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Mapping of Phosphorus at Rya Wastewater Treatment Plant

A Case Study of the Phosphorus Treatment at Rya Wastewater Treatment Plant

Master's thesis in Infrastructure & Environmental Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Rya wastewater treatment plant.

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Abstract

Phosphorus (P) is an essential building stone for humans and plants, but it can cause eutrophication when discharged into water bodies. Wastewater is one of the main inputs of phosphorus into freshwater sources, and treatment of phosphorus through chemical and biological methods is essential to reduce the concentrations reaching recipients. Rya wastewater treatment plant (WWTP) is located in Gothenburg, Sweden, and employs simultaneous chemical precipitation for the reduction of phosphorus with iron(II) sulfate (FeSO4). Sufficient P removal is achieved at Rya WWTP even as the dosage of $FeSO_4$ is low compared to recommended levels of chemical dosing given in literature. A mass balance of the P at the WWTP was constructed combined with laboratory tests measuring P-release/uptake and chemical precipitation with drinking water sludge (DWS) to investigate possible processes within the plant contributing to phosphorus removal besides the chemical precipitation with $FeSO_4$.

The primary reduction of P, around 85% of the total reduction, can be observed after the addition of $FeSO_4$ over the activated sludge (AS) basins and the secondary settling tanks (SSTs) for both total P (Tot-P) and orthophosphate as P (PO_4-P) at Rya WWTP. The remaining reduction of 15% occurs in the denitrifying moving bed biofilm reactor (DMBBR) for the PO_4-P and through the disc filters (DF) for the suspended phosphorus. The P-release and uptake batch test indicated that bio-P bacteria with the ability to release and store P is present in the AS at the plant. Combined with the observed presence of polyphosphate-accumulating organisms (PAOs) at Rya WWTP through participation in the MiDAS project, the results indicate bio-P treatment at the plant, but to what extent remains undecided. The aluminium in the DWS showed that it could precipitate PO_4-P, which means that a reduction of ca. 15-18 tonnes/yearly of PO_4-P occurs before the water reaches the AS basins at Rya WWTP. The contribution from the DWS to PO_4-P reduction, the presence of PAOs in the AS basins and their ability to store and release P are two possible explanations for the low effluent concentrations of P with the sparse dosage of $FeSO_4$.

Keywords: Enhanced biological phosphorus removal (EBPR), chemical precipitation, polyphosphate accumulating organisms (PAOs), drinking water sludge, orthophosphate, Iron(II) sulfate ($FeSO_4$), activated sludge.

Kartläggning av fosfor på Ryavekert
En fallstudie av fosforreningen på Ryaverket

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Sammanfattning

Fosfor (P) är en viktig byggsten för människor och växter, men den kan orsaka övergödning vid utsläpp i vattendrag. Avloppsvatten är en av de största källorna vid utsläpp av fosfor till vattendrag, och rening av fosfor med kemiska och biologiska metoder är avgörande för att minska koncentrationerna som når recipienterna. Ryaverket ligger i Göteborg, Sverige, och använder simultanfällning med järn(II)sulfat ($FeSO_4$) för reduktion av fosfor. Tillräckliga rening av utgående P uppnås vid Ryaveker även om dosen av $FeSO_4$ är låg jämfört med rekommenderade nivåer av kemikaliedosering angiven i litteratur. För att undersöka möjliga processer inom anläggningen som bidrar till fosforavskiljning, förutom den kemiska utfällningen med $FeSO_4$, konstruerades en massbalans över fosfor vid reningsverket kombinerat med laboratorietester som mäter P-släpp/upptag och kemisk fällning med dricksvattenslam.

Den primära minskningen av P, cirka 85% av den totala minskningen, kan observeras efter tillsats av $FeSO_4$ över bassängerna för aktivt slam (AS) och de sekundära sedimenteringstankarna (SST) för både total P (Tot-P) och ortofosfat som P (PO_4-P) vid Ryaverket. Den återstående minskningen på 15% sker i de denitrifierande biofilmreaktorerna med rörlig bädd (DMBBR) för PO_4 och genom skivfiltren (DF) för den suspenderade fosforn. Burktestet för P-släpp och upptag visade att bio-P-bakterier med förmåga att frigöra och lagra P finns i det aktiva slammet vid anläggningen. I kombination med den observerade förekomsten av polyfosfatackumulerande organismer (PAOs) vid Ryaverket genom deltagande i MiDAS-projektet, tyder resultaten på bio-P-behandling vid anläggningen men i vilken utsträckning är ännu oklart. Aluminiumet i DWS visade att det kunde fälla ut PO_4-P, vilket innebär att en minskning med ca. 15-18 ton/år av PO_4-P förekommer innan vattnet når AS-bassängerna vid Ryaverket. Bidraget från DWS till minskningen av PO_4-P, närvaron av PAO i AS-bassängerna och deras förmåga att lagra och frigöra P är två möjliga förklaringar till de låga avloppskoncentrationerna av P med den sparsamma dosen $FeSO_4$.

Nyckelord: Lyxupptag av fosfor (EBPR), kemisk fällning, polyfosfat, polyfosfatackumulerande organismer (PAO), dricksvattenslam/vattenverksslam, ortofosfat, Järn(II) sulfat ($FeSO_4$), aktiv slam.

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Frida Byström, Gothenburg, June 2022

List of Acronyms

AS Activated sludge.

BGT Belt gravity thickening.
Bio-P Biological phosphorus.
BP Biogas plant.

DF Disc filter.
DMBBR Denitrifying Moving Bed Biofilm Reactor.
DP Direct precipitation.
DS Dewatered sludge.
DWS Drinking water sludge.
DWTP Drinking water treatment plant.

NMBBR Nitrifying Moving Bed Biofilm Reactor.
NTF Nitrifying trickling filter.

P Phosphorus.
PAC Polyaluminium chloride.
PAO Polyphosphate-accumulating organism.
PHA Poly-β-hydroxyalkanoate.
PO_4-P Orthophosphate as phosphorus.
Poly-P Polyphosphate.
PS Primary settled.
PST Primary settling tank.

SLT Sludge liquor treatment.
SP Screw press.
SS Suspended solids.

Tot-P Total phosphorus.
TS Dry matter.

VFA Volatile fatty acids.
VSS Volatile suspended solids.

WAS Waste activated sludge.
WWTP Wastewater treatment plant.

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1
Introduction

This chapter introduces the subject of P and the importance of reducing P loads reaching waterbodies through wastewater treatment along with the purpose, aim and limitations.

1.1 Background

P is a nutrient that is essential for both humans and plants as it is part of our bones, nerves and even DNA (Sincero and Sincero, 2002). As P leads to algae growth when discharged into freshwater, there is a risk of eutrophication with excessive P release (Henze et al., 1997; Sincero and Sincero, 2002). Eutrophication is when the concentrations of nutrients, such as P, increase in a water body (Britannica, T. Editors of Encyclopaedia, 2019; U.S. Geological Survey, 2018). One consequence of eutrophication is algae growing in excess due to the nutrient supply, and dissolved oxygen is consumed during the degradation process of algae when it dies, leading to ecosystem degradation. One of the prime sources of P in waterbodies is fertilizers and wastewater treatment plants (WWTPs) (Conley et al., 2009). P ends up in wastewater as it discharges from households, industries and natural runoff (Metcalf and Eddy, 2014).

Treatment of P in WWTPs can be chemical, biological or a combination of the two (Yeoman et al., 1988). A precipitation chemical in the form of metal salts is mixed with wastewater for particles to form larger particles (flocks) that separate from the wastewater during chemical precipitation (Henze et al., 1997). P stores in bacteria called polyphosphate-accumulating organisms (PAOs) with varying aerobic and anaerobic conditions during biological P (bio-P) removal, which makes it possible to separate P from water into sludge (la Cour Jansen et al., 2009).

Rya WWTP is located in Gothenburg, Sweden, and serves wastewater treatment to the 887 442 connected Population Equivalents (PE) from domestic households and 70 000 PE from industry in Västra Götaland County (Gryaab, 2022). Physical, chemical and biological treatment is applied at the WWTP to reduce the nutrients, degradable and organic materials, particles, objects and settleable substances that reach Göta River. Drinking water sludge (DWS) from the drinking water treatment plants Lackarebäck and Alelyckan is also sent to Rya WWTP for further treatment through the wastewater piping system (Pacoste et al., 2020). The physical processes include bar screens, settling tanks and disc filters while activated sludge, nitrifying trickling filters, nitrifying moving bed biofilm reactors, and denitrifying moving biofilm reactors are biological treatments. The chemical treatments consist of simultaneous chemical precipitation and direct precipitation.

Simultaneous chemical precipitation is used at Rya WWTP as P treatment by

adding Iron(II)Sulfate ($FeSO_4$) with a molar ratio between 1.0-1.3 mole Fe/mole incoming P (Gryaab, 2022). The concentration of P in the effluent at Rya WWTP reached 0.18 mg/L on average in 2021, which is lower than the maximum concentration of 0.3 mg/L stated in the environmental permit for Rya WWTP set by the Environmental assessment delegation in Västra Götaland County on January 29, 2020. The necessary molar ratio between Fe and incoming P in literature is 2 mol Fe/mol P to reach an effluent concentration of 0.3-0.5 mg/L (Henze et al., 1997; Metcalf and Eddy, 2014). As the dosage of Fe is low at Rya WWTP compared to literature, the question of any other processes occurring within the plant that reduces the P concentration and makes it possible to achieve a low effluent concentration has emerged.

1.2 Purpose & Aim

This thesis investigates possible reasons for P reduction at Rya WWTP besides chemical precipitation with $FeSO_4$, as the low dosage of Fe indicates that alternative processes contribute to the removal of P.

This thesis aims to map out how P travels within the WWTP and why the dosage of precipitation chemicals is low. The following questions will be answered to reach the aim:

- How does P travel within the plant, and where does reduction occur?
- Does any bio-P treatment occur within Rya WWTP?
- Do the precipitation chemicals in the DWS that reaches Rya WWTP affect the phosphorous treatment?

1.3 Limitations

The results of this thesis are applicable at WWTPs with similar conditions as Rya WWTP, as it consists of a case study. The effects of drinking water sludge on other substances than P treated at the WWTP will not be discussed within the scope of this thesis. The capacity of the activated sludge to biologically treat wastewater is only evaluated for P.

2
Theory

This chapter covers the basics of wastewater treatment, a more in-depth description of the P treatment at WWTPs, the concept of P-release and uptake tests, and an extensive description of the treatment at Rya WWTP.

2.1 Wastewater treatment

Wastewater is purified to remove nutrients, metals, organic materials, hydrogen sulphide and pathogens to avoid eutrophication, odour, toxicity for water living organisms and humans, or bio-accumulation (Henze et al., 1997). The treatment methods of wastewater divide into physical/mechanical, chemical, and biological (Metcalf and Eddy, 2014).

2.1.1 Wastewater composition

The sources of wastewater include domestic/sanitary wastewater, industrial wastewater, infiltration/inflow from leaks in pipes, and stormwater, which is runoff from rain or snow (Metcalf and Eddy, 2014). Stormwater is also diverted to WWTPs for treatment if the stormwater and wastewater collection systems are combined . The main components in wastewater include microorganisms, biodegradable and other organic materials, nutrients, metals, and other inorganic materials (Henze et al., 1997; Sincero and Sincero, 2002). The sources and composition of the wastewater determine what type of treatment is needed to achieve set target values in accordance with laws and regulations.

The characteristics of wastewater are physical, chemical or biological (Metcalf and Eddy, 2014; Sincero and Sincero, 2002). The physical properties include colour, odour, solids and temperature. The chemical properties in wastewater are organics such as pesticides and oils, inorganic constituents such as heavy metals and P, and gases. The biological content of wastewater consists of organic materials, plant components, viruses and protists (Metcalf and Eddy, 2014).

2.1.2 Physical/Mechanical treatment

The physical/mechanical treatments involve no change of the substance as in biological or chemical operations, it is instead moved around and transferred (Metcalf and Eddy, 2014; Sincero and Sincero, 2002). The physical methods include sedimentation, gas transfer, adsorption, mixing and flocculation, and membrane filtration. Mixing is either done rapidly to mix two substances, such as chemicals and wastewater, or to keep contents suspended in e.g. aerobic digesters. Flocculation forms larger particles (flocs) by collisions of particles that make them stick together and at a slower pace than mixing. Membrane filtration can filter both dissolved and

particulate substances by filtration through a medium with hydraulic pressure or vacuum. The substance desired for removal, the adsorbate, is accumulated onto an adsorbent, commonly activated carbon in wastewater treatment, during adsorption (Metcalf and Eddy, 2014). Sedimentation takes place in a rectangular or circular tank as particles sink to the bottom of the tank through gravity (Sincero and Sincero, 2002).

2.1.3 Chemical treatment

There is a chemical change in the composition of substances during chemical treatment (Sincero and Sincero, 2002), with treatment methods such as coagulation, chemical precipitation or ion exchange (Metcalf and Eddy, 2014). Coagulation and chemical precipitation for chemical removal of P are described further in Section 2.2.1. Ion exchange is a process that removes dissolved ionic constituents by replacing dissolved ions with ions from an insoluble material (Metcalf and Eddy, 2014; Sincero and Sincero, 2002).

2.1.4 Biological treatment

It is essential with organic waste, electron acceptors, a temperature suitable for the desired bacteria, a pH between 6 and 8 for most bacteria, and nutrients such as carbon or nitrogen that makes up the structure of bacteria for microbial growth in all biological treatment processes (L. K. Wang et al., 2010). Activated sludge is a popular treatment method where bacteria convert organic matter to gases or cell tissue, removing it from the wastewater (Metcalf and Eddy, 2014). The microorganisms, the activated sludge, are kept suspended through aeration or stirring and form flocs that separate from the water in a settling tank (Henze et al., 1997; Metcalf and Eddy, 2014). Sludge is returned from the settling tank to the activated sludge tank, where the sludge incorporates into the activated sludge. Part of the sludge, called waste activated sludge (WAS), is withdrawn from the system.

Moving bed biofilm reactors (MBBRs) is another biological treatment process, but unlike the activated sludge process, there is no return of activated sludge. The microorganisms instead grow on a suspended media that separate from the effluent water with screens (Metcalf and Eddy, 2014).

Nitrification and denitrification that reduce nitrogen levels take place in the activated sludge process (L. K. Wang et al., 2010). Nitrification occurs during aerobic conditions by autotrophic bacteria, commonly Nitrosomonas and Nitrobacter in wastewater treatment (Henze et al., 1997). The Nitrosomonas oxidize ammonium to nitrite while Nitrobacter oxidizes nitrite to nitrate. These bacteria have a slow growth rate compared to denitrifying bacteria. The denitrifying bacteria are heterotrophic bacteria that oxidize nitrate to atmospheric nitrogen. The denitrification process occur under anaerobic conditions and is anoxic as nitrate is the oxidizing agent. These aerobic and anaerobic zones also make it possible for the growth of P reducing bacteria, further explained in Section 2.2.2.

2.1.5 Sludge treatment

Sludge forms as wastewater pass through different treatment processes and constitutes are separated (Henze et al., 1997; Metcalf and Eddy, 2014). The sludge from the separation of particles through primary sedimentation is primary sludge, the sludge from biological treatment is named secondary sludge (Metcalf and Eddy, 2014), and the sludge from chemical treatment is called chemical sludge (Sincero and Sincero, 2002). As mentioned in Section 2.1.4, there is also return activated sludge and WAS. As the sludge consists of many unwanted components removed from wastewater, it has to go through further treatment before its final disposal (Metcalf and Eddy, 2014). The nutrients in the sludge allow for usage as fertilizer for crops but as it contains toxic substances such as heavy metals, it is essential to reduce the incoming concentrations of these substances to allow for the reuse of sludge.

Even as the sludge consists of particles, it still has a low solids content of between 0.25-12% of its weight and is, therefore, a liquid or semisolid liquid (Metcalf and Eddy, 2014). A large part of the sludge treatment consists of volume reduction and dewatering, with the steps and treatment methods:

- Preliminary operation: grinding, screening, blending, degritting
- Thickening: flotation, centrifugation, gravity belt
- Stabilization: anaerobic digestion, composting, heat drying
- Conditioning
- Dewatering: centrifuge, screw press, drying beds

The preliminary treatments of sludge have the goal of reducing particle sizes, homogenization and removal of grit (Metcalf and Eddy, 2014). The thickening step is applied to reduce the volume of the sludge. Stabilization is for mass reduction, resource recovery and product recovery before the conditioning step that improves the dewatering capacity of the sludge. The dewatering step is a second volume reduction of the sludge before it can be stored or disposed of directly. The end use of sludge is most commonly within agriculture as a fertilizer, incineration or landfilling.

As P is a finite resource and the use of agricultural fertilizers increases, there is a risk of a fertilizer shortage in some parts of the world as prices are pushed up (Childers et al., 2011). The mining of P is carbon-intensive and the refining process where it converts into phosphoric acid requires extensive inputs of other substances. Focus has shifted to recycling the sludge containing P from wastewater to avoid unsustainable mining of P (Childers et al., 2011; Metcalf and Eddy, 2014).

2.1.6 Heavy metal treatment

Heavy metal removal from wastewater occurs through ion exchange (Papadopoulos et al., 2004), chemical precipitation (Fu and Wang, 2011), adsorption, coagulation and flocculation, flotation, membrane filtration, or electrochemical methods (L.

Wang et al., 2007). The method of removal depends on several factors such as cost both for installation and operation, incoming metal concentrations, as well as regulations and threshold values (Kurniawan et al., 2006). Even as metals removes from the water through these processes, they will generate varying amounts of sludge that contains the metals removed from the water, which can affect the end-use of the sludge (Fu and Wang, 2011).

2.2 P treatment

The fractions of P present in wastewater before any treatment, divided into dissolved and particulate P with some examples of the inorganic P, are shown in Table 2.1 (Henze et al., 1997; Metcalf and Eddy, 2014). The total P (tot-P) content in the wastewater is the sum of the concentrations of these fractions in the water. Particulate P contains polyphosphates (poly-P) and orthophosphates that are biologically bound or chemically precipitated, but is only listed as organic in the table as the separation methods for particulate P are not affected by the P composition (Henze et al., 1997). The dissolved orthophosphates are ready to be used as energy by bacteria in their current form, but poly-P goes through hydrolysis to convert into orthophosphate used as energy (Metcalf and Eddy, 2014). Larger molecules, either particulate or dissolved, are degraded to smaller molecules by facultative and obligate anaerobes during hydrolysis. Hydrolysis is a slow process compared to bacterial growth and is often the limiting step in the bio-P treatment (Henze et al., 1997).

Table 2.1: *P fractions in wastewater (Henze et al., 1997; Metcalf and Eddy, 2014).*

Dissolved P	
Orthophosphate	H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}
Polyphosphate (Poly-P)	2+ P-atoms, O-atoms (and H-atoms)
Organic	
Particulate P	
Organic	

To remove P from wastewater the dissolved P must convert into particulate P and be removed with separation methods such as sedimentation or filtration (Henze et al., 1997). Primary settling tanks reduce the particulate P in incoming wastewater with up to a 25% reduction of the incoming tot-P (Svenskt Vatten, 2007). The wastewater has to pass through chemical and biological treatment as described in Section 2.2.1 and 2.2.2 to reduce the concentrations of dissolved P (Henze et al., 1997; Metcalf and Eddy, 2014; Svenskt Vatten, 2007).

2.2.1 Chemical treatment of P

P can be treated chemically through precipitation with metal salts in four steps: precipitation, coagulation, flocculation, and separation (Henze et al., 1997; Svenskt Vatten, 2007). The process operates with direct, simultaneous, multipoint, pre- or post-precipitation and uses aluminium or iron as metal salts. Some of the most common aluminium and iron salts used for chemical precipitation of P in wastewater

treatment are in Table 2.2. The different operating modes are dependent on the point of precipitation chemical addition in the treatment process. To reach an effluent concentration of 0.3-0.5 gP/m^3 a molar ratio of 2 between Fe^{3+} or Al^{3+} and incoming Tot-P is recommended (Henze et al., 1997; Metcalf and Eddy, 2014).

Table 2.2: *Metal salts used for chemical precipitation in wastewater treatment (Svenskt Vatten, 2007).*

Aluminium	
Aluminium sulfate	$Al_2(SO_4)_3$
Aluminium chloride	$AlCl_3$
Polyaluminium chloride (PAC)	$(Al(OH)_xCl_{3-x})_n$; 0<x<3, n $\geq$ 2
Iron	
Iron(III) chloride	$FeCl_3$
Iron(II) chloride	$FeCl_2$
Iron(II) sulfate	$FeSO_4$
Iron(III) sulfate	$Fe_2(SO_4)_3$
Iron(III) chlroide sulfate	$ClFeO_4S$

The first step of precipitation occurs as the precipitant mixes with the wastewater, where metal ions precipitate P (Henze et al., 1997). The simplified reactions of this process for Fe^{3+} and Al^{3+} is shown in the reaction Equations 2.1 and 2.2. The primary reaction is when phosphate reduction occurs, but the side reaction is where the metal ions precipitate with the hydroxide into larger particles that catch smaller particles for settling. When using Iron(II) sulfate in waters with a pH over 8.5, the Fe^{2+} is oxidised to Fe^{3+} rapidly with the same reactions (Svenskt Vatten, 2007). Since there are many competing reactions taking place when a precipitant is added to wastewater, as it consists of a wide variety of substances, the dosage is decided based on either bench-scale or full-scale tests (Metcalf and Eddy, 2014).

$$\text{Main reaction: } Me^{3+} + H_2PO_4^- \rightarrow MePO_4 + 2H^+ \tag{2.1}$$

$$\text{Side reaction: } Me^{3+} + 3HCO_3^- \rightarrow Me(OH)_3 + 3CO_2 \tag{2.2}$$

where:

Me = metal salt

The coagulation process takes place in the same tank as the precipitation, where colloids with a particle diameter of between 10^{-3} µm and 1 µm form larger particles (Henze et al., 1997). During flocculation, the particles grow in size and form flocs, which occur as the particles collide by stirring the water. These flocs separate from the water through filtration or sedimentation.

The process of direct precipitation in Figure 2.1 is when the precipitation chemical adds after the mechanical treatment and no further treatment, such as a biological step, is installed after the sedimentation basin (Svenskt Vatten, 2007). All of

the metal salts in Table 2.2 are possible precipitants with direct precipitation, but polyaluminium chloride (PAC) and iron chloride (FeCl) are the most common. PAC or FeCl is added into a flocculation basin or sedimentation basin and achieves an effluent concentration of Tot-P around 0.4-0.6 g/m^3. Henze et al. (1997) state that direct precipitation is applicable when the receiving water body can withstand an increased oxygen consumption from the higher organic load in wastewater treated with direct precipitation compared to the other operating modes.

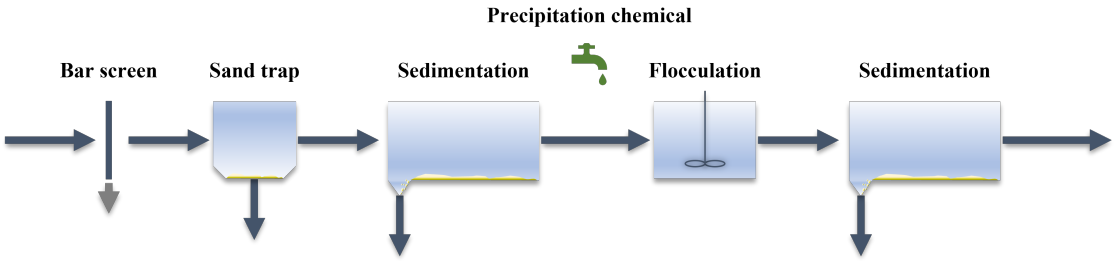


Figure 2.1: *The process of chemical precipitation of P with direct precipitation. Adapted from Svenskt Vatten (2007).*

FeCl or PAC is most commonly added during pre-precipitation before the mechanical treatment, as seen in Figure 2.2 (Svenskt Vatten, 2007). Precipitation and flocculation occur either in the sand trap or at the inlet of the sedimentation basin before it settles. During simultaneous precipitation Fe or PAC is dosed into the activated sludge basin (Henze et al., 1997; Svenskt Vatten, 2007), as shown in Figure 2.2. Both precipitation and flocculation take place in the aerated parts of the basin and separates from the water in the following sedimentation tank, which simultaneously occur for the biologically treated constituents. The activated sludge consists of biological and chemical sludge, leading to increased sludge volumes in the AS basins to achieve sufficient treatment to compensate for the lowered fraction of biological sludge. Fe^{2+} in the form of $FeSO_4$ is applicable in this operating mode, which is the cheapest precipitation chemical as it is a by-product from other processes.

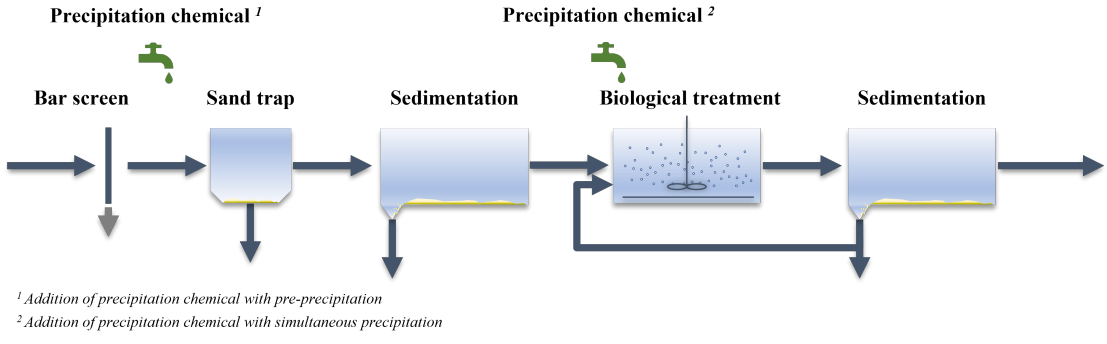


Figure 2.2: *The process of chemical precipitation of P with pre-precipitation and simultaneous precipitation. Adapted from Svenskt Vatten (2007).*

All of the precipitation chemicals in Table 2.2 can be dosed after the biological treatment during post-precipitation, shown in Figure 2.3. The wastewater has to pass through a sedimentation basin in an activated sludge system before adding

the precipitation chemical to avoid chemical sludge in the activated sludge. The precipitation, flocculation and separation occur in a flocculation and sedimentation basin. Multipoint precipitation can be applied when further treatment compared to the already discussed operation modes is required (Metcalf and Eddy, 2014; Svenskt Vatten, 2007). As the figure shows, there are several possible combinations of additional points during this operating mode, depending on the needs of the WWTP.

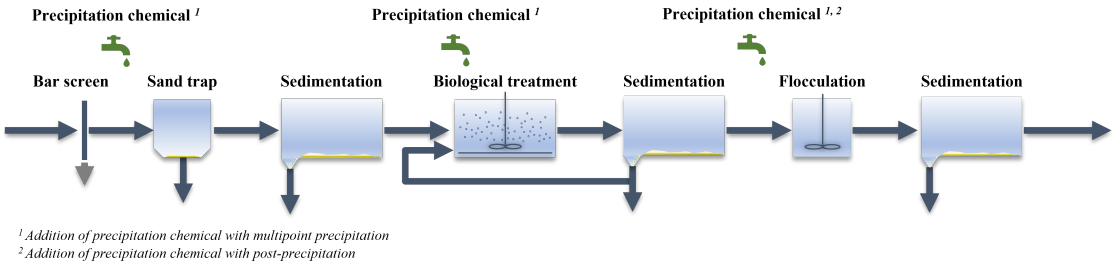


Figure 2.3: *The process of chemical precipitation of P with multipoint precipitation and post-precipitation. Adapted from Svenskt Vatten (2007).*

Besides the operating modes there are several factors that influence the choice of precipitation chemical. Some of these are:

- pH - the metal salts goes through different reactions and their ability to precipitate P depends on the pH of the wastewater (Sincero and Sincero, 2002; Svenskt Vatten, 2007).
- The composition of the incoming wastewater (Svenskt Vatten, 2007).
- Sludge build up - the chemicals create varying amounts of sludge.
- The content of heavy metals in the precipitation chemical.

2.2.2 Biological Treatment of P

Biological P removal builds on altering between aerobic and anaerobic conditions for bacteria to assimilate P into sludge (AnoxKaldnes, 2020; Henze et al., 1997; Metcalf and Eddy, 2014; Svenskt Vatten, 2007). Removal of WAS is the only option to reduce the concentration of P in the wastewater as P is not part of any gas in the same way as nitrogen converts to nitrogen gas (AnoxKaldnes, 2020; Metcalf and Eddy, 2014; Svenskt Vatten, 2007). This process is called Enhanced Biological P Removal (EBPR) and aims to optimize the concentration of P Accumulating Organisms (PAOs), which is the bacteria that stores P (AnoxKaldnes, 2020; Metcalf and Eddy, 2014).

Bio-P has the ability to reduce incoming concentrations of P between 20-50% (Svenskt Vatten, 2007), which often is lower than the reduction needed to reach discharge limits in Sweden (la Cour Jansen et al., 2009). This is significantly lower than the 85-95% reduction that can be achieved through chemical precipitation (Svenskt

Vatten, 2007), and has led to most plants that has adapted biological treatment in Sweden uses it combined with chemical treatment (la Cour Jansen et al., 2009).

As seen in Figure 2.4, PAOs consumes easily degradable organic material, Volatile Fatty Acids (VFAs), and produces an organic polymer called Poly-β-hydroxyalkanoate (PHA) stored within the bacteria during anaerobic conditions (AnoxKaldnes, 2020; Metcalf and Eddy, 2014). The energy needed to produce PHA is formed during the hydrolysis of stored Poly-P into phosphate, which causes a release of phosphate into the wastewater but decreases the organic material as the PAOs consume it (AnoxKaldnes, 2020; Metcalf and Eddy, 2014; Svenskt Vatten, 2007). The stored PHA is oxidized and forms poly-P bonds within the cell, leading to a P-uptake and cell growth when reaching the anaerobic zone. As the PAOs increase in the presence of oxygen, the uptake of P will be higher than the release in the anaerobic tank, leading to a removal of P from the wastewater through the WAS.

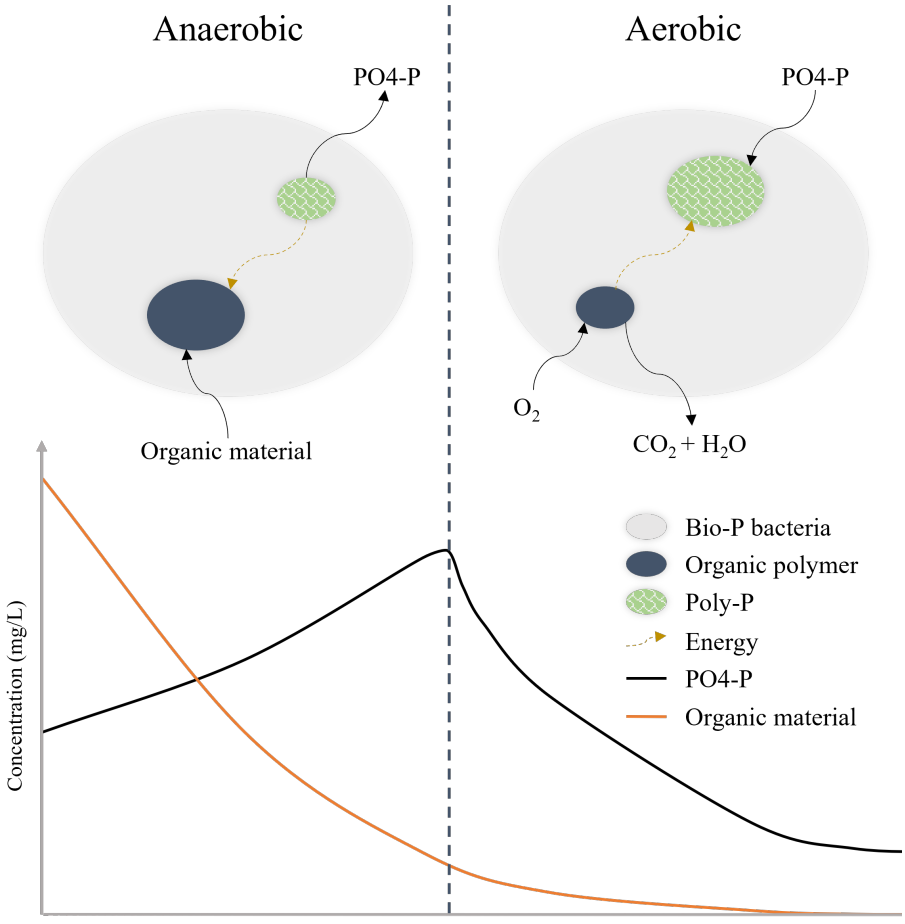


Figure 2.4: *The process of P-release and uptake in a Bio-P process. Adapted from Borglund (2004), Henze et al. (1997) and Svenskt Vatten (2007).*

Some of the more commonly found types of PAOs are Accumulibacter and Tetrasphera (Metcalf and Eddy, 2014). Accumulibacter has been credited as the most important PAO when it comes to EBPR but Tetrasphera has been found in higher quantities at WWTPs in recent studies (Nielsen et al., 2019). Much is still unknown about the Tetrasphera PAO, but studies indicate that they use amino acids (AA)

or glucose as a carbon source compared to Accumulibacter that prefer VFAs (R. Liu et al., 2019; Metcalf and Eddy, 2014). Close et al. (2021) discovered that an activated sludge consisting of only Tetrasphera as PAO could not achieve complete uptake of observed P, while an activated sludge consisting of both Tetrasphera and Accumulibacter could achieve complete uptake during aerobic conditions.

Accumulibacter work as both PAO and glycogen accumulating organism (GAO) when there are limited amounts of P in the wastewater (Kolakovic et al., 2021). GAO stores glycogen during aerobic conditions and consumes glycogen during anaerobic conditions to provide energy for volatile fatty acids (VFA)-uptake and Poly-β-hydroxyalkanoate (PHA) production (Metcalf and Eddy, 2014). EBPR is not achieved with GAO as they, unlike PAO, does not store polyphosphate and use as energy source during VFA-uptake. This means that GAO and PAO compete for VFA under anaerobic conditions and if the population of GAO dominates it will inhibit phoshporus removal.

An anaerobic tank with access to VFAs followed by aerobic or anoxic tanks is needed to achieve EBPR, which can be done both in the mainstream where all of the wastewater passes through or in sidestreams (Metcalf and Eddy, 2014; Svenskt Vatten, 2007). Figure 2.5 shows an example of an Anaerobic/Oxic (A/O) process, which is a mainstream process commonly used in Sweden (Svenskt Vatten, 2007). In the A/O process, the water first passes through an anaerobic tank followed by an aerobic tank to simulate PAO growth before entering a sedimentation tank where the sludge is recycled to the anaerobic tank to supply the bacteria with VFAs (Metcalf and Eddy, 2014).

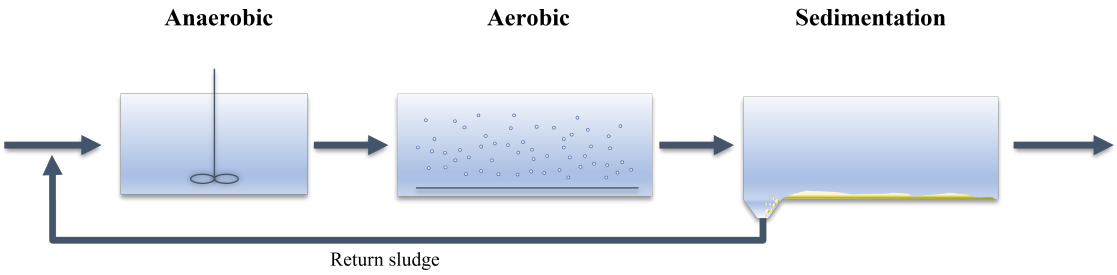


Figure 2.5: *Biological P treatment with a two-stage Anaerobic/Oxic (A/O) process. Adapted from Svenskt Vatten (2007).*

The University of Cape Town (UCT) process shown in Figure 2.6 is a mainstream process combining P and nitrogen treatment (Metcalf and Eddy, 2014; Svenskt Vatten, 2007). The wastewater passes through an anerobic tank to where sludge is recycled from an anoxic tank to avoid nitrate entering the anaerobic tank (Metcalf and Eddy, 2014). An anoxic tank is placed after the anaerobic tank to where nitrate and return sludge is sent from an aerobic tank and sedimentation tank that the wastewater passes through after the anoxic tank.

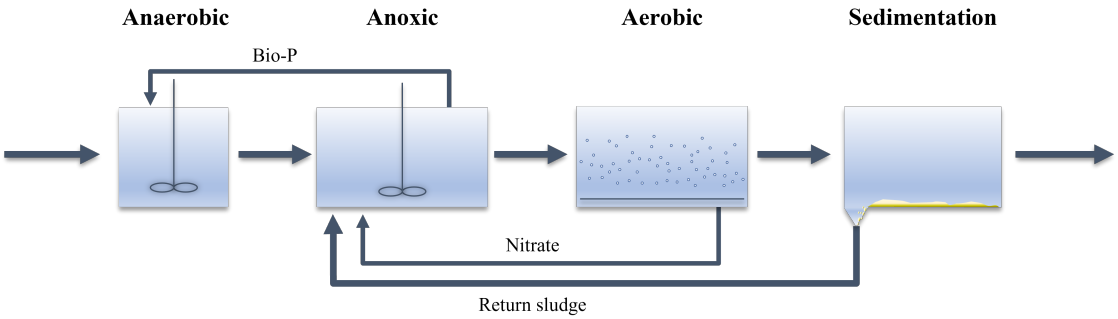


Figure 2.6: *Biological P treatment with the University of Cape Town (UCT) process. Adapted from Metcalf and Eddy (2014 and Svenskt Vatten (2007).*

The PhoStrip process as seen in Figure 2.7 is a sidestream Bio-P process, where not all return sludge is put through anaerobic conditions (Svenskt Vatten, 2007). Part of the return sludge is sent to a stripper tank which is a gravity thickener with anaerobic conditions (Metcalf and Eddy, 2014). The sludge is recycled to the return sludge stream after generating PAO in the stripper tank while the P that is released from the sludge is sent to a mixing tank. The P is treated chemically with lime in the mixing tank and sent back to the start of the process at the first sedimentation tank.

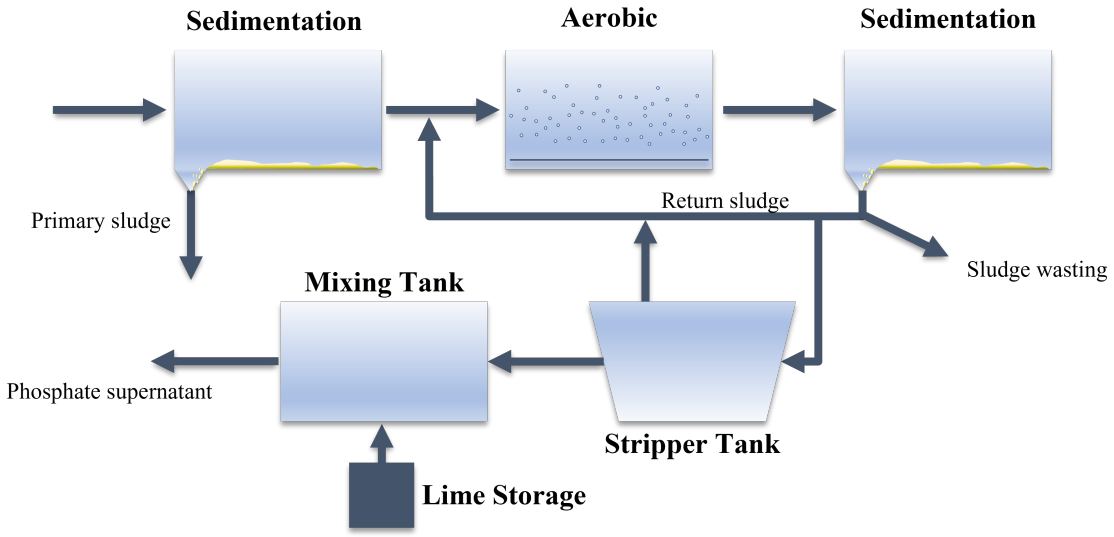


Figure 2.7: *Biological P treatment with the PhoStrip process. Adapted from Levin (1987).*

2.2.3 P-release and uptake tests

P-release and uptake tests can be performed in a laboratory to determine the capacity of an activated sludge to remove P biologically (Tykesson and la Cour Jansen, 2005). The method is not standardised but Tykesson and la Cour Jansen (2005) gives a description of the method that is used by other researchers conducting the tests (Palatsi et al., 2021; Salmonsson et al., 2017; Tomei et al., 2020), and Borglund (2004) presents a more detailed description of the test following a similar procedure. An example of a laboratory setup for the test is presented in Figure 2.8. The out-

put of the test is orthophosphate as P (PO_4-P) release and uptake rates that are compared with literature to determine if biological P removal occur (Tykesson and la Cour Jansen, 2005).

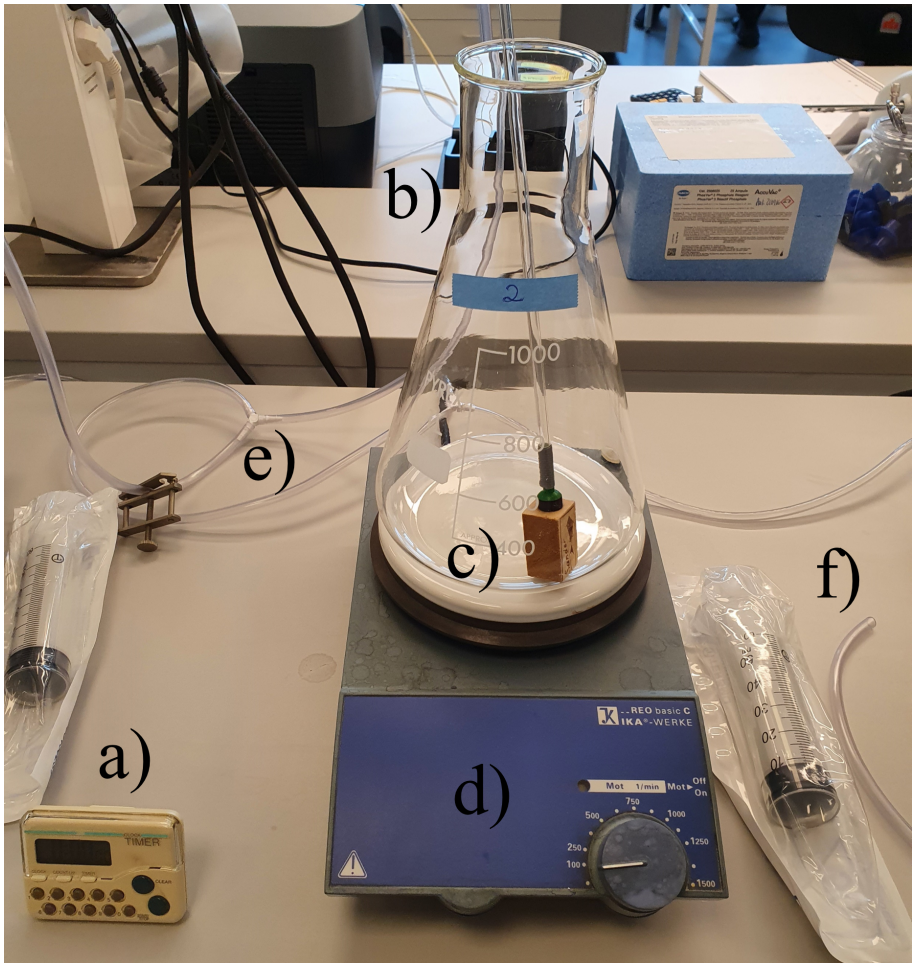


Figure 2.8: *Example of equipment that can be used for a P-release and uptake test as described by Borglund (2004) and Tykesson and la Cour Jansen (2005) with: a) timer, b) glass beaker, c) aerator, d) magnetic stirrer, e) compressed air, f) syringe and plastic tube for sample collection.*

Activated sludge collected from the aerated zone at a WWTP is subjected to one aerated period, an anaerobic period after addition of a carbon source, and another aerated period during the test (Tykesson and la Cour Jansen, 2005). VFA is oxidised and the storage of P boosted during the first aerated period while the addition of a carbon source in excess and lack of oxygen during the anaerobic period trigger a P-release. By supplying the sludge with oxygen during the final aerated period an uptake of P is expected as in the first aerated period. These processes are described in detail in Section 2.2.2. Samples for PO_4-P analyses are collected continuously to monitor the P-release and uptake over time. Figure 2.9 shows a possible pattern of PO_4-P-release and uptake during the aerobic and anaerobic periods in the test over time. SS and VSS of the sludge should also be measured to give a more comparable result as they vary greatly between WWTPs.

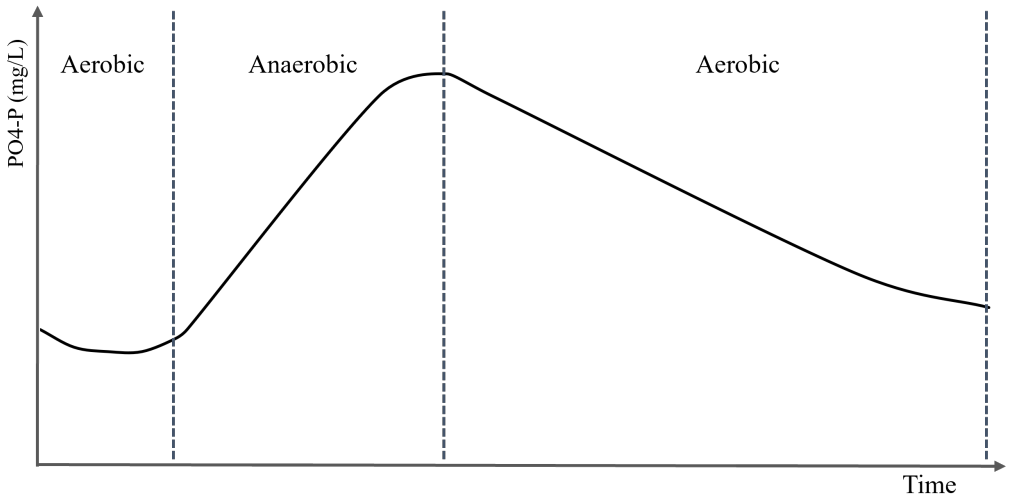


Figure 2.9: *P-release over time during a P-release and uptake test. Adapted from Borglund (2004) and Tykesson and le Cour Jansen (2005).*

The PO_4-P-release rate is calculated from the measured concentrations of PO_4-P in the activated sludge in the samples collected during the anaerobic period (Borglund, 2004; Tykesson and la Cour Jansen, 2005). The PO_4-P uptake rate is calculated in the same way but from the samples collected during the second aerobic period. When comparing rates with other WWTPs they are commonly given the unit of mgP/(gVSS·h) (Borglund, 2004; Tykesson and la Cour Jansen, 2005). Borglund (2004, p.72) presents an equation that can be used to calculate these rates, shown in Equation 2.3. A maximum release rate can also be calculated as the difference between the maximum and minimum PO_4-P concentrations during the anaerobic period with the unit mgP/(gVSS) (Tykesson and la Cour Jansen, 2005).

$$v_{release/uptake} = \frac{P_2 - P_1}{(t_2 - t_1) \cdot VSS} \tag{2.3}$$

where:

$v_{release/uptake}$ = PO_4-P-release/uptake rate $[\frac{mgP}{gVSS \cdot h}]$
P_1 = PO_4-P concentration in the beginning of period 2/3 $[\frac{mgP}{L}]$
P_2 = PO_4-P concentration at the end of the linear period of period 2/3 $[\frac{mgP}{L}]$
t_1 = time of measurement of P_1 [h]
t_2 = time of measurement of P_2 [h]
VSS = Volatile Suspended Solids $[\frac{gVSS}{L}]$

Janssen et al. (2002) presents a classification system, shown in Table 2.3, for the sludge based on P-release/uptake rates. A higher release/uptake rate indicates a higher presence of Bio-P bacteria with a better capacity to remove P. However, other factors such as water characteristics, available carbon sources, and phosphate loads also affect the systems ability to remove P biologically. Table D.2 in Appendix B presents release rates from P-release batch tests conducted in other studies and information regarding the P treatment at the WWTPs in the studies (Borglund, 2004; Gu et al., 2008; Hansson, 2016; Salmonsson et al., 2017).

Table 2.3: *Sludge quality based on P-release/uptake rate (Janssen et al., 2002).*

Release/uptake rate $\frac{mgP}{gVSS \cdot h}$	Sludge quality
<3	Moderate
3-7	Good
>7	Very good

The carbon source, temperature, pre-aeration, pH, and precipitation are factors that influence the results of the release and uptake tests (Tykesson and la Cour Jansen, 2005).

Carbon source
One possible error source when preforming the test is if not all acetate is consumed during the anaerobic period, as it affects the P-uptake rate due to bio-P bacteria storing the acetate as PHB instead instead of using the already stored PHB (Janssen et al., 2002). This inhibits the uptake of P and can lead to an opposite effect where P is released but can be avoided by first doing a release test and then repeating the test. An adjusted acetate amount can be dosed in the second test by measuring the consumption of VFA in the first release test, ensuring there is no acetate in excess when the aerated period starts. If an easily degreadable carbon source, such as acetate, is used it should be degraded rapidly once the oxygen is supplied and have little effect on the uptake rate of the test (E. Tykesson, personnel communication, April 7, 2022). There is also a risk that the carbon source is consumed rapidly when added if anaerobic conditions are not reached beforehand. Nitrogen gas can be supplied to the reactor to ensure no oxygen is present at the start of the anaerobic period (Tykesson and la Cour Jansen, 2005). To avoid this issue during P-release and uptake tests performed by Comeau et al. (1987), they kept the sludge non-aerated during 3.5 hours while mixing it.

Temperature
PAOs have higher release and uptake rates of P during higher temperatures (Janssen et al., 2002), which was shown in batch tests performed by Tykesson (2002) where a higher release rate was noted at a higher temperature when performing the test with the same sludge at different temperatures. The tests should be performed with a constant temperature, either the sludge temperature or a chosen temperature, to make the results comparable even if the same sludge is used for several attempts (Tykesson, 2002; Tykesson and la Cour Jansen, 2005).

pH
pH affects the test both regarding acetate consumption and physical-chemical bounding of phosphate (Janssen et al., 2002). The acetate consumption of the bio-P bacteria increases at a low pH as more energy is required to transport acetate over the cell membrane instead of conversion into PHA (Janssen et al., 2002; Smolders et al., 1994). This means that with the same dosage of acetate, a higher pH leads to an increased P-release rate when comparing tests with different pH (W.-T. Liu et al., 1996; Smolders et al., 1994). A high pH can also lead to a lower P-release rate as

precipitation occur, either due to chemical sludge or high calcium concentrations in the activated sludge (Comeau et al., 1987; Tykesson, 2002; Tykesson and la Cour Jansen, 2005). The precipitation chemicals or calcium present in the chemical sludge removes dissolved P, disguising some of the biological P-release (Janssen et al., 2002; Tykesson, 2002; Tykesson and la Cour Jansen, 2005). To avoid precipitation with calcium the pH should be kept at around 7 while potassium (K) release or uptake can be measured to determine the effect of metal precipitation. If there is a high K/P ratio it indicates that the chemicals has influenced the release or uptake of P.

Pre-aeration
The pre-aeration period is important to achieve a high storage of P when starting the anaerobic period, especially if the sludge has been transported or stored for some time before starting the tests (Tykesson and la Cour Jansen, 2005; Tykesson, 2002). The concentration of VFAs in the wastewater is also reduced through oxidation during the pre-aeration which leads to a known concentration of carbon source when added during the anaerobic period (Tykesson and la Cour Jansen, 2005). However, if the test starts close to collection of the activated sludge the pre-aeration period is less important and can be left out completely to reduce the length of the test (E. Tykesson, personnel communication, April 7, 2022).

2.3 Rya WWTP

Rya WWTP is located in Gothenburg and treats wastewater from the municipalities of Ale, Härryda, Gothenburg, Partille, Kungälv, Lerum, and Mölndal (Gryaab, n.d.-a). 957 442 Population Equivalents (PE) were connected to the plant in 2021 with an average flow of 14 703 m^3/h and a total flow of 135 212 568 m^3/year (Gryaab, 2022). The treatment at Rya WWTP reduces the concentrations of P, nitrogen and degradable organic materials reaching the recipient Göta River as well as removes particles, objects and settleable substances. These substances are treated at the WWTP with the mechanical, chemical, and biological processes as well as sludge treatment as seen in Figure A.1 in Appendix A.

2.3.1 Mechanical treatment

The mechanical treatment steps are numbered 1-4, 7-8, and 17 in Figure A.1 in Appendix A. Incoming wastewater first reaches a course bar screen with 20 mm spacing between the bars that traps objects (Gryaab, n.d.-b). With four pumps the water is pumped into an aerated sand trap that removes heavy solid particles before the water passes through twelve fine bar screens with two millimeter spacing between the bars (Gryaab, 2022). The fine bar screens captures smaller waste such as cotton swabs and condoms (Gryaab, n.d.-b). The course and fine bar screens are cleaned of waste removed from the water with washing and pressing before the waste is sent to an incineration plant in Sävenäs operated by Renova (Gryaab, 2022). To further separate solid particles from the wastewater it passes through twelve primary settling tanks (PSTs), with the properties presented in Table 2.4, and the separated particles generate primary sludge. The final treatment step before releasing the water into Göta River is the 32 disc filters. The automatic filters separate suspended substances from the water as they rotate and are washed clean with a high pressure system.

Table 2.4: *Properties of the settling tanks and disc filters at Rya WWTP in 2021 (Gryaab, 2022).*

Primary settling tanks		
Retention time	h	1.67
Normal flow	m^3/s	3.8
Disc filters		
Mesh size	µm	15
Maximum incoming flow	m^3/s	8
Secondary settling tanks		
Retention time	h	3
Total volume	m^3	72 200

2.3.2 Chemical treatment

The chemical processes steps are numbered 5-6, 9, and 14-15 in Figure A.1 in Appendix A. Iron(II) sulfate (FeSO4 · 7H2O) is used for chemical precipitation of P at Rya WWTP with the quantity consumed during 2021 in Table 2.5 (Gryaab, 2022), and the process is explained further in Section 2.3.5. Direct precipitation with PAC and polymer is applied when the incoming flow of water to Rya WWTP exceeds the capacity of the activated sludge process. Six of the primary settling tanks can be used for direct precipitation which removes phosphorus, organic materials and particles from the wastewater before releasing it into Göta River. The properties of the direct precipitation is presented in Table 2.5. The use of phosphoric acid and methanol is explained in section 2.3.3.

Table 2.5: *Properties of chemical treatment processes at Rya WWTP in 2021 (Gryaab, 2022).*

Chemical precipitation of P		
FeSO4 · 7H2O (90%)	tonnes/year	2970
Direct precipitation		
PAC (Al_2Cl_3)	tonnes/year	490
Polymer (Amide/Amino acrylate, copolymer)	tonnes/year	2.1
Maximum incoming flow	m^3/s	3
Retention time	h	0.5-1

As mentioned in Section 2.1.6, metals can be removed through several treatment processes. At Rya there is not specific treatment of metals but as the metals passes through the plant a reduction can be observed, as seen in Table 2.6 that shows the reduction of metals from the inlet to the outlet at Rya WWTP (Gryaab, 2022).

Table 2.6: *Incoming metal loads, outgoing metal loads, and removal efficiency at Rya WWTP during 2021 (Gryaab, 2022).*

	Pb kg	**Cd** kg	**Cu** kg	**Cr** kg	**Hg** kg	**Ni** kg	**Zn** kg
In	417	15.4	9286	398	13.3	528	13023
Out	37.5	1.26	1367	45	7.00	416	1540
Removal	91.0%	91.8%	85.3%	88.7%	47.4%	21.2%	88.2%

2.3.3 Biological treatment

The biological treatment steps are numbered 10-16 in Figure A.1 in Appendix A. The wastewater is mixed with recirculated water from the nitrifying trickling filters (NTFs) and recirculated activated sludge (AS) from the secondary settling tanks (SSTs) when it reaches the three AS basins, with the flows presented in Table 2.7 (Gryaab, 2022). The water passes through the 40-60 per cent of the activated sludge basins that are anoxic and the remaining aerated part during the retention time seen in Table 2.7. There are 24 SSTs with two levels stationed after the AS basins with the properties presented in Table 2.4. The AS settles in the SSTs and recirculates to the activated sludge basins, with the exception of WAS, which circulates to the inlet of the PSTs.

Table 2.7: *Properties of the biological treatment processes at Rya WWTP in 2021 (Gryaab, 2022).*

Activated sludge		
Maximum incoming flow	m^3/s	8-9
Retention time	h	1.5
Volume	m^3	51 000
Return sludge flow	m^3/s	1-3.5
Flow from nitrifying trickling filters	m^3/s	1-7
Nitrifying trickling filters		
Maximum incoming flow	m^3/s	7
Water/plastic-contact surface	m^2/m^3	230
Depth	m	7.2
Nitrifying MBBR		
Maximum incoming flow	m^3/s	5
Water/plastic-contact surface	m^2/m^3	800
Denitrifying MBBR		
Maximum incoming flow	m^3/s	4
Water/plastic-contact surface	m^2/m^3	500
Methanol (CH3OH, 98-99%)	tonnes/year	2278
Phosphoric acid (H_3PO_4, 75%)	tonnes/year	15.1

A majority of the water pumps to the two blocks of NTFs with the properties

in Table 2.7 (Gryaab, 2022). The water is sprayed through six sections over the corrugated solid plastic material that the filters consist of and percolates through the full depth. Nitrification converts ammonium to nitrate before the water circulates to the AS process or is sent to the denitrifying Moving Bio Bed Biofilm Reactors (DMBBRs). This process also occurs in the Nitrifying MBBRs (NMBBRs) with the properties seen in Table 2.7. The plastic carriers are mobile in the NMBBRs compared to the NTFs, and the water is forwarded to the DMBBRs, with the properties presented in Table 2.7. The DMBBRs are full of mobile plastic carriers with heterotrophic bacteria that convert nitrate to nitrogen gas with the help of added methanol (CH_3OH) and phosphoric acid (H_3PO_4). The amounts of CH_3OH and H_3PO_4 consumed at Rya WWTP during 2021 are presented in Table 2.7. These processes are seen in Figure 2.10.

(a) *NTF*

(b) *DMBBR*

(c) *NMBBR*

Figure 2.10: *The biological treatment steps at Rya WWTP.*

2.3.4 Sludge treatment

The sludge treatment at Rya WWTP consists of thickening, mesophilic anaerobic digestion, and dewatering with the final disposal of the sludge as fertilizer in agriculture or for soil production (Gryaab, 2022). These steps are numbered 18-23 in Figure A.1 in Appendix A. Gravity belt thickeners (GBTs) thicken the sludge by adding 90 tonnes of polymer, increasing the TS of the sludge to around 4-8%. Reject water from this process is recirculated to the channel after the primary settling. The sludge pumps into the three anaerobic digestion chambers, shown in Figure 2.11a, where bacteria convert biodegradable material into biogas consisting of mainly methane and carbon dioxide. This process reduces the sludge by around 60% and leaves the remaining sludge odour free. The digestion chambers are in series, and sludge is pumped for dewatering in the screw presses from the third smaller. The TS increases to around 25-30% through dewatering, and reject water is filtered through drum filters and sent to the sludge liquor treatment before recirculation into the plant. As seen in Figure 2.11b, the dewatered sludge is stacked in piles next to the digestion chambers before trucks transport the sludge for final disposal. The sludge at Gryaab is Revaq certified for use in agriculture.

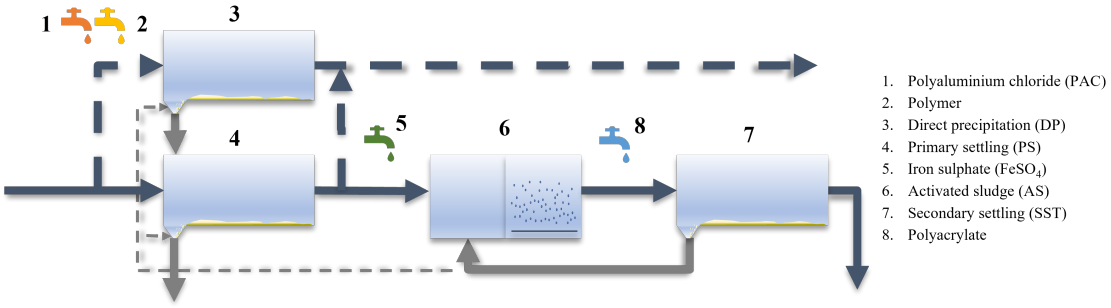
(a) *Digestion chambers* **(b)** *Dewatered sludge storage*

Figure 2.11: *Part of the sludge treatment steps at Rya WWTP.*

2.3.5 P treatment

As stated in Section 2.3.2, chemical precipitation with $FeSO_4$ is applied to remove P at Rya WWTP (Gryaab, 2022). As shown in Figure 2.12a a simultaneous process, further described in Section 2.2.1, is applied where $FeSO_4$ is added before the AS basins where precipitation and coagulation take place. If needed a flocculation chemical can be added before the water enters the secondary settling to improve the flocculation capacity before the P settles in the SSTs and is incorporated in the activated sludge. The dosing of $FeSO_4$ at Rya WWTP, with a molar ratio of 1.0-1.3 mol Fe/mol P, is shown in Figure 2.12b where the $FeSO_4$, which arrives at Rya WWTP in powder form, has already has been dissolved in water. It is the amount of $FeSO_4$ in powder form that is presented in Table 2.5 of 2970 tonnes for 2021. The

$FeSO_4$ is in the form of Iron(II) sulphate when it is supplied to the wastewater flow, but the Fe^{2+} is oxidised to Fe^{3+} in the aerated part of the AS basins as described in Section 2.2.1. Direct precipitation is also used at Rya WWTP for P removal when the capacity of the AS basins are exceeded, which is described in Section 2.3.2.



(a) *Schematic of the P treatment at Rya WWTP.*

(b) *Addition of $FeSO_4$ at Rya WWTP before the AS basins.*

Figure 2.12: *Chemical precipitation of P at Rya WWTP.*

2.3.6 Drinking water sludge (DWS)

DWS is sent to Rya WWTP through the wastewater piping system from the DWTPs Lackarebäck and Alelyckan in Gothenburg as described by operations engineer I. Kjellberg at Kretslopp och vatten (personal communication, February 17, 2022). The drinking water sludge is created at the DWTPs through chemical precipitation with aluminium sulphate (alum), which according to Matilainen et al. (2010) removes turbidity, colour, natural organic matter (NOM), and pathogens from the drinking water. Kjellberg further explains that sludge production varies over the year as, for example, people leave Gothenburg during hot summers and DWS production decreases. The DWS has a low total solids (TS) content of around 1% as there is no dewatering process at the DWTPs.

Data supplied by environmental engineer L.Wellsjö at Gryaab (personnel communication, February 21, 2022) states that the TS of the DWS from Lackarebäck during 2021 was, on average, 0.56% and 1.64% from Alelyckan. The total load of DWS reaching Rya WWTP during 2021 in TS was 1264 tonnes, 719 tonnes from Alelyckan and 545 tonnes from Lackarebäck. This data shows that the DWS production and TS of the sludge are slightly higher at Alelyckan than at Lackarebäck, which Kjellberg confirmed. The use of alum, with a 9% Al content, was higher at Lackarebäck with 1176 tonnes compared to 1154 tonnes at Alelyckan in 2021. The total flow of the solid and liquid parts of the DWS was ca. 96574 tonnes/year or 11.0 m^3/h from Lackarebäck and 43963 tonnes/year or 5.02 m^3/h from Alelyckan. Table 2.8 shows that Alelyckan contributes to higher amounts of Zink (Zn) and Chromium (Cr) to Rya WWTP, while loads are similar for the remaining metals.

Table 2.8: *Metal loads reaching Rya WWTP from the DWTPs Lackarebäck and Alelyckan.*

Metal	**Cu** kg	**Ag** kg	**Hg** kg	**Zn** kg	**Sb** kg	**Cd** kg	**Pb** kg	**Cr** kg	**Ni** kg	**Al** tonnes
Lackarebäck	26.86	0.17	0.04	28.22	1.17	0.10	4.70	3.87	5.34	105.9
Alelyckan	24.62	0.22	0.02	43.67	0.90	0.11	5.97	10.42	8.63	103.9
Total	51.5	0.4	0.06	71.9	2.1	0.2	10.7	14.3	14.0	210

2.3.7 MiDAS project Sweden

The MiDAS (Microbial Database for Activated Sludge) project in Sweden is a collaboration between Anoxkaldnes, the Center for Microbial Communities (CMC) at Aalborg University, and Swedish WWTPs, among those Rya WWTP and Ellinge WWTP, that strives to characterize the microorganisms of greatest importance at WWTPs (MiDAS, n.d.). Ellinge WWTP uses post-precipitation for P removal (VA SYD, 2022, compared to Rya WWTP, which uses simultaneous precipitation. However, neither plant operates bio-P removal. Table B.1 and B.2 in Appendix B shows the presence of PAOs and GAOs at Rya and Ellinge WWTP.

3
Method

This chapter covers the methodologies used to reach the aim of this thesis, including a description of the literature study, the data collection and calculations to achieve the phosphorus mass balance, and the laboratory work and calculations for the P-release and uptake tests and chemical precipitations tests with DWS.

3.1 Literature study

A literature study was conducted to gather knowledge of wastewater treatment, phosphorus in wastewater treatment and Rya WWTP to construct Chapter 2 in this Thesis. Open sources, such as Google and Google Scholar, were used to find scientific articles and books before assessing the source's credibility. This assessment included checking the number of citations, the background of the authors, who published the source, the journal of publication, judging if the source is outdated, if it is a primary source, and if it is peer-reviewed.

3.2 Mass balance

All data for water flows, phosphorus concentrations, and suspended solids (SS) concentrations in the balance are from measurements performed at Rya WWTP, either internally or externally. The researcher did not perform any measurements. Data for 2021 was collected, as more data was available than for 2022, and as daily averages. The data only covered measurements from January to August, as the outgoing sludge flow from the WWTP increased due to the clearance of sludge in the anaerobic digesters in September 2021. The flows studied in the mass balance are shown in Figure C.1, and Table 3.1 shows the equations to calculate each mass flow rate. Equations not presented in this Chapter are in Appendix C.

Table 3.1: *Mass flow rates of phosphorus, concentrations and flows at Rya WWTP and the equation used.*

Tag	From	To	Eq.
$\dot{m}_{Tot-P\ 1}$	Inlet		3.1
$\dot{m}_{PO_4-P\ 1}$	Inlet		3.1
$\dot{m}_{X-P\ 1}$	Inlet		3.2
$\dot{m}_{Tot-P\ 1.2}$	Inlet	PS	C.1
$\dot{m}_{PO_4-P\ 1.2}$	Inlet	PS	C.1
$\dot{m}_{X-P\ 1.2}$	Inlet	PS	3.2
$\dot{m}_{Tot-P\ 2}$	Inlet	DP	3.1
$\dot{m}_{PO_4-P\ 2}$	Inlet	DP	3.1

Continued on next page

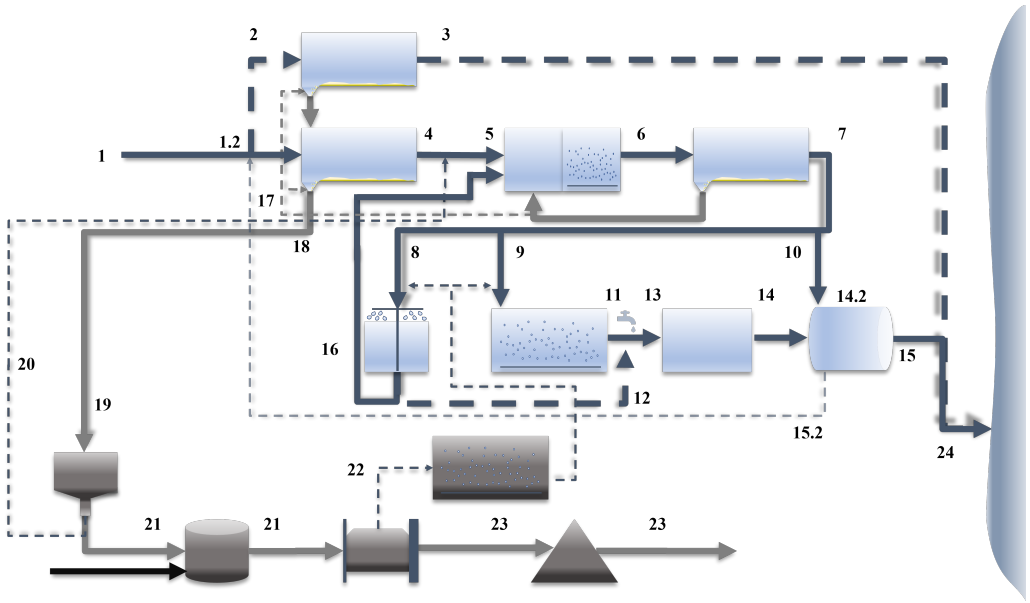
Table 3.1 – continued from previous page

Tag	From	To	Eq.
$\dot{m}_{X-P\ 2}$	Inlet	DP	3.2
$\dot{m}_{Tot-P\ 3}$	DP	Outlet	3.1
$\dot{m}_{PO_4-P\ 3}$	DP	Outlet	3.1
$\dot{m}_{X-P\ 3}$	DP	Outlet	3.2
$\dot{m}_{Tot-P\ 4}$	FS	AS	3.1
$\dot{m}_{PO_4-P\ 4}$	FS	AS	3.1
$\dot{m}_{X-P\ 4}$	FS	AS	3.2
$\dot{m}_{PO_4-P\ 5}$	FS+BGT	AS	C.2
$\dot{m}_{PO_4-P\ 6}$	AS	SST	3.1
$\dot{m}_{Tot-P\ 7}$	SST	NTF+NMBBR+DF	C.5
$\dot{m}_{PO_4-P\ 7}$	SST	NTF+NMBBR+DF	C.3
$\dot{m}_{X-P\ 7}$	SST	NTF+NMBBR+DF	C.4
$\dot{m}_{PO_4-P\ 8}$	SST	NTF	3.1
$\dot{m}_{PO_4-P\ 9}$	SST	NMBBR	3.1
$\dot{m}_{PO_4-P\ 10}$	SST	DF	C.6
$\dot{m}_{PO_4-P\ 11}$	NMBBR	DMBBR	3.1
$\dot{m}_{PO_4-P\ 12}$	NTF	DMBBR	3.1
$\dot{m}_{H_3PO_4}$	NTF	DMBBR	
$\dot{m}_{PO_4-P\ 13}$	NTF+H_3PO_4+NMBBR	DMBBR	C.7
$\dot{m}_{PO_4-P\ 14}$	DMBBR	DF	3.1
$\dot{m}_{Tot-P\ 14.2}$	DMBBR+SST	DF	C.10
$\dot{m}_{PO_4-P\ 14.2}$	DMBBR+SST	DF	C.8
$\dot{m}_{X-P\ 14.2}$	DMBBR+SST	DF	C.9
$\dot{m}_{PO_4-P\ 15}$	DF	Outlet	3.1
$\dot{m}_{Tot-P\ 15}$	DF	Outlet	C.13
$\dot{m}_{X-P\ 15}$	DF	Outlet	3.2
$\dot{m}_{X-P\ 15.2}$	DF	PS	C.12
$\dot{m}_{PO_4-P\ 16}$	SST	AS	3.1
$\dot{m}_{Tot-P\ 17}$	SST	PS-BGT	C.15
$\dot{m}_{PO_4-P\ Bio}$	SST	PS-BGT	C.22
$\dot{m}_{PO_4-P\ Chem}$	SST	PS-BGT	C.23
$\dot{m}_{PO_4-P\ sludge}$	SST	PS-BGT	C.24
$\dot{m}_{X-P\ 17}$	SST	PS-BGT	C.14
$\dot{m}_{Tot-P\ 18}$	SST	BGT	C.16
$\dot{m}_{Tot-P\ 19}$	PS	BGT	C.17
$\dot{m}_{PO_4-P\ 19}$	PS	BGT	C.17
$\dot{m}_{X-P\ 19}$	PS	BGT	C.17
$\dot{m}_{Tot-P\ 20}$	BGT	SST	3.1
$\dot{m}_{Tot-P\ 21}$	BGT BP	BP SP	C.20
$\dot{m}_{Tot-P\ 22}$	SP	SLT	3.1
$\dot{m}_{PO_4-P\ 22}$	SP	SLT	3.1
$\dot{m}_{X-P\ 22}$	SP	SLT	3.2

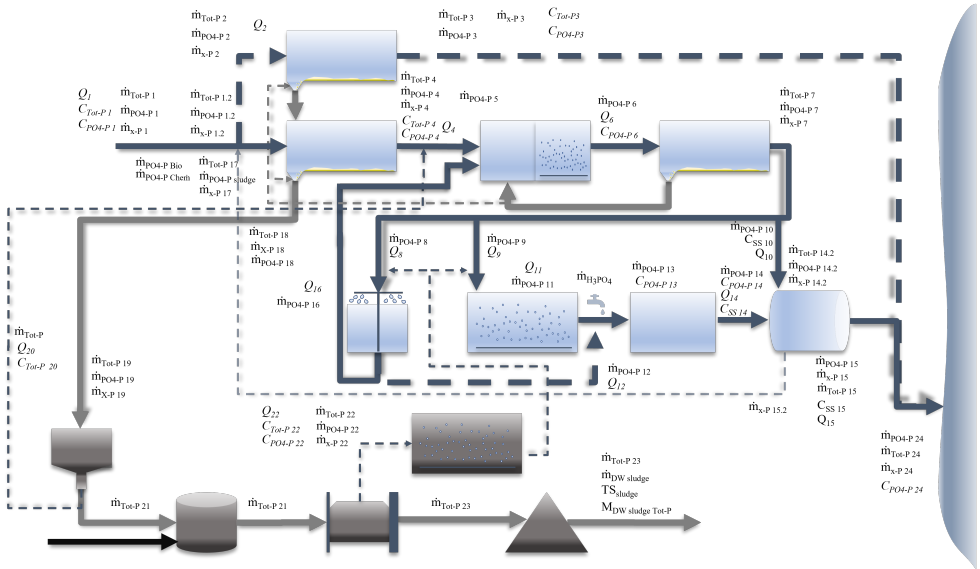
Continued on next page

Table 3.1 – continued from previous page

Tag	From	To	Eq.
$\dot{m}_{Tot-P\ 23}$	SP DS	DS Outlet	C.25
$\dot{m}_{Tot-P\ 24}$	FS	AS	C.26
$\dot{m}_{PO_4-P\ 24}$	FS	AS	C.26
$\dot{m}_{X-P\ 24}$	FS	AS	3.2



(a) *Flows.*



(b) *P mass flow rates, concentrations and flows.*

Figure 3.1: *Schematic with P mass flow rates, concentrations and flows at Rya WWTP.*

Equation 3.1 was applied to obtain the mass flow rates of total phosphorus (Tot-P) and PO_4-P.

$$\dot{m}_{(Tot-P\ x/PO_4-P\ x)} = Q_x \cdot C_{(Tot-P\ x/PO_4P\ x)} \tag{3.1}$$

where:

$\dot{m}_{(Tot-P\ x/PO_4-P\ x)}$ = Mass flow of Tot-P or PO_4-P [kg/day]
Q_x = Wastewater flow [m^3/day]
$C_{(Tot-P\ x/PO_4-P\ x)}$ = Concentration of Tot-P or PO_4-P [kg/m^3]

For mass flow rates with a concentration given the same number in Figure 3.1a, that P concentration is applied. There are no P measurements for the flows in Table 3.2, and the mass flow rates were calculated with the P concentrations in the same table. The P concentration for flow 1, from the inlet, was used for flow 2, as these flows have the same wastewater characteristics. The PO_4-P concentration from the NTFs and NMBBRs into the DMBBRs was used for flows 8, 9, 11, 12, and 16. These concentrations were assumed to be equal as the NTFs and NMBBR are not optimal for PO_4-P reduction, and the incoming P concentration was, therefore, set equal to the outgoing concentration.

Table 3.2: *Concentrations used to calculate mass flows.*

Mass flow	Concentration
$\dot{m}_{Tot-P2}$	C_{Tot-P1}
$\dot{m}_{PO_4-P2}$	C_{PO_4-P1}
$\dot{m}_{PO_4-P8}$	C_{PO_4-P13}
$\dot{m}_{PO_4-P9}$	C_{PO_4-P13}
$\dot{m}_{PO_4-P11}$	C_{PO_4-P13}
$\dot{m}_{PO_4-P12}$	C_{PO_4-P13}
$\dot{m}_{PO_4-P15}$	C_{PO_4-P24}
$\dot{m}_{PO_4-P16}$	C_{PO_4-P13}

The fraction of phosphorus in the wastewater that is not PO_4-P is labelled X-P and the mass flow of that fraction was calculated with Equation 3.2.

$$\dot{m}_{(X-P\ x)} = \dot{m}_{(Tot-P\ x)} - \dot{m}_{(PO_4P\ x)} \tag{3.2}$$

where:

$\dot{m}_{(X-P\ x)}$ = Mass flow of phosphorus fraction that is not PO_4-P [kg/day]

3.3 P-release and uptake batch test

A P-release and uptake batch test was completed to investigate if any Bio-P treatment occurs in the activated sludge treatment step at Rya WWTP. Measurements of VSS and PO_4-P were used to calculate P-release and P-uptake rates that show if Bio-P bacteria are present in the sludge.

3.3.1 Laboratory work

A detailed description of the methodology for the P-release and uptake batch test is given by Borglund (2004, p.72). On March 8^{th} 2022, AS was collected from the aerated zone at Rya WWTP in a two-litre-plastic container from where Suspended Solids (SS) and Volatile Suspended Solids (VSS) were measured. Laboratory personnel at Gryaab performed the SS and VSS analyses following SS-EN 872:2005 (Swedish Standards Institute, 2005b). Two litres of activated sludge were poured into the glass beaker in Figure 3.2 and subjected to an aeration period of one hour, an anaerobic period of three hours, followed by a second aeration period of three hours. The magnetic stirrer was set at 390 rpm during the aerated periods and 540 rpm during the anaerobic period. The test was performed in a room with a constant temperature of 20°C.

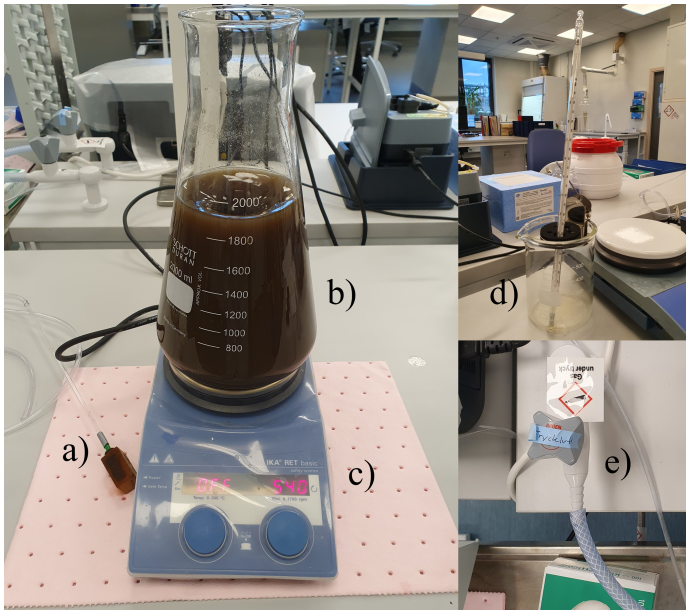


Figure 3.2: *Setup for the P-release and uptake batch test with the following equipment: a) aerator, b) 2L glass beaker, c) magnetic stirrer, d) mercury thermometer, e) compressed air.*

30 ml of sodium acetate (NaAc), with a concentration of 25.625 g/L, was added before the anaerobic period. Laboratory personnel at Gryaab produced the NaAc by mixing acetic acid (CH_3COOH) and sodium hydroxide (NaOH), according to the recipe assembled by the researcher in Table 3.3. The NaOH was in pellet form and diluted with 100 ml of H_2O before mixing 23 ml from the NaOH solution with 10 ml of CH_3COOH. The procedure to compute the recipe is in Section 3.3.2.

Table 3.3: *Recipe for NaAc by mixing NaOH and CH_3COOH.*

Dilution 1		**Dilution 2**	
Compound	Volume/mass	Compound	Volume
H_2O	100 ml	CH_3COOH	10 ml
NaOH	1.8 g	NaOH (aq)	23 ml

Samples for analysis of orthophosphate as phosphorus (PO_4-P) were collected every

20 minutes, which resulted in a total of 23 samples. The researcher prepared the PO_4-P samples for analysis by filtrating 20 ml of activated sludge from the glass beaker with a 50 ml plastic syringe through glass microfiber filters into 100 ml plastic bottles with the equipment seen in Figure 3.4. A plastic tube was put onto the syringe to reach further down the beaker with activated sludge. The mercury thermometer, seen in Figure 3.2, was used to measure the temperature each time a PO_4-P sample was extracted to monitor any drastic temperature changes.

The 100 ml plastic bottles were stored in a fridge with a temperature of 4°C immediately after filtration until completion of the test when they were analysed for PO_4-P by laboratory personnel at Gryaab following SS-EN ISO 6878:2005 (Swedish Standards Institute, 2005a). A SEAL AQ400 Discrete Analyzer, seen in Figure 3.3, is used at Gryaab for PO_4-P analyses.

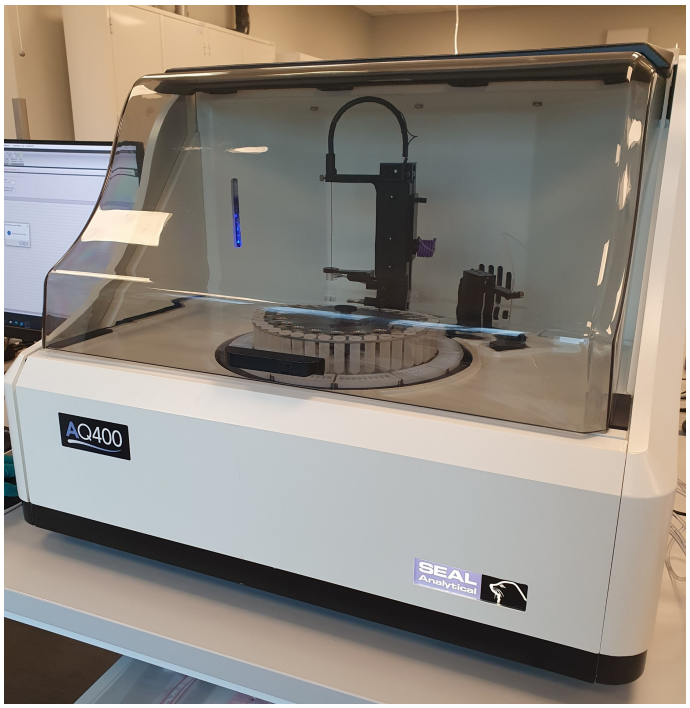


Figure 3.3: *SEAL AQ400 Discrete Analyzer.*

3.3.2 Calculations

Recipe for NaAc

The recipe for producing NaAc, presented in Table 3.3, was put together to reach the concentration 25.625 mg/L of NaAc given in the description by Borglund (2004, p.72). The laboratory at Gryaab had CH_3COOH in 10ml ampules, with a concentration of 62.5 g/L, and limited to using 10 ml for the test due to only having a few ampules in stock. The number of moles of CH_3COOH was computed with Equation 3.3.

$$Number\ of\ moles = \frac{V_{CH_3COOH} \cdot C_{CH_3COOH}}{M_{CH_3COOH}} \tag{3.3}$$

where:

V_{CH_3COOH} = Volume of CH_3COOH [L]
C_{CH_3COOH} = Concentration of CH_3COOH $[\frac{g}{L}]$
M_{CH_3COOH} = Molar mass of CH_3COOH $[\frac{g}{moles}]$

The equilibrium equation for mixing CH_3COOH and NaOH into NaAc is given in Equation 3.4 and shows that 1 mole of NaOH mixed with 1 mole of CH_3COOH produces 1 mole of NaAc, written in its chemical formula $NaC_2H_3O_2$ in Equation 3.4.

$$NaOH + CH_3COOH \rightarrow NaC_2H_3O_2 + H_2O \tag{3.4}$$

With the known number of moles of NaAc, the same as of CH_3COOH, the mass (m) of NaAc was calculated with equation 3.5.

$$m_{NaAc} = M_{NaAc} \cdot number\ of\ moles \tag{3.5}$$

where:

m_{NaAc} = Mass of NaAc [g]
M_{NaAc} = Molar mass of NaAc $[\frac{g}{moles}]$

The volume of NaOH was calculated with equation 3.6 with the known mass of NaAc, the concentration of NaAc, and the volume of CH_3COOH.

$$V_{NaOH} = \frac{m_{NaAc}}{C_{NaAc}} - V_{CH_3COOH} \tag{3.6}$$

where:

V_{NaOH} = Volume of NaOH [L]

NaOH pellets with a molar mass of 40 g/mol, were used. The mass of NaOH was calculated in the same way as in Equation 3.5 but with the molar mass of the NaOH pellets. The volume from Equation 3.6 is the needed volume of NaOH pellets mixed with H_2O, where the NaOH pellets are dissolved and not added to the volume. The concentration of the NaOH solution was calculated with Equation 3.7.

$$C_{NaOH} = \frac{m_{NaOH}}{V_{NaOH}} \tag{3.7}$$

where:

C_{NaOH} = Concentration of NaOH $[\frac{g}{L}]$
m_{NaOH} = Mass of NaOH [g]

The NaOH pellets were diluted with 100 ml H_2O to adapt to the working procedures by laboratory personnel at Gryaab. The mass of NaOH pellets to dilute with 100 ml H_2O was calculated with Equation 3.8 to reach the concentration calculated in Equation 3.7.

$$m_{NaOH_{dilution}} = C_{NaOH} \cdot V_{H_2O} \tag{3.8}$$

where:

V_{H_2O} = Volume of H_2O chosen for dilution [L]
$m_{NaOH_{dilution}}$ = Mass of NaOH for first dilution [g]

The calculated volume of NaOH in Equation 3.6 was the volume extracted from the NaOH dilution and mixed with 10 ml CH_3COOH to reach a concentration of 25.625 mg/L NaAc.

P-release and uptake rates
The PO_4-P concentration in the activated sludge beaker plotted over time combined with Equation 2.3 were used to determine the P-release and uptake rates. A maximum release rate was also calculated as described in Section 2.2.3. To calculate SS and VSS in g/L Equation 3.9 and Equation 3.10, respectively, were used.

$$SS = \frac{m_A - m_B}{V_F} \tag{3.9}$$

where:

SS = Suspended Solids $[\frac{g}{L}]$
m_A = Mass of filter + residue [g]
m_B = Mass of filter [g]
V_F = Volume of sample filtered [L]

$$VSS = \frac{m_A - m_C}{V_F} \tag{3.10}$$

where:

VSS = Volatile Suspended Solids $[\frac{g}{L}]$
m_C = Mass of filter + residue after ignition [g]

3.4 Chemical precipitation with drinking water sludge

Four chemical precipitation tests were performed to investigate the precipitation potential of the DWS that reaches Rya WWTP from Lackarebäck DWTP.

3.4.1 Laboratory work

The same procedure was followed for each of the four precipitation tests, with some variations in the first test conducted on March 11^{th} compared to the three tests conducted on April 11^{th}. The test procedure consisted of the following steps:

1. Water from after the primary settling at Rya WWTP was collected before the start of the tests. Five litres of water were collected in a plastic container for the first test the day before testing by laboratory personnel at Gryaab and stored in a refrigerator at 4°C during the night. For the other tests, 12.5L of water was collected in plastic containers by the researcher on the morning of testing.

2. Analyses of PO_4-P and Tot-P were done the day before testing per SS-EN ISO 6878:2005 (Swedish Standards Institute, 2005a) for the first test, while the same analyses were performed on the same day of testing for the remaining tests. The researcher prepared the samples for PO_4-P analysis by filtration into plastic bottles with the equipment seen in Figure 3.4.

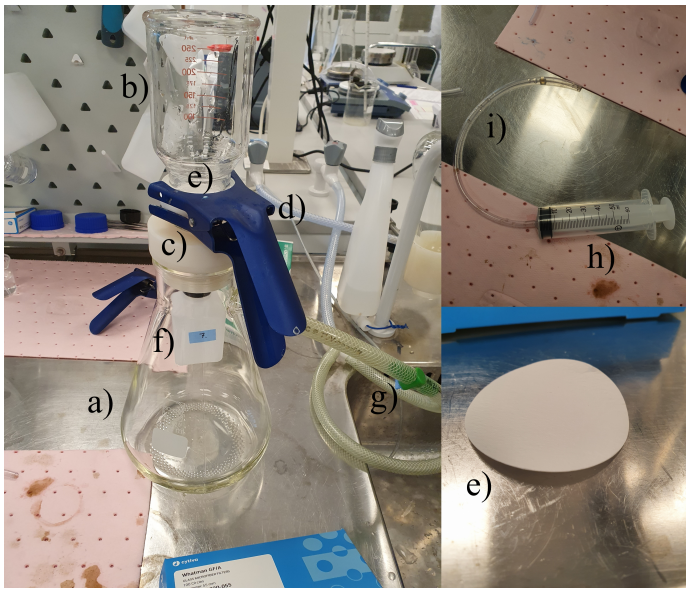


Figure 3.4: *Filtration equipment to prepare for PO_4-P analysis: a) Büchner flask, b) glass filter cup, c) cylinder funnel, d) clamp, e) 55 mm glass microfiber filter, f) 100 ml plasic bottle, g) plastic tube connected to air suction, i) plastic tube, h) 50 ml plastic syringe.*

3. The drinking water sludge used for all tests was collected by personnel at Lackarebäck on March 7^{th} and arrived at Rya WWTP on March 10^{th} where it was stored in a refrigerator at 4°C. Total solids (TS) were measured on the sludge by laboratory personnel at Gryaab following SS 28113 (Swedish Standards Institute, 1981) on March 10^{th} for the first attempt and April 11^{th} for the remaining ones. The pH of the sludge was measured on the same dates by laboratory personnel per SS-EN ISO 10523:2012 (Swedish Standards Institute, 2012).

4. pH analysis of the primary settled water (PS) was done for each beaker before the start of the first test on March 11^{th}, while it was measured from one of the plastic containers on the morning of April 11^{th} for the remaining tests. The pH analyses were performed by laboratory personnel at Gryaab following the same standard as with the pH analyses of the DW sludge.

5. 0.9 litres of phosphoric acid (H_3PO_4) solution was used in the second beaker in test 1 instead of primary settled water to investigate the phosphorus removal capacities of the DW sludge further. The phosphoric acid solution was mixed from water and phosphoric acid by laboratory personnel at Gryaab according to the recipe in Table 3.4 to reach a desired PO_4-P concentration of 11.4 mg/L. The calculations are presented in Section 3.4.2.

Table 3.4: *Mixing recipe for the H_3PO_4 solution.*

Dilution 1		**Dilution 2**	
Compound	Volume	Compound	Volume
H_2O	200 ml	H_2O	1 L
H_3PO_4	1 ml	H_3PO_4 (aq)	5 ml

6. A sample for PO_4-P analysis was collected before test 1 to verify the PO_4-P concentration of the phosphoric acid solution. A pH sample was also collected.

7. The temperature of the drinking water sludge was measured right before the start of the tests with a mercury thermometer, seen in Figure 3.2.

8. Drinking water sludge was pipetted in the volumes and with the molar ratios between Al and PO_4-P presented in Table 3.5 into four one-litre glass beakers containing primary settled water, except for beaker 2 in test 1, with five-minute intervals for each test. The calculations of the sludge volumes and molar ratios are in Section 3.4.2.

Table 3.5: *Molar ratios between Al and PO_4-P, sludge volumes, and Al mass for the four precipitation tests.*

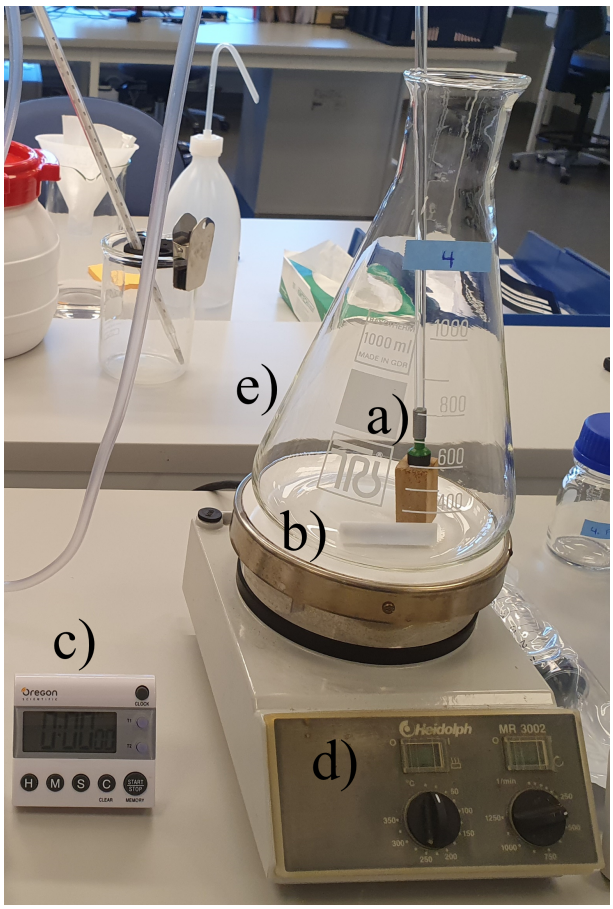
Test 1			
Beaker	Molar ratio Al:PO_4-P	Sludge volume ml	Al mass mg
1 - PS	0:1	0	0
2 - H_3PO_4	3.3:1	81.68	32.33
3 - PS	3:1	10.03	5.26
4 - PS	1:1	3.34	1.75
Test 2			
Beaker	Molar ratio Al:PO_4-P	Sludge volume ml	Al mass mg
1 - PS	0:1	0	0
2 - PS	2:1	3.34	2.65
3 - PS	6.1:1	10.03	7.94
4 - PS	12.2:1	20.05	15.88
Test 3 and 4			
Beaker	Molar ratio Al:PO_4-P	Sludge volume ml	Al mass mg
1 - PS	0:1	0	0
2 - PS	4.1:1	6.68	5.29
3 - PS	8.2:1	13.37	10.59
4 - PS	10.2:1	16.71	13.24

9. The setup for one beaker during the tests is in Figure 3.5. The magnetic stirrers were started at 200 rpm for 120 seconds immediately after the addition of

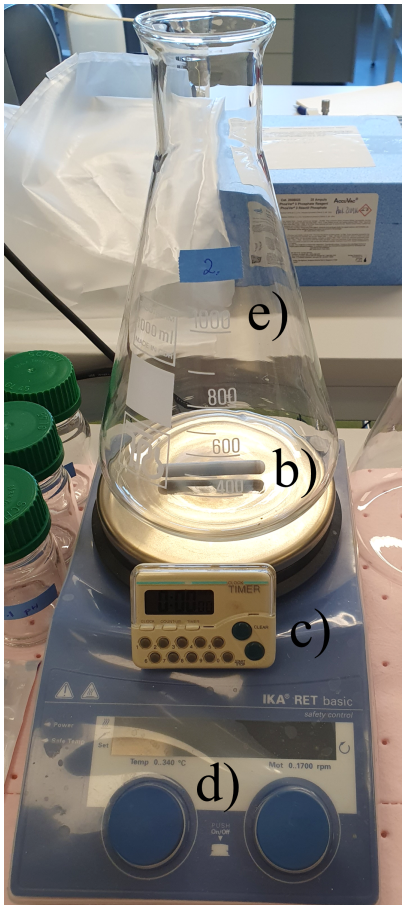
sludge to start the flocculation process. The beakers were aerated during this time period in the first test.

10. After 120 seconds, the stirrer speed was lowered to 50 rpm for 20 minutes. The water temperature was measured after lowering the speed to 50 rpm. The magnetic stirrers were turned off after a flocculation time of 22 minutes and a settling period of an hour started.

11. The water temperature in the beakers was measured, and samples collected for analysis of PO_4-P, Tot-P and pH at the end of the settling period.



(a) *Setup precipitation test 1.*



(b) *Setup precipitation test 2 to 4.*

Figure 3.5: *Setups for precipitation tests with the following equipment: a) aerator, b) magnet, c) timer, d) magnetic stirrer, e) one-liter glass beaker.*

3.4.2 Calculations

Test 1 - Sludge volume

To reach the desired molar ratios for Test 1, given in Table 3.5, the sludge volume addition to each beaker was calculated before test start. Equation 3.11 was used to calculate the number of moles PO_4-P in each beaker.

$$Number\ of\ moles_{PO_4-P} = \frac{C_{PO_4-P}}{M_P} \cdot V_x \tag{3.11}$$

where:

C_{PO_4-P} = Concentration of PO_4-P measured before start of test $[\frac{g}{L}]$
M_P = Molar mass of P $[\frac{g}{moles}]$
V_x = Volume of primary settled water or phosphoric acid solution

Molar ratios between Al and PO_4-P, presented in Table 3.5, were chosen for each beaker to calculate the number of moles of Al with equation 3.12.

$$Number\ of\ moles_{Al} = molar\ ratio_{Al:PO_4-P} \cdot number\ of\ moles_{PO_4-P} \tag{3.12}$$

To calculate the mass of Al added Equation 3.13 was used.

$$m_{Al} = M_{Al} \cdot number\ of\ moles_{Al} \tag{3.13}$$

where:

m_{Al} = Mass of Al [g]
M_{Al} = Molar mass of Al $[\frac{g}{moles}]$

To calculate the concentration of Al of TS in the drinking water sludge data from Lackarebäck provided for the year 2021 by environmental engineer L.Wellsjö at Gryaab (personal communication, February 21, 2022) used in Equation 3.14.

$$C_{Al\ of\ TS} = \frac{m_{Al\ Lackarebäck}}{TS_{Lackarebäck}} = \frac{105.88}{545.4} \tag{3.14}$$

where:

$C_{Al\ of\ TS}$ = Concentration of Al of TS in the drinking water sludge
$m_{Al\ Lackarebäck}$ = Mass of Al from Lackarebäck 2021 [tonnes]
$m_{TS\ Lackarebäck}$ = Mass of TS from Lackarebäck 2021 [tonnes]

The mass of TS in the sludge added to the beaker was then calculated with Equation 3.15.

$$m_{TS} = \frac{m_{Al}}{C_{Al\ of\ TS}} \tag{3.15}$$

where:

m_{TS} = Mass of TS in the beaker [g]

The sludge addition volume into the beaker, to reach the desired molar ratio, was calculated with equation 3.16. As the drinking water sludge has a low TS, it is assumed to have the same density as water.

$$V_{Sludge} = \frac{m_{TS}}{TS_{measured} \cdot \rho_{sludge}} \tag{3.16}$$

where:

V_{Sludge} = Volume of sludge to add in the beaker [l]
$TS_{measured}$ = Measured TS of the drinking water sludge at Gryaab [%]
ρ_{sludge} = Density of the drinking water sludge

Test 1 - Phosphoric acid solution
A phosphoric acid with 85% H_3PO_4 concentration of the mass and H_2O was used to mix the H_3PO_4 solution used in the second beaker in test 1. First, the mass of H_3PO_4 in the first dilution was calculated with Equation 3.17.

$$m_{H_3PO_4} = \rho_{H_3PO_4} \cdot V_{H_3PO_4} \cdot C_{H_3PO_4} \tag{3.17}$$

where:

$m_{H_3PO_4}$ = Mass of H_3PO_4 [g]
$\rho_{H_3PO_4}$ = Density of H_3PO_4 $[\frac{g}{L}]$
$V_{H_3PO_4}$ = Volume of $_{H_3PO_4}$ [L]
$C_{H_3PO_4}$ = Concentration of $_{H_3PO_4}$ [%]

The concentration of P in the H_3PO_4 solution was then calculated with Equation 3.18.

$$C_P = \frac{\frac{M_P}{M_{H_3PO_4}} \cdot m_{H_3PO_4}}{V_{(H_3PO_4+H_2O)}} \tag{3.18}$$

where:

C_P = Concentration of $_{H_3PO_4}$ $[\frac{g}{L}]$
M_P = Molar mass of P $[\frac{g}{mol}]$
$M_{H_3PO_4}$ = Molar mass of P $[\frac{g}{mol}]$
$V_{(H_3PO_4+H_2O)}$ = Volume of H_3PO_4 and H_2O [L]

For the second dilution the same calculations were done with varying volumes of water added to reach a concentration of P around 11 mg/L.

Test 2-4 - Molar ratio
The PO_4-P analysis of the primary settled water used for tests 2-4 was performed the same day as the tests, and the results were delivered after completing the tests. Therefore, the same concentration of PO_4-P as in test 1 was assumed to calculate the sludge volumes before starting the tests. The actual molar ratio in each beaker was calculated after testing. First, the mass of TS in the beakers was calculated from the added sludge volume with Equation C.25.

$$m_{TS} = V_{Sludge} \cdot TS_{measured} \cdot \rho_{sludge} \tag{3.19}$$

The mass of aluminium added was calculated next with Equation 3.20.

$$m_{Al} = m_{TS} \cdot C_{Al\ of\ TS} \tag{3.20}$$

The number of moles of aluminium was then calculated with Equation 3.21.

$$number\ of\ moles_{Al} = \frac{m_{Al}}{M_{Al}} \tag{3.21}$$

The number of moles of PO_4-P was calculated with Equation 3.11 before the molar ratio between aluminium and PO_4-P was calculated with Equation 3.22.

$$molar\ ratio_{Al:PO_4-P} = \frac{number\ of\ moles_{Al}}{number\ of\ moles_{PO_4-P}} \tag{3.22}$$

4

Results

This chapter presents the P mass balance at Rya WWTP and the results from the P-release and uptake test and the chemical precipitation tests with DWS.

4.1 Mass balance

As seen in Figure 4.1, the largest removal of PO_4-P occurs over the AS basins and SSTs as it transfers from being dissolved into particulate matter either chemically or biologically. Over these steps, a significant reduction in X-P can also be observed as suspended solids settle in the SST. The mass flow rate of PO_4-P reduces over the DMBBRs, before reaching the outflow. A reduction in the sludge flow is observed over the screw presses. The fractions of PO_4-P and X-P can not be calculated for mass flows 21 and 22, as there is no measurement of PO_4-P in the reject water from the BGT or in the dewatered sludge. Since the fraction of PO_4-P in the reject from the BGT is not measured, it can not be subtracted from the mass flow of PO_4-P between the PS and the AS basins. This explains the higher value between these processes compared to the mass flow of the inlet.

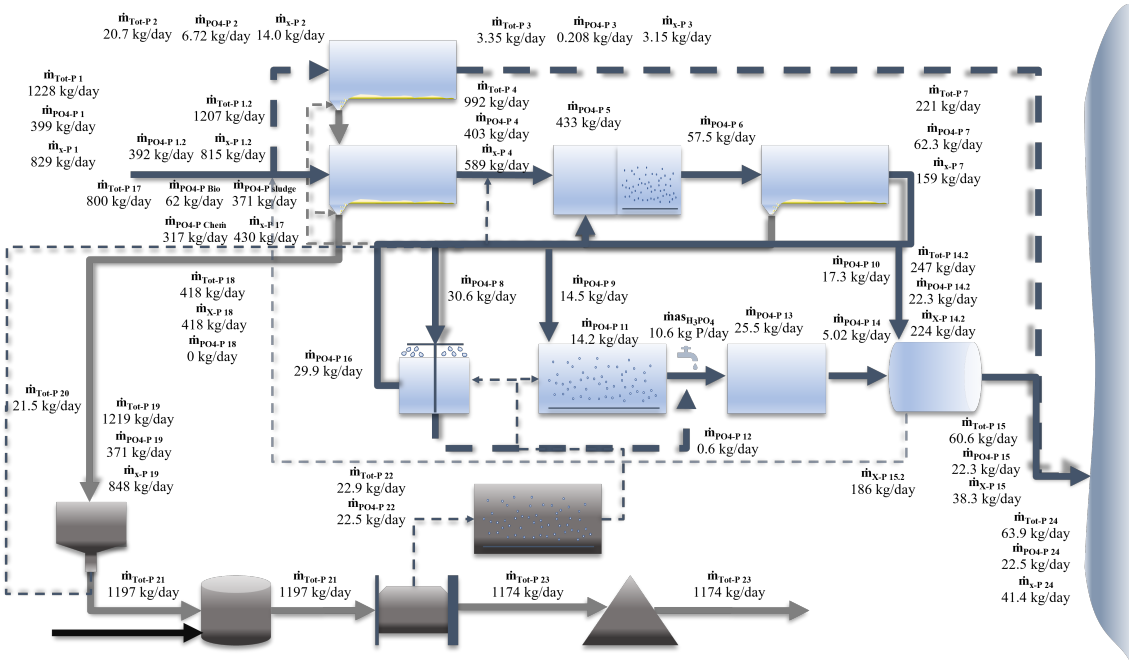


Figure 4.1: *P mass balance at Rya WWTP.*

The total outflow of P in the water was calculated as the sum of flows from the disc filters and direct precipitation in Figure 4.1, but measurements at the outlet can also be used to verify the results for the mass balance. As seen in Table 4.1

the calculated values vary from -0.067% to 2.8% compared to the P flows calculated from measurements at the outlet.

Table 4.1: *Comparison between calculated values at the outlet and measured values.*

Mass flow	**Mass flow rate measurements** kg P/day	**Mass flow rate balance** kg P/day	**Difference** %
$\dot{m}_{Tot-P\ 24}$	63.3	63.9	0.92
$\dot{m}_{PO_4-P\ 24}$	21.9	22.5	2.8
$\dot{m}_{X-P\ 24}$	41.5	41.4	-0.067

Table 4.2 shows a total reduction of all P fractions of around 95%, where over 85% of that reduction occur between the inlet and the secondary settling. About 15% of the total reduction takes place from the secondary settling until the water outlet of the plant.

Table 4.2: *Reduction of P within Rya WWTP.*

Inlet - Outlet water			
	$\dot{m}_{Tot-P}$	$\dot{m}_{PO_4-P}$	$\dot{m}_{X-P}$
Reduction [kg P/day]	1174	387	787
Reduction* [%]	94.8	94.5	95.0
Inlet - Outlet of SST			
	$\dot{m}_{Tot-P}$	$\dot{m}_{PO_4-P}$	$\dot{m}_{X-P}$
Reduction [kg P/day]	1006	337	669
Reduction*[1] [%]	85.7	87.0	85.0
Outlet of SST - Outlet water			
	$\dot{m}_{Tot-P}$	$\dot{m}_{PO_4-P}$	$\dot{m}_{X-P}$
Reduction [kg P/day]	168	50.4	118
Reduction*[1] [%]	14.3	13.0	15.0
Inlet DP - Outlet DP			
	$\dot{m}_{Tot-P}$	$\dot{m}_{PO_4-P}$	$\dot{m}_{X-P}$
Reduction [kg P/day]	17.3	6.51	10.8
Reduction [%]	83.8	96.9	77.5

**Reduction from the inlet to the outlet as a percentage of the incoming P flow.*
**[1] Reduction from the points given as a percentage of the P reduction from inlet to outlet.*

4.2 P-release and uptake batch test

As seen in Figure 4.2, a release of PO_4-P takes place during the three-hour anaerobic period of the test, increasing the PO_4-P concentration from around 0.2 mg/L to 10.6 mg/L. A small PO_4-P release is noted during the first aerobic period as well. The concentration of PO_4-P increased for the first 20 minutes of the final aerobic period

before decreasing the remaining time. The full results with PO_4-P concentrations and temperature measurements, that shows a temperature increase from 13°C to 20°C during the test, are presented in Table D.1 in Appendix D.

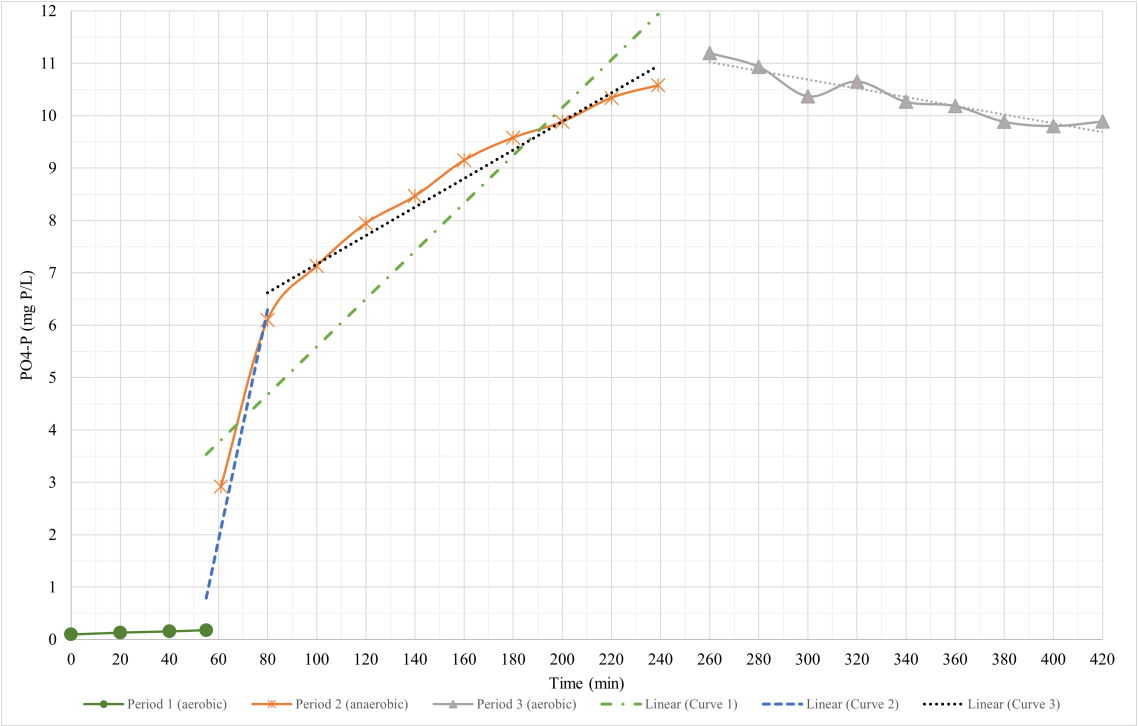


Figure 4.2: *Measured PO_4-P concentrations over time during the P-releae and uptake batch test.*

The calculated P-release rates, presented in Table 4.3 for the curves 1-3 in Figure 4.2, show that the results can vary depending on what part of the curve is used. By classifying the rates according to the system in Table 2.3, the release rates when using curve 1 and 3, as well as the uptake rate, indicates a moderate quality Bio-P sludge at Rya WWTP. Curve 2 indicates a good quality Bio-P sludge.

Table 4.3: *P-release and uptake rates for the batch test.*

Type	Unit	Rate	Sludge Quality
$V_{release\ Curve\ 1}$	$\frac{mgP}{gVSS \cdot h}$	1.4	Moderate
$V_{release\ Curve\ 2}$	$\frac{mgP}{gVSS \cdot h}$	5.8	Good
$V_{release\ Curve\ 3}$	$\frac{mgP}{gVSS \cdot h}$	0.68	Moderate
$V_{maximum\ release}$	$\frac{mgP}{gVSS}$	4.2	
V_{uptake}	$\frac{mgP}{gVSS \cdot h}$	0.20	Moderate

A change in colour of the samples collected for PO_4-P analysis was observed, seen in Figure 4.3, after the addition of the NaAc. The activated sludge darkened between samples 4 to 6 and remained the same colour throughout the test. The filtration capacity through the glass microfiber filters also changed with the NaAc addition. Three filters were required from the anaerobic period until the end instead of two filters, which were required during the first aerobic period.

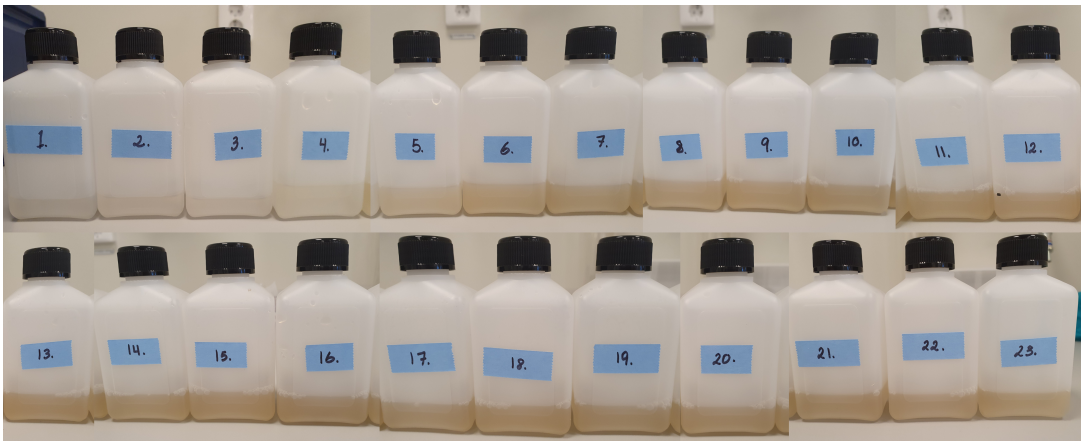
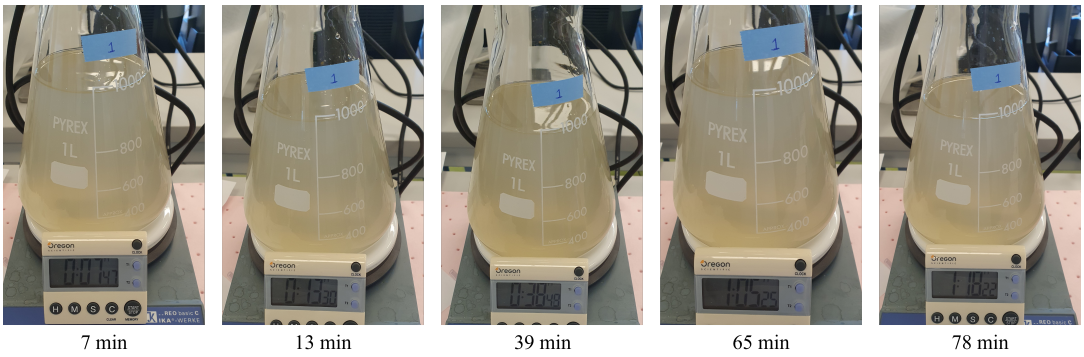


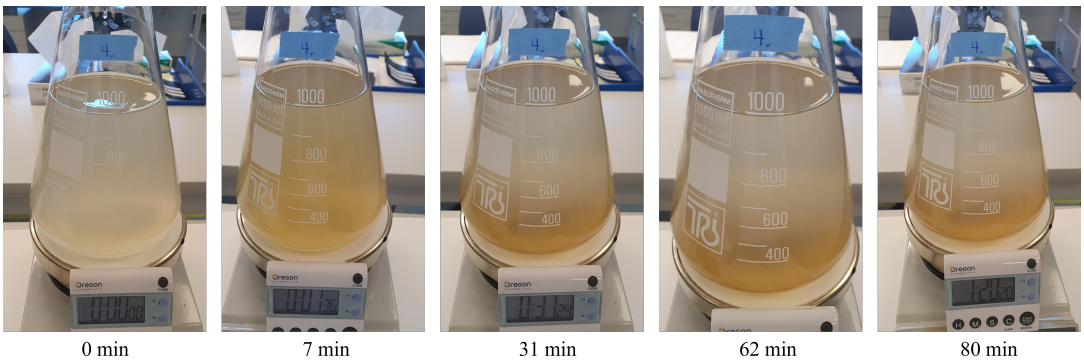
Figure 4.3: *Samples collected in 100ml plastic bottles for analysis of PO_4-P.*

4.3 Chemical precipitation with DWS

There was no noticeable sedimentation in the reference beakers, as shown for the reference beaker in test 4 in Figure 4.4a. Figure 4.4b shows the process for beaker 4 in test 4, where the DWS sinks to the bottom as time passes. As seen in Table E.1, there were no drastic changes in temperature during the test or pH variations with sludge addition to the beakers.



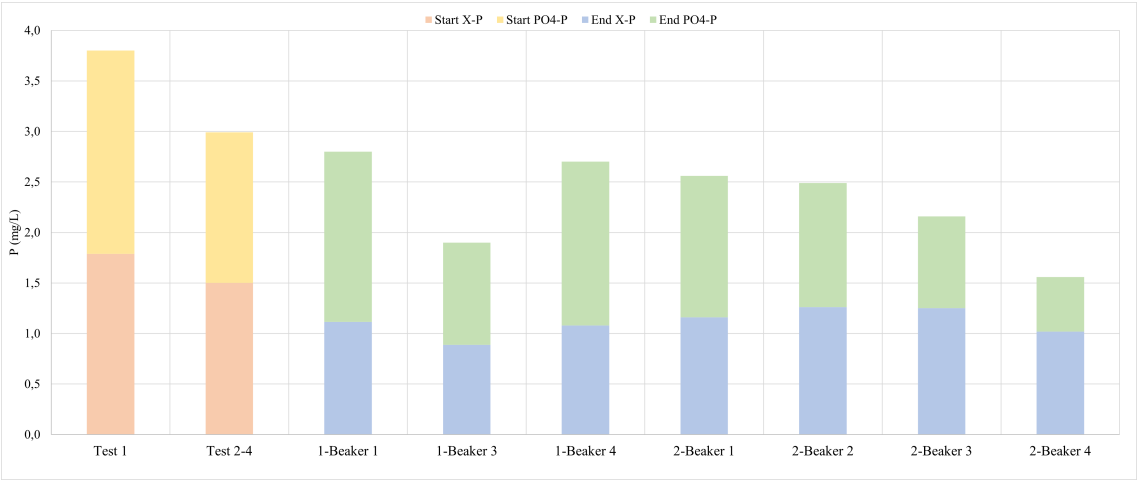
(a) *Test 4 - Beaker 1.*



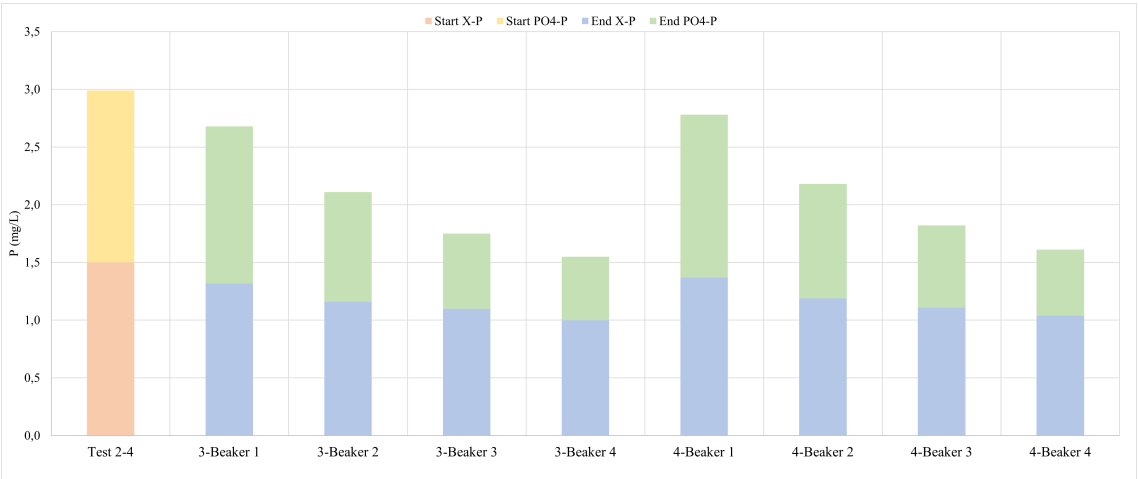
(b) *Test 4 - Beaker 4.*

Figure 4.4: *The precipitation process in beakers 1 and 4 during test 4.*

Figure 4.5 shows the fractions of PO_4-P and X-P in each beaker before the test start and at the end of the test. A higher addition of sludge will have a larger impact on the reduction of PO_4-P than X-P. However, the reduction of X-P is higher in the beakers with more sludge addition when looking at tests 1, 3 and 4. For test 2, the concentration of X-P has reduced equally in beakers 2 and 3 even though three times as much sludge was added to beaker 3. The results show that even as no visible sedimentation was noted in the reference beakers, a significant P reduction occurred. The P concentrations at the start and end of the tests for PO_4-P and Tot-P are also presented in Table E.1.



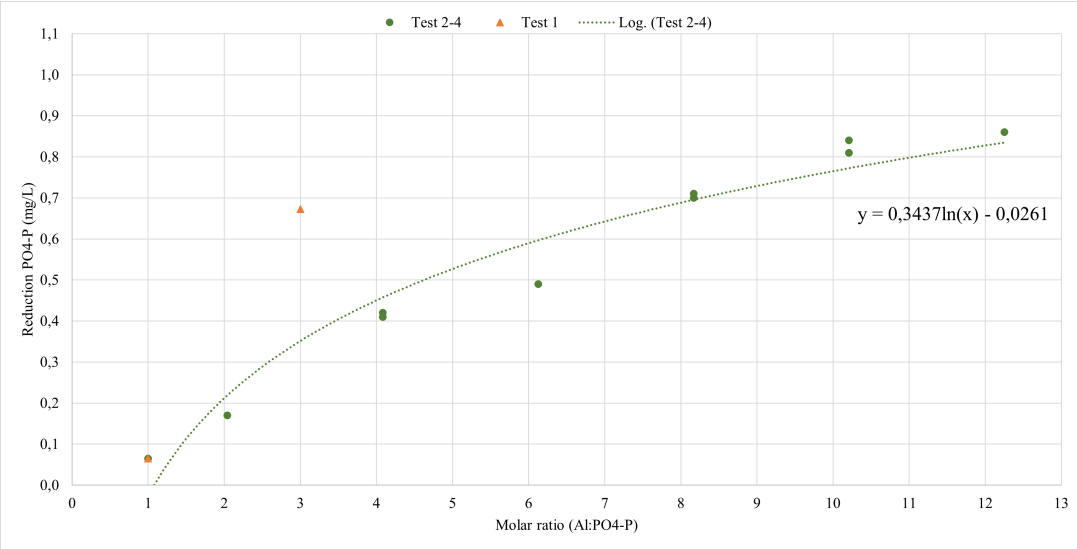
(a) *Test 1 and 2.*



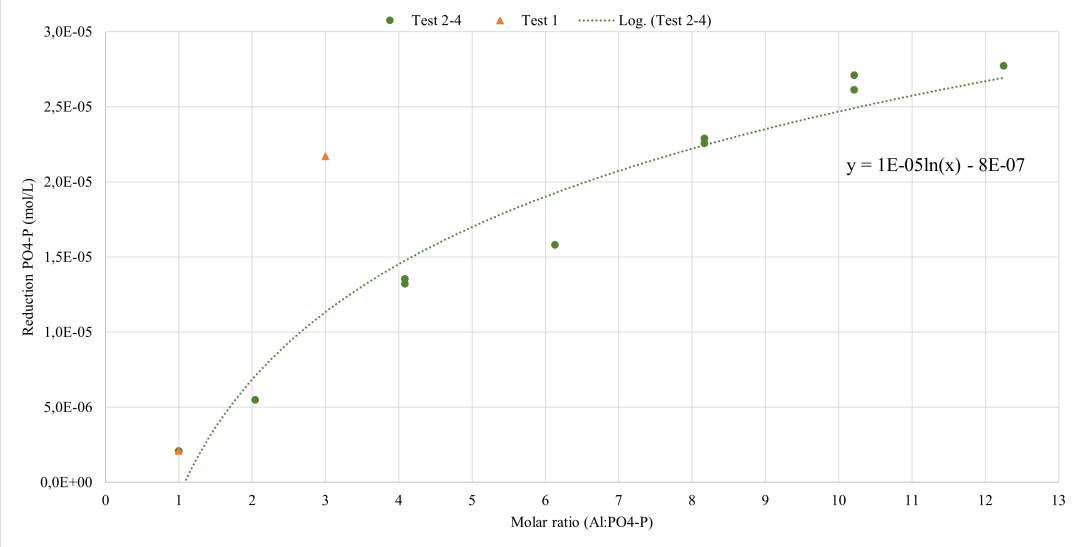
(b) *Test 3 and 4.*

Figure 4.5: *Concentration of P fractions in the beakers before the start and at the end of the tests.*

As seen in Figure 4.6, the reduction of PO_4-P in mg/L or mol/L in the wastewater increases with an increased molar ratio between Al and PO_4-P. At a molar ratio of ca. 13 Al: PO_4-P, there is an implication that the increase rate decelerates and, hence, a logarithmic trendline is plotted. The PO_4-P reduction from test 1 at a molar ratio of 3 that deviates from the other results is not included in the logarithmic trendline.



(a) *Reduction of PO_4-P in mg/L as a function of molar ratio Al:PO_4-P.*



(b) *Reduction of PO_4-P in mol/L as a function of molar ratio Al:PO_4-P.*

Figure 4.6: *Reduction of PO_4-P as a function of molar ratio from the chemical precipitation tests.*

The expected reduction of PO_4-P at Rya WWTP due to DWS with the current molar ratio between Al and PO_4-P in the incoming wastewater at Rya WWTP is seen in Table 4.4. The reduction is slightly higher for Figure 4.6a with 17.5 tonnes/year than 4.6b with 15.6 tonnes/year.

Table 4.4: *Reduction of PO_4-P for the graph in Figure 4.6.*

Graph	**Molar ratio**	**Wastewater volume**	**Reduction PO_4-P**	**Reduction PO_4-P**
	Al:PO4-P	ML	µg/L	tonnes/year
4.6a	1.60	129	135	17.5
4.6b	1.60	129	121	15.6

Figure 4.7 shows the relationship between the Tot-P at the end of the test and the added Al, from which the amount of Al needed to reach a concentration of 0.3-0.5 mgP/L in the effluent was calculated to be 28.0-30.6 mg. From this, a molar ratio between the starting concentration of 2.99 mg P/L for tests 2-4 and the Al addition was calculated to 10.8-11.85:1 Al:Tot-P. The molar ratio between incoming Tot-P and Fe from the addition of $FeSO_4$ at Rya WWTP was calculated to be 0.58:1.

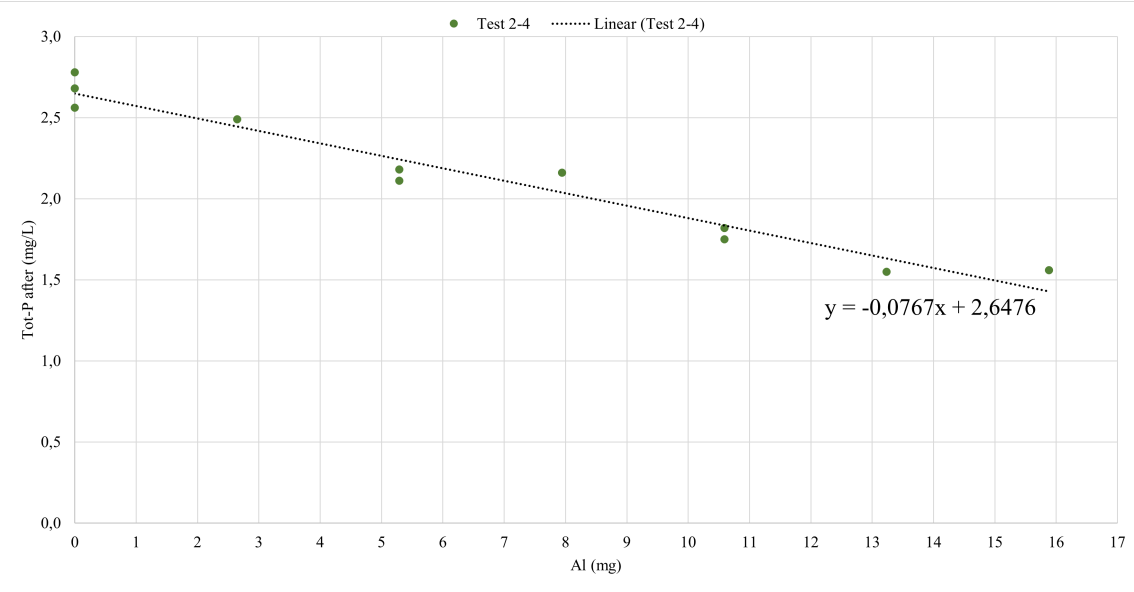


Figure 4.7: *Relationship between Tot-P concentration after the test and Al addition.*

If the flow of DWS to Rya WWTP would stop it would lead to a higher load of PO_4-P reaching the plant that needs treatment. As iron is used as a precipitation chemical to remove PO_4-P at Rya today, Table 4.5 shows how the dosage of iron would have to increase if the reductions from DWS presented in Table 4.4 is assumed to stop. This would lead to an increased iron dosage of ca. 10.3% to 11.6% compared to 2021, depending on the equation used. As the iron is not dosed in its pure form, but as $FeSO_4$, it would lead to a yearly increase of $FeSO_4$ with 308-345 tonnes and a price increase of around 200,000 SEK.

Table 4.5: *Current dosage of Fe and $FeSO_4$ for P removal, required dosage, and change in cost of purchasing increased amounts of $FeSO_4$ if no DWS was sent to Rya WWTP.*

	Unit	**2021**	**Figure 4.6a**	**Figure 4.6b**
Fe	tonnes/year	474	529	536
Increase	tonnes/year		54.9	49.0
Increase	%		11.6	10.3
$FeSO_4$.7H2O	tonnes/year	2798	3323	3286
Increase	tonnes/year		345	308
Cost	MSEK/year	1.91	2.13	2.10
Increase	SEK/year		221,000	197,000

As can be seen in Table 4.6, the DWS has a larger impact on the metal loads at the plant than $FeSO_4$. Removing the DWS would reduce the load of silver, copper,

mercury, and lead from 82 to almost 100% compared to 2021. The only metal loads that noticeably increase with an increased load of $FeSO_4$ are manganese, arsenic, cobalt, and bismuth, which are the metals not measured for the DWS, as can be seen in Table E.2 in Appendix E.

Table 4.6: *Change in the input of metal amounts through increased $FeSO_4$-P dosage and no DWS.*

		2021	Figure 4.6a		Figure 4.6b	
Metal	**Unit**	**Total**	**Total**	**Diff.**	**Total**	**Diff.**
Manganese, Mn	kg	1180	1317	11.6%	1302	10.3%
Antimony, Sb	kg	2.85	0.872	-69.4%	0.862	-69.8%
Arsenic, As	kg	0.781	0.872	11.6%	0.862	10.3%
Lead, Pb	kg	12.6	2.21	-82.6%	2.18	-82.7%
Cadmium, Cd	kg	0.598	0.437	-26.9%	0.432	-27.7%
Cobalt, Co	kg	110	123	11.6%	122	10.3%
Copper, Cu	kg	53.4	2.12	-96.0%	2.09	-96.1%
Chromium, Cr	kg	29.5	16.9	-42.5%	16.7	-43.2%
Mercury, Hg	g	63.0	3.20	-94.9%	3.17	-95.0%
Nickel, Ni	kg	136	136	0.10%	134	-1.02%
Silver, Ag	g	393	1.32	-99.7%	1.31	-99.7%
Zin, Zn	kg	151	88.6	-41.4%	87.6	-42.1%
Bismuth, Bi	kg	0.831	0.928	11.6%	0.917	10.3%

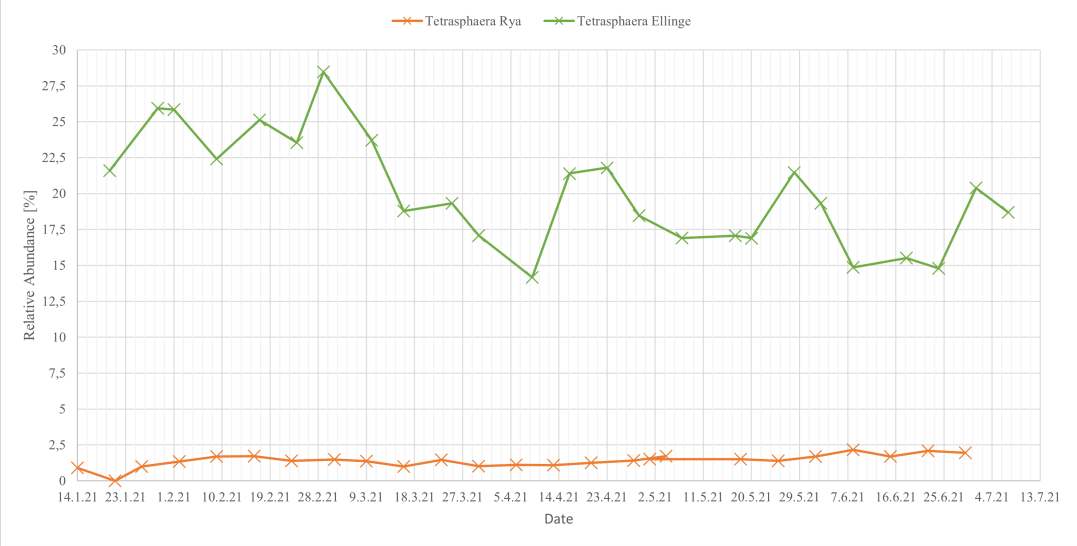
Metal loads from the $FeSO_4$ are not included in Table 2.6, but as seen in Table 4.7, the addition of $FeSO_4$ increases the nickel (Ni) load by around 23% compared to the incoming load for 2021. For the other metals measured at the inlet, the increase from the addition of $FeSO_4$ is not as significant. Removing DWS from the incoming wastewater allows a reduction between around 0.5-3.6% for the metal loads in 2021 presented in Table 4.7. The added amounts of $FeSO_4$, as shown in Table 4.5, combined with DWS removal, would not lead to any drastic changes in metal loads as it at most would reduce loads of chromium with ca. 3% lead and cadmium with 2%.

Table 4.7: *Change in metal concentrations when adding more $FeSO_4$ and removing the incoming DWS.*

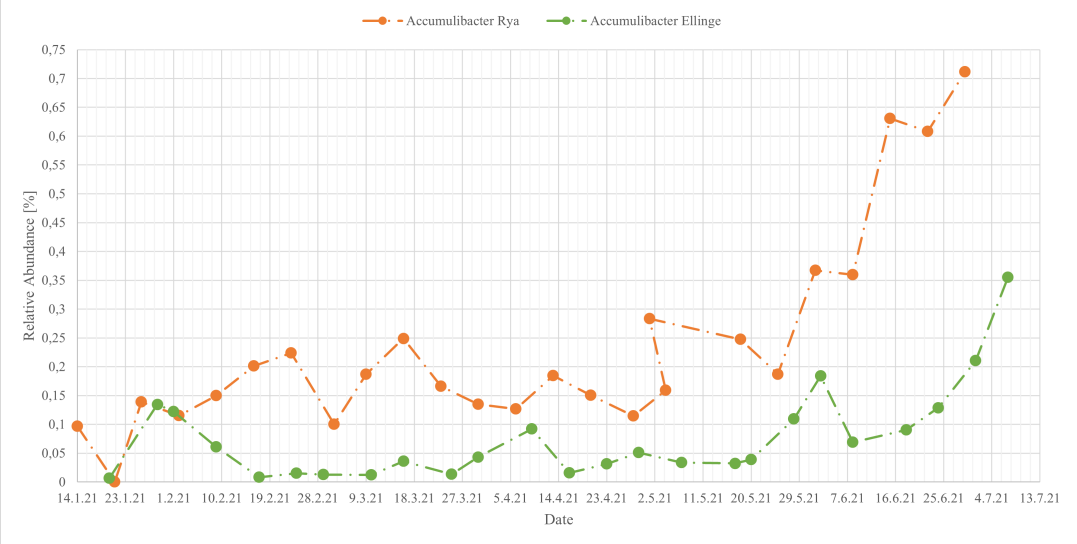
			Pb	**Cd**	**Cu**	**Cr**	**Hg**	**Ni**	**Zn**
	DWS	% of In	2.56	1.34	0.55	3.59	0.45	2.65	0.55
2021	In+ FeSO4	kg	419	15.8	9288	413	13.3	650	13102
	In+ FeSO4	% of In	100	103	100	104	100	123	101
Figure 4.6a	In+ FeSO4-DWS	kg	409	15.6	9237	401	13.2	650	13040
	In+ FeSO4-DWS	% of In	98.0	102	99.5	101	100	123	100
Figure 4.6b	In+ FeSO4-DWS	kg	409	15.6	9237	400	13.2	648	13039
	In+ FeSO4-DWS	% of In	98.0	101	99.5	101	99.6	123	100

4.4 MiDAS Sweden

As can be seen in Figure 4.8a and 4.8b, there is a higher percentage of Tetrasphera than Accumulibacter in the total bacteria content in the AS process at Rya WWTP. It also shows that even though Ellinge WWTP is not designed for bio-P treatment, its AS process consists of around 20% Tetrasphera, which is significantly higher than Rya WWTP with around 2% Tetrasphera. However, these graphs show that Tetrasphera and Accumulibacter are present in the AS at Rya WWTP. Table B.1 and B.2 shows the levels of PAOs are higher than the presence of competing bacteria, GAOs, for both of these WWTPs. This is the case even if Accumulibacter would act as GAOs.



(a) *Presence of Tetrasphera at Rya and Ellinge WWTPs.*



(b) *Presence of Accumulibacter at Rya and Ellinge WWTPs.*

Figure 4.8: *Presence of Tetrasphera and Accumulibacter at Rya and Ellinge WWTP as a percentage of the total bacteria content.*

5
Discussion

This chapter covers the uncertainties and limitations of the P mass balance and laboratory experiments performed in this thesis, reflections on the P removal at Rya WWTP and suggestions for further research to extend the work of this thesis.

5.1 Uncertainties and Limitations

Several assumptions affecting the results in Chapter 4 and other limitations are discussed in this section.

5.1.1 Mass balance

The mass balance in Figure 4.1 and Table 4.1 shows a significant reduction of PO_4-P and Tot-P over the AS basins and SSTs after the addition of $FeSO_4$. Around 15% of the incoming Tot-P and PO_4-P passes through the chemical precipitation step. Removing all of the P is, however, not desirable at this stage as the denitrification process in the DMBBR is fueled by P. Additional P is sometimes added in the form of H_3PO_4 before this step to achieve a desired denitrification capacity of the DMMBR. The lack of PO_4-P measuring points out of the SSTs into the NTFs, NMBBRs, and DFs is uncertain as there are no measurement points until the inlet of the DMBBRs. The assumption that PO_4-P concentrations at the inlet and outlet of these processes are equal to the one at the inlet of the DMBBRs was done on the assumption that no PO_4 reduction occurs over the nitrifying processes. However, since the nitrifying processes are biological, bacteria affecting the concentration of P may be present during these processes. This effect was deemed small enough to be unaccounted for. With a measuring point after the SSTs, it would be possible to determine these flows more precise compared to this thesis. The lack of measuring points after the SSTs into the DFs and out of the DFs also causes uncertainty. These flows are calculated backwards from the PO_4-P concentration in the total outgoing wastewater flow. The results become less reliable as it is impossible to perform calculations in both directions and compare results.

The lack of measurements of PO_4-P at the sludge outlet and reject water from the GBTs affected the mass flow rate of PO_4-P in the reject water circulated into the plant, contra the mass flow rate of PO_4-P in that reaches the sludge outlet. The flow of PO_4-P reaching the sludge outlet is lower compared to at the inlet to the GBTs, as there is a measuring point going into the sludge liquid treatment (SLT) from the screw press that makes it possible to determine that PO_4-P flow. There is, however, no measuring point out of the SLT into the NTF and NMBBR. Since there is a lack of measuring points in these processes, it was determined to not calculate the flow of PO_4-P out from the SLTt. With the lack of PO_4-P measuring points in the sludge

flow, it was not possible to calculate the flow of X-P leaving the plant with the sludge.

Bio-P reduction over AS and DMBBR was compared as they contain the same type of bacteria, heterotrophs. The ratio between COD and biologically bound P may be higher in AS since there is a higher ratio between COD and incoming PO_4-P into AS than DMBBR, 100:1.5 compared to 100:0.26. A ratio between COD and biologically bound PO_4-P of 100:1 was chosen to investigate this possibility. This ratio resulted in a higher reduction of PO_4-P through bio-P removal than chemical precipitation. It is still likely that the ratio is higher than 100:0.26 over the DMBBR but lower than 100:1 but as there are both chemical and biological reactions taking place in the AS basins and SSTs, combined with the design for chemical P-removal, it was deemed the most accurate to use the same ratio and get a more conservative answer for the biologically bound PO_4-P. The data from the MiDAS Sweden project also strengthens the theory that Bio-P reduction takes place at Rya WWTP, as there is a presence of PAOs.

5.1.2 P-release and uptake batch test

As seen in Table 4.3, the release rate is dependent on what part of the curve is used for the calculation. There are two linear parts of the curve, as there is a rapid release immediately after the addition of the acetate before the release slows down after around 20 minutes, where the release rate remains linear until the aerobic period. This can be compared with the curves described in the literature, such as the one in Figure 2.9, where there is only one linear part of the curve. If curve 3, which represents the full anaerobic period, is used, the release rate of 1.4 mgP/gVSS*h is comparable with Skebäcksverket in Örebro which, as seen in Table D.2 in Appendix C, is designed for bio-P treatment. Curve 1 and its rate of 0.68 mgP/gVSS*h is more similar to Käppalaverket in Uppsala operating both chemical and bio-P treatment during the testing period. The highest release rate of 5.8 mgP/gVSS*h is found for curve 2 and is comparable with rates found at Käppalaverket in Lidingö, Skillangaryd and the plant with modified UCT in the US. These plants are designed to operate mainly with bio-P. The maximum release rate of 4.2 mgP/gVSS is similar to those found at Bålsta and Käppalaverket when both chemical and biological treatment is in use. Even though Rya WWTP is designed for chemical P removal, release rates similar to those at WWTPs with bio-P are achieved.

The reason for the rapid release of P at the start of the anaerobic period is hard to determine, as neither pH nor oxygen levels were measured. There is a risk that anaerobic conditions were not reached before the acetate addition, which means that the acetate may have been degraded more rapidly during the first 20 minutes before reaching anaerobic conditions and slowing the release. The oxygen level should be measured until no oxygen is present in the sludge to avoid aerobic conditions as the acetate is added. The first aerobic period can be skipped as the activated sludge is not transported far from the basin until starting the test, since waiting until anaerobic conditions could increase the already long testing time.

A lowered or heightened pH from the NaAc may have affected the test results since the pH was not measured. The NaOH was mixed with the acetate to achieve a

neutral pH, but with no measurements on the NaOH solution, it could have acted as a base or acid when mixed with the sludge. In Figure 4.3, a reaction that changes the colour and consistency of the sludge takes place, making filtration more difficult. A lowered pH due to the NaAc solution could mean that the release rate is higher than the test showed since a lower pH leads to a decreased release rate as described in Section 2.2.3. If the NaAc solution instead increased the pH, the test rate may be higher due to the opposite reason, as a lower pH decreases the rate. Another possibility with an increased pH is that the precipitant chemicals in the sludge, as the activated sludge at Rya WWTP is both biological and chemical, started to precipitate phosphate and disguised some of the releases. This might explain the look of the curve as the release lowers after 20 minutes when the precipitant counteracts the release. To determine if the pH affected the results, pH measurements should be performed on both the NaAc solution and activated sludge before the start of the test and during the test, especially after NaAc addition. The release of K should also be measured, as described in Section 2.2.3, to determine the K/P-ratio and if any precipitation occurred that affected the release rate.

Tetrasphera prefers other carbon sources, such as amino acids and glucose, than Accumulibacter, who prefers VFAs that were used as the carbon source in this test. It is possible that the capacity of the Tetrasphera to release and uptake P was not measured fully due to the choice of carbon source. To investigate the P-release and uptake of Tetrasphera, a more suitable carbon source could be used for the test. As both PAOs are present at Rya WWTP, a combination of the two carbon sources is also an option. The P-release and uptake test should have been repeated several times to eliminate this error source and those stated above, but due to time constraints at the laboratory at Rya WWTP and maintenance of one activated sludge basin, it was not possible to conduct more than one test within the scope of this thesis.

5.1.3 Chemical precipitation with drinking water sludge

There was a significant reduction of P in the reference beakers, as seen in Figure 4.5 and Table E.1, of especially X-P but also of PO−4-P. As the wastewater was gathered after the PSTs, the suspended P should already have settled in the primary settling, which indicates that some other processes took place in the beakers. One possibility is that precipitation chemicals that are part of the WAS recycled into the primary settling get mixed with the water going out of the primary settling. These chemicals got a chance to precipitate P by doing another round of stirring and settling during the tests. This phenomenon or other potential processes taking place was accounted for, as the reductions of PO_4-P in the reference beakers were subtracted from the remaining beakers when calculating the PO_4-P reduction at Rya WWTP from the DWS.

Wastewater was collected after the PSTs to avoid the risk of reactions during storage of the water before test 1. The concentrations of PO_4-P and Tot-P were measured the day before test 1. The incoming wastewater has a higher degree of particles as it has not passed through any sedimentation, which increases the risk of reactions that might affect the results compared to the wastewater after primary settling. The

reduction of PO_4-P was higher during test 1, as Figure 4.6 shows, which could be related to the overnight storage of the water as some reactions might have taken place. Another possibility is an error in the collection of the wastewater sample, as the samples from before and after the PSTs are collected at the same point. There is a risk that wastewater from before the PSTs was collected due to miscommunication. The researcher did not know about the collection point at the time of collection and did not communicate the importance of collecting water after the PSTs to the laboratory personnel. The researcher gained knowledge on the subject before tests 2-4 and could ensure that water from after the PSTs was collected. Since one month passed between the tests, it was impossible to conclude if the wrong water had been used for test 1. This could, however, explain why the reduction is higher for test 1 as the water contains more particles if gathered before the PSTs. Another possibility is that the starting concentration was higher for test 1, as seen in Table E.1, which gives it a higher reduction potential. Since it is unclear if different waters were used for tests 1 and 2-4, the exact reason for the variation between the tests remains undecided.

The molar ratio between Tot-P and the Al from DWS of 10.8-11.85:1 to reach an effluent concentration between 0.3-0.5 mgP/L is significantly higher than the theoretical value of 2:1 from the literature. This is reasonable, as most of the Al should already have gone through precipitation at the DWTPs. A higher amount of DWS is needed to reach the same reduction with the DWS as a pure precipitant. As seen in Table 4.6, when comparing the contents of metals in the DWS and the chemical precipitant at Rya WWTP, a higher load of DWS would lead to a higher load of most metals. However, an increase of DWS to replace the use of $FeSO_4$ is unreasonable, as the DWS production is dependent on the water treatment at the DWTPs. Removing the DWS from reaching Rya WWTP would decrease metal loads coming to the plant. But, as Table 4.7 shows, that reduction would be inhibited by metal loads from increased usage of $FeSO_4$ to replace the DWS. The metal with the greatest impact on the incoming load is Ni from the $FeSO_4$ as it increased the load by 23%, and as Table 2.6 shows, Ni is the metal with the lowest removal efficiency at Rya WWTP. Increased usage of $FeSO_4$ would lead to a higher load of Ni reaching Göta River, even if it in Table 4.7 looks like a reduction would be insignificant. This is due to the subtraction of the Ni load from the DWS from the total load. Therefore, the outgoing and incoming Ni should be studied if the $FeSO_4$ usage or the DWS load into the plant increases in the future. For the remaining metals studied at the inlet and outlet, the loads from other sources are of greater importance than the DWS and $FeSO_4$ loads.

The cost of purchasing precipitation chemicals is impacted by increased usage of $FeSO_4$ and removed DWS, as shown in Table 4.5. As the DWS is a by-product and arrives at Rya WWTP at no cost, the purchase of $FeSO_4$ to compensate for the missing DWS would lead to an increase of up to around 220,000 SEK yearly. However, it is simply possible to compare the purchasing cost, but the DWS contributes to additional volumes of wastewater passing through treatment. By removing the DWS, the total cost for the plant could be decreased through factors such as lower energy consumption, decreased sludge volumes and, as already discussed, lower metal loads when there is less incoming water to treat. To get a better overview of the

possible economical impact of removing the sludge, a more extensive investigation of the composition of the DWS and its effect on other factors besides its capacity to remove P would have to be studied.

5.2 P removal at Rya WWTP

The MiDAS results, the result of the P-release and uptake test, and the results from the chemical precipitation with DWS tests indicate that other processes, besides the conventional chemical precipitation process, contribute to the removal of P at Rya WWTP. The chemical precipitation tests showed that the Al in the DWS can reduce PO_4-P, which means that the concentration of PO_4-P that reaches the AS basins where $FeSO_4$ is added, would be higher without the DWS. The incoming Tot-P concentration would not be affected by the removal of DWS, as it mainly reduces the fraction of PO_4-P. The purpose of chemical precipitation is to convert dissolved P into suspended P, which can partly explain the low molar ratio as the Al in the DWS goes through precipitation and coagulation in the piping system and sedimentation in the primary settling.

The MiDAS project shows that there are PAOs present in the AS at Rya WWTP, and the P-release and uptake test performed in this thesis also shows that the sludge has the capacity to release and bind PO_4-P. Since there are many uncertainties regarding the results of the P-release and uptake test as described earlier, it is impossible with the available data to determine what capacity the AS at Rya WWTP has to remove PO_4-P biologically. Combined with the data collected during a long period from the MiDAS project on the presence of PAOs, there is highly likely that bio-P removal occurs at Rya WWTP. A combination of P removal due to the DWS and biological removal can explain why the dosing of precipitant chemicals is low compared to the incoming Tot-P to Rya WWTP while reaching a low effluent concentration of Tot-P.

5.3 Further research

Possible research points and questions are presented below to continue the work started in this thesis.

- Extensive P-release and uptake tests should be performed to investigate the capacity of the PAOs in the AS at Rya WWTP to release and store P.
- Repeat the P-release and uptake test with sludge from other plants than Rya WWTP to compare release and uptake rates.
- Perform P measurements in the piping system at points before the DWS is discharged and compare with incoming P concentrations at Rya WWTP to investigate the effects of DWS further.
- Chemical precipitation with DWS tests should be performed with incoming wastewater instead of after the primary settling to better simulate the real-life conditions for the reaction of Al in DWS with P at Rya WWTP.

- Do the P-release and uptake test with sludge from other plants than Rya WWTP to compare release and uptake rates
- Conduct measurements of PO_4-P in the incoming water, after the primary settling, out from the secondary settling, in the reject water from the belt gravity thickening and dewatered sludge over a longer period to verify the mass balance in this thesis.
- Study the P composition of the water at Rya more extensively by measuring other fractions besides PO_4-P and Tot-P.
- What happens with the biologically and chemically bound P in the sludge as it passes through the biogas plant?
- How would removing the DWS affect the sludge properties at the WWTP?

6

Conclusion

Of the incoming Tot-P flow of 1228 kg/day only 63.9 kg/day leave Rya WWTP with the effluent water, a reduction with ca. 95%. Almost the same percentage of reduction is seen for PO_4-P, from 399 kg/day to 22.5 kg/day, and the remaining fractions of phosphorus, X-P, from 829 kg/day to 41.4 kg/day from inlet to outlet. This means that the fraction of phosphorus that does not leave the plant through the effluent water is removed through the sludge flow out of the plant. 1174 kg/day of Tot-P is transported out through the dewatered sludge, while the fraction of PO_4-P and X-P in the dewatered sludge could not be determined due to recirculating of phosphorus within the plant and a lack of PO_4-P measuring points in the sludge flow.

The main phosphorus removal from the wastewater, around 86% for Tot-P, 87% for PO_4-P and 85% for X-P of the total removal from inlet to outlet, takes place over the activated sludge basins and secondary settling tanks after addition of $FeSO_4$ at Rya WWTP. That the majority of the reduction takes place over these treatments steps is expected as the plant is designed with simultaneous chemical precipitation for phosphorus removal, where coagulation and flocculation occur in the AS basins and separation in the SSTs. However, additional reduction of phosphorus occur after the secondary settling of both PO_4-P over the DMBBR and of the suspended phosphorus in X-P over the disc filters before discharge into Göta River. The reduction of Tot-P is not as sufficient, with a reduction of ca. 94%, when the incoming flow exceeds the capacity of the AS basins and direct precipitation has to be applied. This is due to a lower capacity to reduce X-P in the DP compared to the normal treatment while the PO_4-P reduction is higher with direct precipitation.

The low dosage of Fe compared to incoming Tot-P, the presence of PAOs in the activated sludge basins in the form of Tetrasphera and Accumulibacter combined with the results from the P-release and uptake test where a release and uptake of phosphorus was observed indicate that bio-P removal takes place at Rya WWTP. The release rate, dependant on what part of the curve is used for calculations, is in line with other WWTPs that has implemented bio-P but the uptake rate is significantly lower than the release rate, which needs to be higher to achieve a reduction of phosphorus in the water. The maximum release rate is in this case better to use for comparison as it can only be calculated in one way, and it is in line with Käppalaverket and Bålsta WWTP that uses a combination of chemical and biological phosphorus treatment.

Even as the P-release and uptake test shows that the bacteria in the activated sludge has similar functions as PAOs, the lack of measurements of pH, oxygen level, K-release and VFA-uptake during the test and lack of opportunity to repeat the test sets a barrier to draw any definite conclusions from the results. It is possible that the

addition of NaAc either decreased or increased the pH, which leads to a lower and higher release rate respectively. A heightened pH can also have caused precipitation from the chemicals in the sludge, masking some of the release. The K-release should therefore had been measured to get the K/P-ratio and see if precipitation affected the results. As the oxygen level was not measured before addition of the NaAc there is a risk that the carbon source was consumed more rapid due to the presence of oxygen, which might explain the lowered release rate 20 minutes into the anaerobic period. Another possibility is that the NaAc was dosed in such an excess that it remained into the final aerobic period and was consumed by the bacteria instead of phosphorus. To determine if all of the NaAc is consumed the VFA-uptake during the anaerobic period should be measured and the dosage adjusted for a second attempt.

The results of the tests with chemical precipitation with DWS shows that it has the ability to precipitate phosphorus, especially PO_4-P. If the flow of DWS were stopped it would lead to an increased load of PO_4-P into Rya WWTP with around 15-18 tonnes/year, which would lead to an increased need with 10.3-11.6% of precipitation chemicals compared to 2021. This would also lead to an increased purchasing cost of $FeSO_4$ with 197 000-221 000 SEK/year, but a more in depth analyses of the effects of DWS on the plant is required to get an economical overview as it may lead to lower costs of treatment regarding energy consumption, smaller sludge volumes for treatment, and lower metal loads as shown in this Thesis. Removing the DWS and increasing the $FeSO_4$ would for a majority of the metals lead to lower loads when comparing the contribution of metal loads between $FeSO_4$ and DWS, but when comparing these loads with the total load of metals reaching the plant the removal of DWS would have a minimal effect. However, the only metal load that is significantly impacted by either DWS or $FeSO_4$ is Nickel which means that increased loads of $FeSO_4$ is noticeable on the total metal load. Increased loads of metals in the outgoing sludge is undesirable as it hinders reuse, which is a crucial part of the reuse of phosphorus to avoid mining of phosphorus.

Additional P-release and uptake tests of the activated sludge at Rya WWTP and precipitation tests with higher molar ratios between Al and PO_4-P, with sludge from both Lackarebäck and Alelyckan, and with incoming wastewater instead of primary settled water should be performed to confirm and develop the results in this Thesis. To advance the research even further it would be beneficial to perform measurements within the plant of PO_4-P and Tot-P to get a more detailed and accurate phosphorus mass balance. Further studies could also include additional effects of the DWS on other compounds than phosphorus and the treatment steps at the WWTP to determine if the DWS should be treated at Rya WWTP.

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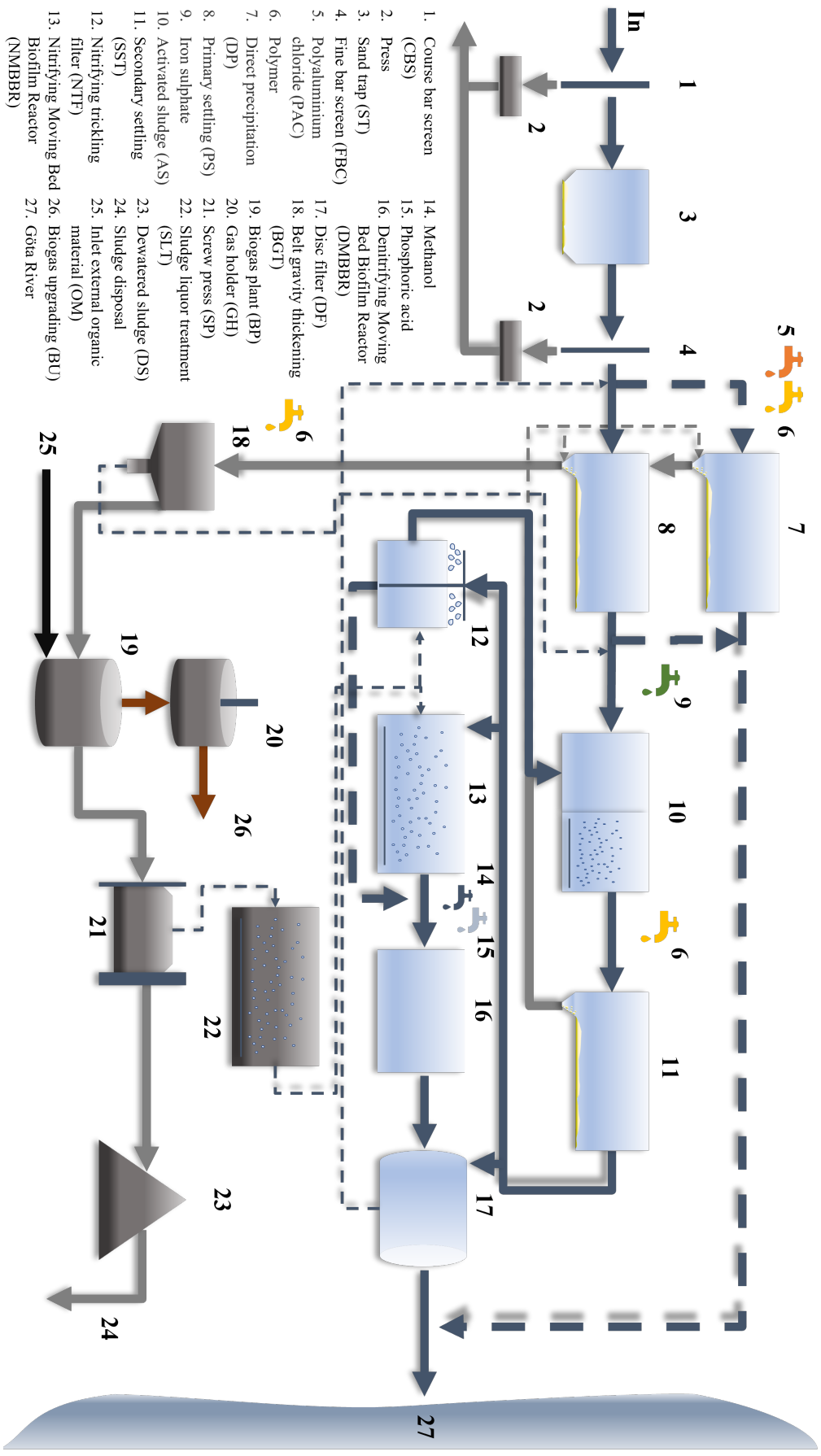
A

Appendix I - Rya WWTP



1. Course bar screen (CBS)
2. Press
3. Sand trap (ST)
4. Fine bar screen (FBC)
5. Polyaluminium chloride (PAC)
6. Polymer
7. Direct precipitation (DP)
8. Primary settling (PS)
9. Iron sulphate
10. Activated sludge (AS)
11. Secondary settling (SST)
12. Nitrifying trickling filter (NTF)
13. Nitrifying Moving Bed Biofilm Reactor (NMBBR)
14. Methanol
15. Phosphoric acid
16. Denitrifying Moving Bed Biofilm Reactor (DMBBR)
17. Disc filter (DF)
18. Belt gravity thickening (BGT)
19. Biogas plant (BP)
20. Gas holder (GH)
21. Screw press (SP)
22. Sludge liquor treatment (SLT)
23. Dewatered sludge (DS)
24. Sludge disposal
25. Inlet external organic material (OM)
26. Biogas upgrading (BU)
27. Göta River

Figure A.1: *Process schematic of Rya WWTP.*

B

Appendix II - MiDAS Project Sweden

Table B.1: *Presence of PAO and GAO bacteria as relative abundance in the activated sludge at Rya WWTP from the MiDAS project.*

Bacteria	Tetra-sphaera	Accumuli-bacter	Competi-bacter	Micro-pruina	Propioni-vibrio
PAO/ GAO	PAO	PAO/ GAO	GAO	GAO	GAO
Date	RA*	RA*	RA*	RA*	RA*
14.1.21	0.9%	0.10%	0.77%	0.08%	0.07%
21.1.21	0.0%	0.00%	1.05%	0.00%	0.00%
26.1.21	1.0%	0.14%	0.38%	0.15%	0.05%
2.2.21	1.4%	0.12%	0.31%	0.24%	0.03%
9.2.21	1.7%	0.15%	0.18%	0.17%	0.07%
16.2.21	1.7%	0.20%	0.19%	0.15%	0.12%
23.2.21	1.4%	0.22%	0.16%	0.15%	0.09%
3.3.21	1.5%	0.10%	0.17%	0.18%	0.06%
9.3.21	1.4%	0.19%	0.15%	0.69%	0.04%
16.3.21	1.0%	0.25%	0.15%	0.12%	0.08%
23.3.21	1.5%	0.17%	0.09%	0.17%	0.10%
30.3.21	1.0%	0.13%	0.10%	0.04%	0.09%
6.4.21	1.1%	0.13%	0.03%	0.15%	0.07%
13.4.21	1.1%	0.18%	0.06%	0.17%	0.07%
20.4.21	1.2%	0.15%	0.04%	0.15%	0.03%
28.4.21	1.4%	0.11%	0.03%	0.11%	0.05%
4.5.21	1.7%	0.16%	0.03%	0.14%	0.03%
1.5.21	1.5%	0.28%	0.04%	0.07%	0.04%
18.5.21	1.5%	0.25%	0.04%	0.16%	0.08%
25.5.21	1.4%	0.19%	0.07%	0.17%	0.07%
1.6.21	1.7%	0.37%	0.05%	0.18%	0.08%
8.6.21	2.2%	0.36%	0.04%	0.10%	0.08%
15.6.21	1.7%	0.63%	0.03%	0.08%	0.06%
22.6.21	2.1%	0.61%	0.03%	0.12%	0.03%
29.6.21	2.0%	0.71%	0.01%	0.08%	0.06%

**RA = Relative Abundance.*

Table B.2: *Presence of PAO and GAO bacteria as relative abundance in the activated sludge at Ellinge WWTP from the MiDAS project.*

Bacteria	Tetra-sphaera	Accumuli-bacter	Defluvii-coccus	Competi-bacter	Micro-pruina	Contendo-bacter
PAO/ GAO	PAO	PAO/ GAO	GAO	GAO	GAO	GAO
Date	RA*	RA*	RA*	RA*	RA*	RA*
20.1.21	22%	0.01%	12.8%	1.2%	0.03%	0.00%
29.1.21	26%	0.13%	10.7%	1.2%	0.04%	0.00%
1.2.21	26%	0.12%	10.4%	1.3%	0.02%	0.01%
9.2.21	22%	0.06%	9.6%	1.2%	0.03%	0.00%
17.2.21	25%	0.01%	6.2%	0.5%	0.01%	0.01%
24.2.21	24%	0.02%	7.0%	0.5%	0.04%	0.00%
1.3.21	28%	0.01%	4.8%	0.5%	0.02%	0.00%
10.3.21	24%	0.01%	6.5%	0.5%	0.03%	0.00%
16.3.21	19%	0.04%	3.8%	0.8%	0.01%	0.04%
25.3.21	19%	0.01%	3.5%	0.8%	0.03%	0.06%
30.3.21	17%	0.04%	3.1%	1.2%	0.01%	0.05%
9.4.21	14%	0.09%	1.5%	1.4%	0.02%	0.16%
16.4.21	21%	0.02%	3.2%	0.7%	0.02%	0.04%
23.4.21	22%	0.03%	3.7%	0.6%	0.02%	0.02%
29.4.21	18%	0.05%	3.6%	0.9%	0.01%	0.03%
7.5.21	17%	0.03%	3.3%	1.1%	0.04%	0.06%
17.5.21	17%	0.03%	2.2%	1.2%	0.03%	0.07%
20.5.21	17%	0.04%	2.2%	1.1%	0.03%	0.06%
28.5.21	21%	0.11%	2.6%	2.2%	0.04%	0.17%
2.6.21	19%	0.18%	3.1%	3.5%	0.03%	0.16%
8.6.21	15%	0.07%	3.4%	4.1%	0.03%	0.12%
18.6.21	16%	0.09%	7.0%	2.0%	0.03%	0.06%
24.6.21	15%	0.13%	6.8%	2.2%	0.03%	0.06%
1.7.21	20%	0.21%	6.0%	1.2%	0.10%	0.03%
7.7.21	19%	0.35%	5.5%	1.3%	0.09%	0.03%

**RA = Relative Abundance.*

C

Appendix III - Mass balance

Table C.1: *Mass flow rates of phosphorus, concentrations and flows at Rya WWTP and the equation used.*

Tag	From	To	Parameter	Unit	Value	Eq.
$\dot{m}_{Tot-P\ 1}$	Inlet		Mass flow rate	kgP/day	1228	3.1
$\dot{m}_{PO_4-P\ 1}$	Inlet		Mass flow rate	kgP/day	399	3.1
$\dot{m}_{X-P\ 1}$	Inlet		Mass flow rate	kgP/day	829	3.2
Q_1	Inlet		Flow	m^3/day	322109	
$C_{Tot-P\ 1}$	Inlet		Concentration	kg/m^3	0.0041	
$C_{PO_4-P\ 1}$	Inlet		Concentration	kg/m^3	0.0013	
$\dot{m}_{Tot-P\ 1.2}$	Inlet	PS	Mass flow rate	kgP/day	1207	C.1
$\dot{m}_{PO_4-P\ 1.2}$	Inlet	PS	Mass flow rate	kgP/day	392	C.1
$\dot{m}_{X-P\ 1.2}$	Inlet	PS	Mass flow rate	kgP/day	815	3.2
$\dot{m}_{Tot-P\ 2}$	Inlet	DP	Mass flow rate	kgP/day	20.7	3.1
$\dot{m}_{PO_4-P\ 2}$	Inlet	DP	Mass flow rate	kgP/day	6.72	3.1
$\dot{m}_{X-P\ 2}$	Inlet	DP	Mass flow rate	kgP/day	14.0	3.2
Q_2	Inlet	DP	Flow	m^3/day	8646	
$\dot{m}_{Tot-P\ 3}$	DP	Outlet	Mass flow rate	kgP/day	3.35	3.1
$\dot{m}_{PO_4-P\ 3}$	DP	Outlet	Mass flow rate	kgP/day	0.208	3.1
$\dot{m}_{X-P\ 3}$	DP	Outlet	Mass flow rate	kgP/day	3.15	3.2
$C_{Tot-P\ 3}$	DP	Outlet	Concentration	g/m^3	0.364	
$C_{PO_4-P\ 3}$	DP	Outlet	Concentration	mg/m^3	24.3	
$\dot{m}_{Tot-P\ 4}$	FS	AS	Mass flow rate	kgP/day	992	3.1
$\dot{m}_{PO_4-P\ 4}$	FS	AS	Mass flow rate	kgP/day	403	3.1
$\dot{m}_{X-P\ 4}$	FS	AS	Mass flow rate	kgP/day	589	3.2
Q_4	FS	AS	Flow	m^3/day	314704	
$\dot{m}_{(AS_{COD_{filtered}})}$	FS	AS	Concentration	g/m^3	100	
$C_{Tot-P\ 4}$	FS	AS	Concentration	g/m^3	3.39	
$C_{PO_4-P\ 4}$	FS	AS	Concentration	g/m^3	1.38	
$\dot{m}_{PO_4-P\ 5}$	FS+ BGT	AS	Mass flow rate	kgP/day	433	C.2
$\dot{m}_{PO_4-P\ 6}$	AS	SST	Mass flow rate	kgP/day	57.5	3.1
Q_6	AS	SST	Flow	m^3/day	314704	
$C_{PO_4-P\ 6}$	AS	SST	Concentration	mg/m^3	59.0	
$\dot{m}_{Tot-P\ 7}$	SST	NTF+ NMBBR+ DF	Mass flow rate	kgP/day	221	C.5

Continued on next page

Table C.1 – continued from previous page

Tag	From	To	Parameter	Unit	Value	Eq.
$\dot{m}_{PO_4-P\ 7}$	SST	NTF+ NMBBR+ DF	Mass flow rate	kgP/day	62.3	C.3
$\dot{m}_{X-P\ 7}$	SST	NTF+ NMBBR+ DF	Mass flow rate	kgP/day	159	C.4
$\dot{m}_{PO_4-P\ 8}$	SST	NTF	Mass flow rate	kgP/day	30.6	3.1
Q_8	SST	NTF	Flow	m^3/day	416409	
$\dot{m}_{PO_4-P\ 9}$	SST	NMBBR	Mass flow rate	kgP/day	14.5	3.1
Q_9	SST	NMBBR	Flow	m^3/day	195567	
$\dot{m}_{PO_4-P\ 10}$	SST	DF	Mass flow rate	kgP/day	17.3	C.6
Q_{10}	SST	DF	Flow	m^3/day	118707	
$C_{SS\ 10}$	SST	DF	Concentration	g/m^3	19.1	
$\dot{m}_{PO_4-P\ 11}$	NMBBR	DMBBR	Mass flow rate	kgP/day	14.2	3.1
Q_{11}	NMBBR	DMBBR	Flow	m^3/day	192830	
$\dot{m}_{PO_4-P\ 12}$	NTF	DMBBR	Mass flow rate	kgP/day	0.584	3.1
Q_{12}	NTF	DMBBR	Flow	m^3/day	7033	
$\dot{m}_{H_3PO_4}$	NTF	DMBBR	Mass flow rate	kgP/day	10.6	
$\dot{m}_{PO_4-P\ 13}$	NTF+ H_3PO_4+ NMBBR	DMBBR	Mass flow rate	kgP/day	25.5	C.7
$C_{PO_4-P\ 13}$	NTF+ H_3PO_4+ NMBBR	DMBBR	Concentration	m^3/day	7033	
$\dot{m}_{PO_4-P\ 14}$	DMBBR	DF	Mass flow rate	kgP/day	5.02	3.1
Q_{14}	DMBBR	DF	Flow	m^3/day	210435	
$C_{PO_4-P\ 14}$	DMBBR	DF	Concentration	mg/m^3	23.6	
$C_{SS\ 14}$	DMBBR	DF	Concentration	g/m^3	17.2	
$\dot{m}_{Tot-P\ 14.2}$	DMBBR+ SST	DF	Mass flow rate	kgP/day	247	C.10
$\dot{m}_{PO_4-P\ 14.2}$	DMBBR+ SST	DF	Mass flow rate	kgP/day	22.3	C.8
$\dot{m}_{X-P\ 14.2}$	DMBBR+ SST	DF	Mass flow rate	kgP/day	224	C.9
$\dot{m}_{PO_4-P\ 15}$	DF	Outlet	Mass flow rate	kgP/day	22.3	3.1
$\dot{m}_{Tot-P\ 15}$	DF	Outlet	Mass flow rate	kgP/day	60.6	C.13
$\dot{m}_{X-P\ 15}$	DF	Outlet	Mass flow rate	kgP/day	38.3	3.2
Q_{15}	DF	Outlet	Flow	m^3/day	210435	
$C_{SS\ 15}$	DF	Outlet	Concentration	mg/m^3	2.75	
$\dot{m}_{X-P\ 15.2}$	DF	PS	Mass flow rate	kgP/day	186	C.12
$\dot{m}_{PO_4-P\ 16}$	SST	AS	Mass flow rate	kgP/day	29.9	3.1
Q_{16}	SST	AS	Flow	m^3/day	408655	
$\dot{m}_{Tot-P\ 17}$	SST	PS-BGT	Mass flow rate	kgP/day	800	C.15
$\dot{m}_{PO_4-P\ Bio}$	SST	PS-BGT	Mass flow rate	kgP/day	62	C.22

Continued on next page

Table C.1 – continued from previous page

Tag	From	To	Parameter	Unit	Value	Eq.
$\dot{m}_{PO_4-P\ Chem}$	SST	PS-BGT	Mass flow rate	kgP/day	317	C.23
$\dot{m}_{PO_4-P\ sludge}$	SST	PS-BGT	Mass flow rate	kgP/day	371	C.24
$\dot{m}_{X-P\ 17}$	SST	PS-BGT	Mass flow rate	kgP/day	430	C.14
$\dot{m}_{Tot-P\ 18}$	SST	BGT	Mass flow rate	kgP/day	418	C.16
$\dot{m}_{Tot-P\ 19}$	PS	BGT	Mass flow rate	kgP/day	1219	C.17
$\dot{m}_{PO_4-P\ 19}$	PS	BGT	Mass flow rate	kgP/day	371	C.17
$\dot{m}_{X-P\ 19}$	PS	BGT	Mass flow rate	kgP/day	848	C.17
$\dot{m}_{Tot-P\ 20}$	BGT	SST	Mass flow rate	kgP/day	21.5	3.1
Q_{20}	BGT	SST	Flow	m^3/day	2644	
$C_{Tot-P\ 20}$	BGT	SST	Concentration	g/m^3	12.6	
$\dot{m}_{Tot-P\ 21}$	BGT BP	BP SP	Mass flow rate	kgP/day	1197	C.20
$\dot{m}_{Tot-P\ 22}$	SP	SLT	Mass flow rate	kgP/day	22.9	3.1
$\dot{m}_{PO_4-P\ 22}$	SP	SLT	Mass flow rate	kgP/day	22.5	3.1
$\dot{m}_{X-P\ 22}$	SP	SLT	Mass flow rate	kgP/day	0.460	3.2
Q_{22}	SP	SLT	Flow	m^3/day	1395	
$C_{Tot-P\ 22}$	SP	SLT	Concentration	g/m^3	15.7	
$C_{PO_4-P\ 22}$	SP	SLT	Concentration	g/m^3	16.4	
$\dot{m}_{Tot-P\ 23}$	SP DS	DS Outlet	Mass flow rate	kgP/day	1174	C.25
$\dot{m}_{DW\ sludge}$	DS	Outlet	Mass flow rate	tonnes/day	131	
TS_{sludge}	DS	Outlet	TS	%	28.9	
$M_{DW\ sludge\ Tot-P}$	DS	Outlet	Mass	gP/kgTS	30.9	
$\dot{m}_{Tot-P\ 24}$	FS	AS	Mass flow rate	kgP/day	63.	C.26
$\dot{m}_{PO_4-P\ 24}$	FS	AS	Mass flow rate	kgP/day	22.5	C.26
$\dot{m}_{X-P\ 24}$	FS	AS	Mass flow rate	kgP/day	41.4	3.2
$C_{PO_4-P\ 24}$	SP	SLT	Concentration	mg/m^3	66.5	

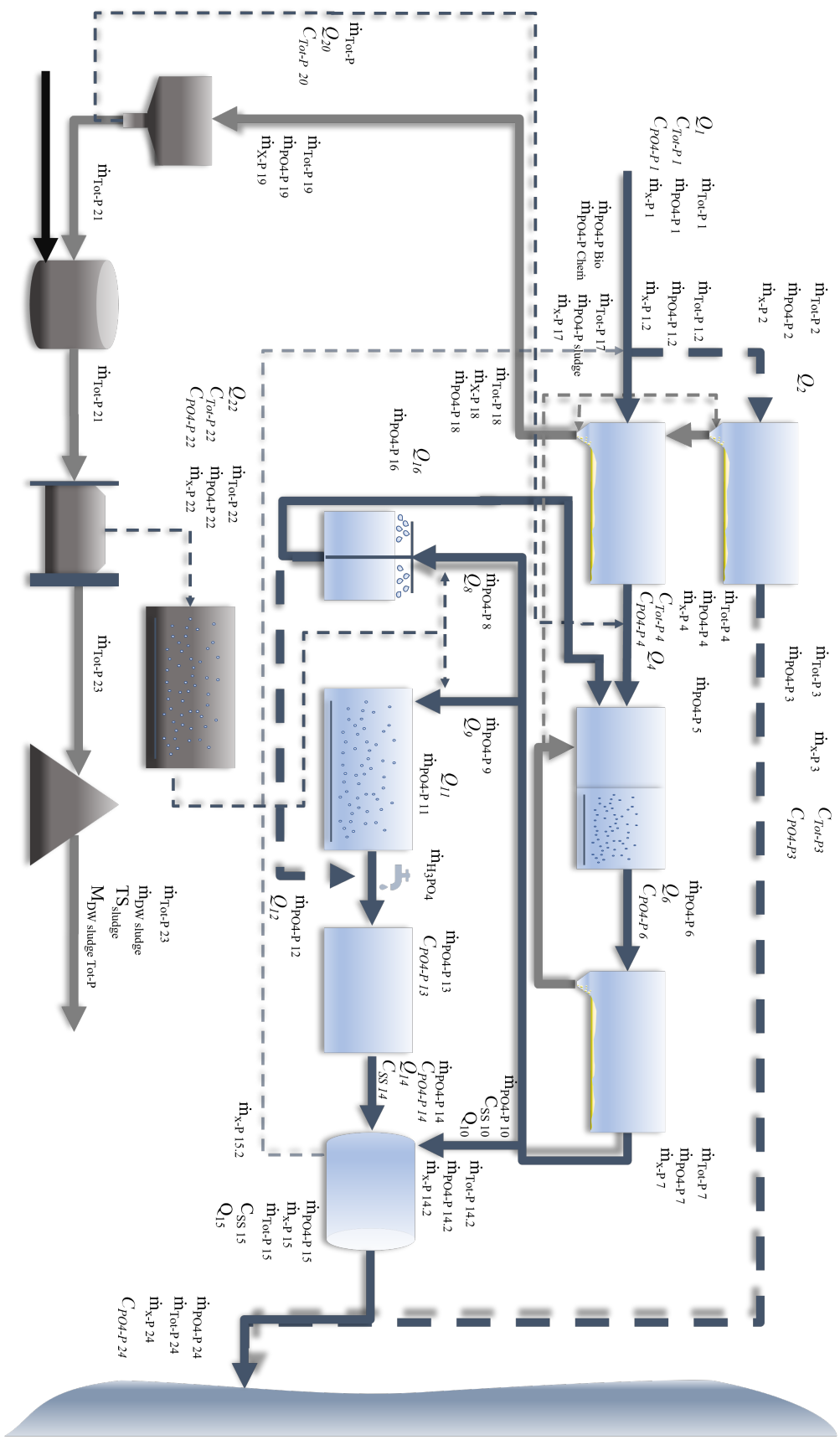


Figure C.1: *Location of the phosphorus Mass flow rates, concentrations and flows presented in Table C.1 at Rya WWTP.*

Some of the flow rates are calculated either by adding or subtracting other mass flow rates in the mass balance. The mass flow rates from the inlet to the primary settling was calculated with Equation C.1.

$$\dot{m}_{(Tot-P\ 1.2/PO_4-P\ 1.2)} = \dot{m}_{(Tot-P\ 1/PO_4-P\ 1)} - \dot{m}_{(Tot-P\ 2/PO_4-P\ 2)} \tag{C.1}$$

The mass flow rate of PO_4-P into the AS process was calculated with Equation C.2.

$$\dot{m}_{(PO_4-P\ 5)} = \dot{m}_{(PO_4-P\ 4)} + \dot{m}_{(PO_4-P\ 20)} \tag{C.2}$$

The mass flow rate of PO_4-p out from the secondary settling was calculated with Equation C.3.

$$\dot{m}_{(PO_4-P\ 7)} = \dot{m}_{(PO_4-P\ 8)} + \dot{m}_{(PO_4-P\ 9)} + \dot{m}_{(PO_4-P\ 10)} \tag{C.3}$$

To calculate $\dot{m}_{x-P\ 7}$, Equation C.4 was applied as the X-P not part of the sludge flow must remain in the wastewater flow out of the secondary settling.

$$\dot{m}_{x-P\ 7} = \dot{m}_{x-P\ 4} - \dot{m}_{x-P\ 17} \tag{C.4}$$

Equation C.5 was used to calculate $\dot{m}_{Tot-P\ 7}$.

$$\dot{m}_{Tot-P\ 7} = \dot{m}_{(PO_4-P\ 7)} + \dot{m}_{x-P\ 7} \tag{C.5}$$

$\dot{m}_{PO_4-P\ 10}$ was calculated with Equation C.6 as no significant reduction of PO_4-P is expected over the disc filters.

$$\dot{m}_{(PO_4-P\ 10)} = \dot{m}_{(PO_4-P\ 15)} - \dot{m}_{(PO_4-P\ 14)} \tag{C.6}$$

By adding the flows of PO_4-P from the nitrifying trickling filters, nitrifying MBBR and H_3PO_4 into the denitrifying MBBR, the total flow of PO_4-P into the denitrifying MBBR was calculated with Equation C.7. $\dot{m}_{H_3PO_4}$ was gathered directly in kg P/h from the data and converted to kg P/day.

$$\dot{m}_{(PO_4-P\ 13)} = \dot{m}_{(PO_4-P\ 11)} + \dot{m}_{(PO_4-P\ 12)} + \dot{m}_{(H_3PO_4)} \tag{C.7}$$

The total flow of PO_4-P into the disc filters was calculated with Equation C.8.

$$\dot{m}_{(PO_4-P\ 14.2)} = \dot{m}_{(PO_4-P\ 14)} + \dot{m}_{(PO_4-P\ 10)} \tag{C.8}$$

The flow of X-P into the disc filters was calculated with Equation C.9.

$$\dot{m}_{(X-P\ 14.2)} = \dot{m}_{(X-P\ 15)} - \dot{m}_{(X-P\ 15.2)} \tag{C.9}$$

To calculate $\dot{m}_{Tot-P}$, Equation C.10 was applied.

$$\dot{m}_{(Tot-P\ 14.2)} = \dot{m}_{(X-P\ 14.2)} + \dot{m}_{(PO_4-P\ 14.2)} \tag{C.10}$$

The relationship between suspended solids (SS) and X-P out from the disc filters were studied to determine X-P in the filter sludge from the disc filters since X-P is in suspended form. First, the relationship between the outgoing SS and X-P from the disc filters were calculated with Equation C.11.

$$\frac{\dot{m}_{X-P\ 15}}{\dot{m}_{SS\ 15}} = \frac{\dot{m}_{(X-P\ 15)}}{C_{SS\ 15} \cdot Q_{15}} \tag{C.11}$$

where:

$\dot{m}_{X-P}/\dot{m}_{SS}$ = Relationship between X-P and SS [kg P/kg SS]

With the relationship between SS and X-P out from the disc filters, the X-P in the reject water from the disc filters was calculated with Equation C.12.

$$\dot{m}_{(X-P\ 15.2)} = \frac{\dot{m}_{X-P\ 15}}{\dot{m}_{SS\ 15}} \cdot (Q_10 * C_{SS\ 10} + Q_14 * C_{SS\ 14} - Q_15 * C_{SS\ 15}) \tag{C.12}$$

The flow of Tot-P from the disc filter to the outlet was calculated with Equation C.13.

$$\dot{m}_{(Tot-P\ 15)} = \dot{m}_{(Tot-P\ 24)} - \dot{m}_{(Tot-P\ 3)} \tag{C.13}$$

To calculate the fraction of X-P in the waste activated sludge Equation C.14 was applied.

$$\dot{m}_{(x-P\ 17)} = \dot{m}_{(Tot-P\ 19)} - \dot{m}_{(Tot-P\ 18)} - \dot{m}_{(PO_4-P\ sludge)} \tag{C.14}$$

The Tot-P in the waste activated sludge was calculated with Equation C.15.

$$\dot{m}_{(Tot-P\ 17)} = \dot{m}_{(x-P\ 17)} + \dot{m}_{(PO_4-P\ sludge} \tag{C.15}$$

To calculate the sludge flow from the primary settling, Equation C.16 was applied.

$$\dot{m}_{(Tot-P\ 18)} = \dot{m}_{(Tot-P\ 1.2)} + \dot{m}_{(X-P\ 15.2)} + \dot{m}_{(Tot-P\ 2)} - \dot{m}_{(Tot-P\ 3)} - \dot{m}_{(Tot-P\ 4)} \tag{C.16}$$

Equation C.17 was used to calculate the total flow of phosphorus from the waste activated sludge and the primary sludge.

$$\dot{m}_{(Tot-P\ 19)} = \dot{m}_{(Tot-P\ 21)} + \dot{m}_{(Tot-P\ 20)} \tag{C.17}$$

The PO_4-P out from the primary settling in the sludge was calculated with Equation C.18.

$$\dot{m}_{(PO_4-P\ 19)} = \dot{m}_{(PO_4-P\ 17)} + \dot{m}_{(PO_4-P\ 18)} \tag{C.18}$$

To calculate the fraction of X-P in the combined primary and waste activated sludge Equation C.19 was applied.

$$\dot{m}_{(X-P\ 19)} = \dot{m}_{(X-P\ 17)} + \dot{m}_{(X-P\ 18)} \tag{C.19}$$

The sludge flow from the gravity belt thickening and biogas plant was calculated with Equation C.20.

$$\dot{m}_{(Tot-P\ 21)} = \dot{m}_{(Tot-P\ 23)} + \dot{m}_{(Tot-P\ 22)} \tag{C.20}$$

The mass flow of biologically bound PO_4 was calculated for the waste activated sludge from the secondary settling by studying the COD:P-ratio in the denitrifying MBBR at Rya WWTP. The PO_4-P reduction over the denitrifying MBBR is assumed to be only biological as no precipitation chemicals are added at this stage. The methanol flow into the denitrifying MBBR was collected to determine the relationship between COD and P in the denitrifying MBBR with Equation C.21.

$$COD : P = \dot{m}_{(COD)} = \frac{\dot{m}_{(PO_4P\ 13)} - \dot{m}_{(PO_4P\ 14)}}{\frac{\dot{m}_{Methanol_{COD}}}{100}} = 100 : 0.21 \tag{C.21}$$

where:

$COD : P$ = Ratio between COD and P
$\dot{m}_{(Methanol_{COD})}$ = Mass flow of methanol into DMBBR [kgCOD/day]

With the mass flow of filtered COD into AS and the COD:P ratio 100:0.21, the mass flow of biologically bound PO_4 was calculated with Equation C.22. The same calculation was also performed with a ratio of COD:P of 100:1, given as a conventional ratio (Metcalf and Eddy, 2014).

$$\dot{m}_{PO_4-P\ Bio} = \frac{C_{AS_{COD_{filtered}}} \cdot Q_4}{100} \cdot 0.21 \tag{C.22}$$

where:

$\dot{m}_{PO_4-P\ Bio}$ = Mass flow of biologically bound PO_4-P in the WAS [kg P/day]
$C_{(AS_{COD_{filtered}})}$ = Concentration of filtered COD into AS [kgCOD/m3]
Q_4 = Flow from PS to AS

The chemically bound PO_4-P in the waste activated sludge was calculated with Equation C.23.

$$\dot{m}_{PO_4-P\ Chem} = \dot{m}_{PO_4-P\ 5} - \dot{m}_{PO_4-P\ Bio} - \dot{m}_{PO_4-P\ 7} \tag{C.23}$$

where:

$\dot{m}_{PO_4-P\ Chem}$ = Mass flow of chemically bound PO_4-P in the WAS [kg P/day]

As a ratio COD:P of 100:1 would result in $\dot{m}_{PO_4-P\ Bio}$ = 296 kg P/day and $\dot{m}_{PO_4-P\ Chem}$ = 73.9 kg P/day, it was deemed an unreasonable ratio as the plant is designed for chemical removal of phosphorus and hence a larger portion should be bound chemically. Therefore the COD:P ratio of 100:0.21 was used. The total mass flow of bound PO_4-P in the waste activated sludge was then calculated with Equation C.24.

$$\dot{m}_{PO_4-P\ sludge} = \dot{m}_{PO_4-P\ Chem} + \dot{m}_{PO_4-P\ Bio} \tag{C.24}$$

where:

$\dot{m}_{PO_4-P\ sludge}$ = Mass flow of totally bound PO_4-P in the WAS [kg P/day]

The mass flow of Tot-P in the dewatered sludge was calculated with Equation C.25.

$$\dot{m}_{Tot-P\ 23} = \dot{m}_{DW\,sludge} \cdot TS_{sludge} \cdot M_{DW\ sludge\ Tot-P\ of\ TS} \tag{C.25}$$

where:

$\dot{m}_{Tot-P\ 23}$ = Mass flow of dewatered sludge [kg P/day]
$\dot{m}_{DW\,sludge}$ = Flow of dewatered sludge [kg/day]
TS_{sludge} = TS of the dewatered sludge [%]
$M_{DW\ sludge\ Tot-P}$ = Mass of Tot-P of the mass TS in the dewatered sludge [kgP/kgTS]

The flow of PO_4-P and Tot-P at the outlet was calculated with Equation C.26.

$$\dot{m}_{(Tot-P\ 24/PO_4-P\ 24)} = \dot{m}_{(Tot-P\ 15/PO_4-P\ 15)} + \dot{m}_{(Tot-P\ 3/PO_4-P\ 3)} \tag{C.26}$$

D

Appendix IV - P-release/uptake batch test

Table D.1: *Time of measurements, temperature and PO4-P concentrations for the P-release/uptake batch test.*

Sample	**Time** min	**Temp.** °C	**PO4-P** $\frac{mgP}{l}$	**Aerobic/ Anaerobic**
1	0	13	0.098	Aerobic
2	20	15	0.13	
3	40	15	0.15	
4	55	15	0.18	
5	61	16	2.9	Anaerobic
6	80	16	6.1	
7	100	17	7.1	
8	120	18	7.9	
9	140	18	8.5	
10	160	19	9.1	
11	180	19	9.6	
12	200	20	9.9	
13	220	20	10.3	
14	239	20	10.6	
15	260	20	11.2	Aerobic
16	280	20	10.9	
17	300	20	10.4	
18	320	20	10.7	
19	340	20	10.3	
20	360	20	10.2	
21	380	20	9.9	
22	400	20	9.8	
23	420	20	9	

Table D.2: *Time of measurements, temperature and PO4-P concentrations for the P-release/uptake batch test.*

WWTP	Location	Biological/ Chemical	Type of P treatment	P-release rate mgP/(gVSS*h)	max P-release rate mgP/gVSS	Date
Bålsta[1]	Bålsta, Sweden	Biological & Chemical	Side stream hydrolysis & postprecipitation with Al3+	2.89	6.28	2015-05-10
Duvbacken	Gävle, Sweden	Biological & Chemical*	Activated sludge main and side stream hydrolysis & coprecipitation	41 29 20.7	40.7 32.5 18.5	2015-06-08 2015-09-14 2015-09-16
Kungsängsverket	Uppsala, Sweden	Biological & Chemical	Activated sludge side stream hydrolysis & postprecipitation	2.16 4.46[2] 2.88 2.91 1.5	1.44	2015-06-30 2010-12-30 2011-11-09 2014-10-08 2015-07-08
Skebäcksverket[1]	Örebro, Sweden	Biological & Chemical*	Side stream hydrolysis & Coprecipitation FeSO4	0.2 0.16	0.47 0.38	2015-08-17 2015-09-15
Skillingaryd	Skillingaryd, Sweden	Biological & Chemical*	Main & side stream hydrolysis & coprecipitation	6.67 8.28	11.3 17.7	2015-05-10 2015-09-01
Käppalaverket[3]	Lidingö, Sweden	Biological & Chemical	Pre-precipitation FeSO4 UCT & Pre-precipitation UCT UCT UCT UCT UCT UCT	3.3 3.2 7.6 7.5 7.1 11 17 16.5	5.9 5.3 12.2 12.4 9.2 11.3 19.1 17	2003-04-08 2003-05-08 2003-05-19 2003-05-26 2003-06-10 2003-10-07 2003-11-11 2003-11-12
Öresundsverket[4]	Helsingborg, Sweden	Biological & Chemical	Hydrolysis in primary settling tanks Hydrolysis in primary settling tanks & coprecipitation FeSO4	17 9	36 20	n.d. n.d.
Unknown - A[5]	USA	Biological	Anaerobic-anoxic-aerobic	16.5		2001-2003*1
Unknown - B			Anaerobic-anoxic-aerobic	13.7		2001-2003*1
Unknown - C			Virginia initiative plant	12.4		2001-2003*1
Unknown - D			Virginia initiative plant	10.8		2001-2003*1
Unknown - E			Modified UCT	5.6		2001-2003*1
Unknown - F			UCT	31.9		2001-2003*1

[1] *Salmonsson et al. (2017).* [2] *Hansson (2016).* [3] *Borglund (2004).* [4] *la Cour Jansen et al. (2009).* [5] *Gu et al. (2008).*
**Chemical treatment in operation only if needed to reach target treatment values.*
*1 *Dates are not specified further by the authors but testing took place sometime between 2001-2003.*

E

Appendix V - Chemical precipitation with DWS

Table E.1: *PO4-P and Tot-P concentrations,temperature, and pH at the start and end of the tests as well as molar ratios between Al and PO4-P and Tot-P.*

		Test 1					Test 2				
Parameter	Unit	DWS	Beaker 1	Beaker 2	Beaker 3	Beaker 4	DW	Beaker 1	Beaker 2	Beaker 3	Beaker 4
PO4-P start	mg/L		2.01	12.4	2.01	2.01		1.49	1.49	1.49	1.49
PO4-P end	mg/L		1.686	0.984	1.01	1.62		1.40	1.23	0.910	0.540
Reduction	mg/L		0.3270	11.4	1.00	0.392		0.0.0895	0.260	0.580	0.950
Tot-P start	mg/L		3.80	16.4	3.80	3.80		3.00	3.00	3.00	3.00
Tot-P end	mg/L		2.80	1.30	1.90	1.70		2.60	2.50	2.20	1.60
Reduction	mg/L		1.00	15.1	1.90	1.10		0.430	0.500	0.830	1.40
Temp. Start	°C		11.0	12.0	12.0	13.0		14.0	14.0	14.0	14.0
Temp. End	°C		16.0	16.0	16.0	17.0		16.0	16.0	16.0	16.0
PH start		6.06	7.49	3.46	7.51	7.51	6.02	7.35	7.35	7.35	7.35
Temp.*	°C	17.2	18.6	18.6	18.7	18.8	19.7	20.7	20.7	20.7	20.7
PH end			7.63	4.53	7.52	7.63		7.32	7.36	7.37	7.46
Temp.*	°C		20.8	20.9	20.9	20.9		20.4	20.6	20.6	20.5
Al:PO4-P	mol:mol		0	3.3	3.0	1.0		0	2.0	6.1	12.2
Al:Tot-P	mol:mol		0	2.5	1.6	0.53		0	1.0	3.0	6.1
		Test 3					Test 4				
Parameter	Unit	DWS	Beaker 1	Beaker 2	Beaker 3	Beaker 4	DW	Beaker 1	Beaker 2	Beaker 3	Beaker 4
PO4-P start	mg/L		2.0125	12.382	2.0125	2.0125		2.0125	12.382	2.0125	2.0125
PO4-P end	mg/L		1.6855	0.9835	1.013	1.621		1.6855	0.9835	1.013	1.621
Reduction	mg/L		0.3270	11.398	0.9995	0.3915		0.3270	11.398	0.9995	0.3915
Tot-P start	mg/L		3.0	3.0	3.0	3.0		3.0	3.0	3.0	3.0
Tot-P end	mg/L		2.7	2.1	1.8	1.6		2.8	2.2	1.8	1.6
Reduction	mg/L		0.31	0.88	1.2	1.4		0.21	0.81	1.2	1.4
Temp. Start	°C		16	16	16	16		12	12	12	12
Temp. End	°C		17	17	17	17		16	16	16	16
PH start		6.02	7.35	7.35	7.35	7.35	6.02	7.35	7.35	7.35	7.35
Temp.*	°C	19.7	20.7	20.7	20.7	20.7	19.7	20.7	20.7	20.7	20.7
PH end			7.43	7.43	7.42	7.51		7.32	7.33	7.32	7.37
Temp.*	°C		20.5	20.4	20.3	20.6		19.8	19.9	19.9	20.0
Al:PO4-P	mol:mol		0	4.1	8.2	10.2		0	4.1	8.2	10.2
Al:Tot-P	mol:mol		0	2.0	4.0	5.0		0	2.0	4.0	5.0

**Temperature at the time of pH analysis.*

Table E.2: *Change in metal loads reaching Rya WWTP with a changes dosage of $FeSO_4$ and no DWS.*

Metal	**Mn** kg	**Sb** kg	**As** kg	**Pb** kg	**Cd** kg	**Co** kg	**Cu** kg	**Cr** kg	**Hg** g	**Ni** kg	**Ag** g	**Zn** kg	**Bi** kg
2021													
FeSO4	1180	0.781	0.781	1.98	0.392	110	1.90	15.2	2.87	122	1.19	79.4	0.831
DWS	0.0	2.07	0.0	10.7	0.206	0.0	51.5	14.3	60.2	14.0	392	71.9	0.0
Tot	1180	2.85	0.781	12.6	0.598	110	53.4	29.5	63.0	136	393	151	0.831
4.6a													
FeSO4	1317	0.872	0.872	2.21	0.437	123	2.12	17	3.20	136	1.32	89	0.928
Difference	137	-1.98	0.0906	-10.4	-0.161	12.8	-51.3	-12.5	-59.8	0.13	-392	-62.7	0.0963
Difference	11.6%	-69.4%	11.6%	-82.6%	-26.9%	11.6%	-96.0%	-42.5%	-94.9%	0.1%	-99.7%	-41.4%	11.6%
4.6b													
FeSO4	1302	0.862	0.862	2.18	0.432	122	2.09	16.7	3.17	134	1.31	87.6	0.917
Difference	122	-1.99	0.0808	-10.5	-0.165	11.4	-51.3	-12.7	-59.9	-1.38	-392	-63.7	0.0860
Difference	10.3%	-69.8%	10.3%	-82.7%	-27.7%	10.3%	-96.1%	-43.2%	-95.0%	-1.02%	-99.7%	-42.1%	10.3%

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