Fractionation of NOM in water from the treatment process at Ringsjöverket

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Picture on front page: Columns used for fractionating NOM. Photo by Stina Karlsson

Preface

This master thesis was written in collaboration with Sydvatten AB and the Department of Chemical Engineering at Lund University. It concludes my education to become an environmental engineer. I am incredibly thankful that I got the opportunity to do this mater thesis and for the opportunity to deepen my knowledge related to drinking water treatment. There are a lot of people that I want to thank when I now realise that I could not have done this alone. Therefore, I want to thank the following people:

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Summary

During the last decades, increased concentrations of natural organic matter (NOM) and colour of surface waters have been reported from northern Europe and North America. Since surface waters are widely used for drinking water production this development has been problematic for drinking water producers. Even though NOM in itself is not harmful, it can cause production of undesirable disinfection by-products, decrease efficiency of UV-treatment and enhance biological growth within distribution systems. Moreover, drinking water treatment plants that use chemical precipitation has been forced to increase their coagulant dosages. This in order to obtain sufficient removal of NOM. In addition to increased concentrations of NOM, the colour of surface waters and UV absorbance have been shown to increase more than DOC values. This is not only an indication of increasing NOM-concentrations but also of that the characteristics of the NOM in surface waters are changing. In order to be able to optimise and improve the performance of the applied processes, it is essential not only to investigate different options of treatment techniques, but also to analyse the characteristics of the NOM in the water.

In this master thesis, the characteristics of water from the process at Ringsjöverket were investigated. Ringsjöverket is a drinking water treatment plant located in Scania and owned by Sydvatten AB. In order to characterise NOM based on hydrophobicity the rapid fractionation method was used. Applying this method, water was fractionated into very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). After fractionation the quantity of each fraction was determined by dissolved organic carbon (DOC) measurements.

This study shows that the raw water from lake Bolmen has a hydrophobic character. The dominating fraction in the raw water, VHA, constitutes together with the SHA, 85% of all DOC in the raw water. Chemical precipitation and the following rapid sand filtration was shown to be effective in separating VHA, SHA and CHA. However, these treatment processes showed no ability in separating the NEU fraction. The subsequent treatment in the slow sand filters showed no significant removal of any of the NOM fractions.

Since 2017, two pilots, one ultra-filtration pilot and one infiltration sand filter pilot, have been running at Ringsjöverket. The purpose is to investigate future options for treatment techniques. However, compared to the more conventional treatment including chemical precipitation and rapid sand filtration, the chemical precipitation followed by ultra-filtration turned out to be less effective in separating NOM. However, small differences in separation of each fraction could be distinguished. The NEU fraction of NOM, which appeared to be unaffected during all other treatment steps, was separated in the ultra-filtration membrane. The sand filter pilot showed no ability of separating any of the fractions of NOM. On the contrary, increased concentrations of the fraction VHA after the sand filter indicated leaching of NOM from the sand filter. However, there are some uncertainties related to the result from the pilots. Therefore, more fractionation of this water is needed for a reliable result.

Sammanfattning

De senaste årtiondena har det rapporterats om att koncentrationen av naturligt organiskt material (NOM) har ökat i ytvatten i norra Europa och Nordamerika. Eftersom att det är vanligt att ytvatten används till produktion av dricksvatten så har denna utveckling varit problematisk för många dricksvattenproducenter. NOM är i sig själv inte farligt, men det kan orsaka att oönskade biprodukter bildas vid desinfektion, minskad effektivitet av UV- desinfektionen och intensifierad tillväxt av mikroorganismer i ledningsnätet. Dessutom har dricksvattenverk som använder sig av kemisk fällning, för att nå önskad reningsgrad av NOM, blivit tvungna att öka doseringen av kemikalier. Förutom ökade koncentrationer av NOM i ytvatten har man också kunnat se att färgen, mätt som UV absorbans, ökat mer än värden på totalt organiskt kol (TOC). Detta indikerar inte bara på att koncentrationen av NOM ökar utan även att karaktären av NOM har förändrats. För att kunna optimera reningsprocesser och förbättra reningen är det därför viktigt att inte bara utreda olika reningsmetoder, utan att också karaktärisera innehållet av NOM.

I detta examensarbete har NOM i vatten från olika steg i reningsprocessen på Ringsjöverket studerats. Ringsjöverket är ett dricksvattenverk beläget i Skåne som drivs av bolaget Sydvatten AB. För att karaktisera vattnet baserat på hydrofobicitet har en metod som kallas snabbfraktionering använts. Med hjälp av denna metod har NOM i vattnet kunnat separeras i följande fraktioner: starkt hydrofoba syror (VHA), svagt hydrofoba syror (SHA), laddat hydrofilt material (CHA) och neutralt hydrofilt material (NEU). Efter fraktioneringen bestämdes storleken på de olika fraktionerna med hjälp av mätningar av löst organiskt kol (DOC) i vattnet.

Denna studie visar att råvattnet som kommer från sjön Bolmen och som används vid dricksvattenproduktionen vid Ringsjöverket har en starkt hydrofob karaktär. Den dominerande fraktionen i råvattnet, VHA, utgör tillsammans med fraktionen SHA, 85% av allt DOC i råvattnet. Kemisk fällning och den efterföljande snabbfiltreringen visade sig vara effektiv när det kommer till separationen av fraktionerna VHA, SHA och CHA. Däremot visade sig mängden NEU efter kemisk fällning och snabbfiltrering vara oförändrad. Den efterföljande reningen i långsamfiltren visade inte på någon märkbar separation av någon av fraktionerna.

Sedan 2017, utför man på Ringsjöverket pilotförsök med ultra-filtrering och sandfiltrering för att utreda dessa reningsmetoder. I den här studien fraktionerades också vatten från dessa piloter. Kemisk fällning kombinerat med ultrafiltrering visade sig med avseende på total DOC reduktion vara mindre effektiv än kemisk fällning kombinerad med snabbfiltrering. Dock kunde små skillnader i separationen av olika fraktioner urskiljas. En utav dessa skillnader var förmågan att avskilja NEU. Denna fraktion visade sig vara opåverkad av alla reningssteg förutom i ultrafiltreringen där mängden NEU på ett ungefär halverades. Den efterföljande sandfiltreringspiloten visade inte på någon förmåga att separera någon av fraktionerna av NOM. Tvärtom, ökade mängden VHA i vattnet efter filtrering vilket indikerar att sandfiltret läcker NOM och framförallt VHA. Det finns dock vissa osäkerheter kopplade till resultatet. För ett mer tillförlitligt resultat bör därför ytterligare fraktioneringar utföras på dessa vatten.

Abbreviations

CHA	Charged hydrophilic acids
DBP	Disinfection by-products
DI water	Distilled water
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWTP	Drinking water treatment plant
MM	Molecular mass
MW	Molecular weight
NEU	Neutral hydrophilic material
NOM	Natural organic matter
SHA	Slightly hydrophobic acids
SUVA	Specific ultra-violet absorption
TOC	Total organic carbon
UF	Ultra-filtration
UV	Ultra-violet
UV_{254}	Ultra-violet absorbance at 254 nanometres
VHA	Very hydrophobic acids

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1 Introduction

Increased and fluctuating concentrations of natural organic matter (NOM) and colour of surface waters have been reported worldwide. This has become an issue for drinking water producers and increased the pressure on drinking water treatment process. In order to meet water quality standards drinking water treatment plants (DWTP), unable to handle these increased and fluctuating concentrations of NOM, need to be upgraded and adapted to this situation. Therefore, to be able to in a sustainable way deliver high quality drinking water independent of the raw water quality, development of reliable and efficient treatment methods is essential.

The most common process used today by DWTP to separate NOM from water is chemical precipitation. As a consequence of increased NOM concentrations in surface waters it has been reported that facilities have increased their dosage of coagulation chemicals, and as a result more sludge is produced from the coagulation process (Lidén, 2016). Even if NOM is not dangerous in itself, it can, for example, during disinfection produce disinfection by-products (DBP), cause problems such as colouring of water, bad taste and odour and in addition enhance biological growth within distribution systems (Sillanpää, 2014). This development is problematic and negative both economically and environmentally, but first and fore most the quality of the water is put at risk.

It has been reported that values of colour and UV- absorbance of surface waters have increased more than values of total organic carbon (TOC). Therefore, it is believed that it is not only the concentration of NOM that is increasing, but also the characteristics of NOM, which are changing towards more coloured substances (Lidén, 2016; Graneli, 2012). In order to be able to optimise and improve the performance of the applied processes it is essential not only to investigate different options of treatment techniques, but also to analyse the characteristics of the NOM in the water.

This thesis was written in collaboration with one of the largest drinking water producers in Sweden; Sydvatten AB. Sydvatten has two large DWTPs; Ringsjöverket and Vombverket. The source water used by Ringsjöverket, from lake Bolmen, is suffering from brownification (Lidén, 2016) which during the past years have been the topic for several investigations and pilot projects. These investigations and projects have been focusing on new treatment techniques and mainly on membrane filtration.

The water from lake Bolmen is transported in a 80 km long tunnel to Ringsjöverket. In the future Sydvatten plans to also transport water from lake Bolmen to Vombverket by expanding the existing tunnel with a pipe. Because of this, pre-treatment of the new raw water is needed at Vombverket. One of the proposed treatment methods are membrane filtration and therefore an ultra-filtration (UF) membrane pilot study has been running since May 2017 at Ringsjöverket. As a complement to the ongoing pilot project, this study aims to characterise and quantify NOM in the treatment processes at Ringsjöverket.

1.1 Objective

In this study, the objective was to investigate the characteristics of NOM in water from the DWTP Ringsjöverket. More specifically, the aim was to fractionate NOM in water from different treatment steps at Ringsjöverket, based on hydrophobicity. The specific research questions in this study were:

- What fractions of NOM do the water contain?
- Where in the treatment process are different fractions separated?

The research questions have been answered through practical experiments in lab. The experimental method used to fractionate NOM was the rapid fractionation method. After fractionation, different analytical methods were used to measure water quality and to determine the quantity of the different fractions of NOM. In addition to analysing how the quantity of NOM changes during treatment, this study will also be able to show a more detailed picture of how different fractions of NOM are separated. This will give a deeper understanding, not only about the NOM, but also about the different treatment processes. This knowledge can then be used during, for example, process evaluation and design.

1.2 Structure of the thesis

This master thesis report starts, in Chapter 2, with an introduction of NOM. In this chapter the characteristics of NOM will be presented and the phenomenon called brownification will be introduced. Moreover, available separation and analytical methods for NOM and the rapid fractionation method will be presented in Chapter 3. Chapter 4 will give a short introduction to the pilot project at Ringsjöverket and a brief presentation of the DWTPs Ringsjöverket and Vombverket. Furthermore, the experimental setup and procedure will be described followed by a presentation of the calculations and the analytical methods used. Then, the results and a discussion about the outcome, including sources of errors, will follow in Chapter 5. Conclusions will be presented in Chapter 6, and the report ends with Chapter 7, with ideas about future work.

2 Natural organic matter

NOM is a shared term for degraded organic matter in nature, originating from animals, plants, bacteria and algae. In nature, NOM is present in soil, water and sediments. Due to the interaction between the biosphere, geosphere and the hydrological cycle, NOM can be found in all fresh waters and especially in surface waters. Therefore, water used as drinking water source usually contain NOM (Sillanpää, 2014). This chapter will start with an introduction of the characteristics of NOM and a brief presentation of characterisation of NOM. Moreover, this chapter will present the phenomenon "brownification". Finally, this chapter ends with a section about NOM related to drinking water production.

2.1 Characteristics of NOM

NOM can be categorised into two classes depending on their origin; allochthonous and autochthonous NOM. Allochthonous NOM originates from leaching and decomposition of organic matter from plants and soil, whereas autochthonous NOM originates from microbial derived NOM within the water body (Aliverti, et al., 2005). NOM therefore consists of various forms of complex macro-organic molecules with extensive variation in structure and molecular size and weight. Moreover, factors such as temperature, pH, biological processes and water chemistry influences the composition of NOM (Sillanpää, 2014). Consequently, the amount and the characteristics of NOM varies both with location and over time. These complex molecules consist of a mixture of both aromatic and aliphatic hydrocarbon structures with different combinations of functional groups, which at neutral pH are mainly negatively charged (Uyguner-Demirl & Bekbolet, 2011).

Natural waters in general, contains both hydrophobic and hydrophilic NOM components. The largest fraction is the hydrophobic acids, which constitute about 50% of all TOC in surface waters. Traditionally these hydrophobic acids have been categorised into three types of humic substances; humic acids, fulvic acids and humins (Sillanpää, 2014).

Hydrophobic acids consist of biostable and high-molecular humic substances. These molecules are of high aromatic character and have high abundance of conjugated double bonds. Consequently, these molecules are assumed responsible for most of the ultra-violet (UV) absorbance and colour in the water. Hydrophilic fractions of NOM, on the other hand, are of lower molecular weight, more biodegradable and they are assumed responsible for fouling of membranes and biological growth (Eikebrokk & Juhna, 2010a).

NOM has an approximated molecular mass (MM) in the range of 100 Da to 100 kDa (Sillanpää, 2014). All waters have their own characteristics and size distribution of NOM, but in general the smaller molecules, <1 kDa, are dominating (Metsämuuronen, et al., 2014). In a study performed by Fabris et al. (2008) on surface waters in Norway and Australia, it was found that the MM of NOM in these waters was in the range from a few 100 Da up to 10 kDa. NOM in the form of polysaccharides, proteins and amino sugars have the largest MM. NOM with high aromatic character are found to be of an intermediate to high MM. Hydrophilic compounds, building blocks and organic acids which are degradation products from humic substances are NOM with the smallest MM (Lankes, et al., 2008 & Sillanpää, et al., 2015).

2.2 Characterisation of NOM

Drinking water treatment facilities today normally control and measure NOM in water through parameters such as TOC, dissolved organic carbon (DOC), chemical oxygen demand, colour and UV-light absorption (Sillanpää, 2014). All these measurements are relatively easy and fast to perform and do not require advanced methods or equipment. These methods provide information about the amount of NOM present in the water, but information given about the characteristics of NOM with these methods are limited (Matilainen, et al., 2011). Since NOM molecules are diverse and normally present in low concentrations in water, characterisation of NOM is problematic. Suitable methods, that have the possibility to characterise NOM in either dilute solutions or by methods that are able to sort out or concentrate NOM, are therefore useful. To characterise every NOM molecule is unrealistic. Consequently, it would be more practical to use methods that can identify NOM with the same chemical and physical properties (Matilainen, et al., 2011).

2.2.1 Specific UV-absorption

The specific UV-absorption (SUVA) is the ratio between UV absorbance at a wavelength of 254 nm and the DOC concentration of the sample. The obtained ratio describes the characteristics of NOM in terms of hydrophobicity and hydrophilicity and it can act as an operational indicator at DWTPs. A value above 4 indicates that the characteristics of NOM in the water is hydrophobic, of high-molecular weight (MW), aromatic and humic. With values below 2 the characteristics of NOM in the water are hydrophilic, of low MW and non-humic (Matilainen, et al., 2011; Eikebrokk & Juhna, 2010a). Table 1 shows how Edzwald and Tobiason (1999) summarise values of SUVA as an operational indicator and the expected removal of NOM by coagulation.

Table 1. Characteristics of NOM at different SUVA-values and expected removals of DOC during alum coagulation. Efficiency is slightly higher for ferric (Edzwald & Tobiason, 1999).

SUVA-value	NOM characteristics	Coagulation efficiency
>4	High hydrophobicity, high MW, Aquatic humic	Greater than 50%
2-4	Mixture of hydrophobic and hydrophilic NOM, mixed MWs	25-50%
<2	Low hydrophobicity, low MW and non-humic	Lower than 25%

2.3 Increased NOM concentrations and brownification of surface waters

Brownification is defined as the increase of the brown colour of surface waters, such as lakes and rivers. The cause of this increase in colour is mainly due to increases in humic material and dissolved organic matter (DOM) in the water (Graneli, 2012).

Since the beginning of the 1980s, there has been a noticed brownification of surface waters in for example Sweden, Norway, North America, Finland and the UK (Lidén, et al., 2015; Forsberg, 1992; Köhler & Lavinen, 2015; Hongve et al., 2004; Driscoll et al.,2003 and

Monteith, et al., 2007). In a few decades, values of colour have in some cases been more than doubled. The concentration of DOM has increased along with colour but not as much, which implies that DOM alone can not explain the brownification (Graneli, 2012). Therefore, the quality, and not only the quantity of DOM, may also influence the colour. Another substance that has been shown to increase the colour of water is iron (Kritzberg & Ekström, 2012).

2.3.1 What causes brownification?
The causes for this brownification of surface waters have up until now not been completely understood, but the proposed causes are linked to climate change. Several studies have shown that increased precipitation is well correlated to increased NOM concentrations and especially to the hydrophobic fraction of NOM (Haaland, et al., 2010; Forsberg, 1992 and Fabris, et al., 2015). This may be due to decreased retention times in lakes as a result of higher flows (Weyhenmeyer, et al., 2012). At extreme rain events, the water will take other pathways and according to Hongve et al., (2004) more coloured acid organic compounds will leach from the upper layer of the soil. Similarly, have Köhler and Lavonen (2015) proposed that more humid conditions in the soil zone near the stream contributes to more humic substances in the water. A study made 2011 in Australia, which is a country with extreme changes in climate conditions, showed that river water quality changes considerably during flood and drought. During flood the DOC values became four times as high compared to during drought. In this study, the hydrophobic fraction of NOM was the cause for increased DOC concentrations during floods. The hydrophilic NOM was instead increased during stable conditions (Fabris, et al., 2015).

Other suggested causes to brownification is decreased acidification (Erlandsson, et al., 2008; Monteith, et al., 2007), land-use or a combination of all mentioned factors (Ritson, et al., 2014). Even though the suggested causes are related to human activities, climatic variability may also influence the brownification in a shorter time scale. Köhler and Lavonen (2015) have for example shown that periods with high precipitation clearly results in more coloured waters. How NOM in surface waters will develop in the future are somewhat uncertain. However, Ritson, et al. (2014) have suggested that catchments that are recovering from acidification will contribute to more DOM with high hydrophobicity and that larger alternation in precipitation is likely to result in larger fluctuations in DOM in waters reaching treatment plants.

2.3.2 Brownification of lake Bolmen
Water quality data from lake Bolmen show that the lake since the 1990s suffers from brownification including decreasing secchi depth, more coloured water and higher TOC concentrations (Lidén, 2016). According to Lidén (2016), colour and absorbance have increased more than TOC, which may indicate that the composition of NOM has changed to contain more humic substances. In response to this increase the DWTP Ringsjöverket has increased its coagulant dosages. Even though increased TOC concentrations have been reported from lake Bolmen, it is according to Figure 1 even more interesting to see the large fluctuations in UV_{254} absorbance during the last twenty years. UV_{254} absorbance have during this period been fluctuating between 20 m^{-1} and 60 m^{-1}. This is an indication of that the concentration of aromatic and hydrophobic NOM in the water is varying considerably.
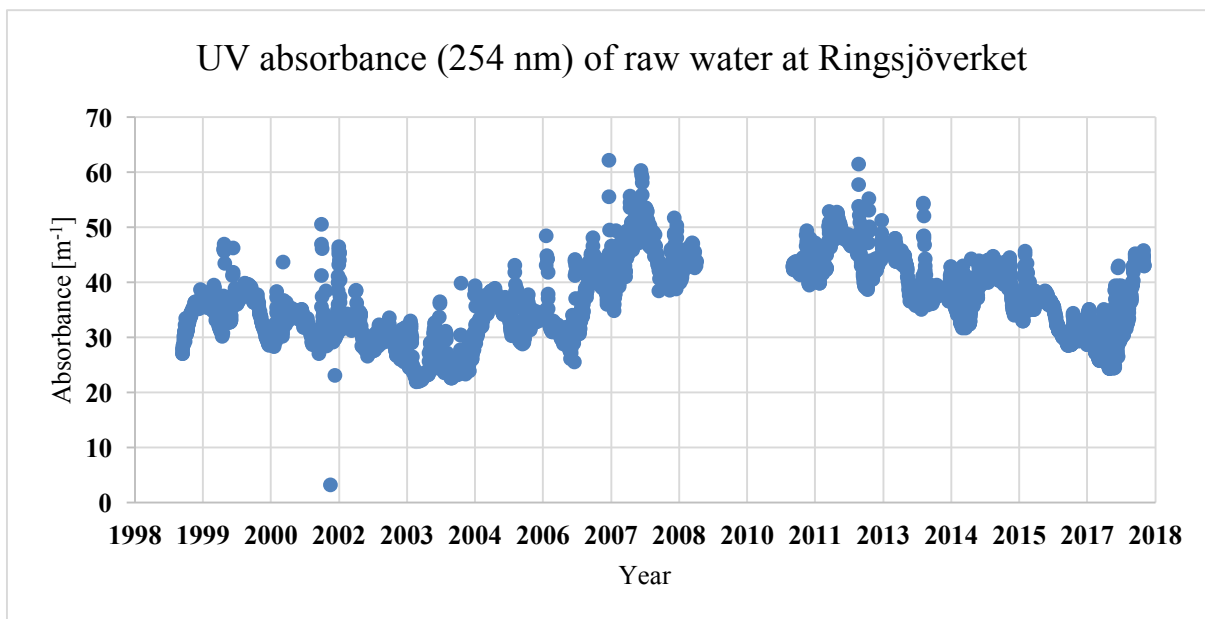
Figure 1. Data on UV absorbance at 254 nm, from year 1999 to 2018, of raw water at Ringsjöverket. Water originates from lake Bolmen. During the period 2009-2011 another raw water source was used, lake Ringsjön, and therefore data from this period is excluded.

2.4 NOM and drinking water production

In this section, the most common available treatment method of surface water will be described and in addition, effects and consequences of NOM in drinking water production will be presented. Since chemical precipitation is one of the most common treatment methods to remove NOM and since an UF membrane pilot is in place at Ringsjöverket, these methods will be further described below.

2.4.1 Drinking water treatment - in general

Of all drinking water produced in Sweden half comes from surface waters, such as streams or lakes, whereas the other half consists of water produced from groundwater. While surface waters are characterised by coloured and turbid water containing humic substances and bacteria, ground water is most often of a better quality since it undergoes a purification process when it is filtered through the ground (Lidström, 2013).

In conventional drinking water treatment of surface water coagulation, flocculation, followed by sedimentation and filtration, is the most common process for NOM removal. Although other treatment options such as membrane filtration, adsorption, ozonation, ion exchange and degradation are available, coagulation has historically been the most efficient and economically favourable option (Ritson, et al., 2014).

2.4.2 Effects of NOM during and after drinking water treatment

Too high concentrations of NOM can cause several problems in the drinking water treatment process and in the drinking water distribution system. In the treatment process, increased NOM concentrations increase the requirements of coagulants, which results in higher volumes of produced sludge. This is negative both economically and environmentally. If disinfection by UV is used, it is, according to Eikebrokk & Juhna (2010a), important to control hydrophobic NOM

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since these fractions have high UV absorbance and colour which might decrease efficiency of UV-disinfection. If NOM is not successfully separated in DWTPs, it could cause aesthetical problems such as coloured water, bad taste and odor as well as biological growth in the distribution system (Sillanpää, 2014).

Disinfection of drinking water has been used widely all over the world. During the twentieth century, it has been one of the most important factors behind advanced public health. However, during the 1970s it also became an issue to public health when it was recognised that chemicals used during disinfection could form DBP when reacting with for example NOM. These findings came at the same time as a relation between cancer and disinfection of drinking water was recognised (Singer, 1994). Oxidants such as ozone, chlorine, chloramines and chlorine dioxide are the most commonly used disinfectants. At the same time as these chemicals are effective in killing microorganisms they are also strong oxidants. Consequently, other components in the water such as NOM can be oxidised and form DBPs (Richardson, et al., 2007). The most commonly found DBPs are trihalomethanes and haloacetic acids (Sillanpää, 2014). In general, NOM and, especially, hydrophobic NOM with high MM and high aromatic carbon content, has been seen as the most important precursor to DBPs. However, all types of NOM seem to form DBPs and therefore it is important to also remove hydrophilic NOM with low MM (Sillanpää, 2014, Hua & Reckhow, 2007, Hua, et al., 2015)

2.4.3 Chemical precipitation

Chemical precipitation is a process which normally includes coagulation, flocculation and sedimentation. The most commonly used coagulants are aluminium and ferric based. Chemical precipitation is the treatment which have been shown to be most efficient in separating NOM. How successfully coagulation separate NOM depends on several factors such as what type of coagulant that is used and in what dosages, the characteristics of NOM, DOC concentrations and pH of the water (Edzwald & Tobiason, 1999; Chow, et al., 2004).

The principle behind coagulation is to reduce the repulsive force between particles enabling production of micro-particles. These micro-particles can thereafter form larger flocs, which could be separated and removed from the water (Matilainen, et al., 2010).

When coagulants such as aluminium and iron salts are added to the water, they are first dissociated to positively charged ions, hydrolysed and thereafter they form positively charged complexes. These complexes can be adsorbed to negatively charged colloids. Thus, the repulsive potential is reduced. During coagulation, there are several mechanisms in which NOM can be removed from the water; charge neutralisation, destabilisation, entrapment, adsorption and formation of complexes with metal ions. In this way micro-particles can be formed. Through collisions by micro particles, larger insoluble aggregates, called flocs, are formed in the flocculation process (Matilainen, et al., 2010; Matilainen & Sillanpää, 2015). Flocs large enough can thereafter be separated through sedimentation. Smaller flocs not able to sediment can be separated by for example sand or a membrane filtration.

Hydrophobic NOM and NOM with high MM are expected to be removed most efficiently during chemical precipitation. The dominating removal mechanism of these types of NOM is charge neutralisation. Adsorption is expected to be the dominating mechanism when removing non-humic NOM and NOM with low MM (Matilainen & Sillanpää, 2015).

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2.4.4 Membrane filtration

Membrane filtration has become more and more common in drinking water treatment processes, including reverse osmosis, nano, ultra (UF) and micro-filtration. All types of filtration methods have different capacities of removing NOM. Fouling of membranes and decreased flux are mayor problems related to membrane filtration (Matilainen, et al., 2010).

Large and uncharged NOM molecules are mostly rejected by the membrane by size exclusion, due to these molecules being larger than the membrane pore size. Moreover, rejection also depends on the interactions between the water and the membrane. Repulsive electrostatic forces between solution and membrane can result in higher rejections than expected. Not only are the properties of the membrane important, but also the properties of the NOM in the water are of importance (Sillanpää, et al., 2015).

NOM properties that enhance the rejection by membranes are high molecular mass, negatively charged, aromatic and hydrophobic structures. Another important factor of membrane filtration related to the solution, i.e. the water, is pH. The pH of the water changes surface properties of both NOM and the membrane and therefore, all the removal mechanisms. Even though high removal rates have been reported at low pH, greater rejection is expected at high pH because NOM, in these conditions, has a larger radius and the membrane surface repulsive forces are stronger. Conditions resulting in positively charged membranes attract hydrophobic NOM to the membrane, which can cause fouling (Sillanpää, et al., 2015).

Micro-filtration membranes have large cut-off values, >100kDa, and a pore size of 0.1-5 μm. These membranes are effective in removing turbidity but less efficient in removing NOM. UF-membranes have a cut-off value of 1-100kDa and a pore size of 10-100 nm. In these membranes, NOM with high molecular mass is rejected. Higher separations of NOM can be achived if coagulation is used before the micro-filtration and UF membranes. Cut-off value for nano-filtration membranes is 100-500 Da. This membrane can remove NOM with high molecular mass but NOM with low molecular mass can pass through (Metsämuuronen, et al., 2014).

DOC removal in surface water filtered through UF membranes, with a cut-off of >60 kDa, have shown to range from 14 to 49% (Metsämuuronen, et al., 2014). In order to increase DOC removal, the UF process have, according to Lidén et al. (2015), to be combined with other treatment processes. The most conventional option is to have coagulation followed by flocculation, sedimentation and then membrane filtration. There are, however, other alternatives; direct filtration, where flocs are not removed before the membrane, and in-line coagulation, where coagulant is added directly to the main stream before the membrane. Direct filtration and in-line coagulation followed by membrane filtration requires less chemicals compared to if only chemical precipitation is used and, in addition, the same treatment results of NOM are obtained. Nanofiltration on the other hand has shown good treatment results even without pre-coagulation (Lidén, et al., 2015). Treatment processes such as adsorption, oxidation and filtration through tighter membranes are also options to combine with micro-filtration and UF (Sillanpää, et al., 2015).

3   Fractionation of NOM

There are several existing methods in which NOM can be separated into different fractions. Membrane filtration, resin fractionation, chromatographic methods, spectroscopic methods and biological testing are some of these available methods. Since the properties of NOM vary widely, the results from separation methods will depend on the origin of the sample and the separation method used. In consequence, understanding of and comparison between studies can be difficult. In this study, a resin fractionation method called the rapid fractionation method is used. This method will in this chapter be further described. Moreover, this chapter will also present what fractions that are expected to be separated in different treatment processes.

3.1   The rapid fractionation method

One common way of characterising NOM is to divide it into hydrophobic and hydrophilic fractions and one method used for this is resin fractionation. The type of resin fractionation used in this study is called the rapid fractionation method. This method includes three types of resins, Superlite XAD-8, Amberlite XAD-4 and Amberlite IRA-958. Water is filtered in series through columns packed with these resins, which allows NOM to separate based on hydrophobicity into the four following fractions:

- Very hydrophobic acids (VHA)
- Slightly hydrophobic acids (SHA)
- Charged hydrophilic material (CHA)
- Neutral hydrophilic material (NEU)

The mechanism in which NOM is adsorbed to the different resins are driven by solubility in the aqueous phase and the ability of the NOM to adsorb to the surface of the resin. Hydrophilic NOM forms strong hydrogen bonds with water, whereas hydrophobic NOM is not forming these strong interactions with water. Hydrophobic NOM are therefore partially separated from the aqueous phase. This instead enables the hydrophobic NOM to adsorb to the surface of the resin by Van der Waal forces (Jarvis, et al., 2010).

By changing the pH, the dissociation of the NOM molecules can be controlled. At acid conditions, the ionisation of acidic groups on the NOM molecule decrease and as a result the charge of the NOM molecule becomes less negative or even neutral. Acid conditions will, therefore, make the NOM molecule more hydrophobic. Alkaline conditions favour dipole forces whilst in acid conditions the Van der Waal forces are dominating. This is the principle behind adsorption to the DAX-8 and XAD-4 resins but for the last resin, the IRA-958, NOM is adsorbed by ionic bonds (Jarvis, et al., 2010).

Washing of the resin or back elution of NOM is driven by the opposite mechanism. A solution with high pH is used which increases the polarity of the NOM molecule which becomes more hydrophilic. The dipole and hydrogen bonds formed with water will overcome the Van der Waal forces and the NOM species are desorbed from the resins (Jarvis, et al., 2010).

In this study, differences in DOC between the influent to the column and the effluent are used to estimate the adsorbed fraction. It should be noted that there are several studies using similar types of resins but with another type of analytic method. In these studies the adsorbed NOM is washed out and the structure and chemical characteristics of the adsorbed NOM are analysed.

In a study by Croué et al., (2003) the isolated fraction by XAD-8 was shown to have the highest C/H, C/O and C/N ratios and also the largest aromatic content of all fractions. The fraction isolated by the XAD-4 had a high content of polysaccharides whereas the neutral hydrophilic fraction, isolated by using a cation exchange resin, was mostly proteinaceous. According to Eikebrokk & Thorvaldsen (2010b), humic acids are adsorbed on DAX-8, fulvic acids on XAD-4 and proteins and amino acids are adsorbed to IRA-958. The material passing through all resins are the polysaccharides. Table 2 summarice what fractions and type of NOM that are separated when using the rapid farctionation method according to Eikebrokk & Thorvaldsen (2010b).

Table 2. Show the separated fractions of NOM by using the rapid fractionation method. In addition the type of resin used and pH is presented for each fraction. The expected type of NOM adsorbed according to Eikebrokk & Thorvaldsen (2010b) is also shown.

Fraction	Abbreviation	Adsorption	Type of NOM
Very hydrophobic acids	VHA	Adsorb to Superlite DAX-8 at a pH of 2	Humic acids
Slightly hydrophobic acids	SHA	Adsorb to Amberlite XAD-4 at a pH of 2	Fulvic acids
Charged hydrophilic material	CHA	Adsorb to Amberlite IRA-958 at a pH of 8	Proteins, amino acids
Neutral hydrophilic material	NEU	Does not adsorb to any of the resins.	Polysaccharides

Even though methods including adsorption to resins are widely used, there are some reported uncertainties with the method. According to Song, et al. (2009), some uncertainties related to the method are irreversible adsorption to resins, bleeding of resin material, size-exclusion effects and chemical reactions of NOM due to changes in pH during the fractionation procedure.

3.2   Separation of NOM fractions during drinking water treatment

Hydrophobic NOM and NOM with high MM is to a higher degree removed in the coagulation process compared to hydrophilic NOM with low MM (Matilainen, et al., 2010, Metsämuuronen, et al., 2014, Köhler & Lavonen, 2015 and Matilainen, et al., 2006).

Eikebrokk & Thorvaldsen (2010b) have used the rapid fractionation method to analyse fractions of NOM at two Norwegian DWTPs; one plant using coagulation followed by UV-disinfection and another with ozonation followed by biofiltration. For both DWTPs, the VHA and SHA were the dominating fractions in the raw water, around 85% of the total DOC concentration. VHA, SHA and CHA fractions were effectively separated during the coagulation process with 83%, 62% and 85% respectively whereas the NEU fractions were unaffected. The total reduction of DOC was for coagulation 72%. The UV treatment had no significant impact on the different fractions. In the ozonation process, the separation of all fractions was low and so also the total DOC reduction. It even turned out that the SHA, CHA and NEU fractions increased during treatment.

Transforming NOM with a hydrophobic character into NOM with a more hydrophilic character have also been reported form a pre-ozonation coagulation process (Matilainen, et al., 2010). Oxidation of NOM by ozone was shown to depend on the ozone dosage. Low ozone dosages transformed hydrophobic NOM to neutral and medium MM compounds of NOM which was

efficiently removed by the following coagulation step. But, on the other hand, at high ozone dosages the concentration of hydrophilic and NOM compounds with lower MM, which are more resistant to the coagulation process, increased.

It has been reported from several studies that the majority of NOM components removed by membrane filtration were aromatic and/or hydrophobic. Negatively charged membranes have been shown not only to remove NOM by size-exclusion but also charge repulsion, since NOM molecules smaller than the membrane cut-off value have been filtered out. It has, furthermore, been demonstrated that hydrophobic NOM has a higher removal potential in membranes due to charge-repulsion since these molecules have a higher charge density. Hydrophilic NOM with low MM is hard to remove by size or charge exclusion. Pre-coagulation followed by membrane filtration has been shown to enhance the performance of membrane filtration. For substantial removal of NOM with micro-filtration or UF this pre-treatment is required (Metsämuuronen, et al., 2014). Tighter membranes such as nano-filtration membranes have shown to have a successful remove of almost all fractions of NOM (Lidén, et al., 2015).

Activated carbon is widely used in drinking water treatment and especially to remove micro pollutants. In Finland, granular activated carbon filtration has been studied by Matilainen, et al. (2006). This water was initially pre-treated by coagulation. This filter was most successful in removing NOM with intermediate MM whereas NOM with high and low MM was not reduced any further. Removal of NOM with granular activated carbon might be at the expense of less micro pollutants adsorbed to the filter and the capacity of the filter is influenced by the regeneration of carbon (Matilainen, et al., 2010; Matilainen, et al., 2006)

4 Material and method

This section will start with a short introduction of the pilot project started at the DWTP Ringsjöverket. Then, in order to add some more background information a presentation of the two DWTPs, Ringsjöverket and Vombverket, will follow. In addition, some information about the two surface water sources used will be given. Where in the treatment process at Ringsjöverket water samples were taken will thereafter be specified. The experiment in the laboratory will also be introduced including the laboratory setup and the lab procedure. Finally, the calculations made and analytic methods used in this study will be described.

4.1 Pilot project- water from lake Bolmen to Vombverket

In order to secure reliable water supply and create redundancy in the system, Sydvatten has planned to construct a pipe transporting water from lake Bolmen to Vombverket. Today Vombverket uses lake Vomb as source water. The purpose of the ongoing pilot project is to investigate the opportunities to infiltrate the water from lake Bolmen in the existing infiltration ponds at Vombverket. Since the two lakes, lake Bolmen and lake Vomb, have different water qualities, particularly when it comes to organic matter, pre-treatment of Bolmen water is necessary. In the project, treatment methods such as coagulation and membrane filtration are investigated. An UF membrane pilot has been running since 2017 at Ringsjöverket. This in order to investigate whether membrane filtration of water from lake Bolmen is possible, where in the treatment process the UF will be best suited and what capacity this treatment method could have. The UF membrane is a hollow fibre membrane with a molecular weight cut-off of approximately 150 kDa and it has a pore size of approximately 20 nm.

In connection to the UF membrane pilot Sydvatten has also employed a sand filtration pilot containing sand and gravel taken from the infiltration ponds at Vombverket. Water from the UF pilot is infiltrated through the sand filter. This in order to see what happens with pre-treated water from lake Bolmen when it is filtered through sand from the infiltration ponds at Vomverket. Water from lake Bolmen and lake Vomb have large differences in alkalinity and hardness, see Table 3. There is a risk that the water after filtration will be corrosive and this need to be avoided. In order to resemble the filtration at Vombverket the water in the sand filter pilot has a retention time of 2-3 weeks.

4.2 Ringsjöverket

The DWTP Ringsjöverket is located in Stehag close to lake Ringsjön in Scania. Today, Ringsjöverket produces in average 1400 L/s in order to supply Eslöv, Helsingborg, Höganäs, Kävlinge, Landskrona, Lomma, Lund, Svalöv, Ängeholm and parts of Malmö and Staffanstorp with drinking water. The treatment plant has a maximum capacity of producing 2400 L/s (Sydvatten, 2018).

Ringsjöverket was commissioned in 1963 and in the beginning lake Ringsjön was used as raw water source. However, after deteriorating quality of the water in lake Ringsjön, raw water was delivered to Ringsjöverket from lake Bolmen. Water from lake Bolmen is transported in an 80 km long tunnel to Ringsjöverket. Today, lake Ringsjön is only used as a reserve water source (Sydvatten, 2018). Figure 2 shows the different treatment steps at Ringsjöverket.
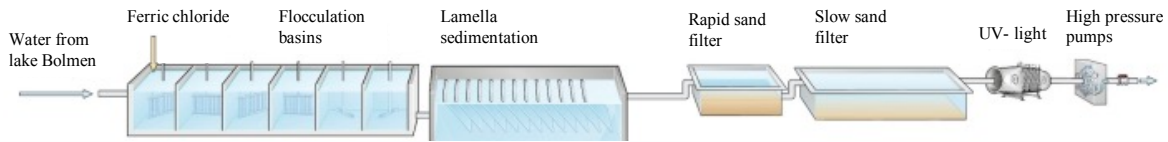
Figure 2. Drinking water treatment process at Ringsjöverket including screening, coagulation, flocculation, sedimentation, rapid and slow sand filtration, UV-treatment and disinfection. Published with permission from Sydvatten.

Before raw water enters Ringsjöverket it is filtered in micro screens (500 μm). The pH is adjusted with sodium hydroxide and then the coagulant ferric chloride is added before the water enters the flocculation basins. Here, the water is mixed in order to create desirable flocs. The water is thereafter entering the lamella sedimentation basins, where the flocs are separated. After sedimentation, pH is increased with lime, in order to get rid of iron residuals. Thereafter, the water is filtered through a rapid sand filter followed by a slow sand filter. Before the water enters the distribution system it is UV treated and disinfected with sodium hypochlorite (Lidén et al., 2015; Sydvatten, 2018).

4.3 Vombverket

Vomverket is located in Veberöd close to lake Vomb. Vombverket supplies drinking water to Burlöv, Malmö, Staffanstorp, Svedala, Vellinge and parts of Lund and Eslöv (Sydvatten, 2018).

Vombverket was commissioned in 1948 and since then water have been treated in infiltration ponds, trying to mimic the principle which occurs in nature when water is infiltrated in the ground and ends up as groundwater. However, from the beginning, infiltration was the only treatment needed, unlike today, when requirements are higher and several other treatment steps are necessary. Vombverket takes approximately 900 L/s from lake Vomb (Sydvatten, 2018). Figure 3 shows the treatment steps at Vombverket.
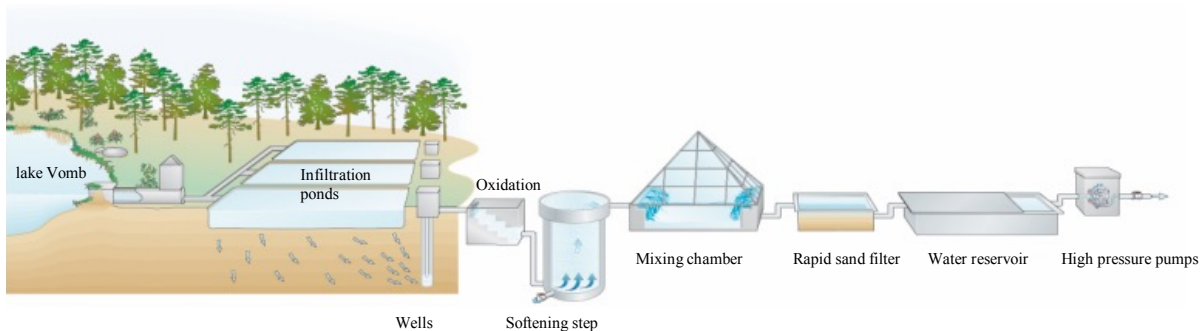
Figure 3. Drinking water treatment process at Vombverket including screening, infiltration ponds, oxidation, softening step, rapid sand filtration and disinfection. Published with permission from Sydvatten.

First, the water from lake Vomb is led in to micro screens before it is distributed over one of about 60 infiltration ponds. The water is infiltrated through sand and gravel layers in the ground, to finally end up in a natural groundwater reservoir. This artificially made groundwater is pumped up through one of the 114 wells to be oxidised in order to treat it from iron and manganese. Subsequently, the water is softened with sodium hydroxide and the dissolved lime is precipitated and removed. After the softening step the water is pumped into a mixing chamber where iron chloride is added. Small particles still remaining in the water is separated in the

subsequent rapid sand filter. Before the water is entering the distribution system, it is disinfected with monochloramine (Sydvatten, 2018).

4.4   Raw water sources

The two surface water sources used by Sydvatten for drinking water production are lake Bolmen and lake Vomb. In Table 3 some water quality parameters of these lakes are presented.

Table 3 Yearly mean values from 2016 of chemical parameters from the three lakes; Bolmen and Vomb. The values are taken from the production report of water quality made by Sydvatten (Sydvatten, 2016). Value marked with * is water from the Bolmen tunnel.

	Lake Bolmen	*Lake Vomb*
Colour [mg/l Pt]	61.7	23.8
COD_{Mn} [mg/l]	-	5.4
TOC [mg/l]	9.1	7.2
Hardness [ºdH]	1.2*	9.3
Alkalinity [mg/l]	14.3	152.9

A previous study done 2017 has shown that mean values of TOC, UV_{254} and colour of water from lake Bolmen are 7.8 mg/L, 0.29 cm^{-1} and 0.019 cm^{-1}, respectively (Söderman, 2017). As mentioned before, the MM of NOM has been shown to range from a few 100 Da up to 10 kDa. Measurements done by Söderman (2017) showed that NOM in water from lake Bolmen had a MM around 1-2 kD.

4.5   Water sampling

In this study water samples were taken at Ringsjöverket and transported to the Department of Chemical Engineering at four occasions; 12th and 19th of March and the 3rd and 10th of April. Figure 4 is a schematic picture of where in the treatment process at Ringsjöverket the samples, were taken. At the first two occasions water samples were taken of raw water (RW), sampling point 1 in Figure 4, of water after the UF membrane pilot (UMP), sampling point 4, and of water after the sand filtration pilot (SFP), sampling point 5. The last two occasions water samples were taken of RW, before the slow sand filters (SSF), sampling point 2, and after the SSF, sampling point 3. As could be seen in Figure 4, incoming water to the pilots, the UMP and the SFP, are taken in between the sedimentation and the rapid sand filtration.
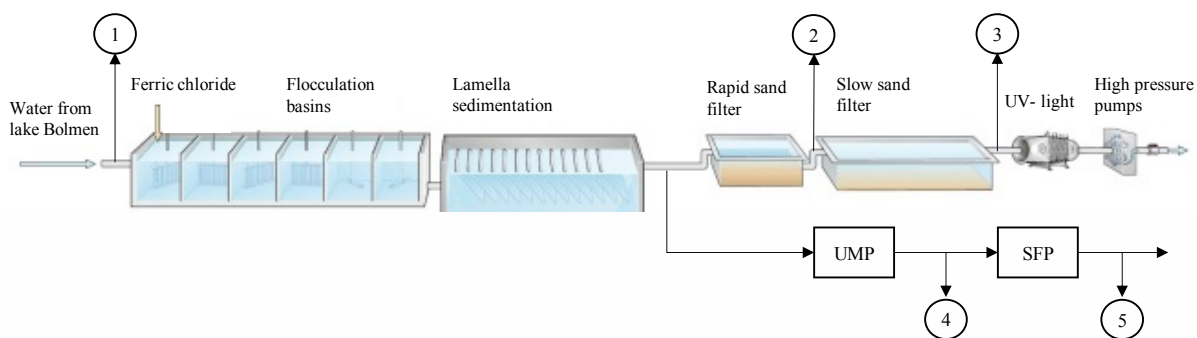
Figure 4. Scheme of sampling along the treatment process at Ringsjöverket, including the two pilots. Sampling points: 1. RW=raw water, 2. Before SSF=slow sand filtration, 3. After SSF, 4. Water after the ultra-filtration membrane pilot (UMP) and 5. after the sand filter pilot (SFP).

After the fractionation procedure and the following analysis the samples were stored for a few days in a cooling room at the department, maintaining a temperature of 6 ºC. Fractionated samples from the 3rd and the 10th of April was after fractionation and UV-analysis frozen for 10 and 22 days respectively before TOC and DOC analyses were performed.

4.6 Laboratory setup

The laboratory setup consists of glass columns packed with three types of different resins: Superlite DAX-8 (DAX), Amberlite XAD-4 (XAD) and Amberlite IRA-958 (IRA). There are six columns of each resin i.e. six columns with Superlite DAX-8, six columns with Amberlite XAD-4 and six columns with Amberlite IRA-958. This enables having duplicates of three types of water sample being fractionated at the same time. The bed volume, i.e. the volume of resin in each column, is 15 ml.

The pump used to pump water through the columns was ECOLINE VC-MS/CA8-6 from Ismatec. A potentiometric titrator from SI analytics, TitroLine 7000, was used to adjust the pH of the water samples. All waters were filtered before entering the columns with 0.45 μm polypropylene syringe filters. Filtering is applied to prevent particles from entering the column and clog the resins. The filters were, before mounted on top of the columns, rinsed with distilled (DI) water.

During the experiment, three different water samples was pumped from glass bottles through plastic tubes, through the filters and into the columns. The effluent from each column was captured in glass bottles. Figure 5 is a photo of the laboratory setup showing sample bottles, pump and the columns packed with resins.

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Figure 5. The laboratory setup when fractionating through the IRA columns. In the front: glass bottles with water samples, in this case from effluent from the previous XAD columns. In the middle: the pump that pumps water from the bottles to the IRA columns. In the back: the IRA columns and the effluent water that is collected in glass bottles.

4.7 Lab procedure

The following section will describe the lab procedure, including pre-cleaning of resins, fractionation, desorption and regeneration of resins.

4.7.1 Pre-cleaning

Pre-cleaning of resins is needed the first time the resins are used or when the resins are coloured or contaminated. During pre-cleaning, the resins are first washed with methanol (HPCL grade) during stirring for one hour. Thereafter, the same procedure is repeated for acetonitrile (HPCL grade) and, lastly, with DIwater before the resins are transferred back to the columns.

4.7.2 Fractionation

During the fractionation procedure, three types of water samples are fractionated at the same time and of each sample, double samples are made. Each fractionation of 1000 ml water samples therefore results in six fractionated samples of 500 ml. Before the samples are filtered through the first column, DAX, the pH of the samples is adjusted to 2 with 2M HCl. Thereafter, the water samples are pumped through the DAX columns at a rate of 3 ml/min. The first two bed volumes, i.e. 30 ml, are discarded. Samples of 100 ml of the DAX effluents are collected for DOC and UV analysis. The remaining 370 ml is, subsequently, filtered through the second column, XAD, following the same procedure as for the DAX column.

The remaining sample volume from the XAD effluent, 240 ml, is first adjusted to a pH of approximately 6 with 2M NaOH and thereafter increased to a pH of 8 with 0.1M NaOH by using the titrator. Then water is pumped through the third column, IRA, following the same procedure as for the previous columns. In Figure 6 the fractionation procedure for one water sample, including all three types of columns, is illustrated.
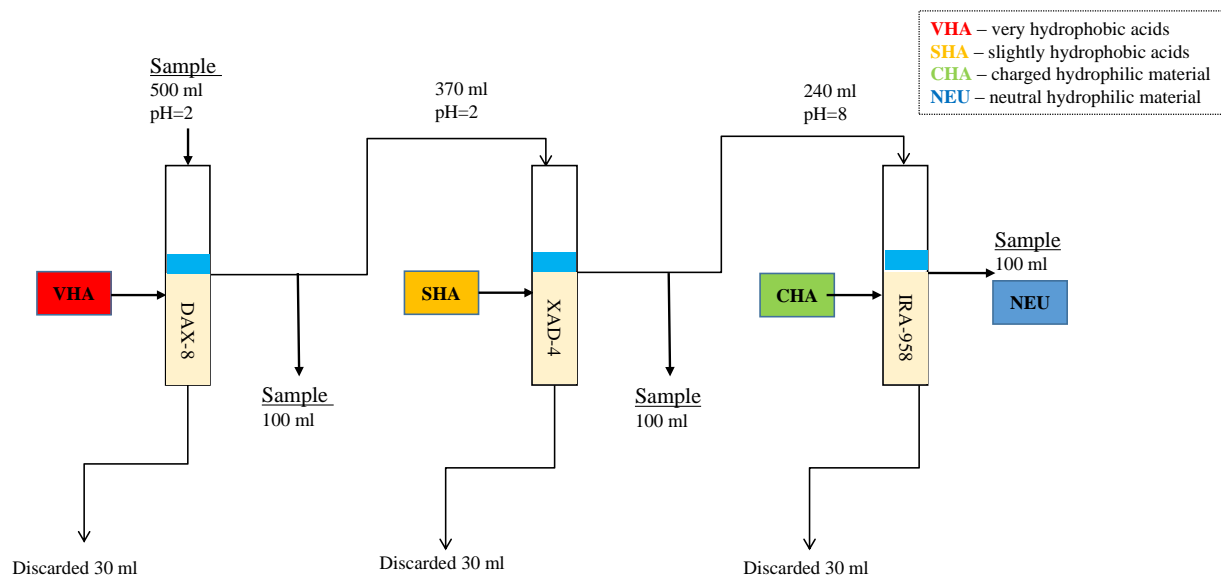
Figure 6. Illustrative picture on the fractionation procedure of one water sample. 500 ml of the water sample with a pH of 2 is pumped through the DAX column and thereafter the XAD column. Before the water sample is pumped through the IRA column pH is increased to 8. The first 30 ml from the effluent from each column is discarded and after each fractionation, 100 ml samples are taken.

4.7.3 Desorption and regeneration

All three resins must after fractionation or pre-cleaning undergo desorption and regeneration. For desorption of DAX and XAD resins, 60 ml (four bed volumes) of 0.1M NaOH is pumped through the columns at a rate of 3 ml/min. After desorption, these columns are rinsed with DI water to prevent formation of salt. For regeneration of DAX and XAD, 60 ml of 0.1M HCl is pumped through the columns at a rate of 3 ml/min.

Desorption and regeneration of the IRA resin follows the same procedure as for DAX and XAD but with different solutions. For desorption, a solution of 1M NaOH and 1M NaCl is used and for regeneration, a solution of 1M HCl and 1M NaCl is used.

4.8 Calculations

After DOC analysis of all samples was done, calculations of the different fractions of NOM was made. Each fraction of NOM was obtained by subtracting the measured DOC concentration in the effluent from the DOC concentration in the influent. The following equations were used to calculate fractions of NOM (mg DOC/L):

$$VHA = DOC_{\text{filtered water}} - DOC_{\text{effluent DAX}} \qquad (1)$$

$$SHA = DOC_{\text{effluent DAX}} - DOC_{\text{effluent XAD}} \qquad (2)$$

$$CHA = DOC_{\text{effluent XAD}} - DOC_{\text{effluent IRA}} \qquad (3)$$

$$NEU = DOC_{\text{effluent IRA}} \qquad (4)$$

4.9 Analytical methods

In this section, methods used to analyse the water before and after the fractionation are presented.

4.9.1 TOC and DOC

TOC is the sum of the DOC and the particulate organic carbon in a sample after inorganic carbon have been removed. DOC is the content of organic carbon after the water has been filtered through a 0.45 μm filter. Since all water samples in this study are filtered prior to fractionation the actual result from the TOC analysis is DOC. Earlier studies by Köhler and Lavonen (2015) have shown good correlation between DOC and TOC. The production report from Sydvatten (2015) confirms that this is the case also in analysed water from Lake Bolmen. It is, therefore, assumed that the NOM lost in the filters is negligible. However, measurements on unfiltered samples were also performed but the calculations of the different fractions need to be performed with values of DOC, see equations 1-4 in section 4.8.

TOC measurements at the department were done by using a Total Organic Carbon Analyser model TOC-5050A and an auto sampler model ASI-5000A, both from Shimadzu. TOC measurements at Ringsjöverket were preformed by using a TOC analyser from Shimadzu model TOC-L CPH/CPN.

4.9.2 UV$_{254}$

The recommended wavelengths used when measuring NOM is 220-280 nm and within this range, it is expected that different structures of NOM will absorb UV-light. Absorbance at 254 nm is related to absorbance by NOM with aromatic structures (Sillanpää, 2014). Measurements of UV$_{254}$ were performed by using a spectrophotometer, namely the UV-VIS-spectrophotometer Hach Lange DR6000. UV measurements were executed in a 5 cm x 1cm^2 quarts cyvett. The spectrophotometer was calibrated before use with DI water. The samples were analysed once and at room temperature.

4.9.3 Colour

Measurements of colour were performed with a spectrophotometer at 436 nm. This analysis method of colour is also used by Sydvatten. The same spectrophotometer and method as for measurements of UV$_{254}$, a Hach Lange DR6000, were used.

5 Results and discussion

In this chapter, the results from the experiment and a discussion about its outcome is presented. First values of TOC, DOC, UV_{254} and colour of unfractionated water samples is presented followed by the results from the fractionation. Detailed information and values from the experiments can be found in the Appendix I-IV. Some figures are also present in the Appendix illustrating these detailed values obtained from the fractionation. Moreover, this chapter will include a discussion about the possible sources of errors in this study.

5.1 Water quality analysis

Measured values of TOC, DOC, UV_{254}, colour and SUVA of unfractionated water samples are presented in Table 4.

Table 4. Mean values including standard deviations of water quality parameters and SUVA values on raw water, before and after slow sand filters (SSF), after ultra-filtration membrane pilot (UMP) and after sand filter pilot (SFP). On outgoing water from Ringsjöverket TOC analysis was made once. For detailed values, see Appendix I-IV.

	TOC (mg/L)	DOC (mg/l)	UV_{254} (m^{-1})	Colour (m^{-1})	SUVA (L/mg*m)
Raw water	11.4 ± 0.54	11 ± 0.11	42 ± 0.46	2.9 ± 0.18	3.7
Before SSF	2.9 ± 0.0075	3.0 ± 0.03	4.5 ± 0.15	0.08 ± 0.02	1.5
After SSF	2.7 ± 0.011	2.8 ± 0.17	4.7 ± 0.32	0.23 ± 0.13	1.6
After UMP	4.2 ± 0.28	3.6 ± 0.28	4.9 ± 0.04	0.13 ± 0.03	1.3
After SFP	5.4 ± 0.025	5.2 ± 0.0015	7.5 ± 0.01	0.28 ± 0.02	1.4
Outgoing water	2.8				

The raw water during this study period had higher values in TOC, UV_{254} and colour compared to in the study by Söderman (2017). However, because of the varying UV_{254} absorbance according to Figure 4, section 3.2, of water from lake Bolmen, higher values on raw water were expected.

TOC and DOC values are reduced by approximately 80% and 70% respectively after coagulation with sedimentation followed by rapid sand filtration, see Table 4. This reduction was expected, since coagulated water with SUVA values around 4 has been reported having a coagulation efficiency of at least 50%. For ferric based coagulants the reduction is reported to be even higher (Edzwald & Tobiason, 1999). Before the SSF, the SUVA value had decreased considerably, from 3.7 in the raw water to 1.5. This indicates that mainly aromatic and/or hydrophobic NOM are separated during chemical precipitation at Ringsjöverket (Matilainen, et al., 2011). Exactly how much TOC is reduced in this process and in the UMP is hard to tell, since no measures were done on water directly after the sedimentation. However, after the UMP the

water has higher TOC and DOC values compared to before the SSF. This imply that the rapid sand filters first of all removes NOM and secondly in a better way than the UMP. The removal of NOM by the SSF are somewhat uncertain. TOC and COD is reduced at the same time as the UV_{254} and colour is increased. It is also worth noting from Table 4 that all measured water quality parameters increase when water passes through the SFP. This may be an indication that the pilot is leaking. Since UV_{254} values increases more than DOC, it is probably aromatic and more hydrophobic NOM that is leaking from the SFP.

TOC analysis was performed on clean outgoing water from Ringsjöverket once. As Table 4 shows, NOM measured as TOC is not changed after the SSF. This means that the concentration of NOM is stable throughout the rest of the treatment processes, including UV treatment and disinfection.

As mentioned in section 4.9.1, previous studies of water from lake Bolmen show no significant difference in TOC and DOC values. Figure 7 show how the TOC and DOC values of raw water differed during this study period.
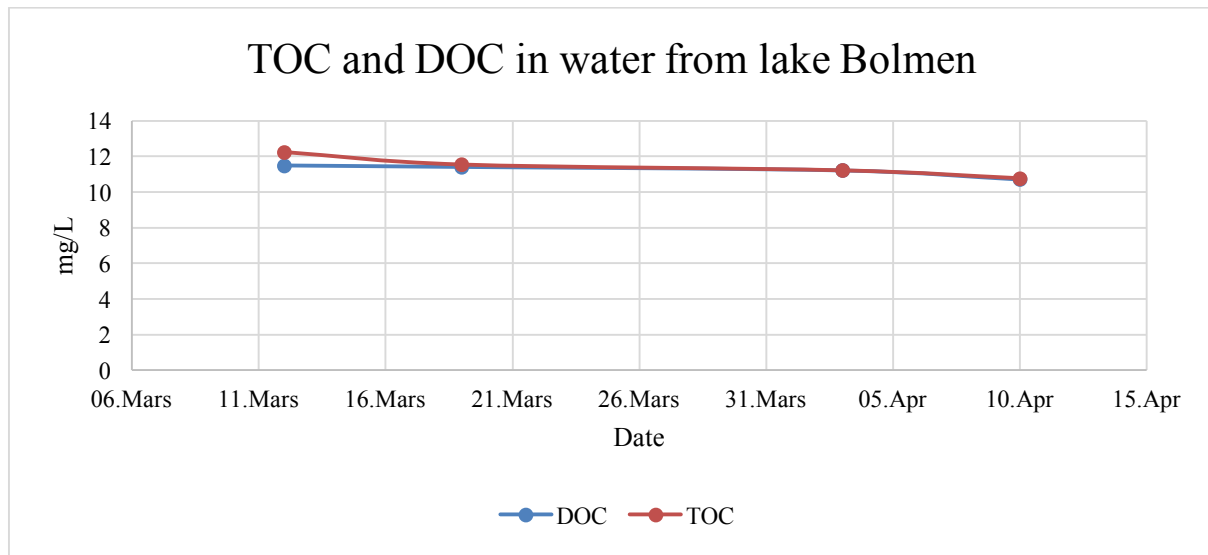
Figure 7. Values of TOC and DOC in the incoming water to Ringsjöverket, from lake Bolmen, during the study period.

As Figure 7 illustrates, there is no significant difference between TOC and DOC in raw water except from in the beginning of the study where small differences were noticed. This indicates that the raw water already before entering the treatment plant, has low content of particulate carbon. The assumption made in section 4.9.1, that there are no significant amount of NOM trapped in the filters, therefore appears reasonable.

5.2 Results from fractionation

The whole fractionation procedure was performed at four occasions with different water samples. After DOC analysis of fractionated water samples equation 1-4, section 4.8, where used to calculate the fractions VHA, SHA, CHA and NEU. During the first fractionation of water samples taken the 12th of March, a mistake was made. The pH was increased to 8 between

fractionation in DAX and fractionation in XAD instead of after fractionation in XAD. Therefore, the analytic results obtained after the fractionation in XAD are not included in the presented result.

The result from the fractionation is presented in Figure 8. This figure illustrates how the different fractions are distributed in the different types of water samples. Figure 8 also show how the fractions are separated during different treatment steps at Ringsjöverket.

Fractionation of water from Ringsjöverket

	RW	before SSF	after SSF	after UMP	after SFP
◼ sum DOC	11,30	2,95	2,84	3,63	5,23
◼ VHA	8,22	1,48	1,43	2,27	3,70
◼ SHA	1,39	0,63	0,57	0,17	0,30
◼ CHA	0,62	0,04	0,11	0,50	0,54
◼ NEU	0,78	0,76	0,67	0,42	0,40

Figure 8. Results from fractionation of water samples from Ringsjöverket. Mean values and standard deviations are presented. DOC concentrations in unfractionated water samples (sum DOC) and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW = raw water, SSF = before and after slow sand filtration, UMP = water after ultramembrane pilot and SFP = water after sand filtration pilot.

The largest fraction of NOM in the raw water is the VHA, and together with the other hydrophobic fraction, the SHA, it accounts for 85% of all NOM in the raw water. Throughout the whole study period there were no large fluctuations neither of the quantity of NOM, see Table 4, nor the different fractions of NOM in the raw water, see error bars in Figure 8. As shown earlier, in Figure 1, water from lake Bolmen has the past years, seen large fluctuations in UV_{254} absorbance. These fluctuations is an indication of that the concentration of NOM is fluctuating and so especially the hydrophobic fractions. In this study these fluctuations were not observed. This is probably because the time period of this study was too short and there were no large rain events during this period. The remaining hydrophilic fractions, the CHA and the NEU, accounts for 6 and 7% of the total DOC content in the raw water, respectively.

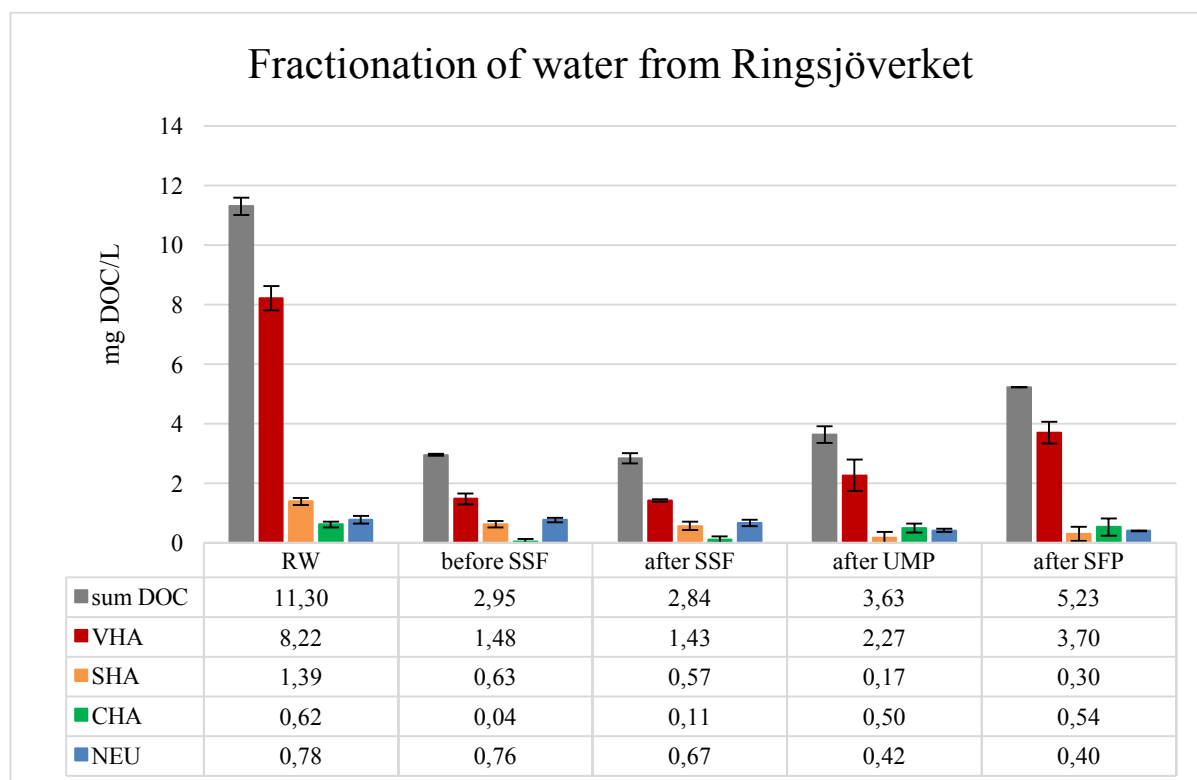Figure 9 illustrates how large each fraction is and how it is changing throughout the treatment process.
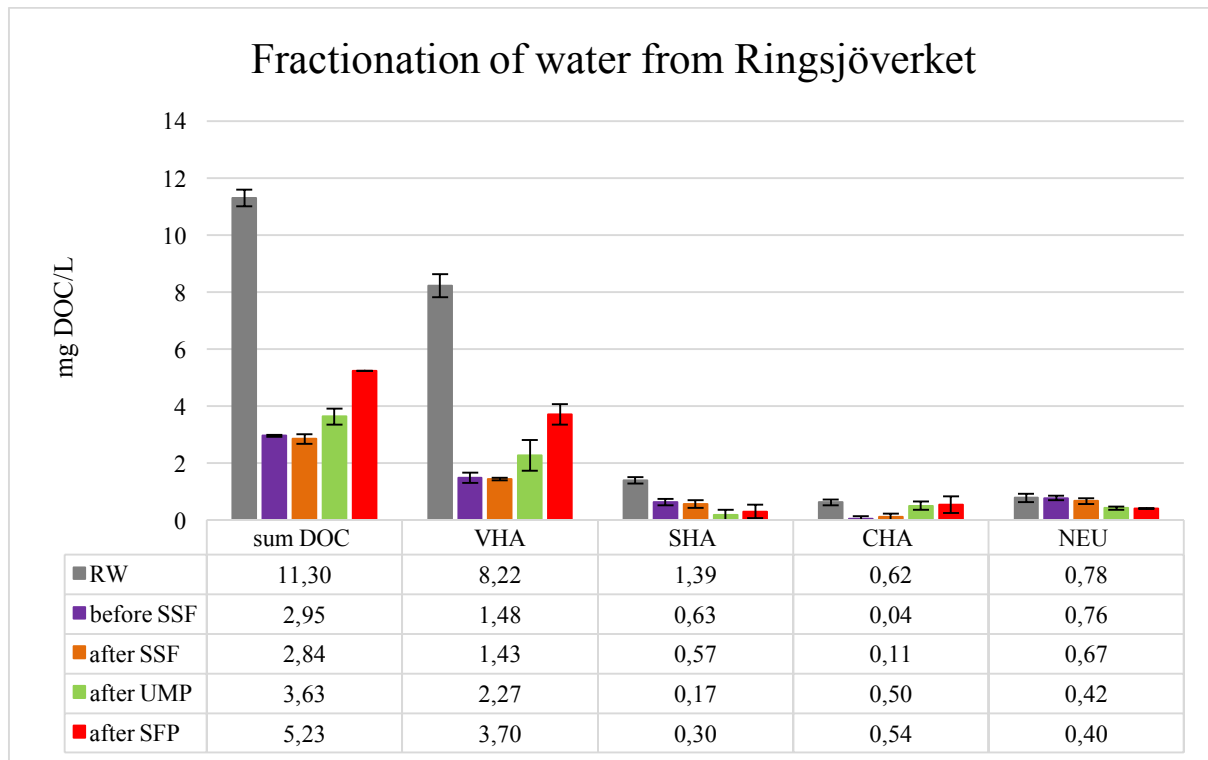
Figure 9. Results from fractionation of water samples from Ringsjöverket. Mean values and standard deviations are presented. DOC concentrations in unfractionated water samples (sum DOC) and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW= raw water, SSF= before and after slow sand filtration, UMP= water after ultra-membrane pilot and SFP= water after sand filtration pilot.

According to these results, the majority of the VHA and CHA are removed during the coagulation, sedimentation and rapid sand filtration processes. This is similar to the reductions reported by Eikebrokk & Thorvaldsen (2010b). The VHA are reduced in average with 82%, SHA with 57% and CHA with 93% and NEU were not reduced at all, see Figure 9. Nevertheless, since the amount of NEU is low in the raw water, the overall DOC removal by coagulation, sedimentation and rapid sand filtration still becomes as high as 74%. Similar DOC reductions, 72%, have also been reported by Lavonen (2015) at Ringsjöverket.

Similar as the water quality parameters in Table 4, all fractions of NOM seem to be more or less unaffected when passing through the slow sand filters, see Figure 8. Previous studies also show that the reduction of DOM in the slow sand filters at Ringsjöverket is low (Lavonen, 2015). However, Lavonen, et al. (2015) have reported that DOC removed by slow sand filters is of an autochthonous origin. NOM with autochthonous origin is believed to be coupled to the hydriphilic fractions, CHA and NEU. In this study, almost all CHA was separated before the SSF, see Figure 9, and no further reduction was seen after the SSF. Neither can any significant reduction of NEU be seen, see Figure 9. The NOM in the water at Ringsjöverket have a hydrophobic character and high SUVA values. NOM with these characteristics may not be suitable carbon substrate for the microorgansims in the SSFs and this can maybe explain the low reduction of DOC in this treatment step.

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The MM of the NOM in the raw water is expected to be around 1-2kD, (Söderman, 2017). With respect to MM the expected separation of NOM by the UMP, which have a cut-off value of 150kD, is therefore low. However, as reported by Metsämuuronen et al. (2014) pre-treatment with coagulation will enhance removal of NOM by UF membranes. Suspended flocs large enough will probably therefore be trapped in the UMP. The UMP can in this way, similar to the rapid sand filter, act as a polishing step after chemical precipitation. However, this study can not specifically show what fractions the UMP separate. Despite this, a comparison between the two processes coagulation/sedimentation/ultra-filtration and coagulation/sedimentation/rapid sand filtration can be made.

Removal of NOM by coagulation/sedimentation/rapid sand filtration are as mentioned 74% and in the process coagulation/sedimentation/ultra-filtration the removal of NOM is lower, namely 68%. When looking at the different fractions, in Figure 8 the coagulation/sedimentation/rapid sand filtration process seems to remove more of the VHA and CHA fractions. Coagulation with sedimentation followed by the UMP, on the other hand, seems to have a better removal of SHA and NEU. To find an explanation for this result is hard, since the expected removal efficiency was supposed to be similar for the two processes. However, the differences do not seem to be related to hydrophobicity.

The NEU fraction of NOM, which is unaffected in all other treatment processes, is reduced with almost 50% in the UMP. NOM and especially the hydrophilic fraction is not, in this type of membrane, expected to be removed by either size exclusion or charge repulsion (Sillanpää, et al., 2015). Larger floccs where NEU are adsorbed on the coagulant are possible (Matilainen & Sillanpää, 2015), but not expected since this fraction was not separated during coagulation and sedimentation. To be able to answer these unexpected results more research and fractionation is needed. More fractionation is needed to see if these results are valid over time or if there are external factors effecting the result, i.e. how the UMP is operated etc. More analysis including a reliable analytic method of the water from the UMP is also needed. This in order to reduce the standard deviations, which for some fractions of water from the UMP are large, see Figure 8. In addition, fractionation of water after sedimentation could also contribute to a better understanding of what fractions that actually are separated by the membrane and the rapid sand filter.

The SHA and the hydrophilic factions, CHA and NEU, seem to be unaffected when passing through the SFP, see Figure 8. However, all water quality parameters presented in Table 4 are increased during filtration in the SFP. As shown in Figure 9, the VHA seem to be responsible for this increase. This means that the SFP is leaking NOM and more specifically VHA. As mentioned before, in section 3.1.2, the sand filter pilot is filled with sand transported from the infiltration ponds at Vombverket. At Vombverket untreated water with a TOC value of around 7 mg/L is infiltrated in the ponds. When the artificial groundwater is pumped up it has a TOC value of 3 mg/L, i.e. a TOC reduction of 4 mg/L is obtained in the infiltration ponds. Compared to the inflowing water to the SFP, which has a TOC content of 4.2 mg/L, the sand in the ponds is used to an inflow of water with higher TOC concentration. Therefore, leaching may be an indication of that the microorganisms and the biofilm are stressed due to the new conditions prevailing in the pilot. This could lead to loss of biofilm from the SFP. If this is the case, it would be interesting to know how long it takes for the sand to adapt and when this happens see what fractions of NOM that can be separated. If fractionation of water from lake Vomb and of infiltrated water at Vombverket, is performed this could give a hint of what to expect when it comes to separation of NOM in infiltrated water from lake Bolmen.

The DOC values obtained in fractionated water after the UMP and the SFP have, as already mentioned, generally larger standard deviations compare to the other fractionated water samples, see Figure 8. The potential cause of this is further discussed in section 5.3. At these low DOC concentrations the obtained standard deviations are considered as too large. Therefore, additional fractionation of this water is needed.

5.3 Sources of error

In this study there are a few sources of errors which potentially could have affected the results. First of all, when DOC analysis was performed on fractionated samples taken the 3rd of April it was noticed that the obtained DOC values differed significantly when comparing results between the double samples. This difference could for example be due to different conditions during the fractionation, contamination of sample or problems with the TOC analyser used. In order to be sure that the TOC analyser during the analysis did not contaminate from one sample to another, samples with DI water were analysed periodically between water samples. This showed, that DOC values of DI water ranged from 0.5 to 2.5 mg/L. This broad range was concluded as unacceptable when analysing water samples with expected DOC values ranging from 0.1 -12 mg/L. Because of this, it could not be excluded that the TOC analyser contaminated the samples and, therefore, analysis of these water samples was performed with a TOC analyser at Ringsjöverket, see Appendix III. Analysis of MilliQ water in between water samples at Ringsjöverket was in an acceptable range, from 0.06 to 0.16 mg/L. From here analytic results performed at Ringsjöverket were used. Since this problem was not discovered until after the analysis of fractionated water samples from the UMP and the SFP, these results are probably more uncertain. As mentioned, this is also reflected in the standard deviations of different fractions in Figure 8, which generally are larger for fractions within water from the UMP and SFP.

Even if the TOC-analyser used at Ringsjöverket seem to give reasonable and reliable results analysis of extremely low concentration of TOC is always problematic and less reliable compared to analysis at higher TOC concentrations. Water samples as clean as the ones obtained during fractionation in this study are also sensitive to contamination. Contamination during storage in glass bottles or during transferring samples from one place to another can not be excluded. In order to avoid contamination freshly made solutions for desorption, regeneration and pH adjustment were always used. To minimize dilution of samples during pH adjustment concentrated solutions where as far as possible used.

As mentioned before, there are some reported uncertainties related to the fractionation method (Song, et al., 2009). To a great extent, these can be avoided by performing the fractionation procedure correctly. However, in the beginning the method is somewhat complicated to perform but with experience problematic situations can be avoided and emerging problems can be handled in a better way. Some of the situations that occurred during this study are listed below.

- Fractionation finished earlier and later than intended.
- Water leaching from the filters on top of the columns as a result of clogged filters.
- Air leaking into the columns from lids, resulting in higher flow rates and lowering of water level in the column.
- Air bubbles in the plastic tubes leading into the columns.

The situations listed above are related to each other and they could potentially have influenced the result. If, for example, there is a problem with one column and NOM is not adsorbed as

expected, this could result in an under and over estimation of fractions. This since all fractions, because of the calculations, see section 4.8, depend on each other. To avoid these problems the equipment, including sample bottles, pump, plastic pipes, filters, lids, connections and the water level in the columns, must be under supervision during the fractionation procedure. In case of, for example, falling water levels, actions can thereby quickly be taken and disturbance of the resins avoided. Faster or slower flow rates are almost always related to air entering the column, or clogged filters. This can be avoided by always using air tight lids and connections and by changing the filters regularly, before they are clogged.

If pH is decreased or increased too much, there is a risk of precipitation of NOM. This was experienced on water samples collected the 12th of March. In this case, the results were not affected, because the pH was increased at the wrong time and hence the result from this fractionation was not used. However, if this happen, during pH adjustment the precipitated NOM could be trapped in the filter and as a result less NOM will be fractionated.

Until the analysis were made waters samples were stored in a cooling room for a maximum of 3 days. This since all samples were planned to be analysed during the same day. Some of the water samples were also freezed before TOC analysis at Ringsjöverket. Preferably, analysis of water samples should be performed as soon as possible. Therefore, there is a risk of that the result has been affected.

Another potential source of error is inadequate desorption of NOM from the resins. Resins in contact with raw water were the ones which appeared most affected after fractionation. After fractionation these resins got a brown colour. This was, however, expected, since the raw water has a more intense colour than all other water samples taken. The colour did not disappear after desorption and regeneration and because of this the DAX resins where, after fractionation, substituted with new and washed DAX resins. However, it cannot be ruled out that the other resins, with no visible discolouration, also after desorption and regeneration still was contaminated. This could potentially have affected the result of the following fractionation.

6 Conclusion

During this study period, incoming water to Ringsjöverket from lake Bolmen had a clear hydrophobic character. The hydrophobic fractions, very hydrophobic acids (VHA) and slightly hydrophobic acids (SHA), were effectively separated during the chemical precipitation process followed by the rapid sand filtration. The hydrophilic fractions, which are less abundant in water from lake Bolmen, were in this process separated to different degrees. Almost all charged hydrophilic material (CHA) was separated whereas the neutral hydrophilic material (NEU) was unaffected. The slow sand filters at Ringsjöverket showed no ability in removing any of the fractions of NOM. TOC measurement on clean outgoing water from Ringsjöverket showed that values of TOC, after the slow sand filters, UV-treatment and disinfection, are not changed. It can, however, not be precluded that the distribution of different fractions of NOM has changed when water reaches the distribution system.

Chemical precipitation followed by treatment in ultra-filtration membranes, appear in this study to be less efficient in separating NOM compared to chemical precipitation followed by rapid sand filtration. The NEU fraction of NOM, which is unaffected during all other treatment processes, seems to be separated well in the UMP. This study shows that the SFP is leaching NOM and, more specifically, the VHA. However, because of uncertainties related to the results from the UMP and the SFP, further studies based on fractionation of these waters are needed.

With the introduction of water from lake Bolmen at Vombverket in mind, this study shows that chemical precipitation of water from lake Bolmen is efficient, and therefore probably also a prerequisite before further treatment. Even though differences exist between rapid sand filtration and membrane filtration, it is expected that these methods have similar capacity. Introducing an ultra-filtration membrane in the pre-treatment of water from lake Bolmen is therefore considered as an option. However, more research is necessary in the future in order to uncover how pre-treated water from lake Bolmen will be affected when infiltrated in the infiltration ponds at Vombverket.

This study has shown that the rapid fractionation method can give a deeper understanding of the characteristics of NOM in raw water and how NOM is separated in the treatment process. The results may, therefore, be useful for future evaluation of treatment methods and as a comparison for future fractionation.

7 Future work

The objective of this study have been to investigate what fractions of NOM the water at Ringsjöverket contains and where in the treatment process different fractions separate. In general, the results appear reasonable and useful. There are, however, some uncertainties related to the results. To avoid some of these uncertainties during future fractionation, it is important to evaluate the performance of the TOC and DOC analyser used. In addition, fractionation of water after sedimentation would be useful, in order to, more in detail, be able to see the differences and similarities between the rapid sand filter process and the UMP. Fractionation of water from lake Vomb and infiltrated water at Vombverket could potentially give a hint of what type of fractions that can be expected to be removed during infiltration.

Since UV_{254} absorbance of water from lake Bolmen have been fluctuating considerably the past twenty years, it is reasonable to believe that also the distribution of different fractions are fluctuating; especially the hydrophobic fractions. However, in this study, larger fluctuations in raw water have not been detected. It will, therefore, be interesting to investigate this further in the future, to see if and how fractions in water from lake Bolmen change with TOC and UV absorbance. In order to cover the fluctuations, fractionation of raw water should be performed regularly during a longer time period. Two of the reported causes to increased NOM concentrations in surface waters have been increased runoff from soil and higher flows in streams as a result of more intense rain events. It will also be interesting to see if higher flows in incoming streams to lake Bolmen can be related to higher NOM concentrations in raw water at Ringsjöverket.

Chemical precipitation is an efficient treatment method for separation of NOM, which has also been shown in this study. The drawback with this method is the increased production of sludge, which is an additional cost for DWTPs. Combining coagulation and membrane filtration has the potential to reduce sludge production since less chemicals have been reported to be needed (Lidén, et al., 2015). It will, therefore, be interesting to investigate how the separation of different fractions of NOM during coagulation depends on the chemical dosage and on, for example, pH. In addition, coagulated water could with or without sedimentation be filtrated trough different types of membranes. In this way, it could be investigated if it is possible to decrease the dosage of chemicals but still have acceptable DOC reductions when coagulation and membrane filtration are combined.

8 Populärvetenskaplig sammanfattning

Under de senaste årtiondena har det i norra Europa och Nordamerika rapporterats om att sjöar och vattendrag blir allt brunare. Den bruna färgen kommer från naturligt organiskt material (NOM), vilket är material från döda djur och växtdelar, som transporterats med vattnet från intilliggande skog och mark. Denna "brunifiering", som den också kallas, tros bland annat kunna vara ett resultat av de pågående klimatförändringarna och av minskad försurning av mark och vattendrag. Även om detta inte är något gemeneman observerat, så orsakar det ändå problem. Sydvatten, som är en utav Sveriges största dricksvattenproducent, har i många år sett att deras råvattenkälla, sjön Bolmen, stundtals blivit allt brunare. Detta har ökat belastningen på de processer som renar vattnet på Ringsjöverket. NOM kan orsaka att dricksvattnet får en oönskad färg, lukt och smak. NOM används också som näringskälla för mikroorganismer och detta kan främja tillväxten av mikroorganismer i ledningsnätet och på så sätt orsaka hygieniska problem. NOM kan också orsaka att cancerframkallande biprodukter bildas vid klorering av vattnet. Höga koncentrationer av NOM kan också minska effektiviteten av UV behandlingen av vattnet. Som en konsekvens av allt högre NOM koncentrationer har man på Ringsjöverket till exempel, för att kunna leverera ett rent vatten till konsumenterna, blivit tvungen öka sin dosering av fällningskemikalie.

Sydvatten planerar att börja leverera och rena vatten från Bolmen till deras andra dricksvattenverk, Vombverket. För att kunna göra det behöver en förlängning av Bolmentunneln byggas och ytterligare reningsprocesser vid Vombverket installeras. För att undersöka detta närmare har Sydvatten startat två testanläggningar på Ringsjöverket, en ultra-filtrerings membran och ett infiltrationssandfilter. Allt detta för att kunna undersöka vilken typ av rening man i framtiden behöver för att rena vatten från Bolmen på Vombverket. Data på vattenkvalitet från Bolmen visar ingen direkt indikation på att NOM koncentrationerna kommer minska i framtiden. Därför är det viktigt att de reningsmetoder man väljer att använda sig av är driftsäkra och effektiva när det kommer till avskiljning av NOM.

I detta examensarbete, vilket är ett samarbete mellan Sydvatten och Institutionen för kemiteknik på Lunds universitet, har det organiska materialet i vattnet från Ringsjöverket närmare studerats. En metod som kallas snabbfraktionering har används för att dela upp det lösta organiska materialet i fyra fraktioner baserat på dess hydrofila och hydrofoba karaktär. Det finns ett antal snabbare och enklare metoder för att mäta hur mycket NOM vatten innehåller men genom snabbfraktionering kan man mer i detalj ta reda på vilka olika typer av NOM som finns i vattnet.

I denna rapport presenteras resultatet från den snabbfraktionering som utfördes på vatten från Ringsjöverket. Snabbfraktioneringen av vattnet har bidragit med kunskap om vilken karaktär råvattnet har och hur de olika reningsprocesserna påverkar olika typer av NOM på Ringsjöverket. Resultatet av denna studie hoppas kunna användas för att på ett bättre sätt kunna utvärdera nuvarande och framtida reningsprocesser.

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Appendix I

In this Appendix I data on measurements performed on water collected the 12th of March are presented.

Table I-1. Analytic results of fractionated water samples collected the 12th of March at Ringsjöverket. Concentration of dissolved organic carbon (DOC) and ultraviolet absorption at 254 nm (UV$_{254}$) and 436 nm (UV$_{436}$). Type of column: DAX= column packed with Superlite DAX-8 resins, XAD= column packed with Amberlite XAd-4 resins and IRA= column packed with Amberlite IRA-958 resins. Sampling points: raw water (RW), after ultra-membrane pilot (UMP) and after sand filter pilot (SFP).

Date yyyy-mm-dd	Type of column	UV$_{254}$ (1/m)	UV$_{436}$ (1/m)	DOC (mg/l)
	DAX 1 RW 1	5.82	0.14	3.54
	DAX 2 RW 2	5.62	0.14	3.23
	DAX 3 UMP 1	1.4	0.04	2.81
	DAX 4 UMP 2	1.36	0.06	1.50
	DAX 5 SFP 1	2.22	0.04	1.78
	DAX 6 SFP 2	2.2	0.04	2.07
	XAD 1 RW 1	3.82	0.06	2.57
	XAD 2 RW 2	3.8	0.08	1.97
2018-03-12	XAD 3 UMP 1	1.16	0.02	1.00
	XAD 4 UMP 2	1.1	0.02	0.85
	XAD 5 SFP 1	1.38	0.02	1.12
	XAD 6 SFP 2	1.44	0.02	1.20
	IRA 1 RW 1	0.38	0	0.60
	IRA 2 RW 2	0.5	0	0.26
	IRA 3 UMP 1	0.44	0	0.16
	IRA 4 UMP 2	0.36	0	0.14
	IRA 5 SFP 1	0.46	0.04	0.28
	IRA 6 SFP 2	0.36	0.02	0.14

Table I-2. Analytic results from fractionation of water collected the 12th of March at Ringsjöverket. Sampling points: raw water (RW), after ultra-membrane pilot (UMP) and after sand filter pilot (SFP).

Sample point	Date yyyy-mm-dd	TOC (mg/L)	UV$_{254}$ (1/m)	UV$_{436}$ (1/m)	DOC (mg/L) Total	#	VHA	SHA	CHA	NEU	SUVA (L/mg*m)
RW	2018-03-12	12.24	42.06	2.8	11.47	1	7.93	0.968	1.971	0.601	3.7
						2	8.245	1.251	1.71	0.264	
UMP	2018-03-12	4.435	4.82	0.16	3.913	1	1.103	1.807	0.847	0.156	1.2
						2	2.416	0.65	0.708	0.139	
SFP	2018-03-12	5.35	7.48	0.3	5.23	1	3.451	0.655	0.849	0.275	1.4
						2	3.156	0.871	1.061	0.142	

	VHA	SHA	CHA	NEU	Sum DOC
■ RW 1	7,93	0,968	1,971	0,601	11,47
■ RW 2	8,245	1,251	1,71	0,264	11,47
■ UMP 1	1,103	1,807	0,847	0,156	3,913
■ UMP 2	2,416	0,65	0,708	0,139	3,913
■ SFP 1	3,451	0,655	0,849	0,275	5,23
■ SFP 2	3,156	0,871	1,061	0,142	5,23
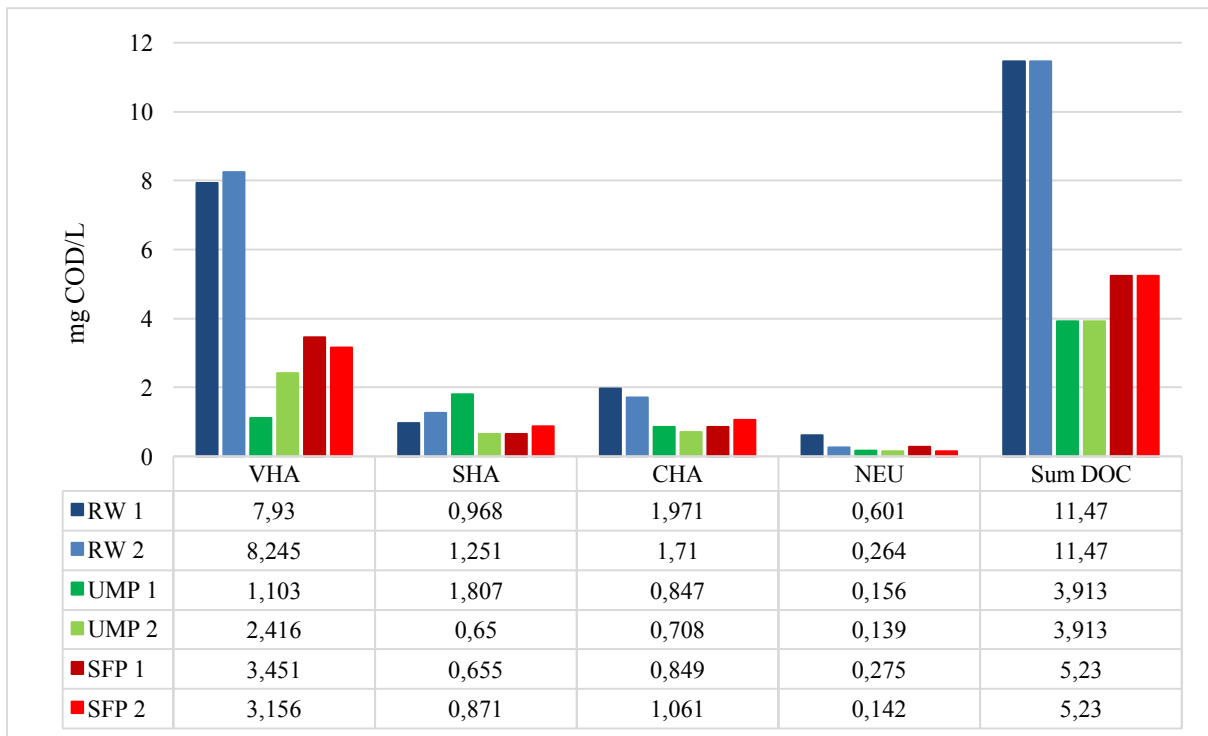
Figure I. Results from fractionation of samples taken the 12th of March at Ringsjöverket. Concentration of dissolved organic carbon (sum DOC) in unfractionated samples and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW= raw water, UMP= water after ultra-membrane pilot and SFP= water after sand filtration pilot.

Appendix II

In this Appendix II data on measurements performed on water collected the 19th of March are presented.

*Table II-1. Analytic results of fractionated water samples collected the 19th of March at Ringsjöverket. Concentration of dissolved organic carbon (DOC) and ultraviolet absorption at 254 nm (UV$_{254}$) and 436 nm (UV$_{436}$). Type of column: DAX= column packed with Superlite DAX-8 resins, XAD= column packed with Amberlite XAD-4 resins and IRA= column packed with Amberlite IRA-958 resins. Sampling points: raw water (RW), after ultra-membrane pilot (UMP) and after sand filter pilot (SFP). Values of DOC marked with * are from remade measurements and these values were used further in the study.*

Date yyyy-mm-dd	Type of column	UV-abs 254 nm (1/m)	UV-abs 436 nm (1/m)	DOC (mg/l)
	DAX 1 RW 1	6.02	0.1	2.44
	DAX 2 RW 2	5.96	0.1	2.45
	DAX 3 UMP 1	1.46	0.02	1.07
	DAX 4 UMP 2	1.4	0.04	1.10
	DAX 5 SFP 1	2.18	0.04	1.19
	DAX 6 SFP 2	2.18	0.04	1.29
	XAD 1 RW 1	2.56	0.02	1.32
	XAD 2 RW 2	2.56	0.04	1.19
2018-03-19	XAD 3 UMP 1	0.54	0.04	0.71
	XAD 4 UMP 2	0.58	0.02	2.014, 1.124*
	XAD 5 SFP 1	0.86	0.02	2.365, 0.659*
	XAD 6 SFP 2	0.88	0.02	3.035, 1.22*
	IRA 1 RW 1	0.5	0.02	0.81
	IRA 2 RW 2	0.38	0.02	0.52
	IRA 3 UMP 1	0.22	0.02	0.36
	IRA 4 UMP 2	0.3	0	0.48
	IRA 5 SFP 1	0.22	0	0.41
	IRA 6 SFP 2	0.3	0	0.39

Table II-2. Analytic results from fractionation of water collected the 19th of March at Ringsjöverket. Sampling points: raw water (RW), after ultra-membrane pilot (UMP) and after sand filter pilot (SFP).

Sample point	Date yyyy-mm-dd	TOC (mg/l)	UV$_{254}$ (1/m)	UV$_{436}$ (1/m)	Total	#	VHA	SHA	CHA	NEU	SUVA (L/mg*m)
RW	2018-03-19	11.53	42.58	2.8	11.39	1	8.953	1.119	0.509	0.809	3.7
						2	8.942	1.262	0.665	0.521	
UMP	2018-03-19	3.875	4.9	0.1	3.355	1	2.282	0.366	0.351	0.356	1.5
						2	2.251	-0.02	0.646	0.478	
SFP	2018-03-19	5.4	7.5	0.26	5.233	1	4.045	0.529	0.245	0.414	1.4
						2	3.942	0.071	0.826	0.394	

	VHA	SHA	CHA	NEU	Sum DOC
RW 1	8,953	1,119	0,509	0,809	11,39
RW 2	8,942	1,262	0,665	0,521	11,39
UMP 1	2,282	0,366	0,351	0,356	3,355
UMP 2	2,251	-0,02	0,646	0,478	3,355
SFP 1	4,045	0,529	0,245	0,414	5,233
SFP 2	3,942	0,071	0,826	0,394	5,233

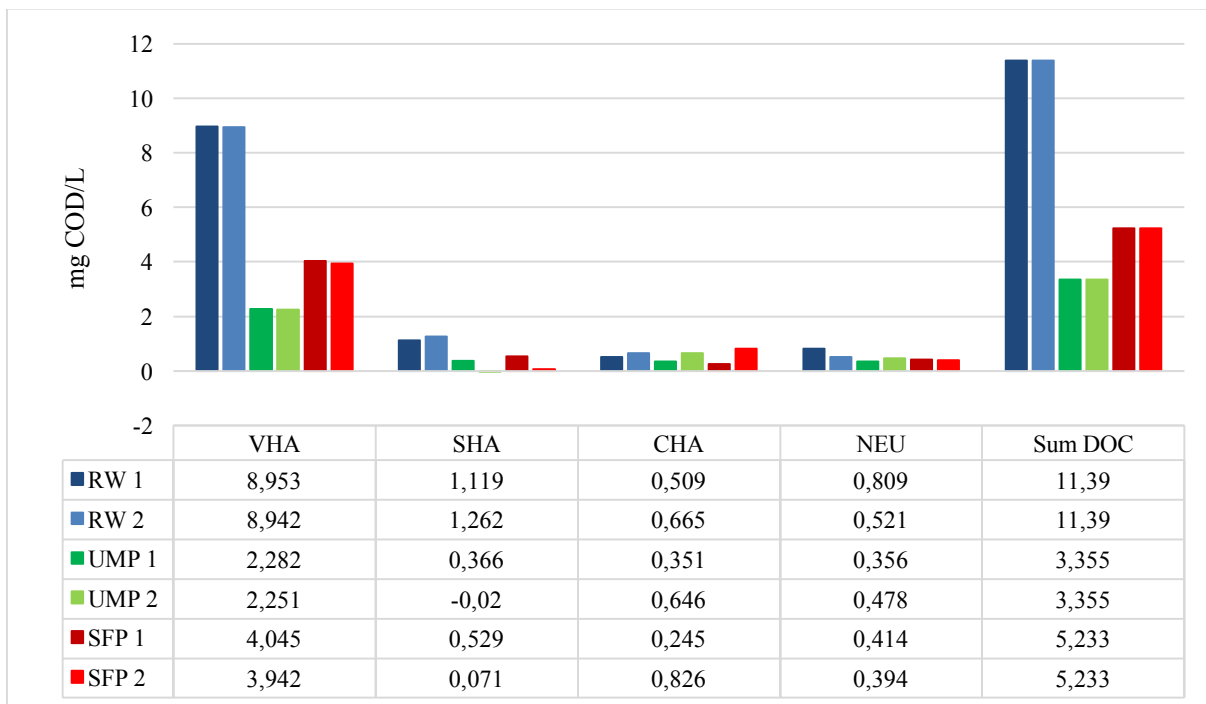*Figure II. Results from fractionation of samples taken the19[th] of March at Ringsjöverket. Concentration of dissolved organic carbon (sum DOC) in unfractionated samples and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW= raw water, UMP= water after ultra-membrane pilot and SFP= water after sand filtration pilot.*

Appendix III

In this Appendix III data on measurements performed on water collected the 3rd of April are presented.

Table III-1. Analytic results of fractionated water samples collected the 3th of April at Ringsjöverket. Concentration of dissolved organic carbon (DOC) and ultraviolet absorption at 254 nm (UV$_{254}$) and 436 nm (UV$_{436}$). Type of column: DAX= column packed with Superlite DAX-8 resins, XAD= column packed with Amberlite XAD-4 resins and IRA= column packed with Amberlite IRA-958 resins. Sampling points: raw water (RW), before and after slow sand filtration (SSF). DOC measurements were performed at the department (DOC) and on Ringsjöverket (DOC Ringsjöverket). Values from Ringsjöverket will be used further in the study.

Date yyyy-mm-dd	Type of column	UV$_{254}$ (1/m)	UV$_{436}$ (1/m)	DOC (mg/L)	DOC Ringsjöverket (mg/l)
	DAX 1 RW 1	5.24	0.08	2.61	3.008
	DAX 2 RW 2	5.26	0.1	2.36	2.899
	DAX 3 before SSF 1	1.54	0.02	1.44	1.625
	DAX 4 before SSF 2	1.34	0.04	1.21	1.616
	DAX 5 after SSF 1	1.12	0	0.98	1.546
	DAX 6 after SSF 2	1.16	0.02	1.96	1.654
	XAD 1 RW 1	2.62	0.14	1.43	1.549
	XAD 2 RW 2	2.66	0.02	2.70	1.521
2018-04-03	XAD 3 before SSF 1	0.72	0	2.28	0.7914
	XAD 4 before SSF 2	0.68	0.06	1.31	0.9336
	XAD 5 after SSF 1	0.58	0.02	1.87	0.9339
	XAD 6 after SSF 2	0.6	0.1	1.35	0.8094
	IRA 1 RW 1	0.42	0.08	1.60	0.7527
	IRA 2 RW 2	0.3	0.04	3.71	0.991
	IRA 3 before SSF 1	-0.08	0.02	3.03	0.9094
	IRA 4 before SSF 2	0.38	0.02	2.72	0.8027
	IRA 5 after SSF 1	-0.26	0.02	0.60	0.6916
	IRA 6 after SSF 2	0.34	0.06	1.07	0.8729

Table III-2. Analytic results from fractionation of water collected the 3th of April at Ringsjöverket. Sampling points: raw water (RW), before and after slow sand filtration (SSF). TOC and DOC values used are those from the analysis on Ringsjöverket.

Sample point	Date	TOC	UV_{254}	UV_{436}	DOC (mg/l)							SUVA
	yyyy-mm-dd	(mg/l)	(1/m)	(1/m)	Total	#	VHA	SHA	CHA	NEU		(m l/mg C)
RW	2018-04-03	11.2	43	3.02	11.2	1	8.192	1.459	0.796	0.753		3.8
						2	8.301	1.378	0.530	0.991		
before SSF	2018-04-03	2.841	4.66	0.06	2.924	1	1.299	0.834	-0.118	0.909		1.6
						2	1.308	0.682	0.131	0.803		
after SSF	2018-04-03	2.725	4.34	0.1	3.018	1	1.472	0.612	0.242	0.692		1.4
						2	1.364	0.845	-0.064	0.873		

	VHA	SHA	CHA	NEU	Sum DOC
RW 1	8,192	1,459	0,7963	0,7527	11,2
RW 2	8,301	1,378	0,53	0,991	11,2
before SSF1	1,299	0,8336	-0,118	0,9094	2,924
before SSF2	1,308	0,6824	0,1309	0,8027	2,924
after SSF1	1,472	0,6121	0,2423	0,6916	3,018
after SSF2	1,364	0,8446	-0,0635	0,8729	3,018

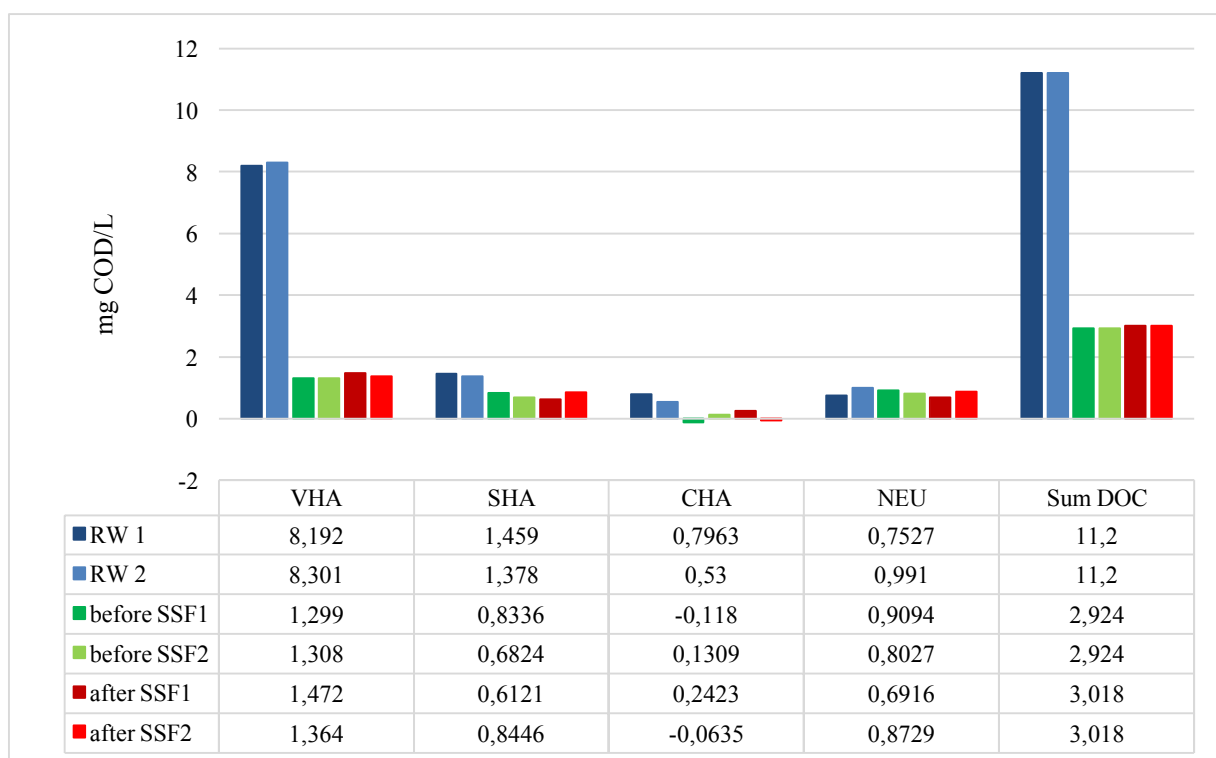*Figure III. Results from fractionation of samples taken the 3rd of April at Ringsjöverket. Concentration of dissolved organic carbon (sum DOC) in unfractionated samples and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW= raw water, before and after slow sand filtration (SSF).*

Appendix IV

In this Appendix IV data on measurements performed on water collected the 10th of April are presented.

Table IV-1. Analytic results of fractionated water samples collected the 10th of April at Ringsjöverket. Concentration of dissolved organic carbon (DOC) and ultraviolet absorption at 254 nm (UV$_{254}$) and 436 nm (UV$_{436}$). Type of column: DAX= column packed with Superlite DAX-8 resins, XAD= column packed with Amberlite XAD-4 resins and IRA= column packed with Amberlite IRA-958 resins. Sampling points: raw water (RW), before and after slow sand filtration (SSF). The DOC analysis was performed at Ringsjöverket.

Date yyyy-mm-dd	Type of column	UV$_{254}$ (1/m)	UV$_{436}$ (1/m)	DOC Ringsjöverket (mg/l)
	DAX 1 RW1	5.6	0.08	2.8
	DAX 2 RW2	5.54	0.08	2.834
	DAX 3 before SSF1	2.14	0.04	1.343
	DAX 4 before SSF2	2.12	0.04	1.298
	DAX 5 after SSF1	1.18	0	1.211
	DAX 6 after SSF2	1.2	0	1.272
	XAD 1 RW1	2.74	0.04	1.392
	XAD 2 RW2	2.68	0.04	1.396
2018-04-10	XAD 3 before SSF1	1.8	0.02	0.7708
	XAD 4 before SSF2	1.38	0.02	0.7436
	XAD 5 after SSF1	0.96	0	0.7094
	XAD 6 after SSF2	0.54	0.02	0.7484
	IRA 1 RW1	0.68	-0.02	0.761
	IRA 2 RW2	0.64	0.02	0.7904
	IRA 3 before SSF1	0.44	-0.02	0.7255
	IRA 4 before SSF2	0.52	0	0.708
	IRA 5 after SSF1	0.2	-0.02	0.6393
	IRA 6 after SSF2	0.22	0	0.5957

Table IV-2. Analytic results from fractionation of water collected the 10th of April at Ringsjöverket. Sampling points: raw water (RW), before and after slow sand filtration (SSF). TOC analysis where also done on outgoing water from Ringsjöverket at the 4th of May.

| Sample point | Date | TOC | UV$_{254}$ | UV$_{436}$ | DOC (mg/l) | | | | | | SUVA |
	yyyy-mm-dd	(mg/l)	(1/m)	(1/m)	Total	#	VHA	SHA	CHA	NEU	(m l/mg C)
RW	2018-04-10	10.75	41.8	3.24	10.71	1	7.91	1.408	0.631	0.761	3.9
						2	7.876	1.438	0.6056	0.7904	
before SSF	2018-04-10	2.856	4.36	0.1	2.985	1	1.642	0.5722	0.0453	0.7255	1.7
						2	1.687	0.5544	0.0356	0.708	
after SSF	2018-04-10	2.747	4.98	0.36	2.67	1	1.459	0.5016	0.0701	0.6393	1.6
						2	1.398	0.5236	0.1527	0.5957	
outgoing water	2018-05-04	2.747									

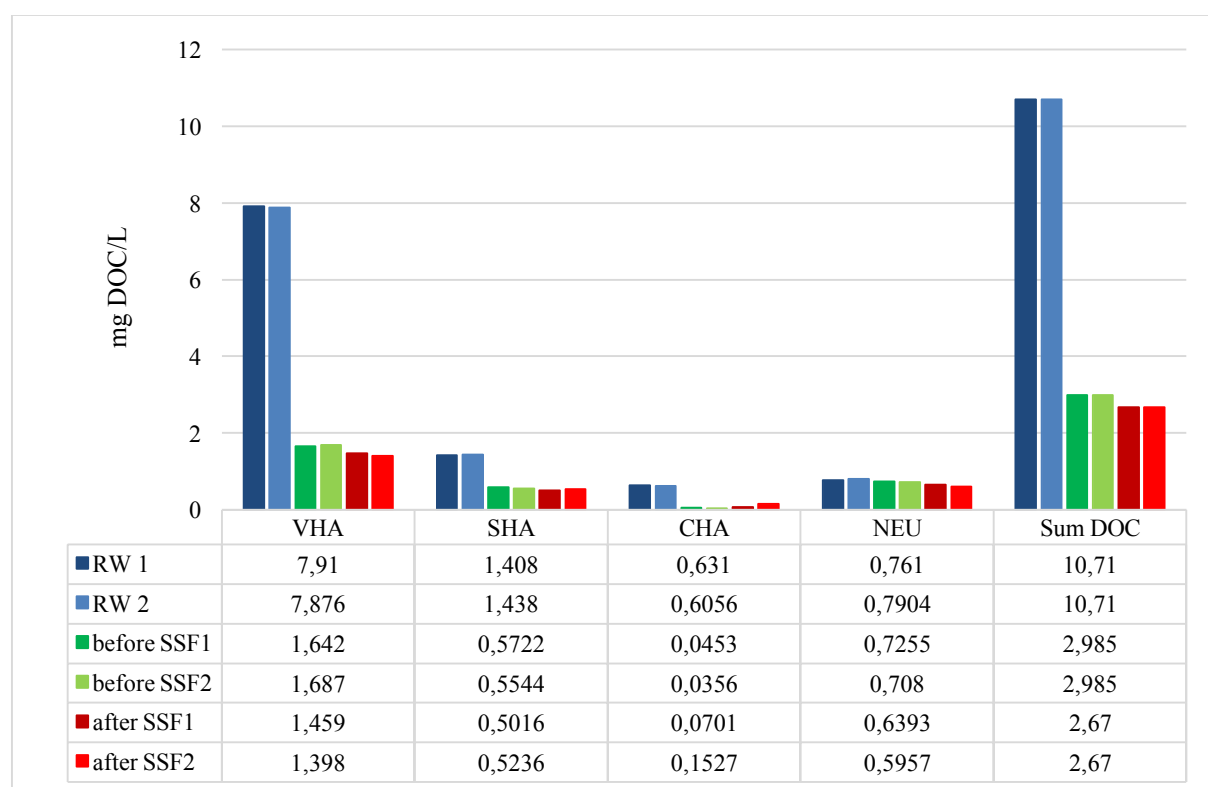|	VHA	SHA	CHA	NEU	Sum DOC
■ RW 1	7,91	1,408	0,631	0,761	10,71
■ RW 2	7,876	1,438	0,6056	0,7904	10,71
■ before SSF1	1,642	0,5722	0,0453	0,7255	2,985
■ before SSF2	1,687	0,5544	0,0356	0,708	2,985
■ after SSF1	1,459	0,5016	0,0701	0,6393	2,67
■ after SSF2	1,398	0,5236	0,1527	0,5957	2,67

Figure IV. Results from fractionation of samples taken the 10th of April at Ringsjöverket. Concentration of dissolved organic carbon (sum DOC) in unfractionated samples and DOC distributed on very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acids (CHA) and neutral hydrophilic material (NEU). RW= raw water, before and after slow sand filtration (SSF).