Evaluation of Dissolved Air Flotation for Water Purification

With Focus on Floc Characteristics and PFAS

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Abstract

In this project, attempts have been made to collect data that allows the municipal association Norrvatten in the decision-making process on the flotation/ sedimentation step of their water treatment process. In this sense, poly- and perfluorinated alkyl substances (PFAS) concentration and the characteristics of agglomerated particles (flocs) have been investigated and compared between the two modes that the process can be operated. For the floc characteristics, the creation and stability of the flocs were investigated, and the particle size, size distribution and zeta potential was identified as important properties and thereafter analysed using the instrument zetasizer. The concentration of eleven different PFAS compounds were analysed. The results of floc characteristics show that there is no major difference in creation and breakage of flocs in the two investigated modes, since the analysed samples had the same zeta potential, -6.45 mV. The results were deemed uncertain because of varying results, and improvement suggestions include using photoanalysis to confirm similar floc appearances and to produce more data so a statistical validity can be quantified. As for the PFAS concentration, the concentration of PFAS were slightly lower in the treatment step in which sedimentation was utilized (7.5 ng/l) compared to when flotation was utilized (9.2 ng/l). The flotation mode did, however, create foam with a high PFAS concentration (3800 ng/l) compared to the liquid samples (5.5-9.2 ng/l), so a potential PFAS removal source was identified. The results were based on one sample series, so improvements of validity can be achieved by gathering more data, analysing more samples, and analysing the same sample in two different instruments measuring PFAS concentrations.

Keywords - Sedimentation, Flotation, Zeta potential, Particle size, Particle size distribution, PFAS

Sammanfattning

I detta projekt har experiment utförts med mål att förse kommunalförbundet Norrvatten med data som kan användas som underlag för beslutsfattande angående om deras fällningslinjer i vattenreningsprocessen ska köras i flotation eller sedimentering. För detta ändamål har koncentrationen av poly- och perfluorerade alkylsubstanser (PFAS) samt karaktär av agglomererade partiklar (flockar) undersökts och jämförts mellan fällningslinjer som körs i olika konfigurationer. För flockkaraktär har skapandet och stabiliteten av flockar varit av intresse, eftersom flotation har ett mer turbulent flöde där flockarna riskerar att brista. Partikelstorlek, storleksfördelning och zeta potential identifierades som egenskaper som reflekterar flockarnas karaktär, dessa analyserades i en zetasizer. Koncentrationen av elva vanligt förekommande PFAS ämnen analyserades i projektet. Resultatet av flockkaraktär tyder på att det ej fanns någon större skillnad i skapandet av flockar samt deras stabilitet mellan de olika fällningslinjerna som undersökts. Detta eftersom zeta potentialen var identisk (-6.45 mV) för de analyserade proverna från respektive process. Analyserna och provberedningen bedömdes ha en hög mätosäkerhet, och några förbättringar som föreslås för att öka säkerheten är genomförande av komplementerande fotoanalys för att bekräfta likheter i utseende mellan flockar, samt att genomföra mer analyser så att en statistisk giltighet av analysen kan kvantifieras. För PFAS koncentrationen så var koncentrationen av PFAS lägre i utgående vatten från fällningslinje som körs i sedimentation (7.5 ng/l), jämfört med prov från linje som körs i flotation (9.2 ng/l). För fällningslinjen som kördes i flotation så skapades skum med höga koncentrationer av PFAS (3800 ng/l) jämfört med analyserade vattenprover (5.5-9.2 ng/l), detta identifierades som en potentiell källa för PFAS-avlägsning. Resultaten av PFAS baserades endast på en provtagningsserie, och förbättringar av validitet kan åstadkommas genom samling av mer analysdata för samma processer, och genom att analysera ett av proverna i två olika instrument, som båda analyserar PFAS koncentration.

Nyckelord - Sedimentering, Flotation, Zeta potential, Partikelstorlek, Storleksfördelning, PFAS

List of Abbrevations

- Sweden National Food Agency - Livsmedelverket
- DAF - Dissolved Air Flotation
- PFAS - Poly- and Perfluorinated Alkyl Substances
- NTU - Nephelometric Turbidity Units
- PDI - Polydispersity Index
- PFOS - Perfluorooctane Sulfonate
- PFOA - Perfluorooctanoate
- PFBS - Perfluorobutanesulfonate
- PFHxS - Perfluorohexanesulfonate
- 6:2 FTS - Fluorotelomer Sulhponate
- PFBA - Perfluorobutanoate
- PFPeA - Perfluoropentanoate
- PFHxA - Perfluorohexanoate
- PFHpA - Perfluoroheptanoate
- PFNA - Perfluorononanoate
- PFDA - Perfluorodecanoate
- CMC - Critican Micelle Concentration
- AFFFs - Aqueous Film-Forming Foam
- Zetasizer - DelsaNano D Zeta Potential and Submicron Particle Size Analyzer
- TOC - Total Organic Carbon

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1 Introduction

Clean drinking water is a necessity for humans, a necessity that unfortunately is not available to every person in the world. At present time, the drinking water quality varies over the world, with some countries offering clean drinking water from the tap, and others not even having an established sewer system. With the increase of population, increasing the production of clean drinking water is crucial.[1]

Sweden has several water treatment plants that produces high quality drinking water by using well established methods. Those plants therefore have the privilege to research about ways to increase the production capacity. This could enable water treatment plants that struggles with achieving a certain water quality demand or production capacity to leapfrog, meaning that they do not have to spend as much time and resources to develop new methods, but instead take parts of the research conducted at other plants.

Norrvatten is a municipal association in Stockholm, Sweden, that produces and distributes drinking water by using raw water from the lake Mälaren and Görvälnfjärden. The plant produces 50 million m^3 water each year that is distributed in the northern Stockholm region over 14 municipalities, to 700 000 users. In the production of drinking water, the raw water goes through several treatment processes before it reaches the quality demand. [2]

The quality sought to be achieved follows the standards set by the national food department (Livsmedelverket) [3]. Livsmedelverket strongly suggest not consuming water or using it for food preparation if the total concentration of poly- and perfluorinated alkyl substances (PFAS) are above 900 ng/l, and they also recommend the water to not exceed a total PFAS concentrations of 90 ng/l. Norrvatten has also set up some environmental policy's that aims to reduce the impact the treatment and distribution have on the environment. Examples of the policy's that Norrvatten has set up is reducing the amount of chemicals and energy that their processes require and to reach the demands of the relevant environmental laws with a good margin. [3, 4]

Among the challenges that the plant faces are the seasonal change of raw water quality as well as change of drinking water demand over the year. This problem requires versatile treatment processes in which production can be changed without decreasing the quality of the outgoing water. The company has set a goal of increasing the production capacity by 10% within the following years. [5]

The precipitation lines are some of the processes that have been identified as the limiting treatment step and measures have therefore been made to increase the production capacity in this step.One of the measures has been to rebuild one of the precipitation basins so it can be run in either sedimentation or flotation mode. The flotation basin was installed in 2019 and in 2020 it got verified that the production capacity increased without the quality parameters of interest deteriorating. [5]

Norrvatten is interested in knowing whether there are advantages of operating the precipitation lines in flotation mode even when a higher production is not required. This project will therefore focus on investigating whether one of the operational modes manages to remove PFAS better than the other, and if the operational modes impact the floc creation and breakage to different extents. [5]

1.1 Aim and scope

The goal of this master thesis is to contribute to the understanding of the precipitation process called dissolved air flotation, DAF, that the company Norrvatten utilizes to remove particles from their water treatment plant, Görvälnverket. The project aims to help the company with the decision of whether DAF is an advantageous process compared to conventional sedimentation, even when the production demand is low. This will be done by analysing key parameters and properties that have been identified as important for the decision making process in this case.

One of the investigated properties are the floc characteristics. The water in DAF undergoes a more turbulent motion compared to conventional sedimentation, and Norrvatten is interested in whether the flocs formed can remain stable under those turbulent motions, or if the flocs break.

The other investigated property is the concentration PFAS in the precipitation lines. Norrvatten wants to investigate if there is a difference in PFAS concentration in the water leaving the precipiation lines run in either mode. Norrvatten is also interested if one of the precipitation modes manages to remove PFAS to a higher degree than the other and if there is any part of the DAF that can be targeted if Norrvatten will implement some removal technique for PFAS in the future.

The parameters that will be investigated in this report are:

- Floc characteristics
- PFAS concentrations

1.2 Research questions

In this report, the following research questions are sought to be answered:

- Are there any charged particles in the DAF that do not agglomerate into flocs, and if so, could this be changed by altering the dosage of coagulant?
- Are there differences in PFAS concentrations in the outgoing water of the precipitation lines run with DAF or sedimentation mode?
- Which part of the DAF should be targeted for eventual future PFAS removal, and how much removal potential could this have?

1.3 System boundaries and limitations

Based on the aim of contributing to the understanding of the DAF at Norrvatten, the system boundaries has been set to Norrvattens water treatment plant, Görvälnverket, with a focus on the water flows before and in the precipitation lines. The main limitation made in this project is that the work will be done without compromising the production of the water treatment plant. To avoid changes of production, no parameters in the processes will be changed, but instead a focus will be put on analyzing the water based on the parameters that the plant has already implemented. Other limitations will be presented throughout the report.

Since there are multiple precipitation lines working at Görvälnverket, one line operated in DAF and one line operated in sedimentation mode were selected to be investigated in this study. For this purpose, precipitation line 1, that can operated in both DAF and sedimentation mode, but is currently operated in DAF mode, has been selected. One of the precipitation line that is operated in sedimentation mode, precipitation line 2, have been investigated. Line 2 was selected as a reference so that all the parameters measured from the water in the DAF could be compared to the water in this line. The rest of the precipitation lines are therefore not contemplated in this project. An illustration of the system boundaries is found in Figure 1.

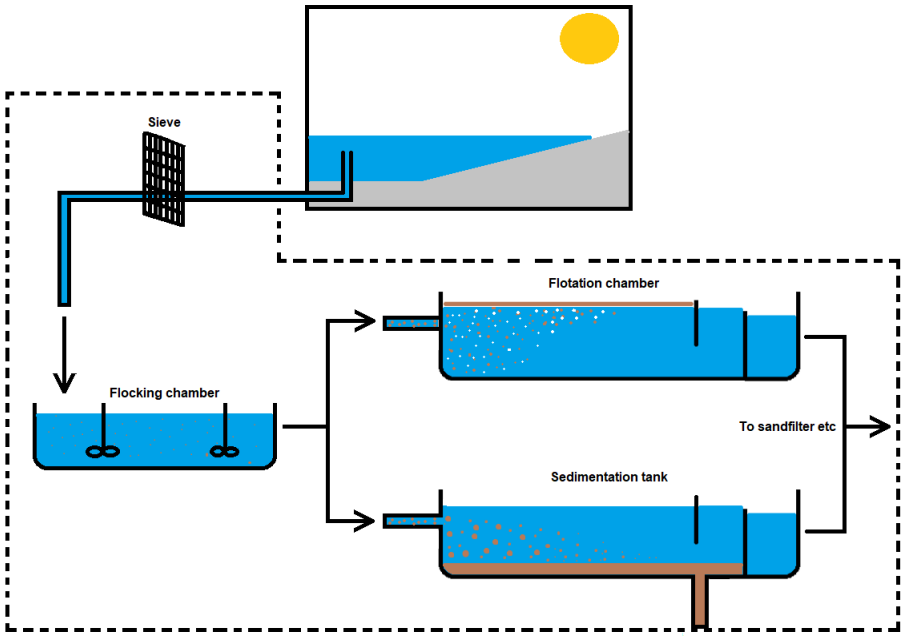


Figure 1: System boundaries

2 Background

2.1 Water treatment at Görvälnverket

Görvälnverket takes raw water from the Görvälnfjärden in the lake Mälaren. The water is taken from two different depths, one at 4 meter below surface and one at 22 m below the surface. Which raw water intake is chosen depends on the water quality. The water is transported to the treatment plant via pipes. The first treatment step is a sieve, in which larger objects, such as algaes or fish, are removed. [2]

The water is pumped to a mixing chute in which a coagulant, aluminium sulphate, is added. The water flows from the mixing chute to the precipitation lines, so all precipitation lines contains water with the same dosage of coagulant. The precipitation lines begin with a flocking chamber, where the coagulant mixes with organic particles, mud, microorganism and more to form so called flocs. In this step, sodium silicate is added as well to make the flocs attach to each other and thus increasing their size, which is beneficial for the removal in the treatment steps to come. [2]

At Görvälnverket, there are two types of precipitation modes, flotation and sedimentation. In sedimentation, the flocs sediment to the bottom, due to gravity, and form a so called sludge. The sludge is then removed from the bottom of the tank. In flotation, some larger flocs sediment, but others float to the surface because of implementation of air bubbles that the flocs attach to. The sludge is thereafter removed from the top of the flotation basin, and at the base of the basin. [2]

After the precipitation lines, the water flows through a sand filter where some particles that did not get removed in the precipitation lines gets removed. After the sand filter, the water flows through a carbon filter in which odour and taste disturbing finer particles are removed. The water continues to a UV reactor, that disinfects the water. One of the last step in the water treatment process is addition of chemicals, lime and monochloramin, that is added to achieve the demanded water quality. The water is thereafter stored in a reservoir where it can be pumped to the user when needed. [2]

The quality of the water are continuously controlled at each treatment step. This is done by utilizing instruments that measures the quality parameters live. The plant also has a SWEDAC accredited laboratory that controls the quality by analysing samples taken from the processes. Figure 2 illustrates the major water treatment steps from the intake of raw water to the finished product. [2]

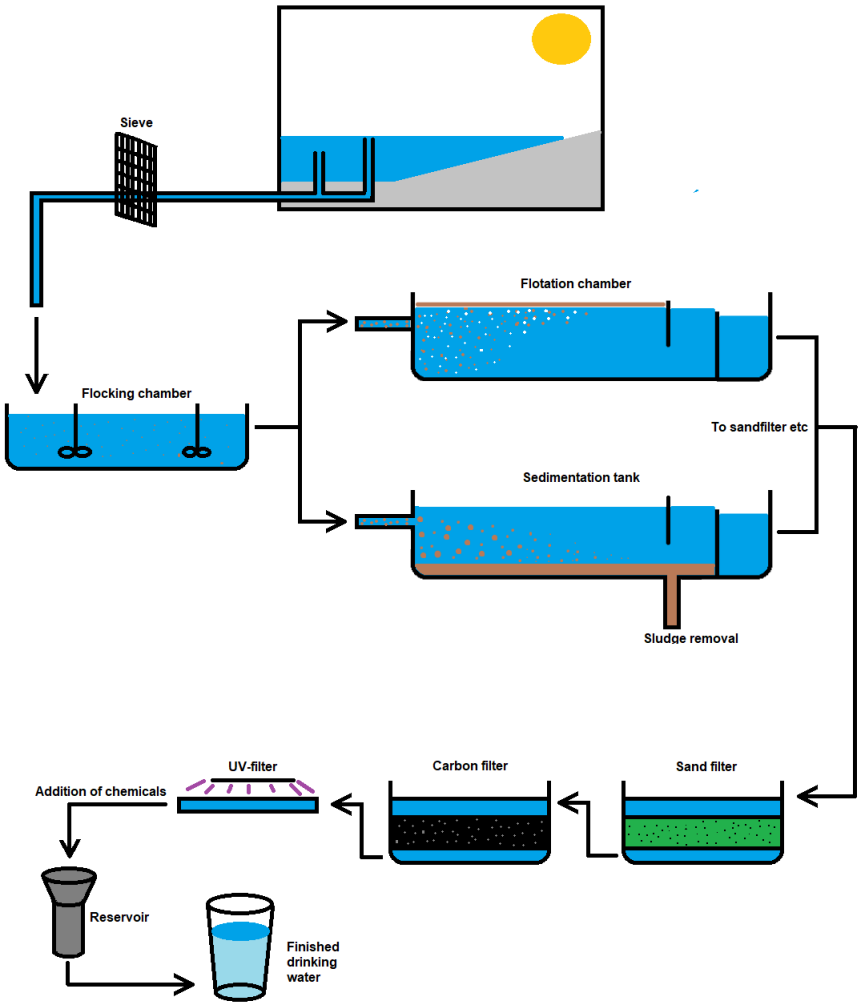


Figure 2: Water treatment at Görvälnverket

2.2 Particle removal

One of the first steps in achieving a water quality demand is the removal of colloidal particles from the water. Colloidal particles have a large surface area, even though their diameter is small. Their size range between 0.001-10 µm. The large surface area of colloids contributes to their ability to adsorb ions from surrounding medium. In water, colloids can adsorb ions that results in a negative charge, thus repulsing other negatively charged colloids because of electrostatic forces. This repulsion results in colloids being stable and dispersed in mediums. [6, 7]

Some well developed methods for removal of particles in water are filtration, sedimentation, coagulation and flocculation. Coagulation and flocculation are not removal techniques per se, but aims to enhance the separation of colloidal particles in some processes by aggregating the particles into so called flocs. In this section, the basic mechanisms of coagulation and flocculation will be described as well as the mechanisms importance for floc characteristics. A brief explanation of how dissolved air flotation and sedimentation works will also be included. [6]

2.2.1 Coagulation and Flocculation

Coagulation and flocculation are two mechanisms that are of importance for the floc characteristics. The mechanisms are utilized in water treatment because they bring particles together so that larger cluster of particles can be formed. Figure 3 illustrates the basic mechanisms of coagulation and flocculation, and also illustrates the difference between those mechanisms. The right part of the figure illustrates how the once formed aggregates can be either settled in sedimentation, or attached to a bubble in flotation. [8]

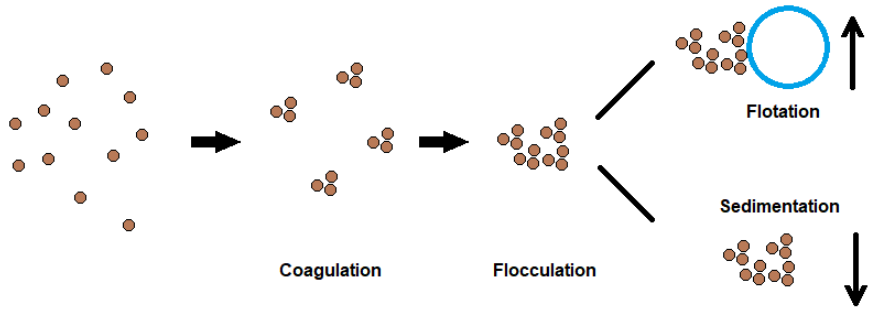


Figure 3: Coagulation and flocculation mechanisms

During coagulation and flocculation, there are three identified mechanisms occuring, charge neutralization, sweeping and bridging [9]. This means that two flocs, that have similar characteristics, could have been created with different mechanisms, and the flocs can therefore have different properties [10]. Figure 4 illustrates how the coagulant acts in each mechanism. In the figure, the coagulants are illustrated below the name of the mechanism, and the colloidal particles are illustrated as brown spheres [11].

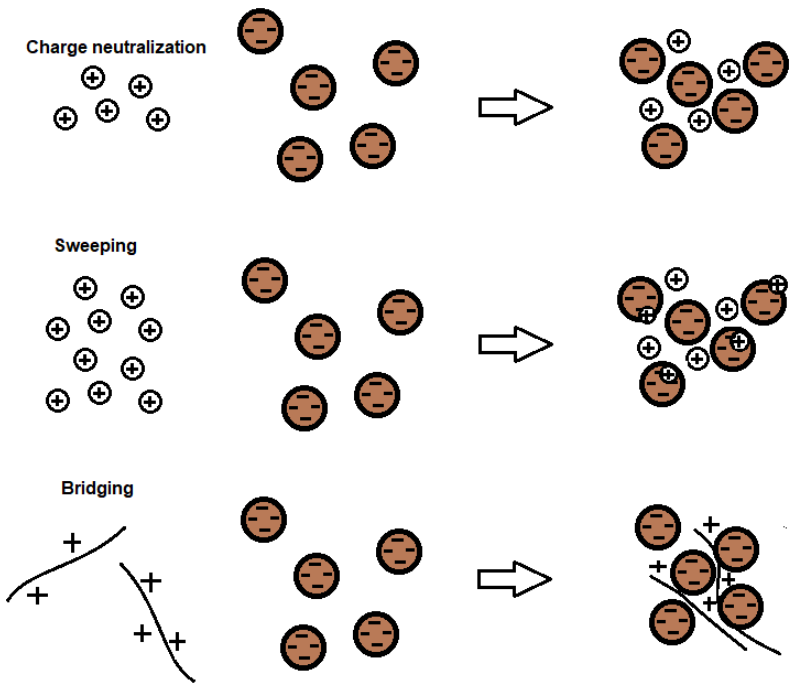


Figure 4: Mechanisms during charge neutralization, sweeping and bridging

Charge neutralization occurs when metal salts are added to the water [9]. The salts dissociate and forms a highly charged hydrolyzed metal cationic species that can adsorb the negatively charged colloids, and thus creating a reduction of charge [6]. The extent of the hydrolysis is a function of pH [6]. A conventional coagulant is aluminium salt ($AlCl_3$) and is the most commonly used coagulant [9].

Sweeping follows the mechanisms of charge neutralization, but the concentration of the metal salt has to be sufficiently high to cause precipitation of metal hydroxide that the colloidal particles can adsorb to. Bridging is a mechanism that is utilized by adding positively charged polymers to the water. The polymers attach to the colloidal particles and aggregates are formed [12].During flocculation, the same mechanisms occur as the ones in coagulation, but with charge neutralization and bridging being identified as the most important mechanisms [6]. As previously mentioned, coagulation and flocculation are used at water treatment plants to make the particles clump together, to enhance the separation in the filters or sedimentation/flotation.

In many plants, the removal of particles is measured by analyzing the turbidity of the water. Turbidity is a measure of a liquids relative clarity and it has a correlation to the amount of particles in a liquid. High turbidity is caused by large number of particles that are generally invisible to the naked eye because of their size. The size, amount of particles and opaqueness has impacts the turbidity of a liquid, but so does the liquids quiescence, since a liquid in motion will prevent particles from settling. Turbidity has a correlation to the amount of particles in a liquid. It is measured in Nephelometric Turbidity Units (NTU) and has traditionally been used as a surrogate measurement to determine the amount of colloidal particles in the water. [13]

Although Turbidity is used to measure particle concentration at many water treatment plants, particle counting has received much attention in recent years since it related directly to the amount of particles in the water instead of using a surrogate measurement [14]. One of the research questions that is sought to be answered in this project is if there are any charged particles that aggregate into flocs and coalescence to the bubbles. Measuring the amount of particles and their sizes would not be enough to answer this question. Instead, another physical property will be investigated, the surface charge. The next subsection includes a background to what factors are important for floc creation, why the surface charge is a property of interest, and how it can be measured.

2.2.2 Floc creation

Several factors affect the degree of coagulation. Below is a list of the influencing factors:

- Temperature
- pH
- Colloid concentration
- Dosage of coagulant
- Affinity of colloids to the water
- Anions or cations in solution

The temperature affects the coagulation by decreasing the viscosity of the liquid and increasing the velocity of the colloids. The pH affects coagulation because the H^+ and OH^- concentrations might affect the charge of the colloids, which is the main driving force, see Figure 4. The optimum pH value for coagulation if aluminium sulfate is used as a coagulant is between 4.0 to 7.0 pH. If the colloid concentration is high, more particles that are charged will be present, and this would require a higher coagulant dose in order to destabilize the colloids. [6, 8, 15]

The affinity of colloids to the water influences the floc creation since a stable molecule will be much more difficult to destabilize and remove from the suspension. The anions and cations affect the floc creation in a similar way as the pH. If there are positive and negative ions in the solution, since the charge difference between colloids and the coagulant is one of the driving forces, this will directly impact the formation of flocs. [6, 8, 15]

The zeta potential is a measure of electrokinetic potential in a colloidal system. If this is high, the repulsive power between colloids is also high, whereas if its closer to zero, the repulsive force is lower. The zeta potential is the relative electric potential form the interfacial double layer of a particles compared to a point in the medium that is away from the interfacial double layer, see Figure 5. The interfacial double layer consists of charged particles and surrounding counter-ions. The total potential on the surface of the colloid is the Nernst potential, followed by a dense layer of counter-ions on the so called Stern layer. The outer layer, that seperates the mobile part of the colloid from the liquid, is the so called slipping plane. The zeta potential is measured at the slipping plane. [16, 6]

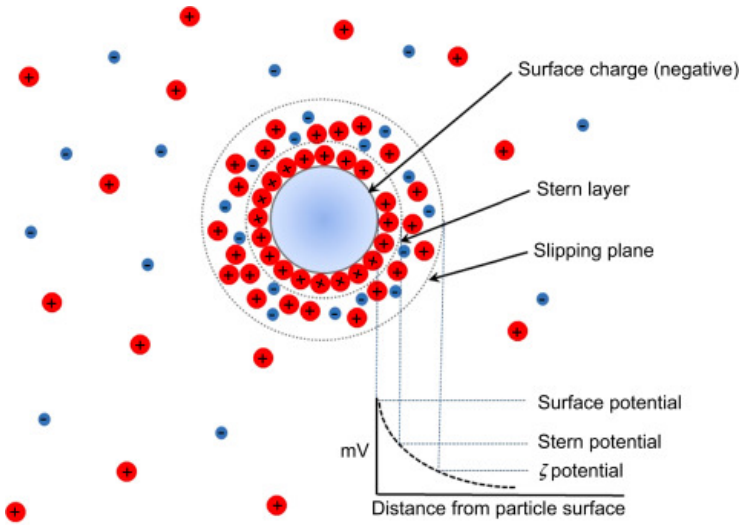


Figure 5: Zeta potential compared to other potentials of a colloid [17]

The zeta potential is often used as a measurement for the stability of a colloid [16, 17]. In water treatment, it is sought to destabilize the colloids, so achieving agglomerates with a zeta potential close to zero is beneficial since the electrostatic repulsion is at its lowest [17]. Guang et al. [2010] claims that emulsions with a zeta potential value of between -11 mV to -20 mV had coagulation and flocculation, and those above had a higher stability and a lower risk of coagulating [16]. K.Pate et al. [2016], Ali.S et al. [2005] and Malvern Panalytical proposes similar ranges. Table 1 summarizes the colloidal stability for given zeta potential that has been observed by three different sources [17, 6, 18].

Table 1: Colloidal stability for different zeta potentials [17, 6, 18]

Source	**Zeta potential [mV]**	**Stability or coagulation**
K. Pate and P. Safier 2016	0 to ±5	Rapid agglomeration
	±10 to ±30	Incipient Stability
	±30 to ±40	Moderate stability
	±40 to ±60	Good Stability
	> ±60	Excellent stability
Saif Ali	+3 to 0	Maximum coagulation
	-1 to -4	Excellent coagulation
	-5 to -10	Fair coagulation
	-11 to -20	Poor coagulation
	-21 to -30	Virtually no coagulation
Malvern Panalytical	+3<	High coagulant dose
	-8 to +3	Good coagulant dose
	-8>	Low coagulant dose

Since the zeta potential can measure stability of colloidal particles, and thus give an indication on whether more colloidal particles can adsorb to the coagulant or not, it is a property of interest for this project. [9]

Another property of interest is the polydispersity index (PDI), which can indicate what distribution the particles have. A low PDI indicates a mono-disperse sample, and a high PDI indicates a poly-disperse sample. Measuring the zeta potential, the size of the particles, and how the size of the particles are distributed can provide an understanding to how the colloidal particles interact with the coagulant. [9, 19, 20]

2.2.3 Dissolved air flotation

Dissolved air flotation is one technique to remove the flocs created through coagulation and flocculation. In DAF, the gravitational force is utilized by decreasing the apparent density of the flocs through implementation of pressurized air bubbles that the flocs attach to. The pressurization of the air is energy intensive but crucial, since the solubility of gas increases with increased pressure according to Henry's law [21].

Traditional DAF mainly has four components, a pump that helps recirculate some of the outgoing water from the DAF, an air supplier that supplies compressed air, an air drum where the pressure can be regulated through a vent, and lastly, the flotation tank. The components of DAF is presented in figure 6.

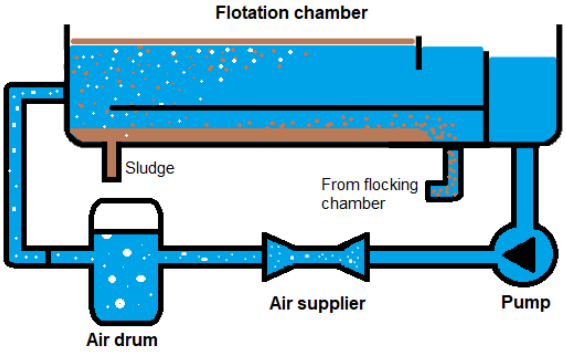


Figure 6: DAF and its major components

The aerated stream enters the flotation chamber together with the stream that contains the flocs. The pressure difference between the pressurized stream and the pressure in the flotation chamber results in the air, that is soluble in water because of the high pressure, not becoming soluble anymore. This releases air bubbles (diameter $< 80\mu m$) to which the flocs attach and rise towards the surface because of the density difference between bubble with attached floc compared to water. Once at the surface, the flocs and bubbles can be removed with scrapers. The attachment of flocs on the air bubbles depend on the surface charge of the particles as well as the bubble-size distribution. [22, 23]

2.2.4 Sedimentation

Sedimentation is another technique that is used to remove flocs created through coagulation and flocculation. In sedimentation, particles are removed from suspension by utilizing gravitation. If there is no addition of chemicals before sedimentation, the technique is commonly referred to as plain sedimentation, which is more popular in wastewater treatment. Because the suspended particles can be small (<10 µm) in surface water and ground water treatment, the addition of coagulants is crucial for sedimentation within a reasonable time limit. Figure 7 contains a simplified illustration of a conventional sedimentation tank.

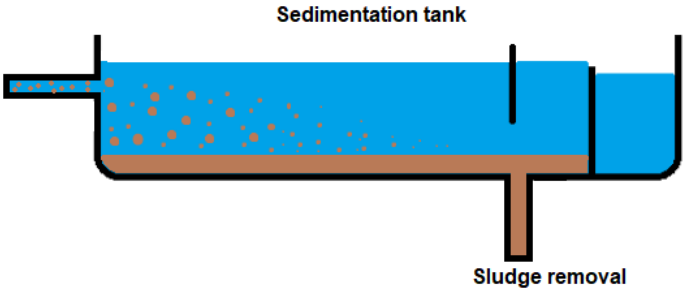


Figure 7: Simplified illustration of a sedimentation tank

The driving force behind sedimentation is gravity, but the settling rate is dependent on the shape, size, viscosity of medium, temperature and what quiescence there is in the medium. Table 2 contains settling times for different type of particles that can be found in water. A temperature of 10°C, specific gravity of 2.65 quiescent conditions and spherical particles are assumed. [22]

Table 2: Settling time of particles in water medium [22]

Material	**Particle diameter[µm]**	**Time to settle 1 m [s]**
Gravel	10 000	1.2
Coarse sand	1000	9
Fine sand	100	120
Bacteria	1	518 400 (6 days)

The flows of water in a conventional sedimentation line is too high for bacteria to settle, therefore, it is not removed via sedimentation to a great extent. For water purification, a treatment method, such as UV-filter and/or addition of chemicals that reduce bacteria growth, is normally added as a complement to deal with this problem. [2]

2.3 PFAS

PFAS is a collective term for poly- and perfuorinated alkyl substances.PFAS are polymers that contain an alkyl chain with one or more fully fluorinated carbon atoms. It has been widely used for over 80 years and it is not until recent years that bans on PFAS in products have been implemented. It has received attention in recent years because of its occurance in water combined with the adverse health outcomes when accumulated in human bodies. [24]

The industry based around organic chemistry of fluorine got its start around 1930 when Midgely and Henne discovered the cooling properties of chlorofluorocarbons. Teflon was discovered in 1938 and a big industry was developed around organoflourine chemistry. As of today, polymers with high fluorine content are widely used around the world. PFAS can be found in consumer products such as fire-fighting foams, anti reflective coatings and textiles. [25]

2.3.1 Physical and chemical properties of PFAS

As mentioned before, PFAS are polymers that contain an alkyl chain with one or more fully fluorinated carbon atoms. Even though they look similar to hydrocarbon chains, the physical and chemical behavior and properties differ majorly. In figure 8, the general chemical structure of PFAS is illustrated.

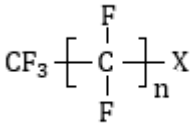


Figure 8: General structure of PFAS [26]

Fluorine is the element with the highest electronegativity, 4.0, and carbon has 2.5. The difference in electronegativity makes the fluorine and carbon bonds polar and also contributes to a high strength, up to 130 kcal/mol. [25] This contributes to a high thermal stability, stability towards corrosion and chemical stability, which is why PFAS has been used extensively in products that require a long lifetime. The most common PFAS in water bodies are the Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). Table 3 presents a summary of some chemical and physical properties of PFOA and PFOS. [25]

Table 3: Physical and chemical properties of PFOS and PFOA [27, 28]

Property	**PFOS**	**PFOA**
Molecular Weight (g/mol)	500.13	414.09
Vapor pressure (mm HG at 25 °C)	0.002	0.525
Boiling Point (°C)	259.0	192.4
Solubility in Water (mg/L)	680	9 500
Atmospheric Halftime (days)	114	90
Halftime in 25°C water (years)	41	92

The most important properties that are presented in the table are the solubility in water, boiling point, and the half time. The halftime is the time it takes for a certain quantity to become half of its initial value. The halftime of PFOS and PFAS in water is as much as 41 and 92 years respectively. The reason to this is its high thermal and chemical stability. They are both anionic surfactants with a strong carbon-fluorine bond which causes a high chemical stability as well as a thermal stability. The substances therefore have a long lifetime in the environment.

The vapor pressure, that indicates what tendency the PFOS and PFOA has to partition into the vapor phase, is low for PFOS, but much higher for PFOA relative to each other. This also indicates that PFOA has a higher risk of long-range gas spreading, since compounds with higher vapor pressure can adsorb to water vapor easier than those that have a lower vapor pressure. The water solubility is much higher for PFOA than for PFOS. The substances both exist in an anionic or neutral form, but the anionic form is significantly more water-soluble than the neutral form [29]. [27, 28]

Some PFAS (PFOA and PFOS) exhibits amphiphilic properties because of their long fluorinated hydrophobic carbon chain and their polar hydrophilic functional group. This explains why they have been used so extensively as surfactants for the last decades [30]. The hydrophobic part in combination with the hydrophilic part of PFOS and PFOA leads to a tendency for the polymers to adsorb at the interface between two liquids that are immiscible or between the interface of an aqueous solution and gas [31, 32].

Figure 9 shows the tendency of amphiphilic polymers to adsorb at the water-gas interface. The red parts illustrated the hydrophilic part, the black parts the hydrophobic part and the blue line the interface.

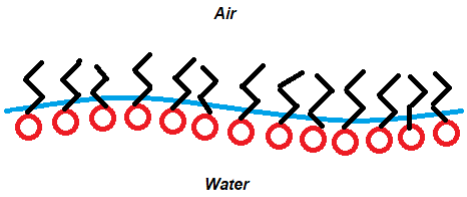


Figure 9: Polymers adsorbing at the Water-Gas interface

The amphiphilic property also enables the substances to form aggregates called micelle. Micelles form when the concentrations of amphiphilic molecules are enough to reach the so called cricical micelle concentration (CMC). This happens when the water/gas interface is filled with amphiphilic molecules and thus sterically hindering more molecules to bind to the interface. Figure 10 illustrates a micelle in an aqueous solution. Left of the micelle is a singular amphiphilic molecule. [27]

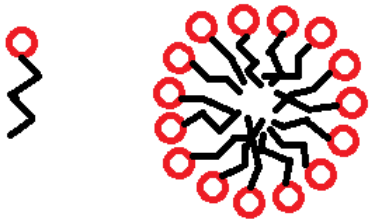


Figure 10: Illustration of a micelle in an aqueous solution

The ability of some PFAS to form micelles is of interest since if the PFAS concentration is enough to reach the CMC, the PFAS might concentrate in micelle aggregates in the DAF basin. The tendency that some PFAS has to adsorb at the aqueous solution/gas interface is of importance for this project since many techniques to remove PFAS from water utilizes this property [31]. This indicates that the PFAS that has amphiphilic properties should adsorb to the bubbles created in DAF because its high affinity to this type of adsorption site [32].

Even though the aim is not to remove PFAS from the DAF basin, some of the techniques that has been used to remove them will be investigated in the next subsection. This is done to contribute with knowledge to eventual additional studies about how PFAS could be removed from the DAF basin if the results are to show high concentrations.

2.3.2 Health effects of PFAS

Drinking water has been identified as a possible source for PFAS to enter the human body. PFOS and PFOA has not only been found in drinking water, but also in air, human breast milk and human blood. [33]

Research has been made on the health effects of PFAS exposure. Two studies report that PFOS has an adverse health effect in the organisms tested,rats and monkeys. The report indicated that high concentrations of PFOS in the test organisms could cause infertility problems, kidney and liver problems, and also tumours. Blood samples were taken from humans, but the PFOS concentrations required for the adverse health effects observed from the test organisms were not reached in the blood samples. Meaning that the people in the study did not have a risk of suffering from the negative health effects that the organisms had, since the concentration was too low. [34, 35]

More recentl research indicates that there are adverse health effects of PFAS exposure, amongst humans [36]. Even though there are reports that present contradictionary results, one thing is certain, when it comes to water quality and health, no unnecessary risks should be taken. Even though PFOS and PFOA are the most abundantly reported PFAS in research, Livsmedelverket, has targeted eleven different PFAS that are of interest to investigate in drinking water, commonly referred to as PFAS11. [37] Table 4 shows the name and abbrevation of PFAS11.

Table 4: Important PFAS to investigate in drinking water according to Livsmedelverket

Name	**Abbrevation**
Perfluorobutanesulfonate	PFBS
Perfluorohexanesulfonate	PFHxS
Perfluorooctanesulfonate	PFOS
Fluorotelomer sulphonate	6:2 FTS
Perfluorobutanoate	PFBA
Perfluoropentanoate	PFPeA
Perfluorohexanoate	PFHxA
Perfluoroheptanoate	PFHpA
Perfluorooctanoate	PFOA
Perfluorononanoate	PFNA
Perfluorodecanoate	PFDA

As of 2021, there is no legally binding limits for how much the PFAS concentration can be in the drinking water in Sweden. There is however, a requirement that it can not be at a concentration that is considered harmful and a risk to human health. Livsmedelverket has recommended that drinking water producers try to keep the PFAS concentration in their drinking water below 90 ng/l. A

suggestion that the water should not be used for food preparation or consumed if the combined PFAS concentration is above 900 ng/l has also been recommended. [37, 38]

The European Union Drinking Water Directive is planning on incorporating PFAS limit values January 2023. In directive 2020/2184, 20 PFAS congeners, referred to as PFAS20 (PFAS11 and an additional 9 PFAS congeners), has been identified as interesting for PFAS removal in drinking water. The directive aims to put a limit of 100 ng/l on PFAS20 and a limit of 500 ng/l on PFAS total. [37, 38]

Because of the adverse health risks that PFAS exposure might have on human health and the future EU limits that will be implemented, the PFAS concentration of the water in the DAF in Görvälnverket will be investigated. The investigation will aim on finding out what PFAS congeners are present in the water and if the concentration of those are reduced throughout the DAF.

Some literature suggest that PFAS can adsorb to the air/liquid interface in the bubbles formed in DAF [31, 32]. A focus will be put on finding the concentration of PFAS in the foam produced in the DAF and thereafter create a material balance of the total PFAS concentration over the DAF. The material balance could provide Norrvatten with an understanding of the PFAS flows in the DAF line at Görvälnverket, this could be used to decide which parts of the DAF should be targeted for future PFAS removal methods.

2.3.3 Removing PFAS from water

Removing PFAS from water has been widely researched [31, 32, 27]. Some of the most common treatment technologies include activated carbon adsorption, ion exchange and high-pressure membranes. There are some novel methods that have been tried for the purpose of removing PFAS from water, such as fractionation, electrocoagulation, advanced oxidation/reduction processes and bioremediation. [27]

As mentioned in the previous subsection, multiple attempts have been made at utilizing the amphiphilic properties of some PFAS to adsorb them to the interface of aqueous solution/gas interface and then remove them from the surface. In one study, Meng.P et al., a combination of aeration and foam collection was used to remove PFOS from aqueous film-forming foam (AFFFs). [31]

In the study, a PFOS removal efficiency of 96% was reached and a concentration of 3.25 g PFOS/l was found in the foam. This indicates that the PFOS concentration can be potentially reduced by 96% just by implementing bubbles into the particle removal step in water treatment. Since DAF already uses bubbles that particles adsorb to and float to the surface, the PFOS concentration could be high in the DAF foam. Meng.P et al. also tried implemented a co-existing

surfactant to increase the removal of PFOS in the water. This proved successful, and a PFOS removal percent of 99.9% was reached by adding a hydrocarbon surfactant. The addition of a co-existing hydrocarbon surfactant seems like a promising removal method if the concentration of PFOS at Görvälnverket is exceeding the limits set by livsmedelverket. [31]

Another study also shows that bubble formation is an efficient way to remove some PFAS in water treatment. Lee.Y et al. removed and recovered PFOS and PFOA from a foam flotation process. The method included addition of metallic activators such as Al (III), Fe(III), La(III) amongst others, and a removal efficiency of 90.2%, 99.5% and 99.0% was reached, respectively, with a dose of 11.5 mM. The study also aimed to look into the pH influence on removal efficiency. According to Lee.Y et al., the optimal removal efficiency was reached at 2.3 pH using Fe(III), with PFOA showing a trend of additional removal at lower pH, but PFOS removal not increasing with pH under 5. [32]

The methods that Meng.P et al. and Lee.Y et al. applied to remove PFOA and PFOS from the water seem promising as a removal method if the concentrations of those PFAS are high in the DAF at Görvälnverket. The DAF creates bubbles and foams, and many studies suggests that PFAS can adsorb to the bubbles in the foam. Therefore, a focus will be put on not only analysing PFAS concentration in the water of the DAF basin, but also analysing the foam created in order to locate where PFAS concentrates in the process. This will create a base for which parts of the process that can be targeted if a method for removal is to be implemented at Görvälnverket.

3 Method

3.1 Particle removal

For the particle removal part of the project, a qualitative method was developed. The method was chosen to be qualitative because the aim was not to identify how many or what particle concentration is in the DAF and sedimentation line. The research question sought to be answered in this part is: *Are there any charged particles in the DAF that do not agglomerate into flocs, and if so, could this be changed by altering the dosage of coagulant?*

3.1.1 Materials

Below is a list of the materials used during extraction of samples, sample preparation and for analysing the samples.

- DelsaNano C Zeta Potential and Submicron Particle Size Analyzer
- Size cell (glass)
- Flow cell (glass)
- Milli-Q water
- Glass flask (250 and 500 ml)
- Lids to flasks
- Plastic pipettes
- Fume hood
- Sample extraction stick
- Bransonic 521 Ultrasonic Cleaner

3.1.2 Experimental design

The size of the particles, PDI and zeta potential was identified as important characteristics for deciding if there are particles that does not agglomerate into flocs in the DAF. For this purpose, the instrument DelsaNano C Zeta Potential and Submicron Particle Size Analyzer (called Zetasizer) were chosen. This instrument is able to analyze both the zeta potential, the PDI and the size of the particles.

For the analysis, six sample extraction points were identified, they are summarized in below list. Figure 11 illustrates where in the process chain the samples were extracted.

- Raw water
- Outgoing water from DAF flocking chamber
- Outgoing water from DAF, line nr 1
- Outgoing water from sedimentation, line nr 2
- Combined sand filter outflow
- Sand filter 4 outflow

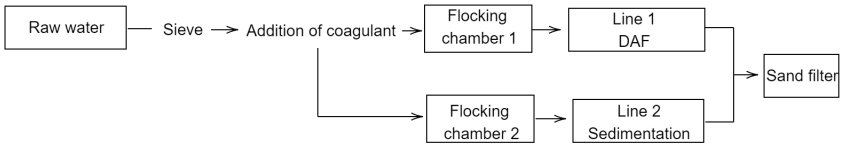


Figure 11: Extraction points for floc characteristic analysis

500 ml were extracted from each sample point and was put in the 500 ml glass flasks. For the outgoing water from line 1 and 2, and the flocking chamber, a sample extraction stick was used. The remaining three samples were easily extracted using a tap connected to each respective process. The date and time when each sample was extracted was noted.

The flasks were sealed with the flask lid and moved to Albanova labs, where the Zetasizer is located. The journey between Görvälnverket and Albanova takes about two to three hours with public transport. During the transport, the samples were handled with care to avoid breakage of flocs.

For the zetasizer analyses, two different type of cells were used. For the size analysis utilizing dynamic light scattering, a Size cell was used. For the zeta potential analysis, utilizing electrophoretic light scattering, a Flow cell was used. Image 12 shows a picture of the size cell (left) and flow cell (right).

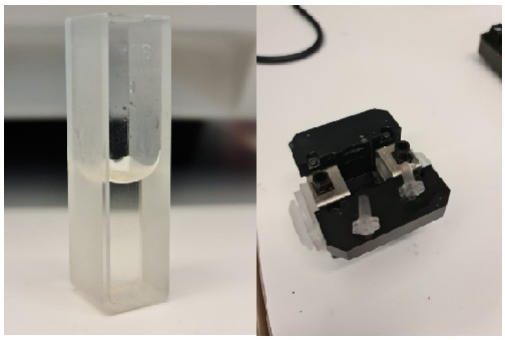


Figure 12: Size cell and Flow cell

The measurement conditions for analysing the size of the particles and the PDI are summarized in table 5. The viscocity and temperature was measured by the instrument, whereas the remaining parameters were set based on the sample characteristics.

Table 5: Measurement conditions for particle size analysis

Condition	**Value**
Sampling time	400 µs
Angle of beam	15°
Attenuator 1	100%
Attenuator 2	3.99%
Temperature	25.1°C
Refractive index	1.33
Viscocity	0.89 cP
Dielectric constant	78.3

For the particle size analysis, the instrument was set to perform 70 measurements on each sample and to iterate this three times, so that a total of 210 measurements were made on each sample. The time domain method was chosen as a correlation method since this method is advantageous for sampling times with many photon counts, for large particles in other words. The correlation method also seemed suitable since the instrument measured a low, fluctuating intensity, which indicates relatively large particles.

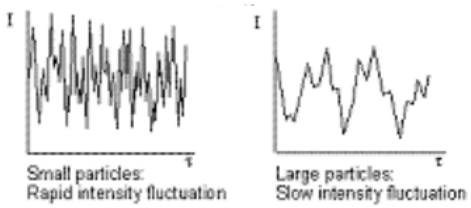


Figure 13: Intensity behaviour for different sized particles [20]

The measurement conditions for analysing the zeta potential of the particles are summarized in table 6. The viscocity and temperature was measured by the instrument, whereas the remaining parameters were set based on the sample characteristics.

Table 6: Measurement conditions for zeta potential analysis

Condition	**Value**
Temperature	25 °C
Cell constant	70
Cell center X (mm)	7.11
Accumulation times	10
Voltage	60 V
Maximum Current	51 mA
Refractive index	1.33
Viscocity	0.89 cP
Dielectric constant	78.3

With the above mentioned settings and conditions, the measurements were made for the flocking chamber sample. The intensity was however, too low. Since the intensity and concentration have a correlation, a conclusion was made that additional methods must be applied to increase the particle concentration in the sample in order to achieve sufficient intensity during the measurement. The changes of methods applied for the floc characteristic investigation is presented in the next subsection.

3.1.3 Method changes for particle removal

The sand filter samples were removed from the study since the intensity was deemed to be too low, even if most of the water were to be removed. The limits were therefore drawn right before the water enters the sieve, to the water that leaves line 1 and line 2. The samples were taken from those four extractions points, using the same technique as previously described.

- Raw water
- Outgoing water from DAF flocking chamber
- Outgoing water from DAF, line nr 1
- Outgoing water from sedimentation, line nr 2

There are several conventional methods for removing water from liquid samples, with distillation being a commonly used one. Boiling the sample in order to evaporate was deemed not applicable in this case, since this could destroy the flocs, thus reducing their size and making the property of interest unrepresentative. A milder form of evaporation is using a so called rotary evaporator that is commonly used to remove solvents from samples. Rotary evaporators lowers the pressure and this reducing the boiling point of water. Unfortunately, even though rotary evaporators has many benefits for this purpose, no rotary evaporator was available for use.

The next best solution was therefore applied, which is natural evaporation, at ambient temperature. The samples were therefore transferred to large, open pickle jars, and places in a fume hood. The temperature in the fume hood was room temperature and the air speed was 0.53 m/s, measured 30 cm above the surface inside the hood. The liquid/gas interface was marked with a marker pen so that the volume lost could be roughly estimated for repeatable purposes. The samples were occasionally checked with the aim of the volume decreasing by 80-90 volume%.

Unfortunately, after two weeks of evaporation in the fume hood, three out of four samples had dried out completely. The raw water sample was still in liquid phase. Because of this, 10 ml of milli-q water was added to the dried samples. Each sample was mixed in order to put the particles back into the solution, the mixing was done with a vortex. The size of the particles were measured using the zetasizer, and the intensity was sufficient. Yet, the intensity was too low for analysing the zeta potential. Since the size of the particles had been measured, an ultrasound bath was used to create a mono-dispersed sample. The ultrasound bath breaks up the agglomerated particles and thus increases the amount of particles in the sample.

The intensity increased sufficiently after using the ultrasound bath. The instrument manual was used to determine whether the results from the measurements

were representative of the samples. This was done by comparing the result of electroosmotic flow curve to the arc shaped curve that it should have. A sample that does not have a symmetric parabolic electroosmotic flow curve might have differently distributed particles due to sedimentation. The samples that had been put in the ultrasound had a symmetric parabolic electroosmotic flow curve which indicates that the particles does not sediment within the cell.

It was hypothesized that treating the samples with an ultrasound bath would not affect the zeta potential of the particles so this was applied. It did however, need verification. The samples had also dried out and the solid particles left in the bottom of the sample jar looked yellow, which could be due to oxidation of the organic matter. This would probably affect the surface charge. Because of the samples drying out, and the ultrasounds impact on zeta potential was unknown, another round of analyses was performed with the goal of verifying the method.

Samples were taken from the same extraction points as before, using the same method and materials. The samples were then taken to the lab and two of them, the raw water and the flock, were analysed on their zeta potential. After that, approximately 2/3 of each samples were put in one pickle jar each and was put in a fume hood. The remaining 1/3 of the samples were sealed. After roughly one week, the samples in the fume hood were sealed so that evaporation to environment would cease.

Half of the volume of the samples that had been evaporated for 7 days were put in the ultrasound bath. The raw water sample and the flocking chamber sample were analysed. The goal was to identify how the result of the untreated, fresh samples differed from letting the samples evaporate for 7 days, and letting the samples evaporate for 7 days + treating the samples in an ultrasound bath. The ultrasound bath would, of course, be the best option if the zeta potential is not affected by it, since it makes the samples more mono-disperse, which will result in a high intensity while being analysed in the zetasizer.

3.2 PFAS

For the PFAS mapping part of the project, a quantitative method was implemented. The method was chosen to be quantitative because the aim was to identify how the concentration of PFAS in each part of the DAF so that an eventual future removal technique can be implemented in the most suitable location. The research questions sought to be answered in this part are:

- *Are there differences in PFAS concentration in the outgoing water of the precipitation lines run with DAF or sedimentation mode?*
- *Which part of the DAF should be targeted for eventual future PFAS removal, and how much removal potential could this have?*

3.2.1 Materials

Below is a list of the materials used during the extraction and storage of the samples. An external lab analysed the samples, and therefore, the equipment and material used for the analysis is not included.

- x18 100 ml specialflask for PFAS, from Eurofins
- x11 250 ml plastic flask for TOC, from Eurofins
- x4 500 ml plastic jar for PFAS soil, from Eurofins
- Flask glass (500 ml)
- Sample extraction stick

3.2.2 Experimental design

The concentration of each respective PFAS in PFAS11 was identified as an important property to investigate in order to map the PFAS flows in the DAF. The total organic carbon (TOC) was also identified as a parameter of interest. PFAS is organic and is therefore a part of TOC, which is measured at the treatment plant, PFAS is not. If a fraction of how much PFAS there is per TOC is calculated, this could be used for the plant to roughly estimate the PFAS content in the water if the TOC content is known.

TOC is however, strongly affected by seasonal changes such as algae blooms or rainfall, and PFAS content is affected by regional effluents [32, 27]. Caution should therefore be applied when an estimation of what the PFAS content is on other days than when the PFAS and TOC was measured. Estimating the PFAS content of a stream for the same or nearby day as the samples were taken could be done with this data.

Analytical methods have been developed for both PFAS and TOC analysis. For PFAS, some methods for analysing drinking water are multilaboratory-validated, such as USEPA 537.1 and USEPA method 533. The lab at Görvälnverket does not have an accredited method for analysing PFAS, therefore, Eurofins was chosen as an external lab that could do those analyses. Eurofins offers accredited analysis' for both TOC, SS EN 1484:1997, and PFAS11, DIN38407-42, UNEP Chemical Branch 2015 mod (HPLC/MS-MS). [39]

The aim is to compare the PFAS flows of the DAF and sedimentation line and to estimate a potential PFAS11 removal from a location in the DAF. It is hypothesized that the PFAS will concentrate in the foam. Based on the hypothesis and the aim, five different sample extraction points were identified:

- Raw water
- Outgoing water from flocking chamber
- Outgoing water line 1 (DAF)
- Outgoing water line 2
- Foam flotation basin

The sample extraction point for outgoing water from line 2 was added to fill the purpose of a reference, so that advantages and disadvantages of using DAF compared to sedimentation with regards to PFAS11 concentration could be compared. A significant difference of PFAS11 concentration between outgoing water in the two precipitation lines would require further investigation of the flows.

The remaining sample extraction points were chosen in order to fulfill that every larger stream from that the water comes into the plant, until it leaves the DAF, is included. Since the analysis of the samples has a monetary cost for the plant, only one sample was taken from each extraction point. This is also the reason to why respective streams for line number two is not analysed.

Sample flasks and jars were ordered by Eurofins. Raw water was extracted from a tap connected to the incoming water into the plant. The remaining liquid samples, sample 2-4 in the above list, were taken from each respective process by using the sample extraction stick together with a large glass flask (500ml). The extraction point of those samples were located in the middle of the walls at the outgoing stream, see Figure 14 for an example of where the extraction point was located for the outgoing water of the DAF line. The other two extraction points were in the corresponding position for that process.

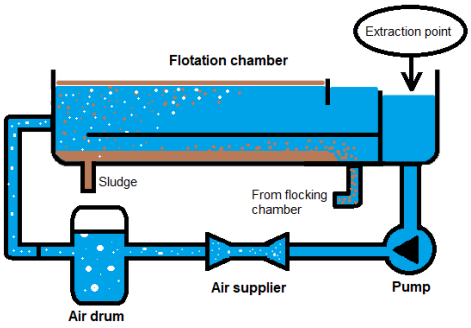
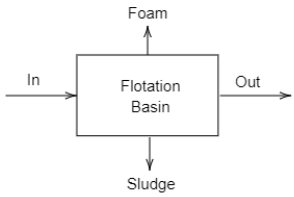


Figure 14: Extraction point of PFAS samples for the DAF outgoing water

The samples were transported to Eurofins labs for analysis the same day as sample extraction. The first set of samples aimed to provide understanding of the PFAS flows in the DAF and in the reference process, sedimentation line 2 as well as calculating a removal potential in the DAF. Flows of flotation foam and outgoing water of the DAF are constantly measured at the plant. The flow of water leaving the flocking chamber and the flow of sludge leaving the DAF is not measured. These flows were approximated by assuming a certain volume flow fraction of sludge vs. foam, and then calculating the mass flows by utilizing equation 1 and 2. The removal potential was calculated using, based on each respectively assumed volume fraction. The equations are presented in Figure 15.



$$\dot{m}_{PFAS,In} = \dot{V}_{In} \cdot C_{PFAS,In} \quad [1]$$

$$\dot{m}_{PFAS,In} = \dot{m}_{PFAS,Out} + \dot{m}_{PFAS,Foam} + \dot{m}_{PFAS,Sludge} \quad [2]$$

$$\dot{V}_{In} \cdot C_{PFAS,In} = \dot{V}_{Out} \cdot C_{PFAS,out} + \dot{V}_{Foam} \cdot C_{PFAS,Foam} + \dot{V}_{Sludge} \cdot C_{PFAS,Sludge} \quad [1] \text{ in } [2]$$

$$\text{Removal potential} = \frac{\dot{m}_{PFAS11,Foam}}{\dot{m}_{PFAS11,In}} \quad [3]$$

$\dot{m}$ – Mass flow

$\dot{V}$ – Volume flow

C_{PFAS} – Concentration of PFAS

Figure 15: Equations to calculate the removal potential of the foam

Another set of samples were extracted, following the same procedure for sample extraction as when the first set of samples were extracted. For the second set of samples, there were two new sample extraction points, and the outgoing water of the flocking chamber was removed as a sample extraction point. The sample extraction points for the second set of samples are summarized below.

- Raw water
- Outgoing water line 1 (DAF)
- Outgoing water line 2
- Under the foam in flotation basin
- Sludge from line 1-5
- Foam flotation basin

The sludge sample was added in order to map all of the flows leaving the DAF. The flows of sludge from precipitation line 1-5 gets combined into one flow, and it is therefore no suitable extraction point for the sludge leaving in the bottom of the flotation basin. Therefore, the PFAS11 concentrationin the sludge sample is assumed to represent the sludge leaving line 1 and 2.

The sample extraction point under the foam in the flotation basin was added to verify if PFAS is trapped in the foam, and not at the liquid-foam/air interface. Some PFAS has surfactant properties, which could create an affinity to the interface and the PFAS might allocate at this interface, instead of the interface in the bubbles. Water was extracted from around 5 cm under the liquid-foam/air interface. A clarification of extraction point for this sample is illustrated in figure 16.

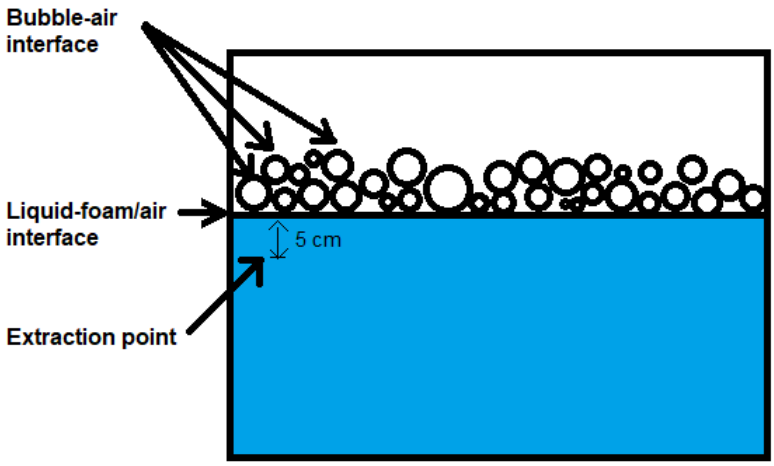


Figure 16: Extraction point for sample "Under surface, flotation foam"

After the samples had been extracted, they were put in the correct sample container and was sent to Eurofins the same day as the sample extraction took place.

4 Results

The results from this section are from samples that were collected and analysed as according to the method described in section 3.1 and 3.2. This section will not include interpretation or discussion of the results, this will be found in section 5, Discussion, of this report.

4.1 Particle removal

For the first analysis with the zetasizer, only one sample, the sample containing water from the flocking chamber 1, had an intensity that was sufficient to execute the analysis. The intensity of the instrument was very low for this run, which resulted in an electroosmotic flow curve that did not have a parabolic shape. The size, PDI, zeta potential and the mobility results are is presented in Table 7. The electroosmotic flow curve from the zeta-potential is presented in Figure 17.

Table 7: Zetasizer results for the flocking chamber water sample

Size [nm]	**PDI**	**Zeta potential** [mV]	**Mobility** [10^{-5} cm^2/Vs]
5841	0.742	-2.63	-1.88

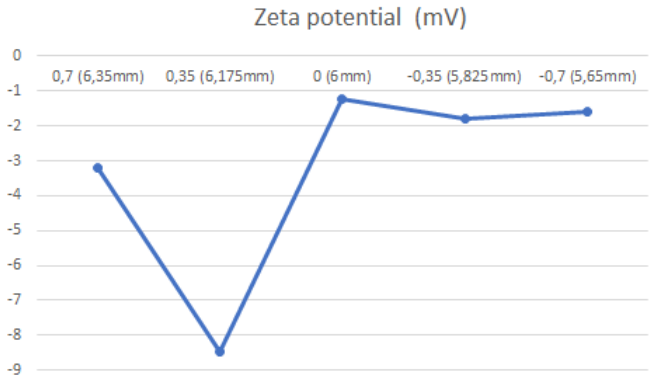


Figure 17: Electroosmotic flow curve from flocking chamber water sample

New samples were taken according to the method description and those samples were left to evaporate for 14 days, then they were analysed. Table 8 contains results of the mean diameter, PDI and the average diameter from each peak as well as the standard deviation of each peak. The sample "Outgoing water line 2" had an insufficient intensity and there were not enough valid data points in the measurement. Therefore, no result could be taken from the analysis of that sample.

Table 8: Zetasizer results of particle size and PDI from four samples

Sample	**Mean diameter** [nm]	**PDI**	**Peak 1** [nm]	**Peak 2** [µm]
Raw water	922.9	0.561	2503 ± 2807	N/A
Outgoing water line 1	2124	0.662	113.4 ± 28.7	N/A
Outgoing water line 2	N/A	N/A	N/A	N/A
Flocking Chamber 1	4035	1.070	1033 ± 236	52 ± 12

Table 9 contains the results of the zeta potential, particle mobility and the electric field of the second sample set. The electroosmotic curve for each of the samples are illustrated in Appendix A.

Table 9: Zetasizer results of zeta potential from four samples

Sample	**Zeta potential** [mV]	**Moblity** [10^{-5} cm^2/Vs]	**Electric Field** [V/cm]
Raw water	-7.99	-6.23	-15.86
Outgoing water line 1	-19.89	-15.51	-15.79
Outgoing water line 2	-7.82	-6.10	-15.56
Flocking Chamber 1	-7.35	-5.73	-15.47

The next measurement had the aim of investigating whether the sample preparation methods have had an effect on the zeta potential of the particles in the samples. One raw water sample was extracted and analysed, with four different sample preparation methods being applied. The results from the zetasizer is presented in table 10. The electroosmotic curve for each of the samples are illustrated in Appendix B.

Table 10: Zetasizer results with aim of verifying method

Sample	**Zeta potential** [mV]	**Moblity** [10^{-5} cm^2/Vs]	**Electric Field** [V/cm]
Raw water "fresh"	-4.46	-3.48	-16.02
Raw water "10 days"	-5.65	-4.41	-15.97
Raw water evaporated	-0.43	-0.34	-16.06
Raw water evap + ultra	-14.23	-11.10	-15.93

Based on the run with the results presented in table 10. Four samples that had stood sealed for 10 days were analysed. The results of that run are presented in table 11. The electroosmotic curve for each sample are illustrated in Appendix C.

Table 11: Zetasizer results, zeta potential measurement of four samples with applied sample treatment method

Sample	**Zeta potential** [mV]	**Moblity** [10^{-5} cm^2/Vs]	**Electric Field** [V/cm]
Raw water	-5.65	-4.41	-15.97
Outgoing water line 1	-6.45	-5.03	-15.96
Outgoing water line 2	-6.45	-5.03	-15.96
Flocking Chamber 1	-11.02	-8.60	-15.96

4.2 PFAS

For the first set of samples for PFAS, five different samples were analysed for PFAS11 concentration. The liquid samples were analysed for their TOC content as well. The measurement uncertainty was 29% for the PFAS analysis and 20% for the TOC analysis. The results of the first PFAS11/TOC analysis are summarized in table 12 and a detailed presentation of the PFAS results are shown in Appendix D. Figure 18 is an illustration of PFAS11 flows for each part of the first treatment steps investigated.

Table 12: Summarized PFAS and TOC results from the first set of samples

Sample	**PFAS11** [ng/l]	**TOC** [mg/l]	**PFAS11/TOC** [10^{-4}]
Raw water	5.5	9.8	5.6
Outgoing water line 1	9.2	5.2	17.6
Outgoing water line 2	7.5	5.6	13.4
Outgoing flocking chamber 1	7.0	9.8	7.1
Foam flotation basin	3800		

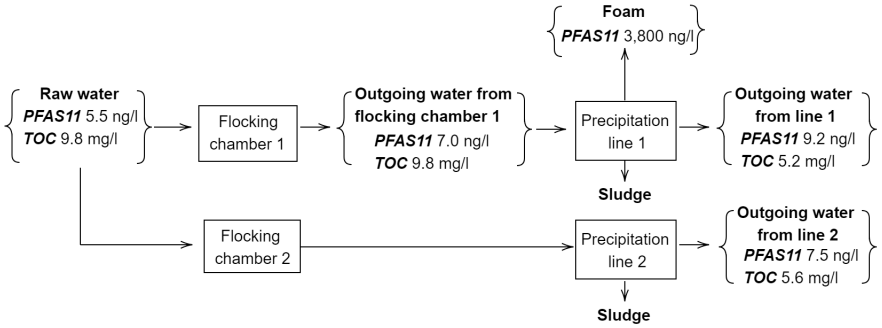


Figure 18: Illustration of the flows with associated results gathered for PFAS and TOC analysis

The data of the flows of the outgoing water of the DAF and the flotation foam were extracted from the online data base at Norrvatten. The flow of outgoing water of the DAF was 280.06 l/s and the flow of flotation foam was 1.06 l/s. The flow of outgoing water of the flocking chamber 1 and the flow of sludge is not measured at the plant. These flows were calculated based on an assumption of a volume relation between foam and sludge. Table 13 contains the calculated flows and the resulting removal potential given each respective assumptions and the results presented in previous table. In the table, "s" represents sludge and

"f" represents foam.

Table 13: Flows and removal potential based on respective assumption of volume fraction of sludge (s) and foam (f)

Assumption	**Sludge flow** [l/s]	**Out flock 1** [l/s]	**Removal potential** [%]
70v% s, 30v% f	2.47	283.59	203
80v% s, 20v% f	4.24	285.36	202
90v% s, 10v% f	9.54	290.66	198
95v% s, 5v% f	20.14	301.26	191
99v% s, 1v% f	104.94	386.06	149

The second set of samples were thereafter collected and sent to Eurofins for analysis. In this set, the foam samples were also analysed for their TOC value. The measured uncertainty for the PFAS analysis was 29% and 10% for the TOC analysis. The summarized results from the analysis of the second set of samples is presented in table 14. Since the instrument failed to quantify specific PFAS11 concentrations, no illustration is presented for the second set of samples. For specific PFAS concentration of each respective substance of PFAS 11, see Appendix E.

Table 14: Summarized PFAS and TOC results from the second set of samples

Sample	**PFAS11** [ng/l]	**TOC** [mg/l]	**PFAS11/TOC** [10^{-4}]
Raw water	<130	10	<130
Outgoing water line 1	<130	5.1	<254
Outgoing water line 2	<130	5.0	<260
Under surface, flotation foam	<130	19	<68
Sludge	<130	260	<5
Foam flotation basin	1400	200	70

The results of the second analysis was presented with higher limits than the previous analysis and were, hence, presented as <130 for many of the samples in table 14. This caused a problem with the results of the whole analysis, since the measurement showed no difference of PFAS11 concentration in the liquid samples. The results gives no indication of a difference in PFAS11 concentrations, therefore, no flows or removal potential could be calculated based on the data from the second analysis.

5 Discussion

In this section, the results and method applied to achieve the results will be discussed. First, the particle removal will be discussed in subsection 5.1 and then the PFAS in section 5.2. After that, a conclusion about the project will be presented together with suggestions of improvements or future research, this is presented in section 6.

5.1 Particle removal

When the first analysis of the size and zeta potential on the sample from the flocking chamber was done, a fluctuating intensity was observed. This indicated that the particles in the sample were large, which had been observed prior to inserting the sample, since there were particles visible to the naked eye. Hence, the time domain correlation method was chosen. This can be both advantageous and disadventageous for the measurement, since the sample from the flocking chamber has relatively large agglomerates, whereas the outgoing water from the DAF most likely has smaller particles. Changing correlation method between runs would be more time consuming since re-calibration is required if changing the correlation method. The time domain was therefore chosen for analysis of all of the samples.

First Zetasizer analysis -The results from the measurements on the flocking chamber samples showed that the average particle diameter was 5841 nm ($\sim$ 5.8 µm), which explains the fact that many particles were visible to the naked eye. The PDI of 0.741 gives indication of a poly-disperse sample, meaning that the size differs greatly between each measured particle. The downside of the low fluctuating intensity is that the majority of the total 210 measurements per sample resulted in a measured diameter of 0 nm. The beam emitting light failed to scatter on any particles and a result of 0 nm was therefore reported for those single measurements.

The measurements resulting in a diameter of 0 nm influences the PDI and mean diameter significantly. The large quantitive of measurements resulting in a diameter of 0 nm indicates that the amount of particles are low, but since this is not something that is sought to be quantified in this report, that type of result does not contribute to the aim. The concentration of particles were, however, not high enough so that the intensity were sufficiently enough to execute the analysis for the sample containing outgoing water from line 2.

The measurements of 0 nm reduces the amount of valid data points and thus decreases the statistical validity of the result. The statistical validity of the analyses is not calculated in this report, but having less amount of measured data for a certain investigated property reduces the accuracy and reliability of the results. The loss of valid data points because of the intensity problem therefore causes an uncertainty of the results.

The zeta potential was measured to be -2.63 mV for the flocking chamber sample. According to the sources presented in table 1, this zeta potential is within the range correlated to the colloids undergoing a rapid and excellent coagulation, and that the coagulant dose is good. This indicates that the coagulation process is adequate and that a higher coagulant dose would not influence the floc creation to a great extent.

The shape of the electroosmotic curve was used to determine whether enough valid data points could be extracted from the measurements. A parabolic electroosmotic curve gives an indication that enough valid data point were extracted. Unfortunately, the curve did not have a parabolic shape. This also indicates that the measured intensity during sample analysis was too low. Thus some new sample preparation methods were applied.

Second Zetasizer analysis -The second performed analysis in the zetasizer was with four samples that had been left under a fume hood for 14 days with the aim of increasing the concentration of particles in the samples, and thus, increasing the intensity during the measurement. The results are presented in table 8 and 9. All samples, except for the outgoing water of line 2, were measured without any intensity problems. The analysis of outgoing water from line 2 resulted in too few valid data points and a final result could therefore not be extracted for that sample.

The particles in the flocking chamber samples had the highest PDI (1.070) and mean diameter (4035 nm), a higher PDI than the previous sample (0.742), but a lower mean diameter then the previous sample (5841 nm). The high PDI of the flocking chamber sample could be explained by looking at the results of the two peaks. The peaks show a clear trend of two different size ranges of particles in the sample. One having a diameter of 1.03 ± 0.24 µm and the other having a diameter of 52 ± 12 µm. The peak with 52 ± 12 µm probably represents the flocs, and the other peak the particles that has not agglomerated into flocs.

The particles in the raw water sample shows a lower mean diameter than the particles in the flocking chamber sample, which indicates floc creation. The mean diameter of the particles in the outgoing water of line 1 and the peak of the same measurement are, however, contradictory. The peak shows that the particles measured are within the range of 113.4 ± 28.7 nm. It is therefore contradicting that the mean diameter can be as high as 2124 nm. This is caused by the data presented in the peaks gets removed by the instrument if they are way outside the range of the other measured particles. Unfortunaltely, this setting could not be changed.

When the realtime size monitor for that run was collected, it could be confirmed that this was the case. Less than 10 out of 70 measurements for one of the runs

gave valid data. That valid data had one particle of 6100 nm and another others giving a result of 150 nm. The particle with 6100 nm has therefore probably been eliminated from the results presented in the peak value, but not from the mean diameter. Few data points were collected for the size and PDI measurements of the outgoing water from line 1 and 2 samples even though methods had been applied to increase the intensity. This shows that those samples probably have too low concentration of particles in order to be analysed with the zetasizer.

The intensity was enough for analysing the zeta potential in all of the samples. The results show that all the samples, except the outgoing water from line 1, had particles with similar zeta potential. While comparing to the sources in table 1, those three samples had a fair coagulation and the dosage of coagulant was good, but on the verge of being too low. The results of the outgoing water from line 1 shows that the particles in that sample had a zeta potential of -19.89 mV. Compared to the sources in table 1, the coagulation is poor, and the coagulant dose is insufficient to reach agglomeration.

For the zeta potential from the particles in the outgoing water from the DAF to be more negative than the one in the flocking chamber shows that the analysed sample might not be representative of the water in the plant. This could be an effect of the flocs breaking, either in the DAF with the turbulent flow, or because of some larger flocs breaking in the sample handling. An ultrasound bath was also used to remove the Van-der waal forces between the agglomerated particles. Whether this broke the agglomeration and thus changing the zeta potential is difficult to know. The velocity of particles is proportional to the charge of the particles, and can therefore be used as a backup measurement to validate that the instrument measures zeta potential correctly.

The mobility and zeta potential are both very high for the particles analysed in the outgoing water from line 1, so the results are probably correct for that sample, but might not be representative of the water in the plant because of sample tampering. The electroosmotic flow curve (Appendix A) shows that all of the measurements had a parabolic shape, so enough valid points must have been extracted during the measurement.

Nonetheless, there are still some uncertainties for the run. The results might be discordant because of the fact that the samples dried out, milli-q water was added, then stirred, then analysed. Some particles went back into the water since there were some valid data points collected for the size and PDI measurement. The zeta potential measurement had many valid points because of the use of ultrasound bath, but if the results got affected by this was determined in the next run.

Another uncertainty was that the sample jars were left open for 14 days in a fume hood. Even though fume hoods provide good ventilation and thus reducing the dust content in the air, leaving a sample exposed to ambient environment for 14 days might have several unknown effects depending on what it is exposed to. Because the size and PDI measurement did not have many valid data points, this analysis was discarded since it was deemed not to provide enough information about whether the particles agglomerate or not. The cost of each analysis was also high, therefore, no further measurements were made on the diameter of the particles nor the PDI.

Run for verifying method - Before the third run of samples from the raw water, flocking chamber, outgoing water from line 1 and line 2, another set of samples were analysed with the aim of investigating how the sample handling might affect the results from the zetasizer. One sample was taken from the fresh water tap at the plant and analysed in the zetasizer around 2 hours after sample extraction. This sample showed particles with a zeta potential of -4.46 mV, which according to table 1 correlates to colloidal particles that will agglomerate rapidly, even though no coagulant had been added. This low negative value indicates that adding coagulant would not do much for the agglomeration potential.

The results differ from the other samples, and the major difference is between the sample that has been partly evaporated over 7 days (-0.43 mV) and the sample that had been partly evaporated, and then put in the ultrasound bath (-14.23 mV). Even though the ultrasound bath provides the most parabolic electroosmotic flow curve (Appendix B), the results differ too much compared to the fresh water sample, and therefore this method was dismissed. The remaining samples had similar electroosmotic flow curves that were slightly parabolic.

The zeta potential of the particles in the sample that had been partly evaporated over 7 days was 4.03 mV higher than the fresh sample. Because their electroosmotic flow curve were both considered acceptable, but the difference in zeta potential was too big, this method was dismissed. The sample that had similar zeta potential as the fresh sample and a similar electroosmotic flow curve was the sample that had been closed with a lid and left alone for 10 days. Since all of the samples were no longer fresh, and no more samples could be extracted because of project time running out, the next run was with samples that had been left alone for 10 days with lids closed.

For this run, there are several uncertainties that might have affected the results. The method that provided that largest change was the one where samples had been evaporated for 7 days and then used in the ultrasound, but it is also the method that is considered the most accurate, since the electroosmotic flow curve follows the parabolic shape. Even if the method resulted in the most accurate measurement, the sample is not a good representation of the water in the plant because it is so different from the results of the fresh raw water sample. The

particle concentrations have caused many problems with the analysis and developing a method were the particle concentration of samples is increased without jeopardizing the zeta potential has been difficult.

A weighing of the usefulness of applying a method to increase particle concentration to produce accurate results vs. the change of zeta potential has therefore been used. Since all of the results presented in Appendix B at least showed a slightly parabolic curve, the accuracy of the measurement has been deemed sufficient, and fresh samples should be used if possible since applying one of the methods investigated in this report will affect the zeta potential. The accuracy of the measurement was also confirmed by comparing the zeta potential results to the mobility and electric field. The mobility was slightly less than the zeta potential in all of the samples, and the electric field, which should be constant, did not differ much from each analysed sample.

Third run - Four samples that had been left with closed lids were analysed, results presented in table 11. The ingoing raw water had particles with a zeta potential of -5.65, which is the highest of the four samples. The flocking chamber is the sample with particles that has the lowest zeta potential, -11.02, and when this is compared to the sources in table 1, this correlates to poor coagulation and a too low coagulant dose. The zeta potential in the outgoing water from line 1 and line 2 are both -6.45, which shows an increase of zeta potential between the flocking chamber and the precipitation lines, which the coagulant aims to do.

The reason to why the flocking chamber has a very low zeta potential can be because the sample extraction point is not representative of the water leaving the flocking chamber. This could result that the coagulation and flocculation mechanisms in the extracted samples had not achieved the agglomeration potential that they have with the corresponding coagulant dose because of the colloidal particles not getting close to the coagulant.

Another explanation might be that the trend that could be seen from the results in table 10 where the sample that had been left for 10 days had a slightly higher zeta potential than the fresh raw water sample. This would not explain the difference in result between the flocking chamber sample and the outgoing water sample, because they all had been left for 10 days with closed lids. It can, however, explain why the zeta potential is so low and why the results might correlate to a poor coagulation and a too low dosage, even if this might not be the case in reality.

The electroosmotic flow curves show, as predicted, a shape that is not smoothly parabolical which indicates few valid data points. Not trying to alter the particle concentration and having a low accuracy of the instrument was deemed better than applying one of the methods mentioned earlier to increase the concentration and thus changing the zeta potential. Each run for the zeta potential

analysis measured $10 \cdot 5 \cdot 3 = 150$ data points, so a loss of accuracy should not be a problem with that many data points. The difference in zeta potential of the flocking chamber and the outgoing water from line 1 and 2 indicates that the coagulant has achieved a charge neutralization between those treatment step. However, the difference in zeta potential between the raw water sample and outgoing water from line 1 and 2 indicates that the colloids have become more negatively charged, and thus more stable in the liquid. This could be a basis for further investigation, and a particle size analysis and PDI could work as a complementary to form a conclusion from this result.

Common uncertainties -All of the samples from table 7 to table 11 share some common uncertainties. One of those are the choice of extraction points. The extraction point for each respective process has been the same for all sample extractions, but whether the extraction point is representative of the part of the process that is investigated remains to be decided. Only one sample was extracted from each point because of economical reasons. Having multiple extraction points for each respective process could improve the study and make the results more representative of that process.

Another problem is that one extraction point that was of interest could not be reached, the sludge leaving the process. If samples could be taken from this part of the process, a mapping of how the particles agglomerate would be easier to achieve. The aim was however, to analyze whether the particles that leave the DAF has a negative charge that correlates to insufficient coagulation so analysing the sludge would not benefit the aim, but it would increase the understanding of the process.

One of the uncertainty, and the one that has been adressed the most, is the low particle concentration in the water and the problems that occur due to it. The zetasizer used should not be used to measure samples with this low concentration. There are zetasizers that operates live and perform online measurements directly on a precipitation line, this could provide more accurate, reliable and representative results for this project. No such equipment was available, unfortunately.

The identified property that would correlate to whether the agglomeration took place or not was successfully measured. It is difficult to reach a conclusion because the results did not follow the anticipated behaviour of the raw water having the lowest zeta potential and then the zeta potential successfully increasing throughout the processes included. This will be brought up in section 6.

5.2 PFAS

Samples were extracted and analysed according to method described in section 3.2, the results are summarized and presented in table 12 and the specific results of the analysis are found in table 15 and table 16.

First sample set - The results show that the concentration of PFAS11 is increasing during the first treatment steps, with it being at its lowest at the raw water intake, 5.5 ng/l, and at its highest at the outgoing water of line 1, 9.2 ng/l. The TOC concentration is decreasing during the first treatment steps which together with the increasing PFAS11 concentration results in an exponentially increasing PFAS11/TOC quota. The most occuring substances of PFAS11 in the liquid samples are PFHxS, PFOS, PFHxA, PFO and PFPeA.

The six remaining substances had a concentration that was too low for the instrument to quantify a specific concentration, these values are therefore presented as <"x" and is not included in the summarized PFAS and TOC concentrations in table 12 and Figure 18. The decreasing TOC concentration and increasing PFAS11 concentration gives indication that organic compounds are removed in the investigated treatment steps, but the treatment fails to remove PFAS11 to the same degree as other organic compounds since the quota is increasing.

The total PFAS11 concentration in the flotation basin foam was 3800 ng/l. This supports the theory that the large surface interface between liquid and air in the bubbles provides a suitable adsorption area for the PFAS11 surfactants. The compounds of PFAS11 with highest concentration in the foam are PFOS: 1900 ng/l, PFOA: 530 ng/l and 6:2 FTS: 880 ng/l.

The concentration of certain PFAS11 compared to the total PFAS11 concentrations greatly differs between the flows. The raw water, outgoing water of flocking chamber, line 1 and line 2, all had a measured 6:2 FTS concentration lower than 1.0 ng/l. The foam in the DAF had a 6:2 FTS concentration of 880 ng/l, so more than 880 times larger than in the liquid samples. 6:2 FTS is considered a long PFAS, and the longer the PFAS, the more hydrophobic the fluorinated carbon chain becomes. This could contribute to a higher affinity for the functional group to adsorb at the gas/liquid interface, and for the chain to avert the liquid.

There is a problem with using concentration as a unit of measurement when comparing the liquid samples and the foam sample, since a large volume of the foam consists of air. This becomes a problem due to the analytical method applied. Liquid chromatography is used, so the liquid part of the samples are analysed. The bubbles are therefore first re-dispersed into liquid before analysis of the sample. This makes the calculation of PFAS mass flow in the DAF foam difficult, because the concentration of PFAS can not be simply multiplied with the volume flow to achieve the mass flow of PFAS.

Even though how well the concentration of PFAS in the foam could relate to the flow of foam was questioned, measures were applied to try to calculate the removal potential. The flow of foam from the DAF was on the same date as the sample extraction 1.06 l/s, and the outgoing water had a flow of 280.06 l/s. With these flows and the assumed fraction between volume flow of settled sludge and floated sludge, the removal potentials were calculated.

The removal potential calculations clearly demonstrates the importance of not comparing the volume flows of liquid samples with the volume flows of foam, since all calculations resulted in a removal potential above 100% for the given assumptions. Attempts were made to assume a larger difference between volume flows of settled sludge and foam, but the problem was not the assumption of relation between the two flows, but rather the assumption that the volume flow of foam could be multiplied with the concentration of PFAS.

Second sample set - The sludge was added as a sample extraction point since the problem with air taking up such a large volume in the foam. This makes the foam concentration ineligible for multiplying with the foam volume flow to calculate the mass flow of PFAS11. The volume flow of sludge is not measured at the plant, but if all the flows around line 1 were analysed regarding their PFAS11 and TOC content, an estimation could be made of how much PFAS is removed in the foam by back-calculating the equations presented in subsection 3.2 and by assuming that the PFAS11/TOC quota is same for each analysis.

Unfortunately, the analysis results had a higher limit than in the first analysis. In the second analysis, the concentration of each PFAS were presented with values of <10 or <20 ng/l, even though the first analysis resulted in specific values when the concentrations were below 10 ng/l.

Eurofins was contacted for a consultancy of how one should interpret those values. Eurofins claimed that the large peak generated from the result of high concentration in the foam scaled the chromatogram after high concentration samples. This caused difficulties in the area measurement of the smaller peaks (from the liquid samples) in the chromatogram because the scale of the chromatogram had adjusted to the large peak.

Based on Eurofins answer, there must have been a difference in which order the samples were analysed in the two sample series made in this project. For future research, it is important to have a dialogue with the lab executing the analyses if one suspects the concentration of PFAS to be high compared to other samples in the same series.

The high limits are problematic because if the results presented as "<x" are used for summarizing the total PFAS11 concentration, the concentration of the liquids are higher than 90 ng/l. This is the the upper limit of total PFAS con-

centration that Livsmedelverket recommends water used as consumption should be below.

In the first analysis, all values reported as "<x" were not included in the calculation of total PFAS11 concentration. If a similar approach was done for the second analysis, the PFAS11 concentrations would be 0. Because of this, all concentrations of <10 or <20 ng/l were summarized so that a total PFAS11 concentration of <130 ng/l was reported.

Another problem that the limits causes are that no difference of PFAS11 concentration can be distinguished in samples taken from the two lines, even though the TOC concentration clearly presents a difference between each sample. The results from the liquid samples can therefore not be used to evaluate whether there is a PFAS concentration difference in the water leaving each process operated under DAF or sedimentation mode.

The results from analysing the second sample set can, however, confirm that the concentration of PFAS is higher in the foam sample compared to the liquid samples. This answers the research question of which part of the DAF should be targeted for eventual future PFAS removal techniques, but the data collected is not sufficient to estimate a removal potential, since further measurements need to be done to calculate this.

Uncertainties - There are some factors that could have contributed to the measured samples not being representative of the part of the process they were extracted. One of those factors is that the analytic method used is HPLC/MS-MS, which is utilized on liquid samples. Before the decision of analytic method was made, Eurofins was contacted for consultancy about which analytical method would be the most appropriate for the purpose of this project. Eurofins claimed that foam samples, such as fire extinguisher foam, are commonly analysed at their labs and that this method could be utilized to investigate the PFAS11 concentrations in the foams from the water treatment plant.

The method of HPLC/MS-MS causes two potential problems with the representative issue of the samples to the foam. One of them is that some PFAS11 might create more stable bubbles than others and is therefore more difficult to re-disperse into the liquid. The other problem is that once the PFAS are dispersed in the liquid, the substances have a high affinity to the liquid-gas interface, and will probably concentrate at this interface. If the sample is extracted from a point beside the liquid/air interface during the measurement, there is a risk that the concentrations are lower than they would be in the foam.

Another reason that could have contributed to the measured samples not being representative is that the sample was only extracted from a few points in each process. For the foam sample, the jar was filled up by scooping a little bit of foam from several locations around the flotation basin. For some locations

closer to the wall of the basin, a thicker foam was observed.

These flocks of foam along the wall seemed to consist of accumulated foam. This could result in the foam closer to the wall having a higher concentration of PFAS relative to the foam extracted from the middle of the basin. Foam could only be extracted from within one meter of the wall, so a wide distribution of collected foam could not be achieved.

Another uncertainty was the scooping that was used to extract the foam sample. The scooping of foam resulted in some of the liquid coming with, and the volume ratio between foam and liquid was not noted. This influences the result of PFAS concentration in the foam sample, since there is more water in the sample and further creates complications to whether the analysed foam sample is representative of the actual foam or not.

The analysis, HPLC/MS-MS, had a high reported uncertainty of 29%. Because this was the analysis available for analysing PFAS concentrations in foam and liquid samples, no efforts were put into trying to reduce the uncertainty, but it was used as caution when interpreting the results.

The uncertainties and the fact that the foam samples might not be as representative of the concentration in the foam might have influenced the results. The aim was, however, to investigate whether the PFAS concentrations were high in some parts of the processes, and to locate a spot in the DAF that should be targeted for future PFAS removal. The results are sufficient to answer those questions since the PFAS concentrations in the foam are significantly higher compared to the concentration of PFAS in the liquid samples. If the plant aims to remove PFAS from their water, the foams in the precipitation lines should be targeted.

6 Conclusion and future research

Methods were developed and used with the aim of investigating differences in floc characteristics and PFAS concentration of the sedimentation/DAF treatment step of the water treatment plant Görvälnverket.

Floc characteristics - The results from the analysis of flocs shows an identical zeta potential of the particles in the samples extracted from the outgoing water of line 1 and 2. The zeta potential indicates that the mechanisms of coagulation and flocculation occuring in both operational modes. The results from analyses of size and PDI supports the theory that the flocs were created since the analysis presented an increase of particle size in the flocking chamber. The turbulent flow in DAF does not seem to break the flocs more than the more laminar flow of sedimentation does.

There are several improvements that can be done to make the results more reliable. Some of those are:

- Using a photoanalysis method to confirm that the floc creation mechanisms occur
- Produce more data by utilizing same method, and quantify a statistical validity of the measurements
- Produce more data by trying other methods, e.g. rotary evaporation, to decrease the water content of the samples,
- Analyse the water with another instrument measuring the same properties, such as an online zetasizer

For future research, experiments can be conducted with the aim of investigating a connection between zeta potential and coagulant/flocculant dose.

PFAS - The results from the analysis shows that the concentration of PFAS11 does not exceed livsmedelverkets recommendation of <90 ng/l total PFAS11 concentration in outgoing water from line 1 or 2. The operational mode sedimentation had a slightly lower PFAS11 concentration compared to the operational mode DAF. The results from analysing the foam in DAF showed a high concentration of PFAS. The foam has therefore been identified as a suitable removal source if the PFAS concentrations in the water are to exceed the limits set by or bound to be set by livsmedelverket or EU in the future.

The data collected has not been sufficient to estimate a reliable removal potential in the foam. In order to calculate such a value, the fraction of volume between air and liquid in the foam must be determined. To increase the reliability of the results, the following procedures can be done:

- Produce more accurate data by using the same method, but ensuring that the liquid samples are analysed before foam samples
- Take samples, and divide them into two sources for each sample. Then send the samples for analysis at two different external, accredited labs, and see the difference in results

Future research suggestions includes: a quantification of the PFAS removal potential in the foam, a development of a PFAS11 removal technique, analysing certain PFAS affinity to the bubbles.

References

[1] WHO. *Drinking-water*. 2019. URL: https://www.who.int/news-room/fact-sheets/detail/drinking-water.

[2] Norrvatten. *Dricksvattenproduktion - Norrvatten.se*. URL: https://www.norrvatten.se/dricksvatten/dricksvattenproduktion/.

[3] Livsmedelverket. *Regler om dricksvatten*. Nov. 2020. URL: https://www.livsmedelsverket.se/produktion-handel--kontroll/dricksvattenproduktion/regler-om-dricksvatten.

[4] Norrvatten. *Miljöarbete - Norrvatten.se*. URL: https://www.norrvatten.se/om-norrvatten/vart-hallbarhetsarbete/mijoarbete/.

[5] Norrvatten. *Fortsättning för flotation - Norrvatten.se*. URL: https://www.norrvatten.se/om-norrvatten/nyheter/nyhetsarkiv/nyheter-2021/fortsattning-for-flotation/.

[6] Saif Ali. "Handbook of Environmental Engineering: Physicochemical Treatment Processes Coagulation and Flocculation". In: *Handbook of environmental engineering* (2005). Ed. by Saif Ali, pp. 103–139. URL: https://d1wqtxts1xzle7.cloudfront.net/62960784/Handbook_of_environmental_engineering_320200414-120806-1jn1vb7.pdf?1586931937=&response-content-disposition=inline%3B+filename%3DPhysicochemical_Treatment_Processes.pdf&Expires=1623223713&Signature=LyY2dVDBjX.

[7] *Colloidal suspensions*. Tech. rep.

[8] Ruyuan Jiao et al. "Roles of coagulant species and mechanisms on floc characteristics and filterability". In: *Chemosphere* 150 (May 2016), pp. 211–218. ISSN: 18791298. DOI: 10.1016/j.chemosphere.2016.02.030.

[9] Tao Li et al. "Characterization of floc size, strength and structure under various coagulation mechanisms". In: *Powder Technology* 168.2 (Oct. 2006), pp. 104–110. ISSN: 00325910. DOI: 10.1016/j.powtec.2006.07.003.

[10] Arman Vahedi and Beata Gorczyca. "Settling velocities of multifractal flocs formed inchemical coagulation process". In: *Water Research* 53 (Apr. 2014), pp. 322–328. ISSN: 18792448. DOI: 10.1016/j.watres.2014.01.008.

[11] Herman E Ries and Bernard L Meyers. "Flocculation Mechanism: Charge Neutralization and Bridging". In: *Science* 160.3835 (June 1968), 1449 LP –1450. DOI: 10.1126/science.160.3835.1449. URL: http://science.sciencemag.org/content/160/3835/1449.abstract.

[12] Emmanuel I. Unuabonah and Andreas Taubert. *Clay-polymer nanocomposites (CPNs): Adsorbents of the future for water treatment*. Sept. 2014. DOI: 10.1016/j.clay.2014.06.016.

[13] *Turbidity and Water*. URL: https://www.usgs.gov/special-topic/water-science-school/science/turbidity-and-water?qt-science_center_objects=0#qt-science_center_objects.

[14] J. D. Eisnor, K. C. O'Leary, and G. A. Gagnon. "Evaluation of particle removal at water treatment plants in Nova Scotia". In: *Water Quality Research Journal of Canada* 36.1 (Feb. 2001), pp. 105–119. ISSN: 12013080. DOI: 10.2166/wqrj.2001.007. URL: http://iwaponline.com/wqrj/article-pdf/36/1/105/229292/wqrjc0360105.pdf.

[15] *Brownian Motion: Langevin Equation*. Tech. rep.

[16] Guang Wei Lu and Ping Gao. "Emulsions and Microemulsions for Topical and Transdermal Drug Delivery". In: *Handbook of Non-Invasive Drug Delivery Systems*. Elsevier, Jan. 2010, pp. 59–94. DOI: 10.1016/b978-0-8155-2025-2.10003-4.

[17] K. Pate and P. Safier. "Chemical metrology methods for CMP quality". In: *Advances in Chemical Mechanical Planarization (CMP)*. Elsevier Inc., Jan. 2016, pp. 1–325. ISBN: 9780081002186. DOI: 10.1016/B978-0-08-100165-3.00012-7.

[18] *Zetasizer WT — Zeta Potential Water Treatment System — Malvern Panalytical*. URL: https://www.malvernpanalytical.com/en/products/product-range/zetasizer-range/zetasizer-wt.

[19] M. Danaei et al. *Impact of particle size and polydispersity index on the clinical applications of lipidic nanocarrier systems*. May 2018. DOI: 10.3390/pharmaceutics10020057. URL: www.mdpi.com/journal/pharmaceutics.

[20] P N B08631aa. *Delsa™Nano Submicron Particle Size and Zeta Potential User's Manual*. Tech. rep. 2011. URL: www.beckmancoulter.com.

[21] *FORENSIC APPLICATIONS OF CONTAMINANT TRANSPORT MODELS IN THE SUBSURFACE — Elsevier Enhanced Reader*. URL: https://reader.elsevier.com/reader/sd/pii/B9780123695222500129?token=8F6AEF7FC67F643FB37D7E95F1BED40D9E5048472B2913BCC6DA485BE3EC21165775ADFA2F8EC445F originRegion=eu-west-1&originCreation=20210525102934.

[22] Edward M- Fahey Lawrence K. Wang and Zucheng Wu. "Handbook of Environmental Engineering: Physicochemical Treatment Processes Dissolved Air Flotation". In: *Handbook of Environmental Engineering: Physicochemical Treatment Processes* (2005), pp. 444–500. URL: https://d1wqtxts1xzle7.cloudfront.net/62960784/Handbook_of_environmental_engineering_320200414-120806-1jn1vb7.pdf?1586931937=&response-content-disposition=inline%3B+filename%3DPhysicochemical_Treatment_Processes.pdf&Expires=1623223713&Signature=LyY2dVDBjX.

[23] Graeme J. Jameson. "Hydrophobicity and floc density in induced-air flotation for water treatment". In: *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Vol. 151. 1-2. Elsevier Science Publishers B.V., June 1999, pp. 269–281. DOI: 10.1016/S0927-7757(98)00503-2.

[24] *Basic Information on PFAS — Per- and Polyfluoroalkyl Substances (PFAS) — US EPA*. URL: https://www.epa.gov/pfas/basic-information-pfas.

[25] David M. Lemal. *Perspective on Fluorocarbon Chemistry*. Jan. 2004. DOI: 10.1021/jo0302556. URL: https://pubs.acs.org/sharingguidelines.

[26] "Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts Scientific Opinion of the Panel on Contaminants in the Food chain". In: *EFSA Journal* 6.7 (July 2008). ISSN: 18314732. DOI: 10.2903/j.efsa.2008.653.

[27] Katarzyna H. Kucharzyk et al. "Novel treatment technologies for PFAS compounds: A critical review". In: *Journal of Environmental Management* 204 (Dec. 2017), pp. 757–764. ISSN: 10958630. DOI: 10.1016/j.jenvman.2017.08.016.

[28] Us Environmental Protection Agency Federal Facilities Restoration and Reuse Office. *Technical Fact Sheet – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)*. Tech. rep. 2017.

[29] V. Gellrich, T. Stahl, and T. P. Knepper. "Behavior of perfluorinated compounds in soils during leaching experiments". In: *Chemosphere* 87.9 (May 2012), pp. 1052–1056. ISSN: 18791298. DOI: 10.1016/j.chemosphere.2012.02.011.

[30] Sierra Rayne and Kaya Forest. *Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods*. Oct. 2009. DOI: 10.1080/10934520903139811. URL: https://pubmed.ncbi.nlm.nih.gov/19847705/.

[31] Pingping Meng et al. "Efficient removal of perfluorooctane sulfonate from aqueous film-forming foam solution by aeration-foam collection". In: *Chemosphere* 203 (July 2018), pp. 263–270. ISSN: 18791298. DOI: 10.1016/j.chemosphere.2018.03.183.

[32] Yu Chi Lee et al. "Recovery of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from dilute water solution by foam flotation". In: *Separation and Purification Technology* 173 (Feb. 2017), pp. 280–285. ISSN: 18733794. DOI: 10.1016/j.seppur.2016.09.012.

[33] Ling Mak Yim et al. "Perfluorinated compounds in tap water from china and several other countries". In: *Environmental Science and Technology* 43.13 (July 2009), pp. 4824–4829. ISSN: 0013936X. DOI: 10.1021/es900637a. URL: https://pubs.acs.org/sharingguidelines.

[34] Gerald L. Kennedy et al. *The toxicology of perfluorooctanoate*. July 2004. DOI: 10.1080/10408440490464705. URL: https://www.tandfonline.com/action/journalInformation?journalCode=itxc20.

[35] A. M. Seacat. "Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys". In: *Toxicological Sciences* 68.1 (July 2002), pp. 249–264. ISSN: 10960929. DOI: 10.1093/toxsci/68.1.249. URL: https://academic.oup.com/toxsci/article-lookup/doi/10.1093/toxsci/68.1.249.

[36] Katherine E. Pelch et al. *PFAS health effects database: Protocol for a systematic evidence map*. Sept. 2019. DOI: 10.1016/j.envint.2019.05.045.

[37] *PFAS in drinking water and self-caught fish - risk management*. URL: https://www.livsmedelsverket.se/en/production-control-and-trade/drinking-water-production-and-control/t?AspxAutoDetectCookieSupport=1#Tolerable_Weekly_Intake_for_PFAS.

[38] *EUR-Lex - 32020L2184 - EN - EUR-Lex*. URL: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32020L2184.

[39] *Högfluorerade ämnen (PFAS) i naturliga vatten - Eurofins utför på nytt dessa analyser i Sverige! - Eurofins Scientific*. URL: https://www.eurofins.se/tjaenster/miljoe-och-vatten/nyheter-miljo/hoegfluorerade-aemnen-pfas-i-naturliga-vatten-eurofins-utfoer-paa-nytt-dessa-analyser-i-sverige/.

7 Appendices

7.1 Appendix A

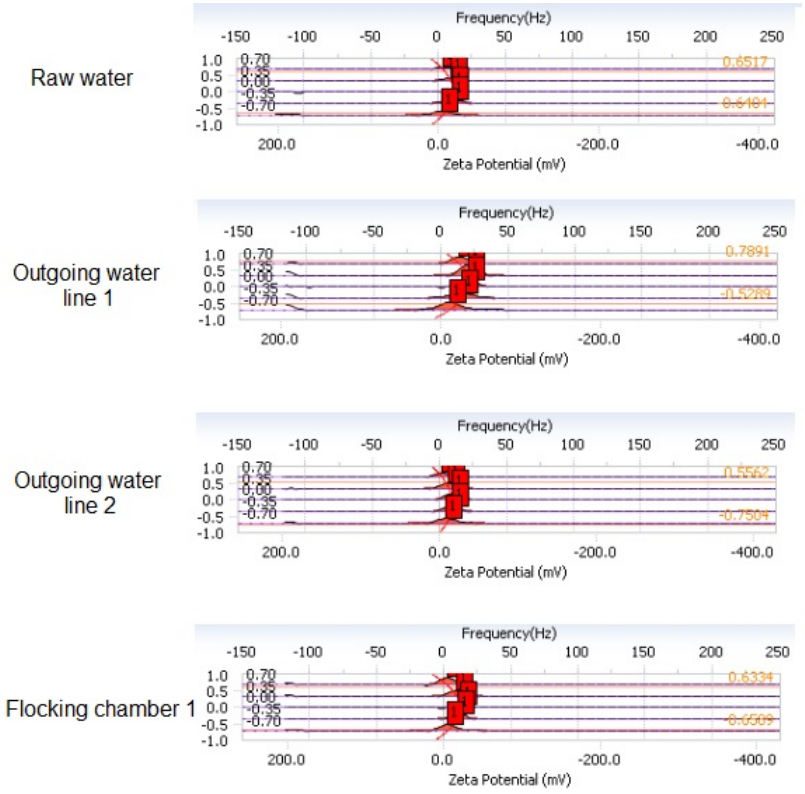


Figure 19: Electroosmotic flow curve from second analysis

7.2 Appendix B

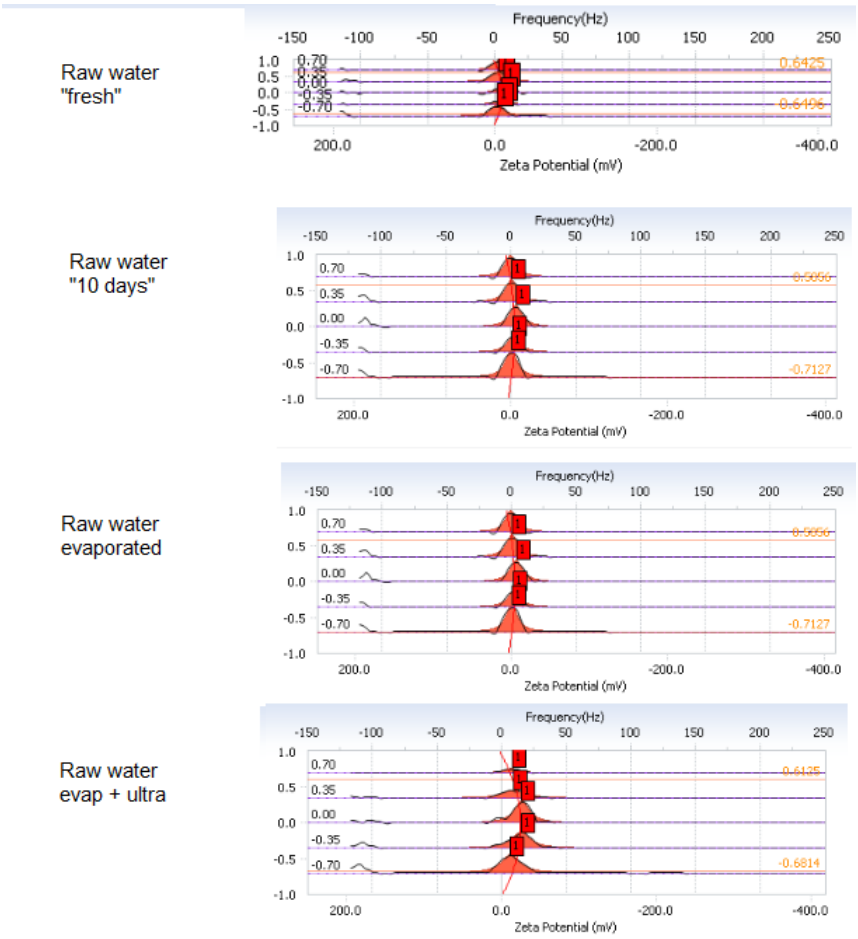


Figure 20: Electroosmotic flow curve from run with aim of verifying method

7.3 Appendix C

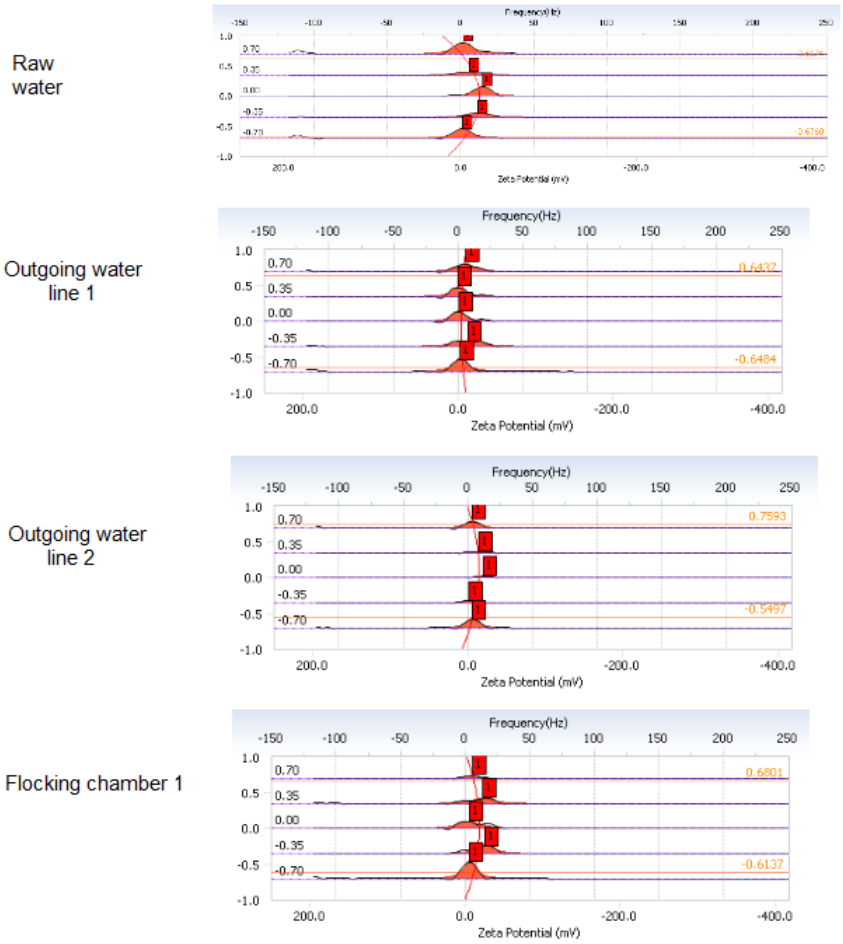


Figure 21: Electroosmotic flow curve from third analysis

7.4 Appendix D

Table 15: PFAS and TOC results from the first set of samples, part 1

Abbrevation	**Raw Water** [ng/l]	**Out Flocking chamber** [ng/l]	**Out line 1** [ng/l]
PFBS	<1.0	<1.0	<1.0
PFHxS	1.2	1.3	2.0
PFOS	1.9	1.9	2.9
6:2 FTS	<1.0	<1.0	<1.0
PFBA	<3.0	<3.0	<3.0
PFHxA	1.2	1.4	1.2
PFHpA	<1.0	<1.0	<1.0
PFOA	1.2	1.1	1.8
PFNA	<1.0	<1.0	<1.0
PFDA	<1.0	<1.0	<1.0
PFPeA	<1.0	1.3	1.3

Table 16: PFAS and TOC results from the first set of samples, part 2

Abbrevation	**Out line 2** [ng/l]	**Foam Flotation** [ng/l]
PFBS	<1.0	<10
PFHxS	1.4	150
PFOS	1.8	1900
6:2 FTS	<1.0	880
PFBA	<3.0	<20
PFHxA	1.5	<10
PFHpA	<1.0	20
PFOA	1.4	530
PFNA	<1.0	230
PFDA	<1.0	44
PFPeA	1.4	<10

7.5 Appendix E

Table 17: PFAS and TOC results from the second set of samples, part 1

Abbrevation	**Raw Water** [ng/l]	**Out line 1** [ng/l]	**Out line 2** [ng/l]
PFBS	<10	<10	<10
PFHxS	<10	<10	<10
PFOS	<10	<10	<10
6:2 FTS	<10	<10	<10
PFBA	<20	<20	<20
PFHxA	<10	<10	<10
PFHpA	<10	<10	<10
PFOA	<10	<10	<10
PFNA	<10	<10	<10
PFDA	<10	<10	<10
PFPeA	<20	<20	<20

Table 18: PFAS and TOC results from the second set of samples, part 2

Abbrevation	**Sludge** [ng/l]	**Under Foam** [ng/l]	**Foam Flotation** [ng/l]
PFBS	<10	<10	<10
PFHxS	<10	<10	48
PFOS	<10	<10	1100
6:2 FTS	<10	<10	<10
PFBA	<20	<20	<20
PFHxA	<10	<10	<10
PFHpA	<10	<10	<10
PFOA	<10	<10	100
PFNA	<10	<10	75
PFDA	<10	<10	27
PFPeA	<20	<20	<20