.48	3.77
	Total Organic phosphates (mg/g)					
AS1	1.92	20.43	7.77	5.11	6.47	4.81
AS2	5.29	1.72	5.66	5.82		
AS3	6.46	5.7	2.61	2.12	5.69	5.46
AS4	5.86	4.05	9.8	5.67	5.08	3.38
AS5	1.06	3.83	4.93	5.4	3.91	4.7
EBPR2	9.33	4.55	6.44	5.66	7.48	3.77

Table 25. Summary of the dissolved calcium and magnesium concentrations before and after thickening.

	Day 1		Day 2		Day 3	
	Undigested	Digested	Undigested	Digested	Undigested	Digested
	Dissolved Calcium (mg/L)					
AS1			138	24	65	35
AS2	55	78	55	66		
AS3	14	22	12	26	12	35
AS4	27	26	26	22	30	36
AS5			459	426	405	419
EBPR2	86	123	124	105	129	160
	Dissolved Magnesium (mg/L)					
AS1			18	162	16	77
AS2	8	26	7	12		
AS3	3	7	2	5	2	8
AS4	3	4	2	3	4	6
AS5			79	96	98	105
EBPR2	4	27	13	30	10	40

Table 26. Comparison of relative standard deviations of the phosphorus data collected in this study versus phosphorus data published in the literature.

Reference	type of biosolids	Analyte	RSD%
This Study	Thickened Undigested	Dissolved Orthophosphate	44
This Study	Thickened Undigested	Particulate Orthophosphate	33
This Study	Thickened Undigested	Particulate Polyphosphate	23
This Study	Thickened Undigested	Particulate Organic Phosphorus	31
This Study	Thickened Digested	Dissolved Orthophosphate	34
This Study	Thickened Digested	Particulate Orthophosphate	10
This Study	Thickened Digested	Particulate Polyphosphate	55
This Study	Thickened Digested	Particulate Organic Phosphorus	57
Lawler and Singer 1984	Digester Supernatants	Total Phosphorus	68
Dueñas et al. 2003	Dewatering Supernatants	Total Phosphorus	40
Dueñas et al. 2003	Dewatering Supernatants	Particulate Orthophosphate	82
Dueñas et al. 2003	Dewatering Supernatants	Dissolved Orthophosphate	38
Danesh et al. 2008	Waste Activated Sludge	Dissolved Orthophosphate	51
Takiguchi et al. 2003	Waste Activated Sludge	Total Phosphorus	11

Table 27. Summary of the dissolved and particulate orthophosphate concentrations for all the sampled biosolids before and after digestion.

		Dissolved Orthophosphate (mg/g)		Particulate Orthophosphate (mg/g)	
		Undigested	Digested	Undigested	Digested
AS1	Day 1	1.2		3.0	
	Day 2	1.6		3.3	
	Day 3	2.3		4.9	
AS2	Day 1	2.9	1.9	6.6	17.3
	Day 2	1.2	1.9	5.8	17.5
	Day 3				
AS3	Day 1	1.7		1.5	
	Day 2	1.7		1.6	
	Day 3	1.9		1.6	
AS4	Day 1	1.0	1.2	2.8	3.2
	Day 2	0.7	1.1	3.1	3.2
	Day 3	0.9	3.0	3.1	4.0
AS5	Day 1	1.8	2.1	2.5	3.5
	Day 2	0.8	0.2	0.5	5.5
	Day 3	0.7	0.5	3.1	7.9
CHEM1	Day 1	0.3		1.7	
	Day 2	0.2		4.3	
	Day 3	1.5		6.3	
CHEM2	Day 1	0.2		4.2	
	Day 2	0.9		5.6	
	Day 3	0.6		5.3	
EBPR1	Day 1	0.7	4.7	3.3	17.2
	Day 2	0.6	4.6	3.1	14.8
	Day 3	0.3	5.0	3.1	14.5
EBPR2	Day 1	0.9		3.6	
	Day 2	0.6		3.1	
	Day 3	1.1		2.0	

Table 28. Summary of the total polyphosphate and organic phosphates concentrations for all the sampled biosolids before and after digestion.

		Polyphosphate (mg/g)		Organic phosphates (mg/g)	
		Undigested	Digested	Undigested	Digested
AS1	Day 1	6.3		20.4	
	Day 2	3.1		5.1	
	Day 3	3.4		4.8	
AS2	Day 1	13.1	8.2	1.7	2.5
	Day 2	10.5	0.0	5.8	1.8
	Day 3				
AS3	Day 1	3.3		5.7	
	Day 2	4.8		2.1	
	Day 3	4.0		5.5	
AS4	Day 1	1.8	0.5	4.1	6.2
	Day 2	2.5	0.9	5.7	4.7
	Day 3	2.5	0.7	3.4	5.7
AS5	Day 1	0.2	0.5	3.8	4.3
	Day 2	5.1	6.5	5.4	0.1
	Day 3	6.4	6.2	4.7	2.7
CHEM1	Day 1	26.6		0.2	
	Day 2	23.3		8.2	
	Day 3	20.3		3.5	
CHEM2	Day 1	15.5		10.8	
	Day 2	5.6		11.8	
	Day 3	14.8		0.2	
EBPR1	Day 1	47.4	6.5	0.0	4.0
	Day 2	23.9	4.0	5.1	0.0
	Day 3	23.0	6.5	6.7	5.4
EBPR2	Day 1	9.2		9.3	
	Day 2	10.8		6.4	
	Day 3	7.5		7.5	

Table 29. Summary of the phosphorus concentrations in thickening and dewatering supernatants.

		Orthophosphate (mg/L)		Polyphosphates (mg/L)		Organic phosphates (mg/L)	
		Thickening	Dewatering	Thickening	Dewatering	Thickening	Dewatering
	Day 1	8.8		0.6		0.3	
	Day 2	5.0		2.0		2.9	
AS1	Day 3	7.5		0.5		0.0	
	Day 1	12.3	46.7	11.3	4.3	6.0	5.2
	Day 2	45.8	31.5	1.6	2.0	20.4	6.1
AS2	Day 3						
	Day 1	4.8	32.8	0.0	7.2	0.8	13.2
	Day 2	5.3	31.3	2.2	4.5	6.1	20.2
AS3	Day 3	7.5	27.9	2.3	8.2	3.8	8.2
	Day 1	7.4	39.9	0.8	4.2	3.3	10.2
	Day 2	6.3	35.3	1.7	8.4	3.0	14.1
AS4	Day 3	6.5		0.8		2.2	
	Day 1	14.2	15.5	5.4	1.6	13.4	5.0
	Day 2	17.0	7.8	7.7	5.3	18.7	4.3
AS5	Day 3	20.4	21.1	4.6	3.4	10.3	4.6
	Day 1	41.8	60.8	10.8	1.7	7.4	5.4
	Day 2	90.6		6.7		0.5	
CHEM1	Day 3	23.9	30.5	7.8	1.8	7.5	4.1
	Day 1		14.5		10.0		0.0
	Day 2		0.9		0.5		1.0
CHEM2	Day 3		1.5		4.9		20.9
	Day 1	7.4	24.1	0.0	13.7	1.9	0.5
	Day 2	9.8	41.7	0.0	0.2	0.2	0.2
EBPR1	Day 3	8.9	38.4	0.2	18.2	0.2	0.2
	Day 1						
	Day 2	2.6		0.0		0.0	
EBPR2	Day 3	2.3		0.0		0.1	

Table 30. Nitrogen to Phosphorus ratios used for the calculations in Chapter 4.

Source	Treatment	P2O5 %	N %	Ratio
Maguire et al. 2001	Conventional Undigested	4.8%	5%	1.0
Maguire et al. 2001	Conventional Digested	5.5%	4%	0.7
Maguire et al. 2001	Chem-P Undigested	2.5%	2%	0.8
Maguire et al. 2001	Chem P Undigested	2.7%	4%	1.3
Maguire et al. 2001	Chem-P Digested	6.6%	4%	0.6
Maguire et al. 2001	Chem-P Digested	4.8%	5%	1.1
Maguire et al. 2001	Chem-P Digested	6.9%	5%	0.7
Maguire et al. 2001	Chem-P Digested	5.5%	5%	0.9
Tchobanoglous	Primary Sludge	2%	3%	1.6
Tchobanoglous	Digested Primary Sludge	2.5%	3%	1.2
Own Measurements	Conventional Undigested	18.4%	32%	1.7
Own Measurements	Conventional Digested	21.2%	31%	1.5
US EPA (1979)	Conventional WAS	7.0%	6%	0.9
Penn and Sims 2002	BNR	4.1%	5%	1.2
Penn and Sims 2002	Conventional digested	4.3%	5%	1.1
Penn and Sims 2002	Chem-P Undigested	1.9%	4%	1.8
Penn and Sims 2002	Chem-P Aerobically digested	3.3%	5%	1.5
Penn and Sims 2002	Chem-P Undigested	3.3%	5%	1.5
Penn and Sims 2002	Chem-P Undigested	1.6%	2%	1.4
Penn and Sims 2002	Chem-P Digested	5.6%	5%	0.9
Penn and Sims 2002	Chem-P Digested	4.4%	3%	0.6
Wang et al. 2010	BNR- WAS Undigested	8.5%	8%	0.9
Wang et al. 2010	BNPR - WAS Undigested	18.7%	7%	0.4
Chinault and O'Connor 2008	Conventional Digested	4.6%	5%	1.2
Chinault and O'Connor 2008	Bio N- Digested	5.3%	6%	1.1
Chinault and O'Connor 2008	BPR Digested	6.0%	6%	1.0
Vincent et al. 2011	Conventional WAS	4.3%	5%	1.2
Schroder et al 2008	Conventional Digested	8.8%	2%	0.2
Uysal et al. 2010	Conventional Digested	3.5%	4%	1.2
Kroiss et al 2008	Not specified	2.0%	1%	0.7
Kroiss et al 2008	Not specified	4.5%	7%	1.4
Debosz et al. 2002	Chem P Digested	6.8%	3%	0.5
Bolzonella et al2012	WAS	4.4%	8%	1.7
Salsabil et al 2009	BPR WAS	20.1%	12%	0.6

Sarkar et al. 2005	BPR DIGESTED	8.0%	6%	0.7
Batziaka et al. 2008	Conventional Digested	1.8%	4%	2.4
Liao et al. 2005	BPR	6.6%	4%	0.6
Liao et al. 2005	BPR	7.0%	4%	0.6
Liao et al. 2005	BPR	21.8%	9%	0.4
Liao et al. 2005	BPR	21.5%	9%	0.4
Elliot et al. 2002	Conventional Digested	6.2%	5%	0.8
Elliot et al. 2002	BPR	6.8%	6%	0.9
Elliot et al. 2002	BPR	7.1%	7%	0.9
Chinault 2007	BPR Undigested	4.6%	7%	1.5
Chinault 2007	BPR Undigested	5.3%	7%	1.3
Chinault 2007	Conventional Undigested	3.9%	4%	1.1

Table 31. Phosphorus recovery efficiencies obtained from the published literature.

	Recovery Efficiency	Source
AIRPREX	90% of dissolved orthophosphate	Stumpf et al. 2009
Stuttgart Process	60 % of total phosphorus	Antakyali et al. 2013
KREPRO	75 % of the total phosphorus	Karlsson 2001

Table 32. Summary of the phosphorus recovery potential calculated for the different technologies of phosphorus recovery using undigested municipal biosolids.

		Phosphorus Recovery Potential (% of total phosphorus)		
		AIRPREX	Stuttgart Process	KREPRO
AS1	Day 1	3%	13%	31%
	Day 2	11%	37%	55%
	Day 3	13%	46%	62%
AS2	Day 1	11%	38%	84%
	Day 2	4%	29%	67%
AS3	Day 1	20%	51%	49%
	Day 2	6%	11%	49%
	Day 3	4%	25%	62%
AS4	Day 1	13%	26%	48%
	Day 2	11%	22%	51%
	Day 3	13%	26%	52%
AS5	Day 1	9%	38%	52%
	Day 2	5%	31%	47%
	Day 3	8%	39%	59%
EBPR1	Day 1	3%	27%	63%
	Day 2	7%	13%	74%
	Day 3	9%	52%	64%
EBPR2	Day 1	4%	19%	54%
	Day 2	3%	17%	62%
	Day 3	5%	16%	55%
Chem1	Day 1	1%	7%	89%
	Day 2	1%	12%	69%
	Day 3	4%	24%	80%
Chem2	Day 1	0%	14%	58%
	Day 2	3%	27%	46%
	Day 3	3%	27%	89%

Table 33. Summary of the potential mass recovered by the different technologies of phosphorus recovery utilizing undigested municipal biosolids.

		Mass recovered (kg of P/metric ton of dry solids)		
		AIRPREX	Stuttgart Process	KREPRO
AS1	Day 1	1.1	4.1	9.4
	Day 2	1.5	4.9	7.3
	Day 3	2.0	7.0	9.5
AS2	Day 1	2.6	9.3	20.4
	Day 2	1.0	6.8	15.7
AS3	Day 1	1.6	4.2	4.0
	Day 2	0.7	1.3	5.7
	Day 3	0.7	3.8	9.3
AS4	Day 1	1.5	3.1	5.8
	Day 2	1.5	3.2	7.3
	Day 3	1.7	3.4	6.8
AS5	Day 1	0.9	3.7	5.0
	Day 2	0.6	3.7	5.6
	Day 3	0.8	3.9	5.8
EBPR1	Day 1	0.3	2.9	6.6
	Day 2	1.7	3.0	17.2
	Day 3	1.9	10.8	13.3
EBPR2	Day 1	0.8	4.4	12.3
	Day 2	0.5	3.6	13.0
	Day 3	1.0	3.0	10.6
Chem1	Day 1	0.3	1.9	25.7
	Day 2	0.2	4.4	25.0
	Day 3	1.3	7.6	25.3
Chem2	Day 1	0.1	4.3	18.1
	Day 2	0.8	6.4	11.0
	Day 3	0.5	5.8	18.7

Table 34. Summary of the estimated nitrogen to phosphorus ratio to be achieved after phosphorus recovery through the discussed technologies when utilizing undigested biosolids.

		N:P2O5 Ratio after recovery		
		AIRPREX	Stuttgart Process	KREPRO
AS1	Day 1	1.3	1.5	1.9
	Day 2	1.4	1.9	2.9
	Day 3	1.5	2.2	3.4
AS2	Day 1	1.4	2.0	7.9
	Day 2	1.4	1.8	4.0
AS3	Day 1	2.1	3.3	3.3
	Day 2	1.8	1.9	3.3
	Day 3	1.8	2.2	4.4
AS4	Day 1	1.5	1.7	2.5
	Day 2	1.4	1.6	2.7
	Day 3	1.5	1.7	2.7
AS5	Day 1	1.4	2.0	2.7
	Day 2	1.4	1.8	2.5
	Day 3	1.4	2.0	3.2
EBPR1	Day 1	1.0	1.2	2.5
	Day 2	1.0	1.0	3.7
	Day 3	1.0	1.7	2.6
EBPR2	Day 1	1.0	1.1	2.0
	Day 2	1.0	1.1	2.5
	Day 3	1.0	1.1	2.1
Chem1	Day 1	1.0	1.1	9.4
	Day 2	1.0	1.1	3.3
	Day 3	1.0	1.3	5.0
Chem2	Day 1	1.0	1.1	2.4
	Day 2	1.0	1.3	1.8
	Day 3	1.0	1.3	9.2

Table 35. Summary of the phosphorus recovery potential calculated for the different technologies s of phosphorus recovery using digested municipal biosolids.

		Phosphorus Recovery Potential (% of total phosphorus)		
		AIRPREX	Stuttgart Process	KREPRO
AS2	Day 1	6%	63%	83%
	Day 2	8%	90%	82%
AS4	Day 1	18%	53%	52%
	Day 2	1%	22%	44%
	Day 3	3%	47%	76%
AS5	Day 1	10%	39%	40%
	Day 2	10%	42%	47%
	Day 3	8%	39%	59%
EBPR1	Day 1	13%	66%	79%
	Day 2	18%	81%	90%
	Day 3	14%	61%	75%

Table 36. Summary of the potential mass recovered by the different technologies of phosphorus recovery utilizing digested municipal biosolids.

		Mass recovered (kg of P/metric ton of dry solids)		
		AIRPREX	Stuttgart Process	KREPRO
AS2	Day 1	1.7	18.8	24.6
	Day 2	1.7	19.0	17.4
AS4	Day 1	1.8	5.3	5.2
	Day 2	0.2	5.5	11.1
	Day 3	0.5	8.1	13.0
AS5	Day 1	1.1	4.3	4.4
	Day 2	1.0	4.1	4.6
	Day 3	1.1	5.2	7.9
EBPR1	Day 1	4.2	20.9	25.1
	Day 2	4.1	19.0	21.1
	Day 3	4.5	19.1	23.4

Table 37. Summary of the estimated nitrogen to phosphorus ratio to be achieved after phosphorus recovery through the discussed technologies when utilizing digested biosolids.

		N:P2O5 Ratio after recovery		
		AIRPREX	Stuttgart Process	KREPRO
AS2	Day 1	1.2	2.6	6.3
	Day 2	1.2	9.1	6.3
AS4	Day 1	1.3	2.1	2.3
	Day 2	1.1	1.4	2.0
	Day 3	1.1	1.9	4.6
AS5	Day 1	1.2	1.7	1.8
	Day 2	1.2	1.8	2.1
	Day 3	1.2	1.7	2.7
EBPR1	Day 1	0.9	1.9	3.7
	Day 2	0.9	3.3	7.8
	Day 3	0.9	1.7	3.1

Table 38. Influent characteristics of Walnut Creek wastewater treatment plant.

Date	Walnut Creek					
	Alkalinity	Ammonia	BOD	TSS	TKN	TP
	mg/L as CaCO$_3$	mg/L as N	mg/L	mg/L	mg/L as N	mg/L as N
1st Q 07		16.7178	159.6829	181.3333		5.422308
2nd Q 07		16.80714	144.8315	192		5.103846
3rd Q 07		17.98145	143.1807	220.4444		6.140769
4th Q 07		21.69672	200.3165	299.4457		7.339231
1st Q 08	205	22.26885	209.8471	235.8022	47.58	8.04923
2nd Q 08	245.84	22.64127	183.8148	262.8352	43.26667	7.20385
3rd Q 08	214.875	25.87143	172.1705	191.1087	46.82857	7.49357
4th Q 08	212.087	23.615	159.2588	214.8043	44.01667	6.88923
1st Q 09	204.7826	24.09836	169.5393	202.9667	45.66667	6.405385
2nd Q 09	204.92	22.73594	176.3708	205.1209	38.83846	6.683077
3rd Q 09	202.5385	22.47937	178.3372	201.8791	38.59231	6.113846
4th Q 09	224.0833	17.69754	171.022	187.4348	37.23077	4.310769
1st Q 10	231.5417	15.83417	168.4545	175.4667	34.26923	3.931538
2nd Q 10	231.24	20.78594	183.4819	208.5934	46.64615	5.334615
3rd Q 10	243.5	20.85641	168.9022	199.4348	40.01538	5.593158
4th Q 10	252.8261	25.58305	199.8293	205.837	43.93077	5.171538
1st Q 11	225.9583	26.33175	249.8202	212.4444	44.8	5.324615
2nd Q 11	260.5357	26.49063	227.954	273.3626	48.31818	5.136154
3rd Q 11	214.75	24.48	162.2857	168.3636		4.590769
4th Q 11	389.22	29.55	192.98	330.91	42.2846	4.22538
1st Q 12	374.08	27.29	198.27	360	42.3538	4.38923
2nd Q 12	388.38	28.45	191.6292	420.0659	45.1538	4.69385
3rd Q 12	401.1	26.55			43.82	
4th Q 12	338.7	26.8				
1st Q 13	472.94	30.08	252.22	489.02	43.83	6.8
2nd Q 13	379.01	28.71	210.97	343.34		5.8
3rd Q 13		29.3				

Table 39. Influent characteristics of South Austin Regional wastewater treatment plant.

Date	South Austin Regional					
	Alkalinity	Ammonia	BOD	TSS	TKN	TP
	mg/L as CaCO$_3$	mg/L as N	mg/L	mg/L	mg/L as N	mg/L as N
1st Q 07	240	18.08955	209.1647	209.1647	33.24545	6.233333
2nd Q 07	243.3333	17.66517	281.2683	281.2683	40.95833	7.009231
3rd Q 07	262.3333	18.66522	204.5432	204.5432	44.38182	5.943333
4th Q 07	233	24.47174	204.85	204.85	45.72	6.992308
1st Q 08	265.6667	26.85495	269.8721	269.8721	81.66364	7.089231
2nd Q 08	260	25.04607	261.48	261.48	51.5	7.045
3rd Q 08	274.5	29.23375	199.0926	199.0926	41.54545	7.403077
4th Q 08	261.6667	31.53516	228.6552	228.6552		6.772308
1st Q 09	244.7778	29.18222	238.9821	238.9821		8.227692
2nd Q 09	256.6667	30.37692	264.6429	264.6429		6.336923
3rd Q 09	270.3333	30.51957	202.0708	202.0708		5.556923
4th Q 09	235.3333	26.52717	184.7882	184.7882		5.961538
1st Q 10	255	26.95955	193.5125	193.5125		5.738462
2nd Q 10	275	27.94318	226.5119	226.5119		6.863636
3rd Q 10	256.6667	28.02717	187.5529	187.5529		6.775385
4th Q 10	240	31.68681	291.9425	291.9425		6.163077
1st Q 11	261	28.82444	311.5758	311.5758		6.209231
2nd Q 11	296.8667	30.73444	244.0123	244.0123	45.33333	6.624615
3rd Q 11	268.2222	33.76977	230.6769	230.6769	49.95455	7.244615
4th Q 11	273.6667	31.47826	409.6625	409.6625	57.63333	10.32923
1st Q 12	273.6667	26.03913	231.2937	231.2937	38.73846	5.769231
2nd Q 12	274.1667	26.73	226.2278	226.2278	42.82	5.84
3rd Q 12	326	27.57				
4th Q 12	256.33	33.44				
1st Q 13	264.33	32.04				
2nd Q 13	276.69	30.44	243.1	243.1	46.88	7.33

Table 40. Water, solid and gas outputs from the wastewater treatment plants modeled in GPS-X.

	Outputs		
	Conventional AS	EBPR	Chem P Removal
	Wastewater Effluent		
Flow (m^3/d)	48000	48000	48000
TSS (mg/L)	0.9	0.9	1.4
BOD (mg/L)	2.2	3.2	2.6
Ammonia (mg/L as N)	1.3	0.4	0.3
Nitrite (mg/L as N)	27.7	2.8	1.8
Nitrate (mg/L as N)	0	8.5	9.1
Phosphate (mg/L as P)	5.1	0.6	0.06
	Digested Biosolids		
TP (kg/day)	202	712	431
TN (kg/day)	757	625	626
	Digester Gas		
Volume (m3/d)	5300	4400	4000
CO_2 (%)	38	44	38
CH_4 (%)	61	56	61

Table 41. Materials and energy requirements to operate the wastewater treatment plants designed in GPS-X.

	Material & Energy Requirements			Source
	Conventional AS	EBPR	Chem P Removal	
Chlorine (gal/day)	340	340	340	GPS-X
Sulfur Dioxide (kg/day)	60	60	60	GPS-X
Ferric Chloride (kg/day)			2614	GPS-X
Sodium Bicarbonate 5% purity (kg/day)		2500	2500	GPS-X
Electricity	(kw-h/day)	(kw-h/day)	(kw-h/day)	
Pumping	2433	2433	2433	GPS-X
Primary Clarifier	11	11	11	GPS-X
Activated Sludge	5448	9396	8711	GPS-X
Secondary Clarification	583	583	583	GPS-X
Filter	482	482	482	Burton 1996
Chlorine Mixing	35	35	35	Burton 1996
Thickening	8.8	8.8	8.8	GPS-X
Digestion	1790	1790	1790	Burton 1996
Dewatering	443	443	443	Burton 1996
Screens	2.3	2.3	2.3	Burton 1996
Grit Chambers	169	169	169	Burton 1996
Lighting and Operations	920	920	920	Burton 1996

Table 42. Percent water extractable phosphorus for the sampled biosolids.

		Percent Water Extractable Phosphorus (%)
AS3	Day 1	2%
	Day 2	3%
	Day 3	3%
AS4	Day 1	3%
	Day 2	3%
AS5	Day 2	9%
	Day 3	7%
EBPR2	Day 1	16%
	Day 2	29%
	Day 3	31%
Chem1	Day 1	8%
	Day 3	4%
Chem2	Day 2	1%
	Day 3	2%
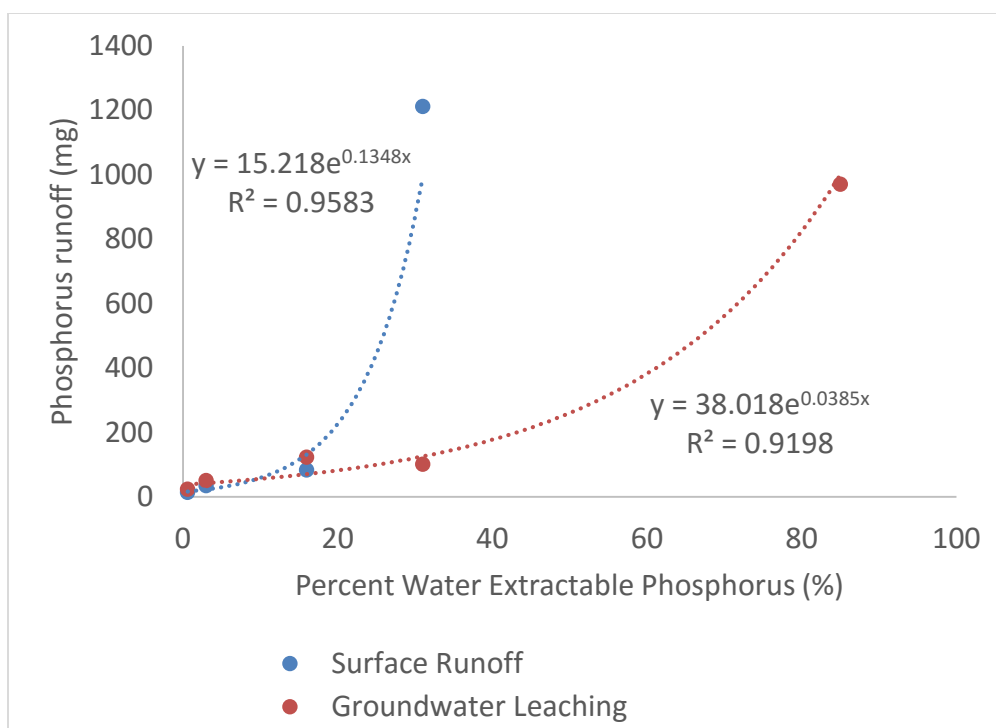
Figure 20. Phosphorus leaching from soils amended with 5.6 g of P from biosolids by surface runoff or groundwater leaching. Adapted from Alleoni et al. 2008.

Appendix B
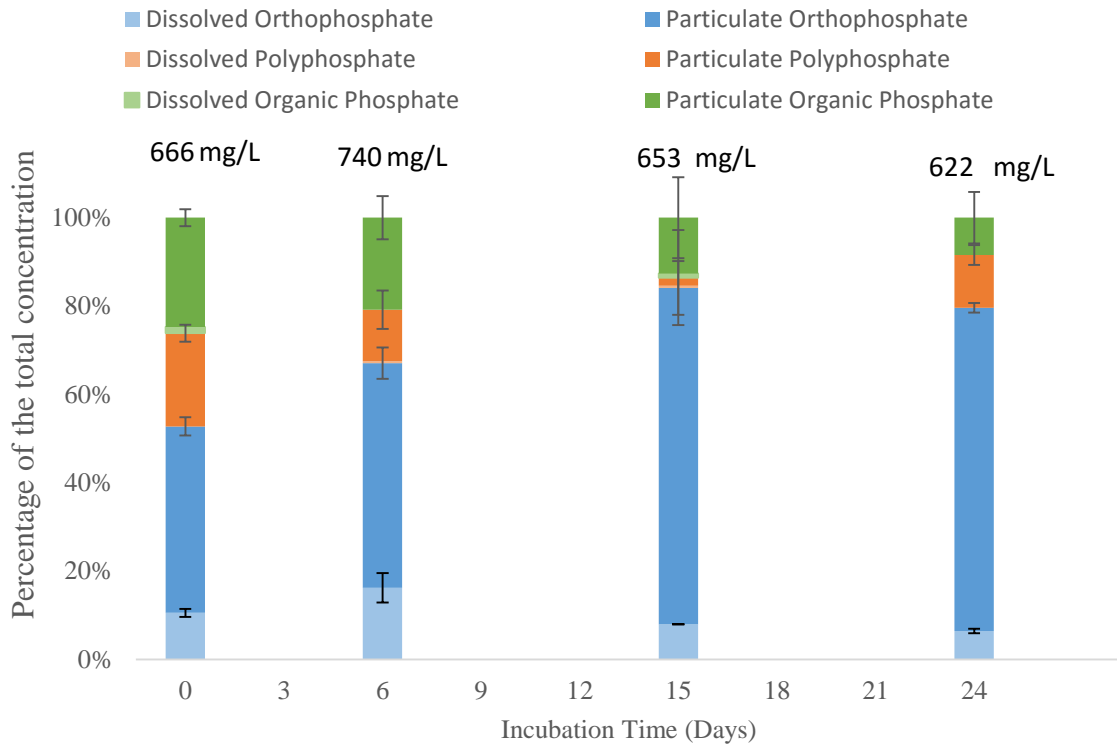
Figure S1. Phosphorus speciation of conventional AS undergoing batch anaerobic digestion as a function of incubation time.
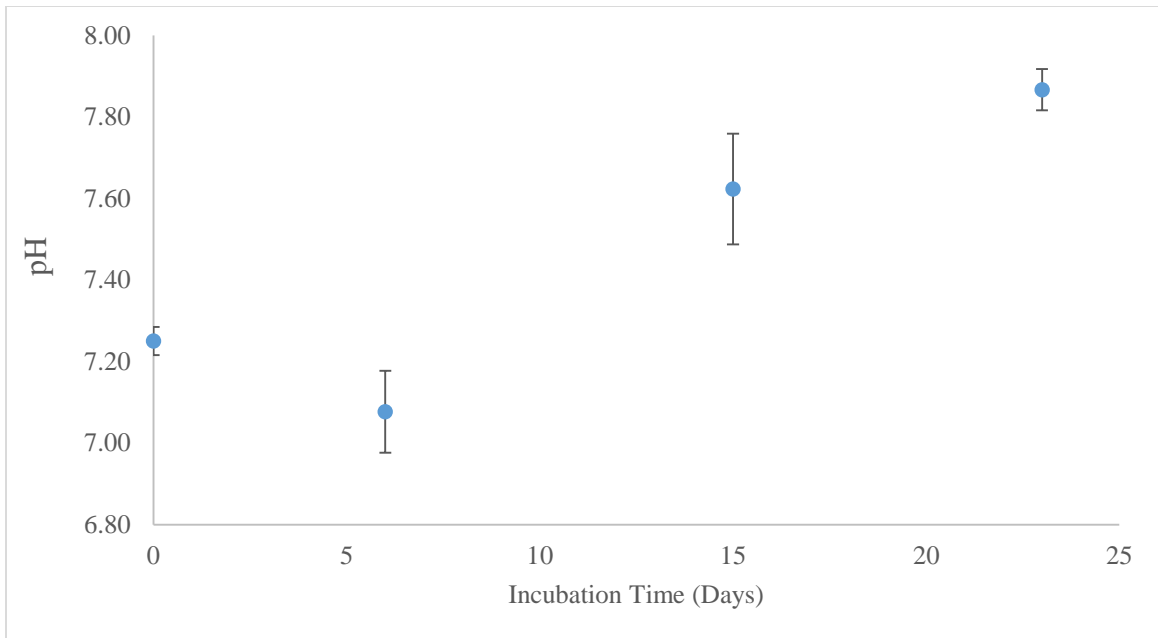
Figure S2. pH of conventional AS undergoing batch anaerobic digestion as a function of incubation time.
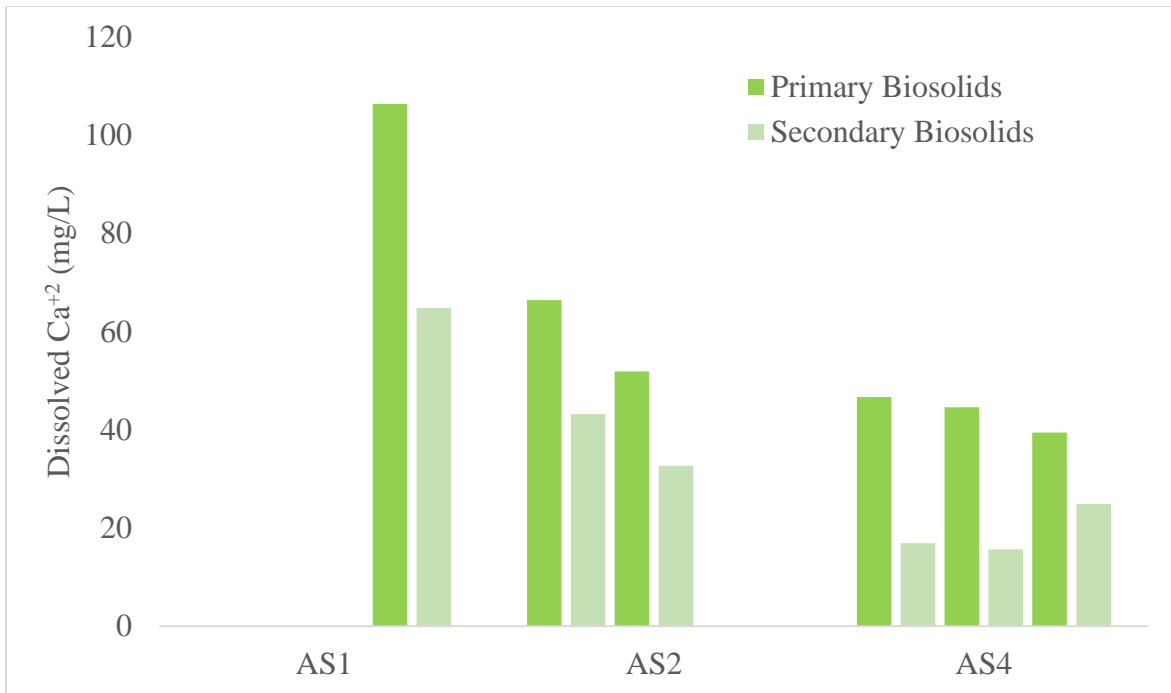
Figure S3. Dissolved calcium concentration in primary and secondary biosolids of conventional AS wastewater treatment plants.

PREDICTED PHOSPHORUS RECOVERY SAMPLE CALCULATION (AS4 + AIRPREX)

$$Dissolved\ orthophosphate\ in\ AS4\ digested\ biosolids = \ 15.6\ \left(\frac{mg}{L}\right)$$

$$Estimated\ recovery\ of\ target\ species\ via\ AIRPREX$$

$$= 90\%\ of\ dissolved\ orthophosphate$$

$$Estimated\ recovery\ via\ AIRPREX\ (mass/vol) = 0.9 * 15.6\ \left(\frac{mg}{L}\right)$$

$$= 14\ \left(\frac{mg\ P}{L\ of\ sludge}\right)$$

$$Total\ Phosphorus\ (TP)in\ AS4\ digested\ biosolids = 173\ \left(\frac{mg}{L}\right)$$

$$Estimated\ recovery\ (\%) = \frac{14\left(\frac{mg}{L}\right)}{173\left(\frac{mg}{L}\right)} * 100 = 8.1\%$$

The same procedure was repeated for all AS WWTPs and an average recovery and standard deviation computed.

PREDICTED N:P2O5 RATIO SAMPLE CALCULATIONS (AS4 + AIRPREX)
Calculating N:P2O5 before recovery
First convert g P to g of P2O5:

$$TP\ in\ AS\ digested\ biosolids = 15 \left(\frac{g\ P}{kg\ dry\ solids} \right) (Uysal\ et\ al.\ 2010)$$

$$TP\ in\ AS\ digested\ biosolids = \frac{15 \left(\frac{g\ P}{kg} \right)}{31 \left(\frac{g\ P}{mol\ of\ P} \right)} * \frac{1}{2} \left(\frac{mol\ of\ P2O2}{mol\ of\ P} \right)$$

$$= \frac{0.25\ mol\ of\ P2O2}{kg}$$

$$TP\ in\ AS\ digested\ biosolids\ (g\ P2O5/kg) = 0.25 \frac{mol\ of\ P2O2}{kg} * 142 \left(\frac{g\ of\ P2O2}{mol} \right)$$

$$TP\ in\ AS\ digested\ biosolids\ (g\ P2O5/kg) = 35.4\ g/kg$$
Then compute the N:P2O5 ratio

$$TN\ in\ AS\ digested\ biosolids = 41 \left(\frac{g}{kg} \right) (Uysal\ et\ al.\ 2010)$$

$$N:P2O2 = \frac{41}{35.4} \left(\frac{g \frac{N}{kg}}{g \frac{P2O2}{kg}} \right) = 1.2$$

The same process was repeated for all conventionally digested AS references found and the N:P2O5 was estimated to be 1.1 ± 0.6

Calculating N:P2O5 after recovery
Compute the moles of P removed by the chosen technology

$$TP\ in\ AS4\ digested\ biosolids\ before\ recovery = 13.3 \left(\frac{g\ of\ P}{kg\ dry\ solids} \right)$$

$$Phosphorus\ recovered\ by\ AIRPREX\ recovery = 13.3 \left(\frac{g\ of\ P}{kg\ dry\ solids} \right) * 8.1\%$$

$$= 1.08 \left(\frac{g \ of \ P}{kg \ dry \ solids} \right)$$

$$Phosphorus \ recovered \ by \ AIRPREX \ in \ mol = \frac{1.08}{31} \left(\frac{\frac{g \ of \ P}{kg \ dry \ solids}}{\frac{g \ of \ P}{mol}} \right)$$

$$= 0.035 \frac{mol \ P}{kg \ dry \ solids}$$

Then compute the nitrogen content (TN) before phosphorus recovery using the N:P2O5 ratio previously determined

$$TP \ in \ AS4 \ digested \ biosolids = \frac{13.3 \left(\frac{g \ of \ P}{kg} \right)}{31 \left(\frac{g}{mol \ of \ P} \right)} = \frac{0.43 \ mol \ of \ P}{kg}$$

$$TP \ in \ AS4 \ digested \ biosolids = \frac{1}{2} * 0.43 \frac{mol \ of \ P2O5}{kg} * 142 \left(\frac{g \ of \ P2O5}{mol} \right)$$

$$TP \ in \ AS4 \ digested \ biosolids = 30.5 \frac{g \ of \ P2O5}{kg}$$

$$TN \ in \ AS4 \ digested \ biosolids \ before \ recovery$$

$$= 30.5 \left(\frac{g \ of \ P2O5}{kg} \right) * 1.1 \left(\frac{\frac{g \ of \ N}{kg \ dry \ solids}}{\frac{g \ of \ P2O5}{kg \ dry \ solids}} \right) = 33.5 \left(\frac{g \ of \ N}{kg \ dry \ solids} \right)$$

$$TN \ in \ AS4 \ digested \ biosolids \ before \ recovery \ (mol)$$

$$= 33.5 \ \left(\frac{g \ of \ N}{kg \ dry \ solids} \right) * \frac{mol}{14 \ g} = 2.4 \ (\frac{mol}{kg \ dry \ solids})$$

Compute the TN and TP after phosphorus recovery

Given that struvite removes nitrogen as well as phosphorus in a 1:1 N/P molar ratio

$$TN \ in \ AS4 \ after \ recovery = \left(2.4 - 0.035 \ \left(\frac{mol}{kg \ dry \ solids} \right) \right) * 14 \frac{g}{mol}$$

$$= 33.1 \left(\frac{g \ of \ N}{kg \ dry \ solids} \right)$$

Calculate the TP after phosphorus recovery

$$TP\ in\ AS4\ after\ recovery = (13.3 - 1.08)\left(\frac{g\ of\ P}{kg\ dry\ solids}\right)$$

$$= 12.22\ \left(\frac{g\ of\ P}{kg\ dry\ solids}\right)$$

Convert to P2O5

$$TP\ in\ AS4\ after\ recovery = \frac{12.22\ \left(\frac{g\ of\ P}{kg\ dry\ solids}\right)}{31\ \left(\frac{g}{mol\ of\ P}\right)} * \frac{1}{2} * 142\left(\frac{g\ of\ P2O5}{mol}\right)$$

$$= 28\ \left(\frac{g\ of\ P2O5}{kg\ of\ dry\ solids}\right)$$

Finally, compute the new N:P2O5 ratio

$$N:P2O5 = \frac{33.5}{28}\left(\frac{g\frac{N}{kg}}{g\frac{P2O2}{kg}}\right) = 1.19$$

The same process was repeated for all treatment plants and the averages computed.

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