

Investigation of the effect of waterwork sludge on the pre- precipitation at the wastewater treatment plant in Norrköping

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Abstract

The aim of this thesis is to investigate the effect of waterwork sludge on the pre-precipitation and how lowering the dosage of FeCl_3 impact the biological wastewater treatment.

The impact of waterwork sludge on the wastewater treatment plant in Norrköping was investigated by creating a pre-precipitation on a laboratory scale by using a flocculator tester and analyzing the water above the sedimented sludge with different analysis methods.

Since the nutrients for the biological wastewater treatment are influenced by the pre-precipitation with precipitations chemicals, the impact of waterwork sludge on the biological wastewater treatment was investigated. This was done by evaluating historical data on biological wastewater treatment, which was provided by Nodra and comparing these with the experimental results. Different quotas were calculated to be able to compare the data and evaluate how well the experiment results mimicked reality.

The conclusion is that all measured components were reduced if waterwork sludge was present, especially phosphate, which indicates that waterwork sludge mainly removes phosphate instead of organic phosphorus. The quotas show that the results from the laboratory-scale experiment differ from reality. However, the same pattern could be seen in both with a decrease in nitrogen, total phosphorus, and phosphate if waterwork sludge was present.

Abbreviations

Table 1. Abbreviations

Wastewater treatment plant	WWTP
Biological wastewater treatment	BWT
Waterwork sludge	WWS

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1 Background

The wastewater treatment plant (WWTP) and waterwork treatment plant for drinking water in Norrköping is managed by Nodra AB, a company owned by the municipality of Norrköping.

Waterwork sludge (WWS) is the residual product from the first step in the production of drinking water and the waterwork treatment plant in Norrköping uses aluminum sulfate as the precipitation chemical. Norrköping has from early 1940 disposed of the WWS into Motala Ström but due to stricter requirements in recent years, WWS has been qualified as operational waste and needs to be disposed of in another way. Nodra identified two alternatives; the first solution was to dispose of the sludge on the waterwork treatment plant by building a dewatering plant close by. The second solution was to transport the sludge to the WWTP via the sewer network, and that is the solution Nodra has started to investigate. Both alternatives required up-concentration of the sludge, and that facility is built and taken into use.

The mean volume of incoming water at the WWTP in Norrköping is 44 000 m³/day and the mean volume of WWS is 300 m³/day, which is almost 1% of the incoming water. Despite this small amount, the processes at the receiving WWTP have been showing taking an impact.

Nodra has transported the WWS to the WWTP during different periods since the start in the autumn of 2021 to investigate how the processes on the WWTP react when receiving WWS. Some of the preliminary results indicate that pre-precipitation is positively affected by WWS. In the pre-precipitation step, ferric chloride is used as the precipitation chemical, and after Nodra started to receive WWS it has become evident that the dosing of ferric chloride could be reduced which also results in reduced chemical costs. However, there have also been some results showing negative effects on the WWTP, for example, on the dewatering of the digested sludge. The dewatered sludge contains more water than before receiving WWS, which results in an increased cost of removal.

Due to these different results, Nodra wanted to investigate what in the WWS is causing these effects on the WWTP plant and if some more pros and cons come with the sludge.

The aim of this master thesis was limited to investigating the impact of the WWS on the pre-precipitation step of the WWTP and how the subsequent biological wastewater treatment (BWT) might be affected by the decreased dosing of ferric chloride.

1.1 Waterwork treatment plant

Motala Ström is a river that starts in Motala and empties into Bråviken, a bay of the Baltic Sea outside Norrköping. Motala Ström passes through several lakes on its way to the Baltic Sea, of which the last one is Glan. A few kilometers downstream from Glan, Nodra has its raw water intake for drinking water to the waterwork treatment plant.

The first step in purifying the water is to mechanically remove bigger subjects like branches, vegetation, and aquatic animals through a grid. After that, the precipitation chemical aluminum sulfate is added during vigorous stirring before entering the flocculation basin where the water is slowly stirred, and smaller particles like viruses, bacteria, algae, and dirt are starting to flock together. The next step is the sedimentation basin where the created flocks clot together into larger flocks and fall to the bottom. The supernatant in the sedimentation basin is led onto two different filters. The first one is called a quick filter and the second is called a slow filter, the purpose of both is to remove pollution and toxins. The water is led on through UV light and before the drinking water is released to the reservoir, lime is added (*Figure 1*).

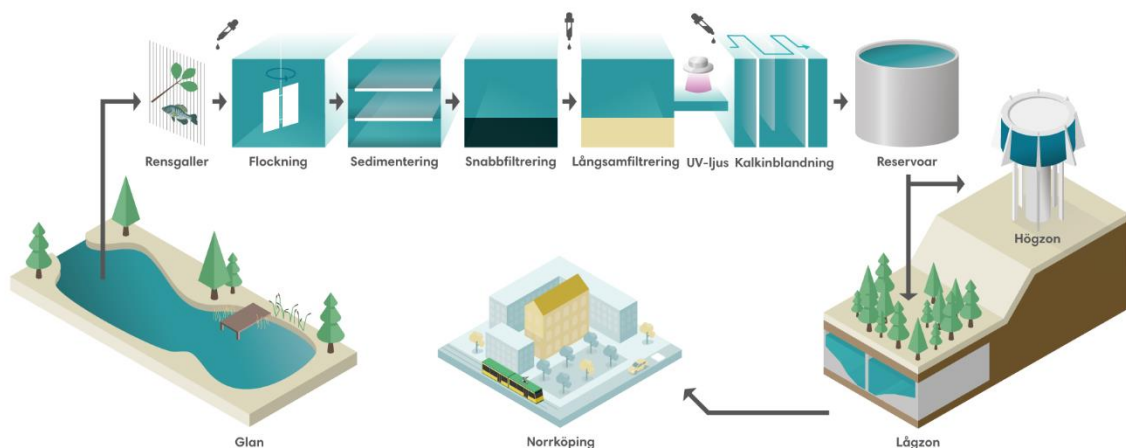


Figure 1. An overview of the processes on Borg, the drinking water treatment plant in Norrköping. Picture from Nodra.

The sedimentation basins have no scrapes that collect the sludge, instead, the basins are emptied and auto-flushed every 6-10 days. The sludge is led onto a collection basin where the sludge is sedimented for a second time. The sludge from the second sedimentation is collected by scrapes into sludge pockets from where the sludge is either released to Motala Ström or pumped through the sewer network to the WWTP (*Figure 2*). The supernatant is released back into Motala Ström.

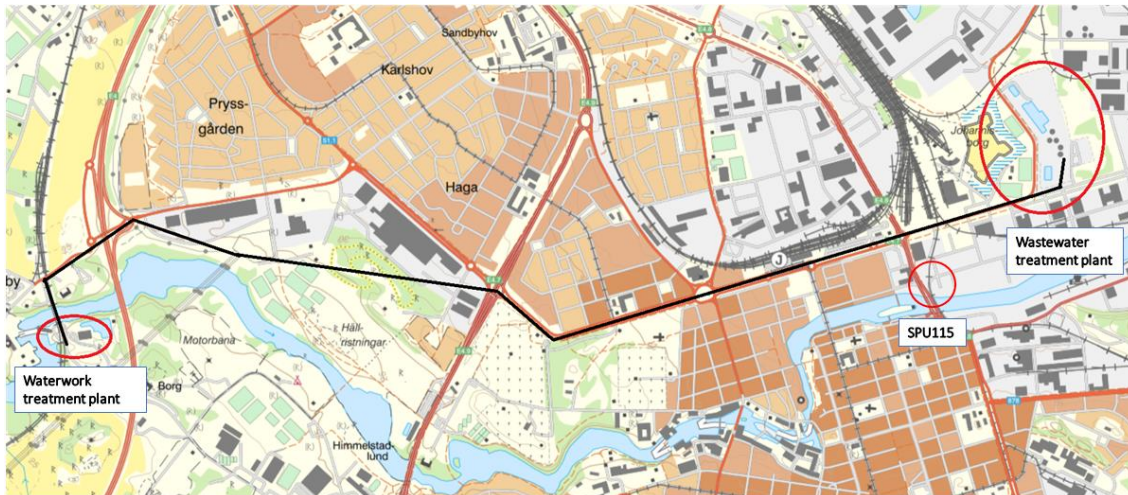


Figure 2. The map shows an overview of the central part of Norrköping. The waterwork treatment plant and the WWTP are circled in red. The black line between the two is the sewer network where the WWS is being pumped. The distance is about 6-7 km. The sewer pumping station SPU115 is also marked with a red circle. The map is from Lantmäteriet, 2022-11-10, the circles and lines are added afterward by the author of the thesis.

1.2 Wastewater treatment plant

The purification steps of the wastewater in Norrköping can be seen circled in green (Figure 3). The incoming wastewater passes firstly through a grind that mechanically removes bigger subjects and then a grit trap where grit is removed to prevent settings or damage to the downstream processes. Before the grit trap, the precipitation chemical, ferric chloride, is added by flow during vigorous stirring. While the wastewater passes through the grit trap, the precipitation chemical is distributed in the wastewater, reacts with particles, and starts to create flocks. Then the wastewater flows into a precipitation basin where the newly created flocks clot together, precipitate, and sediment to the bottom. Scrapes collect the sludge into sludge pockets where it pumps to the sludge process with a digester, circled in red (Figure 3). The precipitation is called pre-precipitation since it occurs before the biological waste treatment (BWT).

After the pre-precipitation, the wastewater is led to the BWT for nitrogen purification with an active sludge process. The BWT contains a pre-denitrification, which means that denitrification is placed before nitrification. With this setup, the nitrate from nitrification can be recirculated back to the denitrification and the carbon in the wastewater can be more fully utilized.

The BWT is followed by post-precipitation, precipitation after the BWT, where ferric chloride also is used and where most of the remaining phosphorus is removed before the water empties into Bråviken.

Parallel to the purification of wastewater, a sludge process is taking place, as seen circled in red (Figure 3). The sludge from the pre-sedimentation and BWT together with external sludge is collected and digested for sludge reduction and to produce biogas. The digestate sludge is dewatered before it is transported from the WWTP, depending on whether it is approved as fertilizer, it is sent to arable land, otherwise to incineration or landfill.

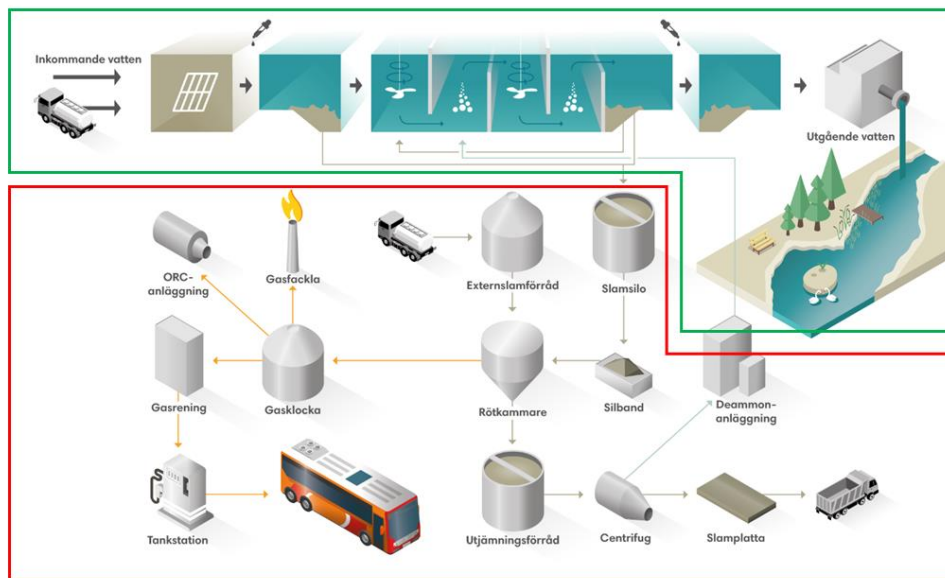


Figure 3. An overview of the processes on Slottshagen, the WWTP in Norrköping. Picture from Nodra.

2 Introduction

In this section, the facts of the project will be introduced.

2.1 Phosphorus

The main part of the phosphorus in the wastewater comes from urine and feces and exists in the form of free phosphate, also called orthophosphate, or bound organic phosphorus. About a third of the amount comes from detergents and exists as polyphosphate, which quickly can break down to orthophosphate [1].

Raw wastewater contains between 6-25 mg phosphorus per liter of water, of which 60-70% is inorganic phosphorus, mainly orthophosphate and polyphosphate. Orthophosphates exist in form of either $H_2PO_4^-$ or HPO_4^{2-} , depending on the pH of the wastewater [1,2]. In the case of the WWTP in Norrköping, where the pH is around 7.4, the ratio is about fifty/fifty.

Organic phosphorus is the next common form and exists as bound in particles, in form of, among other things, bacteria and viruses [3,4]. Bacteria contain phosphor-rich nucleic acids, and the cell membrane has an outer phospholipid bilayer. The virus contains a nucleic acid center with an outer protein layer. The wastewater also contains a smaller amount of phosphor compounds, for example, AMP, ADP, ATP, and free phosphor lipids[1,5]

2.2 Colloidal particles in water

The range of the surface forces between colloidal particles is short, often smaller than the diameter of the particle itself and due to this, the particles have little to no impact on macro transportation. But these surface forces are crucial if the particles either repel or bind when they collide. Most particles and pollutions in wastewater are negatively charged, i.e., they repel each other and stay finely divided in the water, seen as turbidity. If positively charged cations are added, often in terms of ferric salts or aluminum salts, the negative surface charges are lowered or neutralized, and particles that normally repel each other could aggregate[1].

The cations can aggregate both hydrophilic and hydrophobic particles. Hydrophilic particles are naturally negatively charged in wastewater, for example, phosphates or bacteria, but hydrophobic particles lack charges, like lipids. Instead, they bind negatively charged sulfates and orthophosphates through van der Waals bonds, and as result, hydrophobic particles become negatively charged in wastewater [1].

The electrostatic repulsive forces between two negatively charged particles are greater than the attractive forces of van der Waals. After neutralization by adding a cation, the van der Waals forces start to attract and aggregate the particles[1,6]. Compounds with smaller molar mass or non-charged particles are removed during the following BWT system[1].

2.3 Pre-precipitation and flocculation

Precipitation is the process in which the precipitation chemicals neutralized negatively charged particles in the incoming water and make it possible for the particles to aggregate through van der Waals forces. The next part, called flocculation, is the part where the particles will clot together and create larger units (flocs) until they are heavy enough to sink to the bottom by sedimentation. Since sedimentation relies on gravity, it is a slower process than precipitation. It is preferable if the flocs' are larger, as the property of the sludge improves. This is achieved by letting the flocculation be done slowly or with no stirring for a longer time [6].

The purpose of pre-precipitation is to remove phosphorus but consequently, also organic matter is reduced. The reduction of biological matter is measured through the lowered oxygen demand, and in the pre-precipitation, the reduction is around 50%. In the following BWT, the rest of the biological material is removed[6].

2.4 Precipitation chemical

Aluminum sulfate and ferric chloride have been used for decades as precipitation chemicals in precipitation in waterwork treatment plants and WWTPs to remove phosphor, organic matter, and particles [7,8], but the coagulation mechanism behind them is complex and still not fully understood [4,9]. There are certain circumstances where not only the electrical and van der Waals forces are crucial for the precipitation, but also the electrical and colloidal properties of the precipitation chemical itself [9]. This will not be further investigated due to the complexity, the only forces taken into consideration in this report are electrical and van der Waals forces.

There are some important characteristics that a precipitation chemical needs to fulfill to be effective. For example, the metal counter ion should preferably be a trivalent cation, since it is the most effective cation, the compound needs to be non-toxic, and the precipitation chemical should be solvable in the pH range of the treated water[1].

When adding a precipitation chemical to water or wastewater, the colloidal particles will be affected by three coagulation effects, electrical neutralization, adsorption bridging, and sweeping net capture. For instance, orthophosphate and other negatively charged colloidal particles will bind to the positive charge metal ions and be neutralized, they will later aggregate and sink to the bottom. When the precipitation chemical lack substance to react with or is in high concentration, metal hydroxide precipitation will form and induce “sweep floc”, the precipitation acts as a net that sweeps in pollution while it settles at the bottom of the tank [6,10]. A theory is that WWS increases the sweeping net capture, and already in the sewer system binds to negatively charged particles.

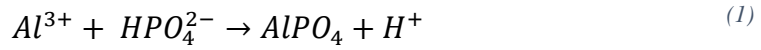
2.4.1 Aluminum salt

The precipitation chemical that is used in the precipitation of the drinking water treatment plant in Norrköping is aluminum sulfate ($Al_2(SO_4)_3$). This product comes as granules and dissolves in water to a concentrated solution before being added to the incoming water and when doing so, aluminum ions (Al^{3+}) and sulfate ions (SO_4^{2-}) are created [6]. In a concentrated solution of aluminum salt, no counterions are bounded to the Al^{3+} -ions. Instead, it has six water molecules tightly bound to each, the chemical designation is $Al(H_2O)_6^{3+}$. Outside of these tightly bound water molecules, there are 10-12 water molecules less tightly bound resulting in very little free water in the solution [1].

When the concentrated solution of an aluminum salt is added to the incoming water at the water treatment plant, different reactions take place depending on if the salt reacts with the negative particles or the water molecule [1].

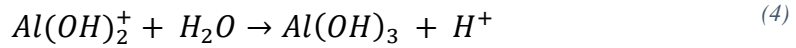
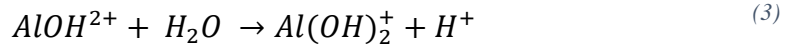
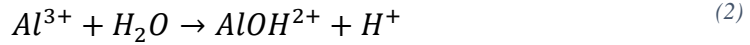
Al^{3+} -ions react with phosphate

If the Al^{3+} -ions react with phosphate, reaction (1) occurs and results in the creation of aluminum phosphate ($AlPO_4$) and H^+ .



Al^{3+} -ions reaction with water

When the Al^{3+} -ions react with the water, a potent reaction occurs and results in splitting the water molecules and creating a proton (H^+) and aluminum hydroxides ($Al(OH)_3$). This happens through a series of reactions, seen in reactions (2)-(4).



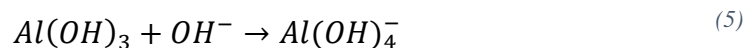
Reaction (2)-(4) happens rapidly, within 1-7 seconds after adding the $Al_2(SO_4)_3$ -solution.

The SO_4^{2-} -ions will not take part in the precipitation reaction, they go through the following purification steps unchanged, the same applies to the chloride (Cl^-) in ferric chloride ($FeCl_3$). described under *Ferric salt*. Therefore, and for the sake of simplicity, they will be ignored in future discussions [1,6]

2.4.2 Importance of pH for the precipitation

Depending on the pH of the water, the $Al(OH)_2^+$ have a positive or negative net charge. At pH 4, the hydroxide has a positive net charge which decreases until pH 9, where the charge changes to being negative. If $Al(OH)_3$ have a positive net charge, they can be used to adsorb orthophosphate and colloidal particles through sweep flocculation, although, Al^{3+} -ions are much more effective than the $Al(OH)_3$. Therefore, and because of the differences in the ratio between water molecules and orthophosphate, the mixing of the precipitation chemical must be done swiftly so that the Al^{3+} -ions react firstly with the orthophosphate and then the water molecules. But even during good mixing, it is impossible to avoid the creation of $Al(OH)_3$. In the beginning, the hydroxide is weakly bounded to the water but after some time they start to aggregate between each other through hydrogen bound, $Al(OH)_3(H_2O)_x$, and where x will increase with time. This is the start of the sweep flocculation [6].

As seen in reactions (1)-(4), when the $Al(OH)_3$ and $AlPO_4$ are created, free H^+ -ions are released. These ions lower the pH of the water and make it acidic. If the water becomes too acidic, the availability of OH^- -ions will decrease. Thus, no $AlOH^{2+}$ can be created, and no sweep flocculation can happen. If the water instead is alkaline and the pH reaches above 8, the $AlOH^{2+}$ starts to react with free OH^- -ions, and aluminate ions ($Al(OH)_4^-$) are created, see reaction (5) [1].



$Al(OH)_4^-$ -ions are solvable at higher pH which means if the pH increases further, the $Al(OH)_4^-$ -ions will dissolve, and the aluminum residue content increase. To obtain

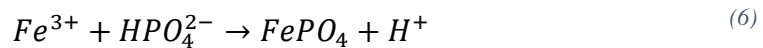
flocculation with aluminum sulfate, a pH between 5-8 is desirable. For optimal flocculation, pH should be between 5,7-6,5 [6].

2.4.3 Ferric salt

The precipitation chemical used at the WWTP in Norrköping is ferric(III)chloride ($FeCl_3$). In comparison to the granules of $Al_2(SO_4)_3$, $FeCl_3$ is supplied as a ready-made solution, so no preparations for the product are required. $FeCl_3$ reacts in the same way with water molecules and orthophosphate as $Al_2(SO_4)_3$ does [6].

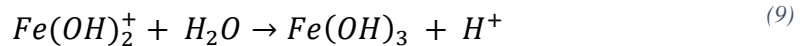
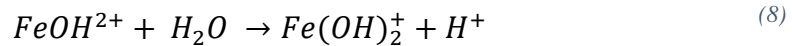
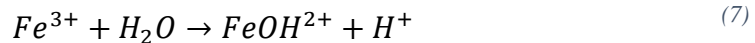
Fe^{3+} -ions react with phosphate

Reaction (6) describes the creation of ferric phosphate ($FePO_4$) and H^+ .



Fe^{3+} -ions reaction with water molecules

The creation of ferric hydroxide ($Fe(OH)_3$) through a series of reactions can be seen in reactions (7)-(9).



A swift mixing of $FeCl_3$ is required as reactions (7)-(9) do occur as rapid as reaction (2)-(4), between 1-7 seconds [1].

Reaction (6)-(9) also lower the pH of the water by releasing H^+ -ions. The precipitation caused by using $FeCl_3$ occur in a wider pH range than $Al_2(SO_4)_3$. A pH over 4,5 is useful but for optimal precipitation, a pH around 5 or a value above 8,5 is favorable. In a wastewater treatment plant, precipitation occurs normally between pH 6-7, it depends on the incoming wastewater [6].

2.5 The biological wastewater treatment system

At the WWTP in Norrköping, the dosage of $FeCl_3$ added before the pre-precipitation is set manually after the output amount of phosphate from the BWT. Then, $FeCl_3$ is added per cubic meter of incoming wastewater. The reason for this is that, in the BWT, the microorganism primarily needs phosphate to be able to work properly. The main purpose of the BWT is to remove nitrogen and organic matter [11].

The BWT in Norrköping consists of four parallel activated sludge lines with pre-denitrification and traditional sedimentation. Activated sludge contains microorganisms that, as they grow, break down organic matter. The active microorganism in the activated sludge process occurs as brownish flocks of sludge and the principle is that the sludge has a longer residence time than the wastewater [11].

For the process of activated sludge to be able to remove organic matter successfully, different functions need to be fulfilled. The first one is the creation of sludge, there needs to be aeration of basins where microorganisms can grow and lump together. The second one is aeration, i.e., oxygen supply for microorganisms during the oxidation of organic matter. The third is aeration and/or stirring to keep the microorganisms floating. Fourth is the sedimentation of the sludge and separation of the purified water from the sludge. Fifth is the return of activated sludge for the regrowth of microorganisms. Sixth and the last one is the collection and withdrawal of excess activated sludge [12].

The activated sludge also adsorbs colloidal particles that cannot sediment on their own. If the mixing of the sludge is effective and the sludge content is high enough, the adsorption requires only a few minutes of contact time. The quality of the sludge in the activated sludge process is also important for the degree of purity of the outgoing water [12].

The word “microorganism” comprises different unicellular eukaryotes and prokaryotes. Eukaryotes include unicellular organisms, like yeast and algae, and multicellular organisms, like fungi and plants. Bacteria and cyanobacteria are differentiated from prokaryotes. The main difference between eukaryotes and prokaryotes is the cell structure and where the DNA is stored. For eukaryotes, the DNA is in the nuclei, and for prokaryotes in the cytoplasm [13]. The most important microorganisms in activated sludge processes are bacteria [5].

The five most important parameters that affect the growth of microorganisms are energy, nutrition, oxygen ratio, temperature, and pH [5]. The ones that will be discussed in this report are energy and nutrition. The nutrition can be controlled before the water enters the activated sludge basins by the number of precipitation chemicals added in the pre-precipitation. The oxygen ratio is controlled during the time the wastewater passes through the activated sludge basins, and the last three parameters, energy, temperature, and pH cannot be altered in any major way as these are influenced by external conditions.

2.5.1 Energy

Energy is about electrons, and energized reactions are where electrons are transferred in redox reactions. For a compound to be able to extract electrons, there needs to be a corresponding compound in excess of electrons. When a substrate reduces its electrons, it is called oxidation. In a redox reaction, the substrate that picks up the electrons is called the electron acceptor, i.e. the electron receiver act as an oxidizing agent, itself becoming reduced in the process. The most effective known electron receiver is oxygen but there are also others like nitrate or sulfate. Bacteria can use different types of electron receivers for oxidation and can use the most effective one available. See Table 2 for different electron receivers of heterotrophic bacteria, bacteria that can access energy from the oxidation of organic compounds [5].

Table 2. Electron receiver and energy exchange of heterotrophic bacteria during the different conditions [5].

Electron receiver	% Energy*	Conditions	Residual product
Oxygen gas	100	-	Water
Nitrate	~90	No O ₂	Nitrogen gas
Chlorate	Maximum 90	No O ₂ , NO ₃ ⁻	Chloride
Sulfate	5-15	No O ₂ , NO ₃ ⁻ , ClO ₃ ⁻	Sulfide
Organic substances	~10	No O ₂ , NO ₃ ⁻ , ClO ₃ ⁻	Organic acids
Metals	<10	No O ₂ , NO ₃ ⁻	Reduced metals

*Compared with O₂ as an electron receiver.

The microorganisms need the energy to survive and grow, and to achieve energy, the microorganisms oxidize organic matter from the wastewater [12].

2.5.2 Nutrition

For a microorganism to grow, in addition to energy, nutrients are also required. Nutrition for bacteria comes in the forms of elements that are included in the cell, the different elements, and the weight percent of the total solids of a bacteria cell (Table 3) [5].

Table 3. Table of relative amounts of the elements that the microorganisms need to grow [5,12].

Element	Weight percent [%]
Carbon	50
Oxygen	28
Nitrogen	12
Hydrogen	6
Phosphorus	2
Potassium	1,5
Sulfur	0,3
Magnesium	0,2
Calcium	0,1
Ferric	0,02
Zinc	0,005
Manganese	0,005
Cobalt	0,001
Copper	0,001
Molybdenum	0,001

The quantitatively essential elements for growth are nitrogen and phosphorus, which makes up 12% respectively 2% of the total solids of a bacterial cell. Trace elements like ferric, manganese, copper, and several others are also required for metabolic functions (Table 3). To meet the need for nitrogen and phosphorus for the microorganisms, a ratio between organic matter, measured in BOD, nitrogen (N), and phosphorus (P) should at least be between 100:10:1 and 100:5:1 (although a higher ratio is acceptable), calculated as BOD/BOD:N/BOD: P/BOD. Depending on how much organic matter, nitrogen, and phosphorus are precipitated in the pre-precipitation, the assets of these elements are often abundant in municipal wastewater [2,5,6]

As mentioned above, pre-denitrification is used at the WWTP in Norrköping and the optimum BOD/N ratio for organic matter to be used for denitrification is 3-3,5 mg BOD/mg N [14].

As mentioned above, for bacteria to access energy and be able to grow, the decomposition of organic materials is required. If the substrate is too large, for example, organic phosphorus or starch, and not able to pass through the cell membrane, the substrate needs to be broken down. This is done mainly by hydrolytic enzymes that are secreted from the bacteria. The rate of degradation of the organic matter is slowed down if the bacteria need to break down the substrate instead of being able to let the substrate pass directly through the membrane, for example, phosphate or glucose. Bigger substrate benefits bacteria that exist in aggregates, whereas scavenging bacteria can use a substrate that the neighbor bacteria have broken down [5].

The substrate concentration is also an important part of the degradation of organic matter, the degradation happens quicker if the substrate concentration is higher than if it is low [5].

3 Materials and Methods

In this section, the trial planning and methods will be introduced.

3.1 Sampling

Since this master thesis will be taking place during times when Nodra receives WWS, and some of the samples need to be without WWS, the wastewater used in the experiments is collected from a sewage pumping station called Hamnbron, or SPU115, (Figure 2). All the wastewater from south of Motala Ström passes through SPU115 which is the largest sewage pumping station without WWS.

New wastewater from SPU115 and WWS from the waterwork treatment plant was collected on the same day as the execution of the experiments. The reason for the collection of new samples was to reduce the sources of error when the experiments were repeated and to obtain repeatable results.

3.2 Trial planning

The trial planning was divided into two parts. The first part was a trial and error to investigate how the experiment should be carried out most efficiently and the second part was the actual experiment which the conclusions in the result were drawn from. For an extensive description of the trial-and-error part, see *Trial planning of the trial-and-error part* in the appendix.

3.3 The experiments

The conclusion from the trial-and-error part resulted in the sample combination of wastewater, WWS, and $FeCl_3$ (Table 4), with settings for the flocculator (Table 5). The WWS concentration was chosen due to the incoming concentration of WWS to the WWTP and the amount $FeCl_3$ depended on the dosage amount on the WWPTS. The preparation and execution of the experiments extend over several days and are described below.

3.3.1 Day one

Preparation of the samples was done by preparing two five-liter containers the day before the precipitation with the flocculator. One with only wastewater and one with wastewater mixed with 50 ml (1%) of WWS, and the last one was stirred overnight with a magnetic flea (Figure 4).

Table 4. The sample with different amounts and contents was used in the second part of the trial planning.

Sample	Amount $FeCl_3$	Concentration WWS
Reference sample	-	-
Wastewater	-	-
Wastewater + 5 μ l/l $FeCl_3$	5 μ l/l	-
Wastewater + 15 μ l/l $FeCl_3$	15 μ l/l	-
Wastewater + 25 μ l/l $FeCl_3$	25 μ l/l	-
Wastewater + WWS	-	1%
Wastewater + WWS+5 μ l/l $FeCl_3$	5 μ l/l	1%
Wastewater + WWS+15 μ l/l $FeCl_3$	15 μ l/l	1%
Wastewater + WWS+25 μ l/l $FeCl_3$	25 μ l/l	1%

Table 5. Settings of the precipitation program for the flocculator. Fast is the length of the first mixing of chemicals, it is measured in seconds and has an RPM of 400 turns per minute. Slow is the length of when the flocculation takes place,

measured in minutes, and has an RPM of 30 turns per minute. Sed is the sedimentation process when the stirrer bar is still and is measured in minutes.

Fast (seconds)	30
Slow (minutes)	20
Sed (minutes)	15
Fast (RPM)	400
Slow (RPM)	30



Figure 4. Picture how the two five-liter containers with and without WWS were prepared, the one to the left contains only wastewater, and the one to the right contains both wastewater and WWS. That container also contains a magnetic flea and was stirred over the night.

3.3.2 Day two

The containers with the prepared samples were transferred to different flocculation jars, one liter each. The flocculator carried out the precipitation program shown in Table 5 and at the beginning of the first 30 seconds, $FeCl_3$ was added to the jars according to the amounts in Table 4. The reference sample was untreated wastewater and did not undergo precipitation.

After the precipitation with the flocculator had ended, 500 ml of the supernatant was extracted. The supernatant was analyzed by different analysis methods to investigate the difference in composition between the samples, see Table 6.

Table 6. The analysis methods were performed on the supernatant with the necessary preparations of the sample.

Analysis method	Preparation of sample
BOD ₇	-
TOC	-
Suspended matter	-
Total Nitrogen	Pressure boiling
Total phosphorus	Pressure boiling
Phosphate	Filtration

More detail about the analysis methods and their purpose of these can be read in the following section *The analysis methods*

3.4 The analysis methods

In this section, the methods used in the preparation and analysis of the supernatant will be described. Nodra uses accredited methods, and they are described by the Swedish Standards Institute, SIS. For the accredited methods below, there will be a reference to the standard from SIS [15].

3.4.1 The flocculator

The flocculator was used for consistent performance of the experiment runs, and to mimic the mixing of precipitation chemicals and the pre-precipitation on the WWTP.

3.4.2 BOD₇

BOD, *biological oxygen demand*, measures the oxygen demand of the microorganisms when oxidizing organic matter and ammonium. In other words, the consumed amount of oxygen the microorganisms use to biochemically degrade organic matter, and can be used as a way to measure the amount of biologically accessible carbon in a sample [14]. In Sweden, the standard analysis takes seven days to complete, hence the term BOD₇ [3].

For details see reference method SS-EN ISO 5815:2019 and 5814:2012 [15].

3.4.3 TOC

TOC, *Total organic carbon*, states the amounts of carbon atoms by oxidizing organic matter to carbon dioxide by heating. By calculating the difference between the carbon dioxide concentration before and after the heating, TOC is determined [14]. TOC includes both biologically accessible carbon, as determined by BOD₇, and biologically inaccessible organic carbon. Example of organic compound in water and wastewater is plastics, pesticides, virus, bacteria, and even fishes [16].

TOC is mainly used as a reference in predicting the dilution of the BOD₇ in this report.

For details see reference method SS-EN ISO 1484 [15].

3.4.4 Total phosphorus

When measuring total phosphorus concentration, the sum of orthophosphate, polyphosphate, and organic phosphorus is measured [1]. By pressure boiling the samples, the organically bound phosphorus and polyphosphate are dissolved into orthophosphate which can be measured.

For details see reference method SS-EN ISO 15681-1:2005 (FIA) [15].

3.4.5 Orthophosphate

By filtering the sample, the organically bound phosphorus and polyphosphate can be separated from orthophosphate. This way, the content of phosphate can be measured.

For details see reference method SS-EN ISO 15681-1:2005 (FIA) [15].

3.4.6 Total nitrogen

When measuring the total nitrogen content, the samples are pressured-boiled to break down bounded nitrogen. The parameter is used when calculating quotas.

For details see reference method SS-EN ISO 11905-1(FIA) [15].

3.4.7 Suspended matter

When measuring the suspended matter, the number of particles in the sample is measured. By measuring this parameter, the sedimentation of different samples can be established, and the results show how well different compositions of precipitation chemicals and WWS precipitate particles and compounds.

For details see reference method SS-EN 872:2005 [15].

3.4.8 pH

pH measures the activity of free H^+ -ions.

For details see reference method SS-EN ISO 10523:2012 utg 1 [15].

3.5 Examination of quotas

In this section, the calculation of quotas will be described.

There are three different quotas, BOD:N:P, BOD:N:HPO₄²⁻ and N:C, which will be calculated. BOD:N:P and BOD:N:HPO₄²⁻ will be calculated from equations (13)-(15), and N:C will be calculated from equation (16).

Both data from the experiment results and historical data from the WWTP in Norrköping will be used to calculate these quotas.

The historical data are from two different periods, one period when the WWTP did not receive WWS and one where it did receive WWS, the aim is to evaluate if the nutrition content from the pre-precipitation into the BWT is affected by the WWS. These quotas will be compared with quotas calculated with experimental data to investigate how well the experiment reflects reality and if the conclusions from this report could be applied to the operation of the WWTP.

4 Results

Every analysis has been repeated three times and the error bars have been calculated with standard deviation. The raw data can be found in the appendix under *Raw data*.

When calculating the standard deviations for the experimental data, the “n-1”-method was used, and the three experiments constituted the entire population. The same method was used when calculating the standard deviations for the historical data, but the arguments constituted a sample from the population.

4.1 Analysis result

The mean results from analyzing total phosphorus and phosphate, respectively (*Figure 5*, *Figure 6*), show very few error bars overlap, which means that the increased amount of precipitation chemicals decreases the concentration of phosphorus and phosphate. Furthermore, when WWS is present, the concentration of phosphorus reduces even more. With these results, the precipitation of phosphorus and phosphate are similar between adding 25 $\mu\text{l/l}$ FeCl_3 as with only WWS.

For graphs of the remaining parameters, see section *Analysis results* in appendix (*Figure 25*-*Figure 28*), since they do not show any differences between the samples as the error bars largely overlap.

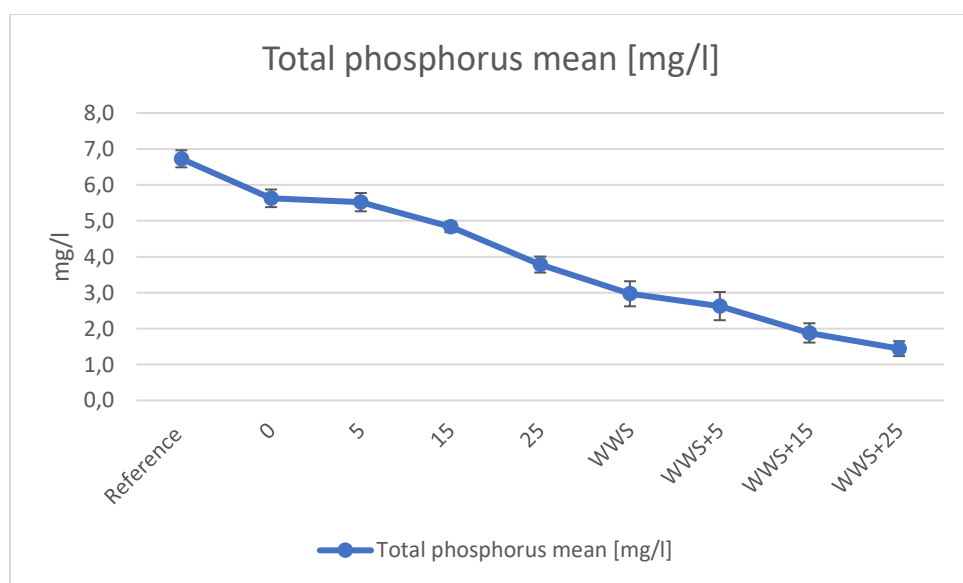


Figure 5. The mean result from analyzing the total phosphorus content with error bars. Explanation of the horizontal axis: “reference” is the reference sample, “WWS” means that the sample contains 1% WWS, and the “0”, “5”, “15” and “25” are the added amount FeCl_3 .

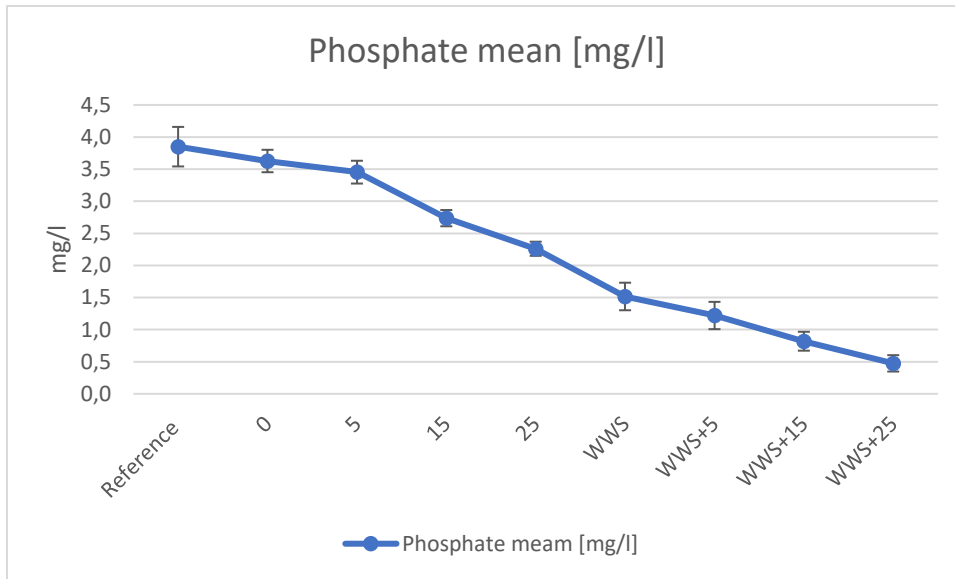


Figure 6. The mean result from analyzing the phosphate content with error bars. Explanation of the horizontal axis: “reference” is the reference sample, “WWS” means that the sample contains 1% WWS, and the “0”, “5”, “15” and “25” are the added amount $FeCl_3$.

4.2 Substance reduction results

To see if any differences could be discerned between the analysis results whose error bars overlapped, the reduction of the parameters were calculated. The reductions are the analysis result normalized to the result of the reference sample (10), and overall, the reduction results indicate a greater difference between the samples than the analysis results since the error bars do not overlap as much.

$$\frac{\text{Reference result} - \text{analysis result}}{\text{reference result}} \quad (10)$$

In the reduction of the BOD_7 (Figure 7), the blue line is wastewater without WWS, and the orange is wastewater with WWS. The precipitation of wastewater with 25 $\mu\text{l/l}$ $FeCl_3$, B41, is close to the precipitation of both wastewaters with only WWS, A1, and WWS with 5 $\mu\text{l/l}$ $FeCl_3$, A2. The precipitation of wastewater with WWS and both 15 $\mu\text{l/l}$ $FeCl_3$ and 25 $\mu\text{l/l}$ $FeCl_3$, A3 and A4, is better than precipitation with only $FeCl_3$, B4. This means that the dosage of $FeCl_3$ could be reduced to zero if one wants to have the same reduction when WWS is present as when 25 $\mu\text{l/l}$ $FeCl_3$ is added.

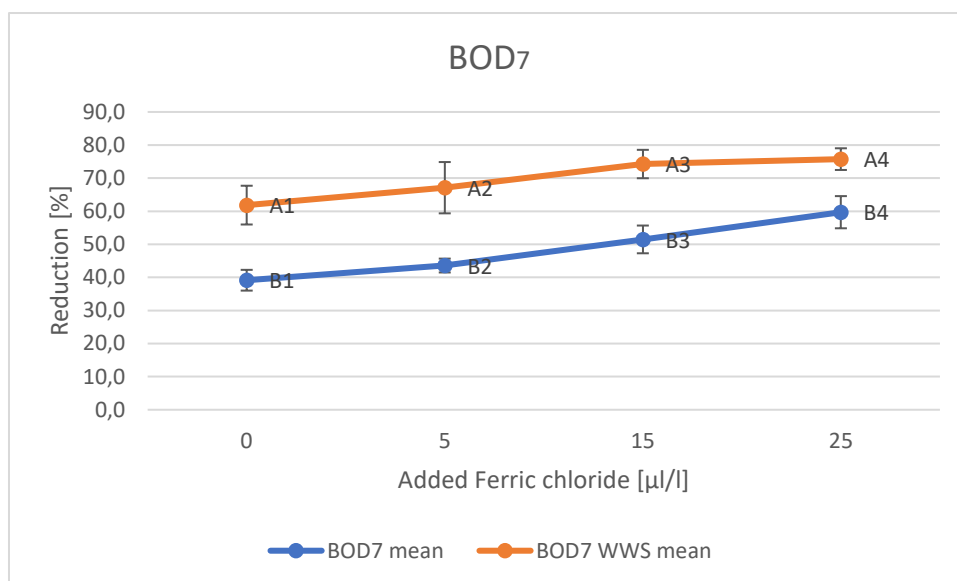


Figure 7. The reduction of the BOD₇ results in error bars calculated from the standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l FeCl₃.

The reduction of suspended matter (Figure 8) indicates that B4 provides a better separation of suspended matter than A1 does. But B4 is similar to A2. The precipitation at A2 and A3, have a similar and higher reduction than all other samples. The conclusion is that B4 could be substituted for the composition in A2.

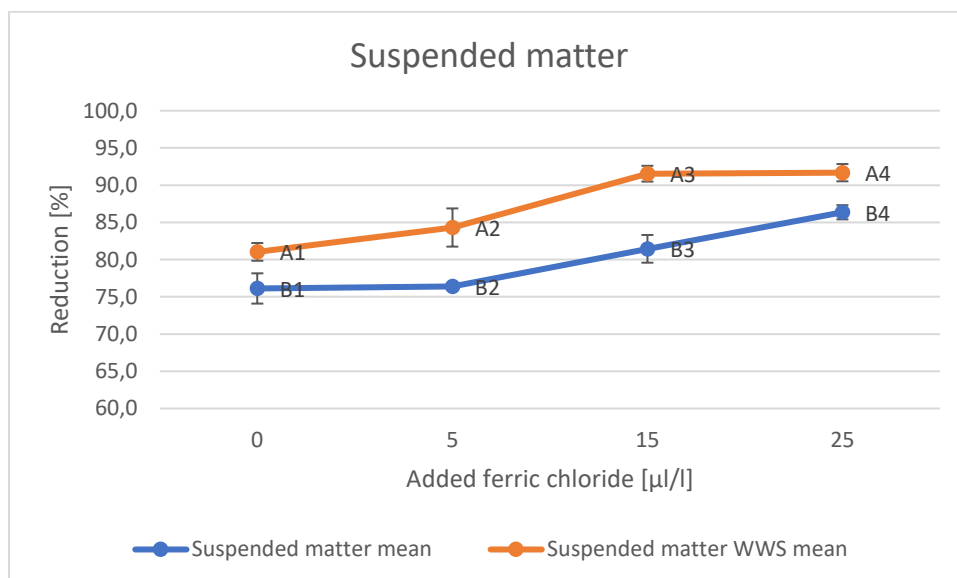


Figure 8. The reduction of the suspended matter results in error bars calculated from the standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l FeCl₃.

The reduction of the TOC (Figure 9), indicates an increased reduction, but due to the error bars, the precipitation of samples with the same amount of FeCl₃ cannot be seen as significantly different. The conclusion is that albeit the biologically accessible carbon is affected, the data obtained does not support that precipitation with FeCl₃ and/or WWS affect the total organic carbon in the wastewater.

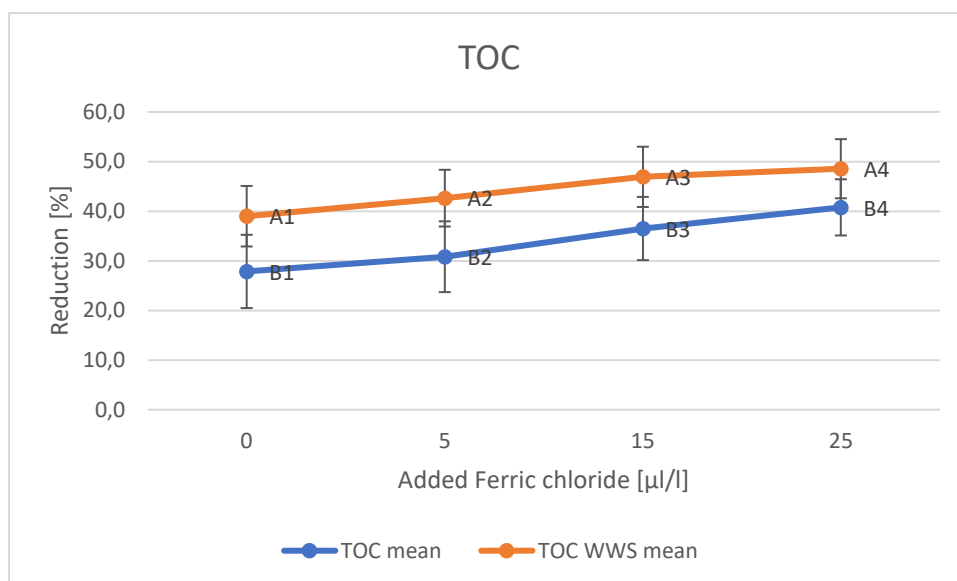


Figure 9. The reduction of the TOC results in error bars calculated from the standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l $FeCl_3$.

The reduction of total nitrogen (Figure 10) shows that B4 has a similar reduction as A1, A2, and A3. A4 has a higher degree of reduction than B4 but is similar to A3. The conclusion is that 25 µl/l $FeCl_3$ could be substituted for only WWS if the aim is the same reduction.

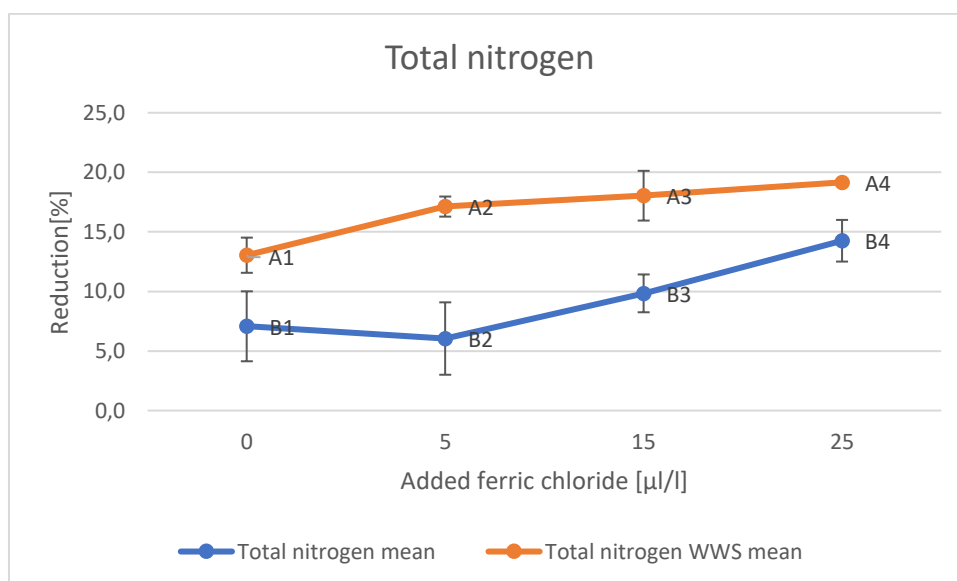


Figure 10. The reduction of the total nitrogen concentration with error bars calculated from standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l $FeCl_3$.

The reduction of the total phosphorus (Figure 11) shows that the reduction in A1 has a significantly higher reduction than in B4. The reduction of A1 is close to the reduction of A2 and the highest reduction has A3 and A4, which also have a similar reduction. The conclusion is that $FeCl_3$ could be substituted for WWS and still give a higher reduction.

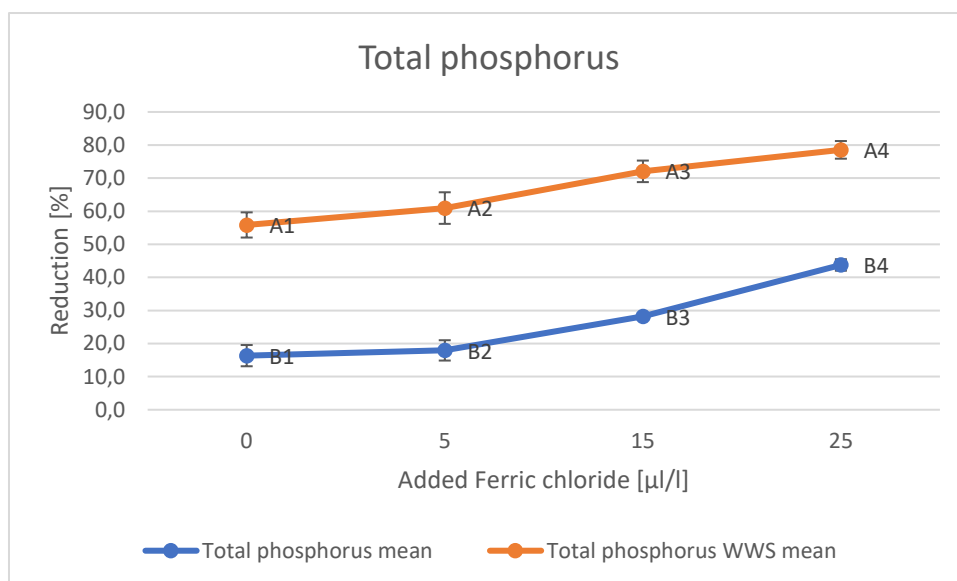


Figure 11. The reduction of the total phosphorus concentration with error bars calculated from standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l $FeCl_3$.

For the reduction of phosphate (Figure 12), B1 overlaps with B2, and A1 overlaps with A2, which means these have a similar reduction and a low dose of $FeCl_3$ (5 µl/l) does not affect the precipitation significantly. The reduction shows that phosphate is being reduced to a larger degree if WWS is present (A1-A4), in comparison to when it is not (B1-B4). The conclusion is that samples containing WWS have reached a higher degree of reduction than samples only containing $FeCl_3$.

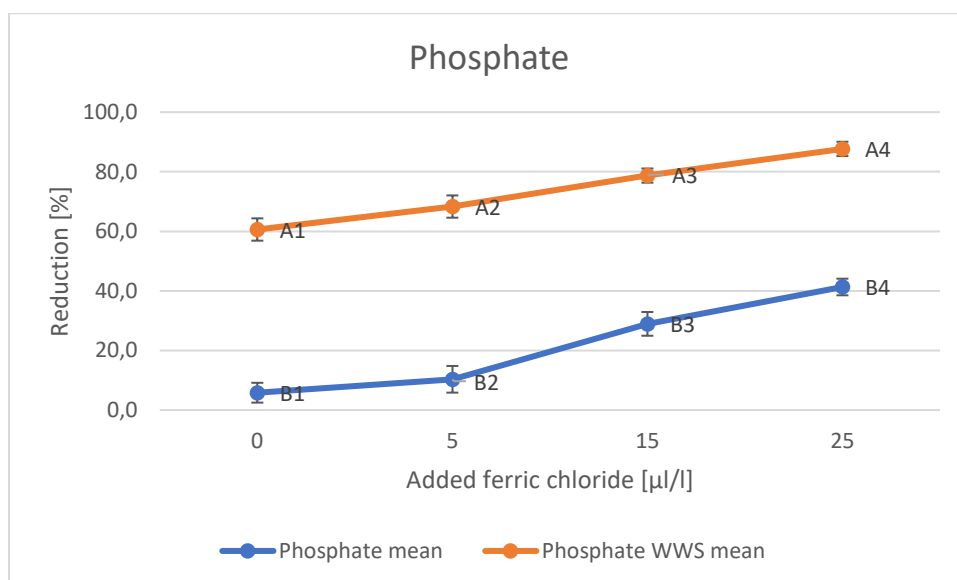


Figure 12. The reduction of the phosphate concentration with error bars calculated from standard deviation. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l $FeCl_3$.

The reduction of organic phosphorus (Figure 13) is calculated by differentiating between total phosphorus and phosphate. B4 has a similar reduction to A1 in this graph as well, but the difference in reduction is smaller than the reduction in the graphs of phosphate. The conclusion is that WWS reduces primarily phosphate and not organically bound phosphorus.

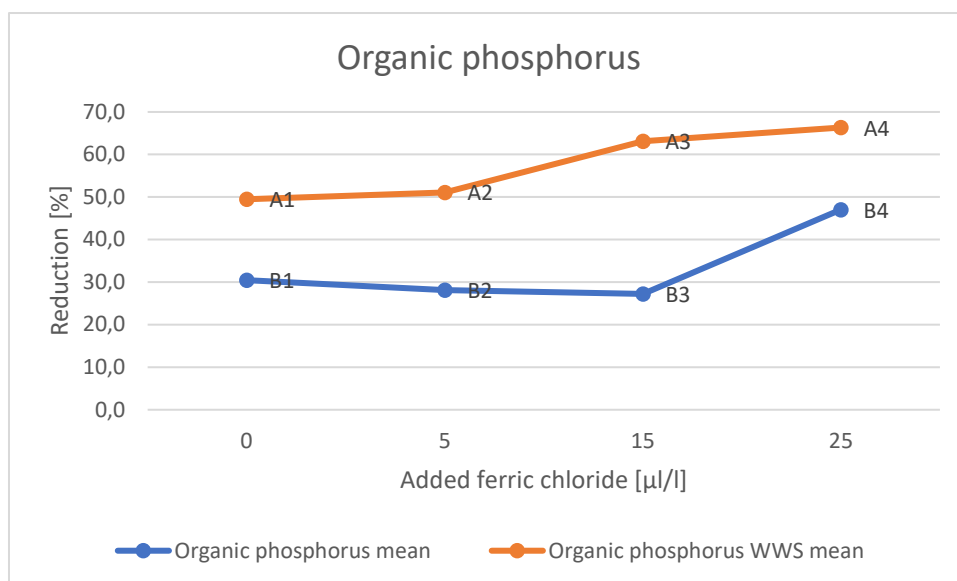


Figure 13. The reduction of the organic phosphorus concentration with error bars calculated from standard deviation. Calculated from the difference between total phosphorus concentration and the phosphate concentration. The blue bottom line is samples without WWS and the samples in the upper orange line contain WWS. The samples have been treated with either 0, 5, 15, or 25 µl/l FeCl_3 .

4.3 The ratio of organic phosphorus to phosphate

The percentage ratio between organic phosphorus to phosphate was calculated to further investigate if the WWS removed bound or free phosphorus. The ratio was calculated by taking the analysis result of phosphate and the calculated results of organic phosphorus and dividing them by the total phosphorus concentration (Figure 14).

The ratio changes drastically after WWS was introduced, which can be seen in the middle of the graph. The percentage amount phosphate is higher than the amount of organic phosphorus when no WWS is present, regardless of the added amount FeCl_3 . But when the wastewater is supplemented with WWS, the ratio between phosphate and organic phosphorus change, and the percentage amount of organic phosphorus is higher than the amount of phosphate.

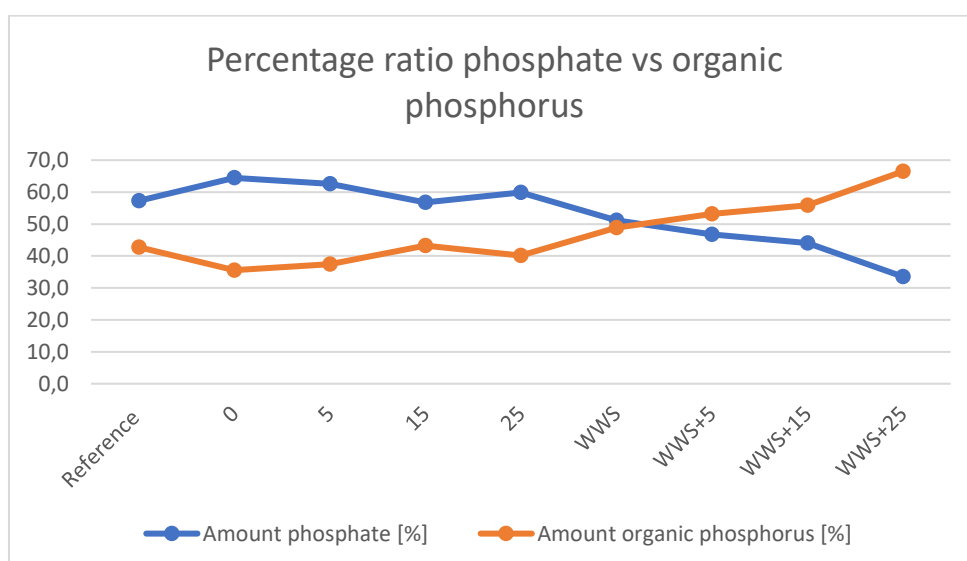


Figure 14. Calculation of the percentage ratio between organic phosphorus and phosphate with total phosphorus concentration as reference. The blue line is the amount of phosphate, and the orange line is the amount of organic phosphorus.

4.4 Changes in pH with and without WWS in the sample

To exclude the influence of pH on precipitation, the impact of WWS on the wastewater was investigated. The differences in pH during a flocculator test were measured by adding $FeCl_3$ to one sample containing wastewater and one sample containing wastewater and WWS (Figure 15). The differences when adding $FeCl_3$ was 0,02 units and after 30 min, the difference was 0,03 units.

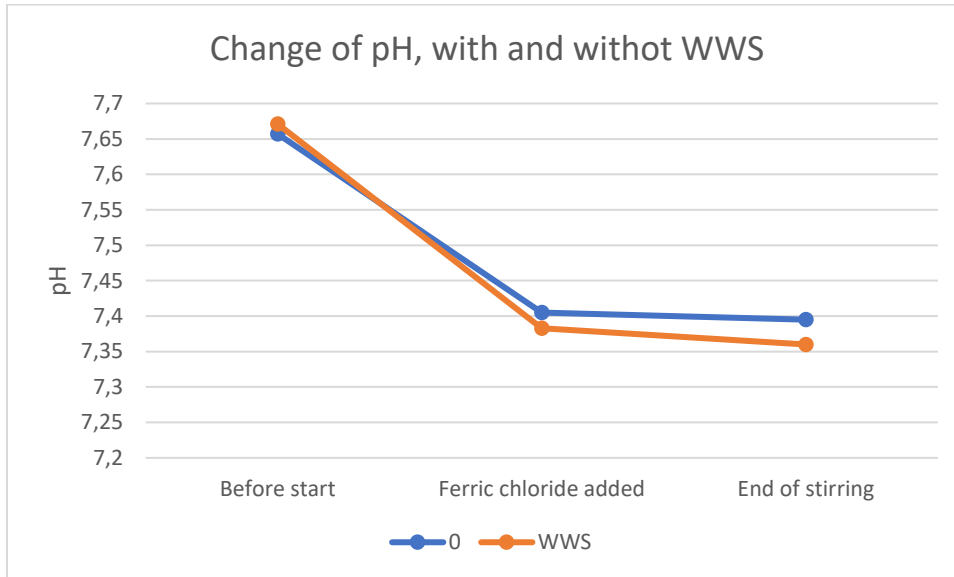


Figure 15. The changes of pH when $FeCl_3$ is added to a sample not containing WWS and one sample containing WWS.

4.5 Calculated results

Due to the results above, the combination of WWS and $5 \mu\text{l/l } FeCl_3$ could be used to replace the dosage of $25 \mu\text{l/l } FeCl_3$ and still, get the same reduction rate, these two will be further investigated by calculating quotas and costs.

The quotas will be calculated from both experiment results and historical data received from Nodra. The historical data are from two different periods, during September and October 2021, when Nodra did *not* receive WWS and the same period during 2022 when Nodra did receive WWS. During the 2021, the mean concentration of $FeCl_3$ was $25 \mu\text{l/l}$, and during 2022, the mean concentration was $20 \mu\text{l/l}$. Due to this, a comparison can not be done but is could give an indication of how the WWS affect the precipitation.

The cost calculations will be based on data from the WWTP.

4.5.1 Calculation of quotas

In the following section, calculations of the quotas BOD:N:P , BOD:N:HPO_4^{2-} (equation (13)-(15) and N:C equation (16), will be presented.

BOD:N:P and BOD:N:HPO₄²⁻

A summary of the calculated quotas from both experimental data and historical data can be seen in Table 7, for details, see *Calculation* in the appendix. The BOD:N-ratio is the same in both quotas.

Table 7. Summary of the BOD:N:P and BOD:N:HPO₄²⁻. The top row describes the minimum quota of nutrition needed for the BWT.

Samples	BOD: [%]	N: [%]	P [%]	HPO ₄ ²⁻ [%]
Recommended range	100	5-10	1	1
Wastewater + 25µl/l FeCl ₃	100	62	5	3
Wastewater + WWS+5µl/l FeCl ₃	100	73	4	2
September 2021 without WWS	100	26	2,5	1,1
October 2021 without WWS	100	27	2,4	1,0
September 2022 with WWS	100	26	1,8	0,4
October 2022 with WWS	100	25	2,1	0,5

To investigate the differences between the samples in Table 7, the standard deviations were calculated from the raw data. The intervals where the values of the quotas could exist were determined by calculating the maximum and minimum of each quota and then visualizing it in block graphs (Figure 16, Figure 17).

The standard deviation for experimental data was greater than the historical data resulting in greater intervals. For the raw data and calculations, see Table 12-Table 15 under *Calculation* in the appendix. In the block graphs, the BOD:N:P and BOD:N:HPO₄²⁻ was divided into BOD:N, BOD:P, and BOD:HPO₄²⁻ for easier overview. The BOD:N quota for all samples in Table 7 is above the minimum quota by a margin and will not be discussed further. If interested, see *Calculation* in appendix (Figure 29).

The intervals of the quota BOD:P (Figure 16) show that all experiment and historical quotas are above the recommended range, even if the historical data are closer than the experiment results. The graphs show that in the experimental results, the quota of sample 25 is higher than the quota of WWS+5. The same pattern with the quotas can be seen in the historical data, the data from 2021 have a higher mean value than the data from 2022, which indicates that WWS affects the ratio between BOD and total phosphorus.

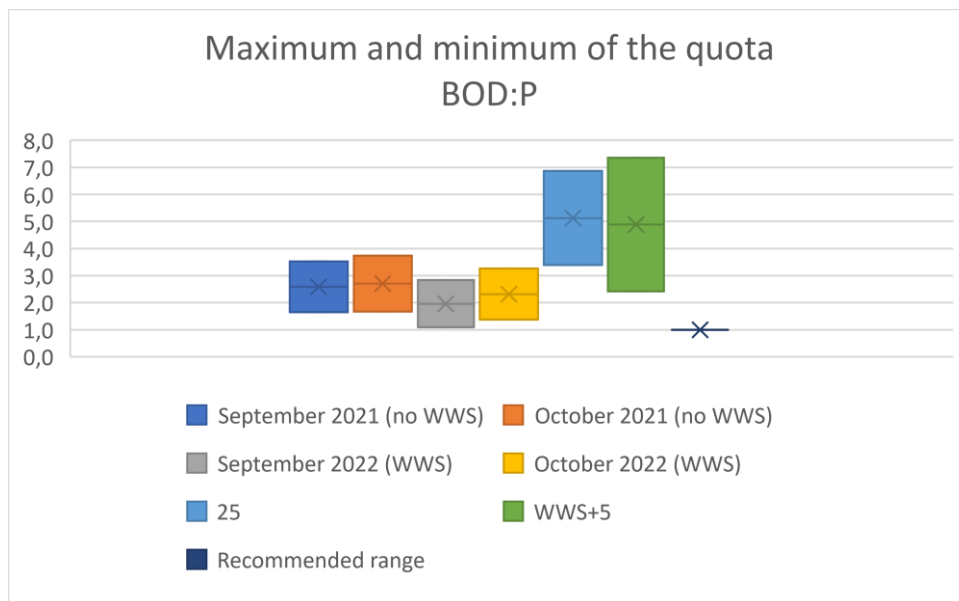


Figure 16. The ranges of BOD:P quota. 25- and WWS+5-blocks are calculated from data represented in Table 12 in appendix. **Fel! Hittar inte referensskälla.** September 2021 (no WWS), October 2021 (no WWS), September 2022 (WWS), and October 2022 (WWS) are calculated from historical data received from Nodra and summed up in the appendix, Table 14.

The pattern from evaluating the BOD:P quota can also be seen in the BOD:HPO₄²⁻, (Figure 17). The differences are that all the BOD:HPO₄²⁻ quotas are closer to the minimum quota, and the lowering of mean values when WWS is present is greater.

For the historical data, when the WWTP did not receive WWS, September-October 2021, the ratio between BOD and HPO₄²⁻ was in line with the minimum quota of 100:1. During the same month in 2022, the interval had fallen below the minimum quota. For the experimental results, both samples had quotas above the minimum, even when WWS was present.

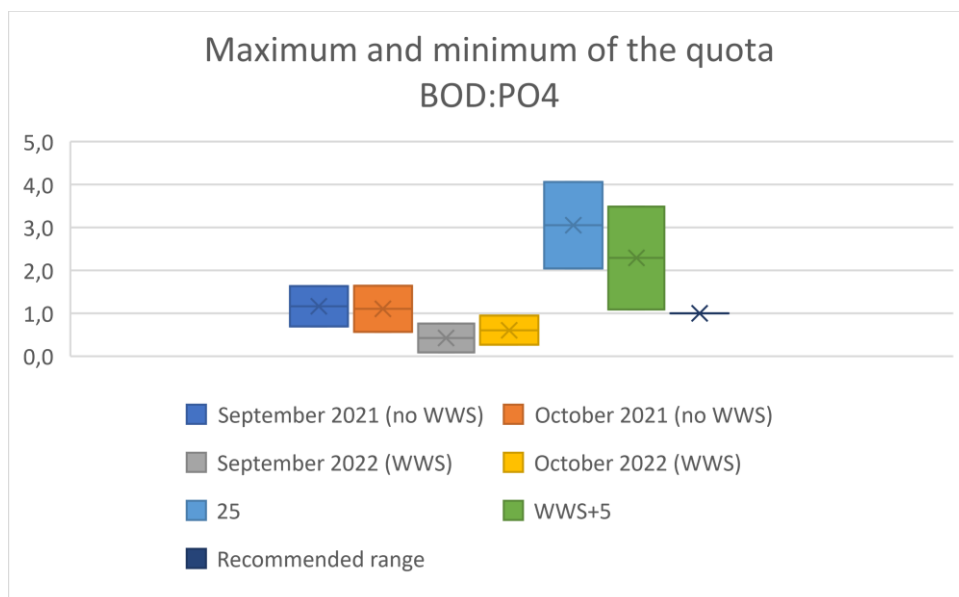


Figure 17. The intervals of BOD: HPO₄²⁻ quota. 25- and WWS+5-blocks are calculated from data represented in Table 13 in appendix. **Fel! Hittar inte referensskälla.** September 2021 (no WWS), October 2021 (no WWS), September 2022 (WWS), and October 2022 (WWS) are calculated from historical data received from Nodra and summed up under the appendix, see Table 15.

C/N

The calculation of quota C/N can be seen in Table 8. BOD is a way to measure carbon content, and, in this calculation, BOD is used when calculating carbon. The maximum and minimum interval of the quotas calculated from standard deviation (*Figure 18*) shows that the quotas calculated from the experiment results are lower than the recommended range of 3-3,5 mg C/mg N. The quotas calculated from the historical data vary but stay around the recommended amount. See *Calculation* in the appendix for more details.

Table 8. Summary of the C/N quotas for different samples, both from experimental results and data received from Nodra. The recommended quota is between 3-3,5 mg C/mg N.

Samples	N:C [mg C/mg N]
Recommended range	3-3,5
Wastewater + 25µl/l FeCl ₃	1,6
Wastewater + WWS+5µl/l FeCl ₃	1,4
September 2021 Without WWS	3,9
October 2021 Without WWS	3,7
September 2022 With WWS	3,8
October 2022 With WWS	4,0

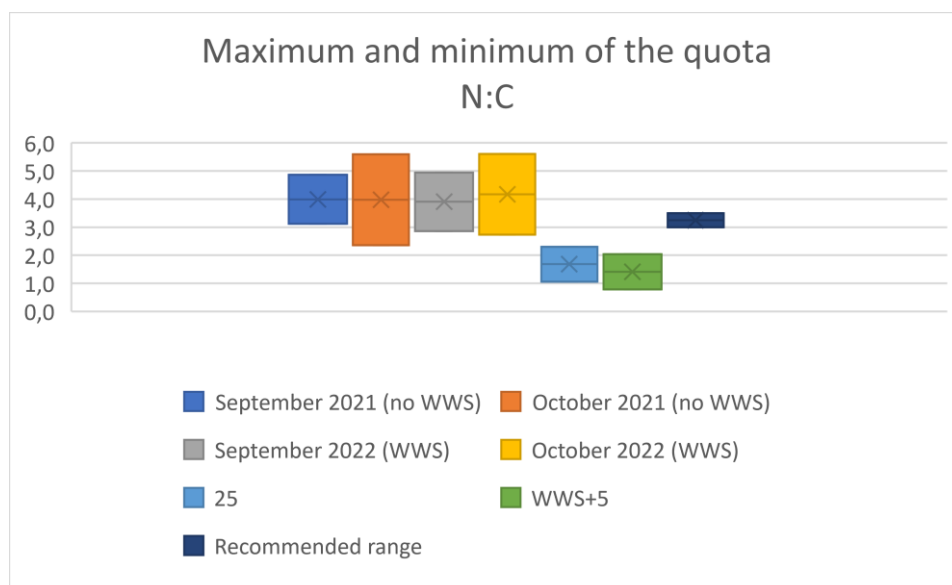


Figure 18. Visualization of the maximum and minimum of the quota N:C, calculated from data in Table 16 in the *Fel! Hittar inte referenskölla*.

4.5.2 Reduced cost of $FeCl_3$

The reduction of cost can be seen in Table 9 and is calculated from equations (11) and (12) under the *Calculation* in the appendix. The reduced cost of using 5 $\mu\text{l/l}$ instead of 25 $\mu\text{l/l}$ of $FeCl_3$ is, when rounding down, 625 300 sek/year.

Table 9. Calculated reduced cost if 5 $\mu\text{l/l}$ $FeCl_3$ /liter wastewater was added instead of 25 $\mu\text{l/l}$ $FeCl_3$ /liter. Calculated from equations (11) and (12).

	Without WWS	With WWS
Mean flow [m^3/day]	44 000	44 000
Cost $FeCl_3$ [sek/ m^3]	1947	1947
Amount added $FeCl_3$ [μl $FeCl_3$ /l wastewater]	25	5
Total cost [sek/day]	2142	428
Total cost [sek/year]	781 721	156 344

5 Discussion

In this section, the results will be discussed and divided into various parts where the analysis result, reduction, and more are discussed by themselves, and at the end of the section, there is an overall conclusion from all the parts.

5.1 Analysis result

The conclusion from analyzing the analysis results is that there is a downward trend for all parameters when adding WWS in comparison to when not doing it, but due to measurement deviations, almost all results of samples overlap. The exceptions are total phosphorus and phosphate, which both display a significant reduction without any data overlapping. The decrease in content indicates that the addition of WWS results in a reduction of primarily phosphorus and phosphate.

5.2 Reduction result

Since no significant differences in most of the parameters could be seen when evaluating the analysis results, the results were normalized with respect to the reference sample, which result in the calculation of the reduction of various substances (*Figure 7-Figure 13*). The conclusion that could be drawn from these graphs is that almost all the parameters, except for TOC, reached a higher degree of reduction when WWS was present in the sample.

For total phosphorus and phosphate, the sample with only WWS had a higher reduction than the sample with added 25 $\mu\text{l/l}$ of FeCl_3 . For BOD_7 , total nitrogen, and organic phosphorus, the sample with only WWS had a similar reduction to only adding 25 $\mu\text{l/l}$ FeCl_3 . And in the case of suspended matter, 5 $\mu\text{l/l}$ FeCl_3 needed to be added to the WWS sample to be similar to the reduction of adding 25 $\mu\text{l/l}$ FeCl_3 .

Another conclusion from the reduction results is that the addition of WWS removes phosphate to a greater extent than organic phosphorus. To further investigate this, the percentage ratio between these two was calculated using the total phosphorus result as the reference (*Figure 14*). The graph shows clearly that the proportion between these two decreases when WWS is present and when adding only 5 $\mu\text{l/l}$ FeCl_3 , the ratio switch and the supernatant contain more organic phosphorus than phosphate. This is not a good thing as the BWT needs phosphate as nutrition for the microorganisms.

Evaluations of the discussion above result in the conclusion that WWS together with 5 $\mu\text{l/l}$ FeCl_3 could replace the dosage of 25 $\mu\text{l/l}$ FeCl_3 , if the intention is to get the same or higher reduction for all measured parameters, and at the same time keep as much phosphate for the BWT as possible.

5.3 Conclusion of the analysis and reduction results

The reason the WWTP must lower the dosage of FeCl_3 to retain the function of the BWT's function is because the addition of WWS otherwise removes phosphate to a greater extent than organic phosphorus.

The theory before the execution of the experiments was that the lowering of phosphorus content depended on sweep coagulations. But if that is the reason, the organic phosphorus should also decrease since it is the larger particles that get caught in the sweep net. A theory is that the nets created by hydrogen bond between $\text{Al}(\text{OH})_3$ in the drinking water process gets destroyed when the WWS is transported through the sewage system to the WWTP and during

the virtuous mixing of $FeCl_3$, resulting in free or a few bounded $Al(OH)_3$. When the $Al(OH)_3$ -fragments entering the WWTP and $FeCl_3$ is dosed, both the fragments and the Fe^{3+} -ions react with the phosphate. The Fe^{3+} -ions react with the phosphate as seen by reaction (6) and $Al(OH)_3$ becomes an induced dipole by the negative charge particle in the wastewater and binds to these.

As seen in the reduction results, all the parameter except for the TOC has an increased reduction with WWS. This could indicate that the $Al(OH)_3$ -fragments exist in both larger and smaller complexes. The larger complex catches the larger particles and suspended matter that contains nitrogen and phosphorus during sedimentations, while the smaller ones bind to the phosphates.

5.4 Changes in pH with and without WWS

As mentioned in the *Introduction*, when precipitation chemicals react with water, free H^+ -ions are released and can cause lowering of the pH. The incoming wastewater on the WWTP in Norrköping has a mean pH of around 7.4, this is a higher value than the optimal pH for precipitation of $FeCl_3$ which is between 6-7. If the pH of the incoming wastewater were lowered by adding WWS, this could be a reason for the improved precipitation. That is the way the impact of WWS on the pH was investigated. The result (*Figure 15*) shows that the differences after adding $FeCl_3$ is 0.03 units. The measurement of uncertainty for the equipment used for measuring pH is 0.2 units, which makes the differences between with and without WWS non-existing. Thus, a lowered pH is not the reason for better precipitation.

5.5 Evaluation of quotas

For the interval of the quotas (*Figure 16-Figure 18*), the experimental data varies more than the historical data. The reason for this is the different quantity of data, the experimental results were based on three experiments and the historical data is based on up to a month of data. The historical data were also based on 24-hour samples, and the experiment results were based on random samples.

Both BOD:P and BOD: HPO_4^{2-} has a higher mean value for the experimental data than the historical data, this could also be seen in the BOD:N quota. The reason for this is probably the withdrawal of supernatant. Only 500 ml was withdrawn to bring up as little sludge as possible from the bottom of the jar. At the WWTP, much more of the sludge follow the wastewater from pre-precipitation to the BWT, which results in a lower reduction of BOD for the historical data compared to the experiment results. The BOD reduction at the WWTP was around 50% and for the experiment results, the BOD reduction was 60-70%.

This affects the quotas when comparing BOD with nitrogen, total phosphorus, or phosphate. That is, although it is obvious that N and P decrease in the supernatant by the addition of WWS, by the results of the decreased quota of C:N and C:P it could be interpreted that they are not efficiently reduced, whereas in reality the ratio results can be deduced to a falsely low BOD. The conclusion is that sampling from the experiments contained too little organic matter to be compared with reality, and if the aim is to mimic reality, more of the supernatant should be extracted for the quotas to be more similar between WWTP data and experimental data. This can also be seen in the N/C-quota, the historical result contains more organic matter than the experiment results.

The difference between quotas when WWS is present and when it is not

In BOD:P and BOD: HPO_4^{2-} , for both the historical data and the experiment results (Figure 16, Figure 17), the mean value of samples containing WWS (approx. 0,5 and 2,3, respectively) is lower than the sample not containing WWS. Thus, the differences are greater in the experimental data but are probably due to the extraction of the supernatant as discussed above. This indicates that WWS has an impact on the ratio of carbon to P and HPO_4^{2-} . For the historical data to a level where there is a lack of phosphate in relation to carbon (100:0,5) and in the case of the experimental data where there is a surplus of phosphate in relation to carbon (100:2,3). Both of these deviates from the recommended value and could, thus, influence the growth of microorganisms in the BWT. However, due to the noted sampling deviations, the quota of the experimental results is most likely closer to one than the number obtained.

25 vs WWS+5

For the experimental results, a comparison between sample 25 and WWS+5 in the BOD:P quota shows that these are close enough and above the minimum quota, which means that WWS+5 could replace 25 without loss of total phosphorus nutrition for the BWT. But when comparing BOD: HPO_4^{2-} quota instead, the loss is greater and closer to the minimum quota and the risk of phosphate deficiency in the BWT needs to be taken into consideration if WWS+5 should replace 25.

The reasons for BOD: HPO_4^{2-} quotas to be closer to the minimum quota is that phosphate is only a part of the total phosphorus content, which results in a lower value of the quota when calculating with phosphate instead of total phosphorus. The quota is interesting to calculate because the microorganisms in the BWT mainly use phosphate as nutrition. The graphs show a distinct reduction of phosphate when WWS is present, both in the experiment and the historical data. This is not as clear in the BOD:P quotas, further evidence that phosphate is reduced by WWS.

The conclusion from the quotas is that the differences between the experiment results and the historical data are too great for the result to be used directly on the operation of the WWTP. It can be seen as a guide, but further investigations are needed if the aim is to mimic reality.

5.6 Cost reduction of lowered $FeCl_3$

As discussed above, the smallest amount $FeCl_3$ added to a WWS sample to keep the same reduction as 25 $\mu\text{l/l}$ $FeCl_3$ for all the parameters is 5 $\mu\text{l/l}$. The reduced cost for adding 20 $\mu\text{l/l}$ lesser $FeCl_3$ is about 625 000 sek/year.

5.7 Conclusion and future outlook

To conclude the investigation of the WWS, the result from experiments performed on a laboratory scale cannot be directly applied to the operation of the WWTP, the reduction of $FeCl_3$ from 25 $\mu\text{l/l}$ to 5 $\mu\text{l/l}$ would not yield the same result. Instead, it showed that the addition of WWS reduce all measured parameters, except for the soluble TOC, compared with the same amount of $FeCl_3$ added without WWS, and specifically, phosphate was reduced. It affects all parameters in the wastewater. The investigation also showed that WWS had an impact on all quotas containing total phosphorus or phosphate.

A suggestion for future investigations is to measure the phosphate in the incoming wastewater at the WWTP before the pre-precipitation and by this be able to calculate the reduction at full

scale. The results could be compared to the results in this thesis and the possibility of lowering the dosage of $FeCl_3$ could be evaluated after that.

6 References

1. Lindquist A. Konsten att rena vatten. Kemira Kemwater; 2003.
2. Winkler M. Optimal nutrient ratios for wastewater treatment. Hach Lange [Internet]. 2012;1–8. Available from: http://www.hach-lange.ma/countrysites/action_q/download;document/DOK_ID/14786173/type/pdf/lkz/MA/spkz/fr/TOKEN/bwHY6wCA68kYX9xFNWsx1uD0UXU/M/8nbj-Q (Accessed: 10 August 2018)
3. Chen G-H, C.M. van Loosdrecht, Mark; Ekama GA, Brdjanovic D. Biological Wastewater Treatment: 2nd edition. 2:nd editi. Chen G-H, C.M. van Loosdrecht M, Ekama GA, Brdjanovic D, editors. London: IWA Publishing; 2020. 899 p.
4. Fytianos K, Voudrias E, Raikos N. Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron. Environ Pollut. 1998;101(1):123–30.
5. Mikrobiologi och avloppsvattenrening. AnoxKaldnes; Veolia Water Technologies; 2020. 124 p.
6. Björnsdotter L, Bennet. M. Introduktion till Avloppsteknik, U14 | Vattenbokhandeln. In: Rutberg B, Westerlund J, editors. Introduktion till Avloppsteknik, U14 | Vattenbokhandeln [Internet]. Stockholm: Svenskt Vatten AB; 2007 [cited 2022 Oct 11]. p. 43–65. Available from: <https://vattenbokhandeln.svensktvatten.se/produkt/introduktion-till-avloppsteknik-u14/>
7. Dentel SK. Application of the precipitation-charge neutralization model of coagulation. Environ Sci Technol [Internet]. 1988 Jul 1 [cited 2022 Oct 20];22(7):825–32. Available from: <https://pubs.acs.org/doi/pdf/10.1021/es00172a013>
8. Jiang JQ. The role of coagulation in water treatment. Curr Opin Chem Eng. 2015 May 1;8:36–44.
9. Duan J, Wang J, Guo T, Gregory J. Zeta potentials and sizes of aluminum salt precipitates – Effect of anions and organics and implications for coagulation mechanisms. J Water Process Eng. 2014 Dec 1;4(C):224–32.
10. Wang S, Fu J, Zhang C, Yang J. Slurry treatment for shield tunnelling and waste slurry recycling. Shield Tunn Eng. 2021 Jan 1;491–521.
11. Fälth E. AV101 Litteraturstudie och nulägesbild biologiskkväverening. Norrköping; 2022.
12. Björnsdotter L, Bennet. M. Introduktion till Avloppsteknik, U14. In: Rutberg B., Westerlund J., editors. Introduktion till Avloppsteknik, U14. Stockholm: Svenskt Vatten AB; 2007. p. 66–75.
13. Chen G-H, Loosdrecht MCM van, Ekama GA, Brdjanovic D, editors. Biological Wastewater Treatment. In: Biological Wastewater Treatment [Internet]. 2nd editio. London: IWA Publishing; 2020 [cited 2022 Dec 7]. p. 11–69. Available from: <https://www.iwapublishing.com/books/9781789060355/biological-wastewater-treatment-2nd-edition>
14. Henze M, Harremoës P, Arvin E, la Cour Jansen J. Wastewater treatment Biological and chemical processes. Third edit. Förstner U, Murphy RJ, Rulkens WH, editors. Lyngby: Springer Science and Business Media; 2002. 430 p.

15. Svenska institutet för standarder, SIS - Svenska institutet för standarder, SIS [Internet]. [cited 2022 Oct 25]. Available from: <https://www.sis.se/>
16. Bisutti I, Hilke I, Raessler M. Determination of total organic carbon – an overview of current methods. *TrAC Trends Anal Chem.* 2004 Nov 1;23(10–11):716–26.
17. Kitchener BGB, Wainwright J, Parsons AJ. A review of the principles of turbidity measurement. *Prog Phys Geogr* [Internet]. 2017 Oct 1 [cited 2022 Dec 16];41(5):620–42. Available from: <https://journals-sagepub-com.e.bibl.liu.se/doi/10.1177/0309133317726540>
18. Omar AF Bin, MatJafri MZ Bin. Turbidimeter Design and Analysis: A Review on Optical Fiber Sensors for the Measurement of Water Turbidity. *Sensors (Basel)* [Internet]. 2009 Oct [cited 2022 Dec 16];9(10):8311. Available from: [/pmc/articles/PMC3292109/](https://pubmed.ncbi.nlm.nih.gov/PMC3292109/)

Appendix 1

1 Trial planning of the trial-and-error part

The trial planning will be described and evaluated.

1.1 Materials and method

During the precipitation testing, a flocculator was used to simulate precipitation (*Figure 19*). Turbidity was used as a method to evaluate the result from the flocculator. It is a simple but fast method, and it gives a hint of how to evaluate the trails from the precipitation test in terms of how well the particles sediment.



Figure 19. Picture of the flocculator. A liter jar with the stirrer inside it and the setting panel. Six identical jars can be run simultaneously.

1.1.1 Turbidity

Turbidity describes the optical clarity of the water sample, that is, the suspended particles, organic matter and dissolved inorganic chemical species [17]. The measurement is based on the optical phenomena that occur when the incident light is scattered after passing through a water body. The optical properties that are causes scattered and absorbed light rather than the light that is transmitted in straight lines are measured. When the turbidity is low, it means that less light is scattered from the straight line, if it is high, more light is scattered by particles in the water [18]. It is a fast method with a fast answer, it does not tell anything about what properties of the particles, just the amount of it.

For details see reference method f.d. SS-EN ISO 7027-1,1990 [15].

1.2 Result

The two different settings for the flocculator, tested in the first part can be seen in Table 10. Setting 1 was the original setting that Nodra had used in previous precipitation tests and setting 2 was based on a discussion about precipitation with a representative from Kemira, Anders Enkel. The second setting has shorter *Fast*-mixing and longer *Slow*-mixing and *Sed*. In the following figures (*Figure 20-Figure 22*), the first three attempts are tested with setting 1 and the last three are tested with setting 2.

Table 10. The two different settings were tested on the flocculator. Fast is the length of the first mixing of chemicals, it is measured in seconds and has an RPM of 350 turns per minute in setting 1 and 400 turns per minute in setting 2. Slow is the length of when the flocculation takes place, measured in minutes, and has an RPM of 30 turns per minute in both settings 1 and 2. Sed is the sedimentation process when the stirrer is still and is measured in minutes.

Setting	Setting 1	Setting 2
Fast (seconds)	60	30
Slow (minutes)	5	20
Sed (minutes)	10	15
Fast (RPM)	350	400
Slow (RPM)	30	30

The results from the precipitations tests with only wastewater, wastewater with $FeCl_3$, and wastewater with WWS can be seen in Figure 20-Figure 22, respectively.

Figure 20 shows the result from the runs with only wastewater as the sample, with no added precipitation chemicals or sludge. The difference between the attempts is the settings, the first three are with setting 1 and the last three are with setting 2. The change in settings between attempts three and four resulted in a halving of the turbidity, the reason for three attempts at each setting was to investigate the repeatability.

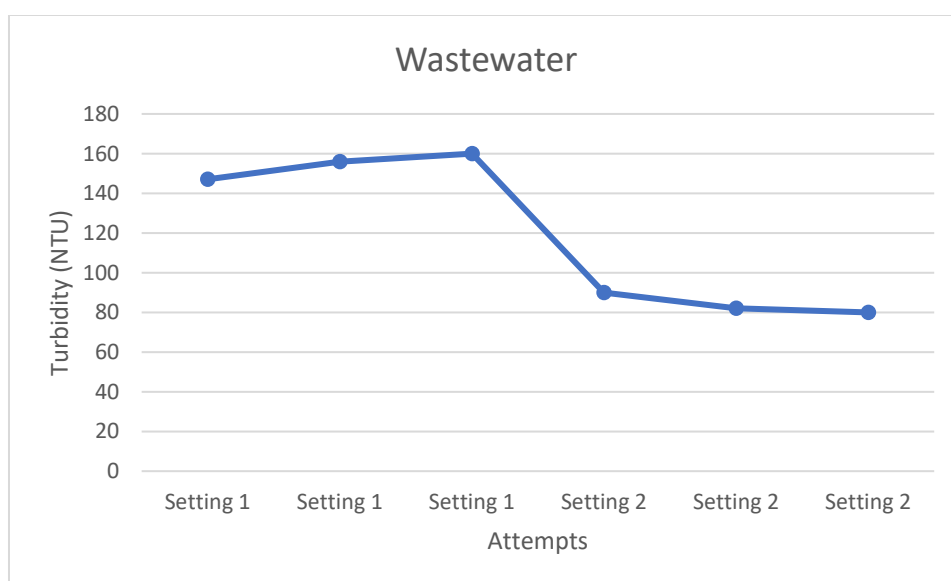


Figure 20. The turbidity of the wastewater only-sample after a run in the flocculator. The first three breakpoints are with setting 1, the last three are with setting 2. The turbidity is halved after the change in settings.

The results from the precipitation test where $FeCl_3$ was added in the beginning (Figure 21). The three first attempts are with setting 1 and the last three are with setting 2. Different concentrations of $FeCl_3$ were used to investigate the impact on the wastewater. During the first three attempts, setting 1 was used and different amounts of $FeCl_3$ was tried out. In the third attempt, 25 $\mu\text{l/l}$ $FeCl_3$ was added since 25 $\mu\text{l/l}$ $FeCl_3$ per liter water is the mean concentration of the WWTP when *not* receiving WWS, the mean concentration when receiving WWS is 20 $\mu\text{l/l}$ $FeCl_3$. The result with setting 1 and 25 $\mu\text{l/l}$ $FeCl_3$ was shown to give an acceptable reading on the turbidity meter which resulted in trying out setting 2 with the same concentration, attempt four-six. The combination was tried out three times to

investigate repetitiveness. The change in settings can be seen in the decrease of turbidity between attempts three and four.

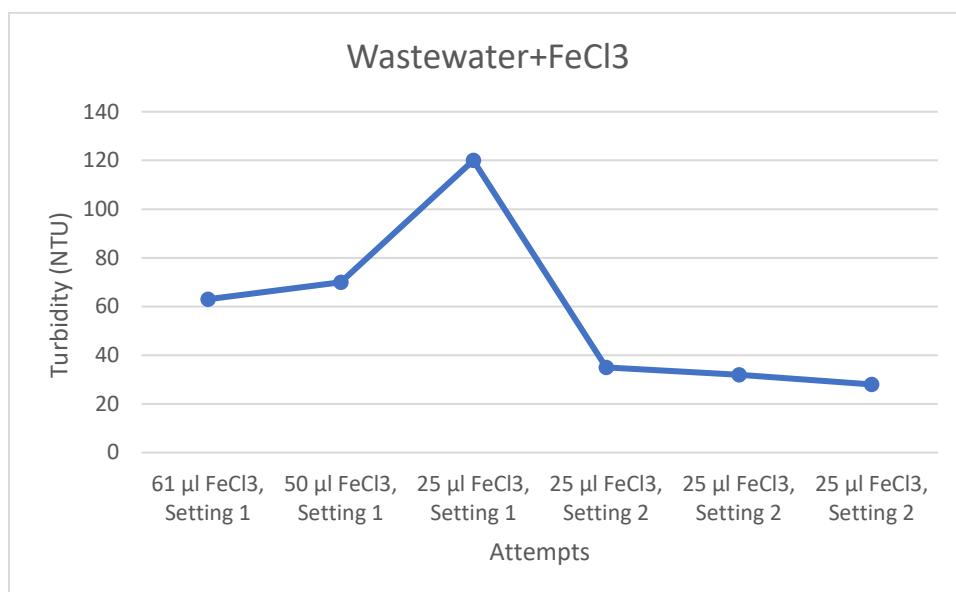


Figure 21. The turbidity of the wastewater sample with added FeCl_3 in different concentrations. The first three attempts are with setting 1 and the last three are with setting 2. The last four attempts are also with the same amount of FeCl_3 . The graph shows that a reduced amount of precipitation chemical increases the turbidity, which was expected. The jump between attempts three and four depends on the changes in settings.

Figure 22 shows the result from precipitation tests with wastewater and different amount of WWS added, and with different settings. In the first three attempts, setting 1 was used and different amounts of WWS were added, the results show an increase in turbidity when the amount of WWS is decreased. The amount of WWS was lowered to 10 ml in attempt three since the concentration on the WWTP is 1% and one wants to mimic the reality as much as possible. The result showed that 10 ml of WWS has an impact on the precipitation, and the amount was used in the investigation of setting 2. The decrease in turbidity depends on the change of setting and indicates that setting 2 has a positive effect on the precipitation. The last three attempts were executed with the same setting and the same concentration of WWS to prove repeatability.

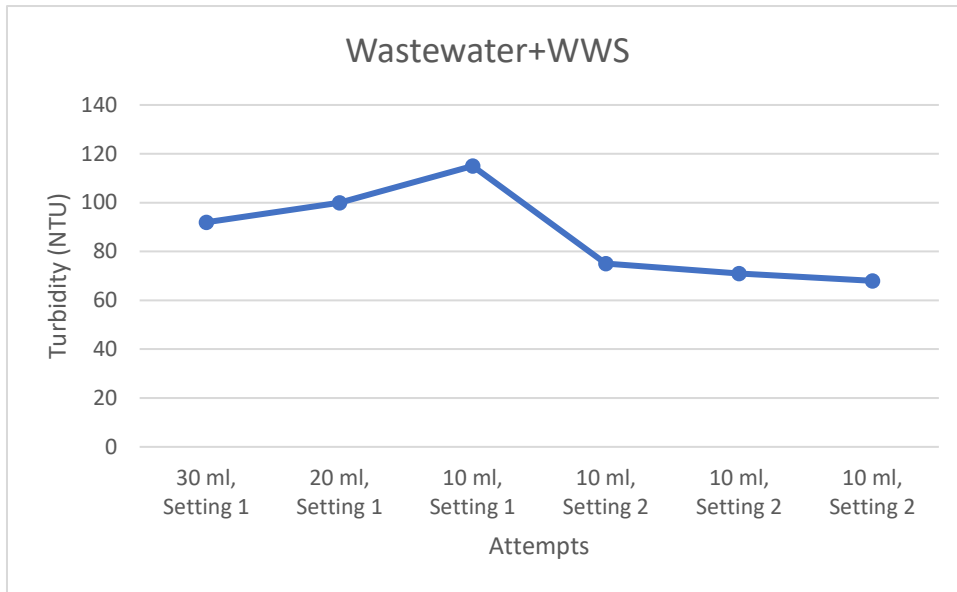


Figure 22. The turbidity of wastewater mixed with different amounts of WWS. The first two attempts have 30 respectively 20 ml of WWS mixed in, the last four have only 10 ml of WWS mixed in. A reduced amount of sludge increases the turbidity and indicated that the WWS has an influence on the precipitation process, seen in attempts one-three. When the settings changed and the same amount of WWS was retained, the turbidity reduces which indicates that the shorter first mixing and the longer sedimentation are positive for the precipitation.

For the experiments to mimic the reality as much as possible, the time of mixing between WWS and wastewater was investigated by preparing jars where WWS was added during different conditions. In two of the jars, one containing a magnetic flea and one not, one liter of wastewater was added together with WWS. In a third jar, one liter of wastewater without any WWS or magnetic flea was added. All three jars were stored in a laboratory hood during the night. On the second day, precipitation tests with $FeCl_3$ were executed, WWS was added to the third jar at the beginning of the precipitations experiment.

The results from the precipitation where WWS was added to wastewater during different times can be seen in Figure 23. Setting 2 was used and $25 \mu\text{l/l}$ of $FeCl_3$ was added in the beginning of the precipitation test, and the turbidity was measured on the supernatant directly after the end of the program. The result shows a greater reduction of particles if the wastewater was pretreated with WWS the day before and stirred during the night, than if not stirred or added at the beginning of the precipitation test.

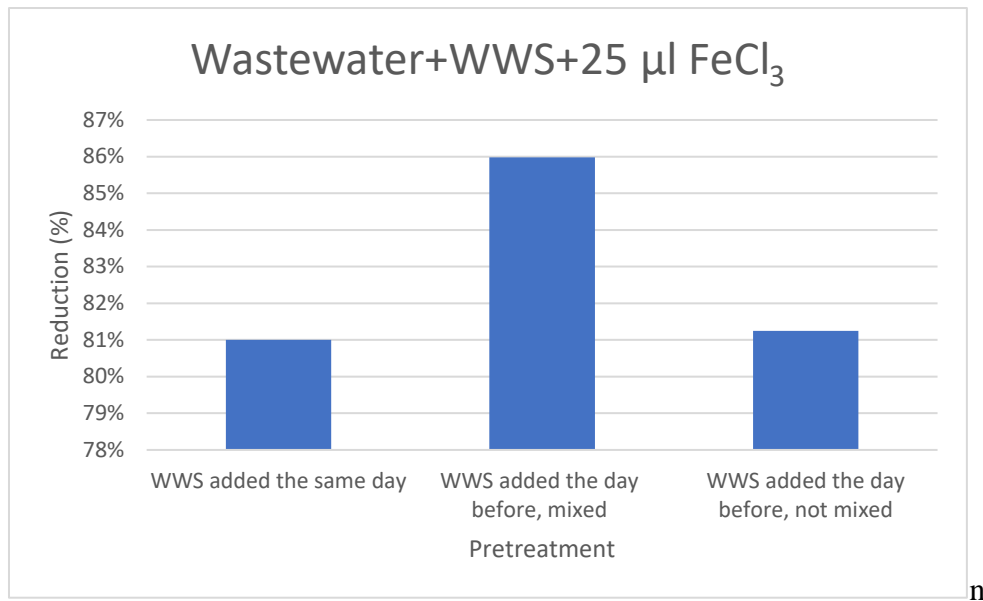


Figure 23. The turbidity reduction with different pretreatment. The same amount, 25 µl/l of $FeCl_3$ was added in the beginning of all the attempts. The best reduction was given by mixing the wastewater and WWS the day before and then stirring during the night with a magnetic flea.

To investigate how much different amounts of $FeCl_3$ affect the precipitation, wastewater and WWS were prepared by adding the WWS the day before the experiment and stirring during the night (Figure 23), and then mixed with different amounts of $FeCl_3$ in the beginning of the precipitation test (Figure 24). The difference in reduction of the turbidity is around 5 units.

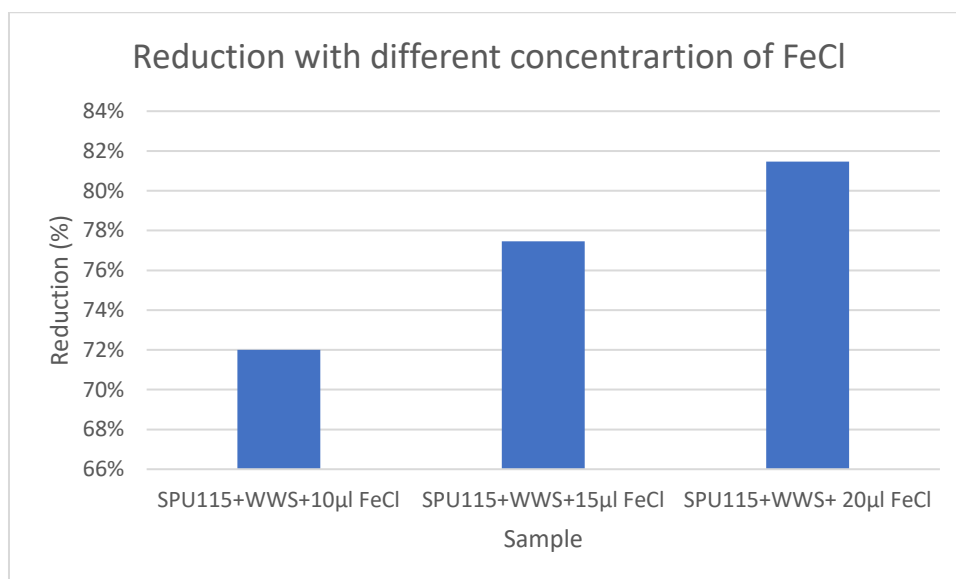


Figure 24. The reduction of turbidity with different concentrations of $FeCl_3$.

1.3 Discussion

Settings

The results between the two settings showed that shorter *fast*-settings and longer *slow*- and *sed*-settings resulted in lower turbidity, which was expected, as the longer *fast*-settings break down the newly created flocks more than if it is shorter, and it takes longer time for the flocks to recreates. Setting 2 also includes longer *low*- and *sed*-settings which is positive for better

precipitation (*Figure 20- Figure 22*). The graphs significantly decrease in turbidity between attempts three and four where setting 1 is changed to setting 2.

The amount $FeCl_3$ and WWS did show an impact on the precipitation when the same ratio used in the WWTP was used in the flocculator. The chosen amount of $FeCl_3$ and WWS can be seen in Table 11 and are based on the results from the first part and are discussed below.

$FeCl_3$ -step

The increasing $FeCl_3$ -step (*Figure 24*) would preferably be larger to be able to secure the differences in concentrations and evaluate these correctly. Thus, the differences in the second part will be 10 $\mu\text{l/l}$ instead of 5 $\mu\text{l/l}$. The conclusion is as follows, a step of 5 $\mu\text{l/l}$, 15 $\mu\text{l/l}$, and 25 $\mu\text{l/l}$ will be investigated. The reasons are that 25 $\mu\text{l/l}$ $FeCl_3$ is the mean amount added per liter at the WWTP when not *receiving* WWS, and 15 $\mu\text{l/l}$ is the lowest amount that has been added during an extended period at Nodra. This is an amount Nodra never dosed below, as it could greatly affect later processes if the dose is too low. Therefore, to see how a dose lower than 15 $\mu\text{l/l}$ affects the precipitation, 5 $\mu\text{l/l}$ of $FeCl_3$ will be investigated. The mean concentration of $FeCl_3$ when the WWTP receives WWS is 20 $\mu\text{l/l}$, but since one wants to secure a difference between the samples, this amount will not be investigated.

Amount WWS

The concentration of WWS used in the experiment will be 1%, based on the concentration on the WWTP (*Figure 22*).

Time of adding WWS

From the result of the experiment with adding WWS at different times (*Figure 23*), the conclusion is that the one with the best reduction would be used which was when wastewater and WWS were mixed the day before and stirred during the night. Also, this mimics the transportation of WWS in the sewer system the best. The preparation of wastewater and WWS was done by mixing 50 ml of WWS with 5 liters of wastewater the day before the precipitation tests and putting it on a magnetic stirrer over the night. To treat all the samples the same, the samples without WWS were also added to a container and stored at the same laboratory hood as the wastewater-WWS mix.

Conclusion

The conclusion of the results from the first part is compiled in Table 11. It shows the nine samples, all with different amounts of precipitation chemicals and WWS.

All samples except for the one at the top, raw wastewater, went through the flocculator before the supernatant was extracted and used in the experiments. The raw wastewater was used as a reference sample for, among other things, calculating reduction.

Table 11. Compilation of the samples and the number of chemicals that will be used in the second experiment.

Sample	Amount FeCl₃	Amount WWS
Raw wastewater	-	-
Wastewater	-	-
Wastewater + 5 µl/l FeCl ₃	5 µl/l	-
Wastewater + 15 µl/l FeCl ₃	15 µl/l	-
Wastewater + 25 µl/l FeCl ₃	25 µl/l	-
Wastewater + WWS	-	10 ml
Wastewater + WWS+5µl/l FeCl ₃	5 µl/l	10 ml
Wastewater + WWS+15 µl/l FeCl ₃	15 µl/l	10 ml
Wastewater + WWS+25 µl/l FeCl ₃	25 µl/l	10 ml

Appendix 2

2 Analysis results

The results of the BOD₇ (Figure 25) have a downward trend but due to the error bar, not much can be said. The runs with WWS contain the same concentrations of organic matter as the ones without it. When comparing 0 with WWS or 5 with WWS+5, and so on, the error bars make the difference disappear and the precipitation of all samples is similar.

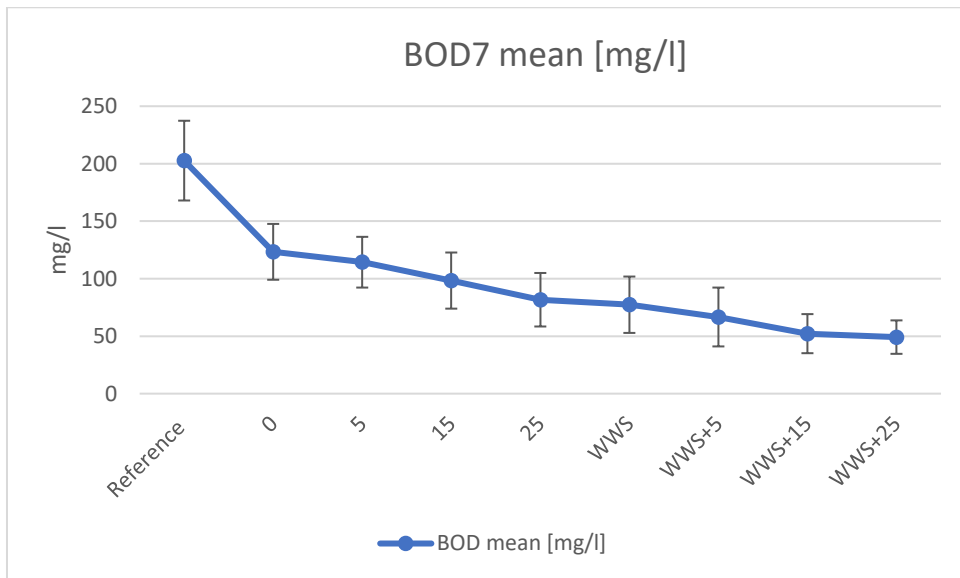


Figure 25. The mean result from analyzing the BOD₇ with error bars.

The result from analyzing suspended matter (Figure 26) is the same as for the BOD₇, not much could be said about the result from suspended matter as the error bars remove the difference between the samples.

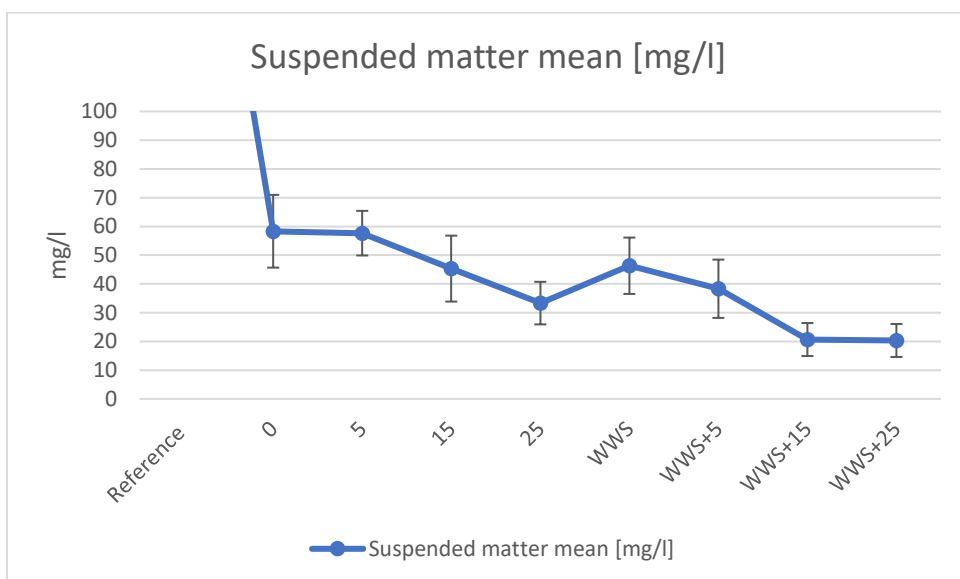


Figure 26. The mean result from analyzing the suspended matter with error bars.

The results from the TOC (*Figure 27*) show a small improvement in the precipitation of the total organic carbon when WWS was added to the samples.

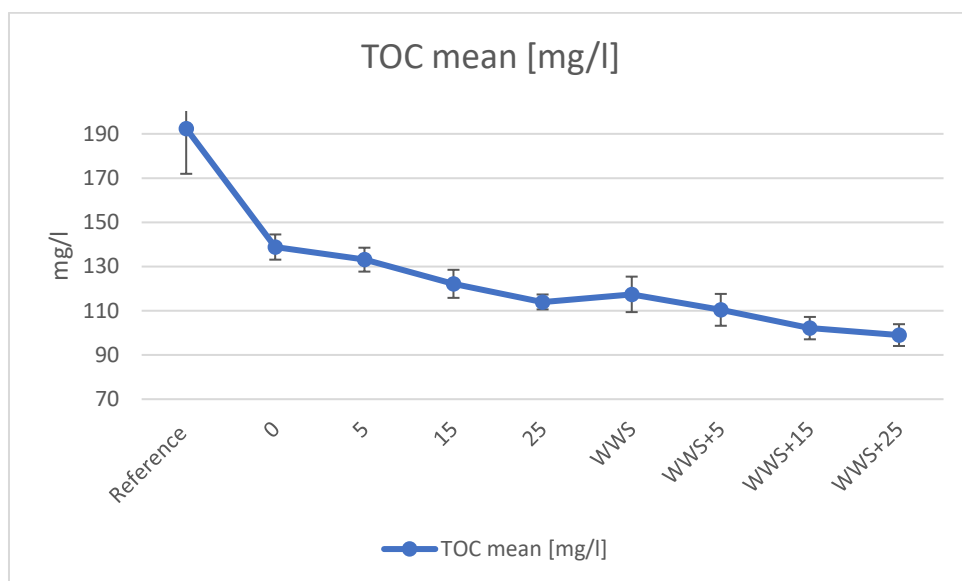


Figure 27. The mean result from analyzing the TOC with error bars.

The result of the total nitrogen (*Figure 28*) shows a little difference in the content of the supernatant between the samples, but it disappears with the error bars. These results were expected as the precipitation chemical does not remove nitrogen in the first place.

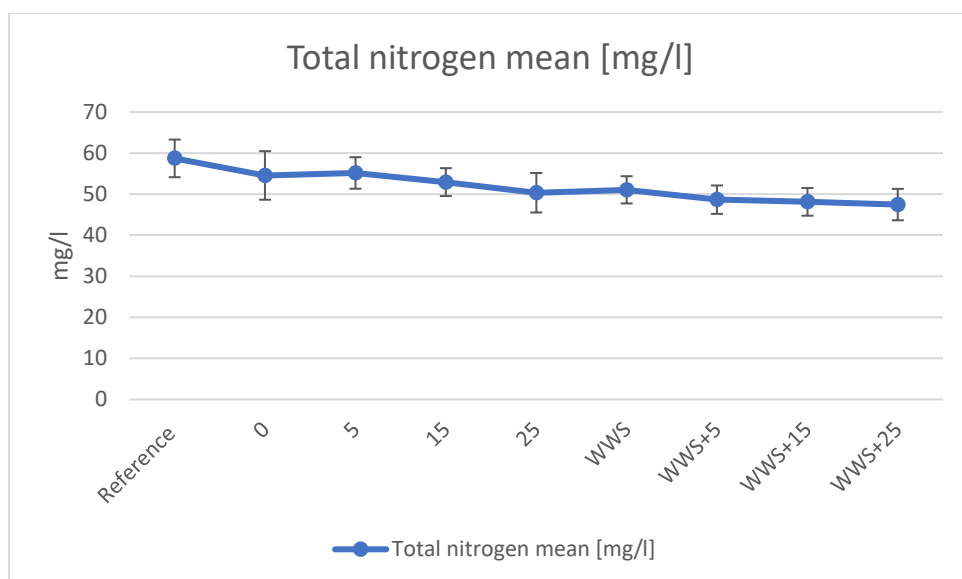


Figure 28. The mean result from analyzing the total nitrogen content with error bars.

Appendix 3

3 Calculations

3.1 Cost

Calculating the cost that could be saved by reducing the amount added $FeCl_3$ on the WWTP in Norrköping.

- Mean flow of incoming wastewater to the treatment plant (MF) [m^3/day]
- Consumption of $FeCl_3$ (Fe) [$m^3 FeCl_3/m^3$ wastewater]
- Cost of $FeCl_3$ (Cost) [sek/ m^3]
- Total cost per day of adding $FeCl_3$ at the treatment plant (Total cost/day) [sek/day]
- Total cost per year of adding $FeCl_3$ at the treatment plant (Total cost/year) [sek/year]

$$\frac{Total\ cost}{day} = Fe * MF * Cost \quad (11)$$

$$\frac{Total\ cost}{year} = \frac{Total\ cost}{day} * 365 \quad (12)$$

3.2 Quotas

To calculate different quotas, equation (13)-(16) was used.

$$BOD_7:P\ ratio = \frac{Total\ phosphorus}{BOD_7} \quad (13)$$

$$BOD_7:N\ ratio = \frac{Total\ nitrogen}{BOD_7} \quad (14)$$

$$BOD_7:BOD_7\ ratio = \frac{BOD_7}{BOD_7} \quad (15)$$

$$N:C = \frac{BOD_7}{Total\ nitrogen} \quad (16)$$

3.3 Calculated quotas of the experiment results

Table 12 and Table 13 sum up the experiment result of the BOD, total nitrogen, total phosphorus, and phosphate together with the standard deviation and the calculated quotas.

Table 12. Summary of some results from the analysis and calculation of the ratio between BOD_7 and total nitrogen in column six, and BOD_7 and total phosphorus in column seven. 25 stands for wastewater with 25 $\mu\text{L/l}$ FeCl_3 added, WWS+5 is wastewater containing WWS and added 5 $\mu\text{L/l}$ FeCl_3 . Equation (13)-(15) was used for calculating columns five to seven.

	BOD means (mg/l) (Standard deviation)	Total nitrogen means (mg/l) (Standard deviation)	Total phosphorus means (mg/l) (Standard deviation)	BOD/BOD [%]	N/BOD [%]	P/BOD [%]
25	81,7 (28,5)	50,3 (5,9)	3,8 (0,3)	100	62	5
WWS+5	66,7 (31,3)	48,7 (4,2)	2,6 (0,5)	100	73	4

Table 13 Summary of some results from the analysis and calculation of the ratio between BOD_7 and total nitrogen in column six, and BOD_7 and total phosphorus in column seven. Equation (13)-(15) was used for calculating columns five to seven.

	BOD means (mg/l) (Standard deviation)	Total nitrogen means (mg/l) (Standard deviation)	Phosphate means (mg/l) (Standard deviation)	BOD/BOD [%]	N/BOD [%]	$\text{HPO}_4^{2-}/\text{BOD}$ [%]
25	81,7 (28,5)	50,3 (5,9)	2,3 (0,1)	100	62	3
WWS+5	66,7 (31,3)	48,7 (4,2)	1,2 (0,3)	100	73	2

Calculated quotas of the historical data

Table 14 and Table 15 show the historical data from the WWTP for the parameter BOD, total nitrogen, total phosphorus, and phosphate, together with standard deviations and calculated quotas.

Table 14. The data is received from Nodra and the calculated ratio between BOD₇ and nitrogen is in column six, and BOD₇ and total phosphorus is in column seven. Equation (13)-(15) was used for calculating columns five to seven. The top two rows are the months without WWS, and the bottom two rows are when the treatment plant receives WWS. The means for each year are highlighted.

Date	BOD means [mg/l] (Standard deviation)	Total nitrogen means [mg/l] (Standard deviation)	Total phosphorus means [mg/l] (Standard deviation)	BOD/BOD [%]	N/BOD [%]	P/BOD [%]
September 2021 without WWS	172,0	44,0	4,2	100	26	2,5
October 2021 without WWS	146,7	39,3	3,6	100	27	2,4
Mean 2021 without WWS	159,4 (31,0)	41,7 (5,0)	3,9 (0,7)	100	26	2,4
September 2022 With WWS	166,0	43,6	3,0	100	26	1,8
October 2022 With WWS	133,3	33,3	2,8	100	25	2,1
Mean 2022 with WWS	149,7 (30,9)	38,5 (3,9)	2,9 (0,7)	100	26	1,9

Table 15. Data received from Nodra and the calculated ratio between BOD_7 and nitrogen is in column six, and BOD_7 and phosphate are in column seven. Equation (13)-(15) was used for calculating columns five to seven. The top two rows are the months without WWS, and the bottom two rows are when the treatment plant receives WWS.

Date	BOD₇ means [mg/l] (Standard deviation)	Total nitrogen means [mg/l] (Standard deviation)	Phosphate means [mg/l] (Standard deviation)	BOD/BOD [%]	N/BOD [%]	HPO₄²⁻/BOD [%]
September 2021 Without WWS	172,0	44,0	1,9	100	26	1,1
October 2021 Without WWS	146,7	39,3	1,4	100	27	1,0
Mean 2021 without WWS	159,4 (31,0)	41,7 (5,0)	1,7 (0,5)	100	26	1,7
September 2022 With WWS	166,0	43,6	0,6	100	26	0,4
October 2022 With WWS	133,3	33,3	0,7	100	25	0,5
Mean 2022 with WWS	149,7 (30,9)	38,5 (3,9)	0,7 (0,3)	100	26	0,4

The range of the quota BOD:N (*Figure 29*) shows that the experiment results vary more than the historical data, but all blocks are well above the minimum of the quota by a margin, see Table 12 and Table 14 for exact numbers.

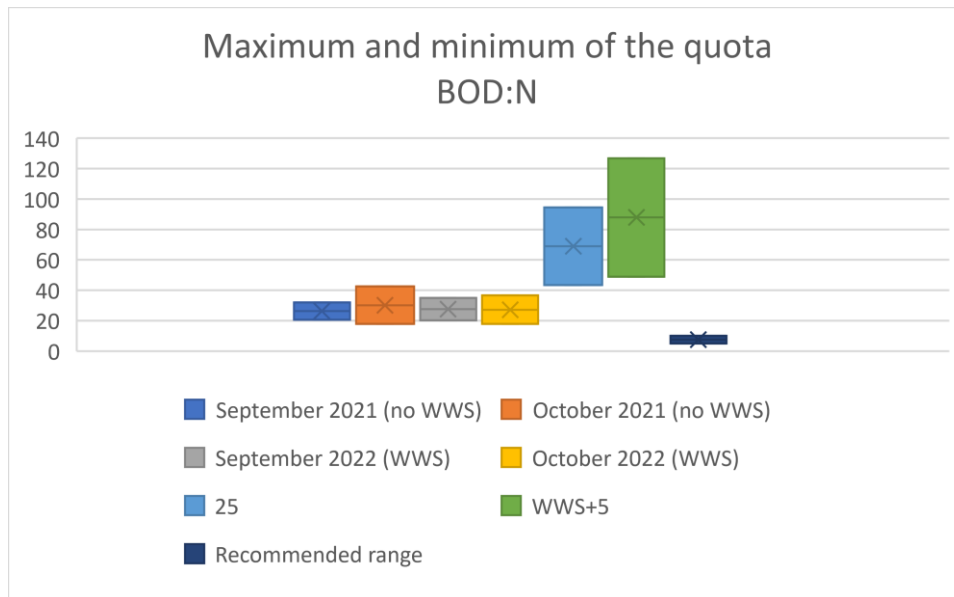


Figure 29. The range where the quota BOD:N for different samples could exist.

3.4 Calculation of N:C

Table 16. Data needed for calculation of the quota N:C, the first rows are data from the experiments, and the lower rows are data received from Nodra. In column four, the result from calculating equation (16).

	Total nitrogen means [mg/l] (Standard deviation)	BOD means [mg/l] (Standard deviation)	N:C [mg C/mg N]
The result of the experiments			
25	50,3 (5,9)	81,7 (28,5)	1,6
WWS+5	48,7 (4,2)	66,7 (31,3)	1,4
The result of data received from Nodra			
September 2021 Without WWS	44,0 (4,2)	172,0 (21,7)	3,9
October 2021 Without WWS	39,3 (5,9)	146,7 (40,4)	3,7
September 2022 With WWS	43,6 (4,0)	166,0 (29,7)	3,8
October 2022 With WWS	33,3 (3,8)	133,3 (32,1)	4,0

Appendix 4

4 Raw data

4.1 Raw data from the experiment

In this section the raw data from the experiments are presented, Table 17 shows the data from the first run, Table 18 from the second run, and Table 19 from the third run.

Table 17. Raw data from the first run.

	BOD₇ [mg/l]	Suspended matter [mg/l]	TOC [mg/l]	Total phosphorus [mg/l]	Phosphate [mg/l]	Total nitrogen [mg/l]
Reference	210	245	171,3	7,05	4,16	64,67
0	119	52	141,9	5,89	3,76	61,96
5	113	58	136,2	5,81	3,7	60,59
15	104	44	124,9	5,03	2,74	57,55
25	82	32	115	4,03	2,41	56,26
WWS	76	47	120,1	3,37	1,82	55,57
WWS+5	72	45	112,9	3,02	1,52	53,31
WWS+15	54	20	106,2	2,14	1,02	51,62
WWS+25	51	21	103,1	1,59	0,64	52,45

Table 18. Raw data from the second run.

	BOD₇ [mg/l]	Suspended matter [mg/l]	TOC [mg/l]	Total phosphorus [mg/l]	Phosphate [mg/l]	Total nitrogen [mg/l]
Reference	157	198	185,8	6,49	3,96	57,96
0	96	47	130,8	5,69	3,74	54,22
5	88	48	125,5	5,56	3,37	52,48
15	66	32	113,4	4,69	2,89	51,76
25	53	25	109,4	3,49	2,22	50,27
WWS	48	34	106,5	2,52	1,37	49,9
WWS+5	33	24	100,6	2,09	1,09	47,66
WWS+15	30,5	14	94,99	1,51	0,769	49,17
WWS+25	30,5	13	92,05	1,15	0,455	46,78

Table 19. Raw data from the third run.

	BOD₇ [mg/l]	Suspended matter [mg/l]	TOC [mg/l]	Total phosphorus [mg/l]	Phosphate [mg/l]	Total nitrogen [mg/l]
Reference	241	290	220,2	6,64	3,43	53,5
0	155	76	143,7	5,3	3,38	47,49
5	142	67	137,6	5,19	3,29	52,41
15	125	60	128,2	4,77	2,58	49,49
25	110	43	117,5	3,83	2,15	44,49
WWS	108	58	125,6	3,02	1,36	47,69
WWS+5	95	46	117,7	2,77	1,05	45
WWS+15	72	28	105,2	1,99	0,67	43,57
WWS+25	66	27	101,8	1,59	0,33	43,15

4.2 Raw historical data received from Nodra

In this section, the historical data that is used in the calculation of quotas is presented. The data are measured on the water exiting the pre-precipitation. Table 20 shows data from the WWTP in Norrköping during September and October 2021, during this time, the WWTP did not receive WWS. Table 21 shows data from the same month but a year later in 2022 and during a time when the WWTP received WWS.

Table 20. Historical data from the WWTP during September and October 2021. During this period, the WWTP did not receive WWS.

Date	Total phosphorus [mg/L]	Phosphate [mg/L]	BOD₇ [mg/L]	Total nitrogen [mg/L]	Dosage <i>FeCl</i>₃ [µl/l]
2021-09-01	4,5	2,5	170	48	25,1
2021-09-05	4,2	1,5			29,0
2021-09-08	4,2	1,8			25,4
2021-09-09	3,6	1,9	170	44	25,9
2021-09-12	5,7	3,4			34,1
2021-09-13	6,4	1,6	200	46	23,1
2021-09-15	4,2	1,5			25,6
2021-09-19	3,4	1,7			25,5
2021-09-21	4,1	2,2	180	45	24,6
2021-09-26	3,8	1,7			25,4
2021-09-28	2,3	1,8			26,3
2021-09-29	4,5	1,4	140	37	40,9
2021-10-03	3,7	1,5			36,4
2021-10-06	3,4	0,99			37,3
2021-10-07	3,2	1,3	140	46	23,5
2021-10-10	3,5	1,7			22,8
2021-10-11	3,8	1,4	190	41	23,5
2021-10-13	4	1,5			23,3
2021-10-17	3,5	1,4			22,5
2021-10-20	3,3	1,4			23,1
2021-10-24	3,6	1,4			22,9
2021-10-25	4,6	2,2			23,3
2021-10-27	3,5	1,5		38	23,5
2021-10-28	3	1,0			22,7
2021-10-31	3,1	0,98			22,6

Table 21. Historical data from September and October 2022, during a period when the WWTP received WWS.

Date	Total phosphorus [mg/L]	Phosphate [mg/L]	BOD₇ [mg/L]	Total nitrogen [mg/L]	Dosage <i>FeCl</i>₃ [µl/l]
2022-09-04	2,2	0,21	130	44	23,5
2022-09-05	2,3	0,17	180	45	23,5
2022-09-11	2,3	0,37			18,7
2022-09-13	4,4	0,38	200	38	33,5
2022-09-14	2,8	0,47			18,8
2022-09-18	2,8	0,53			18,5
2022-09-21	4,7	1,7	180	49	16,5
2022-09-25	2,9	0,7			19,4
2022-09-28	3	0,67			19,2
2022-09-29	2,5	0,7	140	42	19,3
2022-10-02	2,4	0,29			32,1
2022-10-05	3,7	0,65			14,5
2022-10-08	2,2	0,79	110	36	17,8
2022-10-09	2,2	0,55			14,8
2022-10-12	3,1	0,47			12,9
2022-10-16	2,5	0,31	170		22,9
2022-10-19	3,5	1,1			14,8
2022-10-23	2,9	0,94	120	35	17,4
2022-10-24	2,5	0,59		29	29,5
2022-10-26	2,5	0,82			13,3
2022-10-30	3,1	0,85			13,2

Appendix 5

5 Planning report

5.1 Title:

Investigation of the effect of waterworks sludge on the precipitation at a wastewater treatment plant

5.2 Delimitations:

The project will be limited to investigating the influence of waterworks sludge on pre-precipitation and subsequent biological wastewater treatment. The influence on pre-precipitation will be investigated on a laboratory scale. The biological wastewater treatment will be examined by comparing historical data and literature studies.

5.3 Problem formulation:

Waterworks sludge is a residue formed during the first purification step of drinking water production. The precipitating chemical aluminum sulfate is used to separate impurities by precipitation. In the past, the sludge was disposed into the Motala Ström, but due to stricter requirements, the sludge had to be disposed of differently. One of the solutions identified was to send the sludge to the treatment plant via the sewage networks.

Nodra receives an average of 44,000 cubic meters of water per day. The amount of water work sludge sent from the water work treatment plant is about 300 cubic meters per day, and this is approximately 1% of all incoming water, and despite the small amount, changes in the processes of the wastewater treatment plant have been seen in the test results. A positive effect has been seen on the pre-precipitation of the wastewater treatment plant. During the pre-precipitation, the precipitation chemical, ferric chloride, is used to remove, among other things, phosphorus. The dosage of this chemical has been able to be adjusted down, which has led to reduced consumption of precipitation chemicals and reduced chemical costs. Furthermore, a negative effect has been noted on the dewatering of digested sludge in the wastewater treatment plant. The sludge contains more water than before the diversion of the waterworks sludge led to an increased cost for removal. These pros and cons have led to a discussion at Nodra if it is worth receiving the waterworks sludge at the wastewater treatment plant or whether it should be taken care of at the waterworks instead.

Nodra began diverting the waterworks sludge in the autumn of 2021. Since then, the diversion has been on and off for periods to be able to see how the waterworks sludge affects the processes. During the period this project is carried out, the wastewater treatment plant will receive water work sludge.

5.4 Investigation processes:

In this section, the various parts of the project and how they should be carried out will be described.

Pre-precipitation:

To see how the waterworks sludge affects the pre-precipitation, experiments will be carried out on a laboratory scale, to reduce sources of error and to be able to conclude more easily. To be able to scale against the treatment plant, different quotas will be used, including BOD:N:P and C:N. These ratios are rules of thumb to ensure that the microorganisms in the biological

wastewater treatment receive the right nutrition. If, for example, too much phosphorus is reduced in the precipitation, biological wastewater treatment will not work well as a certain amount of phosphorus is required for the bacteria to thrive.

The effects of the waterworks sludge on pre-sedimentation will be investigated by analyzing several parameters on a laboratory scale. The analysis will first take place with the amounts of precipitation chemicals that are received and dosed at the wastewater treatment plant. If this does not produce any results, the dose will be increased to investigate the properties of the chemicals. The parameters that will be analyzed are as follow:

- BOD7: to investigate how the precipitation chemicals affect the organic material in the pre-precipitation. How the precipitation chemicals behave individually and together. What consequences does a changed level of BOD7 have on subsequent purification steps?
- • Phosphorus: total phosphorus and phosphate. If it is organically bound or free phosphorus precipitates, and if there are differences between the amount of phosphorus that precipitates. How is biological wastewater treatment affected?
- • pH: precipitation takes place differently at different pH. Used to investigate if the parameter increases or decreases depending on whether aluminum sulfate or ferric chloride is used, wherein the reaction steps, as well as which reagents are present in the wastewater. How is the parameter affected if you mix the chemicals?
- Suspended matter: a parameter that is influenced by the sludge properties, describes how much sludge is present in a certain amount of water. Do the precipitation chemicals affect this parameter? Separately and together?
- • Precipitation test: evaluation of the sludge's flocculation properties. Do the flocs behave differently between the different precipitation chemicals or when they are together? Different sizes of the flock or sedimentation characteristics?
- • Nitrogen: total nitrogen. Is the amount of nitrogen in the pre-precipitation affected when mixing waterworks sludge and ferric chloride? If yes, how is the nitrogen purification of the biological step affected? It has been seen that the waterworks sludge affects the dewatering of digester sludge, but is the purification also affected? Is the emission of nitrogen increasing? Do you need to add an external carbon source in the biological step?

Biological wastewater treatment

To investigate the biological wastewater treatment, historical data from Nodra will be used for, among other things, calculating the quotas, to see how the biological stage has functioned during the periods with and without waterworks sludge, and if anything more than the dewatering of digested sludge has been affected.

5.5 Literature:

The literature used in the project is provided by Nodra as well as scientific articles found via databases such as Web of science. Articles found via LiU's library or Svenskt Vattens website will also be used.

5.6 GANTT schema

GANTT schedule of the project (*Figure 30*).

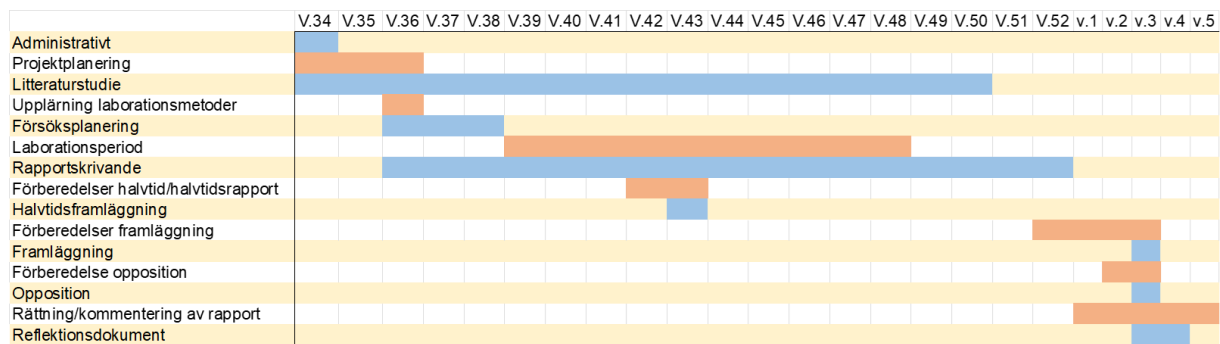


Figure 30. Schematic overview of the GANTT schedule for the project.

Appendix 6

6 Analysis of process

The first step in the thesis was the literature study, which was ongoing almost throughout the whole period. The literature study was laying the ground for how the experiment was executed and was complimented throughout the period.

Two other tasks started in the first weeks, administrative matters regarding the facilities and the planning report. The planning report was based on the knowledge from the literature study and contained a brief description of the aim of the thesis and how it would be executed to achieve this.

During the weeks after the presentation of the planning report, a trial planning was designed. This part is one of the things that did not go as planned since Nodra had only an idea of what they wanted to investigate, the whole laboratory part with how to design the experiments, and how much of the different substrates and reactants needed to be investigated. This took much longer than expected, but when it was done, I had a very clear plan on how to do everything and it was easy to limit myself to the defined task. The trial planning also resulted in easily interpreted results.

The trial planning took about eight weeks to complete, and the experiments, from where the conclusions could be made, took three weeks. The laboratory period included both the trial planning and the actual experiments which resulted in keeping the timetable.

As I had done most of the analysis methods before starting this thesis, I underestimated how long time it would take to do all of them at the same time during the experiment period. This resulted in longer days in the laboratory than I had expected. Thinking back, I would have divided the methods into different days.

The halftime presentation was held as planned and right before the start of the experiments, resulting in it containing the trial planning and, until then, assembled literature study. Otherwise, the project proceeded without any major problems.