

**SIDESTREAM CONTROL OF DISSOLVED NUTRIENTS  
IN ANAEROBICALLY DIGESTED SLUDGE CENTRATE  
USING ANAMMOX AND CHEMICAL PRECIPITATION**

by

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**SIDESTREAM CONTROL OF DISSOLVED NUTRIENTS IN ANAEROBICALLY DIGESTED SLUDGE CENTRATE USING ANAMMOX AND CHEMICAL PRECIPITATION**

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## **Abstract**

The objective of this research was to assess specific side-stream processes for biodegradation and precipitation of dissolved nutrients in dewatering centrate and support the seamless integration of an anaerobic digester (AD) into a biological nutrient removal wastewater treatment plant (WWTP). Anaerobic digestion processes release reactive and non-reactive dissolved nutrients which are returned to the mainstream treatment process in the dewatering centrate. Conventional side-stream treatment processes are typically designed for removal of reactive nutrients (ie, nitrate/nitrite, ammonia and orthophosphate). However, many WWTPs with low total nitrogen and total phosphorus criteria will also be impacted by the non-reactive, difficult-to-degrade nutrient forms such as polyphosphates (poly-P), dissolved organic phosphorus (DOP) and dissolved organic nitrogen (DON).

In this study, characterization was made of a conventional suspended growth deammonification treatment (Anammox) process for transforming poly-P, DOP and DON in two types of dewatering centrate. The first centrate feed studied was from the full-scale Annacis Island WWTP (AIWWTP), Canada. The second centrate feed was from a lab-scale AD fed waste sludge from the existing City of Kelowna Wastewater Treatment Facility (KWTF), Canada. The Anammox process showed similar treatment characteristics for both the KWTF and AIWWTP centrates with excellent DON removal and poor non-reactive dissolved phosphorus (NRDP) removal. A statistical comparison of the DOP and poly-P through the Anammox process suggests that DOP has a higher biodegradation potential. Utilization of a post-Anammox, poly aluminum chloride chemical dosing, optimized based on zeta potential, was able to achieve the objective of precipitating residual DON and NRDP and producing an effluent with lower dissolved nutrients than the pre-digestion KWTF dewatering centrate scenario.

Additional testing was conducted on final effluent to characterize the dissolved phosphorus and determine an optimal coagulant dose. The testing suggests that the dissolved phosphorus in effluent could be associated with colloidal dissolved organic matter (DOM). Furthermore, coagulant batch dosing experiments using poly aluminium chloride (PACL) and poly epichlorohydrin amine (polyepiamine) provides strong support for the use of zeta potential measurements as a way to optimize coagulant dose.

## Preface

The research program, including design and operation of the reactors and data analyses, was executed by myself with assistance from Dr. Cigdem Eskicioglu. From time-to-time, characterization testing was conducted by collaborators, as described below.

A version of Chapter 3 was presented at WEFTEC 2014 and the paper was published as part of the proceedings (Galvagno, G., Eskicioglu, C., Abbott, T., Cella, M., Gosselin, M., 2014. The fate of recalcitrant nutrients through an anaerobic digester and anammox sidestream treatment process. Proceedings of *Water Environment Federation Technology and Exhibition Conference 2014*. Alexandria, Va: Water Environment Federation). The paper writing and all data analyses were performed by myself. Dr. Cigdem Eskicioglu provided feedback and review of the manuscript. The majority of the lab data on which the paper is based was acquired by the first author. Tim Abbott assisted in characterizing waste sludge (COD, VS/TS and biogas) from the anaerobic reactor. Monica Cella prepared samples and coordinated acquisition of scanning electron micrograph images. Mike Gosselin, the managing supervisor of the Kelowna Wastewater Treatment Facility provided access to their in-house lab data and coordinated additional sampling to complete the effluent and centrate characterization.

A version of Chapter 4 was published by Water Research (Galvagno, G., Eskicioglu, C., Abel-Denee, M., 2016. Biodegradation and chemical precipitation of dissolved nutrients in anaerobically digested sludge dewatering centrate. *Water Research*, 96, pp.84-93). The experimental design, reactor operation and all analyses were performed by myself. Marco Abel-Denee assisted in lab testing.

A version of Chapter 5 was accepted as a paper for WEFTEC 2016 (Galvagno, G., Stevens, G., Abel-Denee, M., Eskicioglu, C., Abbott, T.L., 2016. Effluent particulate phosphorus

fractionation and coagulation by optimized chemical dosing. *Proceedings of Water Environment Federation Technology and Exhibition Conference 2016*. Alexandria, Va: Water Environment Federation). The paper was written by myself, including all the analyses, and was presented at the conference on September 28, 2016. The experimental setup was designed by myself with input from Gerry Stevens of AECOM. Gerry provided the initial motivation to characterize colloidal phosphorus and supported the research as a sponsor for the ENGAGE grant. Dr. Cigdem Eskicioglu provided important feedback and review through development of the manuscript. Marco Abel-Denee assisted in the coagulation dosing, phosphorus testing and filtration steps.

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## List of abbreviations

AD	Anaerobic Digestion
Anammox	Anaerobic Ammonia Oxidizing
AIWWTP	Annacis Island Wastewater Treatment Plant
BNR	Biological Nutrient Removal
BOD	Biological Oxygen Demand
CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon dioxide
COD	Chemical Oxidation Demand
DAF	Dissolved Air Flotation
DEMON <sup>®</sup>	DEaMmONification
DON	Dissolved Organic Nitrogen
dTN	Dissolved Total Nitrogen
dTP	Dissolved Total Phosphorus
DOP	Dissolved Organic Phosphorus
FPS	Fermented Primary Sludge
GC	Gas Chromatograph
GHG	Greenhouse Gas
HRT	Hydraulic Retention Time
IC	Ion Chromatograph
KWTF	Kelowna Wastewater Treatment Facility
ML	Mixed Liquor

N	Nitrogen
NRDP	Non-Reactive Dissolved Phosphorus
P	Phosphorus
PACL	Poly Aluminum Chloride
PAO	Phosphorus Accumulating Organisms
PHA	Polyhydroxyalkanoate
poly-P	Polyphosphate
polyepiamine	poly epichlorohydrin amine
PS	Primary Sludge
SBR	Sequence Batch Reactor
SRT	Sludge Retention Time
TKN	Total Kjeldahl Nitrogen
TP	Total Phosphorus
TS	Total Solids
TWAS	Thickened Waste Activated Sludge
UF	Ultra Filtration
UV	Ultra Violet
VFA	Volatile Fatty Acid
VS	Volatile Solid
WAS	Waste Activated Sludge
WWTP	Wastewater Treatment Plant

## **Acknowledgements**

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Financial support for this work was provided by the Natural Science and Engineering Council (NSERC) Strategic Project Grant #396519-10, NSERC Engage Grant (F15-00588) and Pacific Century Graduate Scholarship.

## **Dedication**

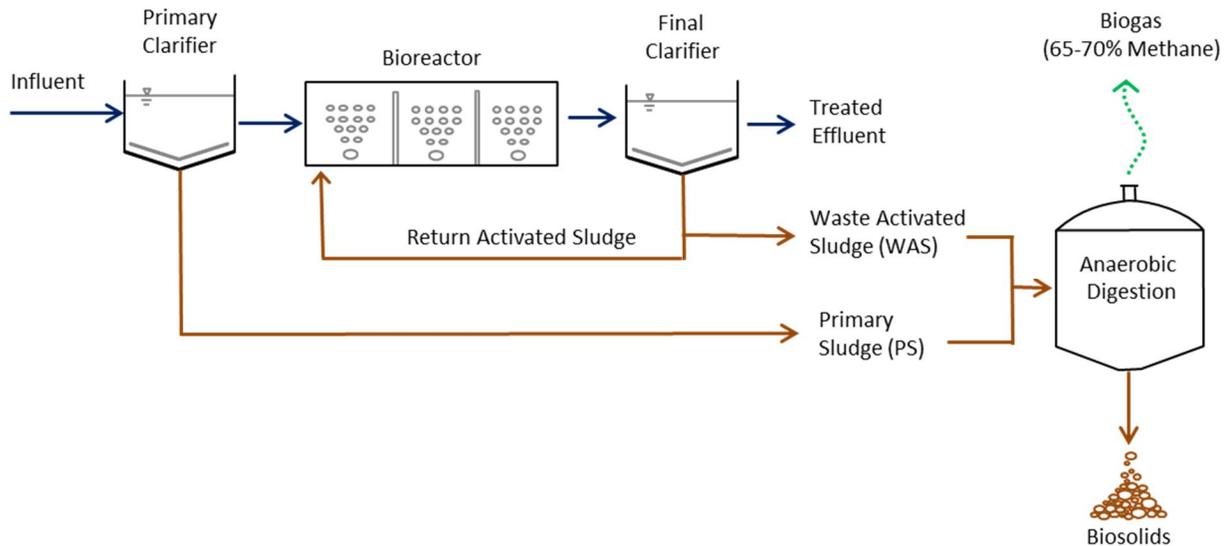
To my wife, children, family and friends who gave me the courage to try and the inspiration to persevere.

## Chapter 1: Introduction

This chapter provides a general description of the wastewater treatment context that serves as the motivation for the research.

### 1.1 Background and context

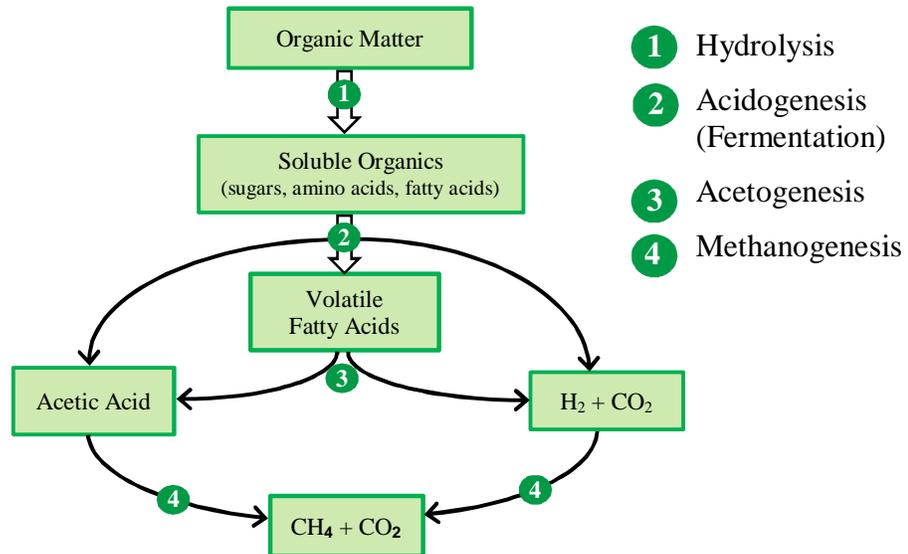
All WWTPs produce organics-rich sludge as a by-product. In general, the treatment process results in two waste sludge streams (Figure 1.1). Primary sludge (PS) consists of the settleable solids removed from the primary clarifier. Waste activated sludge (WAS) is the sludge removed from the secondary clarifier and is the by-product of biological treatment. The WAS consists predominately of the micro-organisms (biomass) which are used in the biological treatment process.



**Figure 1.1 – Generalized wastewater treatment schematic**

As part of the wastewater treatment process, the sludge produced must be stabilized. Solids stabilization involves converting sludge to biosolids which are low in odour and pathogens. AD is a common sludge management technique which produces relatively stable biosolids. The

anaerobic degradation of a complex wastewater or sewage sludge is a multi-step process comprising four major reactions as illustrated in Figure 1.2. Complex organic polymers in the waste are first hydrolyzed by extracellular enzymes of facultative or obligate anaerobic bacteria. The hydrolysis step provides monomeric/oligomeric constituents small enough to allow transport across the cell membrane and is the limiting step in the AD process. These simple soluble compounds are then fermented, or anaerobically oxidized, to short chain fatty acid intermediates, alcohols, carbon dioxide, hydrogen and ammonia (acidogenesis). The short chain fatty acids (other than acetate) are converted to acetate, hydrogen and carbon dioxide (acetogenesis). Finally, methanogenesis occurs from carbon dioxide reduction by hydrogen, and from acetate resulting in the methane and carbon dioxide mixture that constitutes biogas. The biogas consists of 60-70% methane, with the remaining 30-40% consisting of carbon, nitrogen, water vapour and reduced sulphur compounds. In wastewater context, WAS and PS serve as the substrate for AD. The WAS and PS are held in a sealed, oxygen free tank for 10 to 30 days, depending on the temperature, to achieve 40 to 60% volatile solids destruction (Metcalf & Eddy, 2014). During the process biogas is continually removed from the reactor headspace.



**Figure 1.2 – Stages of anaerobic digestion**

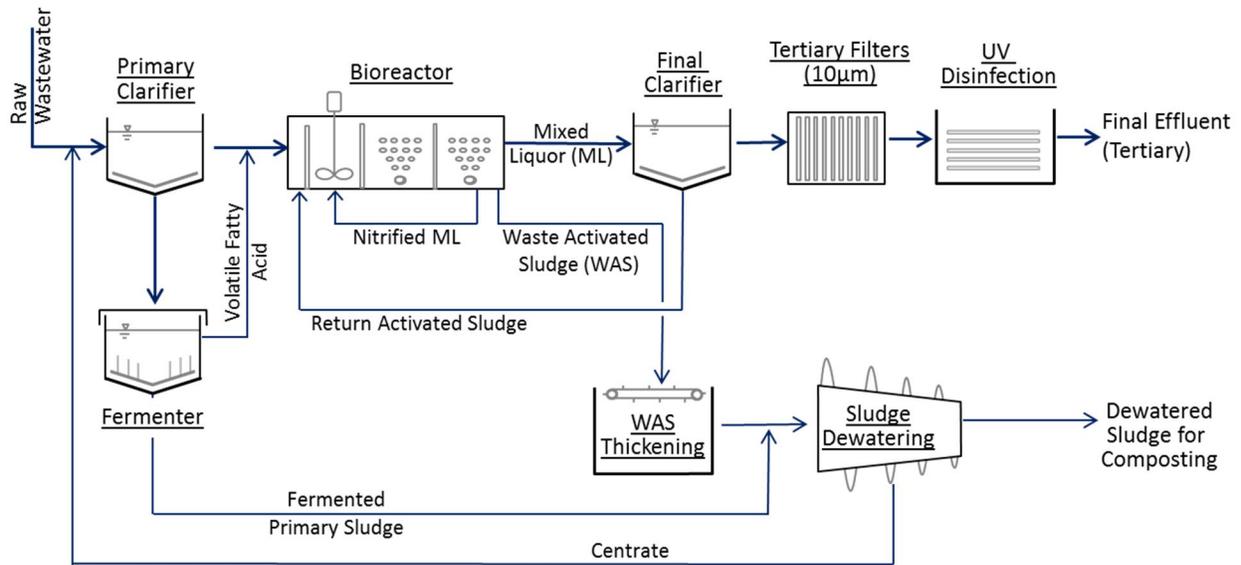
In the United States, it is estimated that approximately 22% of the 16,000 WWTPs utilize anaerobic digesters for stabilizing wastewater residuals. Furthermore, of treatment plants with anaerobic digesters, only 70 (2%) utilize the methane for generating electricity or heat (Lewis et al., 2008). While it is not clear how many facilities utilize the methane for other beneficial purposes, the statistics suggest a low utilization of the methane generating potential in the United States and Canada.

The low utilization of AD for biosolids stabilization reflects the historically poor economic return of constructing and operating an anaerobic digester. Conventionally, the economics of a digester have been evaluated based on comparison of the capital costs against the energy savings. However, rising energy costs, introduction of environmental commodities and markets change the evaluation and outcome (Scanlan et al., 2010).

As the economics and environmental benefits of implementing an anaerobic digester improve in the coming years, technical innovation must also advance to overcome operational challenges,

improve on the efficiencies and fill the knowledge gaps. From an Okanagan perspective, additional work is required to reliably incorporate AD into the biological nutrient removal (BNR) processes which are common in the Okanagan Valley to prevent eutrophication in the Okanagan Lake.

In the Okanagan Valley, dewatered sludge from the BNR treatment plant is taken off-site and composted (Figure 1.3). This approach to biosolids management prevents re-release of phosphorus into the treatment process. Phosphorus is biologically removed in the BNR reactor in a two-step process (WERF, 2010). First, under anaerobic conditions, phosphorus accumulating organisms (PAOs) release their stored phosphate. Volatile fatty acids (VFAs) are simultaneously absorbed and stored as a food source in the form of polyhydroxyalkanoate (PHA). In the second step, the PAOs are transferred to aerobic conditions where they utilize their stores of PHA for cell growth and re-absorb the soluble phosphorus previously released. If the conditions are carefully controlled and sufficient VFAs are available in the anaerobic zone, the PAOs will absorb phosphorus in excess of the amount originally released.



**Figure 1.3 – BNR process schematic**

If stored in the bacterial cell, net removal of phosphorus can be accomplished through normal wasting of biomass. However, if exposed to un-aerated conditions as part of the wasting process the PAOs will re-release the stored phosphorus as with the first step. Consequently, any attempt to anaerobically digest the WAS triggers release of more than 90% of the total phosphorus as phosphate and solubilizes 45% of the total total kjeldahl nitrogen (TKN) (Mavinic et al., 1995). If allowed to return to the mainstream process, the nutrient-rich digester supernatant would eventually overwhelm the WWTP and result in elevated effluent nutrient levels.

Use of composting as a sludge stabilization process eliminates the need to return phosphorus to the main treatment process. The dewatered or thickened WAS is mixed with wood chips and aerated to produce a stabilized biosolids. There are currently six BNR facilities operating in the Okanagan Valley. The stabilized compost material from these facilities is marketed as a soil amendment.

Recycling biosolids as a soil amendment has significant benefits within a BNR context (Pitman, 1999). However, there are disadvantages to the process including relatively high energy expenditure for operation of air blowers in the compost facility and transportation and the potential for foul air emissions.

An alternative option to composting for stabilizing biosolids is AD. In their comparison of anaerobic and aerobic treatment technology, Cakir and Stenstrom (2005) show that from a greenhouse gas perspective, anaerobic treatment is more favourable at higher chemical oxygen demand (COD) concentrations because of the ability to recover methane.

Methane gas could be utilized in a beneficial way (i.e., electricity generation) and digestion could reduce the mass of biosolids by approximately 50%. The smaller volume would reduce the cost and energy associated with transportation and composting while retaining the nutrient value of the final composted product.

The benefits of implementing an anaerobic digester versus maintaining the status quo (composting biosolids) are attractive. However, there are some key challenges that would need to be overcome in a BNR process context that will determine the feasibility of such a system. In particular, the sidestream treatment processes treating digester supernatant need to be able to degrade or remove the recalcitrant species that the mainstream process is not able to efficiently remove.

## **1.2 Research goals & experimental hypotheses**

The main goal of this research was to fill the knowledge gaps associated with dissolved nutrients released through AD of BNR sludge and provide a management approach that would eliminate the risk of the sidestream nutrient loading on the mainstream WWTP. The research is based on the hypothesis that both the reactive and recalcitrant nutrients can be removed through

existing biological sidestream processes or chemical precipitation. However, published research and design manuals do not cover this issue and only a focused lab-scale bioreactor study will provide the required basis for design. Specifically, objectives for this current research are to:

1. Provide baseline characterization of the City of Kelowna's Wastewater Treatment Facility (KWTF) to understand the existing mass loading of nutrients within the mainstream and sidestream flow streams;
2. Characterize the performance of a mesophilic digester fed waste sludge from the KWTF with emphasis on measuring dissolved nutrient concentrations in the waste sludge supernatant;
3. Assess the efficacy of a conventional deammonification sidestream centrate treatment system for bio-transforming or removing dissolved, recalcitrant nutrients; and
4. Characterize final effluent particulate and dissolved phosphorus and determine the efficiency of an aluminum-based coagulant for precipitating dissolved nutrients.

### **1.3 Research scope and methodology**

To achieve the objectives stated in Section 1.2, a research program was proposed utilizing a lab-scale anaerobic digester fed waste sludge from the KWTF and biological deammonification process. The lab-scale KWTF digester would represent the digested sludge characteristics and associated centrate sidestream. Centrate treatment to remove dissolved phosphorus and nitrogen species could then be assessed. The literature review identified the advantage of an ANaerobic AMMonia OXidation (Anammox) process over others for removal of ammonia. The centrate for the lab-scale AD could be fed to a sidestream Anammox process to allow assessment of dissolved recalcitrant nutrient removal. Anammox has the potential to biodegrade recalcitrant nutrients but this has never been measured. Subsequent dissolved phosphorus removal by

precipitation was assessed using aluminum salts. Ideally, phosphate removal by struvite precipitation would be included as part of the process train but was impractical. Based on the general description of the scope provided above, the following methodology was adopted:

1. Collect samples of KWTF mainstream and sidestream flows to assess the mass flow of the various nutrient species. The data serves as a baseline to determine the level of treatment required for the AD centrate. The testing also allows assessment of where the majority of recalcitrant dissolved nutrient originates or is removed.
2. Establish a mesophilic AD using waste mixed sludge from KWTF as a substrate and assess the dissolved nutrient flux through the digestion process.
3. Start-up an Anammox process using centrate from Annacis Island WWTP (AIWWTP). The AIWWTP centrate was used for the start-up to avoid limitations on centrate supply from the lab-scale AD since it was available in unlimited quantities.
4. Once the Anammox reactor stabilizes, collect dissolved nutrient data for the AIWWTP centrate feed and Anammox effluent to assess removal efficiency.
5. After collecting dissolved nutrient data for AIWWTP, slowly change the substrate feed to centrate generated from the lab-scale digester fed mixed sludge from KWTF. Once the Anammox process stabilized, collect dissolved nutrient data for the lab-scale KWTF AD centrate and Anammox effluent.
6. Assess the efficacy of using aluminum coagulants and flocculants for precipitating dissolved nutrients in Anammox effluent and final effluent. Provide a detailed characterization of dissolved phosphorus in final effluent to determine size range and optimized coagulant dosing for enhanced phosphorus removal.

#### **1.4 Novelty of research**

The current body of published research has not clearly documented nutrient flux through AD systems fed WWTP sludge or sidestream treatment processes treating centrate. There is considerable available published research that is focused on removal of dissolved recalcitrant nutrients in the final effluent. However, the approach of optimizing sidestream treatment processes to achieve the same result has not been documented. More specifically, a large amount of published research effort has been devoted to characterizing the performance of various Anammox sidestream processes for removing ammonia but there are no available studies showing the propensity of this process for degrading dissolved recalcitrant nutrients.

#### **1.5 Thesis organization**

Chapter 2 is a detailed literature review which provides context to the issue of sidestream treatment and includes a description of the various treatment options for high-strength nitrogen and phosphorus sidestreams. The literature review lays the ground-work for selecting a conventional biological deammonification process for assessing recalcitrant nutrient degradation. In Chapter 3 and Chapter 4, characterization of the feed and waste sludges for the anaerobic digester and deammonification bioreactors is made. In Chapter 5, particle characterization of NRDP is presented along with the efficacy of coagulants for removing these species. Conclusions and recommendations for additional research are provided in Chapter 6.

## **Chapter 2: Literature review**

The purpose of this chapter is to provide a detailed review of the various conventional and emerging sidestream treatment options for municipal WWTPs. Optimization of wastewater treatment facilities from energy consumption and emissions stand-point necessitates consideration of the impact of the various internal sidestreams. Sidestreams from anaerobic sludge digesters, in particular, have the potential to be a significant ammonia and phosphorus load to the mainstream treatment process. However, the literature suggests that managing sidestreams through their treatment in the mainstream process is not the most energy efficient approach, nor does it allow for practical recovery of nutrients. Furthermore, as effluent criteria become more stringent in some jurisdictions and sludge hydrolysis pre-treatment for digesters more common, an understanding of the fate of recalcitrant carbonaceous and nutrient species in the digester supernatant becomes more important. A variety of sidestream treatment processes described in the literature is reviewed in the context of these considerations.

As a by-product of biological wastewater treatment, various minor and major sidestreams are produced and must be managed through recycling or separate treatment. Sidestreams associated with the solids stabilization processes have the highest potential impact on the mainstream process. Solids stabilization can release significant amounts of nutrients and organics to the liquid stream which must be further treated. As the trend towards greater energy efficiency and higher effluent standards increases, more careful attention of the sidestream characteristics and method of treatment have become necessary. In order to gain a better perspective, a detailed summary from the literature of the various sidestream treatment management options is presented.

## 2.1 Sidestream characteristics

As part of a biological wastewater treatment process, several liquid and solids waste sidestreams are created that are not part of the main liquid or solids treatment trains. Table 2.1 provides a list of conventional sub-processes and associated liquid and sludge sidestreams in a typical WWTP. The sidestreams occur as part of the requirements of the various treatment stages and are typically recycled back or removed from the main treatment process.

**Table 2.1 – Typical sub-processes and associated sidestreams**

Treatment Stage	Sidestreams (Off-Site Removal)	Potential Recycle Sidestream
Screening	Screenings	Screenings dewatering underflow
Grit removal	Grit	Grit wash water
Primary clarification	Scum (FOGs) <sup>a</sup>	Scum dewatering underflow
Bioreactor (activated sludge)		
Bioreactor (membrane)		Membrane backwash
Effluent filter		Filter backwash
Sludge thickener		Thickener underflow
Sludge dewatering		Dewatering centrate
Sludge composting		Leachate
Odour control		Biofilter leachate or scrubber underflow

Notes: a. FOG: Fat, oil and grease

## 2.2 Importance of sidestream management

Treatment stages within the WWTP can produce high-strength waste streams which if unmanaged can degrade the final effluent quality or increase energy demand. In particular, sludge dewatering centrate associated with AD processes are known to contain relatively high concentrations of COD, ammonium and phosphate, as well as other nitrogen and phosphorus species (Table 2.2).

**Table 2.2 – Characteristics of high-strength wastewater liquid sidestreams**

Liquid Sidestream	Flow (% of Influent)	pH	Alkalinity (mg/L)	Temperature (°C)	COD (mg/L)	TSS (mg/L)	Total Nitrogen (mg/L)	Ammonia (mg N/L)	Total Phosphorus (mg P/L)	Orthophosphate (mg P/L)	Reference
DAF underflow (WAS thickening)	4.4	-	-	-	-	6.6	-	2.0	-	0.35	Kelowna (2009/10) <sup>f</sup>
Dewatering centrate:											
BNR without sludge stabilization <sup>b</sup>	0.48	6.3	-	-	2,150	674	4.9	27	208	181	Kelowna (2009/10) <sup>f</sup>
EBPR with alum trimming & mesophilic AD	-	-	-	-	-	-	-	1,200	-	316 - 632 <sup>e</sup>	Bauer 2010
EBPR with mesophilic AD	-	7.3-7.5	-	-	-	-	-	756	-	207	Fujimoto et al. 1991
Trickling filter with mesophilic AD	-	8.1	2,087	-	-	250	-	989	-	88 <sup>e</sup>	Mavinic et al. 2007
Trickling filter with thermophilic AD	-	8.0	3,295	-	-	500	-	1,050	-	140 <sup>e</sup>	Mavinic et al. 2007
Trickling filter with ATAD & alum dosing	0.6	6.0	-	-	-	500	-	700	-	40	Salmon Arm WWTP <sup>g</sup>
Mesophilic AD & thermal hydrolysis	-	7.8	9,500 - 11,500	-	-	<300	-	2,500-3,000 <sup>e</sup>	-	-	Figdore et al. 2010 <sup>a</sup>
Activated sludge with mesophilic AD <sup>d</sup>	-	7.9	-	-	-	-	-	707 <sup>e</sup>	-	157 <sup>e</sup>	Uysal et al. 2010
Activated sludge with mesophilic AD	-	7.7	2,090	31.8	430	580	1,360	590	-	-	Carrio et al. 2003
Biofilter leachate	-	7.2 – 7.8	-	-	-	-	176 - 245	154 - 210	-	-	Shanchayan et al. 2004

Notes: a. Published data provided are design values

b. Sludge taken off-site and composted with no return stream

c. “-“ indicates data not reported

d. Characterization based on the clear liquid component of lab-centrifuged sludge samples

e. Calculated from Authors’ published data

f. Data provided by City of Kelowna, Canada

g. Data provided by City of Salmon Arm, Canada

h. DAF = dissolved air flotation; EBPR = enhanced biological phosphorus removal; BNR = biological nutrient removal; AD = anaerobic digester; ATAD = autothermal thermophilic aerobic digester; TSS = total suspended solids

A review based on data from full-scale facilities and modelling studies (Jones and Takács, 2004) show that substantial ammonia and phosphate is released in anaerobic digesters through

hydrolysis of WAS. Janus and van der Roest (1997) suggests that the nitrogen load from the sludge digestion sidestream contains up to 25% of the total nitrogen load while contributing only 2% of the total flow to a treatment plant. This additional stream increases loading to the mainstream process, resulting in larger bioreactors, increased energy expenditure and a potentially decreased effluent quality.

### **2.3 Potential impacts on final effluent**

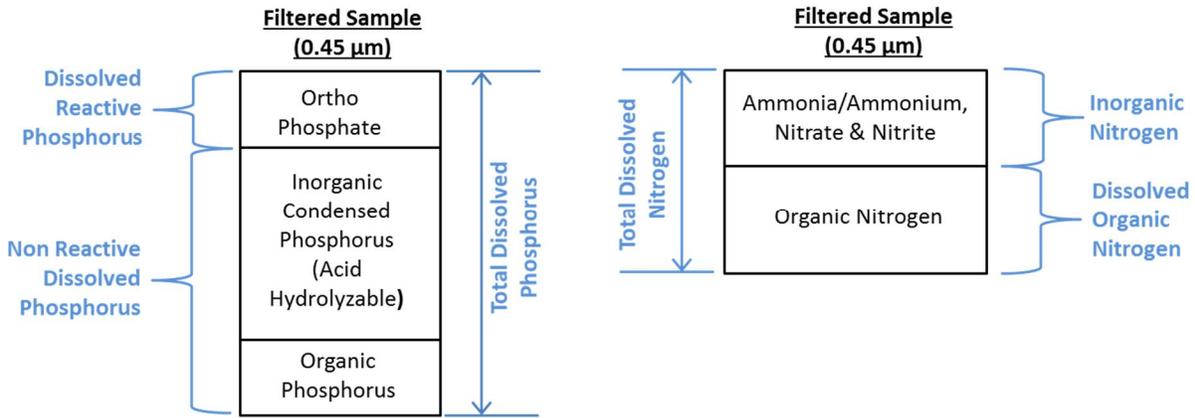
Recent research has highlighted the need to control recalcitrant nitrogen and phosphate species in order to optimize nutrient removal processes and reduce impacts on receiving waters. The trend of a decreasing effluent nitrogen and phosphorus objective for wastewater effluent discharged to surface water bodies has resulted in a focus on understanding the formation and removal of dissolved organic nitrogen (DON) (Pagilla et al., 2008) and non-reactive dissolved phosphorus (NRDP) (Tooker et al., 2010). DON and NRDP make up a significant proportion of the effluent nitrogen and phosphorus in treated wastewater effluent and can be difficult to degrade within a mainstream wastewater treatment process (Neethling and Stensel, 2013). The challenge of managing effluent DON and NRDP is complicated by the secondary objective of beneficially reusing wastewater biosolids through AD. Stabilization of wastewater biosolids through the use of AD can derive significant benefits to the overall WWTP operation in terms of cost and carbon expenditures (Cakir and Stenstrom, 2005; Berg et al., 2013). AD of wastewater sludge represents an opportunity to generate biogenic methane which could be used to offset demand for conventional petroleum-based energy, thereby reducing carbon emissions (Verstraete et al., 2005). In addition, AD is able to reduce the solids content of the sludge, reducing transportation and disposal requirements of the dewatered biosolids. However, AD releases a variety of dissolved nutrients including DON and NRDP (Wilson et al., 2011; Wild et al., 1997).

If returned to the mainstream treatment process, dewatering centrate associated with AD could negatively impact the final effluent quality.

DON consists of the nitrogen fraction which can be difficult to degrade. DON originates in domestic wastewater influent in a variety of forms including urea, amino acids, proteins, aliphatic N compounds and synthetic compounds, such as EDTA, N-containing pesticides and pharmaceuticals; however, DON can also be released into the treatment process through cell metabolism processes that excrete biomolecules, cell decay and cell lysis (WERF, 2009). Non-reactive dissolved phosphorus (NRDP) is also difficult to remove with conventional treatment, requiring advanced treatment processes with multiple stages including filtration, coagulation and adsorption (Neethling et al., 2007). As with DON, NRDP can increase through biological production in the mainstream process (Neethling and Stensel, 2013).

Published data from various full-scale WWTPs indicate a wide range of measured final effluent DON and NRDP concentrations. A survey of 197 nitrogen removal WWTPs in Virginia and Maryland reported an average final effluent DON of 0.93 mg N/L with a range of 0 to 2.5 mg N/L (WERF, 2009). For WWTPs with biological phosphorus removal systems, the range of final effluent NRDP measured in a separate study was 0.015 to 0.050 mg P/L (Neethling and Stensel, 2013). While most of the DON and NRDP enters the mainstream bioreactor as part of the raw wastewater, internal recycle streams, like dewatering centrate and sludge thickener underflow, can also represent significant contributions. Published data of DON and NRDP concentrations in dewatering centrate is not available. However, given the high potential for soluble microbial products produced through cell metabolism and decay of the anaerobic bacteria and WAS (Barker and Stuckey, 1999) it is expected that centrate will contain relatively high DON and NRDP concentrations.

DON is measured as the difference between total dissolved nitrogen and the sum of ammonia, nitrate and nitrite (Figure 2.1). Similarly, NRDP is the difference between total dissolved phosphorus and dissolved reactive phosphorus. The orthophosphate concentration (molybdate reactive phosphate) is generally accepted as a measure of the reactive phosphorus (APHA, 4500-P A).



**Figure 2.1 – Dissolved nutrient speciation**

DON and NRDP can occur as part of the raw wastewater and resist degradation or increase through the biological treatment process, thereby contributing to the final effluent nutrient load (Arnaldos and Pagilla, 2010). Once in the receiving water environment DON can become bioavailable, contributing to algae growth and negatively impacting the receiving environment. Using a 14-day bioassay, Urgan-Demirtas et al. (2008) were able to show that up to 61% of the effluent DON was available for algae growth. The NRDP in WWTP effluent is bioavailable (Ekholm and Krogerus, 2003). Through algae bioavailability studies Liu et al. (2011) demonstrated that 67-90% of the dissolved organic phosphorus (DOP) is bioavailable. This study also showed that DOP is the most recalcitrant form of phosphorus remaining in highly treated effluents and contributes 22% to 89% of the bioavailable soluble effluent phosphorus.

New treatment technologies incorporated into plants can also inadvertently change the formation of DON and NRDP species. For example, Dwyer et al. (2008) determined that the coloured compounds formed during high temperature sludge hydrolysis was found to be melanoidins, a DON compound. The melanoidins were implicated in reduced ultraviolet transmissivity (UVT) and increased DON in the final effluent. Consequently, in this case study, the untreated digester return stream caused a failure of the UV effluent disinfection system. Follow-up research suggested that alum dosing could reduce melanoidin type humic substances in the effluent (Dwyer et al., 2009). Arnaldos and Pagilla (2010) were also able to achieve 69% DON removal using alum at a molar ratio of 1.5. While chemical dosing could be used to control the increased DON production, additional research is needed to better understand and control the formation of these compounds.

#### **2.4 Moving towards “Plant of the Future”**

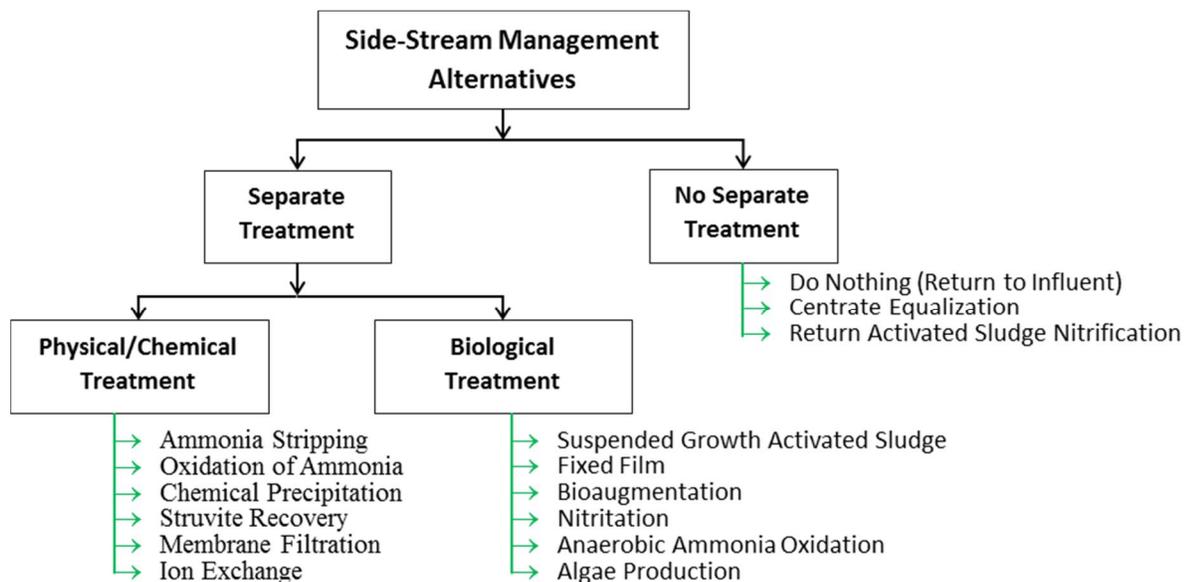
In a Water Environment Research Foundation (WERF) publication, the concept of the “Plant of the Future” is introduced (WERF, 2010). The “Plant of the Future” is a technology concept brainstormed by participants of a workshop attended by a range of experienced researchers, regulators, consultants and equipment manufacturers. The “Plant of the Future” is one that provides for energy self-sufficiency with greatest possible recovery of nutrients while providing effluent of sufficient quality to allow for reuse. These new and innovative approaches serve as vision for sustainable wastewater treatment and identify research needs. Ultimately, the principle objectives are to minimize the carbon footprint and greenhouse gas (GHG) emissions of WWTPs.

In order to achieve sustainability objectives for wastewater treatment, AD will need to feature prominently in the future (WERF, 2010; Verstraete et al., 2005). However, the potential

advantages of AD can be outweighed by impacts of the sidestream processes. For example, implementation of the ANaerobic AMMonium Oxidation (Anammox) process to remove nitrogen from the digester return stream was a key feature in changing the energy balance at the Strass WWTP (Austria) from a net energy consumer to net energy producer (Wett et al., 2007a). Furthermore, selection of a particular sidestream treatment process needs to be considered holistically to overcome the potential dichotomy of principles. Depending on the situation, minimizing energy consumption of the treatment plant may result in the most sustainable approach. In other situations, resource extraction of nutrients or reduction in GHG emissions may need to serve as the priority objective despite the potential increase in energy consumption. Therefore, a clear understanding of the various potential sidestream processes and their implication on the energy balance, effluent quality, emissions and resource recovery are required.

## **2.5 Sidestream treatment processes**

In this section, potential sidestream treatment options documented in the literature are presented and reviewed (Figure 2.2). Particular attention is paid to the implications for resource recovery and energy demand. Many of the sidestream processes documented address only one particular constituent and may necessitate more than one process to address the full spectrum of nitrogen, phosphorus and organic loading. Consequently, this review can serve as a starting point for any specific assessment.



**Figure 2.2 – Sidestream treatment options**  
(adapted from Constantine and Johnson, 2006)

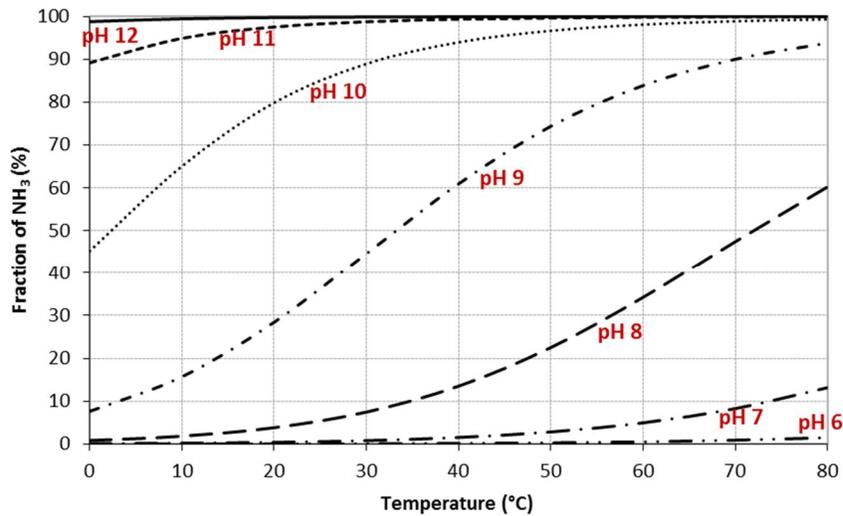
## 2.5.1 Physical and chemical treatment

Many of the sidestream processes that have been researched or implemented rely on physical or chemical removal of nutrients. This section provides an overview of conventional and potential physical and chemical sidestream treatment processes.

### 2.5.1.1 Ammonia stripping

Ammonia gas reacts with water to form ammonium hydroxide ions and exist in equilibrium based on the pH and temperature of the solution. Based on this chemistry, one approach to ammonia removal is to shift the equilibrium toward the gaseous phase and then air strip ammonia from the solution. At high pH and temperature, the equilibrium approaches 100% ammonia in the solution (Figure 2.3). While the stripped ammonia gas can be exhausted to the atmosphere, ammonia gas contributes to smog formation and can impact local ecosystems (Krupa, 2003). Ammonia reacts with strong acidic species in the atmosphere such as nitric and

sulphuric acids, by-products of vehicle and industrial combustion processes, to form ammonium salts. The ammonium salts become fine particulate matter or aerosols. In addition to the health implications associated with breathing the particulate matter, the ammonium salts are known to be deposited locally and can contribute to eutrophication of water bodies and negatively impact terrestrial ecosystems (Krupa, 2003). The Intergovernmental Panel on Climate Change (IPCC) reports that ammonia can also lead to the formation of  $N_2O$  from atmospheric chemical reactions. However,  $N_2O$  formation from  $NH_3$  is not fully understood and there is no method available for estimating conversion in the atmosphere (Intergovernmental Panel on Climate Change, 2006).



**Figure 2.3 – Fraction of unionized ammonia in solution at various pH and temperatures**  
(adapted from Emerson et al., 1975)

Various approaches can be used to strip ammonia gas from a sidestream. However, given the negative impacts associated with uncontrolled ammonia gas discharges, the focus of this section will be on processes which have potential for ammonia recovery; these include acid stripping, steam stripping and vacuum flash distillation processes.

### 2.5.1.1.1 Acid stripping

Air stripping in combination with absorption, can be used to remove and recover ammonia from dewatering centrate. First, the centrate pH is increased to convert the ammonium to ammonia. Through agitation and turbulence the ammonia gas dissolved in the centrate is transferred to an air stream. In a second vessel, the ammonia gas is absorbed from the air into a strong acid solution to generate an ammonium salt. Selection of the acid depends on economics and intended use of the ammonium salt solution. Typical acids and their associated ammonium salt are listed in Table 2.3. Removal of scale inside the tank can add to maintenance of such a system. Also, low temperature conditions can affect performance by reducing the reaction rate.

**Table 2.3 – Typical acids used for ammonia stripping and associated reaction products**

<b>Acid used for ammonia stripping</b>	<b>Associated ammonium salt produced by reaction with acid</b>	<b>Potential reuse of ammonium salt as a bulk solution or dried powder</b>
Sulphuric acid	Ammonium sulphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Fertilizer, flame retardant
Phosphoric acid	Mono-ammonium phosphate NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Fertilizer
	Ammonium phosphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Fertilizer, flame retardant
Hydrochloric acid	Ammonium chloride (NH <sub>4</sub> Cl)	Fertilizer
Acetic acid	Ammonium acetate (NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )	De-icer
Nitric acid	Ammonium nitrate (NH <sub>4</sub> NO <sub>3</sub> )	Fertilizer

Lei et al. (2010) used acetic acid to remove ammonia at a pilot scale and at 25°C achieved almost complete removal (99.95%) of ammonia from the wastewater based on an inlet concentration of 21,006 mg/L ammonia nitrogen. However, it is unclear from the data presented what proportion of the ammonia reacted with the acetic acid and was recovered as ammonium

acetate. The use of phosphoric acid to recover ammonia from a pilot-scale air stripping column was assessed by Minocha and Rao (1988). In this study, two reactors in series were operated to maximize ammonium recovery and minimize ammonia gas emissions.

As part of a sidestream treatment process selection exercise, District of Columbia Water and Sewer Authority (USA) conducted a market assessment for production and sale of ammonium sulphate generated from its Blue Plains Advanced WWTP (Eschborn et al., 2010; Figdore et al., 2010). Based on these assessments, air stripping combined with acid absorption and lime addition for the production of ammonium sulphate, the most economical process of the technologies evaluated. However, product marketing and supply management represented risks which eliminated ammonia stripping as the preferred option. Consequently, biological treatment remains the preferred primary method for sidestream treatment since the nitrogen is destroyed within the plant (Figdore et al., 2010).

The VEAS WWTP in Oslo has been operating a full-scale acid stripping sub-process for more than 10 years to remove ammonia from its anaerobic digester sidestream (Sagberg et al., 2006). The process produces ammonia nitrate as a by-product which is reused as a fertilizer. To minimize operational costs, supply of the acid is tendered and the low bidder is able to receive any volume of the ammonium nitrate solution at a reduced cost. The removal efficiency of the VEAS WWTP ammonia stripping process is limited on a practical basis to approximately 88%. Operating the system beyond a removal efficiency of 88% results in a rapid increase in energy consumption and diminishes return.

#### **2.5.1.1.2 Steam and hot air stripping**

Ammonia can be stripped from centrate through contact with a high temperature carrier liquid or air stream. Typically, a packed tower is used to provide sufficient contact time. As centrate

flows down the packing, the counter-current steam or hot air contacts and vaporizes the ammonia. The vapourized ammonia is transferred to a condensation column by the carrier liquid or air stream to form a concentrated ammonia solution. Alternatively, an acid reaction column could be incorporated into the process to generate a stable ammonium salt.

New York City has evaluated steam stripping of ammonia from dewatering centrate by means of bench and pilot scale facilities and achieved 80 – 85% removal without pH control (Carrio et al., 2003). However, to minimize clogging of the packing, centrate screening and solids removal is required. A similar evaluation of hot air stripping achieved 90% removal but required addition of alkalinity (*ibid.*).

#### **2.5.1.1.3 Vacuum flash distillation**

Vacuum flash distillation can be used as part of an ammonia stripping process to increase the efficiency of ammonia gas liberation from solution (Orentlicher et al., 2009). Flash distillation is applied to the centrate after the pH has been elevated. Dissolved ammonia gas is removed by increasing the temperature and lowering the pressure of the centrate stream. The process is temperature dependent. However, to achieve greater than 80% removal within a 10 minute batch process, the temperature of the centrate must be maintained at 43°C (Orentlicher et al., 2009).

#### **2.5.1.1.4 Summary of ammonia stripping options**

Ammonia stripping has the potential to provide a robust and potentially energy efficient process for centrate treatment. A key challenge that must be overcome for such systems is how to manage the recovered ammonia. Reaction with acid to form ammonium salts has great potential for recovering a fertilizer product provided that the WWTP owner has the resources to market and distribute the product. Under specific circumstances, use of stripped ammonia as a compound for reducing emissions from fuelled electrical generating stations or incinerators may

be possible. Under controlled conditions, ammonia can be reacted with  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{CO}_2$  in the flue gases (Resnik et al., 2004). The by-product of this scrubbing is ammonium sulphate, ammonium nitrate, and ammonium bicarbonate, all of which could be reused as a fertilizer. If the ammonia stripping process associated with a WWTP were in close proximity to a fossil fuelled generating station, the surplus aqueous ammonia could be used to scrub the flue gases. Alternatively, the ammonia could be used for scrubbing exhaust gases from a sludge incineration or biogas co-generation facility. Additional research is required to determine whether using ammonia for exhaust gas scrubbing is a practical solution.

### **2.5.1.2 Oxidation of ammonia**

This section provides a brief overview of options for chemically oxidizing ammonia.

#### **2.5.1.2.1 Break-point chlorination of ammonia**

The addition of chlorine to effluent either as gaseous chlorine or liquid sodium hypochlorite is conventionally used as a disinfectant but if sufficiently dosed will result in ammonia oxidation and removal. Chlorine reacts with ammonia in water to form various chloramines. However, more readily oxidizable compounds such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{H}_2\text{S}$  and organics will react first with the chlorine. If the dose is further increased, chlorine will react with ammonia to form chloramines which contribute to an increase in the combined chlorine residuals. As the chloramines are degraded, the total chlorine residual approaches a minimum which is associated with a maximum ammonia removal. Following this minima, the chlorine residual begins to increase again if chlorine dosing increases. The local minimum that indicates completion of ammonia oxidation is known as the break-point chlorination demand. Chlorine dosing must be sufficient to achieve the characteristic break-point to provide for ammonia removal (Tchobanoglous et al., 2003).

The required chlorine dosing to achieve ammonia removal is dependent on pH and the amount of readily oxidizable compounds. In reasonably clean water with low suspended solids and a pH in the range of 6 - 8, the minimum chlorine dosing on a molar ratio was measured to be approximately 8:1 (Pressley et al., 1972; Brooks, 1999). High alkalinity can increase the chlorine demand to as high as 14.8:1 (Tchobanoglous et al., 2003). The presence of high suspended solids would further increase chlorine demand and increase chlorine by-products.

There do not appear to be any full-scale use of chlorine for ammonia removal in digester sidestreams. However, given that dewatering centrate typically has a moderate level of suspended solids and alkalinity, the chlorine dose would be at the high end of the published ranges. At a dosing rate of 15:1, the amount of required chlorine would be prohibitively expensive to provide removal of the typical range of anaerobic digester centrate ammonia (700 – 4,000 mg/L NH<sub>4</sub>).

#### **2.5.1.2.2 Catalytic oxidation of ammonia**

At a temperature of 800°C and in the presence of a platinum catalyst, ammonia gas can be oxidized to form nitric oxide (NO) which is further oxidized to nitrogen dioxide (NO<sub>2</sub>). The reaction steps are:



A catalytic oxidation system could be used to reduce ammonia gas removed from centrate streams. Under this kind of process, the centrate pH would need to be increased to shift the ion equilibrium toward the gaseous phase. Once liberated from the wastewater stream, the ammonia gas can be oxidized catalytically.

Nitrogen dioxide (NO<sub>2</sub>) is a photochemical oxidant in the atmosphere and in the presence of hydrocarbons UV light is the primary cause of urban smog (World Health Organization, 2005). Consequently, uncontrolled release of nitrogen dioxide into the atmosphere as part of a centrate treatment system could contribute to existing environmental and health impacts in an urban area. To mitigate these impacts, catalytic oxidation of ammonia may require a post-treatment process to mitigate the local impacts of nitrogen dioxide.

#### **2.5.1.2.3 Electrochemical oxidation of ammonia**

Electrochemical oxidation of ammonia could be accomplished by passing a current through a high-strength centrate stream. Lab-scale experiments by Lei and Maekawa (2007) resulted in nearly 100% removal of ammonia after 5 hours of reaction time. The electrolysis process generates hypochlorous acid in the presence of sodium chloride. Hypochlorous acid reduces ammonia to nitrogen gas (N<sub>2</sub>). However, in order to sustain the reaction, the wastewater stream must be dosed with sodium chloride and the electrode must be able to adsorb ammonia (Kim et al., 2006).

Currently, there do not appear to be any full-scale applications of electrochemical oxidation for removal of ammonia in centrate. The potentially high operating energy cost and issues around sodium chloride carry-over into the mainstream process would need to be addressed prior implementing such a system.

#### **2.5.1.3 Chemical precipitation**

Chemical precipitation of phosphorus using a cationic coagulant (iron, aluminum or lime) is a conventional approach in wastewater treatment systems is well documented in the literature. With these systems precipitated phosphorus is typically recovered in the dewatered sludge or dewatering centrate. Depending on the form of phosphorus (ie, dissolved, colloidal or suspended

particulate), coagulation may occur through adsorption destabilization, bridging mechanism or precipitating enmeshment (Bratby, 2006). Metcalf & Eddy (2014) notes that historically dissolved phosphorus coagulation using aluminum and iron salts has been described principally in terms of reactions forming ferric or aluminum phosphate. However, the literature shows that in wastewater systems, the adsorption of reactive and non-reactive phosphorus on to  $\text{Al}(\text{OH})_3$  whether in solution or as part of an alum sludge may be more significant (Galarneau and Gehr, 1996). In wastewater, the reaction of aluminum and orthophosphate formed aluminum hydroxyphosphate which could enhance further phosphorus removal or contribute to organics removal through the formation of soluble and colloidal hydroxyl-aluminum-tannate complexes (Omoike et al., 1999). The finding that surface charge on alum sludge can be used for phosphorus precipitation has led to the notion of re-using water treatment residuals for phosphorus removal in wastewater (Babatunde & Zhao, 2010). Recycled alum sludge introduced into a full-scale wastewater facility was shown to efficiently adsorb soluble phosphorus and continued to be effective even with increasing alum sludge age with the treatment process (Maher et al., 2015).

#### **2.5.1.4 Struvite precipitation**

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is a white, crystalline substance composed of magnesium, ammonium and phosphate. Struvite can precipitate under conditions where the pH is above 7.5 and magnesium ( $\text{Mg}^{2+}$ ), ammonium ( $\text{NH}_4^+$ ) and phosphate ( $\text{PO}_4^{3-}$ ) occur in equal parts (de-Bashan and Bashan, 2004). Historically, struvite formation in WWTPs has been a nuisance and associated with increased maintenance. However, recent research has led to techniques for harvesting struvite from digester supernatant sidestreams, thereby serving as a way to remove both phosphate and ammonia. Digester supernatant tends to be high in ammonia and moderately

high in phosphate but low in magnesium. Consequently, adding magnesium to the supernatant stream in a purposely designed reactor can sustain struvite precipitation and achieve 90% phosphate removal (Ueno and Fuji, 2001). However, due to the stoichiometry and molar mass of phosphorus and nitrogen ammonia will always be less. For every gram of phosphorus removed as struvite, the nitrogen removal will be 0.45 g N. In anaerobic digestion scenarios, struvite recovery provides only nominal ammonia control. For example, in a mesophilic AD scenario that produces centrate with ammonia of 1,050 mg N/L and phosphate of 140 mg P/L (Mavinic et al., 2007), 90% removal of phosphorus as struvite translates to only 5.4% nitrogen removal. Where low nutrient concentrations are desired, struvite recovery would normally need additional ammonia treatment.

A secondary benefit of struvite recovery from centrate is that the recovered struvite can be used as a fertilizer, thereby displacing conventionally produced phosphate fertilizer. Barnard (2007) has highlighted the fact that phosphate is a limiting nutrient in agricultural production with world-wide supplies estimated to be as low as 50 years. The phosphate conversion efficiency increases with pH and optimal struvite occurs at pH 9.5 (Hanhoun et al., 2009). However, control of the removal efficiency can also be achieved through control of the supersaturation ratio (Mavinic et al., 2007). In this experiment, operating the reactor at pH 8 but with a high magnesium dosage achieved over 90% phosphate removal efficiency.

Air stripping of CO<sub>2</sub>, thereby increasing pH has also been studied for process optimization. Stumpf et al. (2009) used a bench-scale, airlift reactor to achieve 90% removal of the available phosphate through struvite precipitation. The availability of a seeding material and adequate mixing energy are also important factors for controlling and optimizing struvite precipitation (Wang et al., 2006).

A commercialization of the struvite recovery process has led to a full-scale implementation at the Durham WWTP (North Carolina, USA) (Bauer, 2010). Bauer describes a successful implementation of the Ostar<sup>®</sup> process (originally developed by the University of British Columbia, Canada) which achieves 89% phosphorus removal and 20% ammonia removal in the dewatered digested sludge centrate stream. Struvite recovery allows the Durham plant to meet its low effluent phosphate limit without the use of chemicals.

### **2.5.1.5 Membrane filtration**

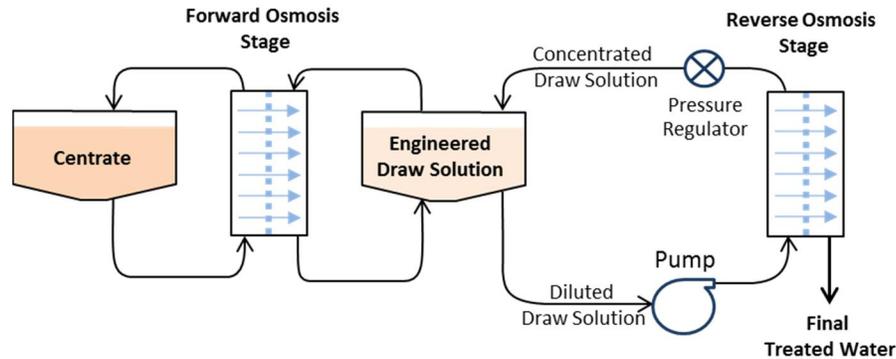
Advances in membrane filtration technology have included processes for centrate treatment. Two processes which have been proposed for centrate treatment include forward osmosis and Liqui-Cel<sup>®</sup>, a proprietary membrane process.

#### **2.5.1.5.1 Forward osmosis**

Forward osmosis (FO) is a technique for using osmotic pressure to concentrate a feed solution. In reverse osmosis (RO), hydraulic pressure is used to overcome the osmotic pressure of an aqueous feed solution and force the movement of water molecules across a membrane to produce purified water. In contrast to this, FO relies on the natural osmotic pressure between the aqueous feed solution and an engineered draw solution (DS) (Cath et al., 2006). The osmotic pressure gradient between the feed solution and DS forces water molecules across a membrane, thereby concentrating the feed solution.

Holloway et al. (2007) applied the principle of FO to centrate treatment to produce a concentrated centrate solution. Because FO is an osmotically driven process that requires very low hydraulic pressure, the effects of fouling are reduced and membrane support and compaction are of less concern. To sustain the osmotic pressure gradient, Holloway et al. introduced a RO membrane (Figure 2.4). In this system, reject water from the RO system is used to maintain a

constant concentration in the DS. Based on Holloway et al.'s research, an optimal water recovery rate of 70% was established. At this rate, power consumption was approximately 4 kWh/m<sup>3</sup>.



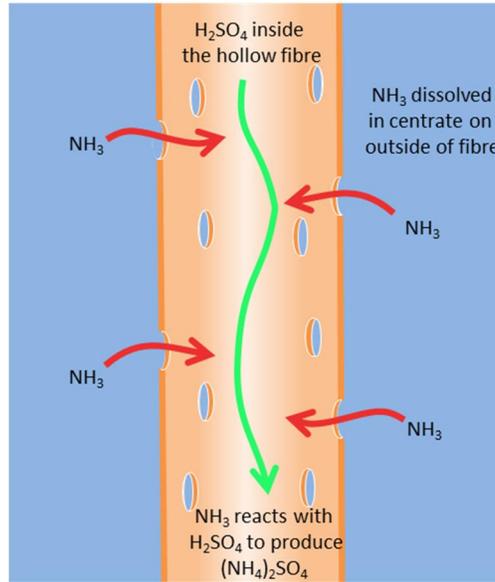
**Figure 2.4 – FO/RO process schematic**  
(adapted from Holloway et al., 2007)

There are no reported full-scale facilities utilizing forward osmosis as a sidestream treatment method. The ability to concentrate the centrate stream would potentially allow for a cost effective sidestream treatment if the concentrated centrate could be used as a liquid fertilizer without additional treatment. While this is technically possible, there would continue to be potential challenges. Suspended solids and other organic constituents would be concentrated together with the nutrients. The odour potential, stability and utility of the concentrated solution is required to assess whether additional pre or post treatment is required.

#### **2.5.1.5.2 Liqui-Cel® membrane contactor**

Liqui-Cel® is a proprietary process which utilizes a membrane contactor to selectively remove ammonia from a wastewater stream (Liqui-Cel, 2009). In this process a hydrophobic membrane separates the centrate solution at high pH (>11.3) and a sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) solution (Figure 2.5). At a pH of 11.3 or higher, the ammonia will be present in the centrate solution as free ammonia gas. The affinity with sulphuric acid causes ammonia to migrate across the porous

membrane and react to form ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ). The membrane pore size and hydrophobic properties are designed to minimize the migration of water molecules or other constituents.



**Figure 2.5 – Membrane contactor process schematic for ammonia removal**  
(adapted from Liqui-Cel, 2009)

As suggested by Figdore et al. (2010), operational costs for such a treatment process will be largely dictated by chemical supply costs due to its heavy reliance on caustic for pH control and sulphuric acid to achieve the ammonia removal. The potential for membrane fouling and the need to pre-filter the centrate have also been identified as potential limitations of this technology (*ibid.*). However, biofouling on the feed side of the membrane should not be problematic given the feed wastewater is at an elevated pH ( $> \text{pH } 11.3$ ). The ability for the process to be contained within a compact, closed vessel and the potential to produce a high quality liquid fertilizer serve as advantages. These characteristics would allow for control of noxious air emissions and potentially provide a revenue source from fertilizer sales.

### 2.5.1.6 Ion exchange and adsorption

Sidestream processes that utilize ion exchange or adsorption as a principle removal mechanism have been investigated or implemented as a sidestream process. Ion exchange processes use resins which have the ability to exchange an ion adsorbed on the resin surface with a specific cation or anion in the centrate. The ion targeted by the process has a stronger affinity for the charged location occupied by the ion and displaces it. In order to be effective, the exchanged ion needs to have little or no impact to the main treatment process or effluent. Adsorption is similar to ion exchange except that no ion is exchanged as part of the process.

The idea of using the ammonium adsorbing properties of vermiculite to create a fertilizer appears to have been first investigated by Allison et al. (1953). Vermiculite is a clay mineral with a high cation exchange capacity for ammonium. Naturally occurring magnesium on the vermiculite surface can be replaced by other cationic elements. The stability of the adsorbed cation is determined by the expansion of the lattice and its hydration properties. Ammonium is relatively stable but can be replaced by sodium cations (*ibid.*). Akerback et al. (2009) investigated the use of spent vermiculite ion exchange media as a fertilizer. Sand-size particles of vermiculite were used to adsorb ammonium and then used as a growing medium for pine seedlings and trees. The average maximum nitrogen content of the vermiculite was 1.44%, suggesting a removal rate of 14.4 NH<sub>3</sub>-N/kg. The growth characteristics of the ammonium-vermiculite amended seedlings were better than the untreated trees and those receiving nutrient irrigation.

The use of vermiculite as a single use ion exchange media and fertilizer has potential as a low-cost method for control of ammonia for small scale facilities. However, on a large scale the mass of required vermiculite makes this approach impractical. Assuming a sidestream flow of 0.5% of

total plant inflow and ammonia nitrogen concentration of 3,000 mg/L, a conventional anaerobic digester for a moderately sized 20,000 m<sup>3</sup>/d treatment plant could produce 300 kg NH<sub>3</sub>-N/d for a treatment plant. At this rate and assuming an adsorption capacity of 1.44% ammonia and removal rate of 90%, 19,000 kg/d of vermiculite would be required to treat the centrate. The effort and cost to transport, stockpile and reuse this mass of vermiculite would be onerous unless a source of vermiculite and demand for the spent material were in close proximity to the treatment facility. Carr et al. (2009) present results from a lab-scale experiment using ochre to adsorb phosphate from wastewater and then as a phosphorus fertilizer substitute. Depending on the source of ochre, adsorption capacities up to 30.5 mg P/g ochre can be achieved. Based on this maximum adsorption rate, 32.8 kg of ochre would be required to remove one kilogram of phosphorus. As with vermiculite for removing ammonia, the economics of a full-scale application of this technology would depend largely on the proximity of the mined ochre.

A more conventional approach is to use a regenerative ion exchange media to remove ammonia or phosphorus ions from the waste stream. Design considerations for ion exchange systems include competition with non-target ions and management of target ion after regeneration. Clinoptilolite, a naturally occurring zeolite, was proposed as a sorption medium by Zorpas et al. (2010) to remove ammonium from digester sidestreams. However, clinoptilolite has a stronger affinity for potassium than ammonium, thereby potentially reducing its efficiency as a centrate treatment method (Guo et al., 2008). Using centrate from a belt press as a waste stream, Thornton et al. (2007) was able to achieve a total loading capacity of 47 to 51 g NH<sub>4</sub><sup>+</sup>-N/kg for MesoLite, a manufactured clay-aluminum ion exchange media. The ion exchange media was regenerated using 5% NaOH solution. At this elevated pH (> 12), the ammonia-ammonium equilibrium would shift to the gas phase. Consequently, regeneration of the ion exchange media

would result in release of ammonia gas. To mitigate the potential health and environmental impacts discussed previously, this approach to ammonium removal should include a secondary process to capture the ammonia gas.

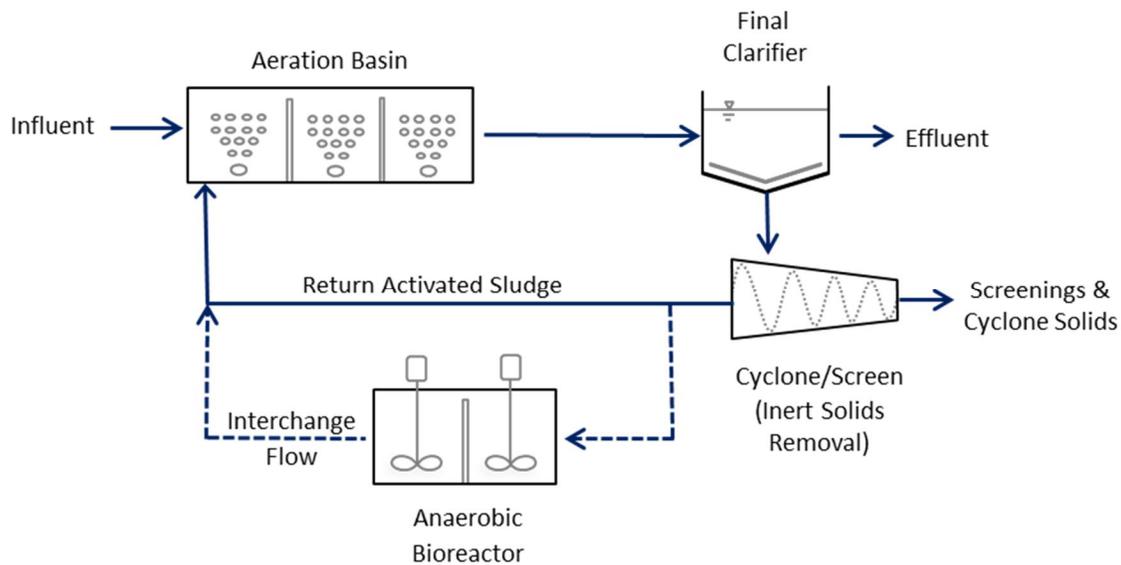
Various approaches have been studied for regeneration of the ion exchange media. Nitric acid and sulphuric acid were assessed to allow nitrogen recovery as ammonium nitrate and ammonium sulphate (Pawlowski, 1979). Biological regeneration of the media has also been considered (Lahav and Green, 1998). Sengupta and Pandit (2010) showed the feasibility of using a polymeric anion exchanger impregnated with iron oxide nanoparticles to selectively remove phosphate and allow for phosphorus recovery. In these tests, regeneration with sodium chloride and sodium hydroxide consistently recovered more than 95.0% of sorbed phosphate within ten bed volumes. Phosphorus can be recovered from the spent regenerant through addition of a chemical to precipitate the phosphate.

## **2.5.2 Biological treatment**

Biological processes have been applied to sidestream treatment. In this section, conventional and new systems are summarized.

### **2.5.2.1 Cannibal® sidestream process**

The Cannibal® process is a sidestream process used to reduce the solids production of a conventional activated sludge treatment plant. By reducing the sludge volume, the process is potentially able to minimize the sidestream loading from the solids digestion process. In the Cannibal® process, approximately 10% of the return activated sludge stream from the secondary clarifier is routed through an anaerobic bioreactor (Figure 2.6) with an optimum hydraulic retention time of 7 days (Easwaran et al., 2009).



**Figure 2.6 – Cannibal sidestream treatment process schematic**  
(adapted from Novak et al., 2007)

At a lab scale, the Cannibal<sup>®</sup> system has resulted in a 60 - 63% reduction in sludge production compared to a control treatment system with aerobic digestion (Novak et al., 2007; Goel and Noguera, 2006a). The lower sludge production results in lower power consumption for operating the aerobic digester; reduced sludge disposal costs; and reduced polymer consumption (Siemens, 2011). The literature does not specifically assess whether there is an increased energy requirement associated with the additional readily degradable organic load. However, Novak et al. (2011) notes an increased air utilization rate in the aeration phase of the mainstream bioreactor.

The reduction in solids is strongly associated with release, under anaerobic conditions, of iron and protein bound up in the extracellular polymeric network of the floc (Park et al., 2006). Under these conditions, the released organic matter, principally proteins are rapidly degraded when returned to the activated sludge tank. Novak et al. (2011) also showed that feed patterns can have a significant impact on the iron release: under a fast feed (high substrate pressure) scenario a

higher iron and protein release was detected in the Cannibal<sup>®</sup> reactor, resulting in a higher solids reduction than the slow feed scenario.

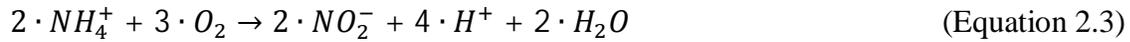
The fermentation that is associated with a sidestream anaerobic process has shown to have benefit to biological phosphorus removal processes by increasing the volatile fatty acid content of the return stream (Goel and Noguera, 2006a; Goel and Noguera, 2006b). The approach of fermenting a slip-stream of return activated sludge to enhance biological phosphorus removal was explored by Barnard et al. (2010a).

An approach similar to the Cannibal<sup>®</sup> process for solids reduction which involved recirculating part of the sludge stream from a thermophilic anaerobic digester at the Rockaway WWTP (New York, US) was reported by the Torpey et al. (1984). In this study, 67% of the sludge on a volatile solids basis from the mesophilic-thermophilic digester was returned to the mainstream activated sludge treatment process and resulted in a 55% reduction in the overall sludge production from the plant. During the five month testing period the overall biogas production increased slightly. Following this pilot study, similar sludge reduction benefits were measured at other treatment plants in the New York area (Carrio et al., 1985). However, the same approach of recycling anaerobically digested sludge was tested at the Hanover WWTP (Pennsylvania, US) and did not result in any overall solids reduction (Prakasam et al., 1990). Due to the reduced operating costs, the Cannibal<sup>®</sup> may be an attractive sidestream process for treatment plants that employ aerobic digesters for sludge stabilization. However, for treatment plants that rely on AD of sludge, the net benefit of recycling anaerobically digested sludge is not assured.

#### **2.5.2.2 Nitrification/denitrification**

In AD, many of the by-products are nitrogen-free ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ) with most of the bound nitrogen released as ammonia (Wett et al., 2010). Conventional biological treatment of ammonia

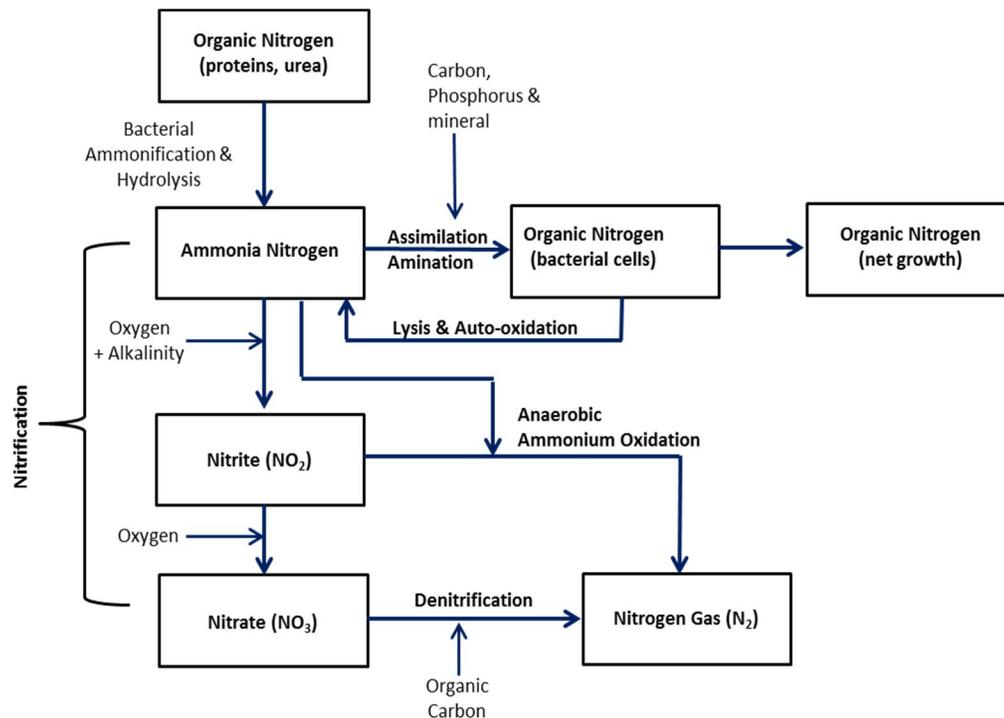
nitrogen involves nitrification of ammonia to nitrate ( $NO_3^-$ ) based on Equation 2.3 and Equation 2.4:



Following nitrification, nitrate ( $NO_3^-$ ) is reduced to nitrogen gas under anoxic conditions with carbon serving as the electron donor (Equation 2.5):



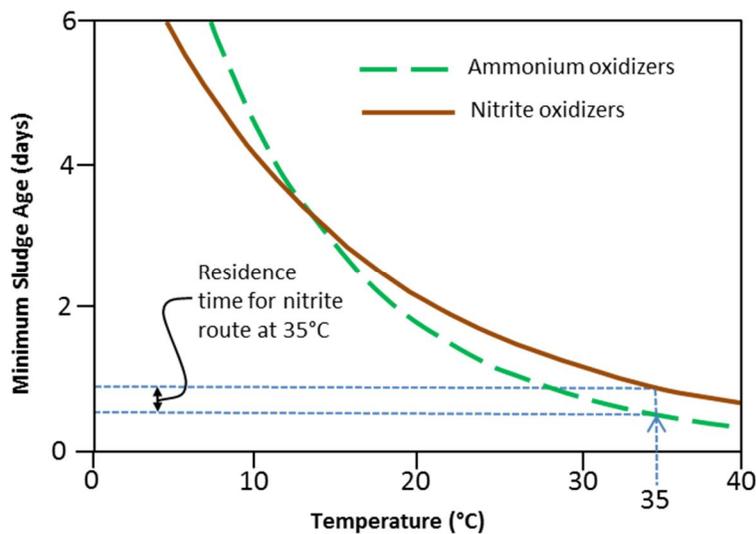
The process converts the ammonia nitrogen to nitrogen gas (Figure 2.7) but requires relatively high energy expenditures. The observed oxygen requirement for removing biochemical oxygen demand (BOD) varies between 0.90 – 1.3 kg  $O_2$ /kg BOD; this compares to 4.57 kg  $O_2$ /kg N for oxidizing ammonia to nitrate (Metcalf and Eddy, 2014).



**Figure 2.7 – Biological transformation of nitrogen**  
(adapted from Stinson, 2001)

### 2.5.2.3 Nitritation

Nitritation is the first step in the nitrification process in which ammonia is oxidized to nitrite (Equation 2.3). The SHARON (Single reactor High activity Ammonia Removal over Nitrate) is a continuous flow, nitritation process originally developed to treat high ammonia in dewatering centrate streams. The process operates at a low sludge retention time (SRT) and relatively high temperature of 35°C (Figure 2.8). The elevated temperature conditions results in high specific growth rates which obviates the need for sludge retention; in addition, ammonia oxidizing bacteria (AOB) out-compete the nitrite oxidizing bacteria (Hellinga et al., 1998). Operating a partial nitrification process to treat high ammonia waste streams reduces aeration requirements and bioreactor sizing over a complete nitrification process.



**Figure 2.8 – Minimum residence time for ammonium and nitrite oxidizers**  
(adapted from Hellinga et al., 1998)

Since ammonium ( $\text{NH}_4^+$ ) rather than ammonia ( $\text{NH}_3$ ) serves as the substrate, pH becomes an important operational parameter (Hellinga et al., 1999). An increased pH will result in a lower ammonium concentration and elevated effluent ammonia concentration (van Dongen et al.,

2001). Furthermore, nitrous acid ( $\text{HNO}_2$ ) is inhibitory to the AOB and used as a substrate for nitrite oxidizing bacteria (NOB). To minimize the inhibition effects of  $\text{HNO}_2$  and ensure the AOB's continue to out-compete the NOB's, the nitrification reactor needs to be operated at an optimum pH between 6.5 and 8 (van Hulle et al., 2007). To provide for pH control, a denitrification stage can be added to replace the lost alkalinity. However, this necessitates addition of methanol as a carbon source. Van Hulle et al. (2007) determined that provision of a denitrification stage with addition of methanol to control pH was more economical than chemical pH control (i.e., NaOH). Recently, Mayer et al. (2009) was able to satisfy the denitrification carbon requirements using a slip-stream of the anaerobic digester feed sludge, thereby further improving the economics.

Garrido et al. (1997) investigated the stability of a fixed film reactor for nitrification as part of a nitrification/denitrification process. At a loading rate of  $5 \text{ kg NH}_3\text{-N/m}^3$ , the lab-scale biofilm airlift suspension (BAS) reactor was able to achieve a stable conversion of ammonia to equal parts nitrite and nitrate.

The nitrification processes took on new significance with the discovery of the anaerobic ammonium oxidation (Anammox) process. This feature is discussed below in greater detail as it is also the sidestream process used in this thesis.

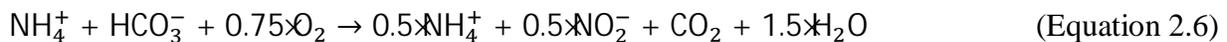
#### **2.5.2.4 Partial nitrification and anaerobic ammonium oxidation (Anammox)**

In 1995, Mulder et al. published a paper that described a new bacterium which can oxidize ammonia under anaerobic (anoxic) conditions. The results were significant because anaerobic oxidation of ammonium was not thought to be feasible (Kuenen, 2008) or at best a theoretical possibility as was suggested by Broda in 1977 (as cited by Kuenen, 2008). The Anammox bacteria were eventually classified as belonging to the group *Planctomycetes* and contain a

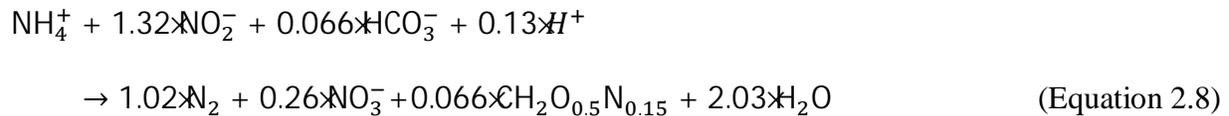
membrane-bound organelle in which ammonium and nitrite are converted to nitrogen gas using hydrazine as an intermediate (Kartal et al., 2010). The newly discovered bacteria were assigned to the sub-group *Candidatus* of the *Planctomycetes* phylum within which five genera have currently been identified: *Anammoxoglobus*, *Brocadia*, *Jettenia*, *Kuenenia*, and *Scalindua* (Kuenen, 2008). From a sidestream treatment perspective, processes which utilize the Anammox bacteria are showing great potential for removing ammonia-N with low consumption of energy and no supplemental carbon addition.

After Mulder's original paper, additional research confirmed that the anoxic oxidation of ammonium is biologically mediated (van de Graaf et al., 1995) and that nitrite was the preferred electron acceptor (van de Graaf et al., 1996). The original research had suggested nitrate was being used as an electron acceptor. The role of nitrate in the ammonia oxidation process is not clear. Research has indicated that under certain conditions Anammox bacteria can also convert nitrate to nitrogen gas while oxidizing an organic energy source (Kartal et al., 2007).

In the late-1990's, the SHARON process was coupled to an Anammox process to achieve denitrification without addition of a supplemental COD source or methanol (Jetten et al., 1997; 1998). The SHARON reactor was used to partially nitrate an anaerobic digester supernatant waste stream. Effluent from the SHARON reactor was then used as an influent to the Anammox reactor following the partial nitritation (Equation 2.6) and anaerobic ammonia oxidation (Equation 2.7) (van Dongen et al., 2001).



Equation 2.8 below describes the Anammox step and accounts for the nitrogen mass balance and cell growth (Strous et al., 1998).



Based on the above reaction rates and piloting of the SHARON-Anammox configuration, the cost of removing nitrogen from waste streams containing high ammonium and low organic matter, like digester supernatant, could be reduced by up to 90% (Jetten et al., 2001).

Factors reported in the literature which have been shown to impact the Anammox process include temperature, dissolved air, pH, nitrite, nitrate, ammonia, phosphate and methanol. Table 2.4 summarizes the range of operation and inhibition values reported in the literature. The available data indicates that dissolved air and nitrite can have a strong inhibitory impact on the Anammox process. Nitrite toxicity is a rate limiting criterion for many Anammox reactor configurations and results in an over-designed bioreactor (van der Star et al., 2007).

Consequently, a better understanding of the factors that result in nitrite, an electron acceptor for oxidation of ammonium, being toxic to the Anammox bacteria could lead to more efficient bioreactor designs. Phosphate and nitrate can also be inhibitory at higher concentrations.

However, the large range of inhibition values reported for nitrite and phosphate should motivate further investigation. Process configurations, testing protocol or the dominant planctomycete genera could all be factors in the variation of nitrite and phosphate inhibition values indicated in Table 2.4.

**Table 2.4 – Operating parameters and observed inhibition thresholds for Anammox processes**

Parameter	Criteria	Observed Impacts	Test Configuration	Reference
Temperature, °C	20 – 43 37 25	-Stable -Optimum at pH 8 -Stable	SBR Fixed volume assays MBBR	Strous et al. (1999) Egli et al. (2001) Szatkowska et al. (2007)
Dissolved Air, mg/L	>0.2 1.2 <sup>c</sup>	-Increasing inhibition -Irreversible inhibition after 64h	UASB <sup>b</sup> Fixed volume assays	Jung et al. (2007) Egli et al. (2001)
pH	6.7 – 8.3 6.5  8.0 8.5	-Stable -61% better N-removal efficiency than pH between 7.5 and 8.1 -Optimum at 37°C -Elevated nitrite concentration	SBR MBBR  Fixed volume assays SBR	Strous et al. (1999) Jaroszynski et al. (2011)  Egli et al. (2001) Lopez et al. (2008)
TSS, mg/L	na	-	-	-
Ammonium-N, mg N/L	980 770 90	-Stable -50% inhibition -No effect	SBR Fixed volume assays SBR	Strous et al. (1999) Dapeena-Mora et al. (2007) Bettazzi et al. (2010)
Ammonia-N, mg N/L	13 - 90 >2	-Inhibition observed -Increasing inhibition	Batch test UASB <sup>b</sup>	Waki et al. (2007) Jung et al. (2007)
Nitrite-N, mg N/L	350 274 185 102 100 70 60 60 30	-50% inhibition -Threshold inhibition -Complete, reversible inhibition -Decreased activity -Complete inhibition -Decreased activity -Strong inhibition -Decreased activity (spiked) -Decreased activity (prolonged)	Fixed volume assays Gel entrapped media Fixed volume assays SBR SBR UASB <sup>b</sup> SBR SBR SBR	Dapeena-Mora et al. (2007) Kimura et al. (2010) Egli et al. (2001) Lopez et al. (2008) Strous et al. (1999) Jung et al. (2007) Fux et al. (2002) Bettazzi et al. (2010) Bettazzi et al. (2010)
Nitrate-N, mg N/L	980 630 57	-Stable -50% inhibition -No effect	SBR Fixed volume assays SBR	Strous et al. (1999) Dapeena-Mora et al. (2007) Bettazzi et al. (2010)
Phosphate, mg/L	1,990 1,900 <sup>a</sup> 155 95	-50% inhibition -No inhibition -Complete inhibition -No inhibition	Fixed volume assays Fixed volume assays Fluidized bed Fluidized bed	Dapeena-Mora et al. (2007) Egli et al. (2001) van de Graaf et al. (1996) van de Graaf et al. (1996)
Hydrogen Sulphide, mg/L	na	-Increased activity	UASB <sup>b</sup>	Jung et al. (2007)
Acetate, mg/L	118 <sup>a</sup>	-16% increase in nitrite-reducing activity	Batch test with purified culture	Güven et al. (2005)
Propionate, mg/L	73 <sup>a</sup>	-24% increase in nitrite-reducing activity increase	Batch test with purified culture	Güven et al. (2005)
Methanol, mg/L	106 <sup>a</sup> 16 <sup>a</sup>	-51% inhibition -Complete loss of activity	Batch test with gel entrapped media Batch test with purified culture	Isaka et al. (2008) Güven et al. (2005)

- Notes: a. Calculated from authors' published data  
b. Upflow Anaerobic Sludge Blanket (UASB); Sequence Batch Reactor (SBR); MBBR: Moving Bed Biofilm Reactor  
c. Calculated based on 18% oxygen saturation value provided by author

Based on the research, phosphate inhibition is an important factor in the design of a full-scale Anammox process treating centrate associated with digested BNR sludge. Bauer (2010) notes

that peak phosphate in the centrate from the Durham Advanced WWTP digester which is fed sludge from an enhanced biological phosphorus removal process can range between 900 and 1,800 mg/L PO<sub>4</sub> (300 – 600 mg/L PO<sub>4</sub>-P). The peak centrate phosphate concentrations measured at the Durham facility are within the range of inhibitory values documented in Table 2.4.

Ammonium has some inhibitory impact but this may be influenced by shifts in the ammonia-ammonium equilibrium caused by changes in pH. Jung et al. (2007) were able to show a clear correlation between free ammonia and Anammox inhibition and suggested a maximum free ammonia concentration less than 2 mg/L. At high ammonium-nitrogen loading and temperature conditions associated with digester supernatant treatment using Anammox, pH control becomes an important operating variable. Under these conditions, small pH increases can result in a relatively large increase in free ammonia potentially leading to ammonia toxicity. Further research is required to support this argument.

Many studies use an operating temperature above 30°C. However, Anammox bioreactors can be operated at lower temperatures but achieve less than optimal nitrogen removal rates. Szatkowska et al. (2007) successfully operated a pilot Anammox reactor at 25°C which was fed digester supernatant. At this temperature the need for external heating was eliminated thereby off-setting the reduced biological process efficiency.

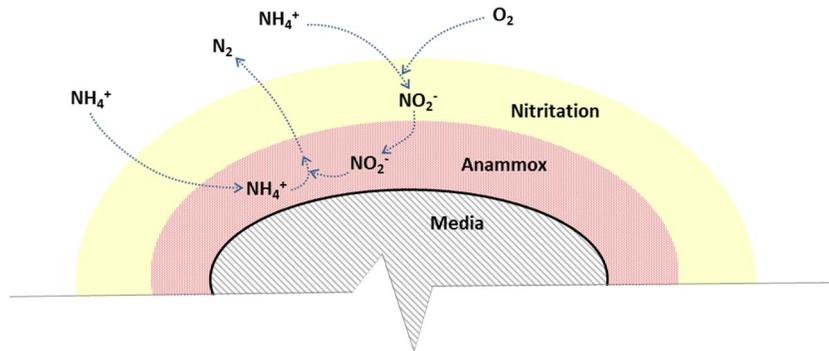
In the presence of propionate, Anammox activity increased, resulting in increased CO<sub>2</sub> production and higher level of nitrite consumption (Güven et al., 2005). The results suggest that the propionate was oxidized to CO<sub>2</sub> using nitrite or nitrate as an electron acceptor. Other research shows that hydrogen sulphide can also enhance Anammox activity by reducing the oxygen reduction potential (Jung et al., 2007).

Single tank nitrification-Anammox processes have been developed as an alternative to the two reactor processes where nitrification is controlled in a separate aeration tank. A completely autotrophic nitrogen removal over nitrite (CANON) process was first described by Third et al. (2001) and utilized a SBR to develop a mixed culture of nitrosomonas-like aerobic and planctomycete-like anaerobic ammonium oxidizing bacteria. The CANON concept of using a single stage reactor has continued to expand to include attached growth fixed film reactors, moving bed biofilm reactor (MBBR), membrane and SBR systems.

DEMON (DeamMONification) is an alternative mixed culture SBR process proposed by Wett et al. (2007) which utilizes Anammox bacteria and incorporates two significant advancements. First, the process control was simplified, using pH as a primary control variable. During nitrification, the mixed liquor pH is allowed to decrease to a lower set-point, after which the aeration is turned off creating the anoxic condition for deammonification which in-turn increases the pH. Similarly, when the pH reaches an upper set-point, the aeration turns on. By cycling the aeration on and off in this way, the nitrification and deammonification stages can be balanced. The second advancement was incorporation of a mechanism for retaining Anammox culture. Anammox bacteria grow slowly, having a doubling time of 10 – 12 days at 35°C (Kartal et al., 2010) which necessitates a long sludge age. However, in order to ensure nitrification is selected over nitrification, a sludge age of approximately 1.5 d is required for the aerobic culture (nitrosomonas population). To recover Anammox bacteria in the waste activated sludge while still achieving nitrification, a technique was developed for using a cyclone-like device as a selector (Wett et al., 2010). The cyclone recovers the granular sludge that is associated with the Anammox bacteria, thereby allowing for a mechanism to increase Anammox biomass concentration.

Anammox attached growth processes have shown good potential because of their ability to retain biomass. Several biofilm reactor configurations have been developed, including granular sludge, fluidized bed biofilm reactors, airlift reactors, and rotating biological contactors. Once the bacteria are established, Anammox systems are robust (van der Star et al., 2007).

Characteristics of an Anammox biofilm were reported by Siegrist et al. (1998) in a rotating biological contactor and later confirmed by Egli et al. (2001). Furukawa et al. (2001) reported the results of research on a biofilm process which utilized Anammox bacteria. Further work by Furukawa et al. (2006) led to a patent for Single-stage Nitrogen removal using Anammox and Partial nitritation (SNAP). Veolia (2011) has incorporated the Anammox culture into a single stage moving bed biofilm reactor (MBBR), known as ANITA™ MOX process. The Anammox bacteria form in an interior layer of the biofilm, below the aerobic layer where any dissolved oxygen is consumed and nitrite is produced through oxidation of ammonium (Furukawa et al., 2001). A schematic of this biofilm concept is provided as Figure 2.9.



**Figure 2.9 – Schematic of Anammox attached growth structure**  
(adapted from Veolia Water, 2016)

The ability of the Anammox culture to form compact, fast settling granules has been studied extensively because of the potential to achieve high biomass concentrations. Microbes grow in granules in response to high velocities that would otherwise wash out the lighter floc and in

effect results in biofilm-type growth (Beun et al., 2000). Imajo et al. (2004) first demonstrated the feasibility of using granular Anammox sludge in an upflow reactor configuration at both the lab and pilot scale. Fernandez et al. (2008) later investigated factors associated with the formation of the granules. Influent with high salt content which promote precipitate formation or zeolite particles which serve as support for biofilm growth resulted in increased biomass retention compared to the control (*ibid.*). Active Anammox granules form gas tunnels as they grow and can result in trapped pockets of gas, leading to sludge floatation (Chen et al., 2010). To avoid the potential reactor instabilities associated with floating sludge, Chen (2010) showed that it was possible to mechanically break-up the granules thereby re-establishing a well-settling granular biomass.

Membrane bioreactors have also been configured to utilize an Anammox process. The membrane is well-suited to biomass retention and results in the fastest start-up of any reactor system at the lab scale (Wang et al., 2009) with low membrane fouling if a granular biomass is achieved (Trigo et al., 2006). However, the high retention efficiency of membrane systems can result in accumulation of non-volatile, inert material which can inhibit Anammox growth (Trigo et al., 2006).

Table 2.5 provides a summary of operating and nitrogen removal data from select pilot-scale and full-scale facilities. Data on large-scale facilities is limited. In some cases the mean reported nitrogen removal efficiencies in Table 2.5 likely under-represent the actual removal efficiencies. For example, the Rotterdam (NL) facility shows exceptional ammonia oxidation efficiency in the Anammox stage (van der Star et al., 2007) but the nitrification stage is likely over-sized since it was originally designed to nitrify full ammonium load (Mulder et al., 2001), a feature not required in an Anammox system. Consequently, the calculated efficiency on a total tank volume

basis of the Rotterdam sidestream treatment system is likely under-estimated. As the collective operational experience increases, it is expected that a more accurate representation of the treatment efficiency for different configurations will become available.

**Table 2.5– Performance of nitrification-anammox systems treating AD digester sidestream**

Facility/ Location	Reactor Type <sup>a</sup>	Nitrification Stage Reactor Volume (m <sup>3</sup> )	Anammox Stage Reactor Volume <sup>e</sup> (m <sup>3</sup> )	Temp. (°C)	Mean Nitrogen Removal Capacity <sup>d</sup> (kg N/m <sup>3</sup> ·d)	Reference
Rotterdam (NL)	GSR	1,800	70	30-40	0.37	van der Star et al., 2007; Mulder et al., 2001
Hattingen (DE)	MBBR	104	158	20-30	0.26 – 0.32 <sup>b</sup>	Rosenwinkel et al., 2005
Himmerfjorden (SE)	MBBR	-	2.1 <sup>f</sup>	25	0.36	Szatkowska et al., 2007
Strass (AT)	SBR	-	500	28	0.61 <sup>c</sup>	Wett et al., 2007b
Zurich (CH)	SBR	2.0	1.6	30	0.30 <sup>b</sup>	Fux et al., 2002

- Notes: a. Granular Sludge Reactor (GSR); Moving Bed Biofilm Reactor (MBBR); Sequence Batch Reactor (SBR)  
b. Calculated from authors' published data  
c. NH<sub>4</sub>-N removal reported  
d. Calculation based on sum of nitrification and Anammox reactor volumes  
e. Total volume for single stage reactors  
f. Does not include volume of final settling tank

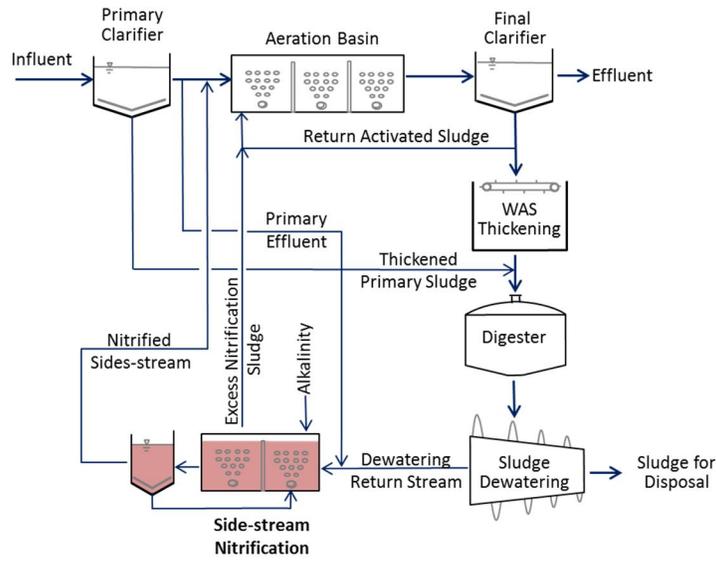
Giraldo (2009) measured bursts of nitrous oxide (N<sub>2</sub>O) generation which was associated with accumulation of nitrite in the culture. The burst of N<sub>2</sub>O is proportional to the concentration of nitrite and is also repetitive. Kampschreur et al. (2009) reported a N<sub>2</sub>O emission rate equal to 1.2% of the nitrogen load to a full-scale nitrification-Anammox sequence batch reactor. However, Slijkers et al. (2002) reported negligible N<sub>2</sub>O emissions (0.05%) from a lab-scale Anammox reactor. Based on the literature, the potential exists for nitrous oxide emissions from the nitrification stage associated with Anammox processes. The research suggests that higher aeration rates increases N<sub>2</sub>O emissions (Kampschreur et al., 2009). As a result, minimizing aeration could minimize N<sub>2</sub>O emissions. In the case of the Zurich WWTP, Joss et al. (2009) show that even

assuming a higher N<sub>2</sub>O emission rate, the total CO<sub>2</sub> equivalent is more favourable for the nitrification-Anammox process over conventional nitrification/denitrification. In large part, this is a consequence of the CO<sub>2</sub> associated with the external carbon source requirement for conventional nitrification/denitrification.

While the factors which contribute to N<sub>2</sub>O production in an Anammox process are not fully understood, the propensity for higher N<sub>2</sub>O emissions could make selection of Anammox unfavourable on a carbon footprint basis under specific circumstances. In particular, if a local, waste by-product were available as a carbon source, the nitrification-Anammox process could result in a higher CO<sub>2</sub> equivalent value than conventional nitrification/denitrification.

#### **2.5.2.5 Bioaugmentation**

Sidestream treatment of high ammonia centrate has been used to augment the mainstream treatment process. In these nitrification/denitrification sidestream treatment systems, excess nitrification sludge is returned to the mainstream process to further increase the overall nitrogen removal capacity of the plant (Figure 2.10).



**Figure 2.10 – Schematic of a bioaugmentation sidestream process**  
(adapted from Kos, 1998)

Centrate treatment combined with bioaugmentation of the mainstream process is particularly advantageous for wastewater treatment facilities located in colder climates since nitrification is highly temperature dependent. The dewatering return stream is at an elevated temperature and allows for a compact nitrification process. Kos (1998) presented the theoretical basis for a bioaugmentation process which suggested a 60% reduction in the required SRT in the mainstream process over a conventional facility. Consequently, a sidestream nitrification process with bioaugmentation could reduce the bioreactor volume of the mainstream treatment plant.

Salem et al. (2002, 2003) undertook model studies to assess the benefits of a bioaugmentation batch enhanced (BABE) sidestream process for upgrade of the Walcheren WWTP and Houtrust WWTP in Netherlands. In the BABE process, part of the return activated sludge (RAS) stream along with the dewatering return stream is routed through a sidestream reactor. The results from these studies indicate that the BABE process could reduce the mainstream bioreactor volume

requirements by lowering the effective SRT and allow for nitrification at lower winter temperatures. A modelling study reported by Sova et al. (2004) showed similar benefits.

Baker et al. (2009) utilized a SBR to treat 1,600 kg/d of ammonia nitrogen from dewatering centrate associated with mesophilic digesters at the North End Water Pollution Control Centre in Winnipeg (Canada). The system was designed to allow the mainstream high purity oxygen activated sludge treatment process to operate at a low SRT time of two days while still achieving nitrogen removal. While the full-scale sidestream SBR operated as designed, the nitrogen removal efficiency of the mainstream treatment process did not change, indicating that bioaugmentation was not taking place. In a separate study, a detailed microbiological assessment of a similar bioaugmentation failure attributed the loss to a shift in the predator-prey dynamics (Bouchez et al., 2000). Bouchez speculates that adding a massive population to the mainstream process in order to induce a biological activity results in a disturbance of the ecosystem equilibrium. Consequently, a successful bioaugmentation process needs to provide for protection of the bacteria from grazing by protozoa. The BABE process addresses this by using a small RAS fraction from the mainstream treatment process and short SRT. This maximizes the cultivation of organisms and a floc structure best suited to the mainstream process (Salem et al., 2003).

#### **2.5.2.6 Algae production**

Centrate has been shown to be a good substrate for algae production and is an approach that has attracted research interest in recent years (Arita et al., 2015). Algae treatment systems have the potential to be low cost, simple and robust. Furthermore, algae grown on centrate could be used as a feed-stock for biofuel production (Kong et al., 2010) or co-digested with municipal sludge to produce methane gas as a fuel (McGinn et al., 2011; Cecchi et al., 1996).

The green algae *Chlorella sp.* has been shown to be well suited to being grown in dewatering centrate from a municipal WWTP (Min et al., 2011; Li et al., 2011). The work suggests that the algae systems treating centrate can remove 89.1% of the total nitrogen and 80.9% of the total phosphorus (Li et al., 2011). The feasibility of recovering algae and the impact of any unrecoverable algae in the effluent on the mainstream process are key considerations for operating such systems (Barnard et al., 2010b). In addition to harvesting and dewatering challenges, other bottlenecks in algae production include changing microbial diversity and abundance with seasonal variations in light, resulting in performance instabilities as measured by nutrient removal (Zhang et al., 2015) and energy output of AD fed excess algae. Also, the more productive algae grown in wastewater have strong cell walls to protect themselves from predators and require pretreatment maximize methane yield of anaerobic digestion (Ras et al., 2011).

### **2.5.3 Summary of the literature review**

As a commodity, ammonia is necessary for production of numerous industrial and agricultural products. Most industrial ammonia is produced through conversion of a hydrocarbon source, usually natural gas but also coal and heavy oil, and requires significant energy input. Any deammonification process ultimately sustains the demand for ammonia from conventional sources and the associated CO<sub>2</sub> emissions. The potential for N<sub>2</sub>O emissions from deammonification processes (i.e., either through atmospheric or biologically mediated conversion of ammonia) further shifts the balance in favour of ammonia recovery processes for high strength sidestream treatment. As our understanding of advanced biological treatment processes and their impact on the environment improves, the best application of a specific process should become clearer. The Anammox process, for example, is showing great potential

as an energy efficient ammonia removal system, therefore has been implemented as the process for the next chapters of this thesis. However, a better understanding of the factors which effect  $N_2O$  emission rates will undoubtedly result in a more optimized process. The impact of the physical and biological sidestream processes on recalcitrant nutrient species (i.e., DON and NRDP) is an area that requires further research. In the context of treatment plants with low nutrient limits, sidestream treatment processes which are able to reduce the recalcitrant nutrient load to the mainstream process will be more desirable. The criteria used for selection of a particular sidestream treatment will be unique to each treatment plant.

### **Chapter 3: Start-up, acclimation and characterization of lab-scale anaerobic digester and Anammox bioreactor performance**

The objective of this chapter is to provide detailed information on start-up, acclimation and dissolved nutrient characterization data from a lab-scale partial nitrification, deammonification (Anammox) bioreactor and anaerobic digester (AD). In addition, results are presented of a sampling program aimed at mapping out the mass flow of dissolved nutrients within the sidestreams of the full-scale City of Kelowna Wastewater Treatment Facility (KWTF). In effect, this chapter provides the context for a more detailed assessment of the effectiveness of Anammox for treating dissolved nutrients described in Chapter 4.

The lab-scale AD was fed waste sludge from the existing KWTF. In parallel to the AD piloting, the Anammox sidestream treatment reactor was operated to assess its efficacy for removing various nutrient species from dewatering AD centrate, including dissolved organic nitrogen (DON) and non-reactive dissolved phosphorus (NRDP). For comparison, dissolved nutrient characterization was made of sidestream and mainstream flows from the KWTF. The KWTF data are intended to serve as a baseline for the research and to understand the mass flux of DON and NRDP through a full-scale process. Reactor studies were conducted at UBC's Bioreactor Technology Laboratory at Okanagan Campus from 2012 to 2016. The results show that the Anammox process is able to degrade a large fraction of the DON (90%) and to a lesser extent the NRDP (12%). The research suggests that additional removal of sidestream dissolved phosphorus (orthophosphate and NRDP) would be required to allow an AD to be incorporated into the KWTF without compromising effluent quality.

### 3.1 Context

Up until the 1980's, increasing nutrient loading to Okanagan Lake (Canada) from the discharge of secondary treated wastewater was resulting in algae blooms and fish kills. Construction of BNR tertiary wastewater treatment plants (WWTPs) in the Okanagan starting in the 1980s was instrumental in reversing the water quality deterioration of the Okanagan Lake system (Oldham and Rabinowitz, 2002). However, the current trend in the Okanagan is towards more energy efficient sub-processes while maintaining or improving the quality of the effluent discharged to Okanagan Lake. Anaerobic digestion of wastewater sludge represents an opportunity to generate biogenic methane which could be used to offset demand for conventional petroleum-based energy, thereby reducing carbon emissions (Verstraete et al., 2005). In addition, AD is able to reduce the solids content of the sludge, reducing transportation and disposal requirements of the dewatered biosolids. Anaerobic digestion is not used as a sludge stabilization process in BNR WWTPs located in the Okanagan because of the potential to re-release nutrients taken up by the process. Instead dewatered sludge is hauled offsite and composted.

The literature review (Chapter 2) highlighted the need to control dissolved recalcitrant nitrogen and phosphate species in order to optimize nutrient removal processes with high effluent quality criteria. In particular, dissolved organic nitrogen (DON) and non-reactive dissolved phosphorus (NRDP) appear to be the more recalcitrant nutrient forms and have the most risk to the final effluent quality. In addition to reactive forms of nitrogen and phosphorus, AD is expected to produce a relatively large fraction of DON and NRDP. However, the literature does not provide a characterization of the DON and NRDP in AD centrate nor the degree of biodegradability in subsequent sidestream treatment processes.

The primary objective of the research described in this chapter was to measure the capacity of a mesophilic AD and Anammox sidestream reactor for producing or removing DON and NRDP. This first part of the research fills a gap in the literature by providing the characterization data needed to assess the impact of an AD on a BNR WWTP. The AD is expected to release a large amount of nutrients into the supernatant, including DON and NRDP. The Anammox process has shown to be an effective and energy efficient process for removing ammonia from AD dewatering centrate (Wett et al., 2007b). However, the literature does not demonstrate if Anammox has the capability to also remove DON and NRDP species. If this potential exists then an Anammox sidestream treatment reactor could support the introduction of an AD in a BNR facility by simultaneously removing ammonia and recalcitrant dissolved nutrients.

To achieve the primary research objective, characterization was made of the supernatant from a lab scale AD fed mixed sludge from the Kelowna Wastewater Treatment Facility (KWTF). The KWTF was selected to serve as the test case; but the proposed approach could be applicable to other similar wastewater and sludge management scenarios. KWTF is one of 6 tertiary WWTPs which operate in the Okanagan Lake basin (BC, Canada), a phosphorus-sensitive watershed. To mitigate impacts to the Lake, the KWTF utilizes a BNR (modified Bardenpho) process. The KWTF has effluent criteria of total nitrogen (TN) < 6.0 mg N/L and total phosphorous (TP) < 0.25 mg /L on an annual average basis. Other WWTPs discharging effluent to the lake system have a similar standard.

The KWTF mixed sludge feed consisted of fermented primary sludge (FPS) and thickened waste activated sludge (TWAS). The AD supernatant characterization attempts to measure the relative concentrations of the various forms of nitrogen and phosphorus species in the AD sludge feed and effluent sludge. A lab scale Anammox reactor was also operated to assess its ability to

remove dissolved nutrient species from dewatering centrate taken from a full-scale thermophilic AD. Comparison of the DON and NRDP characterization results between the lab-scale reactors and KWTF centrate was used to determine on a preliminary basis the feasibility of incorporating an AD at KWTF and assessing the need for additional treatment or research.

A second research objective was to understand the mass flux of DON and NRDP in the full scale KWTF and provide a baseline context to the research. To this end, testing of mainstream and internal sidestream flows was conducted for the KWTF. The data were intended to establish a maximum target concentration for DON and NRDP in the return stream and to understand where the recalcitrant nutrients originate.

## **3.2 Methodology**

In this section, a description of the research setup and testing protocols is provided. In the first two sub-sections, setup and operation of the AD and Anammox reactors are outlined. Following this, testing instruments, protocols and sample preparation techniques are documented.

### **3.2.1 Anaerobic digester**

The 5.0 L anaerobic digester was started up on January 16, 2012. The digester was operated as a mesophilic process (37°C) and fed mixed TWAS and FPS from KWTF at a ratio of 66:34 percent by volume until it was shut-down on June 27, 2015. The solids content of the mixed sludge feed was typically 4.0 to 5.0% by weight. The digester operated at a sludge retention time (SRT) of 20 days. The organic loading rate averaged 9.19 g VS/d (1.84 g VS/L/d).

A New Brunswick BioFlo® 115 glass fermenter/mixer and control centre was used for the digester reactor setup. The digester produced on average 250 mL/d of effluent sludge. The control centre allowed for a semi-continuous automated feeding on an hourly basis. Peristaltic

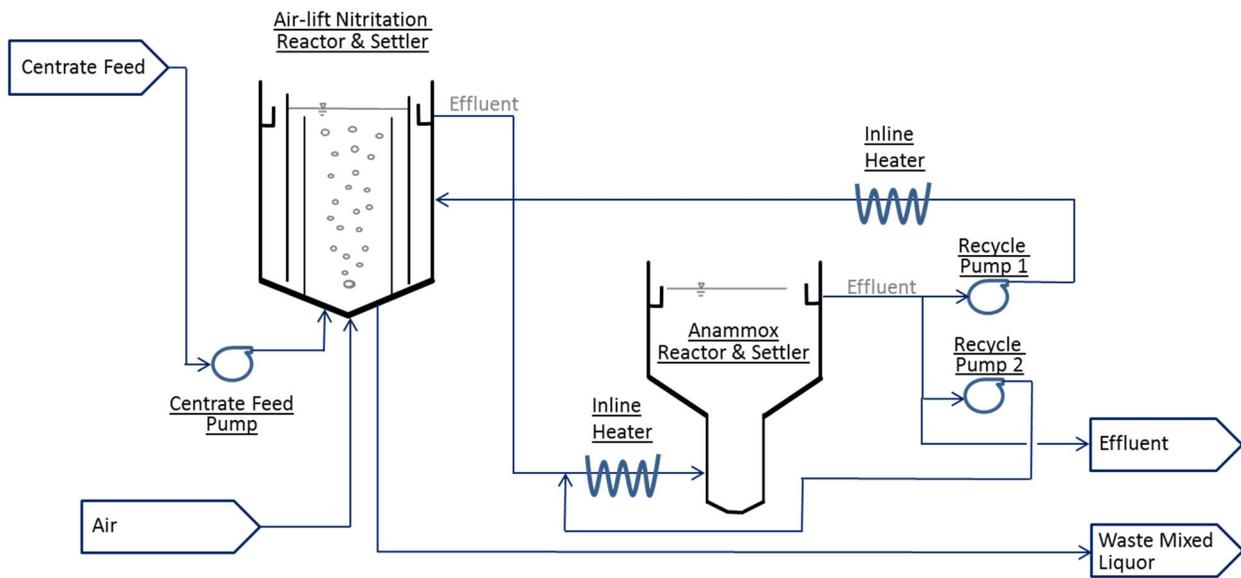
pumps allowed for sludge wasting followed by a feed interval. The waste and feed volumes were checked daily and pump rates adjusted accordingly.

Inoculum used for the mesophilic digester was taken from the City of Penticton (Canada) WWTP. The City of Penticton digesters were operated as mesophilic digesters with an SRT of 14 – 20 days and temperature of 36 - 37°C. The digesters were fed FPS. Total and volatile solids of the mesophilic inoculum was 2.35% and 1.64% at the time of AD start-up.

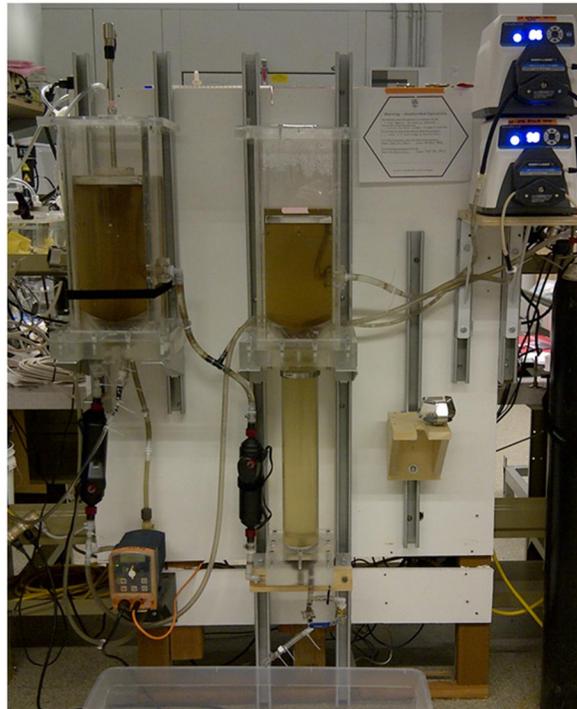
### **3.2.2 Sidestream nitrification-Anammox bioreactor**

The nitrification-Anammox bioreactor was originally designed to be a two-stage reactor with the nitrification and Anammox processes in separate tanks (Figure 3.1, Figure 3.2). The nitrification stage was designed with a settler integrated into the outer annular space. The Anammox tank was an upflow reactor designed to retain the heavier granules in the lower section of the tank.

Centrate was pumped into the nitrification tank at regular intervals with the effluent flowing to the Anammox reactor by gravity. A recycle pump transferred Anammox effluent back to the nitrification tank. By controlling the recycle flow rate, the hydraulic retention time of the centrate in the nitrification reactor could be varied depending on the nitrite concentration. A second internal recycle pump was included to control the upflow velocity, thereby allowing for growth of larger granular sludge. Inline heaters were used to maintain a reactor temperature at 35°C. In theory, separating the nitrification and Anammox stages would allow for more efficient process control.



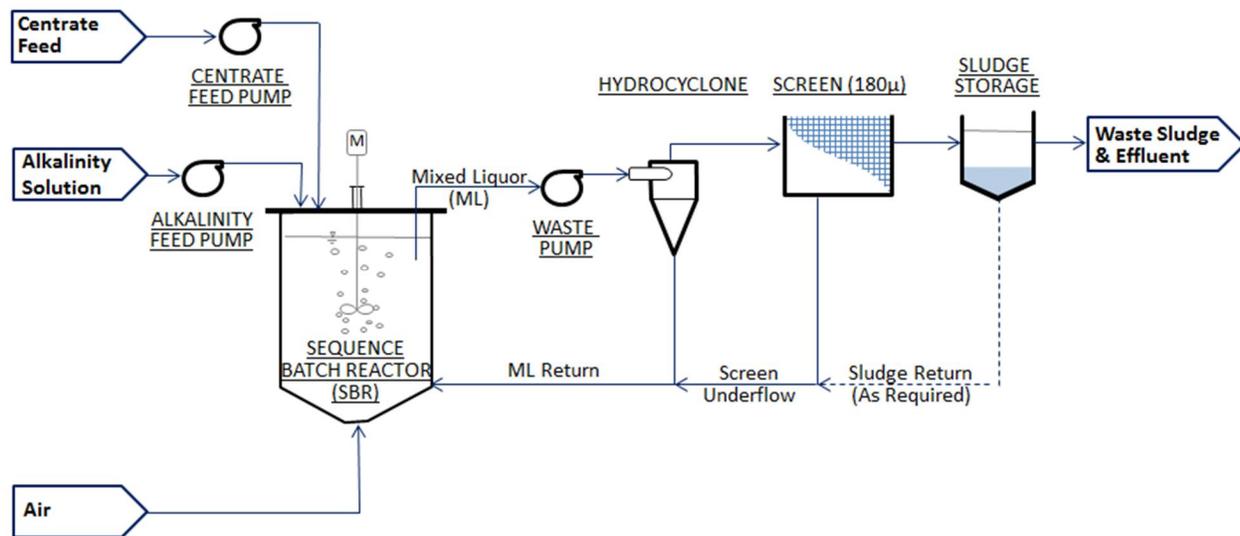
**Figure 3.1 – Process schematic for the two-stage nitrification-Anammox reactor**



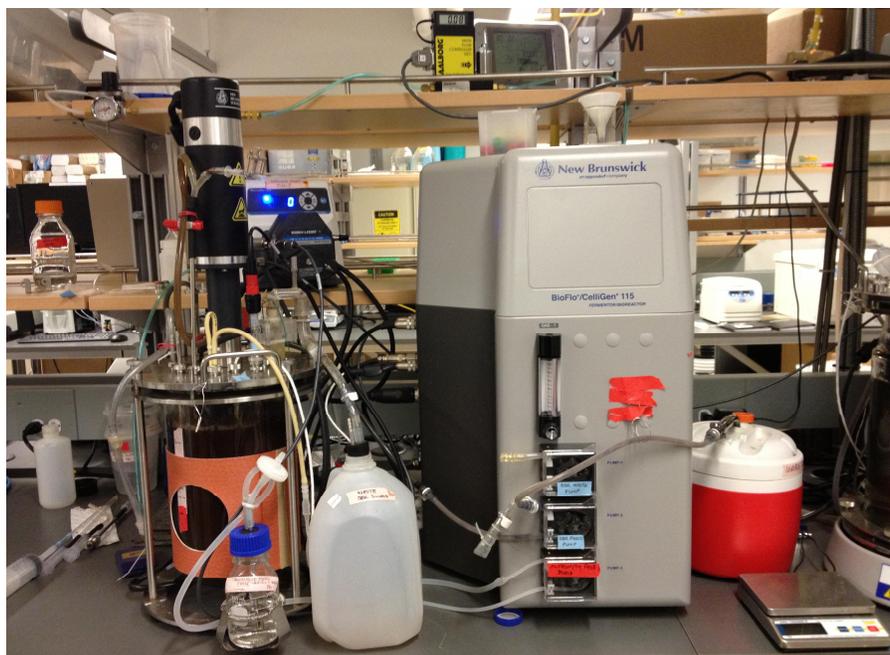
**Figure 3.2 – Photo of the two-stage nitrification-Anammox setup at start-up**

The two stage design was started mid-February, 2011 and by July, 2011, the system was abandoned for a more conventional single stage design. Poor sludge retention in the nitrification reactor resulted in intermittent effectiveness of the two-stage design. The nitrification stage was seeded with activated sludge from the KWTF and initially good aerobic ammonia oxidation capacity was achieved. However, over a week or two the aerobic ammonia oxidizer sludge was washed out and collected in the Anammox reactor resulting in deteriorating ammonia removal performance.

The single stage nitrification-Anammox bioreactor that ultimately proved successful was configured as a 5.5 L sequence batch reactor (SBR), operated at a temperature of 34°C. A New Brunswick BioFlo® 115 glass fermenter/mixer and controller were used for this purpose and the process was started-up in October, 2012. The bioreactor controller and associated computer software allows for automated operation of a centrate feed pump, waste pump, alkalinity feed pump and air valve. Operation of the nitrification-Anammox SBR is based on the DEMON process, as detailed by Wett et al. (2007), also in the literature review Section 2.5.2.4. A flow schematic of the process and photo of the setup used this study is provided in Figure 3.3 and Figure 3.4.



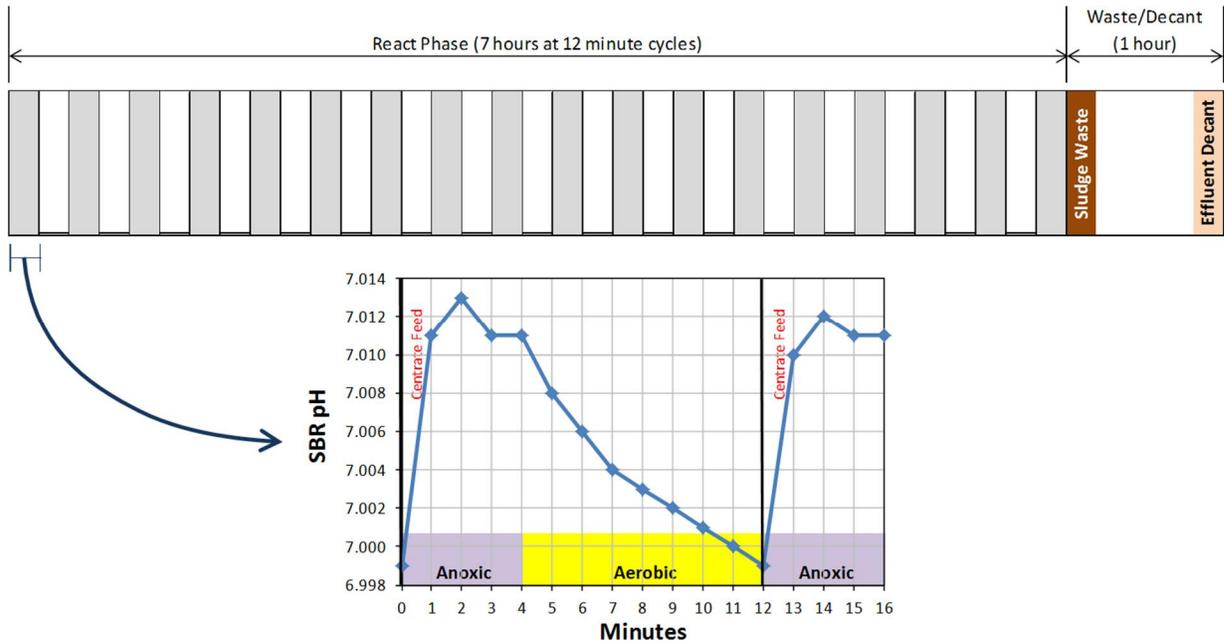
**Figure 3.3 – Process flow schematic for the lab-scale Anammox reactor**



**Figure 3.4 – Photo of the single stage nitritation-Anammox reactor used in the research**

The Anammox SBR operated on 8 hour cycles with 7 hours of biological reaction and one hour for sludge wasting and effluent decant (Figure 3.5). The 7-hour react phase was further divided into 35, 12 minute increments during which an equal volume of centrate was fed to the SBR. The

centrate would cause the pH to increase approximately 0.01 to 0.02 units. For 4 minutes the reactor would slowly mix, allowing for an anoxic phase during which the Anammox bacteria oxidized ammonia using the available nitrite.



**Figure 3.5 – Anammox Sequence Batch Reactor Operation**

Following the anoxic phase, the air valve would open to provide an aerobic phase for the next 8 minutes. The air flow would be controlled by pH and dissolved oxygen (DO). A DO concentration of 0.20 to 0.25 mg/L would be maintained for the duration of the 8 minute aerobic phase. The low DO combined with the relatively high operating temperature (34°C) allows for growth of aerobic ammonia oxidizing bacteria while suppressing growth of nitrite oxidizing bacteria. As a result, if the process is working properly some of the ammonia will have been converted to nitrite during the aerobic cycle and be available for the Anammox bacteria at the start of the anoxic period. Introduction of the centrate at the start of the anoxic period may also

enhance the Anammox process by either providing a source of VFA or reducing the oxygen reduction potential, as suggested by the literature (Güven et al., 2005, Jung et al., 2007).

Nitrate was monitored on a daily basis with ammonia and nitrite assessed 2-3 times per week. Monitoring of the MLSS and SRT were not necessary for process control and were measured intermittently. Sludge wasting was based on measurements of nitrite and nitrate. In general, an increase in nitrate usually signaled the need for additional wasting through the hydrocyclone and screen.

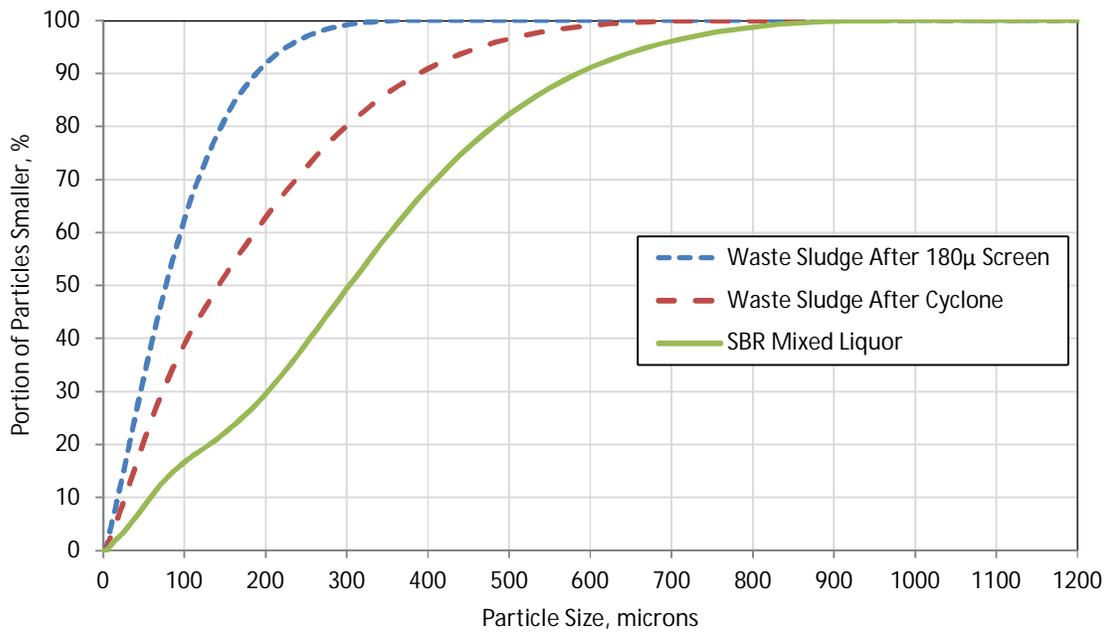
The average hydraulic retention time (HRT) and SRT of the Anammox reactor was 2.6 days and 57 days, respectively, at an average mixed liquor suspended solids concentration of 13,700 mg/L. HRT was measured as the reactor working volume divided by the average volume of centrate feed. SRT was measured as the mass MLSS at the start of the react phase (ie, after wasting is complete) divided by the total wasted mass TSS.

The SBR sludge wasting technique utilized in this research was modified compared to the published DEMON operation in order to resolve issues associated with scale. The DEMON process relies on a hydrocyclone for retention of granular sludge. However, the relatively small waste flow rates of the UBC lab-scale pilot cannot generate sufficient g-forces in the hydrocyclone to provide for adequate retention of the granular sludge. For this lab-scale reactor a 180 micron screen was successfully used to further process the sludge and maximize retention of the granules. This approach of using screens for physically isolating granular sludge was reported by de Clippeleir et al. (2013). A Mastersizer 3000 with a (Malvern Instruments) size range of 0.01 – 3500 micron was used to monitor the size distribution of the mixed liquor in the Anammox bioreactor and the waste sludge. A photo of the reactor sludge is provided in Figure

3.6 and shows the granules in suspension. The relative influence of the hydrocyclone and 180 micron sieve on the retention efficiency of granular sludge is depicted in Figure 3.7.

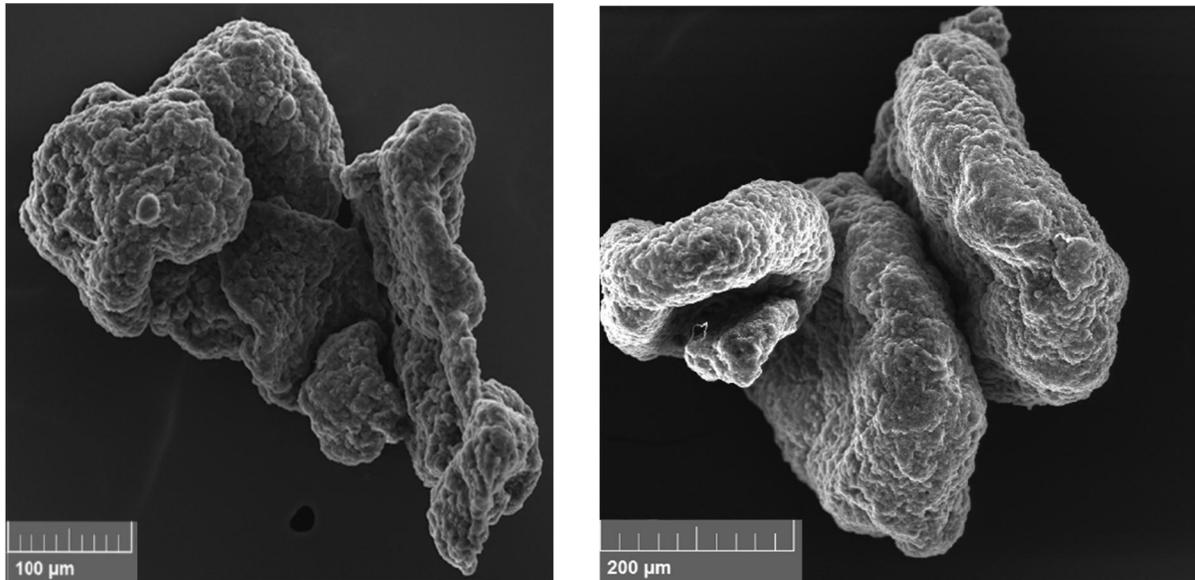


**Figure 3.6 – Photo of Anammox reactor sludge in suspension prior to hydrocycloning**



**Figure 3.7 – Particle size distribution of waste sludge after a cyclone and 180 micron sieve**

A scanning electron micrograph of a typical sludge granule isolated using the 180 micron screen is provided as Figure 3.8. The micrograph shows an asymmetrical structure that appears to be an agglomeration of smaller granules. However, no attempt was made in this study to identify the factors affecting granule morphology.



**Figure 3.8 – Scanning electron micrograph of Anammox granules from the UBC reactor**

As part of the process control, an additional sludge return step was incorporated under specific conditions to control effluent nitrite concentrations. Nitrite levels in the DEMON process above a mean level of 1.7 mg/L have been shown to decrease Anammox activity (Wett et al., 2007b). In this research, it was observed that addition of settled, stored overflow sludge from the 180 micron screen helped to reduce nitrite levels and stabilize the process. Consequently, when nitrite increased above 1.7 mg/L in the SBR, a small amount of reserve sludge was returned to the bioreactor. The flow schematic shown in Figure 3.3 includes this additional, intermittent step.

The Anammox reactor was started in November, 2012 using centrate from the Annacis Island WWTP (AIWWTP), Metro Vancouver, Canada, as a substrate feed. Given the limited volume of

centrate output from the lab-scale AD, centrate from AIWWTP was used as a feedstock to stabilize the Anammox process. Characteristics of the Annacis Island WWTP centrate feed are provided in Table 3.1. The Annacis Island WWTP uses a trickling filter for mainstream secondary treatment and a thermophilic AD process for sludge stabilization. A target centrate loading of 2,750 mg N/d (0.5 g N/L bioreactor volume) to the Anammox reactor was reached on June 28, 2013. Seed Anammox sludge was acquired from World Water Works from their DEMON pilot plant at Pierce County, Washington. The Anammox inoculant was supplied as a dewatered cake at 16% total solids concentration.

**Table 3.1– Annacis Island WWTP centrate feed characteristics**

<b>Parameter</b>	<b>Average of Measured Values</b>	<b>(Standard Deviation, Number of Samples)</b>
pH	8.1	(0.21, 11)
Alkalinity, mg/L as CaCO <sub>3</sub>	5,160	(670, 11)
Total Suspended Solids (TSS), mg/L	340	(51.8, 4)
Ortho Phosphate, mg P/L	181	(7.1, 10)
Ammonia, mg N/L	1,192	(64.0, 27)
Biological Oxygen Demand, mg/L	368	(80.5, 16)
Volatile Fatty Acids, mg/L	32.4	(20.9, 4)

### **3.2.3 Sample preparation and testing**

During the data collection phase, nutrient testing for the AD and Anammox reactor (feed and effluent) was typically undertaken one or two times per week. For consistency, a set of feed and waste (effluent) sample was taken on the same day. Other parameters (i.e., alkalinity, TS/VS, TSS, COD, BOD, VFAs) were sampled monthly to monitor reactor performance. For measurement of the mainstream and sidestream dissolved nutrients at the full scale KWTF, sampling was coordinated with the City’s sampling program between March 11, 2014 and July 10, 2014. Composite influent and final effluent samples collected by KWTF staff were used for

this research. In addition, KWTF's dissolved phosphorus test results on the composite final effluent samples were utilized in the mass flow calculations. KWTF uses the same analytical methods as the UBC lab. The remaining sidestream grab samples were collected on the same day that the composite samples were taken and processed at the UBC lab.

For sample characterization, Standard Methods procedures 2540 B and 2540 E (APHA, 2005) were used for TS and VS determination. TSS was measured according to Standard Methods procedure 2540D. The closed reflux colorimetric chemical oxygen demand (COD) measurements were performed based on Standard Methods procedure 5250D (APHA, 2005) with a Thermo Genesys 10S spectrophotometer and 600 nm wavelength absorbance. Alkalinity was measured according to Standard Methods 2320B (APHA, 2005). Biochemical Oxygen Demand (BOD) was measured using an OxiTop® system, based on pressure measurements in a closed system.

Total volatile fatty acids, calculated as the sum of acetic, propionic and butyric acids, were measured by injecting supernatants (filtered through membrane discs with 0.2 µm pore size) into the Agilent 7890A Gas Chromatograph (GC) with a capillary column (Agilent 19091F-112, HP-FFAP polyethylene glycol TPA column length x ID: 25 m × 320 µm) and a flame ionization detector (oven, inlet and outlet temperatures: 200, 220 and 300°C, respectively, carrier gas flow rate: 25 mL helium/min) equipped with an autosampler (Agilent 7693A). The method developed by Ackman (1972) used iso-butyric acid as an internal standard.

A standard capacity (1.5 - 800 L/d) Wet Tip gas meter was used for measurement of biogas flow from the AD. Biogas volumes were then converted to standard temperature and pressure (STP = 0°C, 1 atm). Biogas composition in the AD headspace was determined in terms of CO<sub>2</sub>,

CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> percent using an Agilent 7820A GC with a packed column (Agilent G3591-8003/80002) and a thermal conductivity detector using helium as the carrier gas.

Samples analyzed for total dissolved nitrogen and total dissolved phosphorus were first filtered using a 0.45 micron syringe tip filter (Millex nylon, 13 mm or 25 mm) and then diluted to match the digestion test range (0.0 to 1.0 mg P/L and 0.0 to 2.0 mg N/L). For liquid streams with high TS, like digested sludge, the sample was first centrifuged at 5,000 ×g for 10 min to extract a supernatant.

Digestion for total nitrogen was conducted using a persulfate method (APHA, 4500-P J). While this method is intended for simultaneous total nitrogen and total phosphorus analysis, it proved insufficient for digestion of dewatering centrate and AD effluent samples for total phosphorus. Consequently, an alternate digestion procedure for total phosphorus was adopted. The digested total nitrogen sample was analyzed for nitrite/nitrate using an Astoria Method A2 autoanalyzer fitted with Multi-Test Cartridge A000-AMT and a cadmium reactor. Ammonia and nitrite/nitrate in the undigested sample were measured using the same autoanalyzer.

Digestion for total phosphorus analysis was based on the Persulfate Digestion Method (APHA, 4500-P B.5). Samples and persulfate/acid solution were dispensed into glass test tube, capped and autoclaved at 120°C for 2 hours. For complex analytes like dewatering centrate and AD effluent, the 2 hour digestion time was necessary to achieve consistent results. The digested solution was cooled and analyzed immediately for orthophosphate using the Ascorbic Acid Method (APHA, 4500-P E) and a Thermo Genesys 10S spectrophotometer with 1.0 cm light path. The original undigested sample was analyzed for orthophosphate in the same way.

Acid hydrolyzable phosphorus (polyphosphates) was measured by digesting samples in a mild acid solution followed by measurement of phosphate (APHA, 4500-P B.2). The polyphosphate

(poly-P) concentration was calculated as the difference between the phosphate concentration of the acid hydrolyzed sample and original undigested sample. Organic phosphorus was measured as the difference between the measured TN and poly-P concentration of the sample.

Characterization of bioreactor influents and effluents were tested for nitrite, nitrite/nitrate, ammonia and orthophosphate using the Astoria Method A2 autoanalyzer. In addition, daily checks of the Anammox SBR effluent nitrate were made using an Accumet nitrate probe (APHA, 4500-NO<sub>3</sub><sup>-</sup> - D). Representative calibration curves for the nitrogen and phosphorus testing are provided in Appendix A.

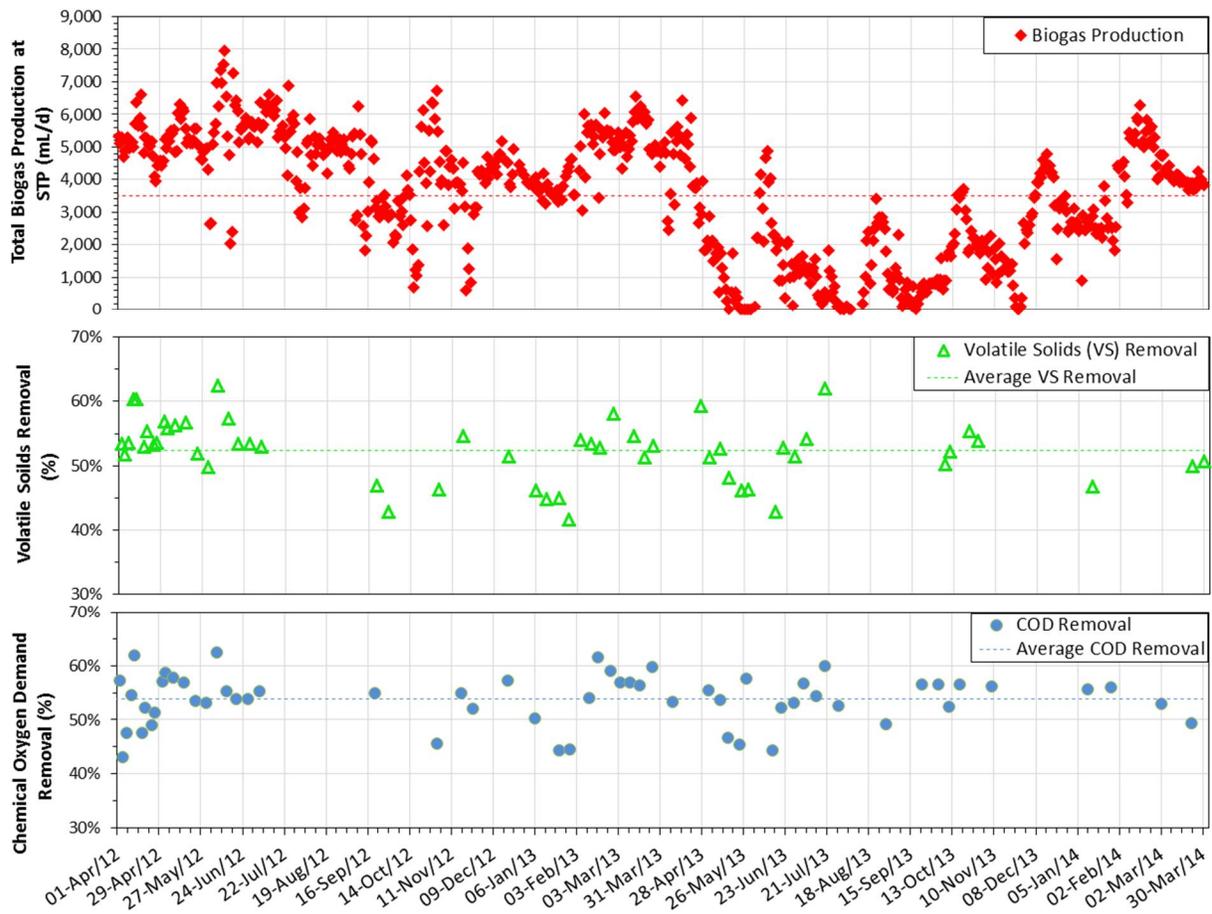
### **3.3 Results**

Presentation of the results is divided into three sub-sections. First, general operational data on the lab-scale AD and Anammox reactors are presented. Following this, results of the lab-scale bioreactor (Anammox and AD) effluent and full-scale KWTF centrate dissolved nutrient characterization are provided. The final sub-section presents results of the NRDP and DON mass flow measurements through the full-scale KWTF.

#### **3.3.1 AD and Anammox reactor operation**

The lab-scale anaerobic digester was operated continuously for more than two years (Figure 3.9). The digester reached stable operation in March, 2012 and showed good biogas production until April, 2013 when the daily production crashed. The large variability in biogas production through year 2013 is attributed to the changes in the sludge feed characteristics and a leak in the bioreactor headspace. During this time, the KWTF was commissioning a new upgrade to its treatment plant. Start-up challenges with the new fermenter and operational changes resulted in fluctuations in the solids content and VFA concentration of the mixed feed sludge through much of 2013. Also, rubber gaskets on the reactor assembly were replaced in September, 2013 to

address a suspected gas leak. Since the latter part of year 2013, biogas generation values showed improvement. While the biogas volume generation measurements fluctuated considerably, the COD and TS/VS removal rates remained relatively stable. Biogas composition through the period of testing, as measured in the AD headspace, averaged 67.1% methane (n = 28, standard deviation = 1.02%). This indicates that organic removal data are more reliable than the biogas volume measurements, a feature which is common for AD operation.



**Figure 3.9 – Operating data for the anaerobic digester**

**Feed and effluent sludge characteristics through the period between April 1, 2012 and April 1, 2014 are provided in Figure 3.10 - SEM images of digester struvite precipitate**

Table 3.2. The digester showed a 54.0% reduction in COD, 52.9% reduction in VS and 44.2% in TS. In addition, on average, ortho phosphate decreased by 131 mg P/L or 22.2%. It is presumed that the phosphate precipitated as struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ). A common feature of the digester operation was the observation of small crystals in the waste sludge. Scanning electron microscope images of the crystals are provided as Figure 3.10. X-ray diffraction confirms the presence of a high proportion of oxygen, phosphorus magnesium and nitrogen, all elements associated with struvite. In addition, the x-ray diffraction also detected sodium, iron and calcium as part of the crystal structure suggesting a variety of chemical precipitates.

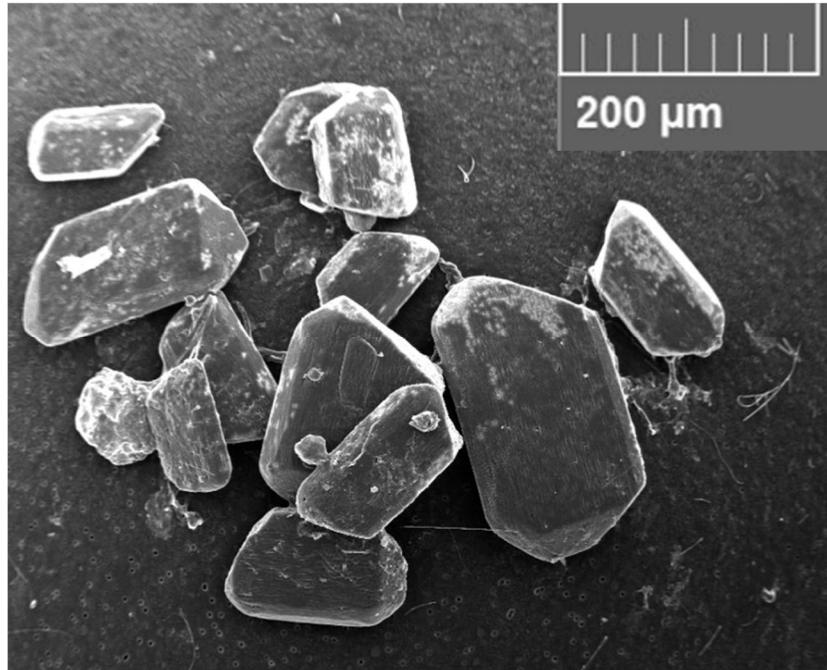


Figure 3.10 - SEM images of digester struvite precipitate

Table 3.2 – Mesophilic anaerobic digester average feed and effluent characteristics

Parameter	Feed Sludge		Effluent Sludge	
	Average Value	(Standard Deviation, Number of Data Points)	Average Value	Standard Deviation, Number of Data Points)
pH	5.47	(0.47, 52)	8.06	(0.20, 35)
Alkalinity, mg/L as CaCO <sub>3</sub>	896	(305, 42)	5,240	(1,090, 35)
Total Solids (TS), % by wt.	4.41	(0.55, 57)	2.46	(0.26, 56)
Volatile Solids (VS), % by wt.	3.67	(0.47, 57)	1.73	(0.13, 56)
Chemical Oxygen Demand (COD), mg/L	57,000	(8,880, 61)	26,200	(3,300, 62)
Ortho Phosphate, mg P/L	591	(130, 28)	460	(105,31)
Ammonia, mg N/L	203	(57, 30)	1,210	(215, 32)
Volatile Fatty Acids, mg/L	1,590	(804, 31)	29.9	(20.9, 21)

Figure 3.11 provides summary plots of the Anammox operation through to the end of the current testing. A series of failures necessitated turning off the bioreactor for most of the month

of August, 2013. Through the months of September and October, 2013, the effluent nitrate and ammonia concentrations remained high. However, by January 1, 2014 the effluent ammonia and nitrate concentrations had stabilized allowing dissolved nutrient testing to commence. During the period between January 1 and April 1, 2014 when the first set of effluent characterization tests were conducted, the ammonia removal rate remained between 83% and 92%. Ammonia removal was calculated based on a mass balance of ammonia-nitrogen loading compared to the mass of effluent nitrogen. Since the main objective of the research was to measure the change in dissolved nutrients through the Anammox process, total nitrogen removal was not monitored. The Annacis Island centrate feed to the Anammox reactor was measured to be 1,566 mg N/L ( $n = 9$ ,  $\sigma = 74.0$ ) compared to a dissolved total nitrogen of 1,320 mg/L and ammonia of 1,130 mg N/L.

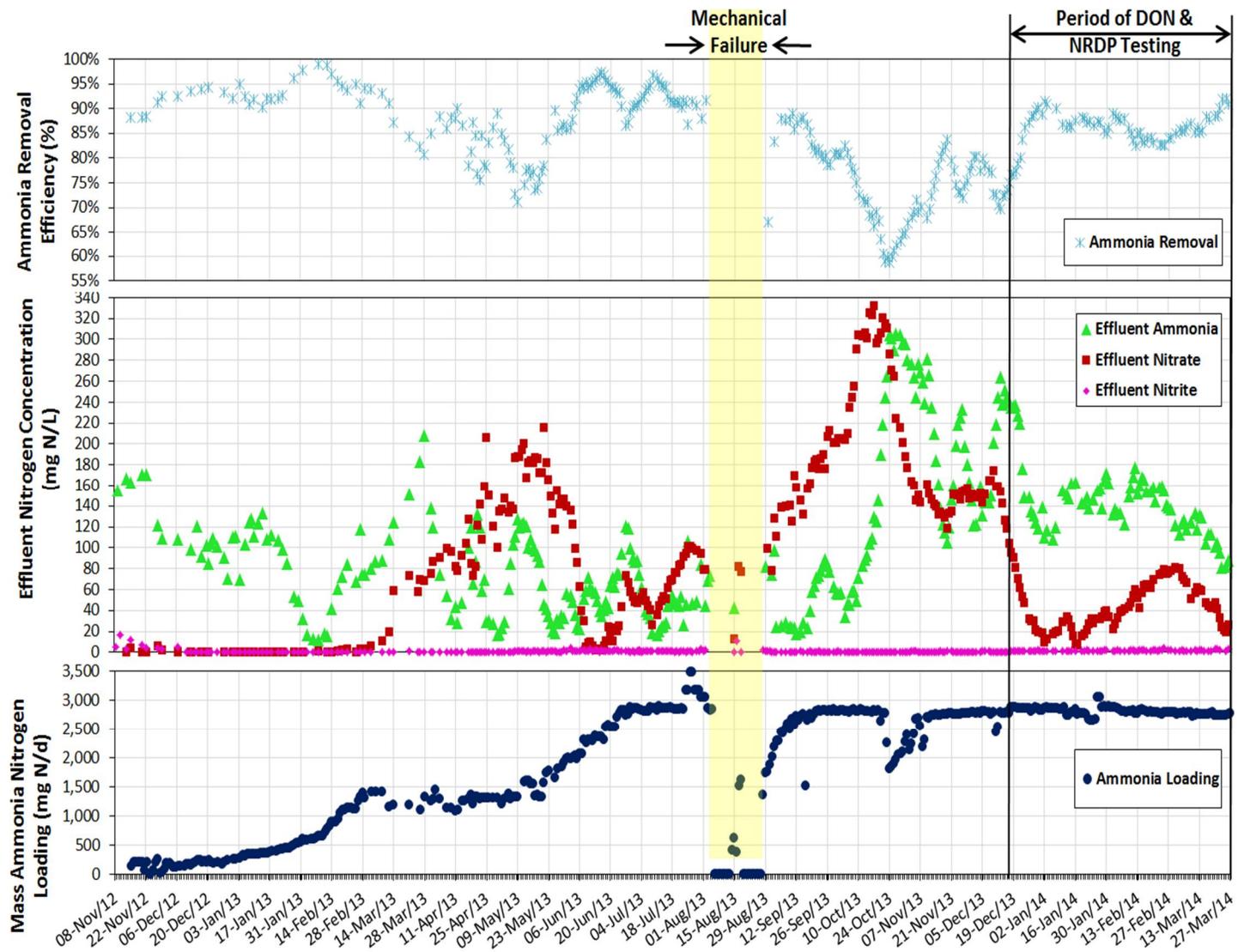


Figure 3.11 – Ammonia removal efficiency and effluent characteristics for the Anammox bioreactor

### 3.3.2 Effluent and centrate characterization results

Table 3.3 provides a summary of the dissolved nutrient testing that was conducted on the anaerobic digester waste sludge, Anammox feed/effluent, and KWTF dewatering centrate. The testing was undertaken to compare the relative concentrations of DON and NRDP and assess whether introduction of an anaerobic digester or Anammox sidestream reactor would have an appreciable impact on the current treatment plant operation.

A summary of the DON and NRDP measurements through the Anammox and AD is also provided schematically as Figure 3.12 and Figure 3.13. The results are discussed in Section 3.4.

**Table 3.3 – Comparison of influent/effluent characteristics for the bioreactors**

Liquid Stream	Dissolved Nitrogen Species				Dissolved Phosphorus Species		
	Dissolved Total N (mg N/L)	Ammonia (mg N/L)	Nitrite/Nitrate (mg N/L)	Dissolved Organic N (mg N/L)	Total Dissolved P (mg P/L)	Ortho- Phosphate (mg P/L)	Non Reactive Dissolved Phosphorus (mg P/L)
Anaerobic Digester Effluent Sludge	1,400 [8,106]	1,190 [8, 59]	0.12 [8, 0.06]	210 [8, 96]	557 [10, 169]	525 [10, 157]	34.2 [10, 23]
Centrate Feed (Annacis Is. WWTP)	1,320 [12, 50]	1,130 [12, 73]	0.13 [12, 0.1]	195 [12, 75]	191 [10, 9.3]	181 [10, 7.1]	10.0 [10, 4.4]
Anammox Effluent	170 [19, 30]	115 [19, 21]	36.0 [19, 15]	19.2 [19, 7.9]	183 [17, 8.3]	174 [17, 7.5]	8.79 [17, 4.5]
KWTF Dewatering Centrate	68.0 [8, 18]	55.8 [8, 20]	0.47 [8, 0.26]	12.0 [8, 6.0]	331 [13, 115]	317 [13, 109]	14.5 [13, 10]

Note: Values in brackets denote sample size and standard deviation, [#, stdev]

Annacis Is. WWTP  
Centrate Feed

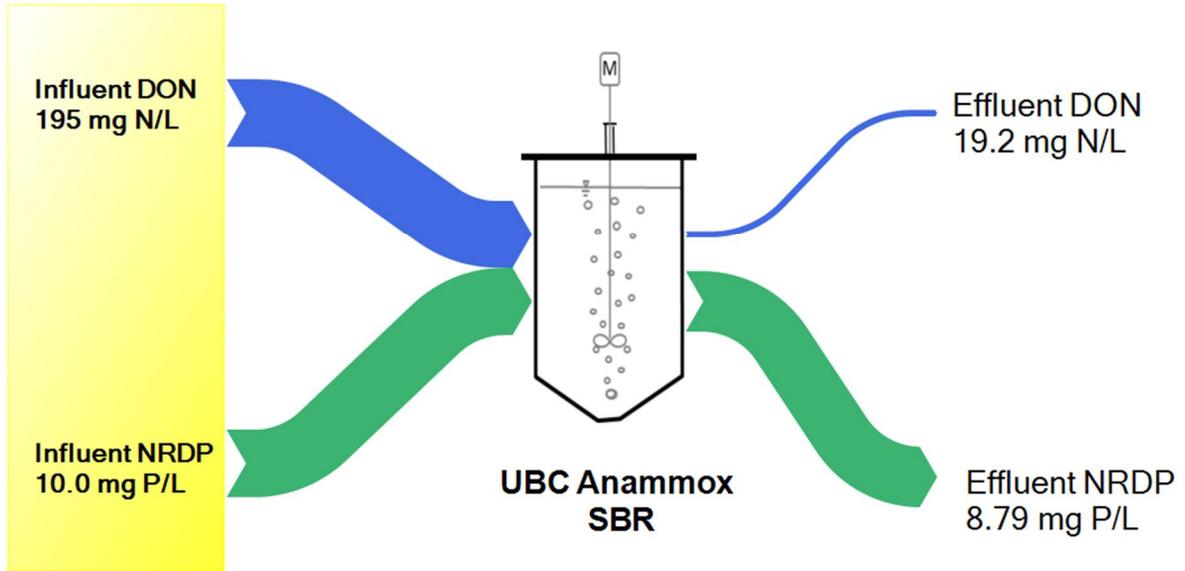


Figure 3.12 – DON and NRDP flux through the Anammox SBR

City of Kelowna  
Mixed Sludge  
Feed

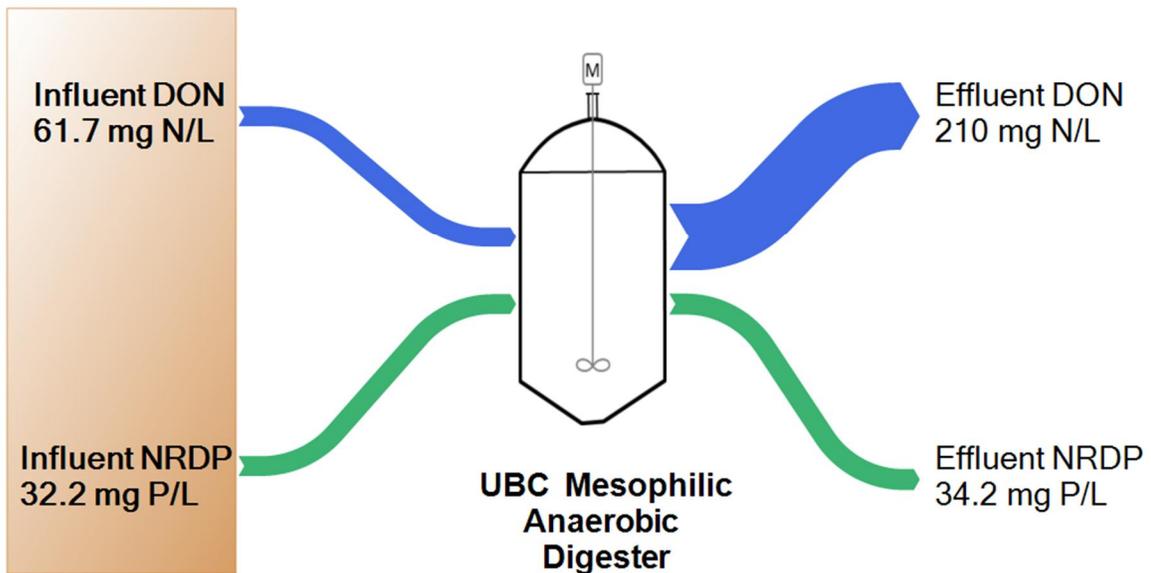
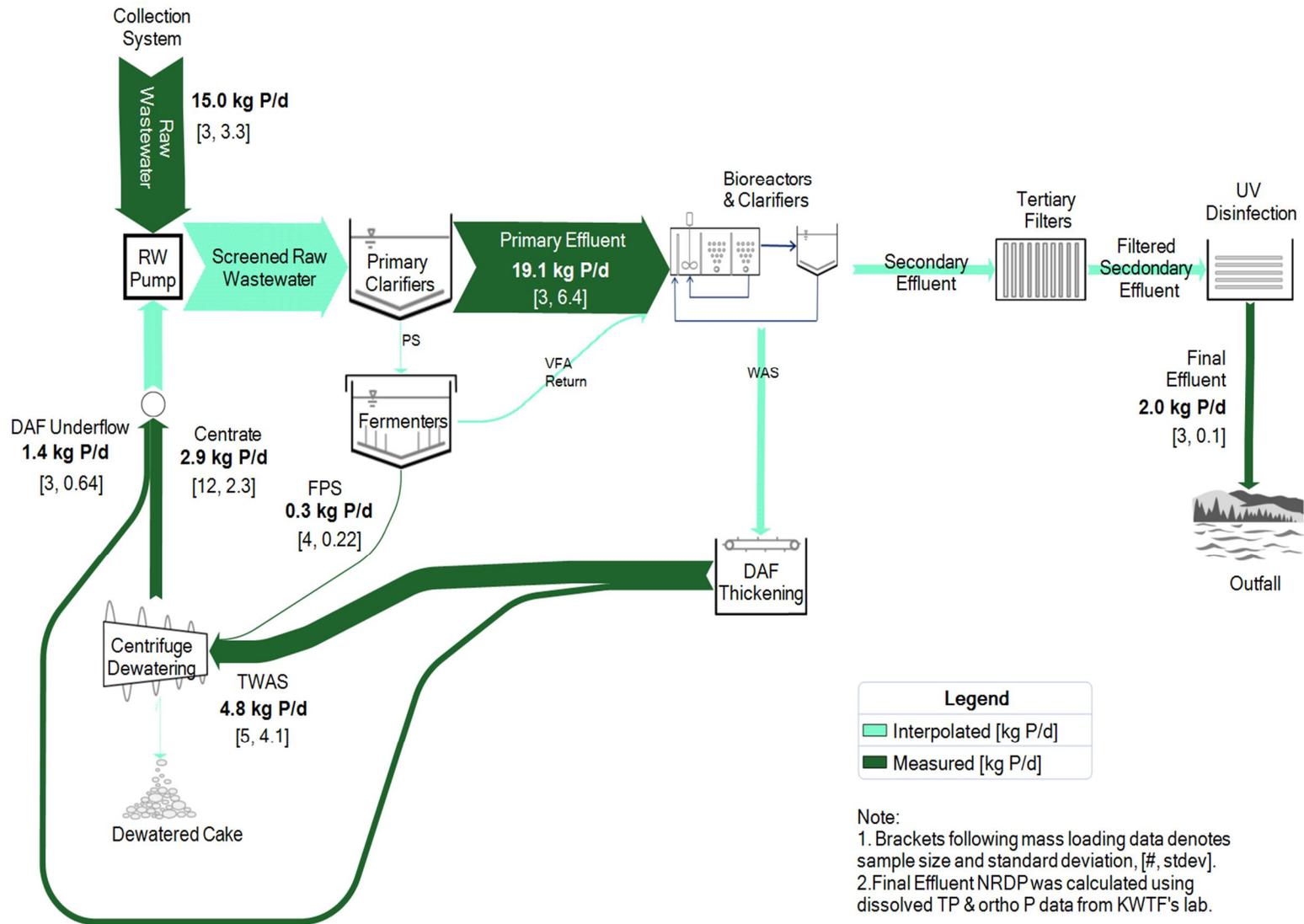


Figure 3.13 – DON and NRDP flux through the mesophilic AD

### **3.3.3 KWTF nutrient mass flow measurements**

As a way to understand the origin of the DON and NRDP species within the KWTF, testing was conducted on the internal recycle and influent streams of the full scale WWTP to measure the mass flow of these species (Figure 3.14 and Figure 3.15). To calculate the DON and NRDP loadings for the KWTF, testing was conducted on composite samples of influent wastewater, primary effluent and final effluent. In addition, grab samples of dewatering centrate, TWAS, FPS and WAS thickener underflow (DAF underflow) were also tested. Flow data for each of the streams tested was provided by KWTF.



**Figure 3.14 – Non Reactive Dissolved Phosphorus Mass Flow Diagram for KWTF**

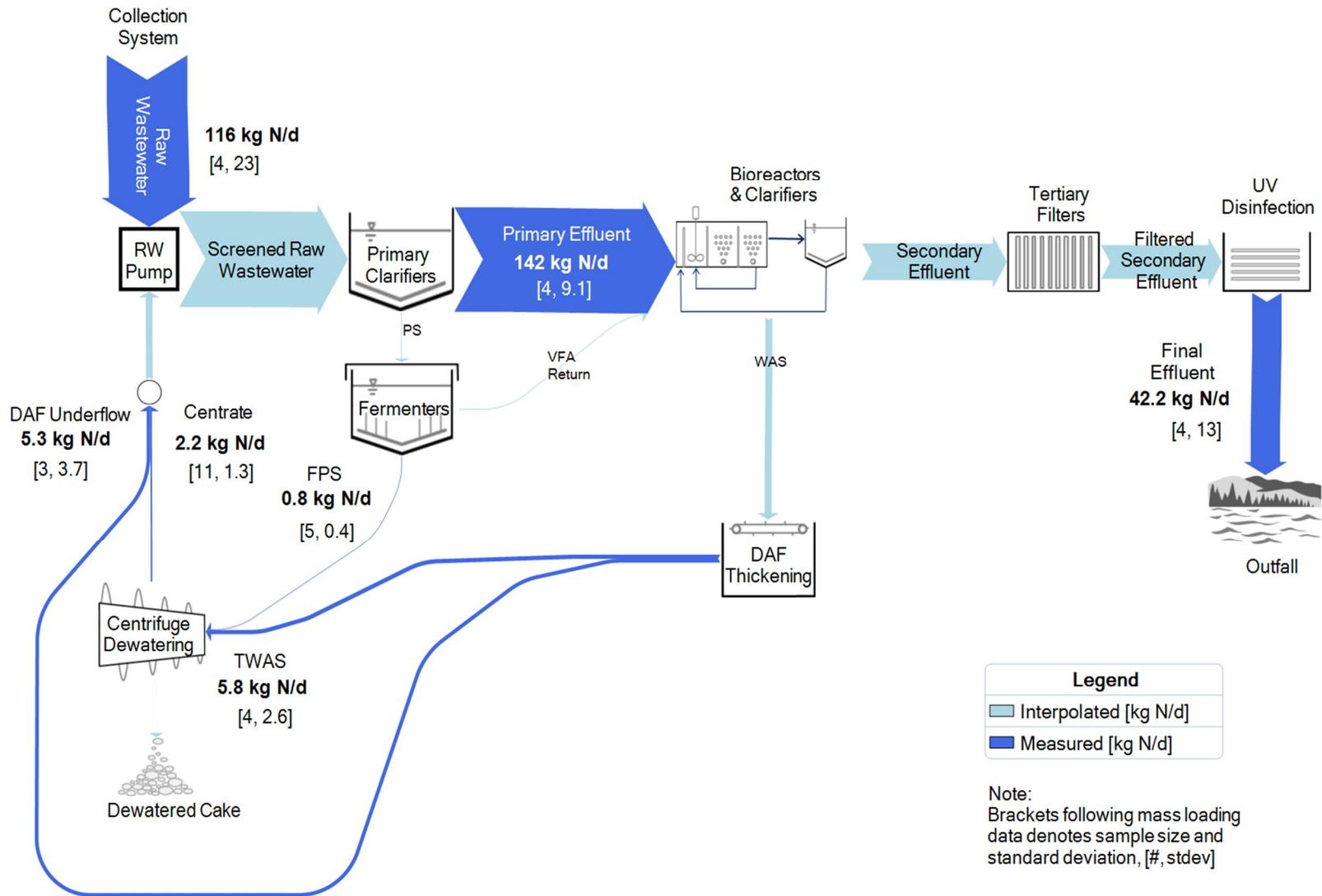


Figure 3.15 – Dissolved Organic Nitrogen Mass Flow Diagram for KWTF

### 3.4 Discussion

The resulting mass flow diagrams indicate that the majority of the DON and NRDP in the KWTF primary effluent originate in the raw wastewater. However, approximately 23% of the primary effluent NRDP mass flow is contributed by the combined internal recycle stream (i.e., dewatering centrate and DAF underflow). A smaller proportion of the DON in the primary effluent (approximately 5%) originates from the internal recycle stream.

The UBC test results for total dissolved phosphorus on the KWTF effluent was inconsistent with the total phosphorus values being measured by the City and therefore were neglected. On the same composite effluent sample, the UBC testing consistently measured higher total dissolved phosphorus than the total phosphorus measured by the City of Kelowna's commercial laboratory (i.e., 0.61 mg P/L versus 0.17 mg P/L, average values). Based on these results, it was concluded that the filtration process probably contributed a positive background interference of polyphosphate and the results were neglected. The KWTF effluent was not filtered using a syringe filter. Since the effluent required no dilution for testing, the relatively large required sample volume meant that a conventional vacuum filtration apparatus was more practical than a syringe filter. Additional final effluent samples were collected and analyzed for dissolved total phosphorus and orthophosphate by the KWTF's lab which uses an autoanalyzer to measure orthophosphate and a commercial lab for TP. The calculated effluent NRDP values in Figure 3.14 are based on these results.

The nutrient characterization confirmed that introduction of the untreated AD waste sidestream would impose a substantial additional nutrient load on the KWTF. The pilot testing also indicated that elevated DON and NRDP concentrations occur in the UBC mesophilic AD sludge effluent. Both DON and NRDP in the digester effluent were significantly higher than the KWTF

centrate. The AD supernatant DON was 210 mg N/L compared to the KWTF centrate of 12.0 mg N/L, 17.5 fold increase. Similarly, NRDP in the AD supernatant was 34.2 mg P/L compared to 14.5 mg P/L for the KWTF centrate, a 2.36 fold increase. Ammonia and orthophosphate concentration also increased significantly through the digestion process. However, a variety of treatment processes for removing centrate ammonia and phosphate are documented in the literature. It is assumed that any increase to the effluent nitrogen or phosphorus concentration due to this loading increases the risk of exceedances.

The influent/effluent characterization indicates that the Anammox process is able to degrade a large fraction of the DON and to a lesser extent the NRDP. On average, the Anammox bioreactor was able to reduce DON by 90% (i.e., from 195 mg N/L to 19.2 mg N/L). The NRDP was reduced on average by 12% (i.e., from 10.0 mg P/L to 8.79 mg P/L). The reduction in both DON and NRDP are statistically significant, based on a paired t-test at a 95% confidence interval ( $\alpha = 0.05$ ). A more detailed statistical assessment is provided in Chapter 4 for a similar set of test results. The work described in Chapter 4 focused on measuring the effluent characteristics from the Anammox reactor fed centrate derived from the pilot AD fed KWTF sludge centrate. This research is more relevant to Okanagan Valley requirements.

Another research consideration is to try to understand the transformation of the removed NRDP and DON compounds through the Anammox process, which is also studied in Chapter 4. In particular, while significant DON removal was measured through the Anammox reactor, it may be shifted to the particulate form (i.e., greater than the 0.45 micron size cut-off) or metabolized and transformed to nitrogen gas. Similarly, the proportion of dissolved organic phosphorus and inorganic condensed phosphorus that is measured as NRDP may change through the AD or Anammox reactor.

Based on results of the lab-scale reactors, the Anammox process shows great promise for DON removal from the return stream of an anaerobic digester. However, in order to mitigate the impacts of the return stream on a BNR process, additional treatment may be required to remove NRDP compounds. Various combinations of coagulation, filtration and absorption have been shown to successfully remove dissolved phosphorus in wastewater effluent (Neethling et al., 2007; Arnaldos and Pagilla, 2010; Gu et al., 2011). Further research is required to assess the suitability of this particular treatment approach for a sidestream flow that is composed of dewatering centrate and WAS thickener underflow. Furthermore, since the return sidestream NRDP at KWTF is greater than the mass contained in the final effluent, removal of most of the NRDP in the sidestream may also reduce the final effluent NRDP concentration. While additional research is required to test this hypothesis (refer to Chapter 4), if it is feasible the reduction in final effluent NRDP could be achieved while treating only a fraction of the mainstream flow.

Although this research is focused on the removal of DON and NRDP, the characterization data indicates the presence of high orthophosphate concentration in the AD effluent sludge. This would translate into a high orthophosphate concentration in the dewatered sludge centrate of a full-scale AD. The orthophosphate concentration in the supernatant of the pilot AD is 525 mg P/L, which is significantly higher than in the Annacis Island WWTP centrate or KWTF dewatering centrate. Since the Anammox reactor had only a very small reduction in the orthophosphate concentration, an alternative removal process is required. The most attractive solution to address the orthophosphate issue is to incorporate a struvite recovery stage upstream or downstream of the Anammox reactor. In one specific lab-scale configuration where the struvite reactor was located downstream of the Anammox reactor, an orthophosphate removal

rate of 86% was achieved (Hassan et al., 2013). Struvite is an equimolar precipitate of ammonium, phosphate and magnesium (*ibid.*). Consequently, a struvite recovery process would have the added benefit of reducing the ammonia concentration in the centrate or Anammox effluent, depending on the process configuration.

### **3.5 Summary of the bioreactor start-up phase**

Results from a lab-scale anaerobic digester fed mixed waste sludge from a BNR treatment plant confirms that the sidestream contains high levels of dissolved nutrients, including NRDP and DON. If untreated the sidestream return flow would likely have a negative impact on the effluent quality of the wastewater treatment plant.

A nitrification-Anammox sidestream process is able to remove a large proportion of the inorganic nitrogen (ammonia and nitrate/nitrite), as well as most of the DON in the Annacis WWTP centrate. Inorganic nitrogen removal through the period of testing averaged 87% while DON removal averaged 90%. However, the Anammox process was only able to reduce NRDP in the centrate by 12% and did not appreciably reduce the centrate orthophosphate concentration. The research suggests that the Anammox sidestream reactor holds promise as a way of reducing DON. Additional removal of sidestream NRDP and orthophosphate would be required to allow an anaerobic digester to be incorporated into the KWTF without compromising effluent quality.

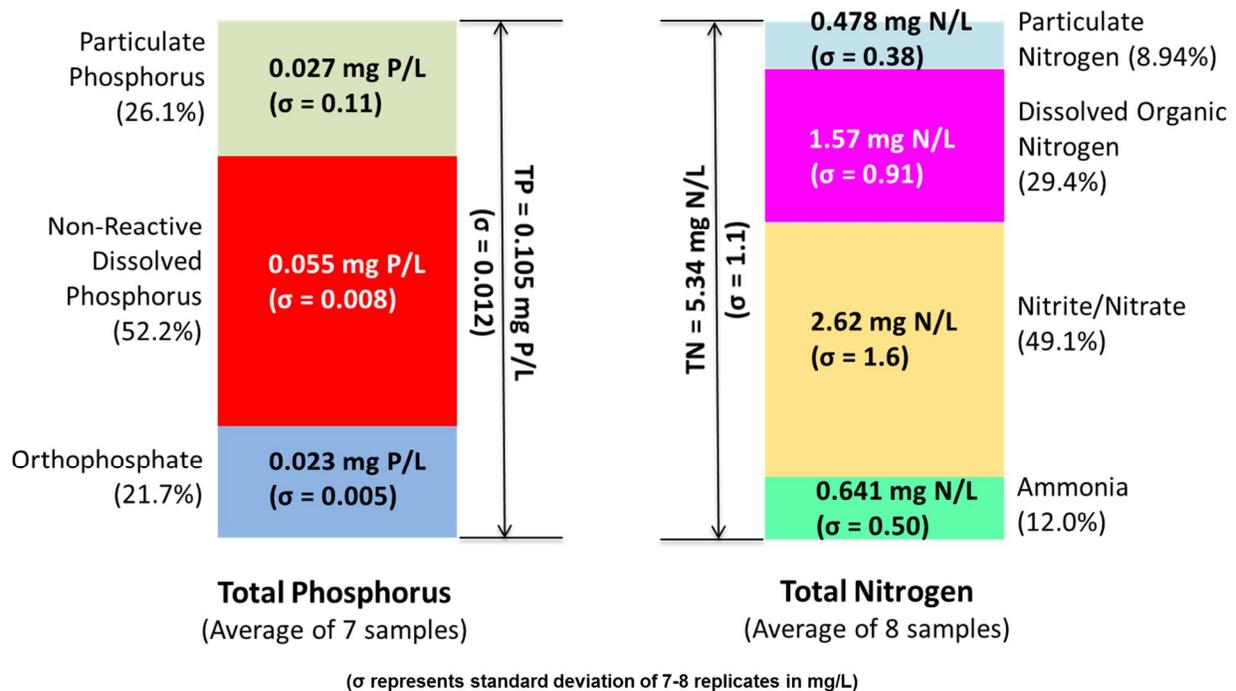
Further testing, including measurements of the inorganic condensed phosphorus and particulate species, is required to understand the transformation pathways of DON and NRDP through the sidestream and anaerobic digestion processes. Additional research could also be conducted to assess the suitability of a coagulation/flocculation/absorption and struvite removal process for removing dissolved phosphorus from the Anammox effluent. The following Chapter 4 was intended to answer questions raised as a result of lab testing in Chapter 3.

## **Chapter 4: Biodegradation and chemical precipitation of dissolved nutrients in anaerobically digested BNR sludge**

The objective of this chapter was to further explore processes for biodegradation and precipitation of dissolved nutrients in dewatering centrate. In this study, characterization was made of a conventional suspended growth deammonification treatment process for transforming dissolved polyphosphate (poly-P), dissolved organic phosphorus (DOP) and dissolved organic nitrogen (DON) in two types of dewatering centrate. The experiments were designed to determine if the initial results generated with Annacis Island WWTP centrate documented in Chapter 3 could be repeated with centrate derived from a nutrient removal treatment plant typical of the Okanagan Valley. The characterization of dissolved phosphorus species through the Anammox reactor was also aimed at determining if the poor NRDP degradation was linked to a change in the relative proportion of DOP and poly-P. Furthermore, poly aluminum chloride (PACL) dosing was assessed to determine if coagulant dosing stage can achieve the objective of precipitating any residual DON and NRDP and producing an effluent that has lower dissolved nutrients than the pre-digestion, dewatering centrate at the Kelowna Wastewater Treatment Facility (KWTF).

## 4.1 Context

The KWTF final effluent contains measured DON that represents 29% of the total nitrogen (TN) on average; similarly, the NRDP represents 52% of the total phosphorus (TP) on average (Figure 4.1). Based on these results, a significant proportion of the effluent nitrogen and phosphorus consists of DON and NRDP.



**Figure 4.1 - Kelowna WWTP final effluent nutrient speciation**

As effluent nutrient standards become more stringent in the Okanagan Lake watershed, understanding the formation, fate and treatment characteristics of NRDP and DON will become more important. Furthermore, as the KWTF service population grows, more energy efficient and compact sludge stabilization techniques are becoming desirable. However, the uncertainty of the fate of DON and NRDP through AD processes and the potential associated impacts on the KWTF effluent quality have served as an obstacle to adopting these technologies.

Suspended growth partial nitrification coupled with an anaerobic ammonia oxidizing (Anammox) step has shown to be an effective and energy efficient processes for removing ammonia from AD dewatering centrate (Wett et al., 2007a). Previous research described in Chapter 3 demonstrated the capacity of a similarly configured deammonification process for removing a large proportion of DON but to a lesser extent NRDP from dewatering centrate. Therefore, the primary objective of this research was to assess the transformation of polyphosphates (poly-P) and DOP through the deammonification process. This aspect of the research was intended to understand the poor NDRP biodegradation capacity of the process. The current investigation focusses on determining whether the relative fraction of poly-P and DOP changes through the deammonification process and if there is a gain in either constituent. The biodegradability of DON and NRDP centrate generated from a bench-scale AD fed BNR sludge was also characterized.

Finally, the success of implementing an AD within a BNR environment will ultimately be measured by the quality of the sidestream treatment effluent. Under ideal conditions, an Anammox process coupled with a struvite recovery process should remove more than 90% of the dissolved nitrogen and reactive phosphorus contained in the centrate (Hassan et al., 2013). Under upset conditions or where the NRDP needs further control, a final treatment barrier would be beneficial. Therefore, as a secondary objective of this research, the impact of dosing the Anammox effluent with poly aluminum chloride (PACL) was assessed. PACL was selected for the following reasons. PACL is supplied as a pre-polymerised liquid with the active aluminum species hydrolyzed with a base which reduces alkalinity demand (Jiang and Graham, 1998). In addition, previous research demonstrated that PACL is superior for TP removal compared to aluminum sulphate (Hatton and Simpson, 1985).

## **4.2 Material and methods**

### **4.3 Anaerobic digester set-up/operation**

The 5.0 L (effective volume) anaerobic digester (New Brunswick BioFlo® 115 glass fermenter) was started up on January 16, 2012 and had been operating continuously throughout the current testing. The digester was operated as a mesophilic process (37°C) at a sludge retention time (SRT) of 20 days and fed mixed sludge from KWTF. The mixed sludge feed consisted of thickened waste activated sludge (TWAS) and fermented primary sludge (FPS) at a percentage ratio of 66:34 by volume, at a total solids (TS) content between 4.0% and 5.0% by weight. Organic loading rate of the digester ranged between 1.73 and 1.93 grams volatile solids (VS)/L of digester/d. Mesophilic sludge inoculum was taken from the City of Penticton WWTP which operated a digester fed FPS as substrate. More detailed set-up/operating data for the AD is documented in Chapter 3.

Waste sludge from the AD was manually dewatered using BASF Zetag 7587 as a flocculant at a dosage of 50 mL, 0.5% solution per litre of sludge. Dewatering was undertaken using a Thermo Sorvall XT centrifuge operated at 3,900 rpm, 3,300 ×g for 20 minutes in 750 mL containers. Prior to dewatering, the waste sludge was stored in a 20 litre plastic container at 4°C. When the container was full, the sludge was batch dewatered to provide approximately 20 litres of centrate feed for the Anammox reactor which was stored in 4 L containers. This approach of batch processing sludge was intended to minimize the variability in centrate feed characteristics.

#### **4.3.1 Sidestream partial nitrification-deammonification bioreactor set-up/operation**

The partial nitrification-Anammox bioreactor was configured as a 5.5 L (effective volume) sequence batch reactor (SBR), operated at a temperature of 34°C. The New Brunswick BioFlo® 115 glass fermenter, controller and associated computer software allowed for automated

operation of a centrate feed pump, waste pump, alkalinity feed pump and air valve. The Anammox reactor configuration used for the experiment in this Chapter was identical to previous work. A more detailed description of the Anammox reactor is provided in Chapter 3.

At the start of operation, the Anammox reactor was operated using centrate from the Annacis Island WWTP (AIWWTP), owned by Metro Vancouver (Canada), as a substrate feed. The AIWWTP uses a trickling filter for mainstream secondary treatment and a thermophilic AD process for sludge stabilization. Once sufficient characterization data was obtained, the substrate feed was switched from AIWWTP centrate to lab-scale KWTF AD centrate. During the transition period, a mixture of AIWWTP and lab-scale KWTF AD centrate was used as feed. The proportion of AIWWTP centrate was progressively decreased over several days to minimize any potential inhibitory effects. In particular, high phosphate concentrations have shown to inhibit the anaerobic ammonia oxidizing bacteria (van de Graaf et al., 1996).

Characteristics of the full-scale AIWWTP and lab-scale KWTF AD centrate feed are provided in Table 4.1. For this study, a target centrate loading of 2,750 mg N/d (0.5 g N/L bioreactor volume) to the Anammox reactor was used.

**Table 4.1 – Full-scale AIWWTP and lab-scale Kelowna AD centrate feed characteristics**

Parameter	Full-scale AIWWTP Centrate		Lab-scale Kelowna AD Centrate	
	Mean	(Standard Deviation, Number of Samples)	Mean	(Standard Deviation, Number of Samples)
pH	8.21	(0.10, 40)	7.84	(0.20, 22)
Alkalinity, mg/L as CaCO <sub>3</sub>	5,047	(147, 11)	3,780	(300, 18)
Total Suspended Solids, mg/L	140	(51.8, 11)	175	(39.4, 21)
Ortho-Phosphate, mg P/L	157	(9.6, 16)	459	(53.0, 21)
Ammonia, mg N/L	1,184	(74.2, 14)	1,045	(147, 16)
Biological Oxygen Demand, mg/L	388	(74.4, 12)	315	(127, 12)
Volatile Fatty Acids, mg/L	32.4	(21, 4)	32.9	(8.1, 4)

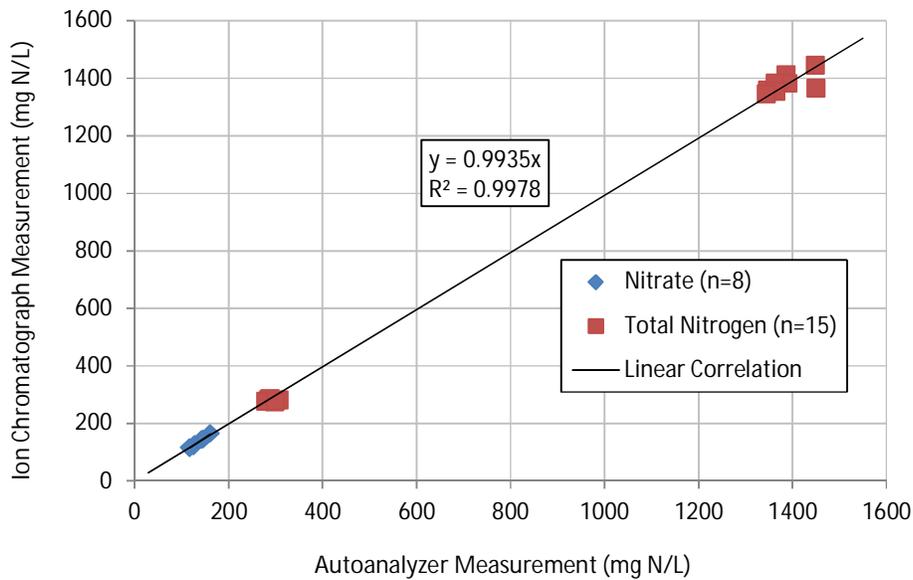
### 4.3.2 Sample preparation and analysis

Testing protocols in this experiment were carried out as described in Chapter 3 with the following modification and observations.

#### 4.3.2.1 Nitrogen & phosphorus testing

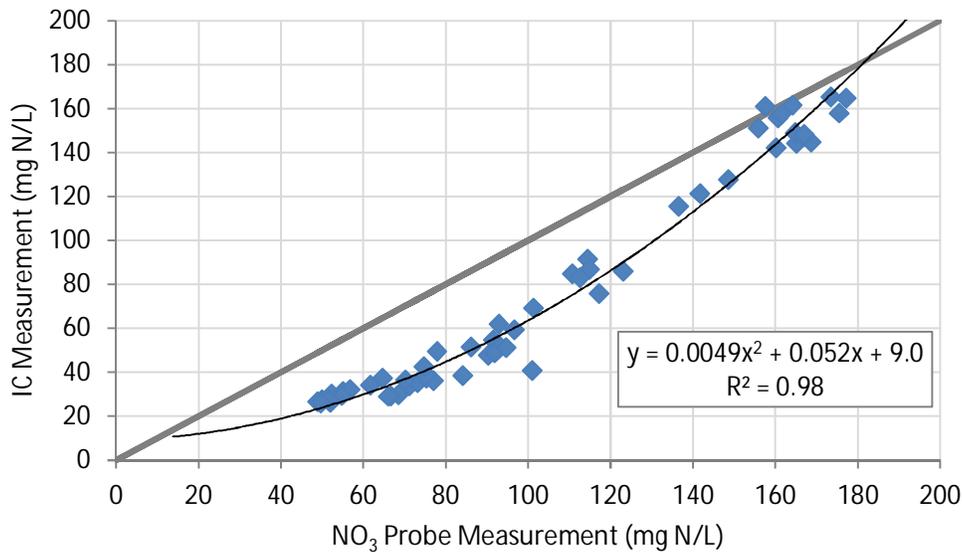
Initially, an Astoria Method A2 autoanalyzer fitted with Multi-Test Cartridge A000-AMT and a cadmium reactor was used to measure nitrate and TN. The persulfate method used for TN measurement (APHA, 4500-P-J) converts nitrogenous compounds to nitrate. TN is measured as the total nitrate concentration of the digested sample. Consequently, accurate TN testing necessitates a reliable method for nitrate. The Astoria autoanalyzer uses the cadmium reactor to reduce nitrate to nitrite. Following reduction of nitrate, nitrite is measured colorimetrically. In this way, TN testing required careful management of the cadmium reactor which over time lost efficiency due to oxidation of the metal surface. However, to simplify the testing and avoid errors associated with drifting of the cadmium reactor efficiency, use of an ion chromatograph (IC) was investigated. The digested TN sample was analyzed for nitrate using a Dionex IC,

Model ICS-2100. By this approach, nitrate could be measured directly and prone to less error. A comparison of TN results obtained using the autoanalyzer and IC showed excellent correlation for a total number (n) of 8 and 15 samples for nitrate and TN, respectively with a correlation coefficient ( $R^2$ ) of 0.9978 (Figure 4.2).



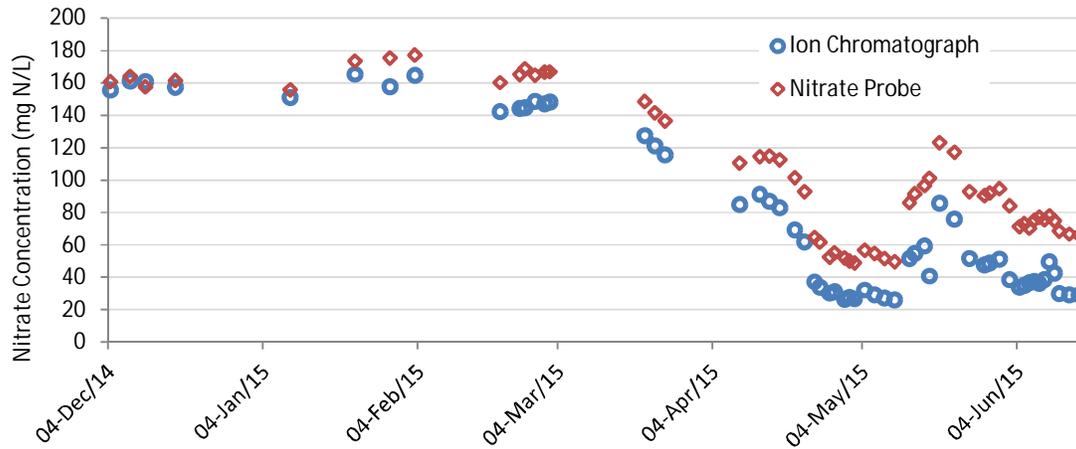
**Figure 4.2 – Comparison of IC and autoanalyzer for measurement of TN**

The use of an Accumet nitrate probe was also tested as a method for measuring nitrate in samples or digested TN samples. Measurements using the nitrate probe were found to not be a reliable measure of the nitrate concentration when compared with the autoanalyzer or IC. In effect, the test results were inconsistent. Figure 4.3 provides a plot of nitrate measurements using the probe and IC. In general, the probe measured nitrate consistently higher than the IC with the relative error increasing with decreasing concentration.



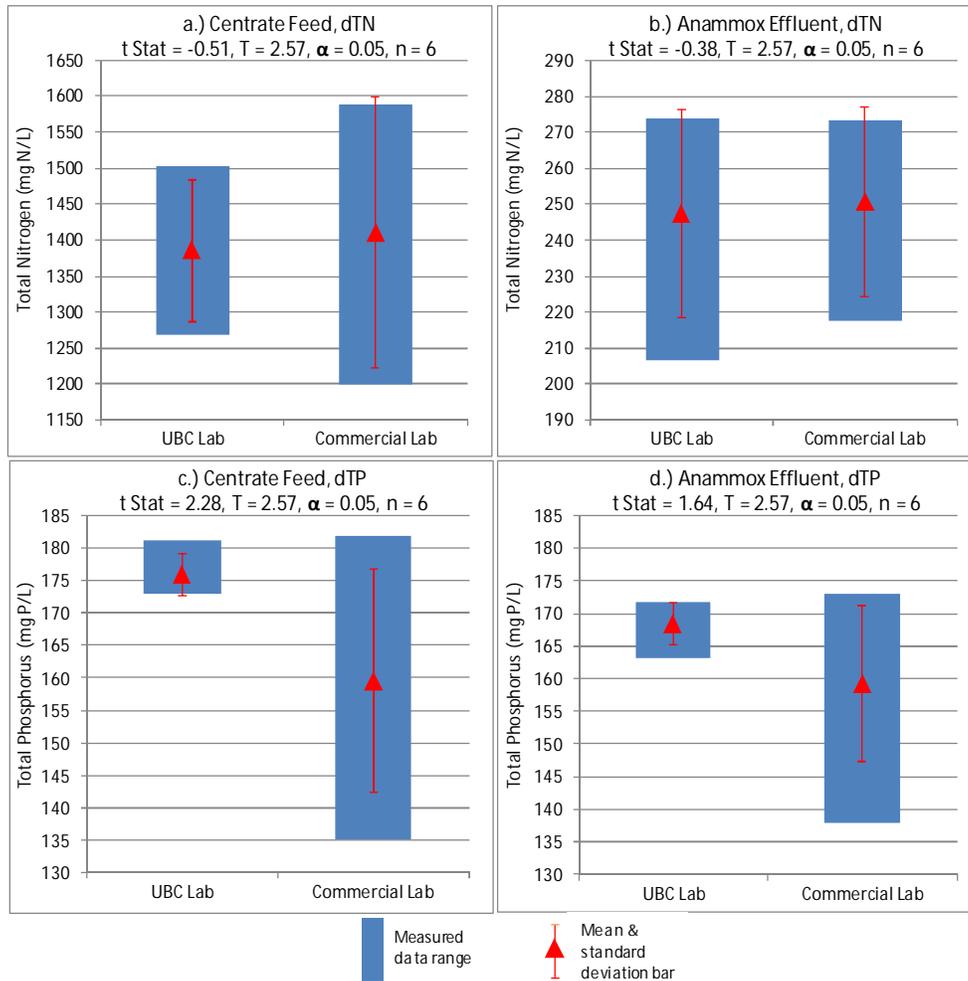
**Figure 4.3 – Comparison of IC and probe for measurement of nitrate**

While results from the probe are a poor measure of the absolute nitrate concentration, it nevertheless provided good value for operation of the Anammox reactor. The probe measurements reliably captured relative changes in the nitrate concentration in the day-to-day operation of the reactor (Figure 4.4). The time required to test Anammox effluent nitrate using the probe was a fraction of the time required to measure a sample using the IC. Effluent nitrate concentration is an important process variable, providing early indication of unusual loading conditions and signaling the need to adjust aeration or sludge wasting. Consequently, the probe was used for convenience to monitor relative changes in nitrate concentration from day-to-day and to allow timely process changes. Duplicate samples were stored and measurements of nitrate made using the IC were used as a check and to calculate nitrogen balance. In addition, ammonia was measured using APHA 4500-NH<sub>3</sub> F and nitrite was measured using APHA-NO<sub>2</sub><sup>-</sup> B.



**Figure 4.4 – Comparison of nitrate measurements made using a probe and IC**

Furthermore, to assess the accuracy of the TN and TP digestion and analysis procedures used in this research, 6 centrate feed and Anammox effluent samples were split and tested by both the UBC lab and a commercial lab. The samples were collected in two clusters within 5 days of each other in late February, 2015 and March, 2015. The commercial lab measurement was based on the summation of total Kjeldahl nitrogen (TKN) (APHA 4500-NORG D) and nitrite/nitrate; TP was measured using persulphate method (APHA 4500-P). A comparison of the measured dissolved TN (dTN) and dissolved TP (dTP) values for 6 centrate feed and 6 Anammox effluent samples is provided in Figure 4.5. The centrate feed for both clusters was part of the same batch of dewatered sludge and the nutrient content would be theoretically similar. The Anammox effluent characteristics would also have been similar for each cluster of samples but the effluent nitrogen had decreased between February and March.



**Figure 4.5 – Centrate feed and Anammox effluent dTN and dTP**

Based on a paired t-test comparison of the dTN measurements, the UBC lab results were not statistically different to the commercial lab result at a confidence limit of 95% ( $\alpha = 0.05$ ). Raw data and summary statistics are provided in Appendix B. The dTP measurements between the UBC lab and commercial lab were also not statistically different at a lower confidence limit of 90% ( $\alpha = 0.10$ ). However, dTP results from the commercial lab exhibit more variability than the UBC lab results. Also, the commercial lab data underestimates the dTP compared to the UBC lab. Given that NRDP is calculated based on the difference of dTP and orthophosphate, the higher variability and tendency for lower values in the commercial lab measurements risks under-estimating NRDP.

### **4.3.3 Dose optimization for nutrient precipitation**

For assessing the effectiveness of PACL on precipitating dissolved nutrients, 100 mL batch volumes of Anammox effluent were used. A pre-mixed PACL product, Isopac (Klearwater Equipment and Technologies Corp.), was used for the testing. Isopac is a non-sulphated PACL solution, 18%  $\text{Al}_2\text{O}_3$  by weight and 45% basicity. The PACL solution was dosed in the effluent and flash mixed in a glass beaker using a magnetic stir rod at 200 rpm for 30 seconds. Following flash mixing, the stir speed was reduced to 25 rpm and the sample flocculated for 25 minutes. A sample was drawn off after settling for 5 minutes for dissolved nutrient testing and measurement of zeta potential. Zeta potential is a measure of the electrostatic charge repulsion and attraction between particles and can be used to monitor coagulant dosing efficiency (Nobbmann et al., 2010). The coagulant dose was incrementally increased and new batch volumes started until a neutral zeta potential was reached. A Malvern Zetasizer (nano ZS) was utilized for measurement of zeta potential. All zeta potential measurements were made at a temperature of 25°C.

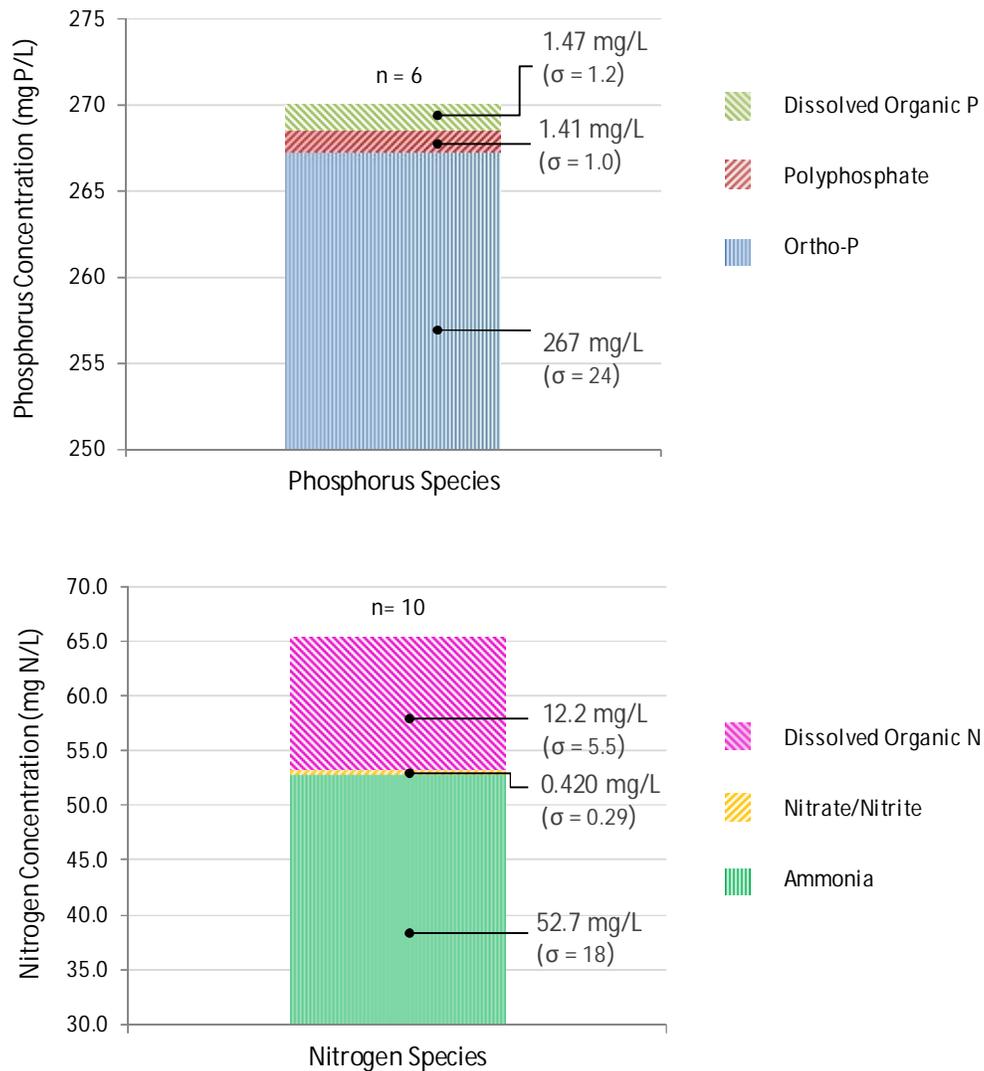
## **4.4 Results**

### **4.4.1 Existing KWTF centrate characterization results**

The potential for increased effluent nutrient concentration associated with introducing an AD into a tertiary WWTP can be minimized by designing a sidestream treatment process to achieve a pre-digestion dewatering centrate quality. The KWTF currently dewateres its primary and waste activated sludge and transports the biosolids off-site for composting. Introducing an AD would impact the WWTP process through changes in the dewatering centrate quality. The existing (baseline) dewatering centrate nutrient load was characterized to assess NRDP and DON concentrations. This exercise was necessary to allow comparison of the Anammox effluent NRDP and DON concentrations with the baseline characterization. The comparison could be

used to assess whether centrate deammonification would be sufficient to reduce nutrient concentrations to baseline levels if KWTF were to implement AD for biosolids stabilization and energy recovery. A graphical representation of the baseline KWTF centrate nutrient fractionation data (no sludge AD) is provided in Figure 4.6. Standard deviation and number of data collected are represented by  $\sigma$  and  $n$ , respectively. Samples were collected from July to September, 2015. To further characterize NRDP, the samples were analyzed for poly-P and DOP. The data indicates that poly-P and DOP make up approximately an equal proportion of the NRDP in the existing KWTF centrate.

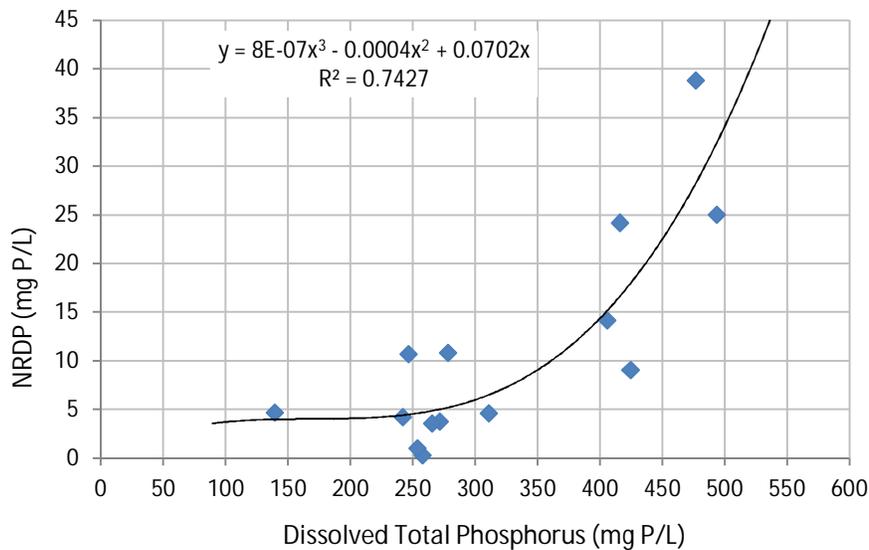
The KWTF centrate also contains a relatively high fraction of ammonia (81%) and phosphate (99%). The ammonia is associated with the fermented primary sludge (FPS). As part of the BNR process, primary sludge is fermented to generate VFAs which are used to enhance phosphate removal in the mainstream process. The fermentation process also releases some ammonia as a by-product. The residual VFAs in the FPS also stimulate release of phosphate in the TWAS when the two sludges are mixed just prior to centrifugation.



**Figure 4.6 – Nutrient fractionation for the existing KWTF dewatering centrate**

Based on the 6 samples of KWTF dewatering centrate that were fractionated to measure dissolved phosphorus species, the NRDP on average was 2.88 mg P/L ( $\sigma = 1.8$  mg P/L). This measured NRDP is less than the 14.5 mg P/L measured over the February-July, 2014 time period. The decrease in NRDP may be explained by process improvements that were implemented at KWTF over this time. In particular, the mixing system in a sludge vault used to

store thickened waste activated sludge (TWAS) when the centrifuge dewatering is off-line (i.e., evenings and weekends) was upgraded to eliminate short-circuiting and suspected fermenting TWAS conditions. After this change, the dTP values decreased from an average of 331 mg P/L ( $\sigma = 115$  mg P/L,  $n = 13$ ) in year 2014 to 267 mg P/L ( $\sigma = 23.8$  mg P/L,  $n = 6$ ) in year 2015. This suggests that dissolved phosphorus release associated with fermenting TWAS also contributes to higher NRDP. The plot of existing KWTF centrate NRDP and dTP values for year 2014 and 2015 (Figure 4.7) provides support to this idea. In the plot, measured NRDP concentration shows a positive, non-linear relationship with dTP. The data suggest that the proportion of NRDP increases as centrate dTP increases above 200 mg P/L.



**Figure 4.7 – Existing KWTF dewatering centrate NRDP and relationship to dTP**

Based on information provided by the KWTF staff, the plant was challenged to meet the final effluent criteria during periods when the centrate dissolved phosphorus exceeded 300 mg P/L. During these times, a backup aluminum sulphate (alum) dosing system was utilized to ensure the final effluent TP objective was met. The use of alum is reserved as a method of last resort due to

the high cost. Once the conditions associated with fermenting TWAS were resolved the KWTF was able to resort to its normal operation without the use of alum trimming to achieve its effluent permit.

#### **4.4.2 Anammox performance results**

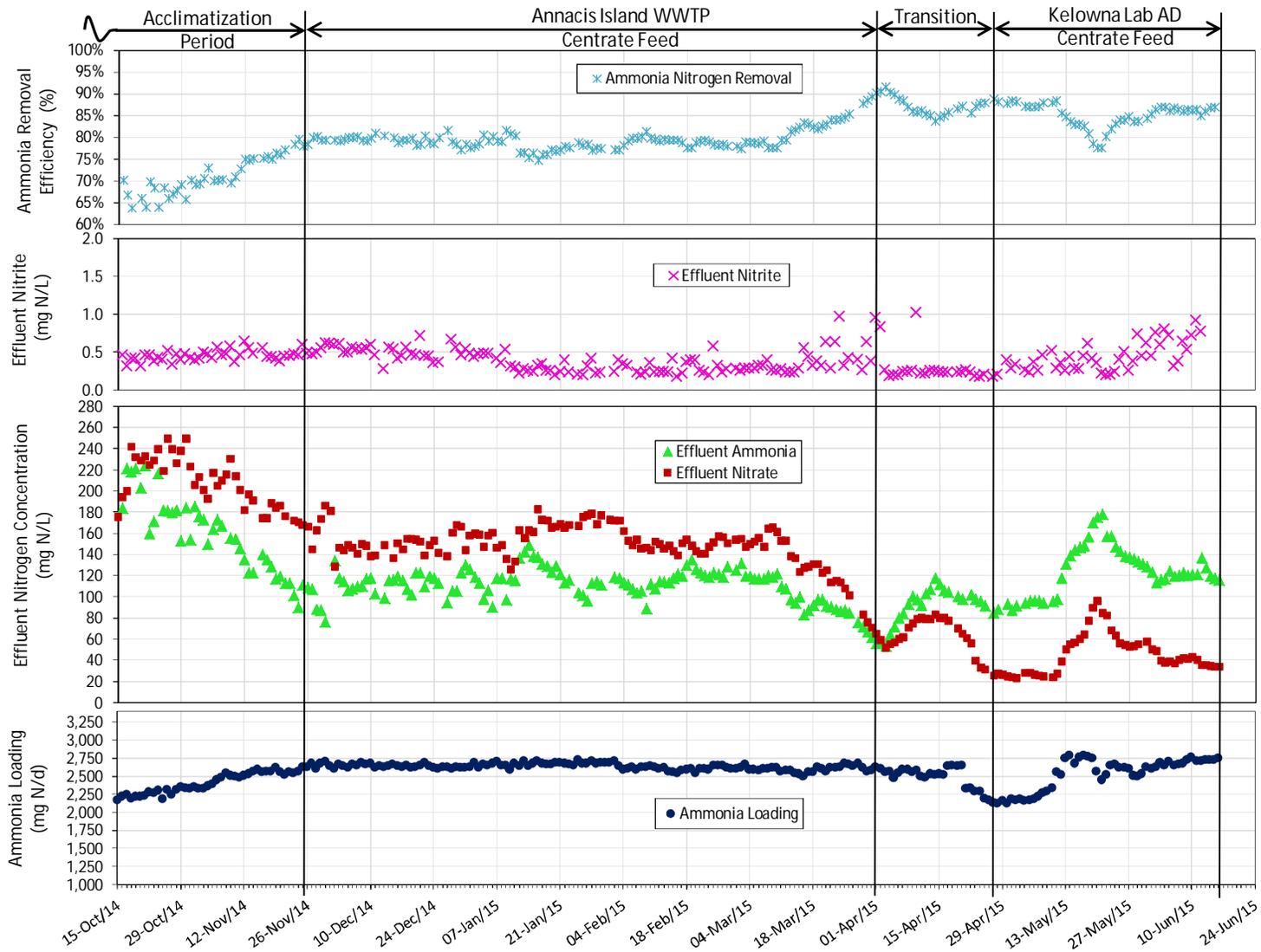
Except for the occasional equipment and power failure event, the lab-scale Anammox reactor operated continuously from November, 2012 to June, 2015, a period of 32 months. The last failure occurred on August 29, 2014 when pH control was lost resulting in excess aeration. Following this upset, the process was slowly re-established using dewatering centrate from AIWWTP, reaching the target loading of 2,750 mg NH<sub>3</sub>-N/d on November 24 (Figure 4.8). From November 24, 2014 to April 2, 2015 AIWWTP centrate feed and Anammox effluent samples were collected and analyzed for dissolved nutrients. Since the principal objective of the research was to understand the flux of dissolved nutrients through the reactor, the testing did not include testing to assess Anammox TN removal.

Once sufficient data had been collected, the feed substrate was transitioned on April 29, 2015 to lab-scale KWTF AD centrate. Through this period of testing, the average ammonia removal rate was 79.4% ( $\sigma = 2.1\%$ ) for the AIWWTP centrate and 85.1% ( $\sigma = 2.8\%$ ) for the lab-scale KWTF AD centrate. The mixed liquor nitrite concentration averaged 0.38 mg N/L ( $\sigma = 0.17$  mg N/L) and ammonia averaged 112 mg N/L ( $\sigma = 21$  mg N/L).

During the transition phase, the proportion of lab-scale KWTF AD centrate was increased over a period of 28 days to minimize the potential inhibition associated with the increased orthophosphate loading. In previous research, van de Graaf et al. (1996) observed inhibition by phosphate on anaerobic ammonia oxidizing bacteria at concentrations as low as 155 mg P/L (i.e., KH<sub>2</sub>PO<sub>4</sub> at 5 mM concentration). Since the KWTF utilizes a BNR process, lab-scale KWTF AD

centrate contains significantly higher concentrations of dissolved phosphorus compared to the AIWWTP centrate. Through the transition period, the orthophosphate loading increased from an average of 157 mg P/L ( $\sigma = 9.6$  mg P/L) in the AIWWTP centrate to 459 mg P/L ( $\sigma = 53$  mg P/L) in the lab-scale KWTF centrate. The Anammox process did experience a temporary decrease in removal efficiency near the end of the transition period. To compensate for the loss, the loading was decreased to around 2,000 mg  $\text{NH}_3\text{-N/d}$  until the process stabilized. The ammonia removal rate associated with the KWTF AD centrate was slightly lower at 79.4% ( $\sigma = 2.1\%$ ) compared to the AIWWTP centrate and 85.1% ( $\sigma = 2.8\%$ ). However, the Anammox reactor operated for 5 months on the AIWWTP centrate feed compared to 2.5 months for the KWTF AD centrate feed. It's possible that in time the difference in removal rates would have closed. The instability in the Anammox process that was observed as the proportion of KWTF AD centrate was increase may suggest some short-term inhibitory event did occur but to which the process was ultimately able to adapt.

During the second testing phase, lab-scale KWTF AD centrate feed and effluent samples were collected from the Anammox reactor and analyzed for dissolved nutrients.



**Figure 4.8 – Operating characteristics and results for the Anammox process**

### **4.4.3 Centrate biodegradation through the Anammox process**

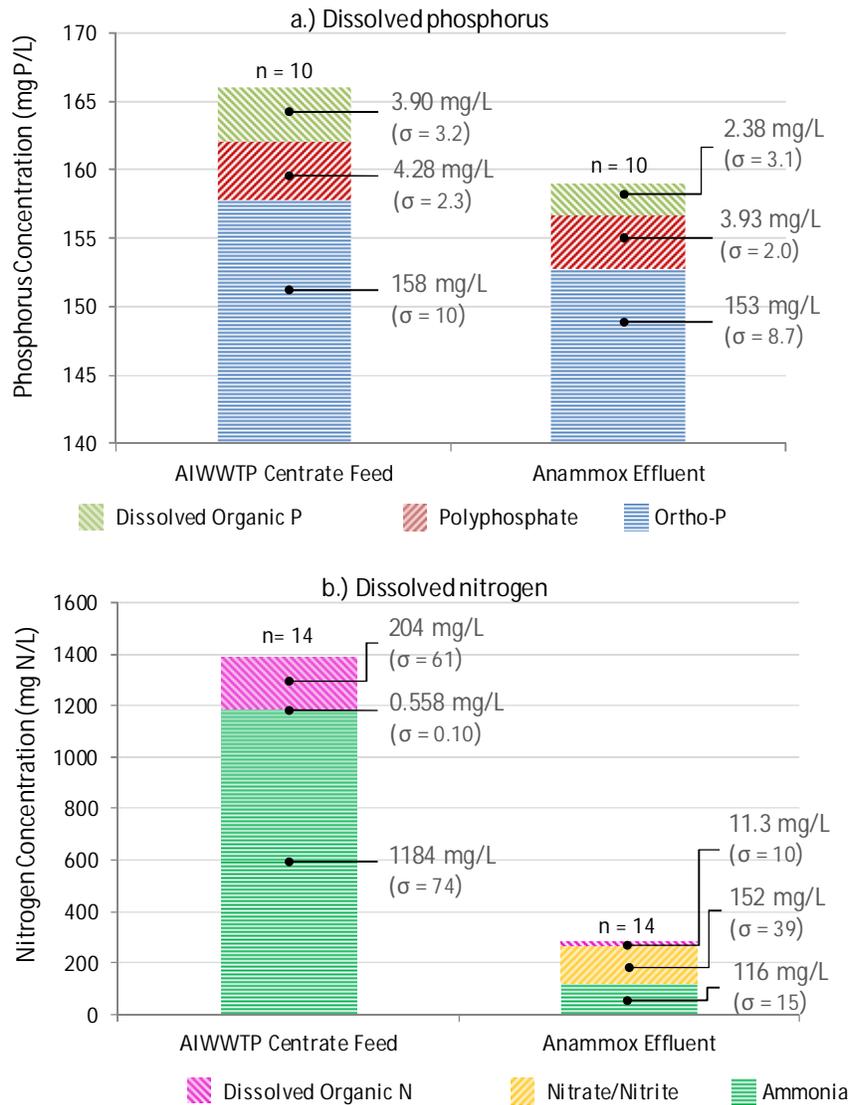
Fractionation of dissolved nutrients in the Anammox centrate feed and effluent was characterized to assess biodegradation capacity of dissolved nutrient species. The underlying assumption of this work is that in a full-scale BNR facility, bio-conversion of the dissolved nutrients into a particulate form will increase the likelihood that it can be removed by the process. The KWTF effluent characterization documented in Section 4.1 indicates that the treatment process is less efficient at removing dissolved nutrients compared to particulate nutrients greater than 0.45  $\mu\text{m}$  in size. The testing necessary to assess TN removal efficiency and particle size characterization of the influent and effluent was not included in the current research. However, future research designed to characterize the change in colloidal and particulate nutrient size distribution through the process could help further optimize removal.

For this part of the research, AIWWTP centrate and the lab-scale KWTF AD centrate were used as feed substrate for the Anammox process. Previous work had shown that the Anammox process was able to degrade AIWWTP centrate DON but had a limited reducing effect on the NRDP (Chapter 3). The current testing was undertaken to determine whether this result could be replicated using the lab-scale KWTF AD centrate feed and to assess whether partitioning of poly-P and DOP changes through the Anammox process.

#### **4.4.3.1 AIWWTP centrate feed**

Results of the dissolved phosphorus and nitrogen fractionation for AIWWTP centrate feed and associated Anammox effluent are summarized in Figure 4.9. The results show a relatively high DON removal rate of 94% by the Anammox process which is consistent with previous work described in Chapter 3. Also, Wadhawan et al. (2015) measured good DON removal (70%) through a nitrification process in secondary effluent and a lesser rate through an anammox

culture under anoxic conditions (27%). The higher removal rate measured in this study may be a consequence of the Anammox process which cycles between aerobic and anoxic processes, thereby maximizing DON degradation through both nitrification and anammox exposure.



**Figure 4.9 – AIWWTP centrate and Anammox effluent dissolved nutrient characterization**

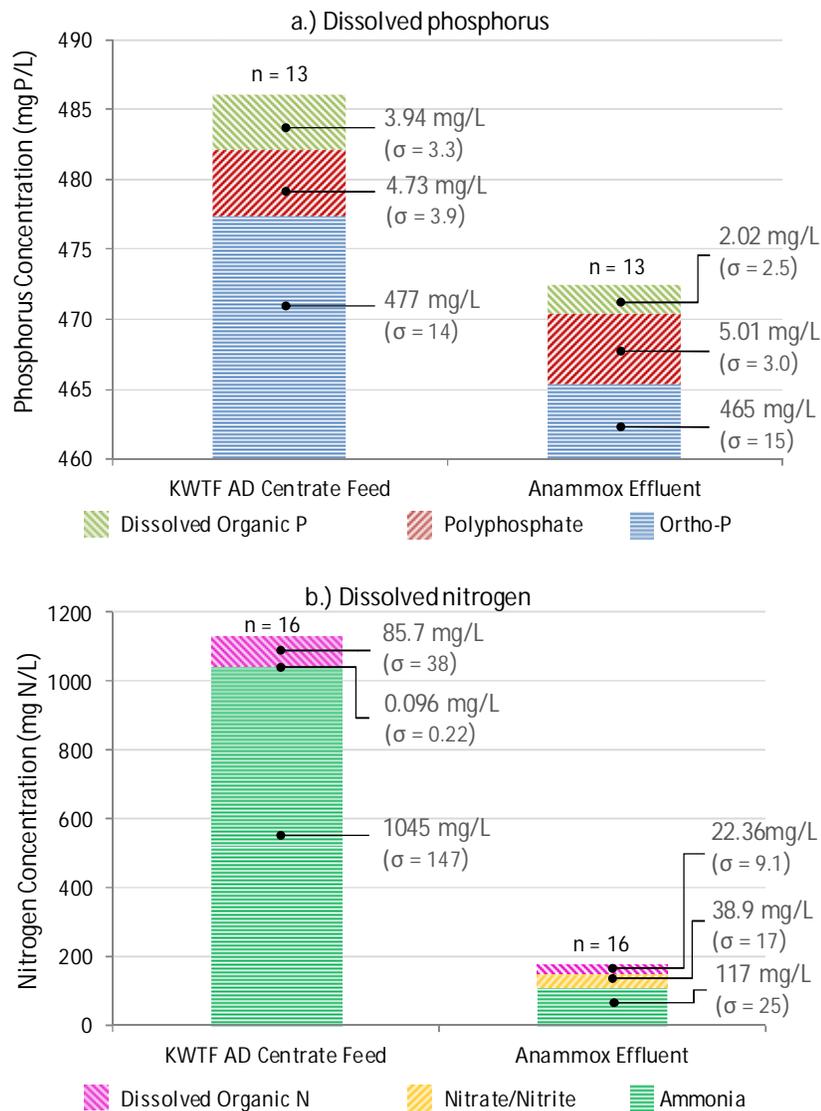
On average, the AIWWTP centrate DON was decreased from 204 mg N/L to 11.3 mg N/L. Overall, the dTN was reduced through the Anammox process by 79.9% (i.e., from 1,389 mg N/L to 279 mg N/L).

A small reduction in dissolved phosphorus species was measured across the Anammox process. The average removal of NRDP was 22.9% (i.e., from 8.18 to 6.31 mg P/L). Based on a paired t-test, the NRDP removal results meet the standard for rejecting the null hypothesis that the means are statistically equal at a confidence limit of 95% (i.e., t-statistic of 2.82 is greater than the T-score of 2.26). In effect, the measured NRDP removal is statistically significant. The poly-P concentration in the centrate feed was not statistically different from Anammox effluent poly-P at a confidence level of 95% (i.e., t-statistic, 0.74 is less than the T-score of 2.26). At the 95% confidence limit, the change in DOP is less certain. The paired t-statistic of 2.17 for DOP in the AIWWTP centrate feed and Anammox effluent is lower than the T-score of 2.26 which indicates the reduction is not statistically significant. However, there is an apparent contradiction in that NRDP reduction is statistically significant but by the same standard reduction in both poly-P and DOP which make up NRDP is not. Consequently, the paired t-test is not definitive but does suggest that additional testing is needed to confirm the reduction potential of DOP through the Anammox process. Raw data and summary statistics are provided in Appendix C.

#### **4.4.3.2 Lab-scale KWTF AD centrate**

In the second trial, the degradation of lab-scale KWTF AD centrate through the Anammox process shows similar characteristics as with the AIWWTP centrate (Figure 4.10). Reduction in DON concentration was 74%, from 85.7 mg N/L in the centrate to 22.4 mg N/L in the Anammox effluent. The precise fate of DON through the Anammox reactor is unclear. The colloidal fraction of centrate DON was not measured as part this research, nor was the TN flux through the reactor assessed. As a consequence, it's not possible to assess whether most of the reduction in DON through the Anammox reactor was associated with colloidal or non-colloidal DON; or to determine how much of the DON was truly removed and oxidized to ammonia, nitrate/nitrite or

nitrogen gas or converted to a suspended solids form (i.e., particle size greater than 0.45  $\mu\text{m}$ ). Additional research could focus on testing colloidal as well as dissolved and particulate nitrogen in order to better assess the impacts. However, in a full-scale application the large reduction in KWTF AD centrate DON, as well as ammonia, through the Anammox reactor does mitigate the potential risk of dissolved nitrogen on the mainstream process and final effluent.



**Figure 4.10 – KWTF AD centrate and Anammox dissolved nutrient characterization**

DON in the lab-scale AD had been measured at higher levels, prior to dewatering using polyacrylamide (PAM) polymer, similar to that used at the AIWWTP. Of the 8 AD sludge samples tested without the use of PAM dewatering polymer, DON averaged 210 mg N/L ( $\sigma = 96$  mg N/L). It's not certain what caused the apparent decrease in DON in the digested sludge supernatant. The influence of dewatering polymer dosing on AD DON is a possible factor that could be tested in future experiments.

The Anammox process fed lab-scale KWTF AD centrate feed, showed a small reduction in effluent NRDP from 8.68 to 7.03 mg P/L. Based on the paired t-test at a confidence limit of 95%, the change in NRDP was statistically insignificant (i.e., t-statistic of 1.70 versus a T-score of 2.18). Using the paired t-test to compare the results, the poly-P concentration in the lab-scale KWTF AD centrate feed is not different from the Anammox effluent at a confidence level of 95% (i.e., t-statistic, -0.23 is greater than the T-score of -2.18). In this case, the change in DOP is more certain compared to the AIWWTP centrate. The paired t-statistic of 3.21 for DOP in the lab-scale KWTF AD centrate feed and Anammox effluent is significantly higher than the T-score of 2.18. Consequently, the measured DOP reduction of 48.7% is statistically significant and may suggest that the Anammox process is able to degrade more DOP than poly-P. Raw data and summary statistics are provided in Appendix C.

#### **4.4.4 Summary of centrate biodegradation study**

The bioreactor studies using both AIWWTP centrate and lab-scale KWTF AD centrate show similar results. The Anammox process is able to degrade most of the centrate DON. The propensity for DON degradability is assumed to be due more to the aerobic ammonia oxidizing bacteria than the anaerobic variety as suggested by research conducted on secondary treatment processes (Wadhawan et al., 2015). Combining both aerobic and anaerobic ammonia oxidizers in

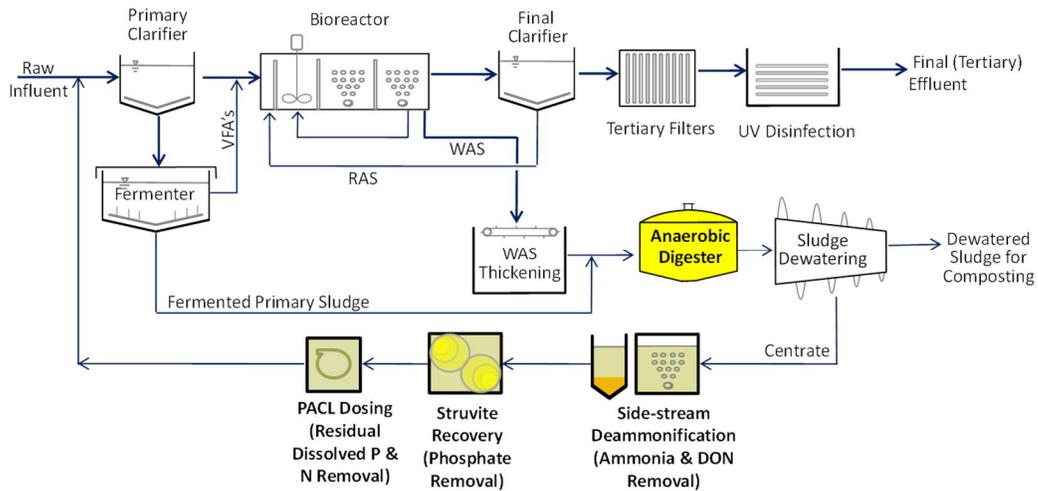
a SBR process such as in the current study may help to maximize DON degradation. It's possible that the ammonia oxidizers have the enzymatic processes to efficiently degrade the organic nitrogen. However, heterotrophs may also be contributing to the higher aerobic degradation of DON.

The testing also shows that DOP is more readily degraded through the Anammox reactor than poly-P. This feature may have application for NRDP removal if DOP degradation can be optimized by process changes like increased HRT.

The nitrogen and phosphorus removal rates were similar for both centrate feeds. This indicates the high phosphate concentration in the KWTF AD centrate did not significantly impact the Anammox process performance.

#### **4.5 Dose optimization for nutrient precipitation**

In addition to characterizing the biodegradability of dissolved nutrient species through the Anammox process, the current research was intended to assess requirements for additional sidestream treatment. When fed lab-scale KWTF AD centrate, the Anammox effluent contains dissolved reactive and non-reactive phosphorus levels that are significantly higher than the existing KWTF centrate. In particular, the Anammox effluent NRDP was 7.03 mg P/L compared to 2.88 mg P/L in the existing KWTF undigested sludge centrate. Consequently, if the results of this lab-scale trial are representative of a full-scale scenario, introduction of AD into the KWTF will need to include additional nutrient removal. In addition to removing NRDP, the centrate has an elevated concentration of phosphate and ammonia. The sidestream treatment paradigm that has guided this research includes struvite recovery and chemical dosing following the Anammox stage (Figure 4.11).

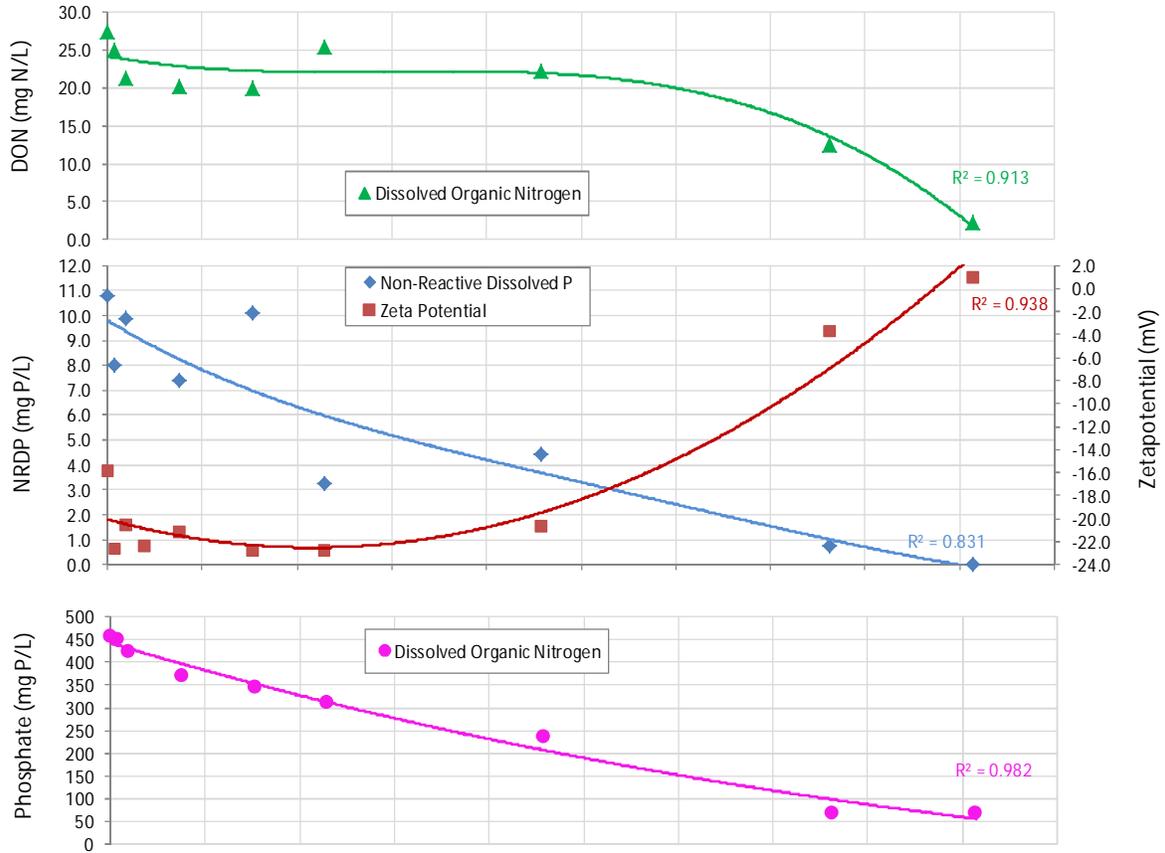


**Figure 4.11 - Modified KWTf schematic incorporating anaerobic digestion and side-stream treatment for centrate dissolved nutrient removal**

Struvite recovery is a conventional approach for phosphate removal and provides an opportunity to recover phosphorus and ammonia in conjunction with biological centrate treatment (Hassan et al., 2013). The Anammox and struvite processes together can treat for centrate ammonia, phosphate and as this research shows a significant fraction of the DON. While Figure 4.11 shows the Anammox as the first stage as the work by Hassan et al. (2013) suggested was better suited for operation of the struvite process, an alternative staged treatment process could prove more optimal.

Dosing the effluent with an aluminum cation like PACL following the Anammox and struvite recovery could serve as a physico-chemical process to polish the treated centrate, minimizing potential impacts of any residual NRDP on the mainstream process and final effluent quality. The effectiveness of coagulant dosing with PACL for precipitating dissolved nutrients in the Anammox effluent was assessed in a series of batch tests. The tests were conducted in the absence of struvite precipitation and therefore illustrate a worse-case scenario for PACL dosing.

Results of the PACL dosing experiment using effluent from the Anammox bioreactor fed lab-scale KWTF AD centrate are provided as Figure 4.12.



**Figure 4.12 – Impact of PACL coagulant dosing on the precipitation of dissolved nutrients**

The testing indicates that a PACL dose of 400 mg Al/L effluent would reduce the NRDP concentration in the Anammox effluent to approximately 1.0 mg P/L, well below the average 2.88 mg P/L currently in the KWTF dewatering centrate. Furthermore, the PACL dosing data also shows a propensity for significant reductions in DON. The 400 mg Al/L effluent PACL dose also reduced the DON concentration in the Anammox effluent to approximately 11.0 mg N/L which is lower than the existing KWTF dewatering centrate. In effect, the combination of Anammox sidestream treatment and PACL dosing together is sufficient to reduce dissolved

phosphorus and nitrogen in dewatering centrate associated with anaerobically digested BNR sludge. If orthophosphate removal by means of struvite recovery were introduced to this treatment train, the PACL dosing requirements would be significantly reduced.

The observation of DON and NRDP precipitation through chemical dosing is supported by previous research by Dwyer et al. (2009) and Arnaldos and Pagilla (2010). In these studies, hydrated aluminum sulphate was used to precipitate DON and NRDP species from wastewater effluent at much lower initial concentrations. The current research concludes that the approach of aluminum dosing the dewatering centrate at higher initial concentrations is an equally effective control for DON and NRDP. Although the dosing concentrations for centrate are significantly higher, there are efficiencies gained from having to dose a much smaller centrate flow compared to the mainstream final effluent flowrate. For KWTF, dewatering centrate represents on average 0.51% of the total mainstream effluent volume. Consequently, under a sludge digestion scenario, the 400 mg Al/L treated centrate dose represents an equivalent dose rate of 2.0 mg Al/L based on the final effluent volume (i.e.,  $0.51\% * 400 \text{ mg Al/L Anammox effluent}$ ).

After dosing the treated centrate with PACL to remove DON and NRDP in a full-scale WWTP, it may be possible to avoid additional sidestream or mainstream filtration to intercept the coagulated nutrients. Instead, the precipitated DON and NRDP could be returned to the primary clarifier and removed through settlement. In this way, the nitrogen and phosphorus precipitates would ultimately be returned to the digester through the normal wasting process. This approach increases the potential for re-release of nutrients in the AD process. Removal of dissolved reactive phosphorus through struvite recovery would reduce the mass of precipitated nutrients returned to the digester and associated risk of nutrient re-solubilization. There are limited published studies which document the hydrolysis potential of aluminum precipitated nutrients in

AD processes. Work by Grigoropoulos et al. (1971) suggests that precipitated phosphorus is stable under mesophilic conditions but additional research is needed to assess the fate of coagulated DON and NRDP through the AD process.

#### **4.6 Summary of the centrate treatment characterization**

Based on a detailed study of centrate treatment through the Anammox, the following summary conclusions were drawn.

- Selection of methods for dissolved nutrient testing was important for achieving consistent results, particularly for TP and nitrate.
- The elevated phosphate concentration in the lab-scale KWTF AD centrate did not appreciably affect the stability of the Anammox process, as measured by ammonia removal.
- The Anammox process showed similar treatment characteristics for both the KWTF and AIWWTP centrates with excellent DON removal but poor NRDP removal.
- A statistical comparison of the DOP and poly-P through the Anammox process suggests that DOP has a higher biodegradation potential. Future research focused on understanding the variables associated with degradation of DOP could lead to better NRDP removal through the Anammox process.
- Both DON and NRDP may be a heterogeneous mixture of dissolved and colloidal compounds and the form may influence biodegradability. Future research should focus on characterizing the relative proportion to TN and TP of dissolved, colloidal and suspended solids DON and NRDP.
- Utilization of a post-Anammox PACL chemical dosing stage can achieve the objective of precipitating any residual DON and NRDP to produce an effluent that has lower dissolved nutrients than the pre-digestion KWTF dewatering centrate.

## **Chapter 5: Final effluent particulate phosphorus fractionation and coagulation by optimized chemical Dosing**

Eutrophication of waterways has prompted many agencies in Canada and the United States (US) to mandate phosphorus removal processes for all the waterways identified as sensitive to phosphorus (P) enrichment. Over the past 30 years these mandates have resulted in many wastewater treatment plant (WWTP) process configurations to convert to chemical, biological and/or physical barriers to enhance P removal. Implementation and optimization of biological process configurations has lowered total P discharges to less than 0.5 mg/L.

Biological nutrient removal (BNR) process configurations when combined with effluent filtration, as depicted in Figure 1.3, have resulted in improved suspended solids removal and reduced total P (TP) to less than 0.25 mg/L. There is a propensity in enhanced nutrient removal treatment plants for a large fraction of the total P in the final treated effluent to be represented by fine particulate and soluble non-reactive phosphorus (Neethling and Stensel, 2013). Consequently, increasing the level of P removal will need to consider ways to remove these forms of effluent phosphorus.

BNR treatment plants typically include a backup coagulant dosing system to chemically precipitate ortho-phosphate in the event of a process upset or effluent polishing. For this application, aluminum sulphate is usually utilized as the coagulant of choice due to its lower cost compared to aluminum chloride and polyhydroxy aluminum chloride (PACL). However, PACL has other characteristics which may make it a more suitable coagulant for dosing at a wastewater treatment plant. PACL is supplied as a pre-polymerised liquid with the active aluminum species hydrolyzed with a base. This feature reduces alkalinity demand compared to aluminum sulphate

or aluminum chloride. The nature of the polymeric species formed depends on a variety of factors but include those with high cationic charge such as  $Al_2(OH)_2^{4+}$ ,  $Al_3(OH)_4^{5+}$  and  $Al_{13}O_4(OH)_{24}^{7+}$  (Jiang and Graham, 1998). In combined phosphorus and nitrogen treatment processes, alkalinity consumption and reduced pH due to aluminum sulphate dosing could destabilize nitrification (Banu et al., 2009).

A further consideration for use of PACL over aluminum sulphate for removal of particulate phosphorus is provided by research conducted by Hatton and Simpson (1985). Their jar test experimentation work comparing phosphorus removal of various aluminum coagulants showed that PACL was superior in removal of TP and equally effective in precipitating orthophosphate. If sufficient charge is available on the PACL floc to adsorb dissolved colloidal P, as suggested by their research, then it may be possible for the PACL floc to become attached to the biological floc and settle-out in the secondary clarifiers.

Within a BNR process environment, the use of PACL may be a good candidate for precipitating the soluble, non-reactive phosphorus that currently is an obstacle for achieving lower effluent criteria. If this is the case then a further improvement in the coagulation process could be the use of a coagulant aid to reduce the PACL dose. This approach is used in the Okanagan Valley at various water treatment plants. The surface raw water of the valley is characterized by a high level of colour. The common treatment method includes using PACL in conjunction with an aqueous solution of poly epichlorohydrin amine (polyepiamine) as a coagulant aid. The polyepiamine has low molecular weight and high cationic charge density which is effective at neutralizing the surface charge of colloids. The proposed research was undertaken in part to determine whether use of a polyepiamine could improve the efficiency of TP precipitation.

Measurements of zeta potential could also be used to monitor and optimize the coagulant dose. Zeta potential is a measure of the charge potential at the plane of shear between a particle and surrounding liquid and depending on characteristics of the suspension the magnitude of the charge can be used as a measure of stability (Bratby, 2006). The cationic coagulants proposed in this research destabilize the phosphorus particle charges, thereby allowing them to agglomerate and settle. By monitoring zeta potential, it may be possible to control coagulant dosing by targeting a specific zeta potential value associated with the desired effluent total P objective. A similar approach has been successfully used to minimize coagulant usage in water treatment plants (Nobbmann et al., 2010). In a wastewater treatment context, optimizing the coagulant dose could also minimize any potential negative effects of elevated concentrations of coagulant on nutrient removal. For example, other research has highlighted a potential for reduced denitrification capacity by PACL at 19.5 mg Al<sub>2</sub>OH<sub>3</sub>/L (Guo et al., 2015).

## **5.1 Research objectives & approach**

The research detailed in this paper focuses on measuring the efficacy of PACL (Isopac, 18% Al<sub>2</sub>O<sub>3</sub>, 45% basicity) in combination with polyepiamine (Magnafloc LT 7990, 50% solids medium molecular weight polyepiamine product) for coagulating particulate and dissolved phosphorus. The main objective will be to establish an optimum coagulant dose for removing soluble, non-reactive phosphorus in final effluent from the Westside Regional WWTP. A secondary objective is to characterize the colloidal material that makes up dissolved, non-reactive phosphorus (NRDP). Westside Regional WWTP effluent rather than KWTF effluent was used in this part of the experimentation work to satisfy the research partner's (AECOM) interest in adding to their operational understanding of the Westside Regional WWTP. However,

the Westside Regional WWTP and KWTF are based on a similar design and the results would be applicable to both facilities.

## **5.2 Methodology**

This section provides a description of the proposed testing methods and apparatus. In general, the testing was intended to generate data of sufficient quality to characterize effluent particulate size distribution, both dissolved ( $< 0.45 \mu\text{m}$ ) and suspended ( $> 0.45 \mu\text{m}$ ). As part of this work, the effluent was fractionated to determine the distribution of total P by particulate size. The intention was to develop a baseline picture of the particulate matter in final effluent from Westside Regional WWTP and to determine if there is a propensity for TP to concentrate in a specific size range. Conventional filtration and ultrafiltration techniques at the lab scale were used to fractionate effluent samples for testing.

In addition, various blends of PACL and polyepiamine were tested to determine their efficiency for agglomerating colloidal particles in the dissolved range ( $< 0.45 \mu\text{m}$ ) and shifting the size distribution toward the suspended solids size range.

### **5.2.1 Phosphorus testing**

Digestion for total phosphorus analysis was based on the Persulfate Digestion Method (APHA, 4500-P B.5). Samples and persulfate/acid solution were dispensed into glass test tube, capped and autoclaved at  $120^{\circ}\text{C}$  for 2 hours. The digested solution was cooled and analyzed immediately for orthophosphate using the Ascorbic Acid Method (APHA, 4500-P E) and a Thermo Genesys 10S spectrophotometer with 1.0 cm light path. The raw undigested sample was analyzed for orthophosphate in the same way.

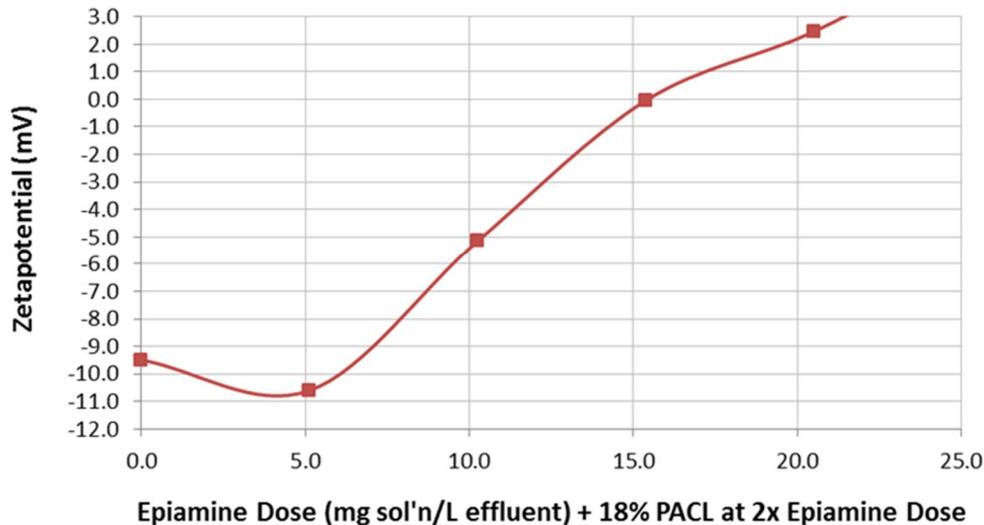
Except where noted, 24 hour composite samples were used for testing. Composite samples were collected in the morning from the Westside Regional WWTP and tested the same day.

### **5.2.2 Particle size and zeta potential characterization**

A Malvern Zetasizer, (nano ZS) was utilized for measurement of zeta potential and particle size. The Zetasizer is able to characterize the size distribution for a sample between 0.01  $\mu\text{m}$  and 10  $\mu\text{m}$ . All Zetasizer measurements were made at a temperature of 25°C.

### **5.2.3 Coagulant Dosing**

Coagulant dosing was conducted in two ways. For assessing the effectiveness of various PACL and polyepiamine blends, 100 mL batch volumes of final effluent were used. The coagulant blend was dosed and flash mixed in a glass beaker using a magnetic stir rod at 200 rpm for 30 seconds. Following flash mixing, the stir speed was reduced to 25 rpm and the sample flocculated for 25 minutes. After settling for 5 minutes, a 5 mL sample of supernatant was drawn off using a syringe and used to measure of zeta potential. The settled, coagulated particles would not contribute to the zeta potential measurement. The coagulant dose was incrementally increased and new batch volumes started until a neutral zeta potential was reached. An example of the zeta potential response curve for a 2:1 coagulant blend of PACL to polyepiamine is provided as Figure 5.1.



**Figure 5.1 – Example of zeta potential response curve using a 2:1 ratio of PACL to polyepiamine**

For fractionation of effluent, dosing was conducted using a jar testing apparatus (Phipps & Bird) and 1 litre glass beakers. The same time interval for flash mixing and flocculation were used with the jar testing apparatus as with the batch experiments.

#### **5.2.4 Conventional filtration apparatus**

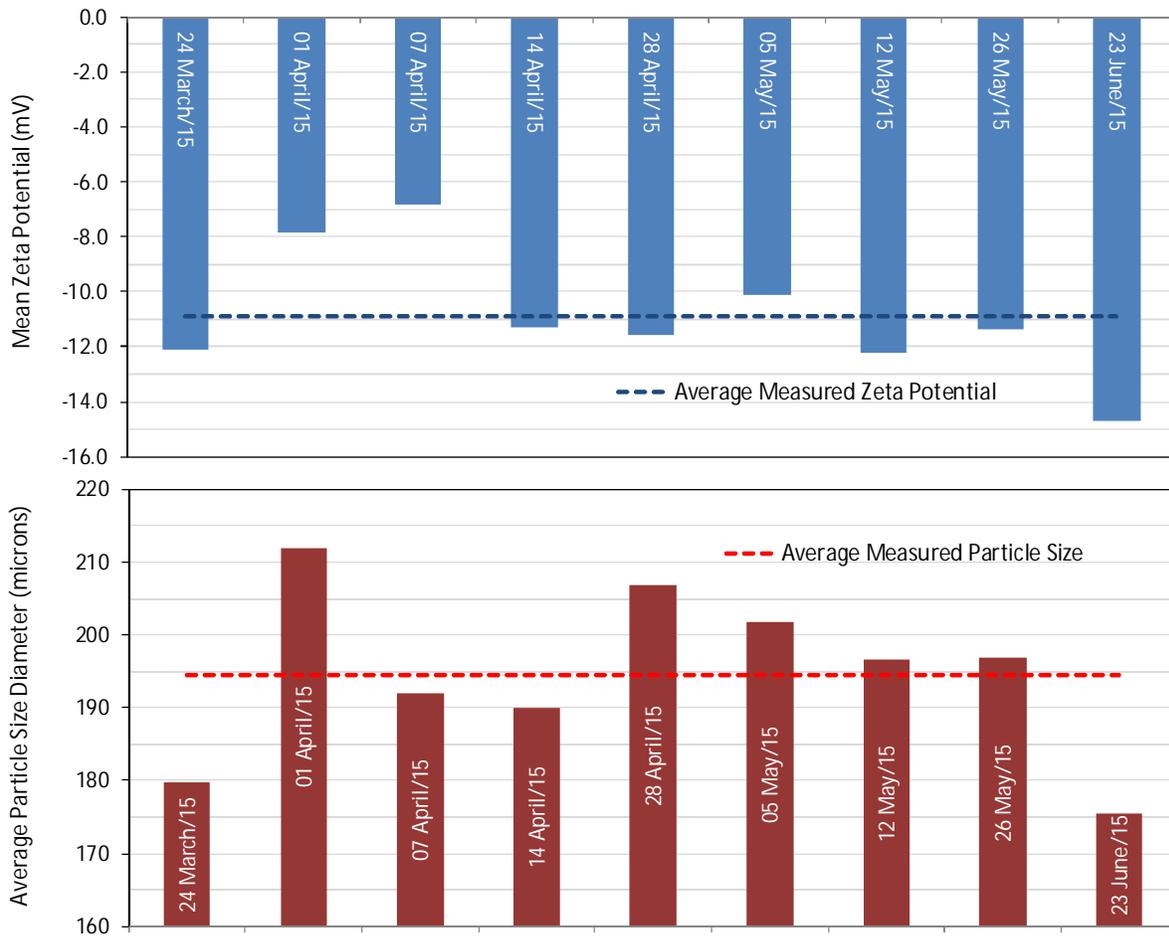
A conventional vacuum filtration system was used to fractionate suspended particulate using three filter cut-off sizes, 0.10, 0.22 and 0.45  $\mu\text{m}$  (Millipore, Durapore). The pore sizes for the conventional filtration were selected based on the manufacturers' availability of membranes with hydrophilic and low particle binding properties. To minimize error associated with hold-up of particles on the membranes, filtration was conducted in parallel (Barker et al., 1999). For each cut-off, a starting volume of 100 mL was used to obtain sufficient filtered sample volume for phosphorus testing. The phosphorus concentration for each filter cut-off was obtained through subtraction of concentrations between cut-offs (for example, 0.45  $\mu\text{m}$  > TP > 0.22  $\mu\text{m}$  was calculated as the difference between the 0.45  $\mu\text{m}$  filtrate TP and 0.22  $\mu\text{m}$  filtrate TP).

### **5.2.5 Ultra-filtration (UF) fractionation**

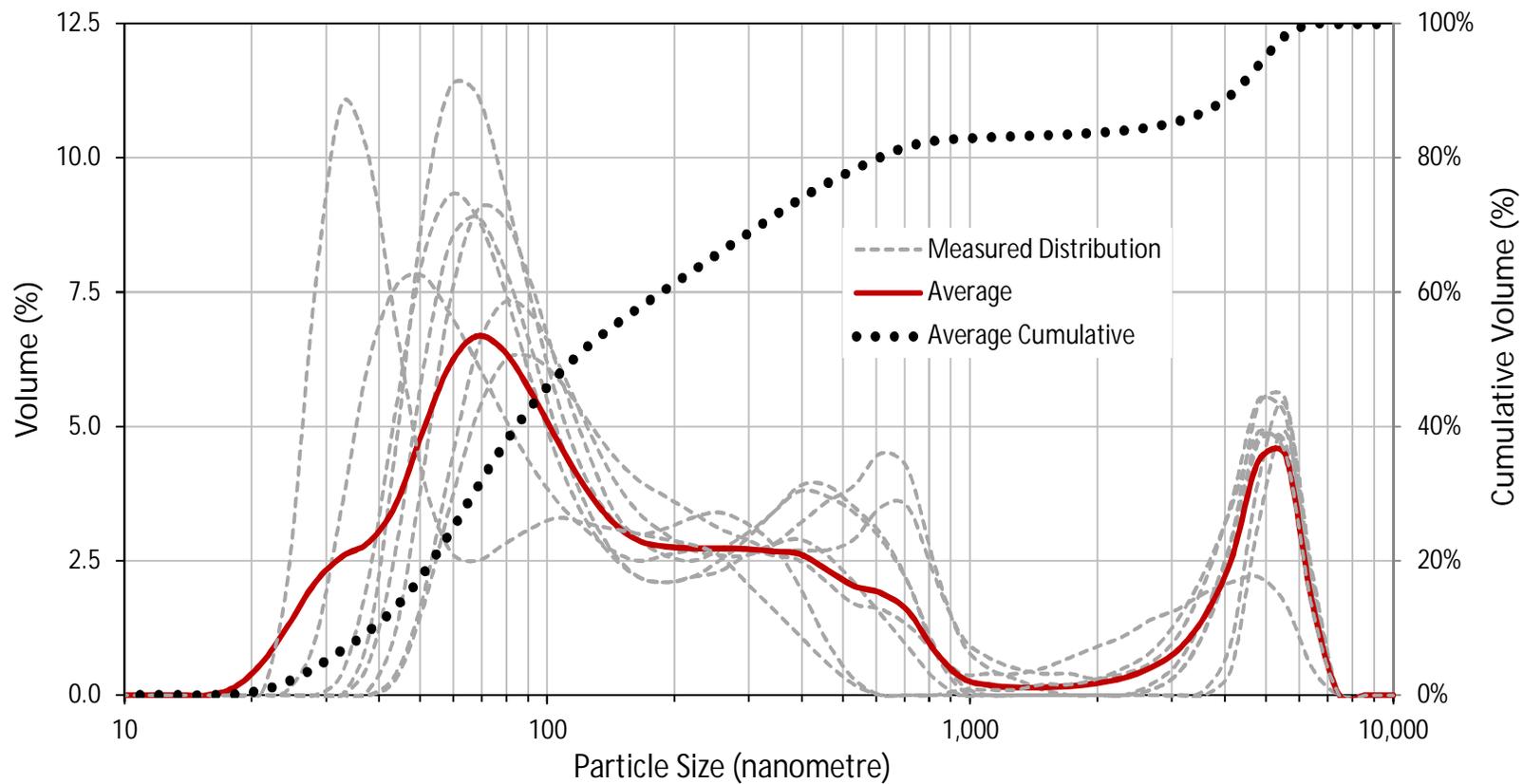
Effluent fractionation was conducted using UF membranes housed in a 400 mL Amicon model 8400 stirred cell [Amicon Corp., MA, USA] using flat (7.6 cm diameter), high recovery, low organic adsorption hydrophilic membranes [Millipore, MA, USA]. Membranes with molecular weight cut-off of 10,000 Da (YM10), 100,000 Da (YM100) and 300,000 Da (PES300) were set up in parallel to minimize hold-up of particles and cross-contamination of samples. Cut-off concentrations were calculated using the subtraction method described in Section 5.2.4. UF membranes were first rinsed with distilled water in a beaker for at least 1 hour with the water changed three times. Rinsed membranes were placed into the Amicon model 8400 cell followed by a 200 mL sample volume and the head space pressurized with nitrogen gas. Nitrogen gas pressures were maintained at a maximum 10 psi for PES300 and YM100 membranes and 50 psi for YM10 membranes as recommended by the manufacturer.

### **5.3 Results & discussion**

Results of the effluent particulate characterization and coagulant dosing experiments are presented in this section. Baseline zeta potential and particle measurements were made on 9 composite effluent samples (Figure 5.2). The average zeta potential measurement was -10.9 mV ( $\sigma = 2.4$  mV) and average particle size was 195 nm ( $\sigma = 11.3$  nm). Both average zeta potential and average particle size values are provided as output by the Zetasizer instrument. The variability was calculated from the results obtained from the 9 samples. The size distribution plots suggest a trimodal distribution with peaks occurring between 30 to 100 nm, 200 to 800 nm and 4,000 to 6,000 nm (Figure 5.3). Based on a cumulative average of these data, 75% of the particulate fraction occurs in the dissolved range (i.e., less than 0.45  $\mu\text{m}$ ).

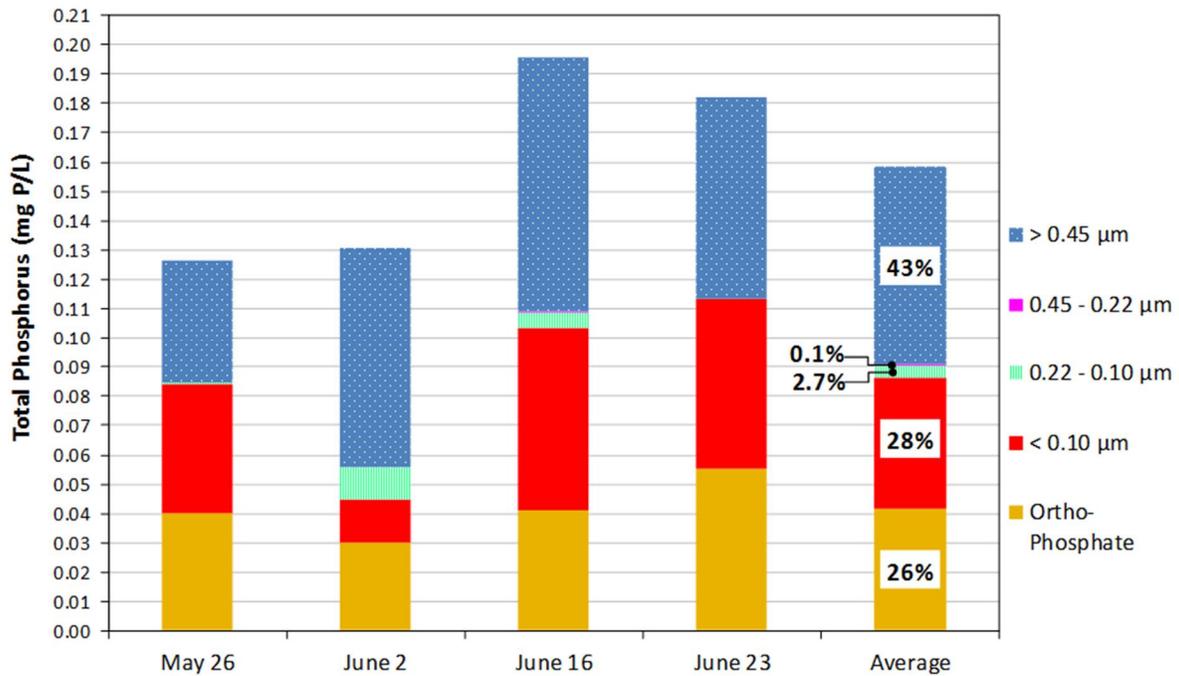


**Figure 5.2 – Average zeta potential and particle size of Westside Regional WWTP final effluent samples**



**Figure 5.3 – Particle size distribution of Westside Regional WWTP final effluent samples**

Fractionation of final effluent samples was conducted to determine the propensity for P to occur around the various peaks observed in Figure 5.3. Filter cut-offs of 0.10  $\mu\text{m}$ , 0.22  $\mu\text{m}$  and 0.45  $\mu\text{m}$  were used to assess phosphorus distribution (Figure 5.4). Of the average measured TP, 43% consists of particles having a diameter greater than 0.45  $\mu\text{m}$ . Based on the Zetasizer measurements (Figure 5.3), on average only 25% of the total particulate volume is greater than 0.45  $\mu\text{m}$ . This suggests that in the fractionated samples, a large part of the TP is concentrated in the suspended fraction ( $> 0.45 \mu\text{m}$  diameter).

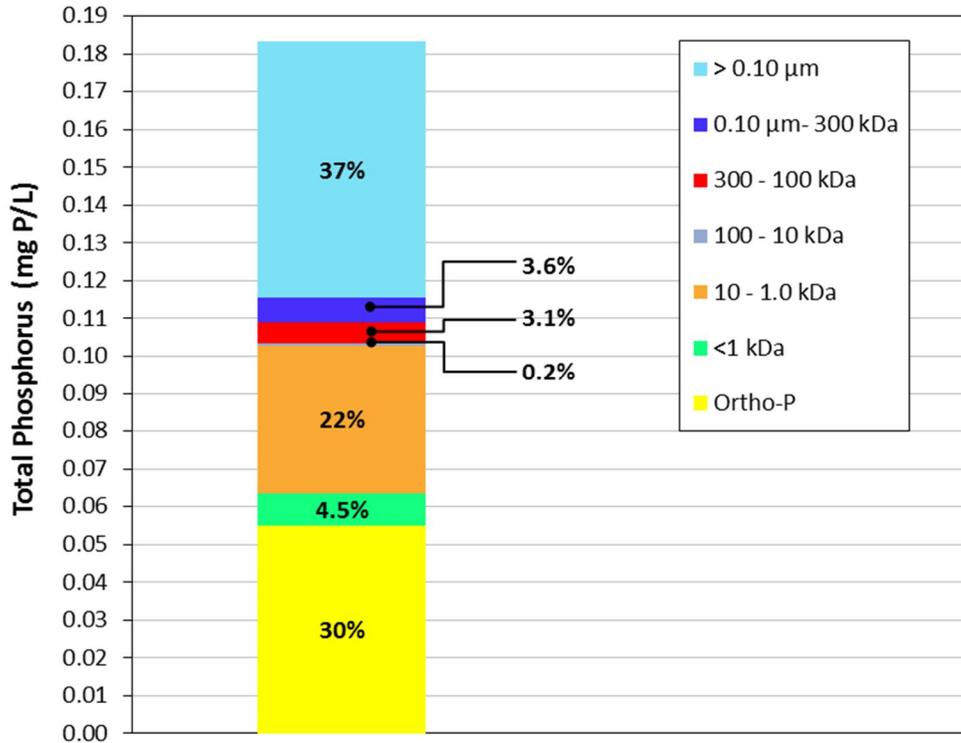


**Figure 5.4 – Fractionation of composite final effluent sample from Westside Regional WWTP**

An unexpected outcome of the filter fractionation was the observation that a relatively small amount of measured TP occurs in the size range between 0.45  $\mu\text{m}$  and 0.10  $\mu\text{m}$ . The Zetasizer measurements (Figure 5.3) suggested a relatively large proportion of the colloidal particle size range volume occurred in this range (ie, approximately 30%). However, according to the testing,

most of the dissolved P is associated with colloidal particle sizes smaller than 0.10  $\mu\text{m}$ . To further characterize dissolved P, final effluent was fractionated using ultrafiltration membranes and tested for TP. Molecular weight cut-offs of 300 kDa, 100 kDa, 10 kDa and 1 kDa were used for this testing. The results indicate a relatively high proportion (22%) of the TP measured in the composite effluent sample occurred within the 1 kDa to 10 kDa molecular weight range (Figure 5.5). Due to the complexity of the testing, the results are based on one effluent sample conducted in triplicate. Additional testing was not conducted to determine additional chemical properties of the dissolved material. However, the research indicates that dissolved organic matter (DOM) in wastewater effluents includes a variety of recalcitrant organic compounds which can vary with the raw water characteristics, land-use composition within the sewerage area and treatment process (Michael-Kordatou et al., 2015). In other research characterizing wastewater effluent DOM, 64% of dissolved organic matter occurs at a MW less than 1 kDa with 10.9% occurring in the 1 kDa to 10 kDa range (Kim et al., 2009). Humic-like colloidal material was also shown to be a dominant in three wastewater effluents and occurred at a MW size range of 1.6 to 2.6 kDa (Worms et al., 2010). Other research characterizing aquatic organic matter suggests that the molecular weight range between 1 kDa and 10 kDa is associated with fulvic and humic acids (Thurman et al., 1982).

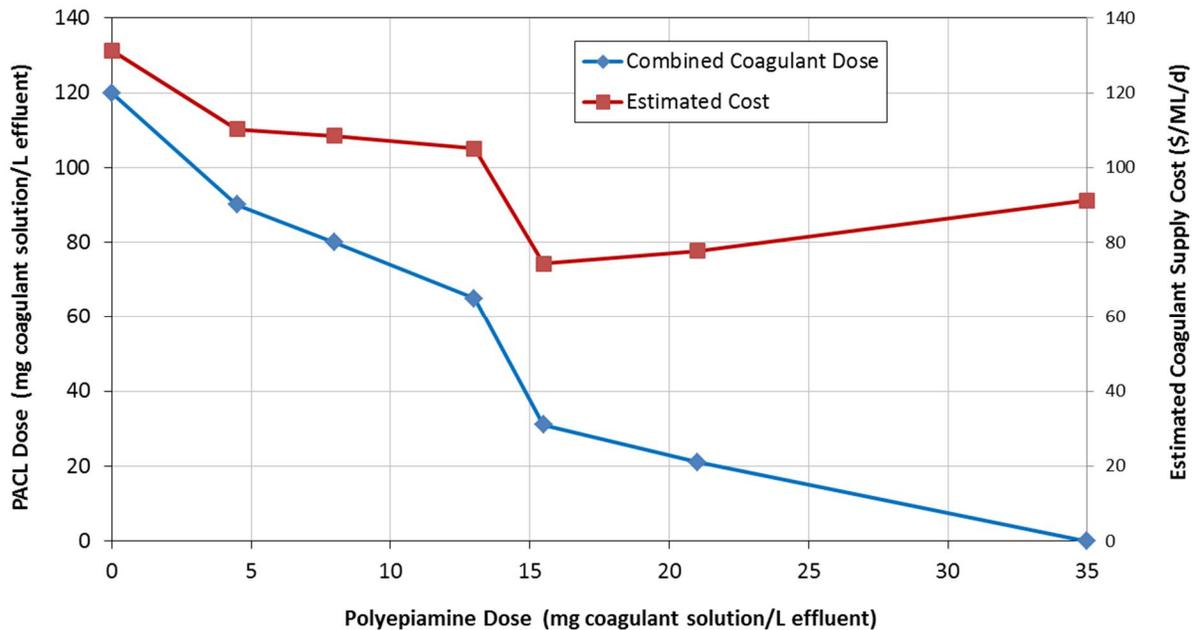
The ability of DOM and humic substances to complex a variety of dissolved compounds, including metals (Brown et al., 2000), micropollutants (Zheng et al., 2008) and phosphorus (Lévesque, 1969) has also been described. Consequently, in addition to removal of phosphorus, coagulation of humic substances using PACL and polyepiamine could result in removal of many other potentially harmful compounds.



**Figure 5.5 – P fractionation of composite final effluent from Westside Regional WWTP using ultrafiltration**

Various mixtures of PACL and polyepiamine were added to 100 mL batch volumes of the Westside Regional WWTP final effluent to test their performance. After dosing a specific concentration of coagulant blend and allowing for flocculation and settlement time, the zeta potential was measured on the supernatant. The dose was increased as required and the process repeated until a neutral zeta potential was reached. Based on this testing, the concentration of PACL and polyepiamine required to achieve neutral zeta potential could be recorded for a variety of mixtures. A plot of this data is provided as Figure 5.6. The dosing performance plot on its own provides no clear optimum dose preference. However, as a secondary performance criteria cost was also assessed. Based on chemical supply cost information provided by the supplier (Klearwater Equipment and Technologies Corp.), a 2 to 1, PACL to polyepiamine ratio

by active chemical mass was calculated to be the least cost scenario to achieve a neutral zeta potential (Figure 5.6)



**Figure 5.6 – Concentrations of coagulant blends that result in neutral zeta potential and associated costs**

Using the results of the batch dosing tests, a blend of 2 parts PACL to 1 part polyepiamine was tested to assess its ability to coagulant dissolved and suspended particulate P. A jar testing apparatus was used to dose 1 litre beakers of Westside Regional WWTP final effluent. The flocculated effluent was fractionated using conventional filtration equipment using filter cut-offs of 5  $\mu\text{m}$ , 0.45  $\mu\text{m}$  and 0.10  $\mu\text{m}$ . The filtrate was tested for P and zeta potential and from these values the fraction of P within each size range was calculated. The fractionated P results are provided as Figure 5.7. The results show the proportion of TP associated with ortho-P and colloidal particles less than 0.10  $\mu\text{m}$  decrease with the first coagulant dose. This indicates that the dissolved P which may be associated with colloidal material (ie, DOM) could be removed provided is can be filtered or settled.

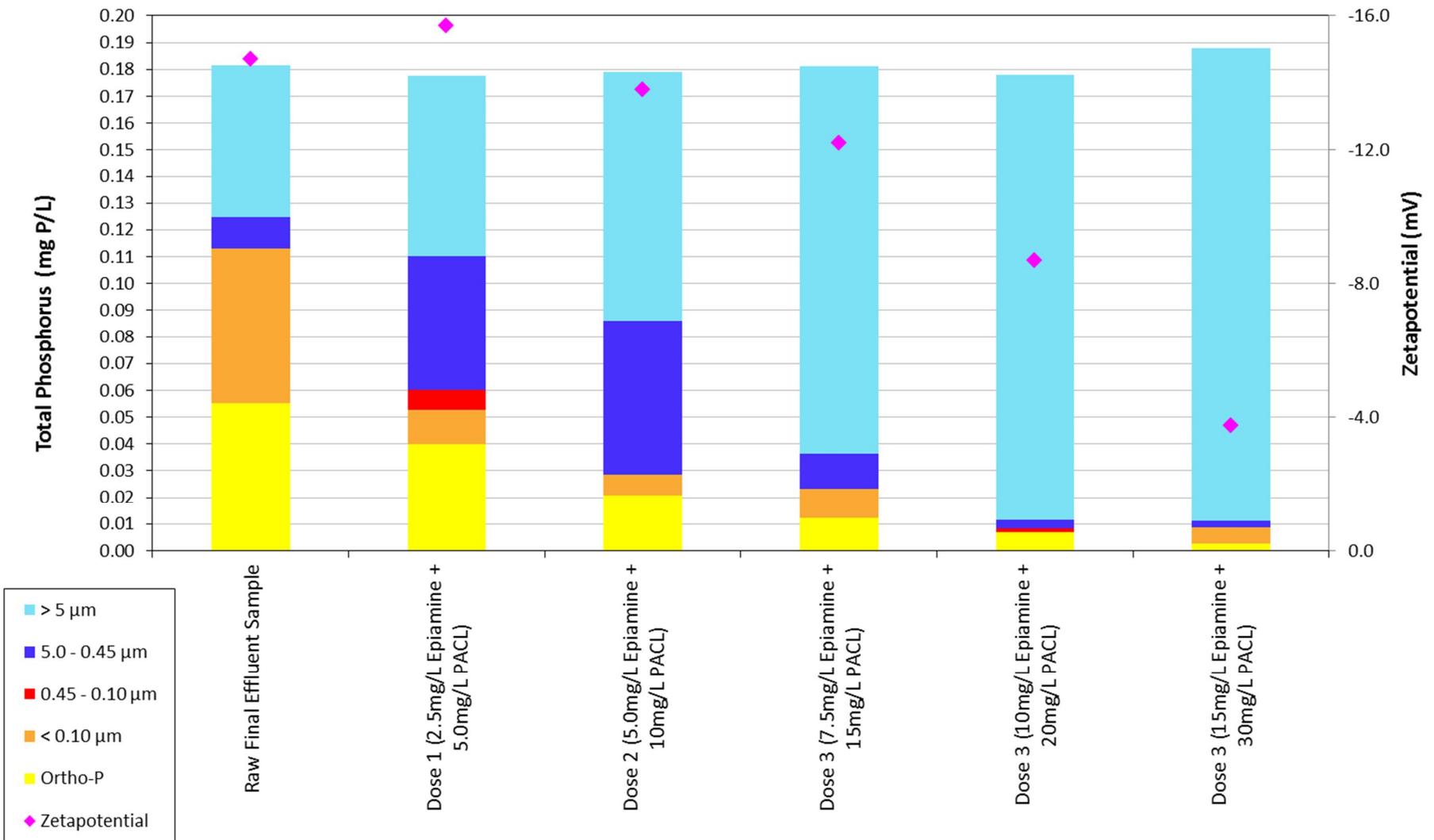


Figure 5.7 – P fractionation of coagulated effluent using a blend of 2 parts PACL to 1 part polyepilamine

The results also indicate that after Dose 3, the effect on total P precipitation diminishes even though the zeta potential is well below a neutral charge. Therefore, optimization of the coagulant dosing for the purposes of total P precipitation could target a specific zeta potential. In the case of Westside Regional WWTP, the target zeta potential would be approximately -8.0 mV. Additional testing would be required to optimize the coagulant dose to target this zeta potential since the current testing was optimized for zeta potential neutrality.

#### **5.4 Summary of the effluent particulate characterization**

The research supports the idea that a significant proportion of the final effluent non-reactive dissolved phosphorus consists of colloidal particles, less than 0.10  $\mu\text{m}$  in size. Ultrafiltration characterization of the final effluent further suggests that a relatively large fraction of dissolved TP may be bound up with DOM. However, this is speculative and additional TP fractionation combined with DOM characterization is needed to test this theory.

Batch dose testing of PACL and polyepiamine, two common coagulants used for potable water treatment, were effective at precipitating the dissolved phosphorus. The testing showed that coagulation of dissolved phosphorus was correlated to zeta potential. These results indicate that coagulant dosing for final effluent phosphorus trimming at BNR facilities could be optimized through zeta potential measurements.

Given the effectiveness of PACL and polyepiamine for coagulating TP and the potential use of zeta potential for optimizing dose, it may be possible to use this combination at BNR facilities for dissolved phosphorus control. Further research at the full-scale would help to clarify the impacts of dosing a blend of PACL and polyepiamine on the BNR process. Specifically, it would be useful to know how the coagulated PACL/polyepiamine floc interacts with the biological floc and how sludge wasting would need to change in order to optimize treatment.

## Chapter 6: Conclusions

### 6.1 Summary and conclusions

The research described in this thesis fills a gap in the literature by providing a detailed characterization of DON and NRDP production from a mesophilic anaerobic digestion process. Furthermore, the current research provides a measure of an Anammox process for the biodegradation potential of DON and NRDP species. Based on the experimental work described in the foregoing chapters, the following conclusions can be drawn:

1. NRDP and DON are significant sources of nitrogen and phosphorus in the existing KWTF final effluent and additional input through production associated with an anaerobic digester will risk effluent quality. In particular, the KWTF is more sensitive to additional NRDP loading to the lower effluent objective for total phosphorus. In addition, a higher proportion of the existing total effluent was measured as NRDP (ie, 52%), thereby providing less of a buffer capacity.
2. The Anammox process showed similar treatment characteristics for both the KWTF and AIWWTP centrates. The side-stream treatment process showed excellent DON removal and poor NRDP removal of the dewatering centrate that would be represented by a full-scale anaerobic sludge digestion scenario. The Anammox process biodegraded 74% of the KWTF AD centrate DON and 94% of the AIWWTP centrate DON. However, the NRDP removal rate was 19% for the KWTF AD centrate and 23% for the AIWWTP centrate. These results suggest that the Anammox would work well as a sidestream treatment process to control all nitrogen concentrations in the return stream but an additional treatment strategy is required for the NRDP.

3. The elevated orthophosphate concentration in the lab-scale KWTF AD centrate did not appreciably affect the stability of the Anammox process, as measured by the ammonia removal efficiency.
4. A statistical comparison of the DOP and poly-P through the Anammox process suggests that DOP has a higher biodegradation potential. Future research focused on understanding the variables associated with degradation of DOP could lead to better NRDP removal through the Anammox process.
5. Utilization of a post-Anammox PACL chemical dosing stage can achieve the objective of precipitating any residual DON and NRDP and producing an effluent that has lower dissolved nutrients than the pre-digestion KWTF dewatering centrate scenario.
6. Based on a detailed characterization of final effluent particulate phosphorus, most of the NRDP appear to occur in a size range that is associated with DOM and humic substances. This result further lends itself to the idea that the same conventional approach for colour removal in water treatment systems could work well for controlling NRDP. Coagulant dosing of the final effluent with polyepiamine and PACL, combined with phosphorus testing shows a strong propensity for shifting the colloidal phosphorus associated with the NRDP to the non-dissolved size range (i.e.,  $> 0.45 \mu\text{m}$ ). Furthermore, the testing suggests zeta potential could be used as a monitor to optimize the coagulant dosing.

Based on the results of the experimental work, it is possible to integrate an anaerobic digester into a BNR wastewater treatment plant provided sufficient care is taken to controlling recalcitrant dissolved nutrients from the supernatant back to the mainstream process. Use of a conventional Anammox sidestream treatment process coupled with PACL dosing provides the required level of nutrient reduction, as compared to the existing centrate.

## 6.2 Limitations

Additional work is suggested by the research work but was not pursued due to limitations in time and resources.

- The current research did not incorporate a method for phosphate removal from the AD centrate but it is assumed that struvite recovery will provide the required level of removal. While PACL can effectively remove all dissolved phosphorus, additional research is required to confirm the optimal staging of the Anammox and struvite recovery processes for the digested BNR sludge centrate.
- Due to lab space limitations the experimental setup used in this research utilized an AD and Anammox process that were mismatched in terms of capacities. The Anammox centrate feed rate was higher than the centrate production capacity of the AD reactor. This feature required that AD sludge be stored in order to generate a sufficient volume of centrate for continuous Anammox operation. Future research that provided for a larger AD reactor would produce a more representative centrate and remove the variable associated with the lag-time.
- The experimental results indicate that DOP does degrade through the Anammox process and may be influenced by hydraulic retention time. Future work could test this theory by systematically decreasing the feed rate in conjunction with DOP and poly-P measurements. Under this scenario, there likely will be a practical limit where the ammonia removal capacity of the Anammox process would be negatively affected but the testing may hint at an optimal operating strategy.
- Due to funding constraints, the research did not incorporate characterization of the Anammox bacterial activity in the bioreactor using molecular techniques. Availability of molecular testing for specific genetic biomarkers would have provided a means to measure the presence

of Anammox genera and allowed for a more complete understanding of the factors for achieving optimal nitrogen removal rates.

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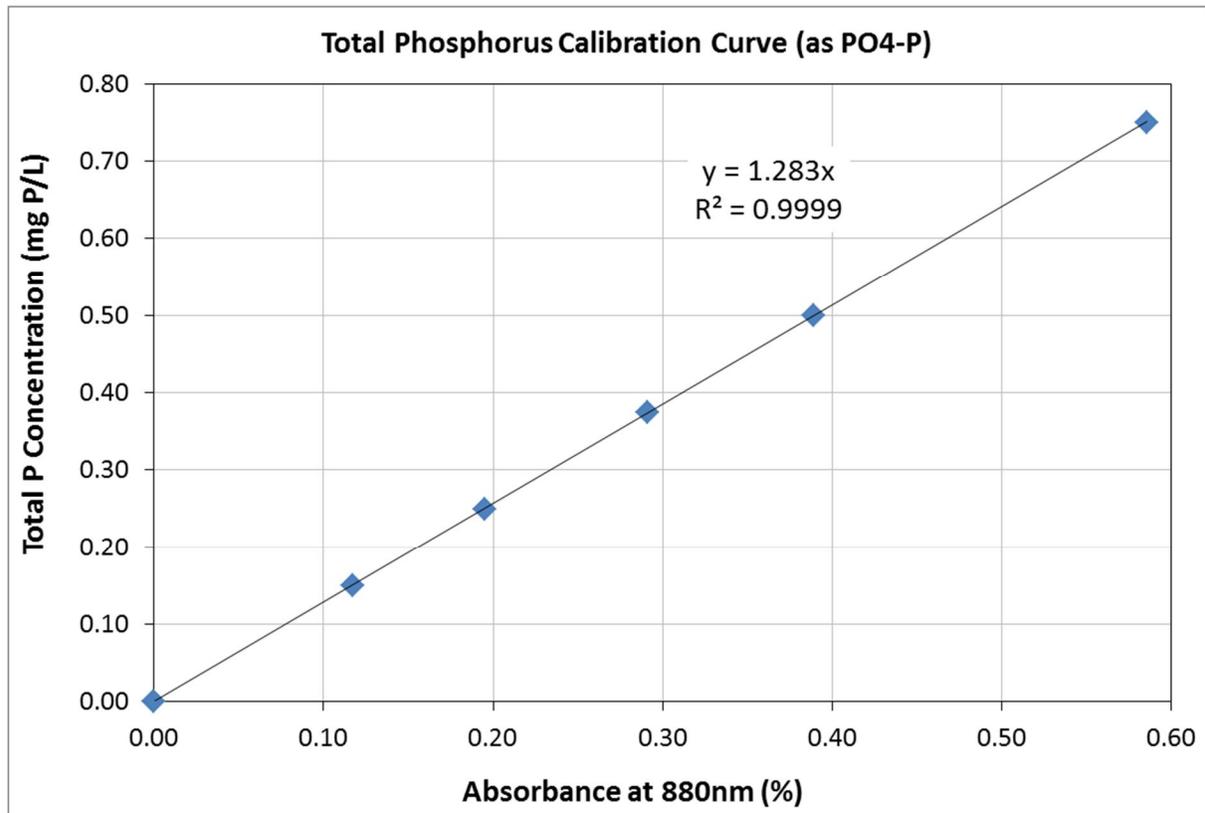
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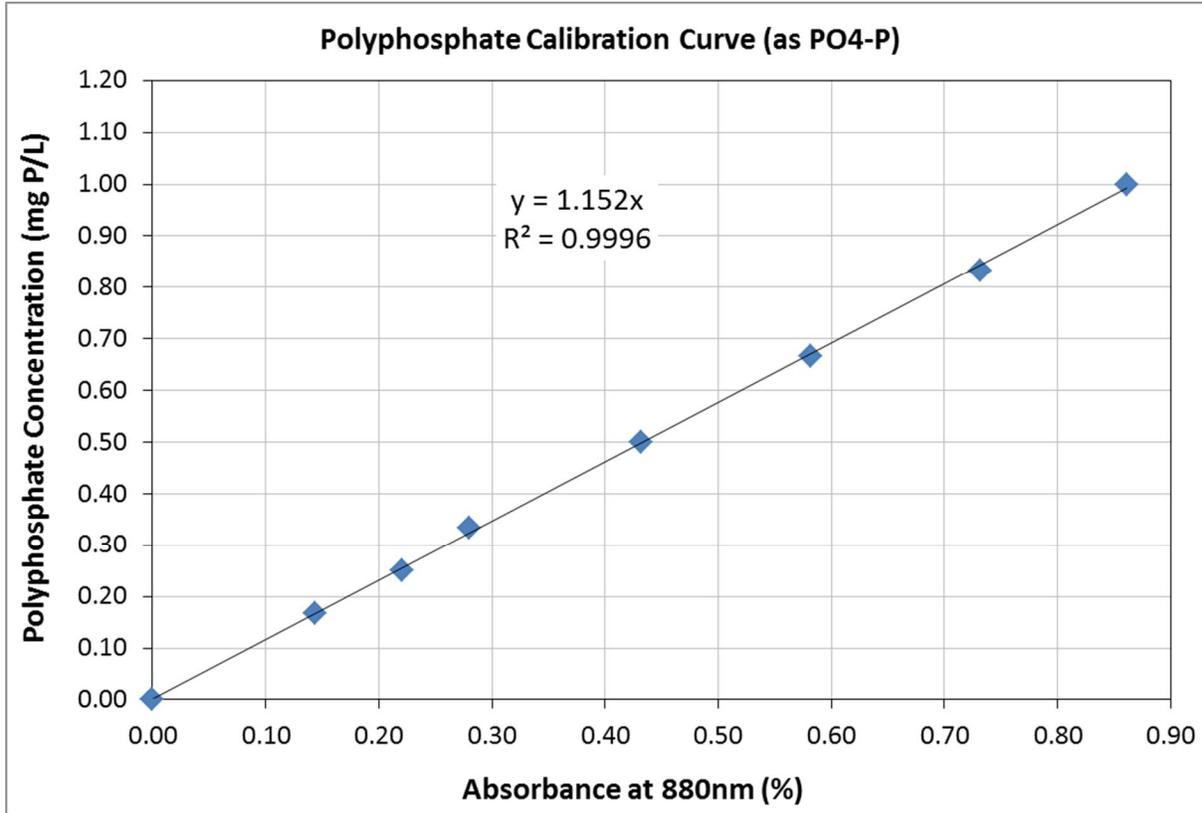
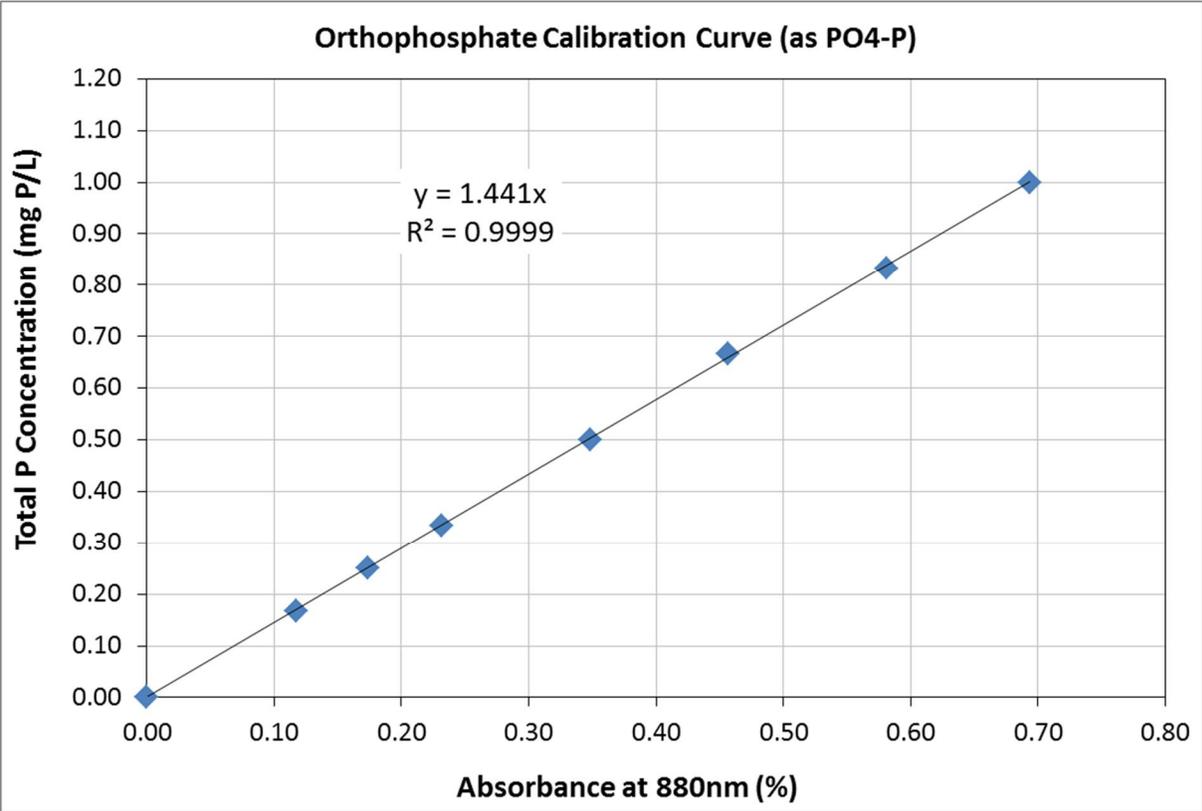
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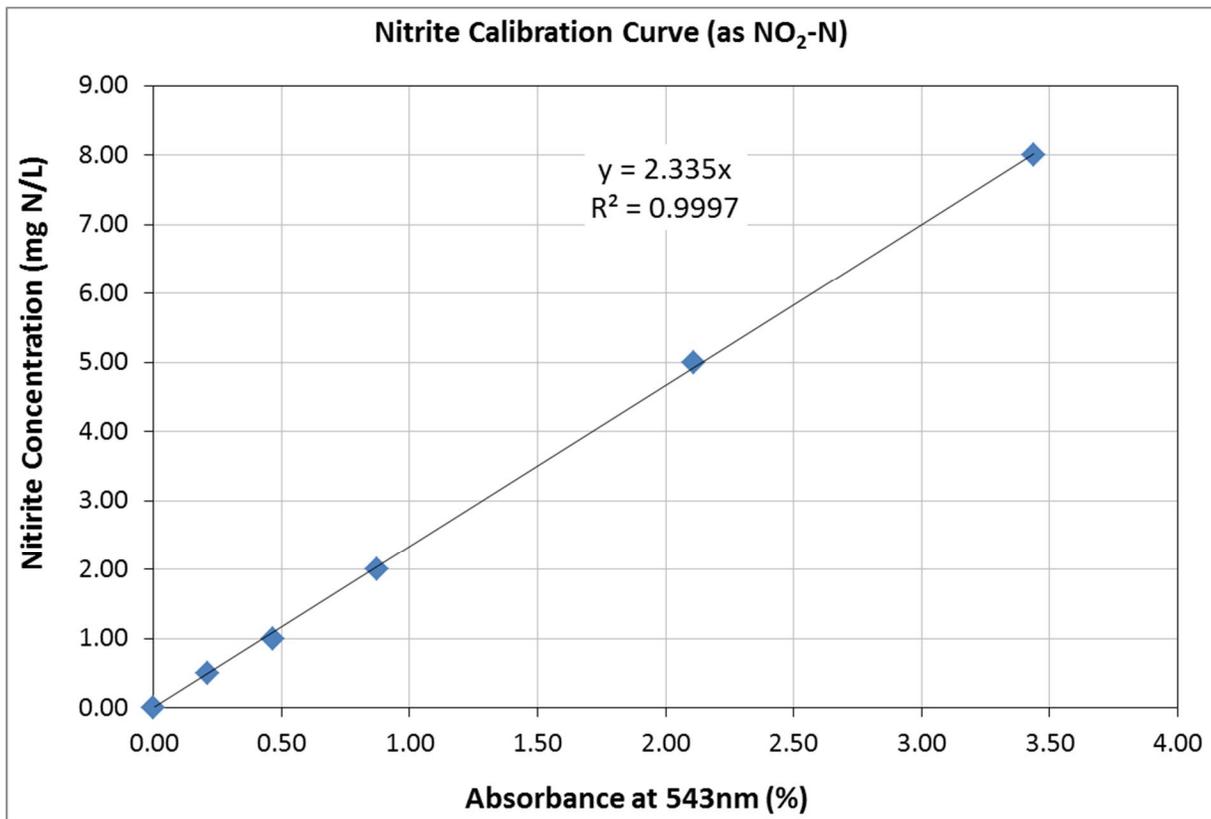
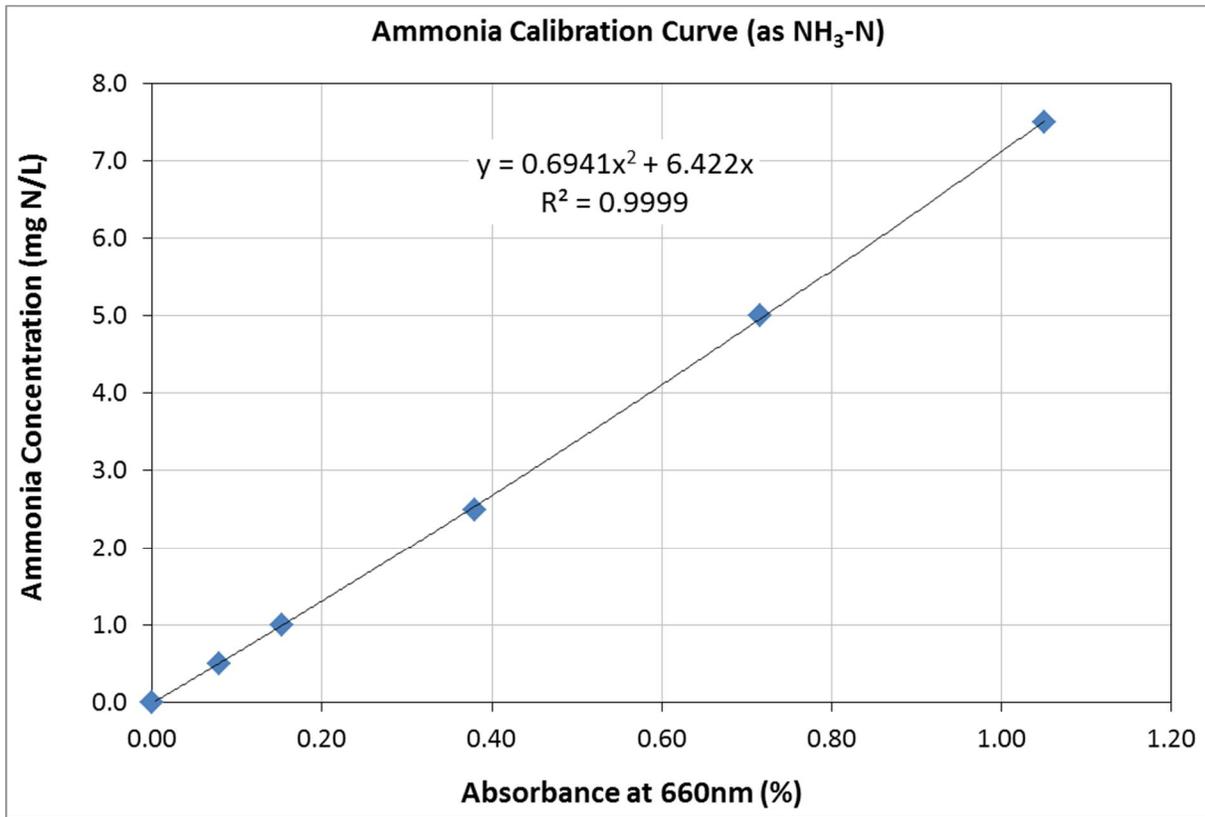
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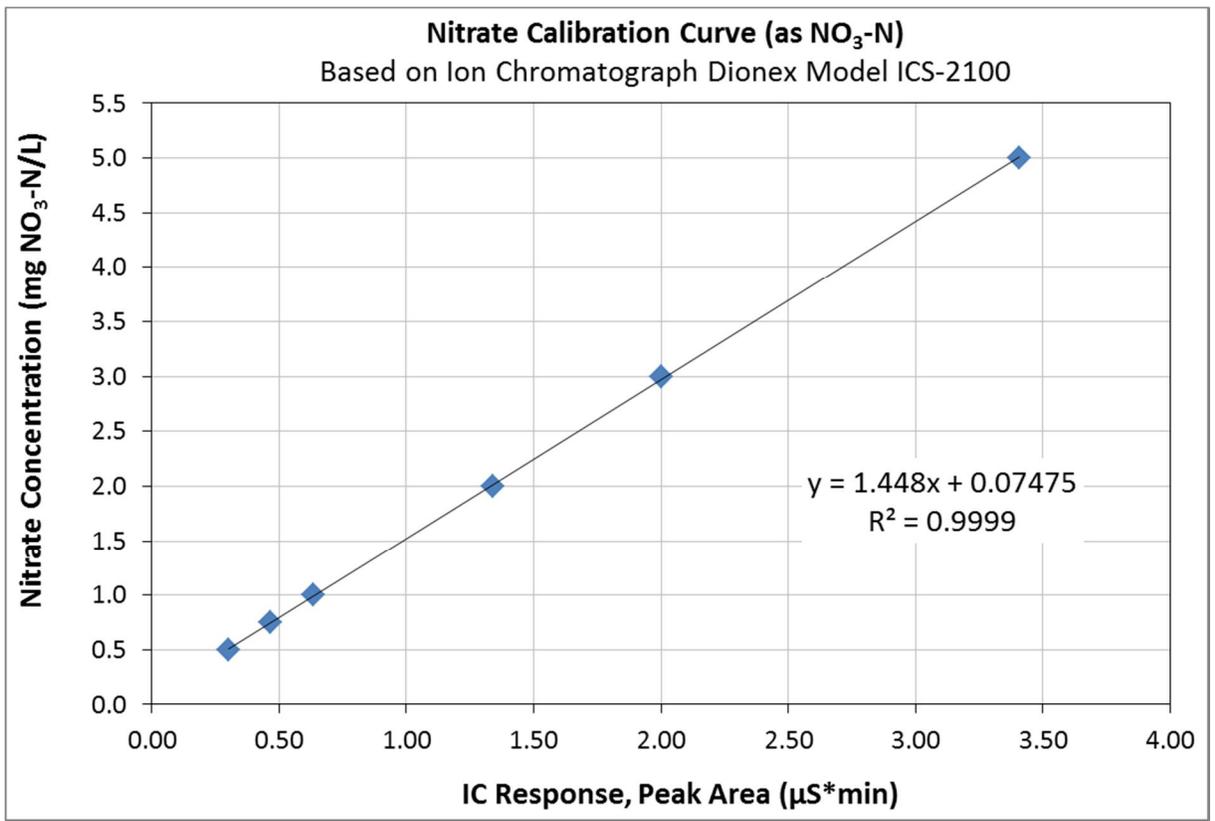
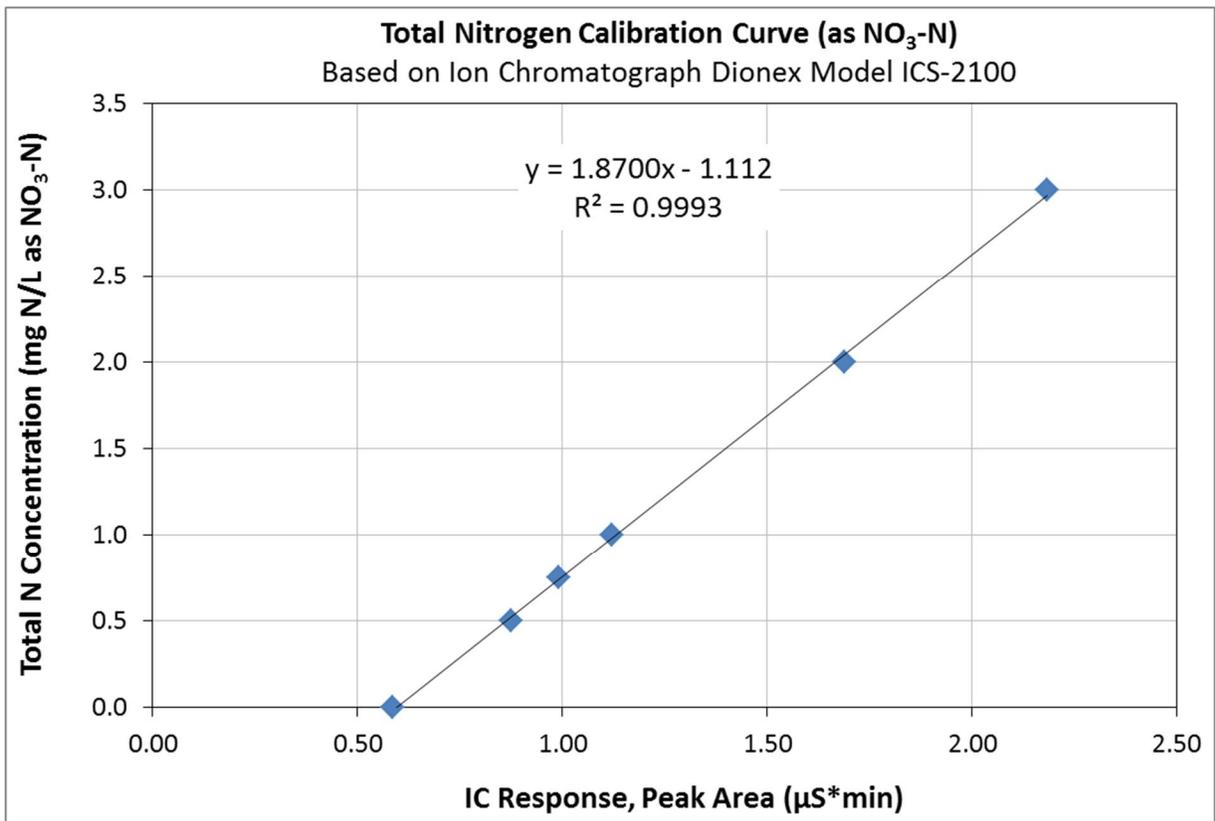
## Appendices

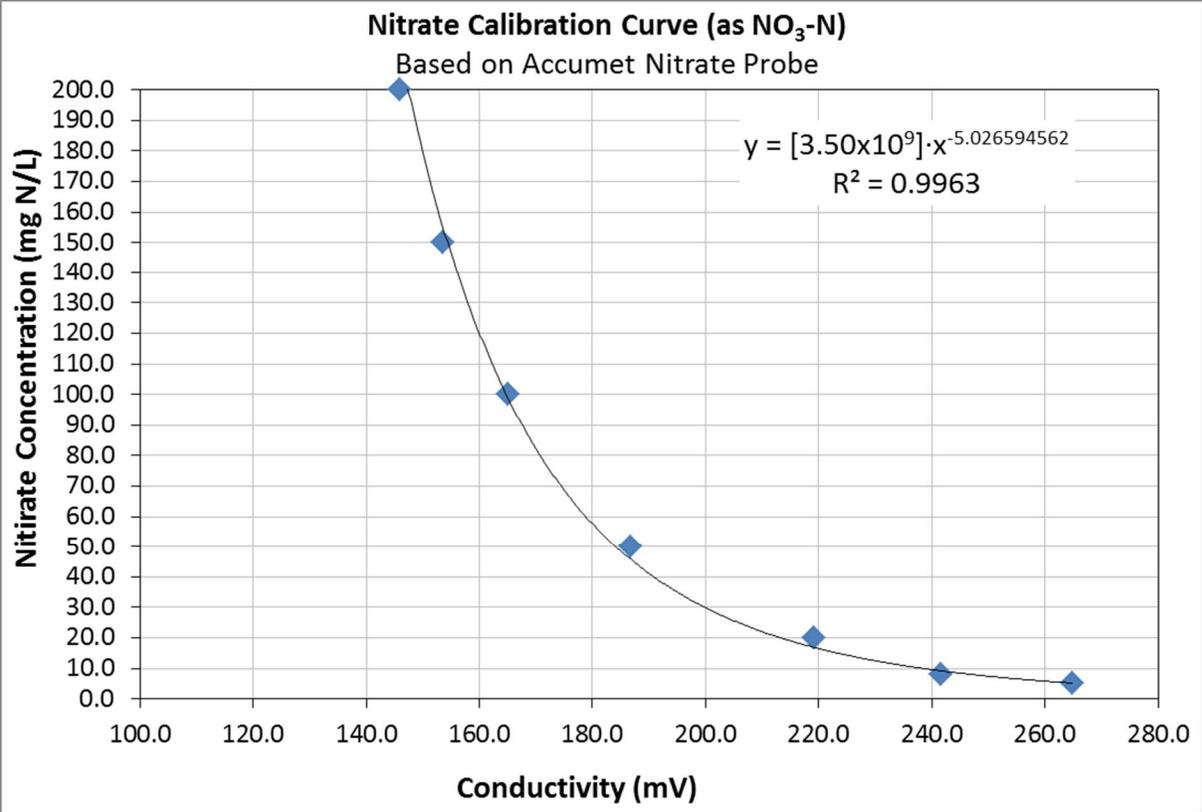
### Appendix A – sample calibration curves











**Appendix B – data & statistical analyses for autoanalyzer and IC measurements**

Date	Sample ID	Total Nitrogen Measurements	
		Autoanalyzer Measurement	Ion Chromatograph Measurement
		Average of Duplicates (mg N/L)	Average of Duplicates (mg N/L)
Nov. 25	Centrate Feed	1347	1358
Dec. 4	Centrate Feed	1450	1365
Dec. 8	Centrate Feed	1387	1413
Dec. 11	Centrate Feed	1391	1381
Dec. 11	Centrate Feed	1363	1383
Dec. 16	Centrate Feed	1365	1354
Jan. 9	Centrate Feed	1345	1344
Jan. 9	Centrate Feed	1449	1445
Nov. 25	Anammox Effluent	287	284
Dec. 4	Anammox Effluent	299	275
Dec. 8	Anammox Effluent	308	280
Dec. 11	Anammox Effluent	286	284
Dec. 1	Anammox Effluent	289	287
Dec. 16	Anammox Effluent	279	277
Jan. 9	Anammox Effluent	300	277

Comparison of Measured SBR Effluent Total Nitrogen  
t-Test: Paired Two Sample for Means

	<i>Autoanalyzer Measurements</i>	<i>Ion Chromatograph</i>
Mean	292.3	280.4
Variance	99.19	20.49
Observations	7	7
Pearson Correlation	-0.299	
Hypothesized Mean Difference	0	
df	6	
t Stat	2.587	
P(T<=t) one-tail	0.021	
t Critical one-tail	1.943	
P(T<=t) two-tail	0.041	
t Critical two-tail	2.447	

Comparison of Measured Centrate Total Nitrogen  
t-Test: Paired Two Sample for Means

	<i>Autoanalyzer Measurements</i>	<i>Ion Chromatograph</i>
Mean	1387	1380
Variance	1757	1145
Observations	8	8
Pearson Correlation	0.604	
Hypothesized Mean Difference	0	
df	7	
t Stat	0.542	
P(T<=t) one-tail	0.302	
t Critical one-tail	1.895	
P(T<=t) two-tail	0.605	
t Critical two-tail	2.365	

## Appendix C – data & statistical analyses for dissolved phosphorus testing

	Centrate Feed						Anammox Effluent					
	Total Dissolved Phosphorus mg P/L	Acid Digested Phosphorus mg P/L	ortho-P mg P/L	Poly-P mg P/L	DOP	nrDP mg P/L	Total Dissolved Phosphorus mg P/L	Acid Digested Phosphorus mg P/L	ortho-P mg P/L	Poly-P mg P/L	DOP	nrDP mg P/L
AIWWTP CENTRATE	158	156	154	1.91	1.64	3.5	150	149	148	1.46	0.17	1.63
	148	146	143	3.31	2.03	5.3	147	145	143	1.68	1.80	3.48
	151	143	140	3.00	8.35	11.3	143	142	137	4.74	0.95	5.69
	160	158	154	4.17	2.18	6.3	159	158	154	4.40	0.80	5.20
	161	161	156	4.92	0.08	5.0	152	151	148	3.14	0.42	3.55
	175	165	165	0.07	10.27	10.3	164	153	151	1.29	10.95	12.24
	178	174	168	5.58	4.03	9.6	170	168	163	4.75	2.66	7.40
	173	171	166	4.95	2.45	7.4	167	165	160	5.27	1.39	6.66
	173	170	162	7.95	3.34	11.3	168	166	161	4.96	1.59	6.55
	181	176	170	6.90	4.67	11.6	172	169	161	7.61	3.03	10.64
LAB-SCALE KWTF AD CENTRATE	485	484	479	4.92	1.33	6.3	445	445	442	3.26	0.30	3.56
	481	477	474	3.02	3.93	7.0	458	456	452	4.13	2.59	6.72
	486	479	477	2.12	6.82	8.9	467	466	463	3.49	1.14	4.63
	486	485	485	0.38	0.66	1.0	475	475	473	2.38	0.22	2.60
	482	478	475	3.47	4.15	7.6	473	473	466	7.38	0.17	7.54
	510	508	506	1.75	2.30	4.1	496	494	490	4.39	2.11	6.49
	510	510	505	4.37	0.58	5.0	497	497	494	2.44	0.13	2.57
	478	468	463	4.22	10.83	15.0	487	479	473	6.40	7.57	13.97
	488	479	474	5.15	8.66	13.8	474	467	462	4.83	6.74	11.58
	478	476	474	1.84	2.20	4.0	465	462	460	2.21	2.81	5.03
	474	474	459	15.11	0.48	15.6	469	468	465	2.76	1.36	4.12
	481	475	470	4.88	5.89	10.8	469	468	458	10.36	0.45	10.81
	477	474	464	10.33	3.44	13.8	466	465	454	11.13	0.66	11.79

Comparison of AIWWTP Centrate Feed & Anammox Poly-P		
t-Test: Paired Two Sample for Means		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	4.28	3.93
Variance	5.42	4.08
Observations	10	10
Pearson Correlation	0.778	
Hypothesized Mean Difference	0	
df	9	
t Stat	0.742	
P(T<=t) one-tail	0.238	
t Critical one-tail	1.833	
P(T<=t) two-tail	0.477	
t Critical two-tail	2.262	

Comparison of AIWWTP Centrate Feed & Anammox DOP		
t-Test: DOP		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	3.90	2.38
Variance	9.96	9.90
Observations	10	10
Pearson Correlation	0.749	
Hypothesized Mean Difference	0	
df	9	
t Stat	2.17	
P(T<=t) one-tail	0.03	
t Critical one-tail	1.83	
P(T<=t) two-tail	0.06	
t Critical two-tail	2.26	

Comparison of AIWWTP Centrate Feed & Anammox NRDP		
t-Test: Paired Two Sample for Means, NRDP		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	8.18	6.30
Variance	9.06	10.49
Observations	10	10
Pearson Correlation	0.776	
Hypothesized Mean Difference	0	
df	9	
t Stat	2.819	
P(T<=t) one-tail	0.010	
t Critical one-tail	1.833	
P(T<=t) two-tail	0.020	
t Critical two-tail	2.262	

Comparison of Lab-scale KWTF AD Centrate Feed & Anammox Poly-P		
t-Test: Paired Two Sample for Means		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	4.73	5.01
Variance	15.60	8.88
Observations	13	13
Pearson Correlation	0.250	
Hypothesized Mean Difference	0	
df	12	
t Stat	-0.230	
P(T<=t) one-tail	0.411	
t Critical one-tail	1.782	
P(T<=t) two-tail	0.822	

Comparison of Lab-scale KWTF AD Feed & Anammox DOP		
t-Test: Paired Two Sample for Means		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	3.94	2.02
Variance	10.72	6.07
Observations	13	13
Pearson Correlation	0.751	
Hypothesized Mean Difference	0	
df	12	
t Stat	3.208	
P(T<=t) one-tail	0.004	
t Critical one-tail	1.782	
P(T<=t) two-tail	0.008	

Comparison of Lab-scale KWTF AD Centrate Feed & Anammox NRDP		
t-Test: Paired Two Sample for Means		
	<i>Centrate Feed</i>	<i>Anammox Effluent</i>
Mean	8.68	7.03
Variance	22.50	14.69
Observations	13	13
Pearson Correlation	0.686	
Hypothesized Mean Difference	0	
df	12	
t Stat	1.70	
P(T<=t) one-tail	0.06	
t Critical one-tail	1.78	
P(T<=t) two-tail	0.12	