



Comparison and Optimization of Removal of Natural Organic Carbon from Raw Water with Ultrafiltration in Pilot Scale Experiments

Tamara Kristin Voigtländer

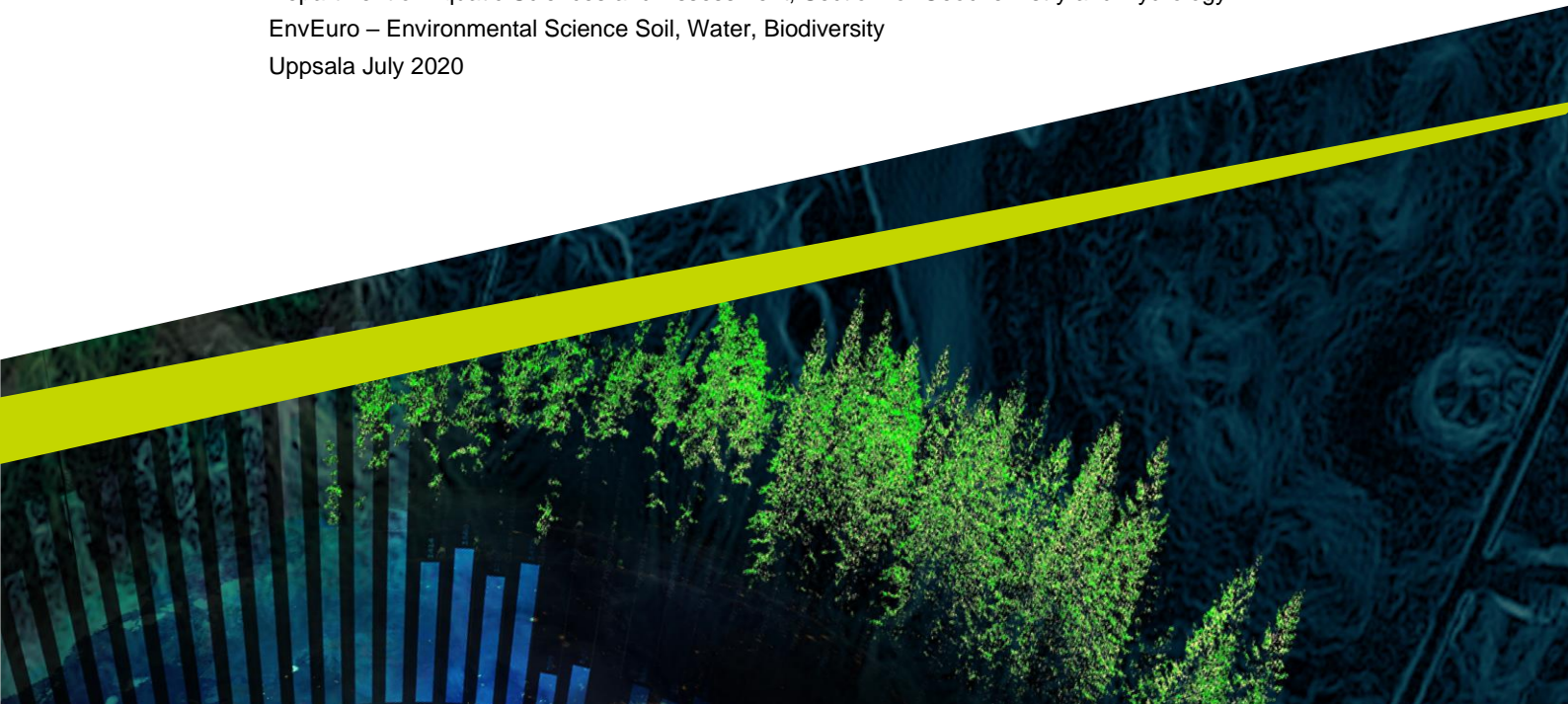
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Swedish University of Agricultural Sciences, SLU

Department of Aquatic Sciences and Assessment, Section for Geochemistry and Hydrology

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Abstract

The removal of natural organic matter (NOM) from Swedish surface waters has become a large challenge for drinking water treatment plants (DWTP), as NOM content has been rising in surface waters all over Northern Europe. In the last decade, membrane technologies, often combined with coagulation, have become more and more common. The DWTP Norrvatten in Stockholm treats water from lake Mälaren with conventional coagulation and sedimentation. However, they are currently testing an online coagulation-ultrafiltration system in a large pilot plant container at Görvålverket in Stockholm to find out whether it can serve as a future technology in times of increasing NOM levels in Mälaren and increasing need for drinking water.

In this study, a compact table-scale water treatment pilot plant working with a hollow-fibre ultrafiltration membrane was used to investigate and optimize the removal of NOM from raw water. NOM removal was quantified using online sensor detection of FDOM and via DOC grab samples. It was documented that the removal of NOM with the small-scale pilot plant is highly comparable to the results from the large container-scale pilot plant at Norrvatten. Therefore, it is a valuable tool to conduct fast, easy, and cheap pretests in the future. Optimal coagulation conditions across an ultrafiltration membrane with polyaluminium chloride were identified (6 mg/l and pH=6) and three different raw waters of varying quality and NOM content were tested using high-frequency multiparameter analysis, spectrofluorescence and total organic carbon analysis. Removal efficiencies of up to 57% fluorescent dissolved organic matter could be achieved. However, raw waters with NOM contents over 15 mg/l will remain a challenge with this treatment technology, because the remaining NOM contents are higher (7,6 mg/l) than the legal threshold (ca. 5mg/l).

Keywords: Dissolved Organic Carbon, online coagulation, drinking water treatment, fluorescence indices, raw water quality, high-frequency sonde

Popular Scientific Summary

Lake water is one of the most important sources for drinking water production in Sweden. However, lake water contains many substances that are derived from soil or plants, called “natural organic matter” (NOM). During rain, these small substances are washed into the lakes. They lead to a yellowish colour of the water and make it smell.

Removing them for drinking water production is challenging, because these substances are too small to be removed by a conventional filter. The drinking water treatment plant (DWTP) Norrvatten in Stockholm is testing a filter technology called “ultrafiltration” that became more and more popular in DWTP in the last years. They are hoping to use this technique in the future when water consumption will increase.

In ultrafiltration, water is pressed through a tight layer of synthetic material, that has very small pores. Through these pores, only water and other very small substances can pass, but most particles, and a portion of larger NOM, are held back and get filtered out. Thus, this filtration is a very effective way to remove virus and bacteria and is therefore popular for drinking water treatment. To improve the NOM removal, a chemical is added to the water beforehand, that allows to produce aggregates of some small NOM substances and form bigger flocs that do not pass the filter.

In this study, a small pilot of a water treatment plant, as big as a desk, was tested, to see if results are comparable with the large container pilot already in use at Norrvatten. The small pilot is easier, faster and cheaper to use and thus, many different variations in the usage can be tested.

Here, it was tested that adding 6 mg/l of the chemical polyaluminium chloride beforehand leads to the highest removal of NOM and gives the cleanest water. Adding more did not improve the removal any further. Additionally, we tested the technology under acidic and neutral conditions and found that the best result is reached at a pH = 6. More precisely, 10 % more NOM were removed than under neutral conditions.

Furthermore, lake water from three different parts of lake Mälaren where tested. They had varying contents of NOM and it was shown that if the NOM content in lake water is above 15 mg/l, too much NOM will remain in the filtered water than legal restrictions allow. This could be problematic in the future if NOM content in the lake would rise and might require another cleaning step.

To sum up, the small pilot showed very similar results as the large pilot at Norrvatten (maximum 10% difference). Thus, the small pilot is recommended as a useful tool for pretests of ultrafiltration in drinking water treatment.

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Abbreviations

Al	Aluminium
ANOVA	analysis of variance
$\beta:\alpha$	freshness index
cDOM	coloured dissolved organic matter
DOC	dissolved organic carbon
DOM	dissolved organic matter
DWTP	drinking water treatment plant
EDTA	ethylenediaminetetraacetic acid
EEM	excitation-emission-matrix
fDOM	fluorescent dissolved organic matter
FI	fluorescence index
FNU	Formazin Nephelometric Unit
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
HIX	humification index
IFE	inner filter effects
LMH	$l/(h \cdot m^2)$
MF	microfiltration
MQ	milliQ water (highly purified water)
NOM	natural organic matter
NF	nanofiltration
SUVA ₂₅₄	specific ultraviolet absorbance at 254 nm
TOC	total organic carbon
UF	ultrafiltration
UVA ₂₅₄	ultraviolet absorbance at 254 nm
WTP	water treatment plant

1. Introduction

In the last two decades, increases of natural organic matter (NOM) in surface waters have been reported all over Northern Europe (Roulet & Moore 2006; Ledesma *et al.* 2012; Lavonen *et al.* 2015; Keucken *et al.* 2017). NOM are organic compounds, partly originating from decomposed soil organic matter, partly being produced and metabolized by plankton and microorganisms in lakes. Reasons for an overall increase were widely discussed and possible explanations include climate change, affecting temperature and precipitation, a decline in acid deposition or ongoing land use changes (Lavonen 2015; Keucken *et al.* 2017).

NOM increases are a large challenge for drinking water production from surface waters due to several reasons. Firstly, NOM affects odour, colour, and taste of the drinking water and thus, reduces its quality. Secondly, there is a higher risk of biological growth in the distribution system if NOM is present. Lastly and most importantly, NOM can form harmful disinfection by-products (DBP) during the disinfection step in the water treatment plant (Jacangelo *et al.* 1995; Lavonen *et al.* 2013).

Therefore, NOM concentrations in drinking water have to be kept low, in Sweden a concentration below 5 mg/l carbon is recommended (Köhler *et al.* 2016). However, the removal of NOM is difficult due to the huge chemical variety of NOM. Conventional methods become insufficient more and more often.

Additionally, the need of drinking water in urban areas in Sweden is constantly increasing. Right now, 2 million people need to be supplied with drinking water in Stockholm and its surroundings and the population of Stockholm is expected to increase by another million people in the next two decades (Ledesma *et al.* 2012). Efficient technologies that can treat large amounts of lake water with high NOM content at stable costs are needed. In the last decade, membrane technologies, such as nano- and ultrafiltration became more and more popular. The DWTP Norrvatten is currently testing an online coagulation-ultrafiltration system in a large pilot plant container at Görvålnverket in Stockholm.

In this study, a small-scale water treatment pilot plant working with a hollow-fibre ultrafiltration membrane is used to investigate and optimize the removal of NOM

from raw water. Firstly, this study aims to evaluate the comparability of the large-scale pilot at Norrvatten with the small-scale pilot plant. Could the small-scale pilot plant serve as a fast, easy and cheap pre-testing facility? As the same membrane technology is used, UV₂₅₄, fDOM, and TOC contents in the permeate are expected to be very similar, allowing precise predictions from the small-scale pilot data. Slight differences might occur due to a different stirring set up and hence different flocculation times and stirring velocities. This might affect size and stability of the flocs.

It is more difficult to maintain constant flux and pressure on the small-scale pilot and backwashes are performed manually and according to the membrane pressure instead of the permeability. Thus, similar, but more varying fluxes and permeabilities are expected. Due to membrane fouling, permeability should decrease during operation and increase during backwash again. A faster decrease is expected for higher coagulant dosages, as more flocs will be formed and accumulate on the membrane.

A second aim of this study is to find the optimal conditions for the ultrafiltration, more specifically the optimal coagulant dosing and pH, as this is expected to be directly transferable to a large-scale application.

Thirdly, three water types from different lake areas, sampled this summer, are tested to study the efficiency of the ultrafiltration membrane under varying DOM concentrations and compositions. The water from lake Ekoln has a high DOM content and hence, contains probably a higher portion of terrestrial DOM, but also more absolute amounts of other, unremovable DOM. Therefore, Ekoln permeates are expected to have the largest NOM remains. However, the removal efficiency should be similar or higher, compared to the water at Görvåln. This is because the membrane is expected to remove terrestrial originated NOM easily, whereas autochthonous NOM does not flocculate with polyaluminium chloride and is therefore not filtered out (Lavonen 2015; Keucken *et al.* 2017). As water from Prästfjärden is supposed to be younger and contains more autochthonous NOM than the mixed water at Görvåln, NOM should be slightly less efficient.

Lastly, the coagulant polyaluminium chloride, that is used for most experiments, is replaced by iron chloride, which is reported to be more efficient (Park *et al.* 2002; Matilainen *et al.* 2005). Thus, a higher removal efficiency of around 10 % is expected. However, iron chloride might lead to a higher irreversible fouling of the membrane. Accordingly, this study aims to evaluate if iron chloride could be an alternative coagulant in large-scale application.

2. Background

2.1. What is Natural Dissolved Organic Matter?

Lake Mälaren is one of the three largest lakes of Sweden and supplies drinking water to 2 million people in and around Stockholm (Ledesma *et al.* 2012). However, to fulfill the necessary high standards of drinking water, lake water must be cleaned from natural organic matter, microorganisms, and nutrients, among others.

Natural organic matter (NOM) occurs either as particles or is dissolved in the water. Whereas particulate organic matter can be easily removed with a conventional 0,45 µm filter, the removal of dissolved organic matter (DOM) is more challenging for drinking water treatment plants (DWTP). DOM is a general term for a heterogenous class of organic material, including humic substances, as well as carbohydrates, lipids, and amino acids. Part of it originates from terrestrial, soil organic matter, that is decomposed and washed out into water bodies and is called allochthonous DOM. However, DOM is also produced in the water body itself by decomposition and metabolization of aquatic microorganisms – commonly known as autochthonous DOM. The detailed composition of DOM and the structure of its compounds is still mostly unknown (Matilainen *et al.* 2010; Köhler *et al.* 2013; Lavonen 2015).

Common methods to measure DOM are the analysis of the amount of dissolved organic carbon (DOC), as well as optical spectroscopic methods. Compounds containing conjugated double-bonds absorb light at the UV-Vis spectrum, and thus, absorbance can give important information about the coloured DOM (cDOM) content. Furthermore, fluorescence can be used to analyze fDOM – fluorescent dissolved organic matter, a subset of cDOM that contains aromatic rings (Cascone 2019). Most autochthonous compounds are aliphatic, but a high proportion of allochthonous DOM is coloured. As mainly allochthonous DOM is removed during drinking water treatment, absorbance and fluorescence techniques are commonly used for the characterization of NOM removal (Lavonen *et al.* 2015; Cascone 2019).

2.2. Conventional Removal by Coagulation

DOM is conventionally removed by chemical coagulation and flocculation – the method currently applied at the DWTP Görvålnverket. A coagulant, usually a metal salt with aluminium or iron, is added to the raw water and hydrolyzes. The highly positively charged metal ions then destabilize the small particles suspended in the water to form aggregates, so called flocs. These flocs eventually settle down or float and thus, become easily removeable by sedimentation or filtration (Crittenden *et al.* 2012).

There are three main mechanisms that are responsible for coagulation: charge neutralization, adsorption and interparticle bridging, as well as sweep coagulation (Crittenden *et al.* 2012).

The suspended particles are mostly negatively charged and, by repulsing each other, are prevented from settling down and stay in suspension. They have an electrical double layer, meaning a first layer of cations that are tightly bound to the negatively charged particle surface and a second, looser layer. Within the loose layer, the still negative net charge creates an electrical field, that attracts cations and repels anions. This loose layer charge slowly phases out into solution.

Highly positively charged metal ions from the coagulant now adsorb to the surface of the particle and neutralize the charge. Hence, the electrical double layer is destabilized and the repulsive forces are reduced.

Furthermore, metal hydroxides can form large polymerized complexes. These complexes bind several particles at different sites and thereby create “bridges” between particles. In presence of high concentrations of metal ions, they form insoluble precipitates, entrapping particulate matter in them. This process is called “sweep coagulation” (Matilainen *et al.* 2010; Crittenden *et al.* 2012; Lavonen 2015).

In Norrvatten, conventional coagulation and flocculation is performed with aluminium sulphate as coagulant. After flocculation, the water is transferred into a specific sedimentation tank where flocs settle. The water is then passed on and filtered through a sand filter to remove remnants of flocs. After another filtration step with activated carbon filters, the water is disinfected with UV light. In a final step, the pH of the now clean water is adjusted to approximately 8 with lime water and from there the drinking water is transferred into the supply system (Norrvatten 2020).

2.3. Functioning and challenges of ultrafiltration membranes during online coagulation

Nowadays, modern membrane filtration technologies become more and more common alternatives in drinking water treatment. They are classified by their pore size into microfiltration (0,1 μm), ultrafiltration (10 nm), nanofiltration (1nm) and reverse osmosis (nonporous). While MF only filters larger particles, algae, and bacteria and UF additional smaller colloids and viruses, NF and reverse osmosis can actually remove DOM. However, their operation needs high pressure, large amounts of energy and the flow rate is rather small – challenging aspects for large scale DWTPs, like Görvälnverket (Crittenden *et al.* 2012).

A distinction is made between two different operating types: cross-flow filtration and dead-end filtration. In cross-flow filtration, a high flux of raw water is pumped alongside the membrane. A small part of the flow is thereby pressed through the membrane, while more than 75 % of the flux is recirculated to the feed, taking solid particles with them that consequently enrich in the flow. In dead-end filtration, all feed water is directly filtered through the membrane, while solid particles accumulate on the membrane's surface. I

n this study, a hollow-fiber UF membrane was used in dead-end mode. A hollow fiber membrane consists of many narrow, hollow tubes. The water is filtered by passing through small pores inside the membrane walls.

To be able to remove DOM with UF, the membrane system can be combined with online coagulation. A coagulant is mixed into the raw water and stirred for a short time before the mixture is passed on into the membrane. Thereby, small DOM compounds are bound in larger flocs beforehand and can then be filtered out by the membrane. Naturally dissolved organic molecules are smaller than 0,01 μm , whereas the resulting colloids have a size of 0,1 – 1 μm . This increases not only the removal efficiency of the UF membrane, but also requires far less coagulant dosages than in conventional coagulation (Huang *et al.* 2009; Bergamasco *et al.* 2011).

While operating a membrane, its permeability will be reduced over time due to fouling. During filtration, particles and NOM enrich on the surface of the membrane, forming a so called “cake”. Large particles also clog single pores and small, colloidal matter enters the pores and adsorbs to the membrane material. This leads to narrowed and eventually completely plugged pores. Online coagulation reduces fouling, because large particles form and prevent small, unbound NOM to enter the pores (Dong *et al.* 2007; Gao *et al.* 2011).

Fouling mechanisms are mostly reversible by conducting regular backwashes. A usual backwash is performed by pushing water of permeate quality in opposite direction through the membrane, to wash out the accumulated cake and clogging particles. To increase the membrane recovery and prolong membrane use time, a chemically enhanced backwash with alkaline hypochlorite solution helps to dissolve and remove more resistant fouling (Gao *et al.* 2011). However, over a longer time span a membrane's permeability will decrease due to light irreversible fouling and eventually, the membrane has to be exchanged.

3. Materials and Methods

3.1. Water Sampling

For most experiments raw water from the eastern part of Lake Mälaren, Sweden was used which is the raw water for the drinking water plant (DWTP) Görvålnverket. At this point of the year the intake depth is at -22m. The water is a mixture from the large western (70%) and the northern (30%) basins. Mälaren water has a usual pH between 7.6 to 7.8 and a high alkalinity (around 1.3 mM) (Köhler *et al.* 2016). During this study, the raw water had a turbidity between 2-3 FNU and a TOC around 7-8 mg L⁻¹. At the site, all water is prefiltered with 200 µm microfilter.

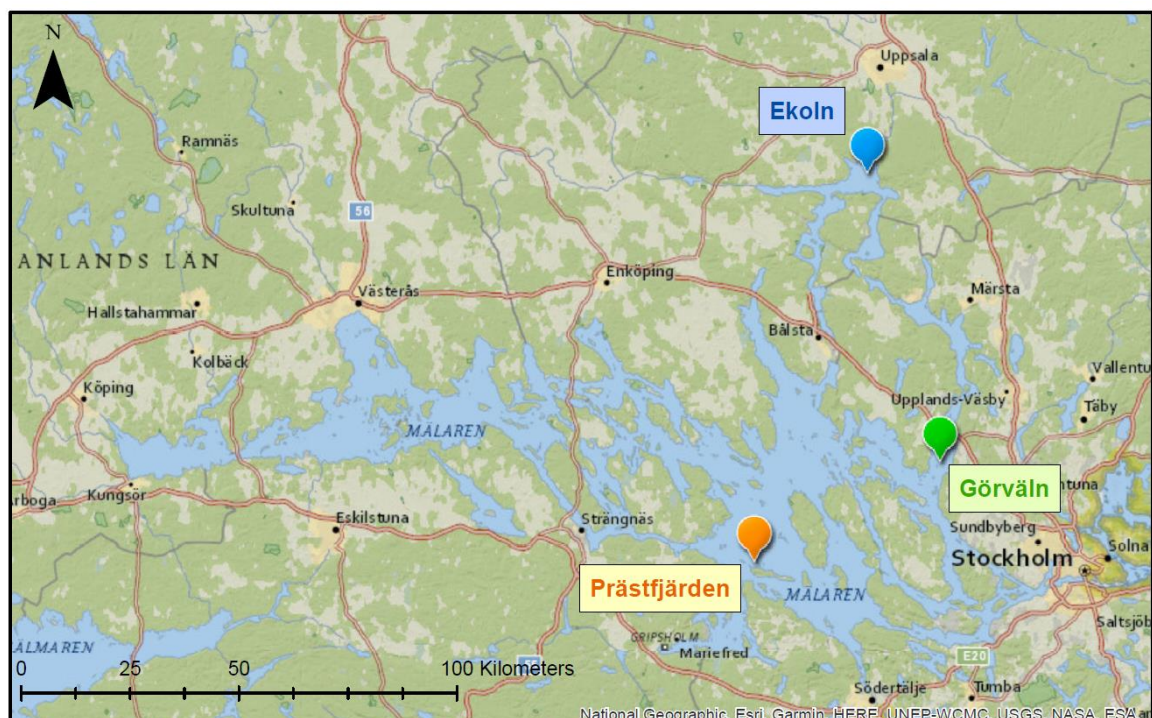


Figure 1: Map of Lake Mälaren in Eastern Sweden, showing the sample sites Görvåln, Ekoln and Prästfjärden

For comparison of UF performance, different unfiltered water types, surface water samples from Lake Ekoln, feeding the northern basin of Mälaren, and from a bay in the centre of Mälaren, Prästfjärden, were analysed as well (Fig. 1).

3.2. Quantification of Organic Matter

3.2.1. High-Frequency Multiparameter Analysis

Permeate water quality was assessed with an EXO2 Multiparameter Sonde from YSI with high frequency (20 sec intervals) and evaluated with the corresponding KorEXO 2.0 software. This multisensor sonde measured the parameters temperature, pH, fDOM (QSU), conductivity ($\mu\text{S}/\text{cm}$) and turbidity (FNU). Coagulant dosage and pH were kept constant for approximately 30 minutes to ensure a complete exchange of the measured permeate in the sonde tank. After 30 minutes, when the dead volume of the sonde tank had been exchanged three times, a sample of the permeate was taken for further analysis.

fDOM (QSU) was corrected afterwards for interferences with differing temperature, turbidity and self-shading (IFE) afterwards (Lee *et al.* 2015). Therefore, the following equations with the respective EXO2 sensor-specific coefficients were used, based on empirical pre-trials in previous studies (Hoffmeister *et al.* 2020):

$$fDOM_{corr_temp} = fDOM_{meas} + fDOM_{meas} \cdot 0,012 \cdot (T_{meas} - 25)$$

eq. (1)

$$fDOM_{corr_temp_turb} = \frac{fDOM_{corr_temp}}{(0,7225 \cdot e^{(-0,004687 \cdot Turb_{meas})} + 0,3041 \cdot e^{(-0,0003624 \cdot Turb_{meas}})}$$

eq. (2)

$$fDOM_{corr_IFE} = fDOM_{corr_temp_turb} + fDOM_{corr_temp_turb} \cdot \left(\frac{0,2508 \cdot UVA_{254}}{100} \right)$$

eq. (3)

With $fDOM_{corr_temp}$ as the temperature corrected fDOM, $fDOM_{corr_temp_turb}$ as temperature and turbidity corrected fDOM and $fDOM_{corr_IFE}$ as temperature, turbidity and IFE corrected, where T_{meas} is the measured temperature in $^{\circ}\text{C}$, $Turb_{meas}$ is the measured turbidity in FNU, $fDOM_{meas}$ is the measured fDOM in QSU and UVA_{254} is the absorbance at 254 nm.

3.2.2. Total Organic Matter

TOC content of raw water and permeate samples were analyzed with TOC Analyzer Shimadzu TOC-V CPN. The analyzer was calibrated before each run with 20 mg/l potassium hydrogen phthalate solution, that was automatically diluted to 0 mg/l, 0,5 mg/l, 1 mg/l, 5 mg/l, 10 mg/l and 20 mg/l samples.

30 ml vials were filled with the samples and 500 μ l 2M HCl added to remove inorganic carbon content. During a sparge time of 15 min the samples got stirred which leads to a complete removal of inorganic carbon present in the sample. The samples were then automatically injected into the combustion tube, which was heated to 680°C. In an oxygen-rich environment, the TOC was converted into carbon dioxide and measured by a non-dispersive infrared (NDIR) gas analyzer. The NDIR output peak area is proportional to the TOC concentration. This was automatically calculated with the calibration curve of potassium hydrogen phthalate. The accuracy of the TOC analyzer is $\pm 1,5$ %.

10 mg/l EDTA solution was used as standard solution to control for the quality. The measurement was accepted, if the measured concentration of EDTA was in a range of 9.5 – 10.5 mg/l.

To analyze DOC content, raw water samples were filtered beforehand with glass microfiber filters GF/F 0.7 μ m (Whatman, CAT No.1825-047). The filters were burnt in advance at 450°C for 240 min to remove organic carbon remains that could potentially be present on the filter.

3.2.3. Fluorescence Analysis

To determine fluorescence and absorbance spectra of permeate and raw water samples, an AquaLog® spectrofluorometer was used.

Raw water samples were filtered beforehand (see above).

Samples were measured in a 10 mm \times 10 mm quartz cuvette. Depending on the fDOM content of the samples, they were measured at integration times between 1 and 5 sec. MQ was used as a blank and a 10 mg L⁻¹ Potassium hydrogen phthalate solution as an absorbance control. The measured values were then corrected automatically with the supplied software for IFE and Rayleigh scattering effects.

The excitation-emission-matrices were used to calculate the fluorescence indices HIX, FI and $\beta:\alpha$ (Zsolnay *et al.* 1999; Parlanti *et al.* 2000; McKnight *et al.* 2001; Cory *et al.* 2010).

$$HIX = \frac{EM(435) - EM(480)}{EM(300) - EM(345) + EM(435) - EM(480)}; \text{ at EX 254}$$

eq. (4)

$$\beta:\alpha = \frac{EM(380)}{\max. I(420 - 435)}; \text{ at EX 310}$$

eq. (5)

$$FI = \frac{EM(470)}{EM(520)}; \text{ at EX 370}$$

eq. (6)

HIX gives insight into the humic substance content of the sample. A high HIX resembles a low H:C ratio, it is redshifted and therefore has a high degree of humification (Zsolnay *et al.* 1999). The $\beta:\alpha$ ratio shows the age of DOM. A high ratio is a sign for more recently derived DOM, whereas a ratio below 1 shows a higher share of more decomposed DOM (Parlanti *et al.* 2000). Lastly, a FI index ≈ 1.8 refers to a microbial origin of DOM, whereas a FI ≈ 1.2 indicates a rather terrestrial source (McKnight *et al.* 2001).

Furthermore, the resulting absorbance spectra gave UVA₂₅₄ data, which were then used to calculate the SUVA₂₅₄ by normalizing UVA₂₅₄ to DOC content. It has been shown, that SUVA₂₅₄ is a valid indicator for aromaticity of NOM and is a proxy for the proportion of allochthonous NOM (Weishaar *et al.* 2003):

$$SUVA_{254} \left[\frac{l}{mg \cdot m} \right] = \frac{UV_{254} [m^{-1}]}{DOC [mg/l]}$$

eq. (7)

3.3. Ultrafiltration Pilot Plant – Small Scale

Raw water samples were filtered using online coagulation and an hollow-fibre UF membrane with dead-end operation.

The employed membrane in the UF pilot is a X-Flow RX300 0,83UFC from Pentair. It is composed of 130 polyethersulfone and polyvinylphenol elements (PENTAIR, personal communication). Each single membrane element has a hydraulic membrane diameter of 0,83 mm and total membrane area is 0,08 m². The whole element is 300 mm long and has an outer diameter of 23,9 mm. For more details on the membrane, the Membrane Element Datasheet is supplied in the Appendix.

The whole small pilot plant was operated at a flow rate of 6 L/h, with 60 ml/h coagulant and 5,94 L/h raw water feed flow rate. Coagulant and raw water were premixed and stirred to allow flocculation before entering the membrane element (Fig. 2).

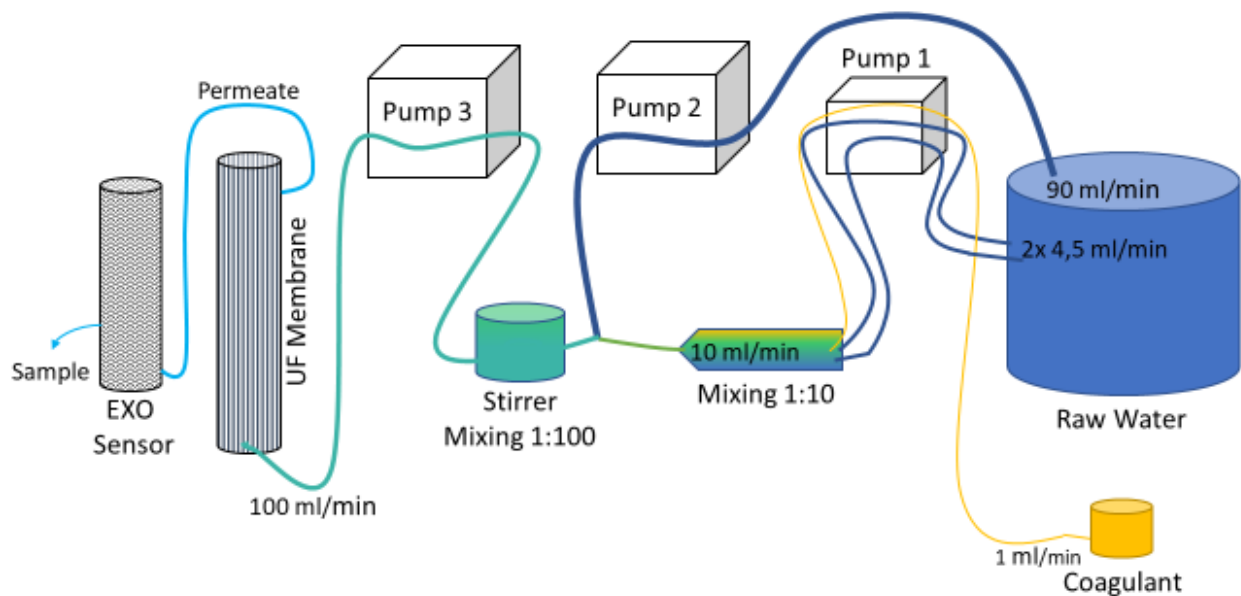


Figure 2: Model of the small drinking water pilot plant, water is flowing from right to left. 9 ml of raw water are pumped to a mixing device and are mixed with 1 ml coagulant. The mixture is then pumped into a stirrer where 90 ml raw water are added. During stirring, flocculation takes place. The solution is then pumped through the UF membrane and the permeate is measured in the EXO sensor.

The filtration flux, as the flow rate per membrane area, was calculated as

$$Flux \left[\frac{l}{h \cdot m^2} \right] = \frac{Flow\ rate \left[\frac{l}{h} \right]}{0,08\ m^2}$$

eq. (8)

The transmembrane pressure (TMP) over the membrane is described as the difference between the feed pressure and the permeate pressure, which were read off from the manometers at the pilot (see Fig. X):

$$TMP = P_{feed} - P_{Permeate}$$

eq. (9)

The permeability of the membrane module was then calculated as the flux per TMP. Permeability is affected by water viscosity and physical expansion which are both dependent on temperature. Hence, a correction for temperature (T) was performed, according to the large pilot plant manual (PENTAIR 2015):

$$Permeability \left[\frac{l}{h \cdot m^2 \cdot bar} \right] = \frac{Flux}{TMP * TempCorr}$$

eq. (10)

$$TempCorr = 2,024 \cdot 10^{-3} \cdot (42,5 + T)^{1,5}$$

eq. (11)

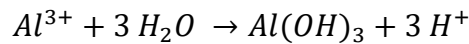
On regularly basis (every 15 min to 2 h), the membrane was backwashed with MQ for 20 minutes at 0,5 bar. It was backwashed firstly from the permeate outflow through the membrane surface. Then the hollow fibres were flushed additionally from top to bottom to remove cake remains with a higher flux. Intermittently, the outflow was shortly blocked to increase pressure up to 0,8 bar, so that stuck particles got pushed out.

Every time before storage, a standard chemical enhanced backwash was conducted with 200 ppm sodium hypochloride (NaClO) solution for 20 minutes, followed by a backwash with mQ water for another 20 minutes.

3.4. Experimental Conditions – Coagulant Dosages and pH

As coagulant polyaluminium chloride ($\text{Al}(\text{OH})_{1,2}\text{Cl}_{1,8}$) or iron chloride (FeCl_3) are used in varying final metal concentrations between 2 - 16 mg/l ($[\text{Me}^{3+}]$). The feeding coagulant solution is diluted 1:100 in the pilot plant (Fig. 2). The feeding coagulant solutions were therefore prepared in 100-fold concentrations.

The addition of $\text{Al}(\text{OH})_{1,2}\text{Cl}_{1,8}$ leads to a decrease of pH:



eq. (12)

Thus, in most experiments, pH was adjusted with 0,5 M NaHCO_3 , 0,5 M Na_2CO_3 and 0,5 M HCl solutions, respectively, added to the raw water in advance. As experiments on the large scale pilot plant were conducted at a pH of approximately 7 to minimize the amount of chemicals used, regular experiments on the small pilot plant were also conducted at a pH of 6,8 – 7,2. This ensures comparability.

With changing pH, size and stability of the formed flocs differ (Crittenden *et al.* 2012). To evaluate how this affects the efficiency of NOM removal by the membrane, two set of experiments with varying pH-values of 6,0 – 7,0 were tested under constant AlCl_3 concentration of 4 mg/l and 16,7 mg/l Al^{3+} , respectively.

3.5. Ultrafiltration Pilot Plant – Large Scale

Permeate samples from the small-scale pilot plant were compared to permeate samples from a large-scale container pilot plant that is located at Görvålnverket, Stockholm. The pilot plant facility was supplied by Pentair X-Flow (Keucken *et al.* 2017). The UF membrane element has a membrane area of 64 m² and an operational flow rate of up to 100 l/(m²*h).

4. Results

4.1. fDOM Calibration

As fDOM is used as proxy for the efficiency of NOM removal from raw water by the UF membrane, an appropriate fDOM calibration is crucial. Fig. 3 shows the distribution of all measured values against UVA₂₅₄. Prästfjärden and Görvåln samples seem to be very similar, however, Ekoln samples are shifted.

To verify the correction for temperature, turbidity, and IFE for all fDOM measurements, the correlation of fDOM_{corr} with UVA₂₅₄ was tested by performing an analysis of variance (ANOVA) (Fig. 4). Raw waters and the samples coagulated with ironchloride were excluded.

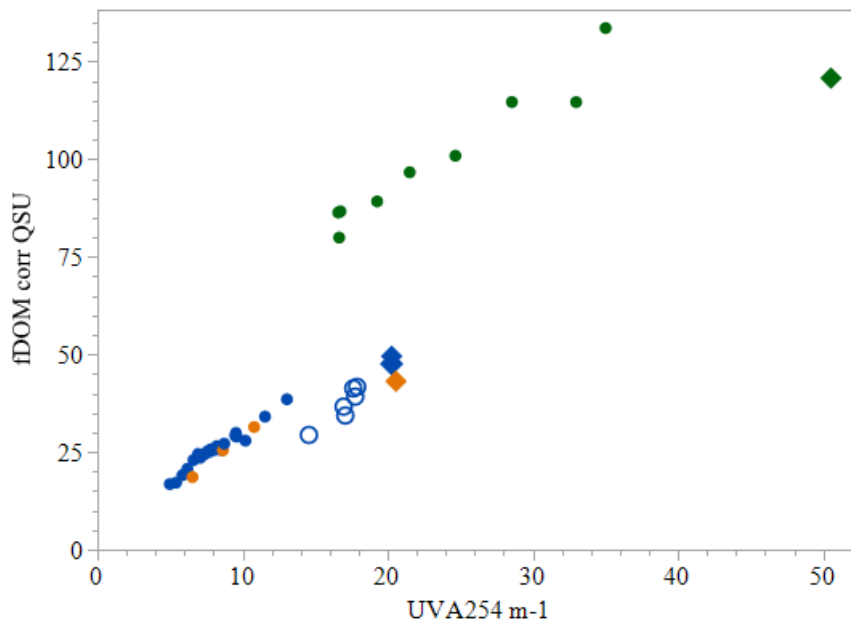


Figure 3: fDOM_{corr} against UVA₂₅₄ for permeates from Ekoln (green), Görvåln (blue) and Prästfjärden (orange) water and their respective raw waters (squares). Görvåln waters coagulated with iron chloride are shown as unfilled circles.

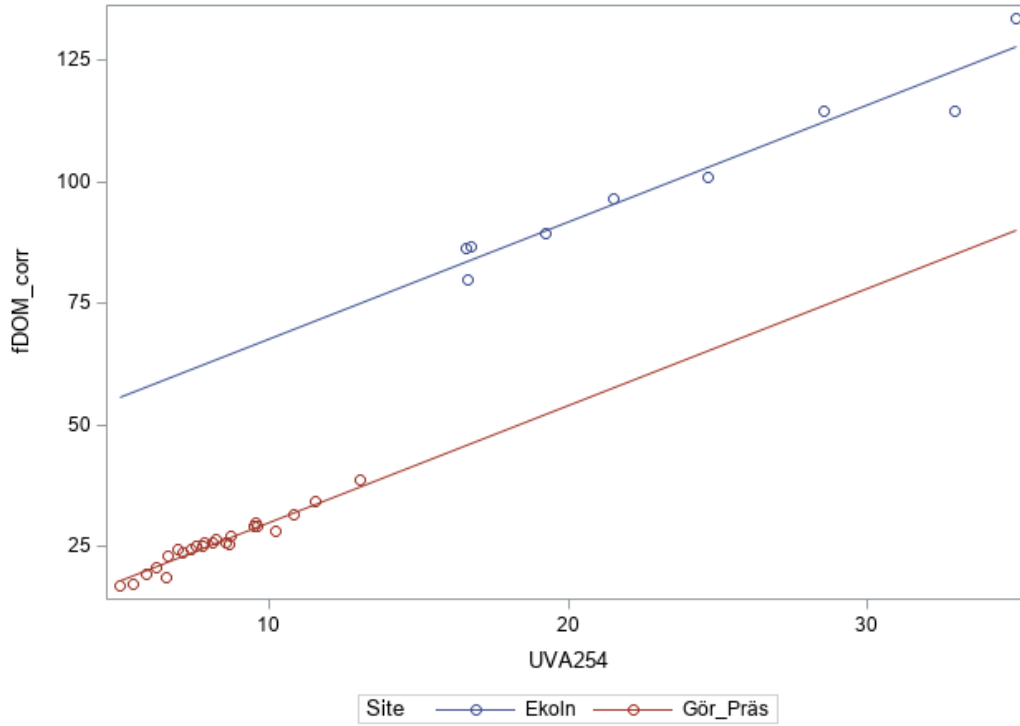


Figure 4: Analysis of Covariance for $fDOM_corr$ against UVA_{254} for all three water types. They share the same slope, but Ekoln samples differ from Görvåln and Prästfjärden samples in the intercept with the y-axis. Prästfjärden samples are not significantly different from Görvåln samples.

The resulting ANOVA table (Tab. 1) shows a high correlation of $fDOM_corr$ with UVA_{254} for all three water types ($r^2 = 0,995$), sharing the same slope. ANOVA tests with differing slopes for each water type were not significant (see Fig. A1, A2). Whereas the regression line for Prästfjärden and Görvåln samples are identical (differing intercepts were not significant, see Fig. A3, A4), the regression for Ekoln samples is shifted by 37,86 QSU. This implies that the performed correction for IFE is not sufficient for Ekoln water samples. Hence, all measured $fDOM$ values are further corrected as:

$$fDOM_{corr_{Ekoln}} = fDOM_{corr_{IFE}} - 37,86 \quad \text{eq. (13)}$$

Table 1: ANOVA table for UVA254 against fDOM_corr for the water types Görvältn/Prästfjärden and Ekoln.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
UVA ₂₅₄	1	2877.252736	2877.252736	481.49	<.0001
Site	2	2729.389562	1364.694781	228.37	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t	95% Confidence Limits	
UVA ₂₅₄	2,39863226	0,10931291	21,94	<,0001	2,17538551	2,62187901
Ekoln	43,82029500	2,70031814	16,23	<,0001	38,30550964	49,33508036
Görv/Präst	5,95674404	1,02473388	5,81	<,0001	3,86395826	8,04952982

R-Square	Coeff Var	Root MSE	fDOM_corr Mean
0.995472	5.317334	2.444538	45.97300

After correction of the fDOM values of all Ekoln samples, they share the same regression line with Görvältn and Prästfjärden samples (Fig. 5).

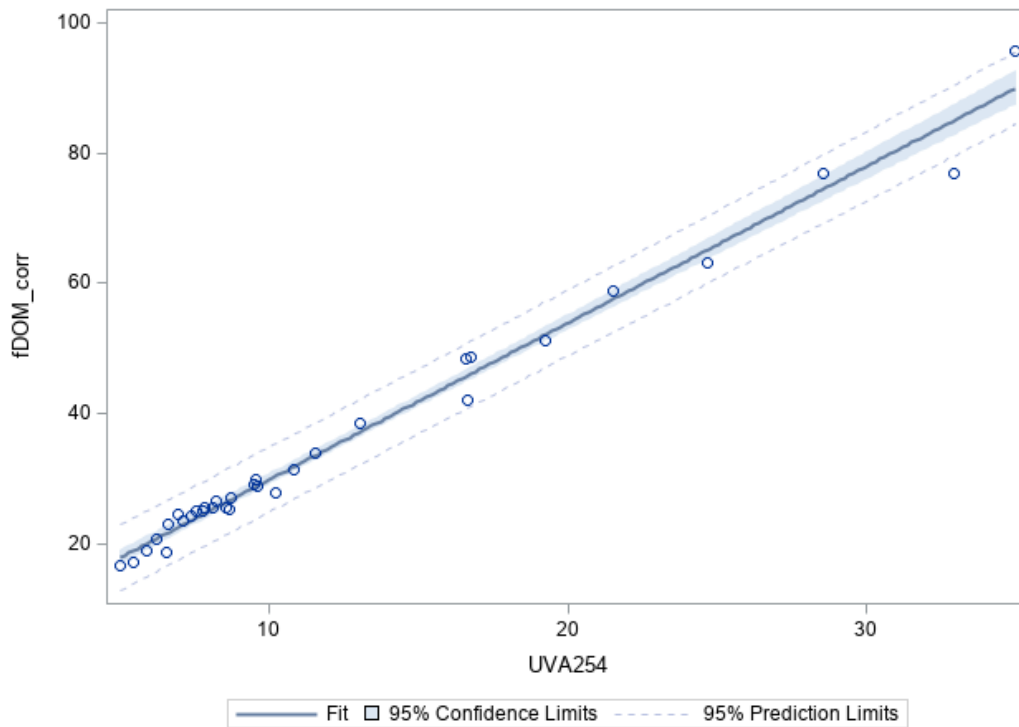


Figure 5: Regression of all UVA254 measurements against fDOM_corr, including samples from Görvältn, Prästfjärden and Ekoln.

The regression equation is: $fDOM_corr = 5,956 + 2,399 * UVA254$; $r^2 = 0,985$

Comparing the regression of UVA_{254} against TOC for all water samples, Prästfjärden and Görväln water samples share the same line (data not shown), but Ekoln water samples follow a significantly different regression ($\alpha < 0,0001$, Fig. 6).

The two resulting equations are:

$$\text{Görväln/Prästfjärden: } UVA_{254} = (2,071 \pm 0,176) \cdot TOC \quad \text{eq. (14)}$$

$$\text{Ekoln: } UVA_{254} = (-18,506 \pm 1,568) + (4,602 \pm 0,419) \cdot TOC \quad \text{eq. (15)}$$

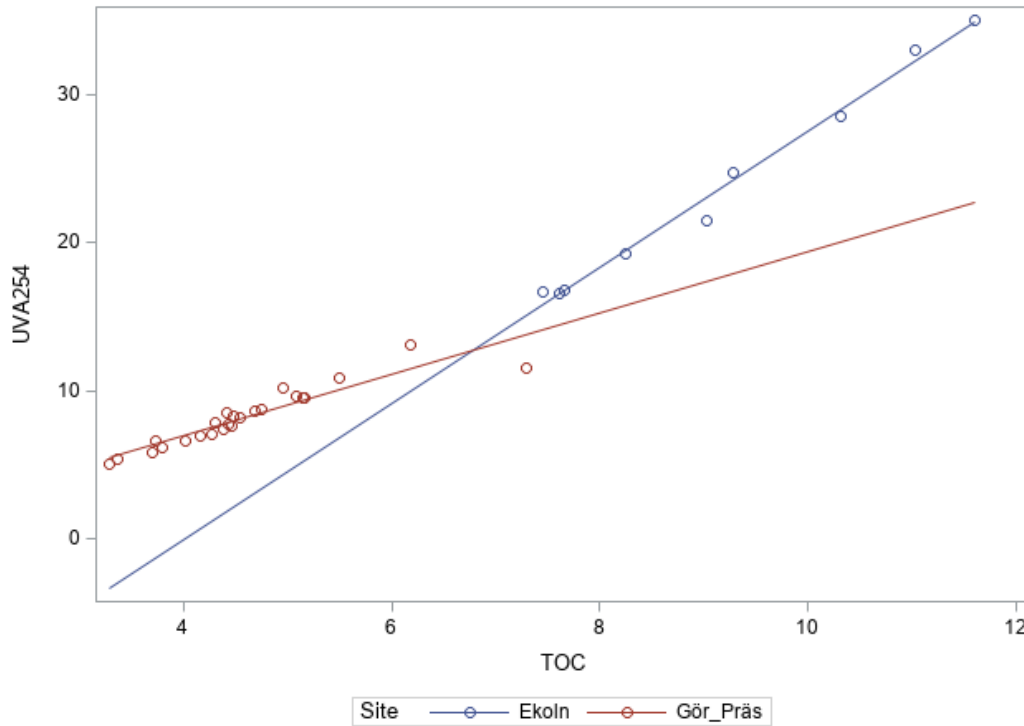


Figure 6: Regression of UVA_{254} against TOC for different water types. Görväln and Prästfjärden samples show no significant difference, while the regression with Ekoln samples is significantly different ($\alpha < 0,0001$).

4.2. Aluminiumchloride Dosage

Different aluminium concentrations were tested under a constant pH of 7, to evaluate the optimal dosing condition. The results from these trials are shown in Fig. 7. With increasing Al^{3+} concentration, a higher amount of NOM was removed from the raw water. However, around 6 mg Al^{3+}/l a saturation is reached. Higher coagulant dosages cannot improve the removal efficiency significantly further. With a maximal dosage of 16,7 mg/l, the permeate had a remaining fDOM content of 24,53 QSU and a TOC content of 4,16 mg/l, which is approximately half of the raw water value.

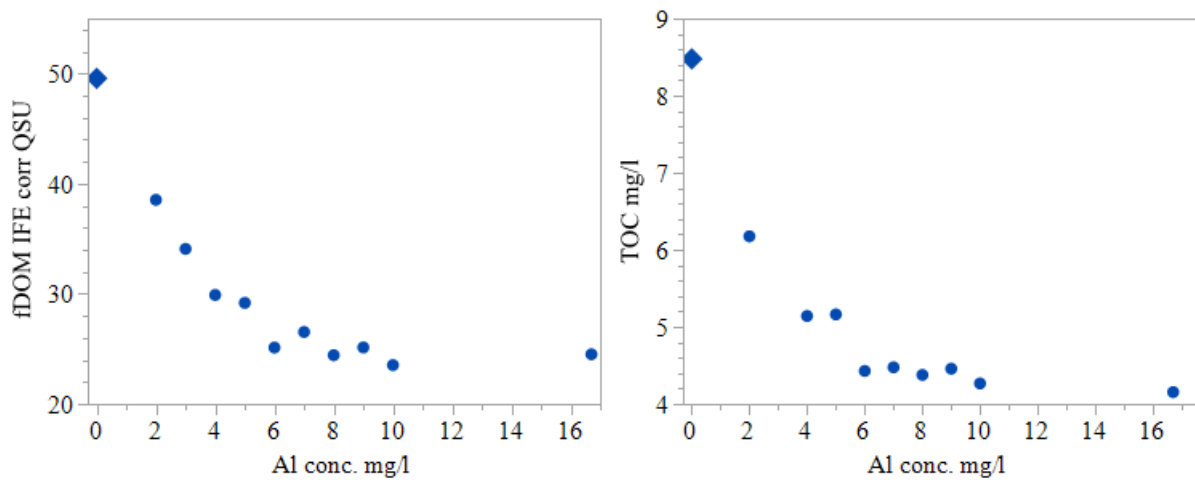


Figure 7: Remaining fDOM and TOC content in Görväln permeate water under varying Al concentrations at pH = 7 after UF, compared to raw water content (black square).

4.3. pH Adjustment

As the pH affects the formation and stability of flocs, it is an important aspect in finding optimal conditions for a maximal NOM removal. The effect of pH on the removal efficiency of NOM was tested with trials of varying pH at a constant medium Al^{3+} dosage (4 mg/l) and at a maximum Al^{3+} dosage (16,7 mg/l) (Fig. 8). It is clearly visible, that a higher pH decreases the removal of both, fDOM and TOC from the raw water, regardless of the coagulant concentration. At a pH = 6,1 the removal efficiency of TOC was 61% with 16,7 mg Al/l and 49% with 4 mg Al/l, whereas at a pH = 7, only 51% and 39% of TOC were removed, respectively. This gives a decrease of both, fDOM and TOC removal of 10% from pH 6 to 7.

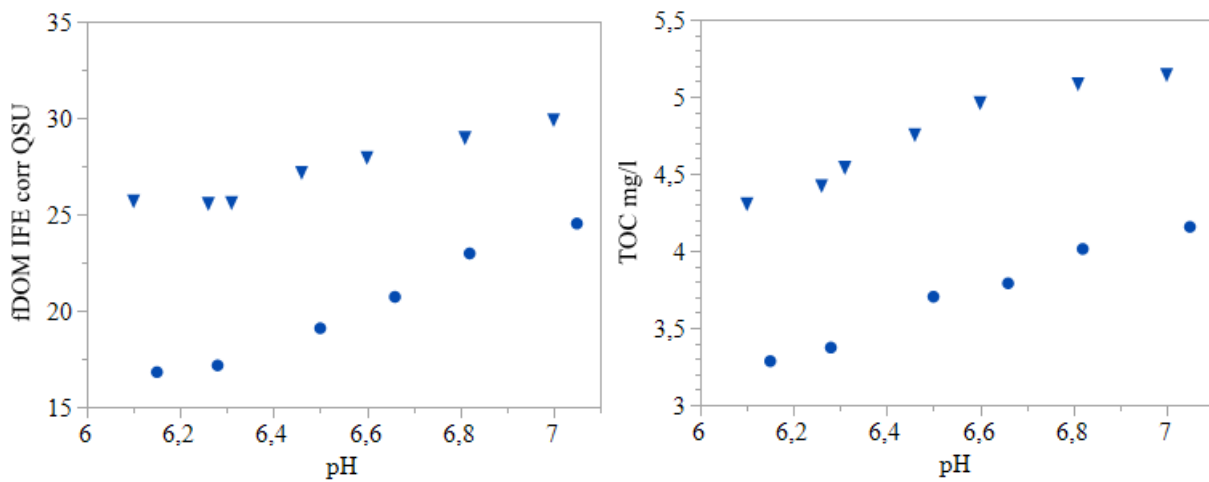


Figure 8: Remaining fDOM and TOC content in Görväln permeate water under varying pH with 4 mg Al/l (triangles) and 16,7 mg Al/l (circles), respectively.

4.4. Operation with Varying Water Qualities

Raw water from three different sample sites were filtered and analysed to evaluate the performance of the UF membrane for varying water qualities. This is of special interest, because the raw water quality for drinking water treatment might change over the years and the TOC content might increase. Characteristics of the three raw water types are shown in Table 2. The raw water samples from Görväln and Prästfjärden show only minor differences. Water from Görväln is slightly more alkaline and contains 0,47 mg/l more TOC. Noticeable is also a higher turbidity of ca. 1 FNU in the Prästfjärden water. More striking differences were found for the Ekoln samples. Ekoln water contains almost the double amount of TOC and more than double fDOM, compared to the other two water types. It is also highly alkaline (2,12 meq/l) and shows a much higher turbidity and colour. Moreover, it has a SUVA₂₅₄ of 3,52, indicating a large portion of aromatic humic substances (Weishaar *et al.* 2003).

Table 2: Raw water characteristics from Görväln, Prästfjärden and Ekoln.

Raw water	Görväln	Prästfjärden	Ekoln
pH	8,11	8,12	7,83
Alkalinity (meq/l)	1,09	0,73	2,12
DOC (mg/l)	8,08	7,66	14,36
TOC (mg/l)	8,48	8,01	15,52
Turbidity (FNU)	1,6	2,53	11
fDOM IFE corr (QSU)	49,58	43,16	82,96
UVA ₂₅₄ (m ⁻¹)	20,27	20,57	50,54
SUVA ₂₅₄ (l/(mg*m))	2,51	2,69	3,52
HIX	0,895	0,888	0,938
β:α	0,645	0,634	0,548
FI	1,5	1,46	1,48

The results of trials with all three water types treated with varying Al³⁺ concentrations at pH = 7 are shown in Fig. 9. The permeate from Prästfjärden water had lower fDOM and TOC than the Görväln water, however, the raw water also contains less NOM. Apparently, they follow a similar trend with increasing Al³⁺ concentrations, although slightly shifted on the y-axis. Nevertheless, a steeper decrease of fDOM and TOC was observed for the Ekoln samples, reaching a saturation at approximately 8 mg Al/l, compared to 6 mg Al/l for Görväln water. The relative removal efficiency of maximum 49 % fDOM and 47 % TOC from Ekoln waters is similar to the efficiencies for Görväln with 51 % fDOM and 46 % TOC, but remains lower than the values for Prästfjärden (57 % fDOM, 51 % TOC). Overall, the permeate from Ekoln water contains almost double the absolute amount

of TOC (7,6 mg/l) and fDOM (42,1 QSU) than in the ultrafiltrated Görvåln water under maximum Al dosage. Remarkably is also, that all Ekoln permeates still showed a slightly yellow colour, whereas Görvåln and Prästfjärden samples were transparent.

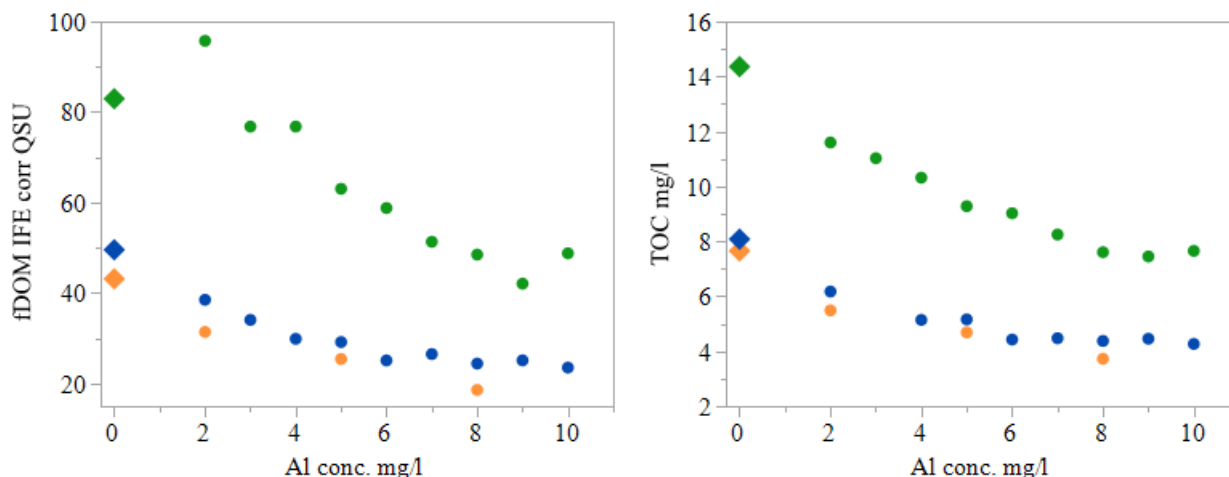


Figure 9: Remaining fDOM and TOC content in different permeate water types under varying Al concentrations at pH = 7 after UF, compared to raw water content (squares). Origin of raw waters: Ekoln (green), Görvåln (blue), Prästfjärden (orange).

A linear regression of the corrected fDOM values of the permeates against the amount of TOC in the three water types gives insight into the NOM that gets removed. The intersection with the y-axis gives the amount of non-fluorescent DOM that remained in the permeates after UF (Fig. 10). Interestingly, both, Görvåln and Prästfjärden samples show a leftover of approximately 1,2 mg/l non-fluorescent DOM, whereas 3,73 mg/l non-fluorescent DOM remain in Ekoln water samples. Comparing the raw water samples with the linear regression of the respective permeates indicates three times less removal of non-fluorescent DOM from Ekoln samples than from Görvåln or Prästfjärden waters. Remarkably, all three raw waters lay slightly above the linear regression of the permeates, showing that some non-fluorescent carbon could be removed. Most non-fluorescent carbon was removed from the Ekoln samples.

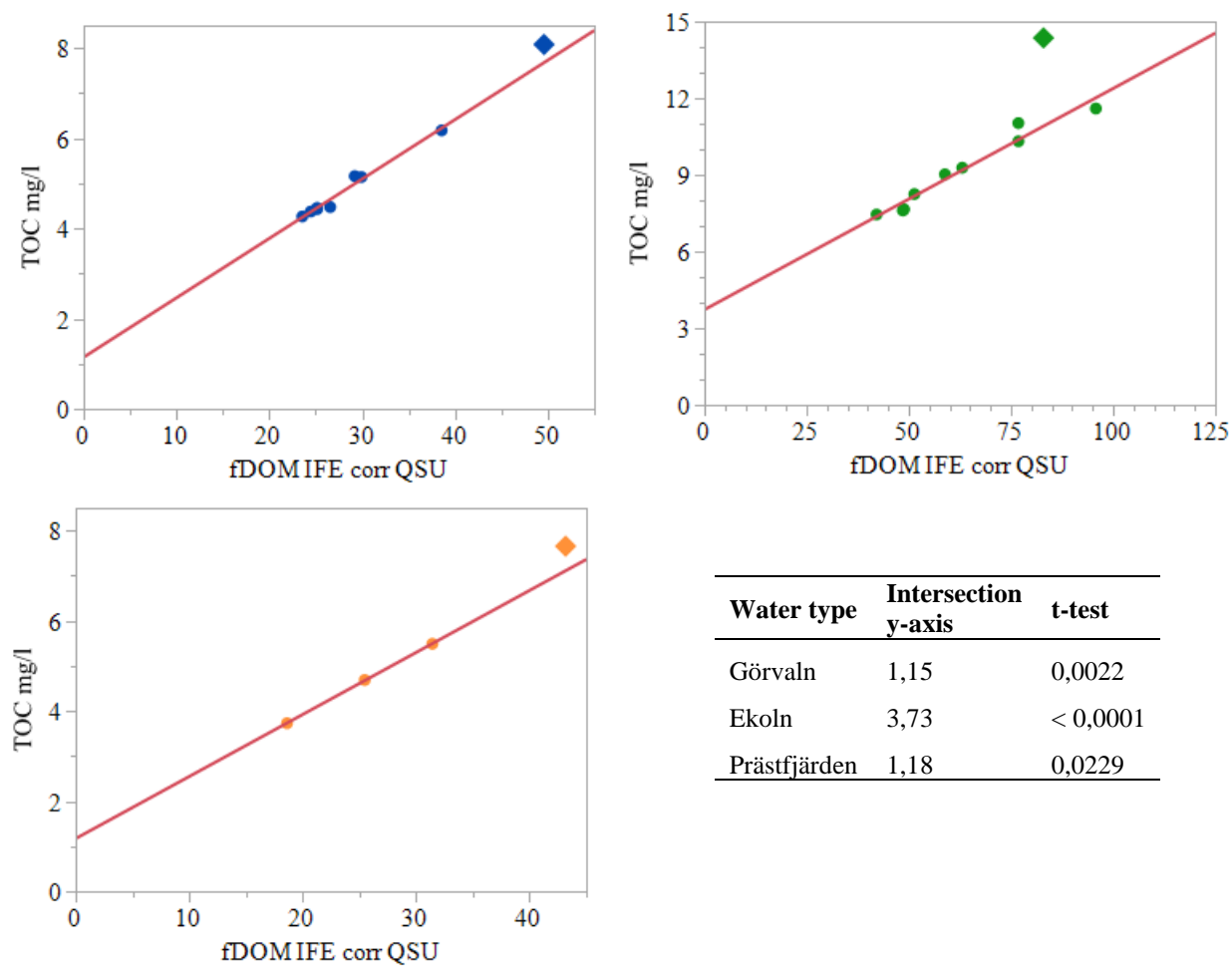


Figure 10: Linear regression of TOC as a function of fDOM IFE corr for all three water types (Görvaln: blue, Ekoln: green, Prästfjärden: orange). The intersection with the y-axis shows the proportion of non-fluorescent DOM in the permeate. The squares show raw water as reference (excluded from regression).

4.5. Fluorescence Measurements

Fluorescence and absorbance analyses of the raw water samples and permeates were done to investigate the nature of NOM that was removed or remained in the waters even after UF.

The $SUVA_{254}$ is clearly reduced for all three water types (Fig. 11). For Görväln and Prästfjärden waters it was reduced from 2,51 and 2,67 l/(mg*m) to 1,67 and 1,75 l/(mg*m), respectively. The strongest reduction was observed in the Ekoln water samples from 3,52 to 2,18 l/(mg*m), nevertheless the absolute $SUVA_{254}$ level remains the highest.

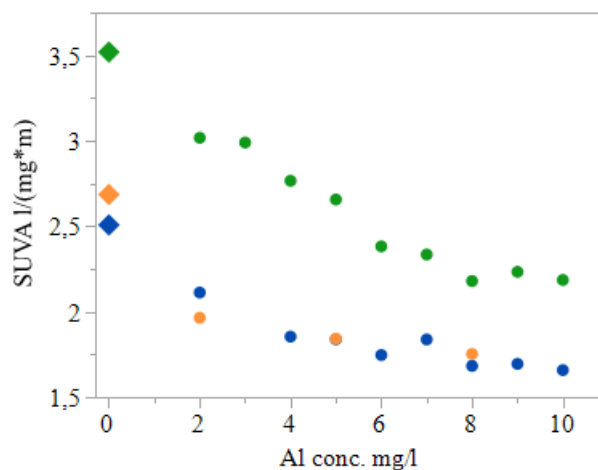


Figure 11: Specific ultraviolet absorbance at 254 nm after UF with varying Al concentrations for different water types, compared to their raw waters (squares). Origin of raw waters: Ekoln (green), Görväln (blue), Prästfjärden (orange).

Regarding the type of NOM that is removed from raw water, fluorescence indices from all water types give important hints (Fig. 12) The degree of humification was slightly, but significantly decreased with increasing coagulant dosing for all three water types ($\alpha < 0,05$). More obvious are the changes for the freshness and fluorescence indices. All three waters show a clear shift towards more recently derived DOM after UF, showing that with increasing Al^{3+} concentration the proportion of decomposed DOM decreases. Furthermore, the share of microbially derived DOM increases with increasing coagulant dosing. More and more terrestrially derived DOM is removed from the waters. Generally speaking, all three water types show the same relative shifts for the three fluorescence indices, however the absolute values of Ekoln water samples differ. The raw water as well as the permeates show a higher degree of humification, a higher share of

decomposed DOM and, despite of similar FI values in the raw water, more terrestrially derived DOM remaining in the permeate.

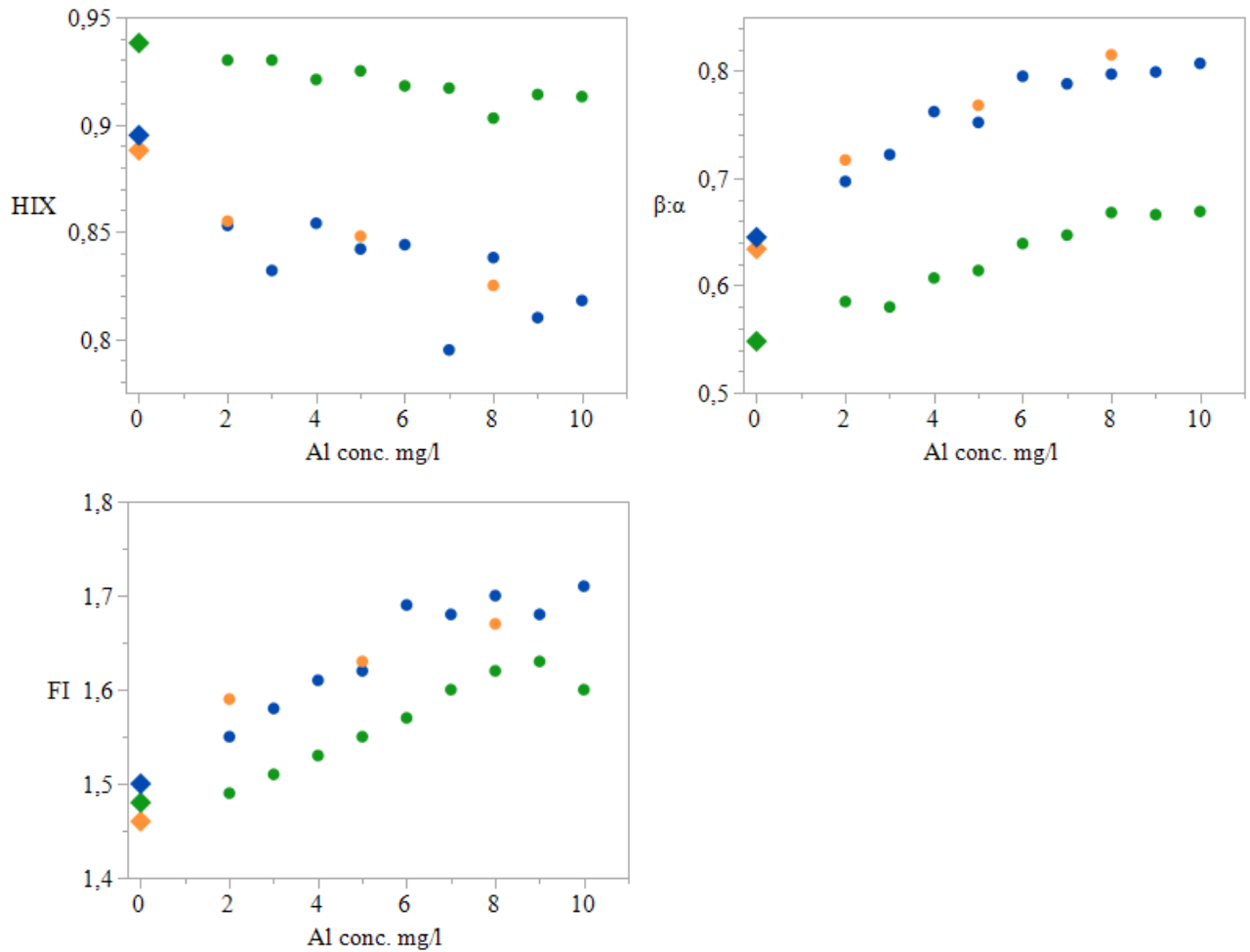


Figure 12: Fluorescence indices of the permeates of Görvåln (blue), Ekoln (green), Prästfjärden (orange) under varying Al conc. and the respective raw waters (squares).

4.6. Iron Chloride as Coagulant

A better performance of iron chloride compared to aluminium sulphate as a coagulant for in-line UF was reported by literature lately (Park *et al.* 2002; Matilainen *et al.* 2005). Thus, a trial with iron chloride was carried out for comparison. However, our findings rather show a slightly reduced efficiency of NOM removal with iron chloride as coagulant (Fig. 13). At a concentration of 8 mg Fe^{3+}/l , 5,01 mg/l TOC and 29,41 QSU fDOM were left in the water, compared to 4,378 mg/l TOC and 24,44 QSU fDOM with 8 mg Al^{3+}/l . This is equivalent to a reduced removal efficiency with iron chloride of 7 % for TOC and 12 % for fDOM, compared to aluminium chloride as coagulant.

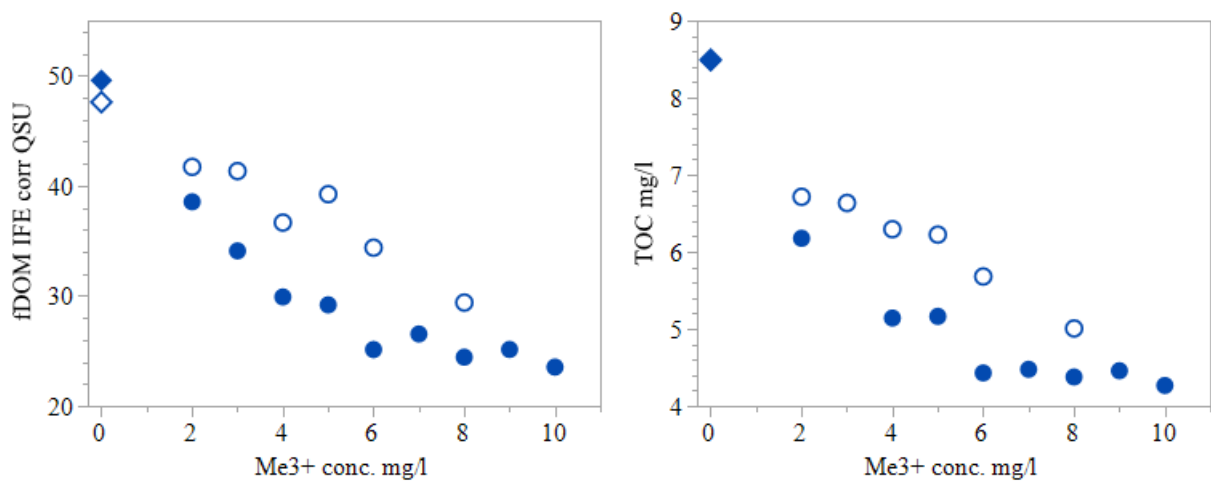


Figure 13: Comparison of the remaining fDOM and TOC content after online UF with the coagulants aluminium chloride (filled) and iron chloride (unfilled), and the respective raw water (squares).

Remarkable is also, that the formed flocs with iron appeared to be smaller and less dense than those with aluminium (fig. 14).

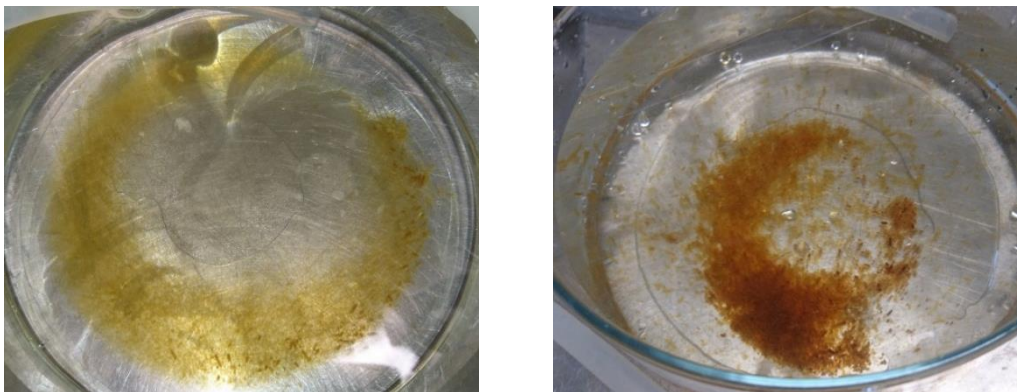


Figure 14: Flocs that were washed out of the UF membrane during backwash. Coagulants: aluminiumchloride (left) and ironchloride (right)

4.7. Pressure and Permeability

TMP and permeability were documented and calculated, to compare how these are influenced by differing pH, coagulant dosing, or the membrane module itself. However, all results are scattered in a range of 0,09 – 0,15 bar TMP and permeabilities between 500 to 900 LMH/bar. In comparison, in the large pilot plant permeabilities are measured in a range of 300 to 500 LMH/bar, which is circa one-fold less than in the small pilot. A correlation between either TMP or permeability and coagulant dosing, pH or the membrane module itself could not be found (Fig. 15).

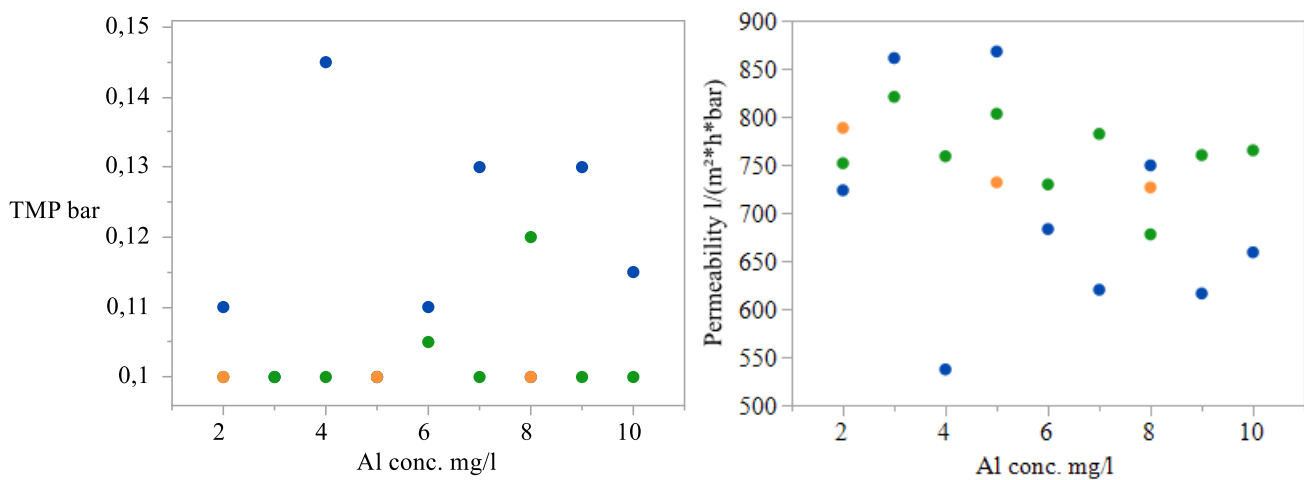


Figure 15: TMP and Permeability against aluminium concentration for the water types Görvåln (blue), Ekoln (green) and Prästfjärden (orange). There is no correlation visible.

4.8. Comparing the Small and the Large Pilot Plant

To examine the comparability of the small pilot plant to the large pilot plant, samples from the large pilot plant were analyzed for UVA₂₅₄ and DOC content as well. These results correlate highly with the respective analyses that were performed by the lab at the DWTP Norrvatten and hence can be seen as reliable (Fig. 16).

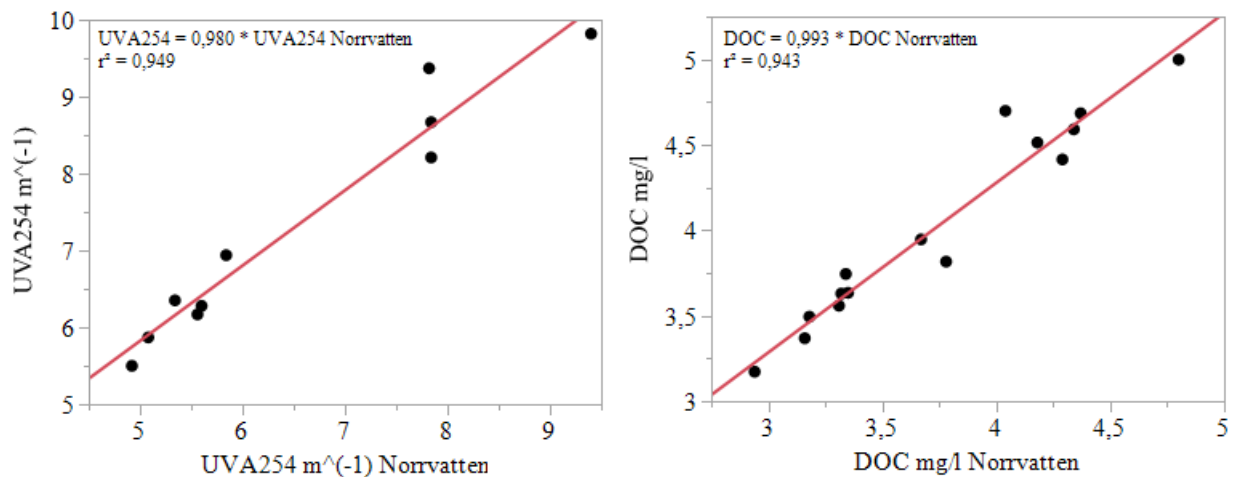


Figure 16: Correlation of measurements from SLU and Norrvatten, for UVA₂₅₄ (left) and DOC (right), respectively. Differences are around 2% for UVA₂₅₄ and 0,7 % for DOC.

Figure 17 shows the removal of UVA_{254} and DOC for varying Al concentrations by the large pilot plant, compared to the small one. The curve shapes are similar for both pilot plants. However, the removal efficiency by the large pilot plant is generally ca. 8 – 10 % higher, than by the small pilot plant. Taking the SUVA_{254} into account, a significant tendency cannot be observed for the large pilot plant data, but the absolute values of filtered samples are found within the range of 1,6 to 2 $\text{l}/(\text{mg}\cdot\text{m})$, such as the values from the small pilot plant (Fig. 18).

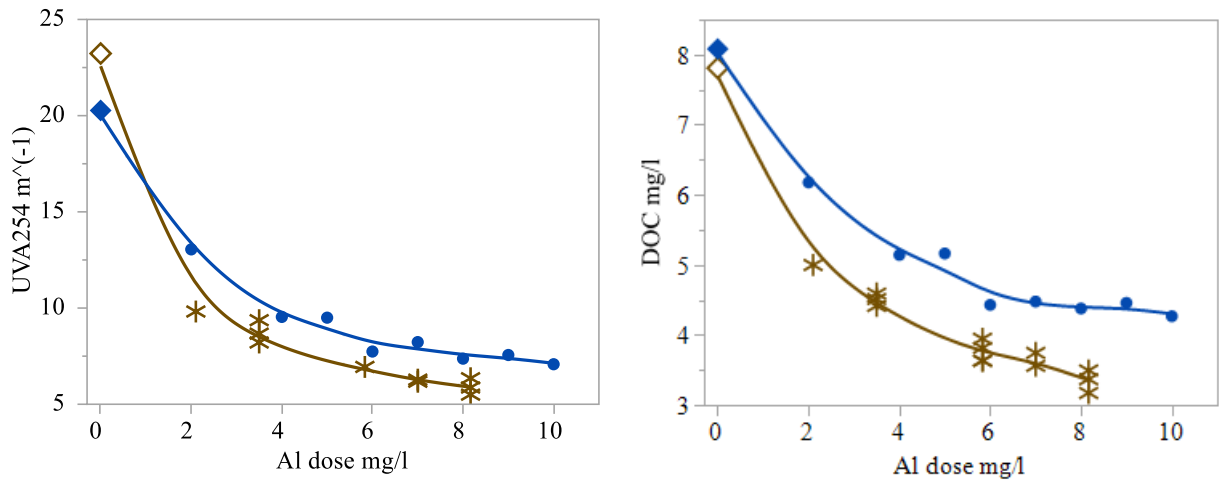


Figure 17: Comparison of the small (blue) and the large (brown) pilot plant, regarding the remaining UVA_{254} (left) and DOC (right) in permeate against Al dosage at $\text{pH} = 7$.

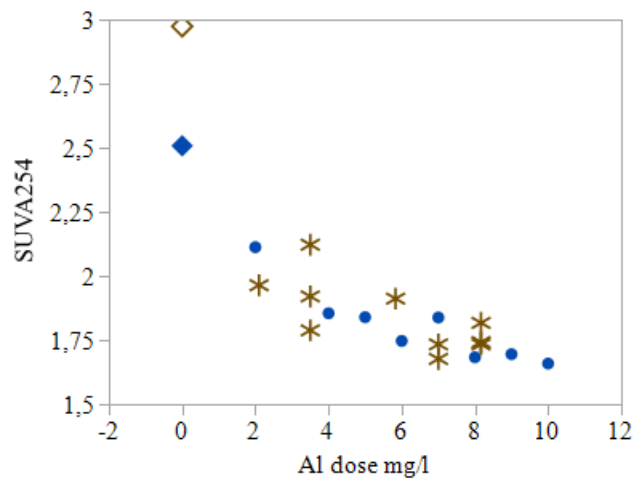


Figure 18: Comparison of the small (blue) and the large (brown) pilot plant, regarding the remaining SUVA_{254} against used Al dosage at $\text{pH} = 7$

5. Discussion

5.1. fDOM Calibration

fDOM is a subset of cDOM and cDOM is well detectable by UV absorbance at a wavelength of 254 nm (Lavonen 2015; Cascone 2019). Therefore, it has to be assumed that some measured fluorescence in the Ekoln samples does not originate from fDOM (Fig. 3). Thus, a correction of the Ekoln samples was necessary to ensure comparability. However, a constant offset but similar slopes (Fig. 4) is very surprising and points to some unknown fluorescent substance that does not absorb light at 254 nm and is unaffected by coagulation and ultrafiltration.

One possible explanation is an interference with fluorescent iron compounds in the water. Water from lake Ekoln contains approximately 0,5 mg/l iron, whereas Görvåln and Prästfjärden water only contains 0,05 mg/l.

Another interesting aspect is that Ekoln samples have a much higher chlorophyll content. Chlorophyll from hydrolized cells would actually pass the UF membrane and might have a significant influence on the fDOM measurement. In a previous study with Mälaren water samples, modelling TOC from fDOM and chlorophyll content was preciser than modelling TOC only from fDOM values (Köhler & Hoffmeister, personal communication). This shows that Chlorophyll has an influence on fDOM measurements, indeed. However, they didn't observe a constant offset, but models showing differing slopes.

This should be further elaborated in laboratory experiments with Ekoln and Görvåln raw water samples and varying Chlorophyll concentrations.

5.2. Comparability with the Large Pilot Plant

The measured fDOM and TOC results compared to measurements with the large pilot strengthen the assumption that the performance of the small pilot plant is highly comparable to the large pilot plant, as they follow very similar trends of UVA₂₅₄ reduction and TOC removal for an increasing Al dosage.

Both curves flatten at around 6 mg Al/l, although the saturation seems to be a little later for the large pilot plant (Fig. 17). This, as well as the systematic 8-10 % lower removal by the small pilot plant could have several reasons. Firstly, the stirring velocity and the retention time in the stirrer differ in the two pilots. They are very difficult to adjust similarly, as the structure of the pilot prior to the membrane module varies in size and construction. The velocity of stirring can influence the floc formation, but also the possible breakage of already formed flocs (Hémion 2017). In a previous study with the small pilot plant, Hémion (2017) could not find any effect of the stirring velocity on NOM removal from Mälaren water with aluminium sulphate. However, he showed an impact of stirring on a different water type with ferric chloride. As the influence of stirring on polyaluminium chloride has not been tested before, this should be considered. Finding the optimal stirring condition is a balancing act and should be taken into account in further comparative studies.

Another aspect is the differently performed backwashing, which could affect the cake formation and cake structure on the membrane. The automated backwash program performed by the large pilot plant can maintain continuous, high pressure and is performed whenever the TMP increases above 0,6 bar. Whereas the small pilot plant is regularly backwashed every 30 minutes or if the absolute outflow pressure increases above 0,65 bar. This means that the time span between two backwashes differs for both pilot plants. A longer operating time without a backwash would result in a thicker and denser cake layer (Gao *et al.* 2011). This could improve the filtration through the cake on the one hand but might also increase the reversible fouling of the membrane.

The high similarity of the SUVA₂₅₄ values from both pilot plants (Fig. 18) indicate that the type of removed NOM is similar. Thus, it can be assumed that the removal mechanisms are the same for both pilot plants.

All in all, the main purpose of the small pilot plant is its use as a fast, easy and cheap testing facility for online-coagulation performance studies under varying conditions. Highly precise predictions for the large pilot are not required. The systematic differences are therefore unproblematic and can be cross-calibrated in future studies. The small pilot plant proved to be a useful tool to predict general

trends for online coagulation. Such pretrials could support the DWTP Görvålnverket from Norrvatten in their decision-making and implementation of future treatment technology.

5.3. Optimal Operating Conditions

With a maximum Al dosage of 16 mg/l at pH = 6 the highest reduction of NOM was reached (< 20 QSU fDOM). However, applied on large scale water treatment, this would also mean a production of huge amounts of sludge and a high consumption of chemicals, which is neither ecologically nor economically desired (Keucken *et al.* 2017). Additionally, a pollution of the produced drinking water with surplus Al^{3+} -ions has to be avoided to fulfil the legal limit values for aluminium.

Therefore, a dosage should be selected that allows a greatest possible NOM removal with minimal use of resources. Increasing the dosage over 6 mg Al/l only leads to a minimal further increase in NOM removal, as most removable NOM is already bound. Hence, we recommend a dosage of maximum 6 mg Al/l.

At a pH of 7, a removal efficiency of almost 50 % is still reached. In this study, 4,5 mg /l DOC remained in the permeate, which is just below the recommended limit of 5 mg /l carbon for Mälaren water in Sweden (Köhler *et al.* 2016). The removal efficiency could be further increased by maximal 10 % in a more acidic (pH = 6) environment.

Without pH adjustment, a UF with 6 mg Al/l would take place at a pH of approximately 6,7 with a slightly increased NOM reduction. Taking the even better performance of the large pilot plant into account, we recommend avoiding a further acidification by adding H_2SO_4 , as the legal limits should already be fulfilled under these conditions. This saves not only acid, but also base in the necessary alkalization step after treatment. Still, an acidification could be a useful measure to improve the UF efficiency. Especially in cases of sudden decreases in raw water quality, as they occur for example during extreme weather events, this should be considered.

5.4. Membrane Performance with Differing Water Quality

Dealing with strong and long-term changes in raw water quality in the future might be more challenging. Increases of TOC concentrations in Nordic lakes were often studied and predicted for the future (Ledesma *et al.* 2012; Valinia *et al.* 2015). However, there are numerous proposals on the reasons and mechanisms and thus,

the predictions are still vague (de Wit *et al.* 2007; Finstad *et al.* 2016; Meyer-Jacob *et al.* 2019).

The water from Ekoln serves as an example for a raw water of lower quality. It has almost double the TOC content of raw water used at Görvålnverket. This explains that a higher Al dosage of at least 8 mg Al/l is necessary to bind all free NOM and reach saturation in the Ekoln water (Fig. 9).

Interestingly, the relative removal efficiencies are very similar for all three water types. This indicates that regardless the total amount of TOC in the raw water, only specific types of NOM can be removed by coagulation and ultrafiltration, making up around 50 % of the TOC content. The other half is more difficult to remove and seems to be consistent all over Mälaren. Further pilot trials with water from other Swedish lakes or streams in varying catchments could give further insight.

The high remaining absolute TOC content in Ekoln permeates is problematic, as it is far above the legal limit. Further cleaning steps and decolouring would therefore be necessary.

The linear regression analysis of TOC as a function of fDOM revealed, that Ekoln permeate contains a higher amount of non-fluorescent organic carbon of 3,37 mg/l, compared to 1,2 mg/l in Görvåln and Prästfjärden permeate samples (Fig. 10). It also shows that more non-fluorescent organic carbon was removed from Ekoln water than from the other water types, because the raw water sampling point is furthest above the respective regression line.

5.5. Optical Characterization of Removed NOM

The specific ultraviolet absorbance and optical indices give important hints on the composition of NOM in lake waters and on the removal of NOM for drinking water cleaning.

A removal of NOM by coagulation from waters with high SUVA₂₅₄ values is more efficient and becomes more difficult for waters with low SUVA₂₅₄ values (<2) (Lavonen 2015). This can also be seen in this study, as the SUVA₂₅₄ decreases with higher amounts of coagulant, but stagnates around 1,7 (Fig. 11). The decrease of SUVA₂₅₄ after inline coagulation shows that mainly humic, aromatic DOM of high and medium molecular weight is removed (Weishaar *et al.* 2003; Ghernaout *et al.* 2009). These compounds are characterized by a high O:C-ratio, but low H:C-ratio and occur typically in lignin-derived, terrestrial DOM (Lavonen *et al.* 2015).

This assumption is strengthened by the observed slight decrease of HIX (Fig. 12), an indicator for the degree of humification and a low H:C-ratio (Fellman *et al.* 2010).

The $\beta:\alpha$ index was reported as a valuable tool to report the removal of NOM from lake water, as it correlates with the used Al dosage (Köhler *et al.* 2016; Keucken *et al.* 2017). Similar correlations were also found in this study for both, the $\beta:\alpha$ index and the fluorescent index. This indicates a higher removal of decomposed, allochthonous over more recently derived, autochthonous DOM, which is mostly left over in the permeates.

All three indices show a worse water quality of the Ekoln permeate, compared to Görvåln and Prästfjärden waters and a higher remaining proportion of humic, terrestrially derived and decomposed DOM, but similar relative changes for FI and $\beta:\alpha$. Nevertheless, only a minor decrease of the HIX is reached through ultrafiltration. This might indicate that the Ekoln raw water contains additional humic substances, that are more difficult to remove.

5.6. Iron chloride as an Alternative Coagulant?

A better performance of iron chloride compared to aluminum chloride, as found for instance by Park *et al.* (2002) and Matilainen *et al.* (2005), could not be verified in this study (Fig. 13). The overall removal efficiency was significantly worse, compared to the trials with aluminium chloride.

A possible explanation for this is the high pH, at which the flocculation took place. In beaker trials, that were conducted at the DWTP Norrvatten, samples with iron chloride showed a lower remaining DOC after flocculation and filtration at a very low pH of ca. 5,5, compared to aluminium sulphate and -chloride. However, conducted at a high pH of ca. 7,5, the filtrate had a three times higher remaining DOC content, which was also significantly higher than under usage of aluminium sulphate and -chloride (Hugg 2019).

From this information, it can be inferred that flocculation with iron chloride is more pH-dependent and the floc quality decreases strongly in neutral or slightly alkaline conditions.

Probably, trials with iron chloride at low pH would show a better removal efficiency, but this would lead to a higher consumption of acids and bases for pH adjustment (as discussed in 5.2.). Therefore, from the current state of results, aluminium chloride is to be preferred over iron chloride for in-line coagulation.

Additionally, it should be considered that the used polyaluminium chloride has been prepolymerized and hence, bigger flocs will form and the formation will be faster. Whereas the iron chloride used has not been prepolymerized. This is strengthened by the observation that iron flocs seemed smaller and less dense than aluminium flocs (Fig. 14).

5.7. Pressure and Permeability

Meaningful pressure and permeability differences for the small membrane could not be found (Fig. 15). This is probably due to the great imprecision of the analog manometers that are read off by hand.

Thus, an error calculation for flux, TMP and permeability is performed. The accuracy of the pressure values is around $\pm 0,04$ bar. The flow rate is also measured by hand and has a precision of approximately $\pm 0,06$ l/h. The temperature sonde has a comparable high accuracy of $\pm 0,01$ °C and due to the minor correcting effect and high accuracy of temperature on the permeability, it is neglected for the error calculation here.

$$\Delta f_{Flux} = \frac{0,06 \text{ l/h}}{0,08 \text{ m}^2} = 0,75 \frac{\text{l}}{\text{h} \cdot \text{m}^2}$$

eq. (16)

$$\Delta f_{TMP} = \sqrt{(\Delta x)^2 + (\Delta y)^2} = \sqrt{0,04^2 + 0,04^2} \text{ bar} = 0,057 \text{ bar}$$

eq. (17)

$$\frac{\Delta f_{Perm}}{f_{Perm}} = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2} = \sqrt{\left(\frac{0,75}{75}\right)^2 + \left(\frac{0,057}{0,108}\right)^2} = 0,528$$

eq. (18)

The results show a mean flux of $75 \text{ LMH} \pm 0,75 \text{ LMH}$, a TMP of $0,108 \text{ bar} \pm 0,057 \text{ bar}$ and a mean permeability of $734 \text{ LMH/bar} \pm 52,8 \%$. Consequently, the pressure and permeability data are not meaningful or evaluable.

The analog manometers installed on the small pilot plant are valuable to control the overall pressure applied on the membrane. This is important to protect it from pressure damage. However, to evaluate the TMP and permeability development

under changing coagulant conditions and over a longer time span, a more precise pressure measuring instrument would be needed, as it is installed in the large pilot plant. Permeability and TMP can be important indicators for the functionality of the membrane and can help to find out when a backwash or CEB is needed.

5.8. Possible Future Applications and Challenges

Further experiments should include a more differentiated study with several different raw water qualities, to deepen the understanding of DOM removal from waters with high DOM content and with higher contents of autochthonous DOM. Moreover, mass spectrometry, such as FT-ICR-MS performed by Lavonen *et al.* (2015), could give further insight into the chemical structures, size and element ratios of unremoved DOC compounds. This might be useful to evaluate the limits of online coagulation in more detail and find solutions for their removal in a possible further treatment step, if needed.

Additionally, iron chloride could be considered as alternative coagulant at low pH, especially for raw water with high DOM content. It is possible that it can remove significantly more DOC, if operated at a low pH around 6. This could be tested on the small pilot to prevent damage of the large membrane.

Another important aspect in the water treatment process with ultrafiltration is the removal of bacteria and viruses. Ultrafiltrated samples should be analyzed for example with flow cytometry, to see if any bacteria or viruses are left over. If the membrane is able to remove them completely, a disinfecting step with UV-light might be unnecessary in the future. This would also solve the problem of disinfection by-products that form regularly during UV-treatment from DOM residues in drinking water (Jacangelo *et al.* 1995; Lavonen *et al.* 2013).

6. Conclusion

The removal of NOM is an ongoing challenge in drinking water treatment, as NOM is increasing in surface waters in Northern Europe. In the DWTP Norrvatten in Stockholm, a large-scale container pilot plant with online UF is currently tested for future drinking water treatment.

The main goal of the present study was to compare a table-scale UF pilot plant with the container-scale pilot plant in Stockholm. The removal of NOM from lake water by a hollow-fibre membrane and polyaluminium sulphate as coagulant was examined.

Optimal operating conditions include high coagulant dosing (≥ 6 mg/l) and an acidic environment (pH=6). Yet, an operation at pH=7 is recommended to reduce the need for pH adjustments and to save resources.

Comparing water types of differing quality and NOM content, similar removal efficiencies of up to ca. 50 % were documented. Treating raw waters with high TOC contents (≥ 15 mg/l) may be challenging, because of the quite high absolute TOC remains after filtration (7,6 mg/l in Ekoln permeate). Additional cleaning steps might be necessary if the raw water quality decreases strongly in the future.

Fluorescence and absorbance measurements proved to be helpful techniques to characterize NOM. Increasing $\beta:\alpha$ and freshness indices with increasing coagulant concentration showed a preferred removal of allochthonous, aromatic NOM, whereas autochthonous, aliphatic NOM mainly remains in the permeate.

Iron chloride was tested as an alternative coagulant, but showed less effective NOM removal at a pH=7. A better flocculation and thus, improved NOM removal might occur at lower pH. This should be studied further in the future.

All in all, the small-scale pilot plant proved to be a valuable system to pretest any challenging aspects, before it is applied on the large pilot or on a future DWTP. One sample can be tested within 1 hour, including necessary preparations. Furthermore, risky trials, where the effect on the membrane is unknown and a

damage is possible, can be pretested on the small pilot. A membrane module exchange is much cheaper and easier than in the large pilot plant.

The study contributes to the deeper understanding of NOM removal by ultrafiltration. The small-scale pilot plant described in this study may be of assistance to Norrvatten in their decision-making and implementation of online ultrafiltration as a future water treatment technology.

7. Acknowledgements

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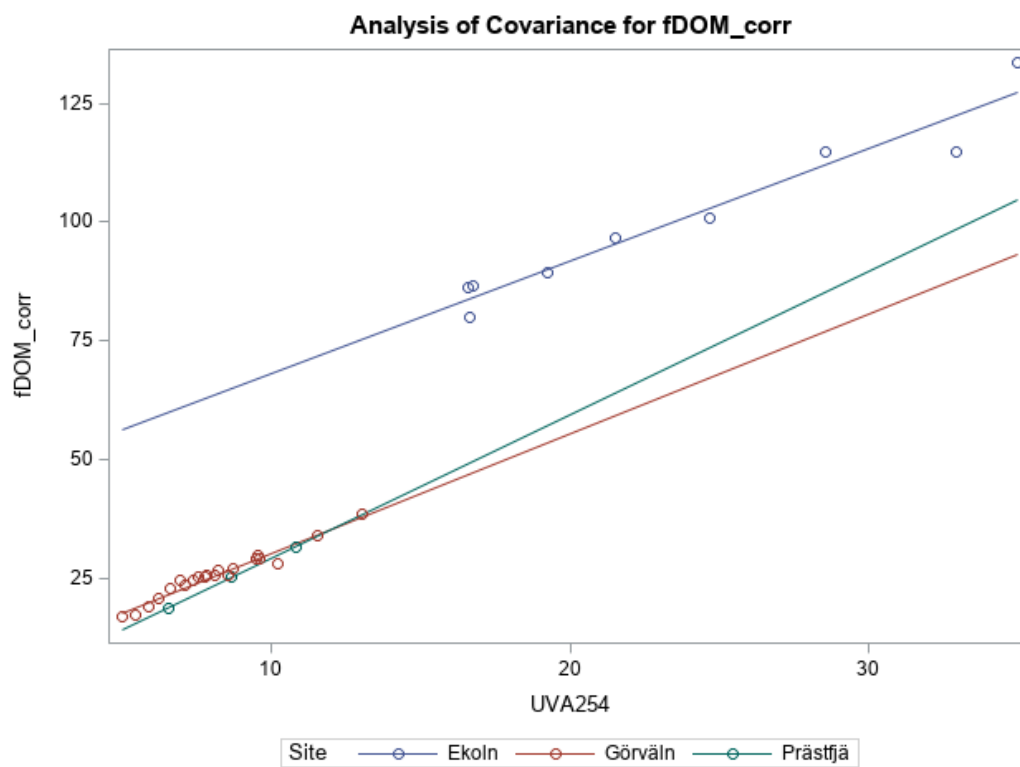
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9. Appendix

a. fDOM Calibration

- ANOVA for fDOM against UVA254 – Do the slopes differ among the different water types?

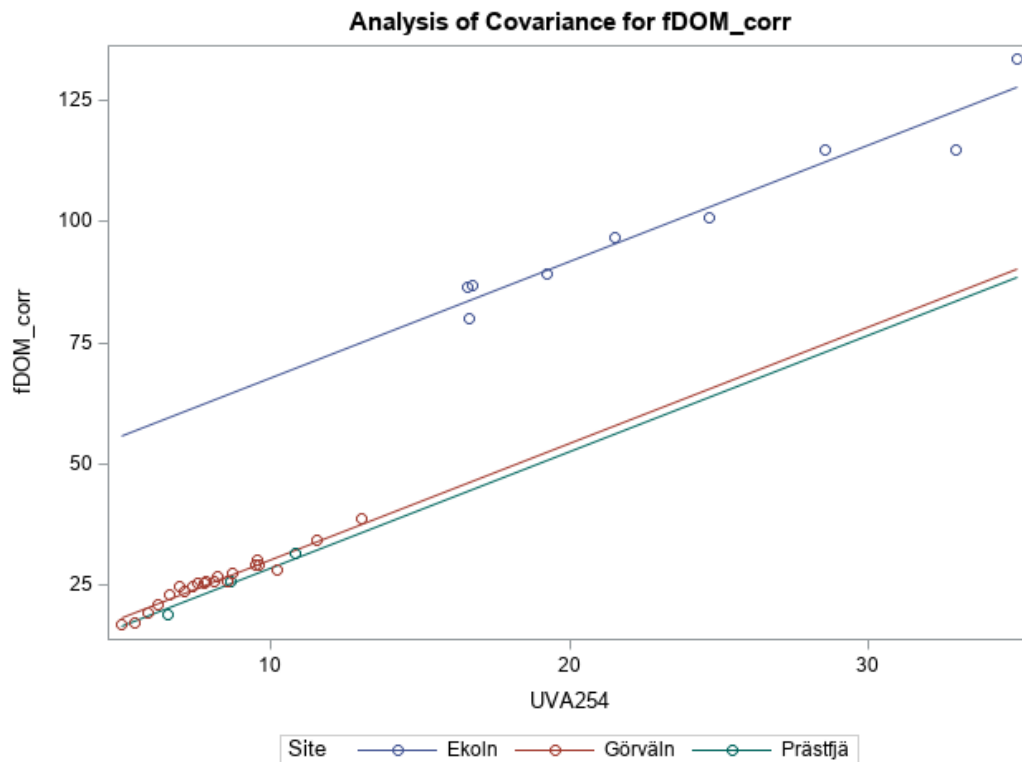


A 1: ANOVA for fDOM against UVA254 – Do the slopes differ among the different water types?

A 2: ANOVA table for fDOM against UVA254 – the slopes are the same for all three water types.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
UVA254	1	495.2463902	495.2463902	80.42	<.0001
Site	2	705.0564718	352.5282359	57.24	<.0001
UVA254*Site	2	4.7402444	2.3701222	0.38	0.6842
R-Square					
0.995801					
Coeff Var	5.397931				
Root MSE	2.481591				
fDOM_corr Mean		45.97300			

- ANOVA for fDOM against UVA254 – Do the intercepts with the y-axis differ among the different water types?

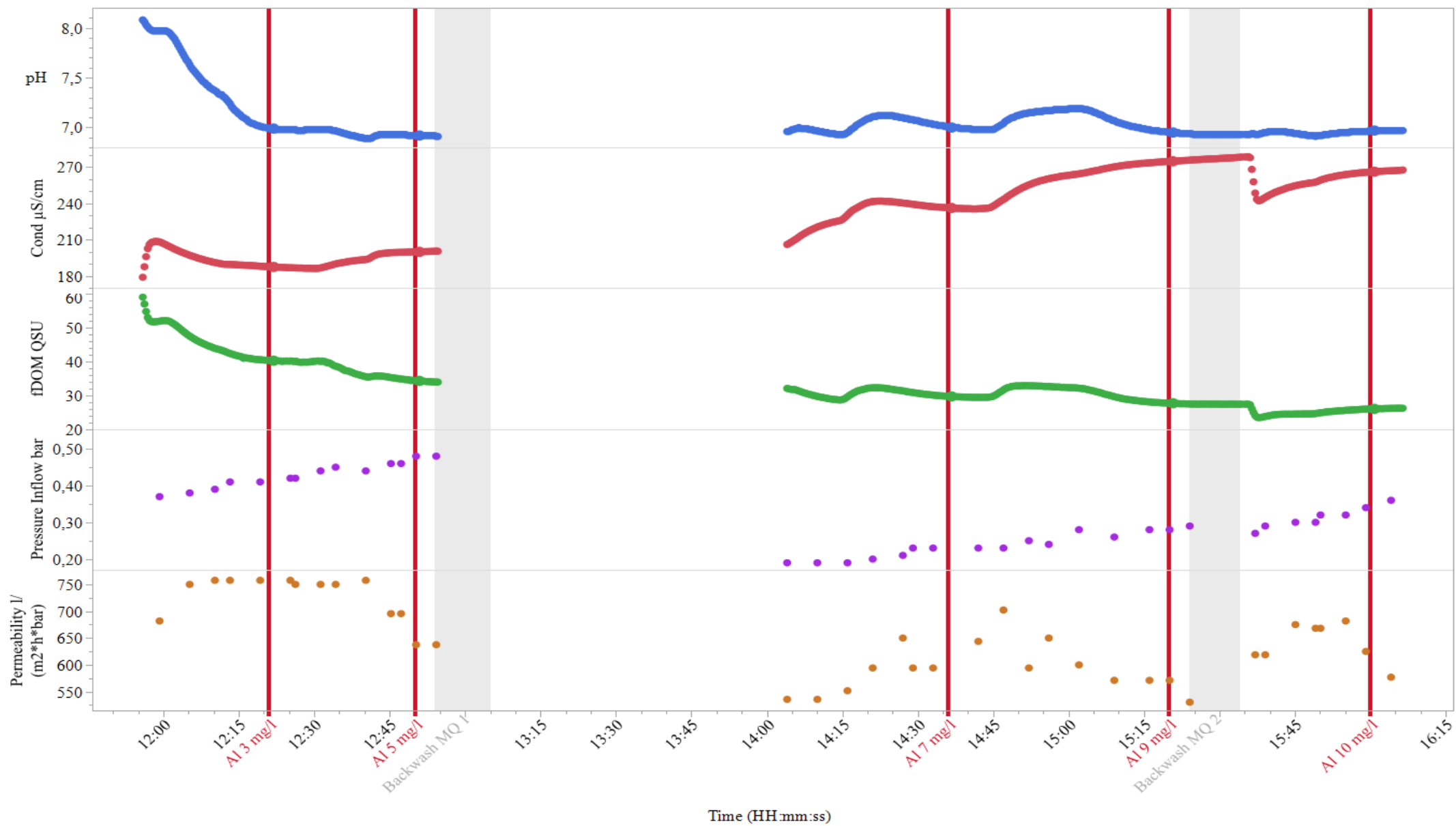


A 3: ANOVA for fDOM against UVA254 – Do the intercepts with the y-axis differ among the different water types?

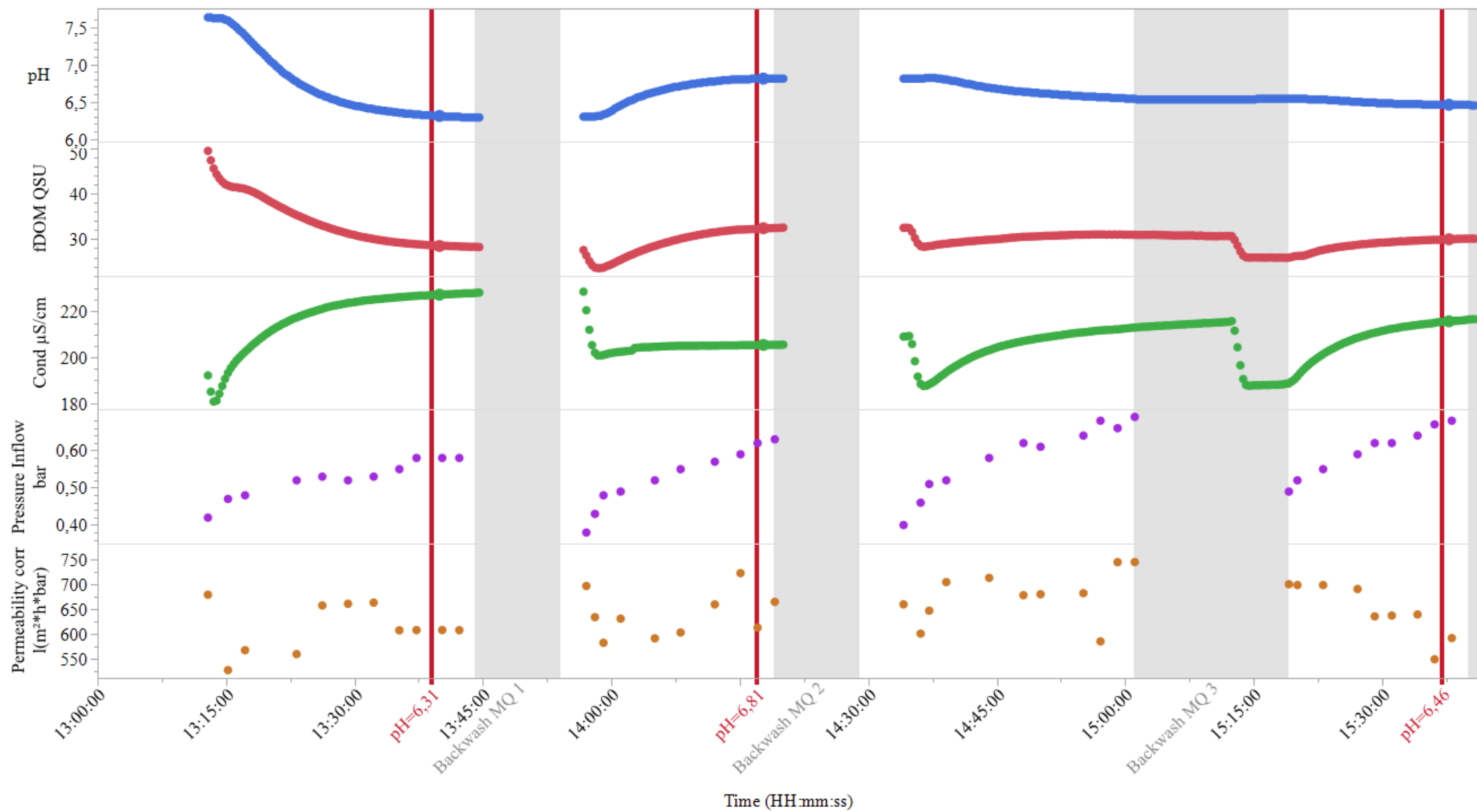
A 4: ANOVA table for fDOM against UVA254 – only Ekoln water samples have a different intercept with the y-axis than Prästfjärden and Görvältn samples. For Prästfjärden and Görvältn, the intercepts are not significantly different.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
UVA254	1	2884.888439	2884.888439	489.21	<.0001
Site	2	2303.011680	1151.505840	195.27	<.0001
Parameter	Estimate		Standard Error	t Value	Pr > t
Intercept	4.36265932	B	1.68839365	2.58	0.0151
UVA254	2.40362467		0.10867239	22.12	<.0001
Site Ekoln	39.34005880	B	2.28928392	17.18	<.0001
Site Görvältn	1.77509448	B	1.49996071	1.18	0.2463
Site Prästfjä	0.00000000	B	.	.	.
R-Square	Coeff Var	Root MSE	fDOM_corr	Mean	
0.995681	5.282192	2.428382		45.97300	

b. High Frequency Analysis - Examples



A 5: Trial with varying Al^{3+} dosages at constant $\text{pH} = 7$, measured with a high-frequency EXO sonde



A 6: Trial under varying pH at maximal Al^{3+} dosage of 16,7 mg/l

c. Membrane Element Datasheet

X-FLOW RX3000.83UFC ULTRAFILTRATION MEMBRANE

MEMBRANE ELEMENT DATASHEET

1" RX300 0.83UFC 0.83mm
ARTICLE CODE : 1051BL895A

GENERAL INFORMATION

RX300 0.83UFC is an ultrafiltration pilot module, used for production of process and potable water. Typical applications are the filtration of surface water, potable water and WWTP effluent. Mode of operation is feed-and-bleed with a minor crossflow or dead-end mode with regular backwash (permeate only) and chemically enhanced backwash.

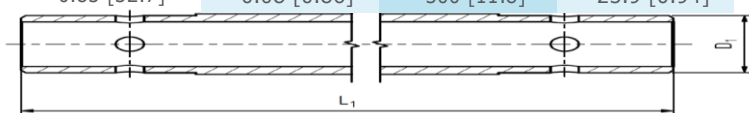
MEMBRANE CHARACTERISTICS

Materials of Construction

Housing	PSF
Potting	EP resin
Membrane	PES/PVP

ELEMENT SPECIFICATIONS

Hydraulic membrane diameter [mm/mil]	Membrane area [m ² /ft ²]	Element length L ₀ [mm/Inch]	Element outer diameter [mm/Inch]
0.83 [32.7]	0.08 [0.86]	300 [11.8]	23.9 [0.94]



OPERATING SPECIFICATIONS

Max. system pressure	Max. trans-membrane pressure	Max. backflush pressure	Max. temp.
[kPa/psi]	[kPa/psi]	[kPa/psi]	[°C/°F]
at 20 °C 800 [116]	at 0-30 °C 300 [43]	at 0-30 °C 300 [43]	60 [140]
at 40 °C 600 [86]	at 30-60 °C 200 [29]	at 30-60 °C 150 [21.5]	
at 60 °C 400 [58]			

- Final maximum operating limits are determined by the lowest values of the membrane and element pressure and temperature specifications

PROCESS CHARACTERISTICS (WATER 20 °C)

Membrane diameter	Flow rate (*)	Pressure-drop across module at 1 m/s	Pressure-drop across module at 2 m/s
[mm/mil]	[m ³ /h/gpm]	[kPa/psi]	[kPa/psi]
0.83 [32.7]	0.27 x v [1.19 x v]	11 [1.6]	24 [3.5]

(*) superficial velocity (v) in m/s [ft/s]

- Backwash water should be free of particulates and should be of permeate quality or better
- Backwash pump should preferably be made of non-corroding materials, e.g., plastic or stainless steel. If compressed air is used to pressurize the backwash water, do not allow a two-phase air/water mixture to enter the element
- To avoid mechanical damage, do not subject the membrane module or element to sudden temperature changes, particularly decreases. Do not exceed 60 °C process temperature. Bring the module or element back to ambient operating temperature slowly (typical value 1 °C/min). Failure to adhere to this guideline can result in irreparable damage

X-FLOW RX300 0.83UFC

ULTRAFILTRATION MEMBRANE

MEMBRANE ELEMENT DATASHEET

STORAGE

New membrane modules can be stored as supplied in the original packaging. The membrane modules contain an aqueous preservation solution of glycerine (20wt%) and sodium metabisulfite (1wt%) to prevent dehydration and control bacterial growth. The membrane modules are packed in plastic bags which are vacuum sealed to keep the moisture in the module. Membrane modules should be stored in a dry, normally ventilated place, away from sources of heat ignition and direct sunlight. Storage temperature should be between 0 and 40 °C. Pentair instructions for transport and storage are to be followed at all times and available upon request. It is recommended to have the membrane modules installed into the UF skids and commissioned as soon as possible. The membrane shelf life is maximum 8 months from the date the modules are announced ready for delivery ex works Pentair warehouse. After expiry of the shelf life all warranties are null and void.



X-FLOW BV

P.O. BOX 739, 7500 AS ENSCHEDE, NETHERLANDS WWW.X-FLOW.COM

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d. Raw Data of all Samples

Date Trial	Type	Sample Site	Sample	fDOM corr QSU	UVA254 m ⁻¹	TOC mg/l	HIX	Freshness Index	FI
13.05.2020	pH 16 mg/l	Görvaln	6,15	16,81509	4,98	3,285	0,837	0,851	1,73
13.05.2020	pH 16 mg/l	Görvaln	6,29	17,16369	5,41	3,373	0,84	0,874	1,73
13.05.2020	pH 16 mg/l	Görvaln	6,5	19,09038	5,85	3,703	0,846	0,852	1,72
13.05.2020	pH 16 mg/l	Görvaln	6,66	20,71774	6,19	3,79	0,847	0,841	1,71
14.05.2020	pH 16 mg/l	Görvaln	6,82	22,9739	6,61	4,013	0,86	0,824	1,7
14.05.2020	pH 16 mg/l	Görvaln	7,05	24,52586	6,93	4,156	0,861	0,812	1,69
12.05.2020	pH 16 mg/l	Görvaln	Raw filtered		21	8,45	0,903	0,637	1,48
12.05.2020	pH 16 mg/l	Görvaln	Raw unfilt	54,65708		8,882			
18.05.2020	Conc mg/l	Görvaln	2	38,54931	13,05	6,177	0,853	0,697	1,55
22.05.2020	Conc mg/l	Görvaln	3	34,09753	11,54	7,294	0,832	0,722	1,58
18.05.2020	Conc mg/l	Görvaln	4	29,90863	9,54	5,143	0,854	0,762	1,61
22.05.2020	Conc mg/l	Görvaln	5	29,19626	9,5	5,164	0,842	0,752	1,62
18.05.2020	Conc mg/l	Görvaln	6	25,13227	7,74	4,43	0,844	0,795	1,69
22.05.2020	Conc mg/l	Görvaln	7	26,55134	8,23	4,4768	0,795	0,788	1,68
18.05.2020	Conc mg/l	Görvaln	8	24,4445	7,37	4,378	0,838	0,797	1,7
22.05.2020	Conc mg/l	Görvaln	9	25,14481	7,56	4,459	0,81	0,799	1,68
18.05.2020	Conc mg/l	Görvaln	10	23,54516	7,08	4,268	0,818	0,807	1,71
15.05.2020	Conc mg/l	Görvaln	Raw filtered		20,27	8,082	0,895	0,645	1,5
15.05.2020	Conc mg/l	Görvaln	Raw unfilt	49,57736		8,479			

Date Trial	Type	Sample Site	Sample	fDOM corr QSU	UVA254 m ⁻¹	TOC mg/l	HIX	Freshness Index	FI
25.05.2020	Conc mg/l	Ekoln	2	95,76806	35,01	11,6	0,93	0,585	1,49
26.05.2020	Conc mg/l	Ekoln	3	76,80341	32,98	11,03	0,93	0,58	1,51
25.05.2020	Conc mg/l	Ekoln	4	76,81764	28,55	10,32	0,921	0,607	1,53
26.05.2020	Conc mg/l	Ekoln	5	63,06359	24,66	9,282	0,925	0,614	1,55
25.05.2020	Conc mg/l	Ekoln	6	58,81888	21,51	9,027	0,918	0,639	1,57
26.05.2020	Conc mg/l	Ekoln	7	51,36474	19,27	8,251	0,917	0,647	1,6
25.05.2020	Conc mg/l	Ekoln	8	48,51359	16,59	7,61	0,903	0,668	1,62
26.05.2020	Conc mg/l	Ekoln	9	42,09624	16,65	7,453	0,914	0,666	1,63
25.05.2020	Conc mg/l	Ekoln	10	48,8106	16,74	7,657	0,913	0,669	1,6
19.05.2020	Conc mg/l	Ekoln	Raw filtered		50,54	14,36	0,938	0,548	1,48
19.05.2020	Conc mg/l	Ekoln	Raw unfilt	82,95954		15,52			
01.06.2020	Conc mg/l	Prästfjärden	2	31,42942	10,79	5,491	0,855	1,59	1,59
01.06.2020	Conc mg/l	Prästfjärden	5	25,46225	8,64	4,689	0,848	1,63	1,63
03.06.2020	Conc mg/l	Prästfjärden	8	18,61844	6,54	3,73	0,825	1,67	1,67
27.05.2020	Conc mg/l	Prästfjärden	Raw filtered		20,567	7,656	0,888	0,634	1,46
27.05.2020	Conc mg/l	Prästfjärden	Raw unfilt	43,16438		8,006			
04.06.2020	pH 4mg/l	Görvaln	6,08	25,69216	7,79	4,305	0,861	0,783	1,64
03.06.2020	pH 4mg/l	Görvaln	6,26	25,556	8,54	4,423	0,857	0,785	1,65
04.06.2020	pH 4mg/l	Görvaln	6,30	25,6021	8,12	4,541	0,858	0,784	1,65
04.06.2020	pH 4mg/l	Görvaln	6,46	27,17487	8,73	4,754	0,866	0,776	1,65
03.06.2020	pH 4mg/l	Görvaln	6,60	27,94842	10,19	4,96	0,863	0,76	1,66
04.06.2020	pH 4mg/l	Görvaln	6,81	28,97214	9,588	5,084	0,867	0,759	1,63

Date Trial	Type	Sample Site	Sample	fDOM corr QSU	UVA254 m ⁻¹	TOC mg/l	HIX	Freshness Index	FI
29.05.2020	pH 4mg/l	Görvaln	Raw filtered		20,27	8,116	0,895	0,646	1,5
29.05.2020	pH 4mg/l	Görvaln	Raw unfilt	47,60496		8,494			
09.06.2020	Conc mg/l Fe	Görvaln	2	41,72569	17,88	6,716	0,877	0,669	1,53
10.06.2020	Conc mg/l Fe	Görvaln	3	41,34937	17,62	6,636	0,884	0,685	1,55
09.06.2020	Conc mg/l Fe	Görvaln	4	36,66742	16,96	6,295	0,876	0,704	1,56
10.06.2020	Conc mg/l Fe	Görvaln	5	39,25073	17,75	6,225	0,883	0,696	1,58
09.06.2020	Conc mg/l Fe	Görvaln	6	34,39062	17,07	5,682	0,873	0,72	1,61
10.06.2020	Conc mg/l Fe	Görvaln	8	29,41007	14,56	5,008	0,862	0,754	1,65
08.06.2020	Conc mg/l Fe	Görvaln	Raw filtered		20,26	8,066	0,899	0,642	1,52
08.06.2020	Conc mg/l Fe	Görvaln	Raw unfilt	47,60496		8,493			

Author's Declaration

I, Tamara Kristin Voigtländer,

declare that I have followed the Principles of Good Scientific Practice while writing the present Master Thesis.

I have written the thesis independently and have used no other sources or aids than those given and have marked the passages taken from other works word-for-word or paraphrased.

Supervisor: Prof. Dr. Stephan Köhler

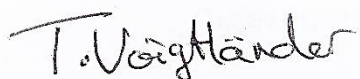
Co-Supervisor: Prof. Dr. Thilo Streck

Examiner: Dr. Brian Huser

Topic of the thesis: Comparison and Optimization of Removal of Natural Organic Carbon from Raw Water with Ultrafiltration in Pilot Scale Experiments

I give my consent to this electronic version being checked for plagiarism with analytical software.

Ofterdingen, 24.07.2020

A handwritten signature in black ink, reading "T. Voigtländer". The signature is written in a cursive style with a large, stylized 'V'.