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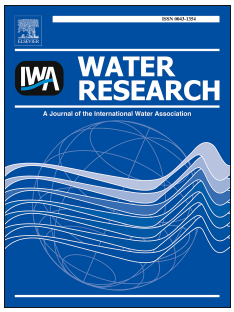

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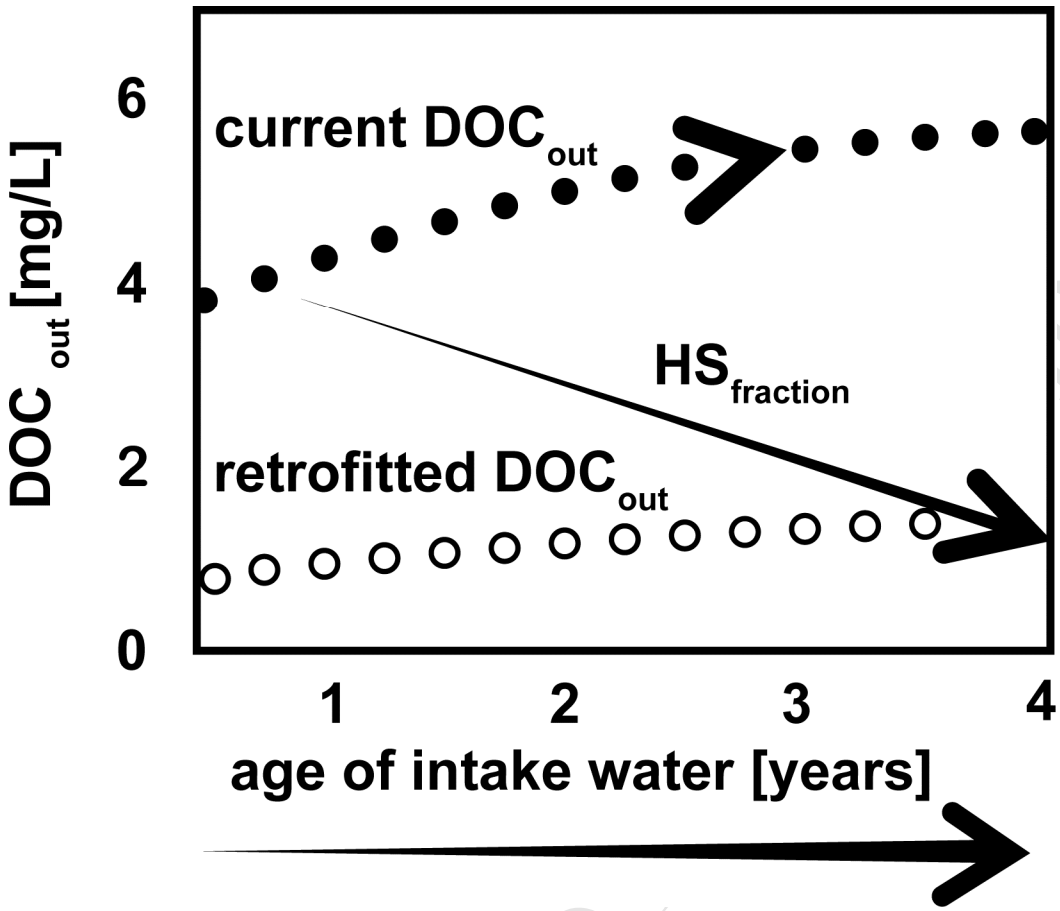

Upgrading coagulation with hollow-fibre nanofiltration for improved organic matter removal during surface water treatment

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Abstract

Rising organic matter concentrations in surface waters in many Nordic countries require current drinking water treatment processes to be adapted. Accordingly, the use of a novel nanofiltration (NF) membrane was studied during a nine month period in pilot scale at a

large drinking water treatment plant in Stockholm, Sweden. A chemically resistant hollow-fibre NF membrane was fed with full scale process water from a rapid sand filter after aluminum sulphate coagulation. The combined coagulation and NF process removed more than 90% of the incoming lake water dissolved organic carbon (DOC) (8.7 mg C L^{-1}), and 96% of the absorbance at 254 nm (A254) (0.28 cm^{-1} incoming absorbance). Including granulated active carbon GAC) filter, the complete pilot plant treatment process we observed decreases in DOC concentration (8.7 to 0.5 mg C L^{-1}), SUVA (3.1 to 1.7 mg^{-1} L m^{-1}), and the average nominal molecular mass (670 to 440 Da). Meanwhile, water hardness was practically unaffected (< 20% reduction). Humic substances (HS) and biopolymers were almost completely eliminated (6510 to 140 and 260 to 10 µg C L^{-1} respectively) and low molecular weight (LMW) neutrals decreased substantially (880 to 190 µg C L^{-1}). Differential excitation emission matrices (EEMs), which illustrate the removal of fluorescing organic matter (FDOM) over a range of excitation and emission wavelengths, demonstrate that coagulation removed 35 ± 2% of protein-like material and 65 ± 2% of longer emission wavelength, humic-like FDOM. The subsequent NF treatment was somewhat less selective but still preferentially targeted humic-like FDOM (83 ± 1%) to a larger extent than protein-like material (66 ± 3%). The high selectivity of organic matter during coagulation compared to NF separation was confirmed from analyses with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), and liquid chromatography with organic carbon detection (LC-OCD), as coagulation exclusively targeted oxidized organic matter components while NF removed both chemically reduced and oxidized components. DOC removal and change in DOC character in the GAC filters showed marked differences with slower saturation and more pronounced shifts in DOC character using NF as pre-treatment. Fluorescence derived parameters showed a similar

decrease over time of GAC performance for the first 150 days but also indicated ongoing change of DOM character in the post NF GAC filtrate over time even after LC-OCD indicated steady state with respect to outgoing carbon. During our trial iron concentrations were low (< 30ppb) and thus A254 could be directly related to the concentration of HS (R^2 = 0.9). The fluorescence derived freshness index (β:α) proved to be an excellent variable for estimating the fraction of HS present in all samples. Given the recommended limit of 4 mg L^{-1} for chemical oxygen demand (COD) for Swedish drinking water, coagulation will need to be supplemented with one or more treatment steps irrespective whether climate change will lead to drier or wetter conditions in order to maintain sufficient DOC removal with the current increasing concentrations in raw waters.

Keywords: Nanofiltration (NF), Hollow fibre, Humic substances (HS), drinking water, fluorescence EEM, GAC.

1. Introduction

Rising levels of dissolved organic matter (DOM) in boreal and north European surface waters (Hongve *et al.* 2004,) pose a number of technical and chemical challenges for drinking water production. Water treatment costs have increased and are expected to continue to rise, especially when using coagulation techniques which require higher chemical doses that results in more sludge (Eikebrokk *et al.* 2004). In addition, climate change is expected to lead to larger fluctuations in dissolved organic carbon (DOC) concentrations, commonly used as a proxy for DOM, and thus, further degradation of raw

water quality in the future (Delpla *et al.* 2009). Intensity, timing and duration of fluctuations in DOC concentration and composition in surface waters are of vital economic interest for drinking water producers but difficult to foresee. DOC removal through coagulation treatment, which is the most commonly used method at Swedish water treatment plants (WTPs), is affected by organic matter composition and the removal efficiency is commonly reported to increase with the DOC-normalized absorbance at 254 nm (SUVA), an indicator of aromatic carbon and a terrestrial origin (Matilainen *et al.* 2010, Weishaar *et al.* 2003). The fraction of terrestrially derived DOC decrease with water turnover time in lakes (Gondar *et al.* 2008, Tang *et al.* 2013, Köhler *et al.* 2013), leading to lowered removal efficiency during the coagulation treatment. Lakes with varying turnover times are thus more prone to temporal changes in DOC character. This is the case for Mälaren, the third largest lake in Sweden, which is used as raw water source for three large WTPs supplying the Swedish capital city Stockholm with drinking water. Raw water DOC concentration is currently approximately 9 mg C L^{-1}, of which only roughly half can be removed through coagulation treatment. Lake water retention time has been identified as a key driver of DOM quality in this lake (Köhler *et al.* 2013, Lavonen *et al.* 2015). In Sweden, WTPs have to comply with a recommended limit of around 4 mg C L^{-1} organic matter measured as chemical oxygen demand (COD) for drinking water. In the case of Mälaren this is equivalent to 5 mg C L^{-1} DOC. Future climate or land use driven changes in DOC concentration and composition are thus large challenges for drinking water producers. Lower outgoing DOC will lead to decreased unwanted consumption of disinfectant and, reduced microbial regrowth potential in the distribution network. Improved DOC removal prior to treatment with granular activated carbon (GAC) filters may furthermore decrease fouling by irreversibly bound DOM components which diminish the ability of GAC filters

to remove micro-pollutants such as perfluorooctanesulfonic acid (PFOS), algal degradation products or fuel residues, all which may occur in Mälaren.

High pressure (>10 bar), NF membranes with low molecular weight cut-off (< 300 Da) have been used for a number years to remove organic matter for drinking water purposes (Meylan *et al.* 2007). These tight membranes are efficient in removing DOC and hardness (e.g. Ca^{2+}, Mg^{2+}, > 80% removal) as well as a number of organic micro-pollutants (Zhang *et al.* 2006). Commercially available spiral wound NF membranes are designed for DOC removal at the expense of undesirable retention of hardness for drinking water production from soft raw waters. Furthermore, the spiral wound membranes are characterized by low chlorine stability, limited disinfection and chemical cleaning possibilities, e.g. pH 3-8 for cellulose acetate filters as compared to pH 2-12 for polysulfonate (Regula *et al.* 2014). Intensive pre-treatment is necessary due to limited hydraulic cleaning options. Capillary, hollow fibre NF membranes have been applied for direct filtration of highly colored surface water during the last decade (Meylan *et al.* 2007). One of the latest concepts in NF for highly effective removal of organic matter, the so called Color Removal Package, is based on capillary NF membranes, combining the chemical resistance of hollow fibre membranes with the organic carbon retention of spiral wound units (De Grooth 2015). These membranes are modified for enhanced organic matter removal and limited retention of bivalent metal ions from the feed water. As they are operated using outside in flow, they may be flushed inside out which is ideal when retrofitting an existing treatment scheme. They do not require pretreatment other than 300 micron safety screen and can directly be fed with raw surface water. In summer 2013, a HFW 1000 membrane pilot plant was installed at Görväln WTP, situated in Stockholm, Sweden, to evaluate the organic matter removal and performance of NF

filtration following conventional coagulation and rapid sand filtration. Organic matter quality and quantity in all steps from raw to drinking water were evaluated with a large range of analytical techniques. These included total and dissolved organic carbon (TOC, DOC), online ultraviolet and visible (UV-VIS) absorbance (250-700nm), 3D fluorescence, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and liquid chromatography with organic carbon detection (LC-OCD).

This study aims to a) evaluate the performance of a retrofitted new generation HFW 1000 nanofilter membrane, b) study the selective removal of DOM fractions in the combined coagulation NF process and the currently used coagulation technique; c) identify DOM characterization techniques that are informative for validating membrane and GAC performance, and d) use the acquired data to estimate removal of DOC with varying composition in the studied raw water as a function of lake water retention time.

2. Material and methods

2.1 NF pilot plant

The membrane material is composed of sulfonated polyether sulfone. The presence of sulfonate groups on the benzene ring structure renders them hydrophilic and leads to a negative zeta potential at pH above 5. The zeta potential further decrease to around -20 mV with the raw water pH 7.5 used in our study and the membrane therefore effectively rejects molecules with negatively charged functional groups such as DOC (De Grooth 2015). The separating layer of the membrane is on the inside of the fibres, thus allowing operating inside-out. The internal hydraulic diameter of the membrane fibers is 0.8 mm and the molecular weight cut-off is approximately 1000 Da based on Dextran permeation.

The HFW 1000 NF membrane module is 0.20 m (8”) in diameter and 1.54 m (60.5”) long. It contained 40 m^2 of membrane surface area with the 0.8 mm fibers. The test module was equipped with surface flow collectors. The test facility (a QuickScan pilot plant, supplied by Pentair X-Flow) had a capacity of 600 L h^{-1} (permeate production). During the pilot trials the test membrane was continuously operated at feed flow rate of 1.2 m^3 h^{-1} with a flux range of around 15 L m^{-2} h^{-1} , a cross-flow velocity of 0.5 m s^{-1}, an intermittent forward flushing interval of every 60 minutes and a recovery rate of 50 %. We chose to protect the membrane and operate at this low recovery even if higher recoveries of up to 80 were successfully tested, With operating pressures around 4 bar and permeability rates of 10 L m^{-2} h^{-1} bar^{-1} the transmembrane pressure typically increased with 0.17 bar and the permeability decreased with 1.0 L m^{-2} h^{-1} bar^{-1} at low water temperatures of around 1-3 °C during a filtration period of 42 days. The cleaning procedure is explained in detail in the appendix.

2.2 Mälaren as drinking water source

Görväln WTP is located in the eastern part, close to the outlet of Lake Mälaren, Sweden, where water from a northern basin (16%) and the large western basin (84%) mix. Varying water quality in the raw water intake is due to different processing of DOC within the lake (Köhler *et al.* 2013). Mälaren raw water (2002-2013) has high pH (7.6-7.8), high alkalinity (1.3 mM) and a DOC that varies between 6-12 mg L^{-1}. Raw water turbidity varies between 2 and 10 FNU depending on the raw water intake depth. A more detailed description of the water quality and different water sources that contribute to the raw water at Görväln WTP can be found in Ericsson *et al.* 1984.

2.3 Full scale drinking water plant

The raw water (RAW) from Mälaren is taken in at two different intake depths (-4 and -22m) depending on the water quality. After passing a micro sieve (200 μm nominal pore size) the water is coagulated with $Al_2(SO_4)_3$ at doses varying from 40 to 70 mg L^{-1}. The coagulant dose is controlled by measuring turbidity after the following rapid sand filtration (SF) (0.6 m h^{-1}), which is used to remove residual flocs. Downstream, the water is filtered through a Norit 1240W GAC bed (CF), and disinfected with UV irradiation (25 mJ cm^{-2}) and monochloramine (NH_2Cl; 0.2-0.35 mg L^{-1}) to produce drinking water (DW) as shown on the left side in Figure 1.

2.4 Pilot scale drinking water treatment plant

The feed water for the NF pilot plant water is recovered from the SF full-scale plant as displayed in the right side of Figure 1. NF membrane module was followed by a pilot scale GAC filter (CF2). A fraction of the rapid sand filtrate was filtered directly by another GAC filter (CF4) so that the effect of NF on the activated carbon filter could be compared under the same conditions regarding GAC age (Figure **1**). Granulated activated carbon (GAC) filter beads of approximately 2.5m height were filled with 1 m GAC (Norit 1240 W) and at a hydraulic load of 10 m h^{-1} this resulted in an empty bed contact time of approximately 6 minutes at a flow rate of 1 L min^{-1} in accordance with the full scale plant conditions. This setup was studied from August 2013 to May 2014.

2.5 Online sensors

The pilot plant was equipped with a number of sensors including an S:can absorbance probe (spectro::lyser™; s::can Messtechnik GmbH), pH-meter, pressure transducers and a conductivity probe. Absorbance spectra was acquired with the S:can sensor using a flow

183 through cell with 4cm path length in the wavelength range 230-750nm. Empirical
184 relationships from particle rich waters were used to calibrate the absorbance measurements
185 against both TOC and turbidity.

186 **2.6 Organic matter characterization**

187 Organic matter was characterized using a number of techniques. Regular and compulsory
188 samples monitoring the WTP performance (n >30) between treatment steps were analyzed
189 for pH, alkalinity and UV absorbance at 254nm. S:can recorded absorbance spectra at the
190 raw water intake for the period July 2010 to June 2014 with one minute resolution.
191 Additionally, grab samples (n = 20) were analyzed for a number of DOC characteristics at
192 eight different sampling points throughout the drinking water train (Figure 1). Samples were
193 taken every month and at specific days prior to or after important adjustments in the setup,
194 such as change of active carbon in the filters or change of intake depth from level A to level
195 B (15.01.2013: 22 m ➔ 4m, 25.04.2013: 4m➔ 22m, 04.02.2014: 22m ➔ 4m, and
196 25.02.2014: 4m ➔ 22m), shown as vertical lines in Figure A. **1**. All samples were analyzed
197 for total and dissolved organic carbon (TOC and DOC) using a Shimadzu TOC-V_{CPH}. DOC
198 samples were filtered using pre-washed (MilliQ water, <18.2 Ω cm^{-1}) cellulose acetate 0.45
199 µm filters (Minisart, Sartorius). Filter blanks were within 0.1 mg C L^{-1} of the DOC content
200 of MilliQ water. As TOC and DOC were always within the analytical precision of the
201 measurement (0.3 mg L^{-1}) we will only mention DOC in the subsequent text. Fluorescence
202 excitation emission matrices (EEMs) were collected using an Aqualog (Horiba Jobin Yvon)
203 spectrofluorometer (Lavonen *et al.* 2015). Previously established indices were calculated
204 from the corrected EEMs, namely HIX, fluorescence index (FI) and β:α according to Ohno
205 2002, Cory and McKnight 2005, and Parlanti *et al.* 2000. Changes in fluorescence spectra
206 over the whole measured range were assessed using differential EEMs (Lavonen *et al.*

2015) for the coagulation, NF and GAC treatments. To compare the removal of shorter emission wavelength, protein-like autochthonous FDOM and longer emission wavelength, terrestrially derived humic-like FDOM we looked at the % decrease in fluorescence signal (differential EEM divided by measured EEM before a treatment process) at excitation = 276 nm, emission = 320 nm (protein-like) and excitation = 350 nm, emission = 550 nm (humic-like). As the raw water was low in dissolved iron (< 30 ppb) and all treatment processes studied here involved only small changes in pH (6.6 < pH < 7.2) we expect no significant effect on the fluorescence spectra from the chemical conditions of the samples.

Approximately 1-20 L samples (depending on DOC concentration) were filtered through pre-combusted (4 hours at 450 °C) GF/F filters (effective pore size of 0.7 μm) and acidified to pH 2 using 37% HCl, p.a., before gravitationally loaded to solid phase extraction cartridges (Agilent Bond Elut PPL). DOM was eluted with methanol according to Dittmar *et al.* 2008. The methanol extracts were kept in a freezer until analyses were conducted. Ultrahigh resolution MS analyses were performed at the Helmholtz Centre in Munich using a 12 Tesla SOLARIX FT-ICR mass spectrometer (Bruker, Bremen, Germany) with an Apollo II electrospray ionization source in negative ion mode. Chemical formulas were assigned to the m/z peaks based on $^{12}C_{0\text{-}100}$, $^{16}O_{0\text{-}80}$, $^{1}H_{0\text{-}\infty}$, $^{14}N_{0\text{-}3}$, $^{32}S_{0\text{-}2}$. For further details regarding FT-ICR-MS analyses, formula assignment and data processing, see Lavonen *et al.* 2015. Relative abundances of m/z peaks were calculated by dividing the signal intensities by the intensity of the most abundant peak in each sample. Changes in relative abundance during the different treatment processes are expressed in percentage points by subtracting the relative abundance of an m/z peak in the sample after treatment from that in the sample before treatment. Following Lavonen et al. 2015, where the same mass spectrometer was

used, we only considered changes in relative abundance by more than 2.5 percentage points as significant, based on measurements of double samples where differences between signal intensities were, on average, 0.9 ± 1.5 percentage points.

Liquid chromatograph organic carbon detection (LC-OCD) was used to analyze a large number of samples (n = 100) from the pilot plant and the full scale process. LC-OCD quantifies the elution as a function of size and column affinity of carbon and nitrogen from a Sephadex column using a buffered (pH = 6.85 using a potassium-dihydrogenphosphate and sodium-hydrogenphosphate buffer with an ionic strength of 2.5 mM) carrier solution (Huber *et al.* 2011). This method has been calibrated using both standard IHSS and polystyrene sulfonate standards and widely applied (Baghoth *et al.* 2011). UV absorbance (254nm), C and N are measured online, and allow quantifying the elution of DOC over time. The acquired chromatogram is separated into different apparent size fractions using the Chrom_CALC software (Huber *et al.* 2011) that divides DOC into the following apparent size fractions as a function of elution time: Biopolymers, HS, building blocks, low molecular weight neutrals and low molecular weight acids that are noted together as LMW.

3. Results and discussion

3.1 Performance of the retrofitted NF pilot plant

The pilot scale membrane plant produced treated water with constant water quality during the whole 9 month experimental period, thus fulfilling one of the main objectives of the study: stable removal of color and DOC over time. The stable DOC character is exemplified by the data in Table 2 and 3 and Figure A.1 Both outgoing DOC concentration (0.6±0.1 mg C L^{-1}) and DOC character (i.e β:α = 0.95±0.04) of the NF permeate are very stable during the whole study period. Raw water DOC concentration of around 8-11 mg C L^{-1} was

reduced to below 0.5 mg C L^{-1} after NF. Of this removal, the full scale coagulation treatment accounted for approximately 50% while NF removed additionally 40% of the DOC, only slightly lower than what can be achieved using conventional spiral would membranes (Meylan *et al.* 2007, Schafer *et al.* 2004, Metsamuuronen *et al.* 2014). In contrast to the former membranes, the hollow fibre NF membranes used here succeeded to retain less than 80% of incoming hardness (results not shown), as is desirable for soft raw waters, thus avoiding a post-membrane alkalinisation step. DOC concentration in the GAC filter feed was significantly reduced (compare SF and NF-P in Table 2). Incoming DOC in the water fed to the pilot plant GAC was eight times lower than that of the full scale GAC, which was approximately 4 mg C L^{-1}. Across the whole pilot plant around 93% of incoming HS, 86% of incoming DOC and 87% of A254 was removed.

3.2 Selective removal of DOC across the whole and pilot plant treatment train

3.2.1 DOC concentration in the raw water

Raw water DOC varied between 8.1 and 11.1 mg L^{-1} (10-90% quartiles respectively) during our experiment period and was composed of approximately 70% HS (Table 2, Table A. **1** and Figure 2). The observed variation in DOC during the study period is thus very relevant for dealing with the recently increasing raw water DOC (Figure A. 7) and for testing how retrofitting a NF membrane may counteract this rise in DOC.

3.2.2 Changes in DOC composition during coagulation

DOC characterization using LC-OCD indicates that the coagulation treatment was, apart from small quantities of large biopolymers, almost exclusively removing HS from the raw water (Figure 2). A selective removal of UV-absorbing substances (Figure 2, SUVA in Table 2) is in accordance with many previous studies (Baghoth *et al.* 2011, Shutova *et al.*

2014). Within the HS fraction, larger compounds were preferentially removed during the coagulation step. Median nominal molecular weight for HS was 452 ± 30 Da after coagulation, compared to 660 ± 70 Da in the incoming water (Table 2). Targeted removal of larger components was also seen from the FT-ICR-MS data were the average nominal molecular weight of CHO components that decreased significantly (were selectively removed) was 440 Da (range from 302-578 Da) while the average mass for components that increased significantly (were not/poorly removed) was 380 Da (range from 256-454 Da). There was, furthermore, a clear shift in abundance from components with a positive average carbon oxidation state to those with negative values (more reduced), in accordance with a previous study of another WTP (Lovö) that also use eastern Mälaren as raw water source and the same coagulation chemical as Görväln WTP (Lavonen *et al.* 2015). Comparing the components that decreased during coagulation at Görväln and Lovö WTP formula by formula showed that 82% (n=114) of those decreasing with >2.5 percentage points at Görväln also decreased significantly at Lovö despite being sampled different years and seasons. This shows that coagulation is a rather stable process, repeatedly targeting similar components. Differential EEMs indicate a strong preferential removal of terrestrial FDOM with emission at long wavelengths (Figure 3 and Figure A. 4), as demonstrated by low β:α (0.48 ± 0.01) and FI 1.37 ± 0.02, and HIX close to 1 (0.94 ± 0.01) for the calculated removed fraction (Table 3), in line with Lavonen *et al.* 2015. Removal ranged from 35 ± 2% for protein-like material to 65 ± 2% of longer emission wavelength, terrestrially derived FDOM (Figure 3, left).

3.2.3 GAC in full and pilot scale

Detailed analysis of full scale or pilot scale long term experiments involving GAC filters are rare (Gibert *et al.* 2013). In the full scale treatment Görväln WTP aims to use their GAC

filter as a chemical barrier. However, due to the relatively high DOC concentration in the GAC feed (4.8 ± 0.3 mg C L^{-1}), the filters commonly become saturated with irreversibly bound DOM compounds within 1 month after regeneration (Matilainen *et al.* 2006) and do not remove any DOC (Table A. 1). The current GAC thus functions as a biofilter, where microbes adsorbed to the GAC surface remove e.g. compounds causing taste and odor, and in some case smaller amounts of DOC e.g. (Camper 2004, Matilainen *et al.* 2006, Gibert *et al.* 2013). The pilot reference GAC filter (CF4) reduced 75% of the incoming DOC when the activated carbon was new, but after being used for just 1 month the removal had been lowered to 11% (0.5 mg C L^{-1}). After one additional month until the end of the experiment period hardly any (0.1 ± 0.8 mg C L^{-1}) was removed (Figure A. **6**). The pilot GAC filter that was fed with NF permeate (CF2) showed a similar reduction in DOC removing capacity over time with the largest removal when the activated carbon was new (72% = 1.4 mg C L^{-1}), which decreased to 0.5 mg C L^{-1} removal the next coming two months and thereafter the reduction in DOC was only 0.1 mg C L^{-1} until the end of the trial period, similar to CF4. Both GAC filters in the pilot plant initially removed large amount of both humic-like (77 and 96% for CF4 and CF2 respectively) and protein-like FDOM (70 and 61% respectively) (Figure 4, left panel). Our LC-OCD analysis confirmed the results from Gibert *et al.* 2013 who also observed preferential removal of HS during the early phase (Figure 4, right panel). The Norit 1240 W seems to have a higher affinity for HS than Norit Row 0.8 supra used in (Gibert *et al.* 2013 under the given conditions. This was not studied further but could be due to differences in water quality such as pH, presence of cations that change the conformation of HS in solution (Schafer, 2004) and differences in the GAC pore size distribution. According to Camper 2004, HS may support the same amount of microbial growth in a biofilm as readily available smaller LMW substances. Even if no change in DOC could be

quantified across the full scale GAC filter, there was still a clear pattern in FDOM removal demonstrated by a decrease in 15 ± 11% for protein-like material and 3 ± 1% for humic-like material, indicating that the GAC mainly had acted as a biofilter as humic material primarily is removed through adsorption (Velten *et al.* 2011, Matilainen *et al.* 2006): Both fluorescence and LC-OCD data are thus valuable for indicating changes in GAC saturation and functioning.

3.2.4 Changes in DOC concentration and composition across the NF membrane

In the pilot plant 40% of the incoming DOC was removed with the NF membrane. The two main fractions that were retained (>90%) were biopolymers and HS (Figure 2). Similar or higher removals are observed in tighter spiral wound membranes (Schafer *et al.* 2004) and (Meylan *et al.* 2007). Up to 80% of the smaller constituents - building blocks and low molecular weight compounds were removed (Table 2,Table A. **1**). UV absorbing compounds were removed slightly more than bulk DOC with SUVA decreasing from 2.1 to 1.7 (Table 2). This and the significant increase in FI and β:α during membrane treatment demonstrates selective removal of terrestrial DOM (Table 3). FI in the treated water was 1.84 ± 0.03 which indicates that so much terrestrial DOM was removed in the combined coagulation NF treatment that the permeate (Table 3) resembled organic compounds from extracellular release and leachate from algae and bacteria defined as a microbial endmember (McKnight *et al.* 2001). Even if NF was selectively removing terrestrial DOM, indices calculated from differential EEMs show that the removed DOC still had a rather microbial fingerprint (high FI (1.64 ± 0.02) and β:α (0.71 ± 0.02)). This demonstrates that NF can remove a wide range of DOM components, reflected in 83 ± 1% removal of humic-like FDOM and 66 ± 3% reduction in protein-like material (Figure 3). This is supported by FT-ICR-MS results, showing that more than 90% of the components that decreased

significantly in relative abundance during coagulation (n = 139) further decreased with NF. Also, 93 components that were not targeted during coagulation decreased significantly during NF. The coagulation treatment was highly selective towards oxidized components with a weighted (against the relative abundance) mean average carbon oxidation state (**Error!**) of 0.35 for decreasing components (maximum 0.78 and minimum -0.10 for components that decreased significantly). Meanwhile, NF removed a wider range of both reduced and oxidized components (weighted mean **Error!** = -0.05, maximum 0.63 and minimum -0.61 for components decreasing significantly). Hence, we can show that NF with the employed membrane is more efficient than coagulation, both continuing to remove material reactive during coagulation, as well as additional components. All components that increased in relative abundance during NF treatment had m/z<400 Da (Figure 5). This indicates that these components do not aggregate significantly and have therefore not been removed through size exclusion. There were also components that had m/z<400 Da that decreased in abundance, however, these had significantly higher O/C (>0.50) (right panel in Figure 5). A higher removal of smaller but highly charged molecules is in line with expected repulsion on negatively charged membranes (Schafer *et al.* 2004).

3.3 Identifying useful spectroscopic information for DOC character

From August 2012 the S:can was used to control the $Al_2(SO_4)_3$ dosing for improved DOC removal in the full scale WTP. From then on dosing efforts were increased and controlled by the online UV signal. Two thirds of HS were removed using a coagulant dose of around 50 mg/l $Al_2(SO_4)_3$. The removed DOC was almost entirely composed of HS (96%) (Figure 2). This explains why the relative removal of DOC is well correlated to both %HS, Al_{DOS} and to A254 (Table 1). On average, the online sensor controlled dosing was higher than the turbidity controlled dosing (75 versus 50 mg L^{-1} $Al_2(SO_4)_3$ and led to a 12% higher DOC

372 removal (around 1 mg L^{-1} on average). Controlling the coagulant dose with absorbance
373 measured online will allow the WTP to remove more DOC under periods with high A254
374 when DOC is easy to coagulate as shown below.

375 Due to the importance of HS for DOC removal during coagulation we analyzed whether any
376 of the optical parameters could be coupled to the LC-OCD data. When comparing the
377 average β:α with average fraction of HS of total DOC in the raw water, rapid sand filtrate
378 and NF permeate and concentrate as well as the drinking water we obtained a linear
379 relationship (Figure 6). Using average data (Table 3) from delta EEMs from raw water to
380 coagulation (RAW/SF) and from coagulation to NF (SF/NF-P) we may produce two
381 additional data points using mass balance calculations of changes in HS (Figure 6). There
382 were a number of other interesting relationships (e.g. prediction of molecular weight of HS
383 as a function of increasing HIX, HS as a function of A254 (Table 1) in line with the results
384 of (Baghoth *et al.* 2011). We focused on another important aspect for finished drinking
385 water, notably the presence of low molecular weight compounds (LMW) in the permeate. In
386 our study we found that LMW determined by LC-OCD in the permeate may be estimated
387 from HIX and β:α (Figure A. **6**). In line with Baghoth *et al.* 2011 and Baker *et al.* 2008 our
388 results confirm that fluorescence signals may be coupled to NOM properties.

389 Both GAC and membrane performance may thus be followed using fluorescence as a faster
390 and cheaper indicator of DOC quality on site. While these relationships (e.g. UV versus
391 DOC (Figure A. **2**), DOC versus building blocks etc.) are useful for individual WTPs, we
392 agree with Shutova *et al.* 2014 that further work is needed to exclude that they are only site
393 specific. Complicating factors in such an analysis would be the presence of dissolved iron
394 (Weishaar *et al.* 2003), pH (Pace *et al.* 2012) and presence of cations (Schafer *et al.* 2004)

that all may influence absorbance and fluorescence due to either changes in organic matter conformation or metal binding.

3.4 Effect of lake water retention time on coagulation efficiency as one aspect of climate adaptation

Both Gondar *et al.* 2008 and Köhler *et al.* 2013 have noted that lake water NOM may be described as two endmembers that are mainly controlled by lake turnover and flow. Dry spells may have a significant effect of lake water quality as lake water NOM during those periods usually contain more hydrophilic NOM (Tang *et al.* 2013, Ritson *et al.* 2014) and less of hydrophobic HS. Removal of incoming DOC during coagulation treatment is controlled by the fraction of HS present in the raw water. The abundance of HS can be estimated from A254 (Figure A. **3**). A254 is, however, affected by the presence of iron (Weishaar *et al.* 2003) and during periods of high iron concentrations (> 300ppb) as was observed in the year 2000 (personal communication Görväln WTP) this relationship will fail. Both β:α and DOC concentration, however, have previously been shown (Figure 6) to be controlled by lake water retention time (Köhler *et al.* 2013) This information could be combined to estimate how shorter or longer lake water retention times may control raw water DOC concentrations and $Al_2(SO_4)_3$ doses. Using a series of linear regression that relate age with DOC and β:α (Figure 7), β:α with HS (Figure 6) and HS with dosing and DOC removal (Table **1**) we may estimate outgoing DOC from raw water DOC and β:α that both change with the age of incoming raw water. As β:α proved to be an excellent indicator of the percentage of HS present, we selected this optical variable to further evaluate its usefulness to assess coagulation treatability of DOM. Two different scenarios with varying water age as surrogates for high respective low flow conditions and varying DOC concentration and their respective β:α and %HS are displayed in Figure **7**. Despite varying

incoming DOC in our scenario (7-14 mg C L^{-1}), drinking water DOC is expected to vary between 3.3 and 4.7 requiring $Al_2(SO_4)_3$ doses between below 10 to almost 100 mg L^{-1}, twice the average dose used today. Wet years with short lake WRT (< 1 year) will lead to exceptionally high $Al_2(SO_4)_3$ dosing due to the increased presence of HS while dry years with long WRT (> 3 years) will lead to low $Al_2(SO_4)_3$ dosing but almost similar outgoing DOC. Should the current observed trend of increasing DOC that has been recorded at the outlet of Mälaren (Figure A. **7**), and large areas of Sweden and Norway continue for several years, outgoing DOC will be above 5 mg L^{-1} irrespective of the chosen scenario.

Another important question of interest is how the fraction of hydrophilic and neutral DOC giving rise to biologically degradable organic carbon will vary in the future. The most relevant fraction is probably that determined as LMW through LC-OCD. Applying the regression in Figure A. **6** and using lake water HIX and β/α LMW decreases from 0.8 to 0.6 mg L^{-1} across the lake. Lake water retention time thus only has a minor effect on LMW. Future studies will need to address that question in more detail.

3.5 Remaining questions and challenges with hollow fibre membrane filtration

Fluorescence EEMs and LC-OCD analyses indicate that the NF permeate consists of microbial derived low molecular weight components, rich in organic nitrogen that might affect the biological activity (regrowth potential) and chemical reactivity (disinfectant stability, corrosion of pipes) in the distribution network. There are recurrent algal blooms in Mälaren and the lake also receives waste water from a number of smaller cities and one large hospital within the catchment. The NF membrane used in this study would allow removing at least some of the larger hydrophilic micropollutants such as microcystines and large PFCAs (Perfluorodecanoate 513 Da) and PFOS (Perfluorooctane sulfonic acid 500

Da). Other typically occurring, smaller compounds such as ketoprofene (pK_a = 4.5, 250 Da), or danofloxazine (pK_a = 6.0, 360 Da) might permeate. In the future we will analyze the fate of a number of micro pollutants through todays and the new proposed water treatment train to test the ability of NF to either retain or improve the removal efficiency of GAC filters.

4. Conclusions

Improved removal of organic matter from surface water is important for surface waters in Nordic countries that currently undergo show increasing trends of organic carbon. Stockholm produces its drinking water from raw water (DOC = 9 mg L^{-1}) taken in Mälaren, Swedens third largest lake. DOC has increased over the last 19 years from 6 to 10 mg L^{-1} and we expect larger temperature and flow driven variations in DOC concentration and character over time in the future. At current full scale operation using aluminum coagulation indicate removal of larger (> 500 Da and HS only) terrestrial (FI = 1.4, β:α = 0.5) and with a higher mean average carbon oxidation state (**Error!**= 0.5) carbon. Using β:α that relates to the presence of HS in the studied water we may estimate the outgoing DOC concentration as a function of incoming DOC character in the incoming water based on established coagulation dose DOC and colour relationships. The existing aluminum coagulation (outgoing DOC 4.5 mg C L^{-1}) and granular active carbon (outgoing DOC 4.0 mg C L^{-1}) process alone might not be able to handle these future changes. Longer water retention times during dry spells will decrease the fraction of hydrophobic DOC that is easy to flocculate.

We chose to use a novel and more resistant hollow-fibre polysulfone nanofilter (HFW 1000) instead of spiral wound membranes as they would affect hardness too much in the studied soft waters. The coupled coagulation-NF pilot plant produced stable outgoing water quality (0.5 mg L^{-1}) during the nine month test trial. The removal of carbon with a much larger

range of size (350-500 Da) and properties (**Error!**= -0.07, FI = 1.65, β:α = 0.5) during NF as compared to coagulation was confirmed using a large array of methods including LC-OCD, FT-ICR-MS and fluorescence. Even if the fluorescence derived parameters and correlations probably are site specific they are reliable, fast to determine and comparably cheap complement to the more advanced techniques used here (FT-ICR-MS and LC-OCD). DOC removal and change of DOC character in the GAC filters in full scale, the current coagulation scheme and pilot plant setup showed marked differences with slower saturation and larger changes in DOC character using fresh GAC. The removal of potentially elevated concentrations of organic contaminants such as diesel, microcystines or persistant organic micropollutants in Mälaren may thus improve using the proposed new scheme.

5. Acknowledgements

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573

574 **Dummy Figures and tables:**

575 Figure 1. Water treatment train for the full scale drinking water plant and the pilot scale
576 drinking water plant at Görväln waterworks. The codes for raw water (RAW), sand filter
577 (SF), full scale active carbon filter (CF), nanofilter concentrate (NF-C), nanofilter permeate
578 (NF-P), the other two carbon filters (CF2 and CF4) and drinking water (DW) are used
579 throughout the paper

580 Figure 2. Selected results of median values for changes in DOC [ppb] quantity and quality
581 across the WTP and pilot plant from the raw water (RAW) through the sand filter (SF), the
582 nanofilter (NF-P) and through the full scale activated carbon (SF-CF4) to the final drinking
583 water (DW) and after the activated carbon filter of the pilot plant (NF-CF2) for all samples
584 in the period August 2013 to June 2014. DOC quality parameters in order of decreasing
585 molecular size are codes as biopoly = Biopolymers, HS = Humic substances; LMW = low
586 molecular weight neutrals; build = building blocks.

587 Figure 3 Fraction of removed fluorescent dissolved organic matter for coagulation (left) and
588 NF (right) treatments. Dark red colors indcate strong removal (> 75%) while blue-purple
589 colors indicate less removal (< 40%). The excitation/emission wavelength pairs chosen to
590 represent humic-like (Ex = 350 nm, Em = 550 nm, marked “H” in the EEMs) and protein-
591 like (Ex = 276 nm, Em = 320 nm, marked “P” in the EEMs).

592 Figure 4 Removal (left panel) of protein-like (triangles) and humic-like (circles) fluorescent
593 dissolved organic matter and (right panel) removal of low molecular neutrals (triangles),
594 humic substances (circles), building blocks (diamonds) and biopolymers (squares) across
595 granulated activated carbon (CF) filters in the full scale treatment (black symbols), as well

596 as the pilot plant reference (CF4, white symbols), and downstream from the NF membrane
597 (CF2, grey symbols).

598 Figure 5 CHO components that increased (left) and decreased (right) during the pilot scale
599 nanofiltration of, with chemical coagulation, treated water. White and black bubbles
600 demonstrate significant changes in relative abundance while gray bubbles show non
601 significant changes. Bubble size represent the magnitude of the change in relative
602 abundance (maximum 52 percentage points decrease and 24 percentage points increase).

603 Figure 6 Left: Measured fraction of humic substances (HS_{frac}) for Raw, SF, DW and NF-P
604 as a function of β:α (black diamonds) and mass balance derived HS_{frac} for the material that
605 was removed during coagulation and NF treatments versus β:α calculated from differential
606 EEM (white diamonds). The regression line is very close to that estimated from all
607 individual data shown to the right. HS_{frac} (predicted) was estimated using β:α (HS_{frac} = 1.52
608 – 1.33* β:α) for all samples except CF2 where DOC concentrations were low.

609 Figure 7 Measured and fitted DOC and β:α across Mälaren as a function of water age to the
610 left (Data from Köhler et al 2013). Black circles and black stars display measured DOC and
611 measured β:α respectively (left panel). Both DOC and β:α are read out as a function of water
612 age (x-axis in left panel) using the horizontally pointing arrows in the left panel. On the
613 right: predicted fraction of DOC composed of HS (HS_{frac}) (x-axis) estimated from as a
614 function of incoming β:α (left y-axis) (blacks stars) and DOC (right y-axis) (black circles)
615 using eqs. 2,3, and 8 in Table A. 1 that relate β:α , HS, DOC and aluminum dose. Vertically
616 downwards pointing arrows indicate the amount of DOC (difference between black and
617 white circles) that can be removed through coagulation treatment for two different situations
618 (A and B); The predicted outgoing DOC (white circles in the right panel) is illustrated for A

(a "young" water 0.7 months of age with high DOC and high HS_{frac} = 0.8, requiring around 90 mg L^{-1} $Al_2(SO_4)_3$ and outgoing DOC of around 3.3 mg L^{-1}) and B (an "old water" with lower DOC, lower HS_{frac} = 0.65 leading to a low dose of 40 mg L^{-1} $Al_2(SO_4)_3$ and outgoing DOC of around 4.7 mg L^{-1}).

Table 1 Correlations between different relationships that concern changes in DOC or, character of DOC used in this study.

Table 2 Median DOC, A254, SUVA and DOC character during the different treatment steps for the period August 2013 to end of May 2014 (5-9 measurements per treatment). Pilot scale sampling sites in brackets (NF permeate (NF-P), activated carbon filtrate for pilot column fed with NF permeate (CF2), activated carbon filtrate for pilot column fed with rapid sand filtrate from the full scale process (CF4) and concentrate from the NF NF-C).

Table 3 Median and standard deviation for fluorescence derived data of raw and processed water (SF = sand filtrate, NF-P = NF permeate). Indices from differential EEMs (Raw/SF = coagulation and SF/NF-P = NF) demonstrate characteristics of the removed FDOM. The step NF/CF2 is not included here as DOC is very low and we observed clear trends over time.

636

637 Figure A. 1: a: S:can modelled modeled platinum color (mg L^{-1}) , b: Time series of S:can
638 modelled DOC (mg L^{-1}) in the raw water (grey), sand filter (black), including measured
639 DOC in raw water (black circles), sand filter (black triangels) and NF permeate (white
640 diamonds for the full pilot study period starting in September 2012 to July 2014. The HFW
641 1000 was installed in August 2013. Vertical black lines indicate change of intake depth and
642 hyphenated vertical lines changes in the NF pilot setup. The black horizontal arrow in the
643 lowest panel indicates the nine months experimental period of the HW 1000 nanofilter pilot.

644

645 Figure A. 2: A254 against DOC for all different sampling points. The black hyphenated line
646 indicates the linear relationship (A254 = -0.0073 + 0.0198*DOC, r^2 = 0.99) between A254
647 and DOC after coagulation. The grey arrows indicate either the concurrent removal (NF-P)
648 or increase (NF-C) in A254 with DOC (lower two arrows) during NF. In contrast during
649 coagulation a preferential removal of A254 is observed (upper arrow).

650 Figure A. 3: Amount of HS [ppb] quantified from LC-OCD against measured A254 for all
651 samples. The hyphenated line is the regression curve HS [ppb] = 100 + 22900*A254; r^2 =
652 0.99.

653 Figure A. 4 Typical EEMs for RAW, SF, NF-P and NF permeate followed by active carbon
654 filter water (CF2) displaying data from 2013-08-14 after installation of a fresh active carbon
655 filter (left: raw and processed waters (Raw, SF, NF, CF2 from top to bottom) and right: the
656 removed fraction of FDOM calculated from differential EEMs displaying the amount of

FDOM that has been removed during the different treatment steps (Raw-SF, SF-NF, NF-CF2 from top to bottom)

Figure A. 5 Predicted concentration of low molecular weight (LMW) neutrals from fluorescence derived parameters humification index (HIX) and freshness index (β:α) for the NF permeate (LMW = -16 + 1450*HIX – 1050*β:α; n = 13; $p < 0.01$)

Figure A. 6 Removed DOC over time after change in GAC filter in CF2 and CF4 indicating similar low removal of DOC after just a few months despite different feed DOC concentration.

Figure A. 7 Change in median annual (n=12) TOC concentration during the period 1996 to 2014. The red line describes the change in TOC over time with a slope of 0.12 mg L^{-1} $year^{-1}$ $r^2 = 0.56$ and $p < 0.001$.

Table A. 1: Median and standard deviation of the different DOC fractions obtained from LC-OCD [ppb] for the period August 2013 to July 2014.

Table 1. *Correlations between different relationships that concern changes in DOC or, character of DOC used in this study.*

No	Equation
1	COD_{Mn} [mg L^{-1}] = 0.666 + 5.26*A_{254}; r^2 = 0.94 RMSE = 0.5 [mg L^{-1}]; n = 115
2	%DOC removed = 0.788 – 0.00489*Al_{DOS} [mg L^{-1}]; r^2 = 0.91 RMSE = 1.3%; n = 249
3	%DOC removed = 2 – 2.09*HS_{frac} ;r^2 = 0.75 RMSE = 2.2%; n = 24
4	HS [ppb] = 307 + 21800*A_{254}; r^2 = 0.99 RMSE = 200 [ppb]; n = 29
5	SUVA-HS = 16.2 - 8.19*FI; r^2 = 0.93 RMSE = 0.17; n = 28
6	MW-HS [Dalton] = -4190 + 5240*HIX; r^2 = 0.80 RMSE = 38 [Dalton]; n = 29
7	LMW neutrals [ppb] = 124 + 0.489*Build-Blocks [ppb]; r^2 = 0.86, RMSE = 99 [ppb]; n = 29
8	%HS = 1.52 - 1.33*β:α; r^2 = 0.86, RMSE = 0.032; n = 29

Table 2. *Median DOC, A254, SUVA and DOC character during the different treatment steps for the period August 2013 to end of May 2014 (5-9 measurements per treatment). Pilot scale sampling sites in brackets (nanofiltration permeate (NF-P), activated carbon filtrate for pilot column fed with NF permeate (CF2), activated carbon filtrate for pilot column fed with rapid sand filtrate from the full scale process (CF4) and concentrate from the nanofiltration NF-C).*

Sample	DOC (mg C L^{-1})	A_{254} (m^{-1})	SUVA (L mg^{-1} m^{-1})	%HS	MW_{HS} (Da)	%build	%LMW
Raw	8.8±0.1	26.7±3.5	3.1±0.1	71±3	660±70	3.1	9.4
SF	4.3±0.1	8.9±0.5	2.1±0.1	50±4	450±50	3.6	15.0
NF-P	0.6±0.0	1.1±0.2	1.7±0.3	27±3	420±40	1.4	34.9
CF2[#]	0.5±0.1	0.5±0.6	1.2±1.3	30±14	420±50	2.1	36.3
NF-C	8.1±0.3	17.4±1.5	2.0±0.2	54±4	450±50	3.3	13.7
CF4[#]	4.2±0.8	8.4±0.7	2.1±0.2	54±4	450±50	3.2	14.8
DW	4.4±0.2	8.6±0.4	1.9±0.1	52±4	407±60	3.5	15.2

[#]these data have clear trends over time when fresh granular activated carbon is used but are displayed as median values in this table.

Table 3. *Median and standard deviation for fluorescence derived data of raw and processed water (SF = sand filtrate, NF-P = nanofiltration permeate). Indices from differential EEMs (Raw/SF = coagulation and SF/NF-P = nanofiltration) demonstrate characteristics of the removed FDOM. The step NF/CF2 is not included here as DOC is very low and we observed clear trends over time.*

Sample	FI	HIX	β:α
Raw	1.48+0.02	0.91+0.01	0.61+0.02
SF	1.68+0.03	0.88+0.01	0.76+0.02
Raw/SF	1.37±0.02	0.94±0.01	0.48±0.01
NF-P	1.84+0.06	0.83+0.02	0.95+0.04
SF/NF-P	1.65±0.02	0.90±0.01	0.70±0.02
CF	1.67 ± 0.03	0.88 ± 0.01	0.75 ± 0.01
SF/CF	1.80 ± 0.25	0.84 ± 0.09	1.07 ± 0.22
DW	1.67 ± 0.03	0.88 ± 0.01	0.75 ± 001

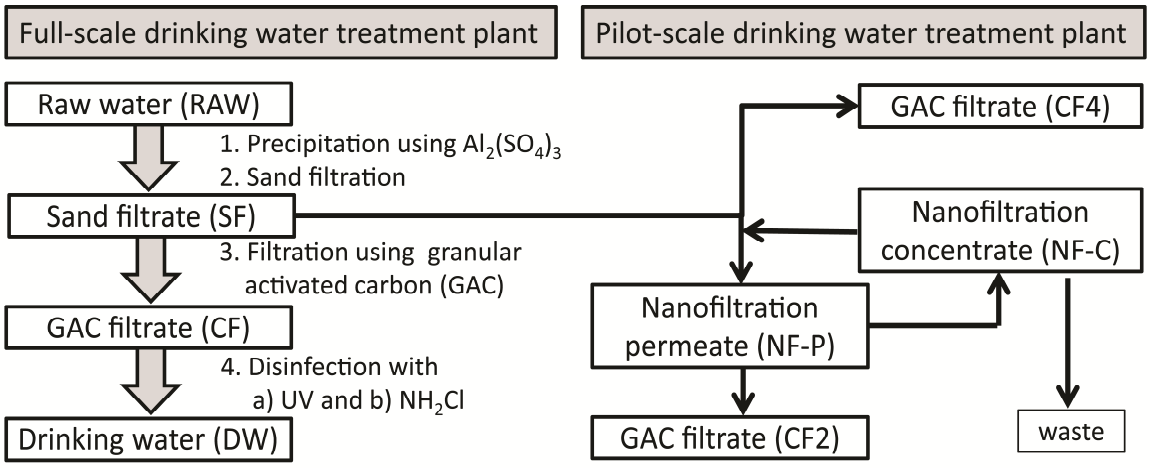

Figure 1. Water treatment train for the full scale drinking water plant and the pilot scale drinking water plant at Görväln waterworks. The codes for raw water (RAW), sand filter (SF), full scale active carbon filter (CF), nanofilter concentrate (NF-C), nanofilter permeate (NF-P), the other two carbon filters (CF2 and CF4) and drinking water (DW) are used throughout the paper

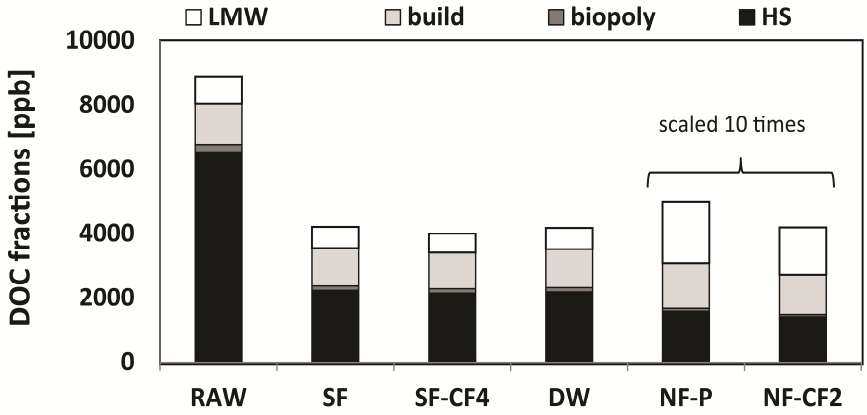

Figure 2. Selected results of median values for changes in DOC [ppb] quantity and quality across the WTP and pilot plant from the raw water (RAW) through the sand filter (SF), the nanofilter (NF-P) and through the full scale activated carbon (SF-CF4) to the final drinking water (DW) and after the activated carbon filter of the pilot plant (NF-CF2) for all samples in the period August 2013 to June 2014. DOC quality parameters in order of decreasing molecular size are codes as biopoly = Biopolymers, HS = Humic substances; LMW = low molecular weight neutrals; build = building blocks.

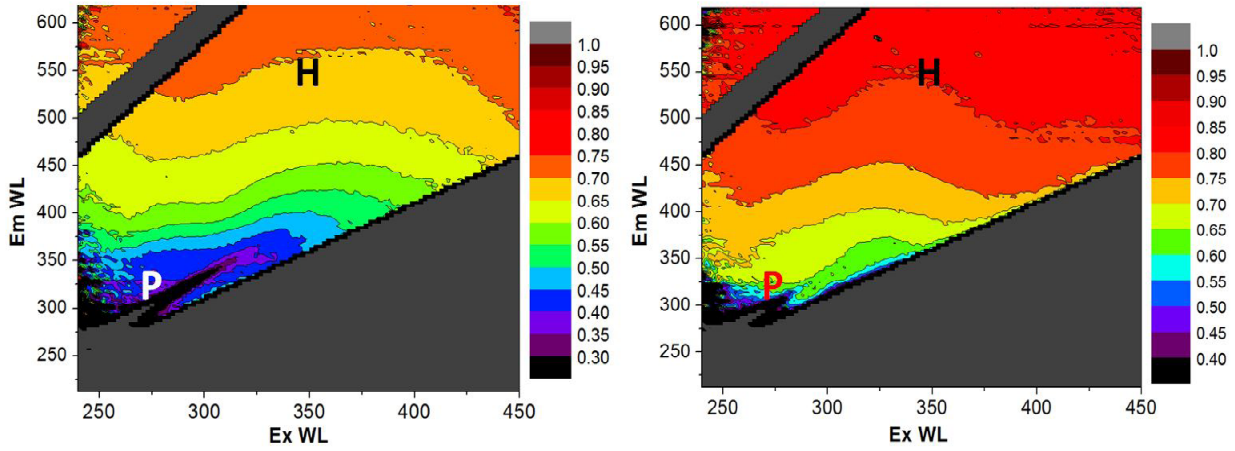

Figure 3: Fraction of removed fluorescent dissolved organic matter for coagulation (left) and NF (right) treatments. Dark red colors indicate strong removal (> 75%) while blue-purple colors indicate less removal (< 40%). The excitation/emission wavelength pairs chosen to represent humic-like (Ex = 350 nm, Em = 550 nm, marked “H” in the EEMs) and protein-like (Ex = 276 nm, Em = 320 nm,

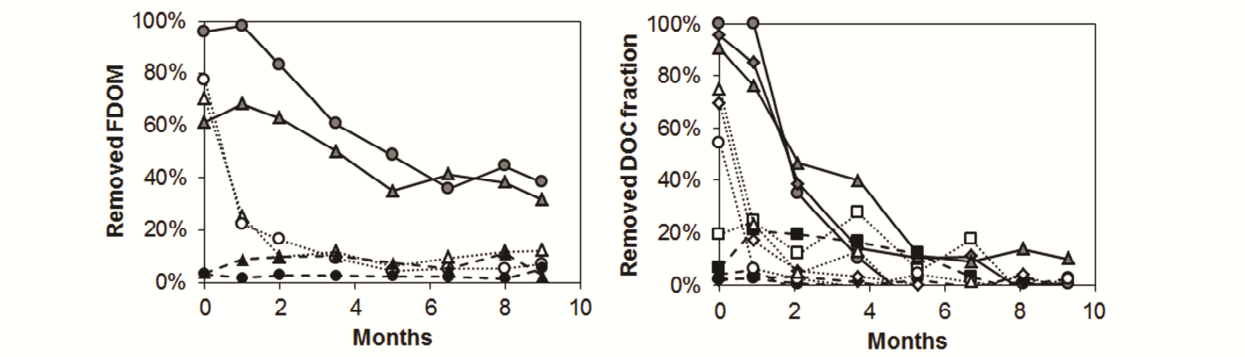

Figure 4 Removal (left panel) of protein-like (triangles) and humic-like (circles) fluorescent dissolved organic matter and (right panel) removal of low molecular neutrals (triangles), humic substances (circles), building blocks (diamonds) and biopolymers (squares) across granulated activated carbon (CF) filters in the full scale treatment (black symbols), as well as the pilot plant reference (CF4, white symbols), and downstream from the NF membrane (CF2, grey symbols).

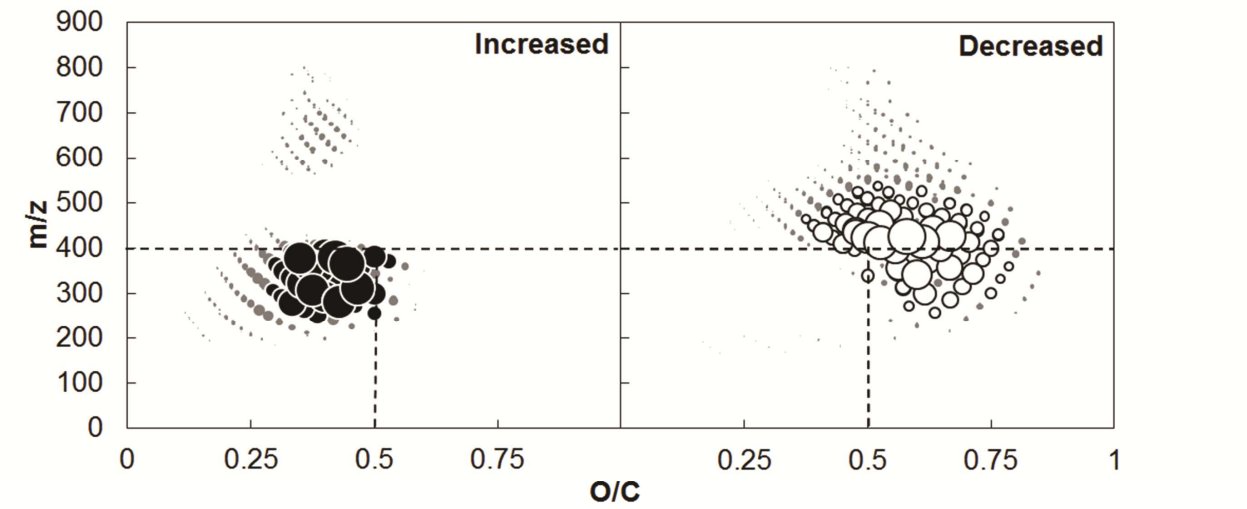

Figure 5: Left: Change in relative abundance as a function of the mass to charge ratio (m/z), left & right = relative change in relative abundance (bubble size) for components that decreased (right, white bubbles) and increased (left, black bubbles) during the pilot scale NF.

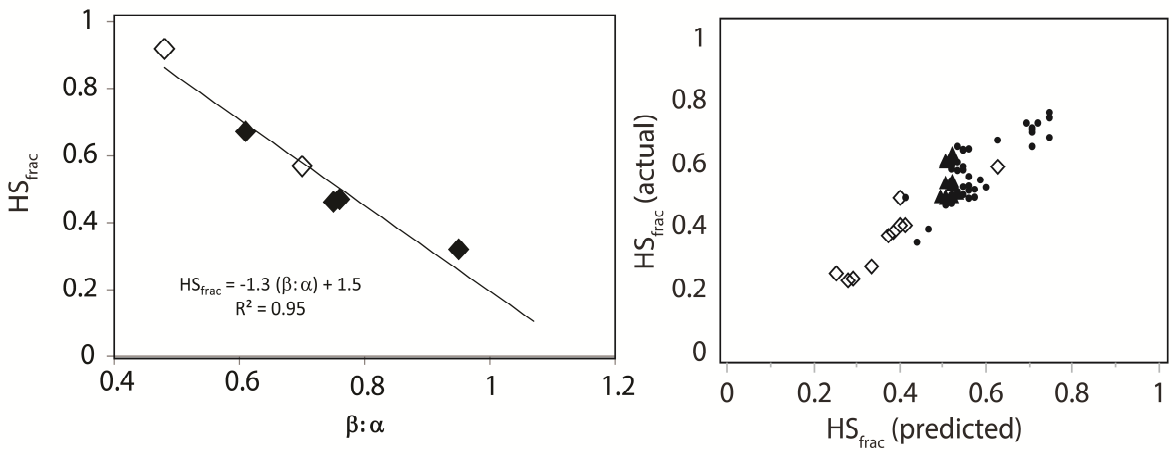

Figure 6: Left: Measured fraction of humic substances (HSfrac) for Raw, SF, DW and NF-P as a function of β:α (black diamonds) and mass balance derived HSfrac for the material that was removed during coagulation and NF treatments versus β:α calculated from differential EEM (white diamonds). The regression line is very close to that estimated from all individual data shown to the right. HSfrac (predicted) was estimated using β:α (HSfrac = 1.52 – 1.33* β:α), for all samples except CF2 where DOC concentrations were low.

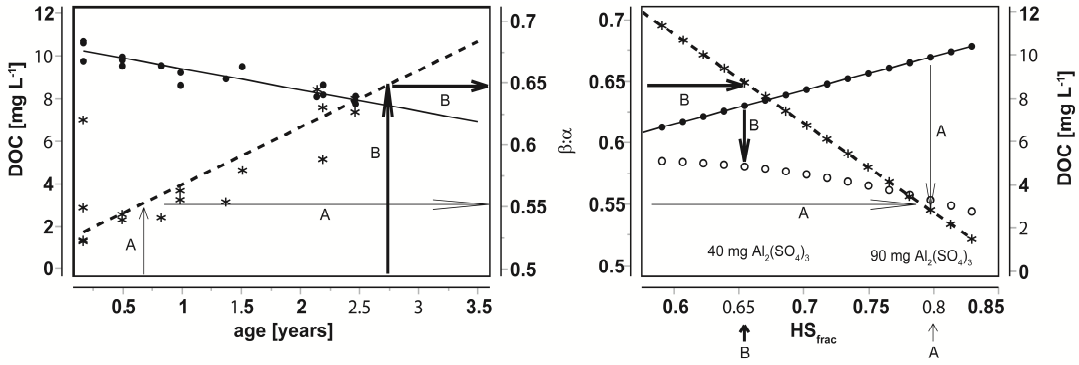

Figure 7: Measured and fitted DOC and β:α across Mälaren as a function of water age to the left (Data from Köhler et al 2013). Black circles and black stars display measured DOC and measured β:α respectively (left panel). Both DOC and β:α are read out as a function of water age (x-axis in left panel) using the horizontally pointing arrows in the left panel. On the right: predicted fraction of DOC composed of HS (HS_{frac}) (x-axis) estimated from as a function of incoming β:α (left y-axis) (blacks stars) and DOC (right y-axis) (black circles) using eqs. 2,3, and 8 in Table A. 1 that relate β:α , HS, DOC and aluminum dose. Vertically downwards pointing arrows indicate the amount of DOC (difference between black and white circles) that can be removed through coagulation treatment for two different situations (A and B); The predicted outgoing DOC (white circles in the right panel) is illustrated for A (a "young" water 0.7 months of age with high DOC and high HS_{frac} = 0.8, requiring around 90 mg L^{-1} $Al_2(SO_4)_3$ and outgoing DOC of around 3.3 mg L^{-1}) and B (an "old water" with lower DOC, lower HS_{frac} = 0.65 leading to a low dose of 40 mg L^{-1} $Al_2(SO_4)_3$ and outgoing DOC of around 4.7 mg L^{-1}).

Highlights

In this manuscript we document, evaluate and compare the stable performance of a newly developed nanofiltration membrane under a continuous nine month period using a pilot plant with the current full scale treatment in one the largest Swedish water treatment plants in Stockholm.

As we propose to increase the use of spectroscopic techniques, a special effort was put into identifying good spectroscopic proxies for the change in organic matter concentration and character.

We document the performance of the whole treatment train (raw water, coagulation, nanofiltration and active carbon filter both in the pilot and full scale process) with respect to organic matter removal and change in organic carbon character. It is the combination of a number of techniques LC-OCD, high resolution mass spectroscopy and fluorescence spectroscopy that allows us to derive which spectroscopic parameters may be used to control and evaluate the performance of the pilot and full scale plant.

At current full scale operation using aluminum coagulation indicate removal of larger (> 500 Da and HS only) terrestrial (FI = 1.4, β:α = 0.5) and with a higher mean average carbon oxidation state (**Error!**= 0.5) carbon. The coupled coagulation-NF pilot plant produced stable outgoing water quality (0.5 mg L^{-1}) during the nine month test trial. The removal of carbon with a much larger range of size (350-500 Da) and properties (**Error!**= -0.07, FI = 1.65, β:α = 0.5) during NF as compared to coagulation. Fluorescence derived parameters and correlations are reliable, fast to determine and comparably cheap complement to the more advanced techniques used here (FT-ICR-MS and LC-OCD). DOC removal and change of DOC character in the GAC filters in full scale, the current coagulation scheme and pilot plant setup showed marked differences with slower saturation and larger changes in DOC character using fresh GAC.

Climate change is predicted to change lake water residence time and thus organic carbon character in the lake. Based on the current process scheme we estimate how both factors will effect DOC in the finished water.