Comparison between ultrafiltration and nanofiltration hollow-fiber membranes for removal of natural organic matter: a pilot study

A. Lidén and K. M. Persson

ABSTRACT

Increasing trends of natural organic matter (NOM) in surface water in Nordic countries may cause future problems for drinking water producers. Emerging membrane technology, such as ultrafiltration (UF) and nanofiltration (NF), has the potential to produce safe drinking water of good quality from sources with high organic concentrations. In the present pilot study, surface water from three sources was treated by direct filtration on a hollow fiber ultrafilter (HFUF) and/or a hollow fiber nanofilter (HFNF). UV-absorbance (UVA) and total organic carbon (TOC) showed a high percentage of NOM removal by HFUF/coagulation, with retentions of around 75% for UVA and 55% for the TOC. NOM removal was notably greater by HFNF; with 93% in UVA retention and 88% in TOC retention. Regrettably, the water treated with HFNF retained 20–35% of the desired hardness. HFUF achieved retention comparable to traditional flocculation and sedimentation steps, while HFNF achieved even better removal of NOM. Importantly, results indicate that a membrane process with only an additional polishing step would result in decreased concentrations of NOM in the drinking water, even with higher organic loads in the raw water.

Key words | drinking water, nanofiltration, natural organic matter, ultrafiltration

A. Lidén (corresponding author)
K. M. Persson
Division of Water Resource Engineering,
Sydvatten AB, Lund University,
Lunds Tekniska Högskola, Box 118,
221 00 Lund,
Sweden
E-mail: angelica.liden@tvrl.lth.se

INTRODUCTION

New technology for drinking water treatment is required to tackle the changing quality of surface waters. In Sweden, most surface water treatment plants (WTPs) still use the same processes as when constructed decades ago. Common processes in Swedish WTPs, such as flocculation/sedimentation, activated carbon, and rapid and slow sand filtration, have limitations in their removal efficiencies, so new methods, such as enhanced coagulation, ozonation and continuous filters, have been introduced. Regrettably, the increased demand of removal of substances is costly, and with increasing natural organic matter (NOM) in the raw water, the removal will not reach satisfactory levels.

A major issue regarding the changing surface water quality is the increasing concentrations of NOM. This increase has been evident across Scandinavia (Hongve *et al.* 2004;

Ledesma *et al.* 2012), the UK (Worrall *et al.* 2004; Evans *et al.* 2006) and North America (Evans *et al.* 2005), and the rise has been related to a few probable causes. Increased organic concentrations have been found for watersheds with less acidification (Monteith *et al.* 2007), increased rainfall from climate changes (Köhler *et al.* 2009) and land use changes (Friberg *et al.* 1998). Such findings are alarming since the climate change will continue, and although NOM has no inherent hazardous implications, it entails other risks. One major issue is contamination, since bacterial growth in the distribution system is nourished (Camper 2004); higher concentrations of NOM can effect UV-disinfection, since NOM has a high absorbance at 254 nm, which is commonly the main output for UV lamps (Hijnen *et al.* 2006). In addition, NOM may react with chlorine used for

disinfection, increasing the demand for chemicals and lead-ing to the formation of disinfection by-products (DBPs), which have suspected adverse health effects (Nikolaou et al. 2004; Richardson et al. 2007; Hrudey 2009). Several types of these DBPs have been detected in the outgoing water from Swedish WTPs, some supplying half a million people (Lavonen et al. 2013).

Membranes introduce the possibility for increased NOM removal. One alternative is ultrafiltration (UF), which has been integrated into WTPs across Europe (Salehi et al. 2006): however, ultrafilters with low molecular weight cut off (MWCO), 10 kDa, has been shown to have little effect on the UV-absorbance (UVA) and total organic carbon (TOC) (Cho et al. 1999; Mijatović et al. 2004). To be able to remove NOM by UF, a coagulation step must be added, which has proven successful (Guigui et al. 2002; Kabsch-Korbutowicz 2006; Koncieczny et al. 2007), while spiral-wound nanofiltration (NF) has achieved a color removal of 80% over time in Norwegian WTPs (Ødegaard et al. 1999). Previous studies comparing UF and NF mem-branes have shown that although direct filtration by UF has a good NOM removal, NF shows a much higher general removal, including DBP precursors, suggesting that NF is the better option for WTP process (Mijatović et al. 2004; de la Rubia et al. 2008). NF has also been shown to be more selective towards hydrophobic fractions of NOM while no such difference has been seen for UF (Lee et al. 2005). The bio-stability may be improved by the NF, as it removes a large part of the biodegradable dissolved organic carbon (BDOC) and the assimilable organic carbon (AOC) from the feed water (Park et al. 2005).

Although NOM removal is the major motivation for implementing membrane filtration in Sweden, it is also cru-cial that this process does not exacerbate microbial contamination. UF used within drinking water production is commonly via hollow fiber membranes that are possible to backwash and clean with chlorine, which ensures a safe process and limits bacterial growth. In contrast, NF is usually via a spiral-wound type which would be destroyed if backwashed. A new hollow fiber nanofilter (HFNF) has been developed to address this issue (Frank et al. 2001; Fut-selaar et al. 2002; Veríssimo et al. 2005). The hollow fiber type permits good cleaning conditions, it is tight enough to retain small fractions of NOM, but retains fewer ions than

is traditionally achieved from NF (Veríssimo et al. 2005). Since NOM consists of numerous types of molecules with varying sizes, formations and moieties that differs between sources (McKnight et al. 2001), it is not yet possible to pre-dict the efficiency for local conditions. Using the boreal lakes of Sweden for drinking water, with soft waters and low temperatures for part of the year, challenges membrane treatments and the advantages and disadvantages for UF and HFNF need to be investigated for an understanding of under which circumstances one is preferable to the other.

This paper evaluates the advantages and disadvantages of hollow fiber ultrafilter (HFUF) and HFNF; mimicking a full scale process as far as possible and using membranes of commercial dimensions. In a single pilot plant, a new hollow fiber nanofilter is compared to a coagulation/ultrafil-tration combination for three different surface water sources, by evaluating TOC, UVA, and hardness of the resulting water qualities. The water qualities produced by the two types of membranes are compared, including how water quality may differ depending on the water sources.

MATERIAL AND METHODS

Membrane modules

The ultrafilter (Aquaflex 55) from Pentair X-flow (Pentair 2015) is an inside-out hollow fiber membrane, with an MWCO of 150 kDa and a membrane area of 55 m^2: around 15,000 fibers, each with a diameter of 0.8 mm, are encased in a plastic cylinder. The nanofilter is a newly com-mercialized hollow fiber module (HFW 1,000), from Pentair X-flow. The MWCO is 1 kDa, while the fibers and the casing have the same dimensions as the Aquaflex, but the number of fibers is around 10,000 and the membrane area is 40 m^2.

Pilot plant

All trials, running the modules sequentially, were conducted in a pilot plant from Pentair; an automated system in a 6.1 m long isolated container. A schematic diagram of the pilot is shown in Figure 1. A steering system with a software made for the X-flow modules, called ViCA, controlled programs
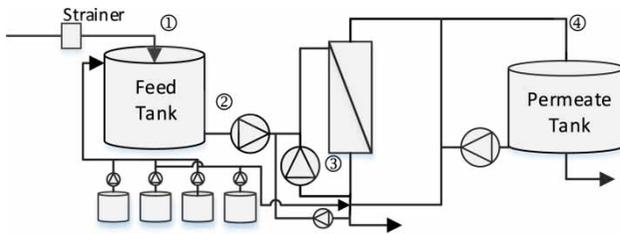
Figure 1 | Schematic diagram of the pilot plant. Numbers show locations of sampling points.

for the two modules. The transmembrane pressure (TMP) was adapted by the system to maintain the flux and cross-flow. Filtration cycles were programmed with set intervals for hydraulic and chemical cleans (Table 1), and levels of coagulant dose and pH were regulated. Additionally, the pilot had a program for air integrity testing (AIT) which could be initiated manually. The AIT was used for both membranes to monitor the integrity of the fibers.

Incoming water passed a strainer of 300 μm before entering the feed tank, in which coagulant was added and pH adjusted by addition of HCl or NaOH (for HFUF). From the feed tank, the water was fed into the vertically orientated membrane module from the top. The HFUF was run in a dead-end process while the HFNF needed the circulation pump to create a crossflow with a bleed flow. The permeate was collected in a permeate tank to be used for hydraulic and

chemical cleans (Table 1). The chemical cleans (CEB and CEFF) were performed as two different types; *type A* was performed with a base (NaOH) and an oxidants (NaOCl), while *type B* was performed with an acid (HCl).

Sampling and analyses

Four sampling locations were used: (1) raw water before feed tank; (2) feed with coagulant (only for HFUF); (3) concentrate from circulation pump (only for NF); and (4) permeate just before permeate tank (Figure 1). These samples were analyzed for TOC, color, UVA at 254 nm and hardness (from Mg and Ca concentrations). For one of the raw water sources (Stångån), alkalinity and concentrations of iron (for iron based coagulant) or aluminum (aluminum based coagulant) were measured.

Raw water sources

A brief presentation of the raw water sources and their chemical character is presented below. More information on the NOM character in the water from Lake Bolmen is presented in Lavonen (2015), no corresponding data for the remaining two water sources have yet been published.

Table 1 | Cleaning regimes for the programs in the pilot plant

Cleaning regimes	Chemicals	Duration	Steps	Module
Hydraulic clean (HC)	None	1.5 min (30 s for each step)	(1) down-to-top flushing (2) top-down flushing coupled with backwash (3) top-down flushing coupled with backwash and air sparging	Both
Chemical enhanced backwash (CEB)	Sodium hydroxide and sodium hypochlorite (A) Hydrochloric acid (B)	15 min for each of A and B	(1) Module filled with permeate with chemical dosed into it (2) 10 min soaking (3) Backwashed (4) Rinsed	HFUF
Chemical enhanced forward flush (CEFF)	Sodium hydroxide and sodium hypochlorite (A) Hydrochloric acid (B)*	70 min for each of A and B	(1) Module filled with permeate and chemicals (2) Chemical mix circulated slowly over membrane surface (3) Flushed (4) Backwashed	HFNF

*CEFF B rarely performed due to the low metal contents of the raw waters.

Table 2 │ Mean values for the raw water from Stångån (October 2012–March 2013, n = 24)

Color	TOC	UVA	Hardness	Ca	Turbidity	Temp
30 mg/l Pt	9.4 mg/L	0.30 cm^{-1}	46 mg/L	15 mg/L	4.4 FNU	3.3 °C

Stångån

Stångån is a watercourse in south-eastern Sweden. It runs from south to north, through a lake system and woodlands, into the city of Linköping where Råberga WTP is located. Turbidity, color and organic content (Table 2) are affected by precipitation and turbidity may increase from six Formazin Nephelometric Units (FNU) to 80 FNU within hours.

Bolmen

Water from Lake Bolmen is led to Ringsjö WTP through an 80 km long bedrock tunnel (crystalline basement), the water consists of around 6% groundwater due to intrusion. The water is soft and has low alkalinity but has NOM concentrations demanding treatment (Table 3).

Ringsjön

The lake Ringsjön is the reserve water source for Ringsjö WTP. This raw water is different from the Bolmen water; alkalinity and hardness are higher due to the limestone containing bedrock (Table 4). The NOM load is smaller, but in the summer the lake has problems with algal blooms due to the surrounding agricultural landscape.

Trial set ups

The experiments took place at two different locations with the three raw water sources and the two module types described here.

Stångån

Ultrafiltration

The first trials in Linköping were direct filtration on HFUF. Ferric chloride was chosen as coagulant since it is the best coagulant in reducing NOM in water, is less sensitive to changes in temperature (Matilainen *et al.* 2010) and is efficient at a wider range of pH (Eikebrokk 1999). Due to iron fouling, the trial was stopped and PACl was chosen as replacement to avoid further fouling. The flux was changed from 40 to 75 L/(m^{2}h) and different coagulant doses and pH levels were tested. Filtration time was set to 20 min between backwashes and CEB A + B were performed around 12 h apart.

Nanofiltration

First, the HFNF was trialed according to a scheme that, in this paper, will be referred to as the *20-point experiment*,

Table 3 │ Mean values for the raw water from Lake Bolmen (July 2013–January 2014, n = 39)

Color	TOC	UVA	Hardness	Ca	Turbidity	Temp
56 mg/L Pt	9.6 mg/L	0.39 cm^{-1}	23 mg/L	6.7 mg/L	2.0 FNU	10.5 °C

Table 4 │ Mean values for the raw water from Ringsjön (November 2014, n = 8)

Color	TOC	UVA	Hardness	Ca	Turbidity	Temp
37 mg/L PT	8.0 mg/L	0.23 cm^{-1}	98 mg/L	34 mg/L	3.5 FNU	10.1 °C

with varying flux and crossflow. Four crossflows (0.25, 0.5, 0.75 and 1.0 m/s) and five fluxes (5, 10, 15, 20 and 25 L/m^{2}h) were coupled and filtration was run for 1.5 h. After sampling, the module was refilled and the next filtration started, changing both flux and crossflow for any new experiment. When the 20-point experiment was finished, the pilot ran with a flux of 20 L/(m^{2}h) and crossflow of 0.5 m/s for 2 weeks, with regular hydraulic clean but no chemical clean.

Lake Bolmen

Ultrafiltration

The HFUF module was tested with water from Lake Bolmen. Aluminium sulphate (alum) was chosen as coagulant since it was accessible at the treatment plant and settings between 2 and 3.5 ppm Al were tried and pH was stable around 6.2. Filtration cycles were 20 min, and chemical cleans were 5 h apart.

Nanofiltration

The trial with the HFNF module and Bolmen water started in mid-July 2013. Flux and crossflow were kept from earlier, i.e. a flux of 20 L/m^{2}h and a crossflow of 0.5 m/s. In the beginning of the trial period, the CEFF A intervals were varied between 2–4 days with an intense sampling. A 2-day interval was the limit between the CEFF A, and the interval was set to 36 h for the continuing trial.

The 20-point experiment was performed as previously, but the water conditions only allowed a maximum flux of 23 L/m^{2}h, hence the fluxes were adjusted (5, 10, 15, 19 and 23 L/m^{2}h). After the experiment, settings were change to 15 L/m^{2}h, 0.5 m/s, and a CEFF A once a day.

Ringsjön

Nanofiltration

The 20-point experiment was also performed for Ringsjön. After this, the pilot plant ran with a flux of 20 L/m^{2}h, a crossflow of 0.5 m/s and CEFF A every 36 h for 3 weeks.

The HFUF was not trialed with water from Ringsjön due to lack of time at the site.

RESULTS AND DISCUSSION

With a continuing changing raw water quality, the WTP processes will have to be adapted. Parameters such as TOC, absorbance (254 nm) and hardness can be used to assess a specific method, giving an indication of how successful the method would be in a full scale treatment plant.

Below follows separate presentations and discussions of the HFNF and HFUF results, and subsequently the modules are compared from a water qualitative perspective. All results from the turbidity measurements of the permeate samples were close to or below 0.1 FNU for both membranes; therefore, turbidity is not included as a basis for comparison.

In addition to the actual fluxes, normalized fluxes are also presented to allow comparisons with other studies. Fluxes have been normalized for 20 °C according to:

$$J_{20} = J_T \cdot \frac{\mu_T}{\mu_{20}}$$

where J_{20} is the normalized flux, J_T the flux at temperature T, μ_T the corresponding viscosity at temperature T, and μ_{20} the viscosity at 20 °C.

HFNF

Figure 2 shows the membrane resistance for a 2-day period at Ringsjö WTP, Lake Bolmen (flux 20 L/m^{2}h and crossflow 0.5 m/s). The start and ending of the filtration cycle can be seen from the resistance change of around 1.5×10^{12} m, due to the chemical cleaning of the membrane in a CEFF ACEFF A. An increase in the resistance can be seen for any new filtration cycle due to fouling of the membrane. No effect from the hydraulic clean can be seen on resistance; this was performed every hour, yet no pattern from this can be seen in Figure 2.

Variations in water chemistry in the permeate

Figures 3 and 4 illustrate that the overall removal of NOM was successful for all 20 experiments in both of these water sources. The UVA-data are all lower than what is found for the produced water from the respective WTP
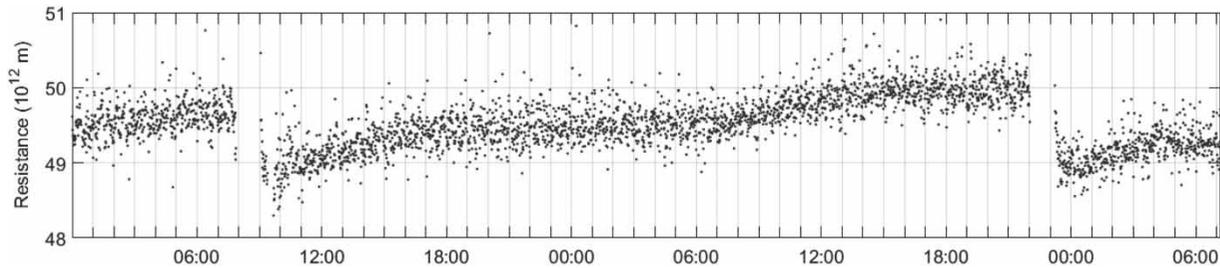
Figure 2 │ Membrane resistance over the HFNF for a filtration cycle in the trial with water from Lake Bolmen, September 16–18 (normalized flux: 22.1 L/m²h).
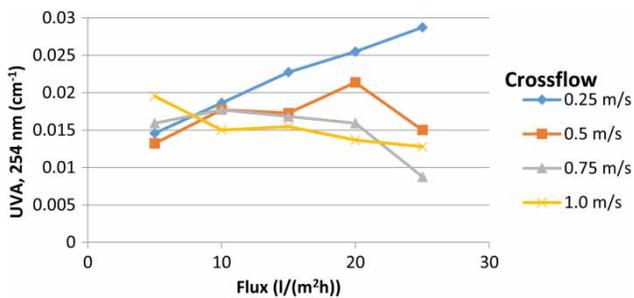

Figure 3 │ UVA in the HFNF permeate for the 20 experiments – the effect from changing flux or crossflow (Stångån). Maximum UVA 0.028 cm⁻¹ and highest TOC concentration 1.6 mg/L (normalized fluxes: 7.8; 15.6; 23.5; 31.3; 39.1 L/m²h).
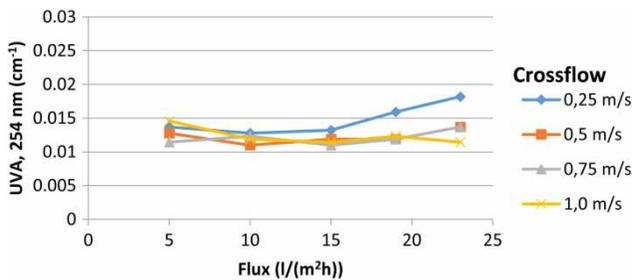

Figure 4 │ UVA in the HFNF permeate for the 20 experiments – the effect from changing flux or crossflow (Bolmen). Maximum UVA 0.018 cm⁻¹ and highest TOC concentration 1.1 mg/L (normalized fluxes: 6.7; 13.4, 20.1; 25.5; 30.9 L/m²h).

(UVA around 0.05 cm^{-1} and TOC around 3.0 mg/L), and the TOC concentrations in the permeates were below or close to 1 mg/L. These results show that all of the included settings in the 20-point experiments could achieve high standard water quality.

Further, Figures 3 and 4 give an indication to the degree of fouling at the different settings; both figures show an increasing UVA with increasing flux at a crossflow of 0.25 m/s. A possible reason for this increase is a higher concentration polarization on the membrane surface; the shear stress did not remove enough of the matter accumulated on the membrane surface. This can lead to degradation of the membrane from fouling, increasing the risk for irreversible fouling. Crossflows higher than 0.25 m/s in Figure 4 resulted in stable UVA with changing flux, and in Figure 3 UVA decreases with increasing flux. Thus the results underline that the choice of flux and crossflow should be chosen with consideration for the energy consumption and lifespan of a module rather than the water quality, since only minor differences can be seen for the latter within this range.

Overall, the results for the water samples from the rest of the HFNF study show a retention of the same level as the 20-points experiments. The samples from the permeate showed that UVA was between 0.025 cm^{-1} (Ringsjön) down to 0.009 cm^{-1} (Lake Bolmen), and the TOC concentration was below 1.5 mg/L with only a few exceptions. Due to the difference in the raw water, the retention varies between the sources.

Water temperature affects the operations of a membrane filtration process, and the differences in operation conditions may affect the resulting water quality of the permeate. Continuously, the chemical differences between the three water sources may be more tangible during parts of the year. In general, the membrane process is harder to operate during the cold half of the year, due to higher viscosity. Low temperature also increases the solubility of calcium, which may affect the hardness removal. The trials took place in different parts of the year, hence the comparison may have been affected. The trial at Stångån took place in March 2013, at the end of a cold winter with a water temperature of 2 °C. The Lake Bolmen trial started in mid-July, and was carried out to the end of October. It was resumed again in the end of November, and continued for two more weeks. The water temperature in the summer reached 20 °C and then decreased during the autumn to 8 °C at the beginning of December. However, no

major changes could be noticed for the permeate water quality with decreasing water temperatures. The trial for Ringsjön took place in October–November. During this time, the water temperature decreased from 11 to 9.5 °C.

The 20-point experiment was performed with water from Ringsjön as well. Unfortunately, it was concluded that during the days for the experiments, the incoming water was intruded by water from Lake Bolmen due to a nearby outlet. Therefore, the results from the 20-point experiment are not reliable for Ringsjön. However, for the rest of the trial, there were no other disruptions, and no intrusion in the following 3 weeks.

HFUF

Figure 5 shows the development of the membrane resistance over a period of 3 days for the trial at Ringsjö WTP (flux 50 L/m^{2}h). A cake layer is seen developing, but the resistance increase is reversed with every chemical cleaning, and no lasting fouling is shown. The hydraulic cleans could not decrease the resistance to the initial magnitude, however a decrease in the resistance was seen from flushing and backwashing of the membrane.

Variations in water chemistry in the permeate

In Figure 6 it is shown that the NOM removal from PACl can be optimized by a low pH: the TOC concentration in the permeate has the same pattern as the pH. A pH of around 6.2 gave the best results, TOC concentration of 4.5 mg/L and UVA of 0.07 cm^{-1}, while an even lower pH gave no improvement of the TOC retention, and only a small additional retention of species with high UV-absorbance (Figure 6), but these conditions affected the operations of the pilot rather negatively since the TMP rose rapidly.
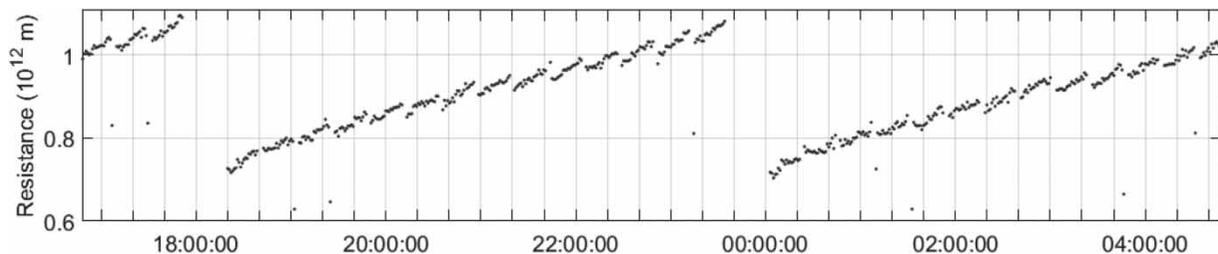

Figure 5 | Membrane resistance of the HFUF during one filtration cycle on December 24–25 (Lake Bolmen, alum 2.8 mg Al, normalized flux: 73.5 L/m^{2}h).
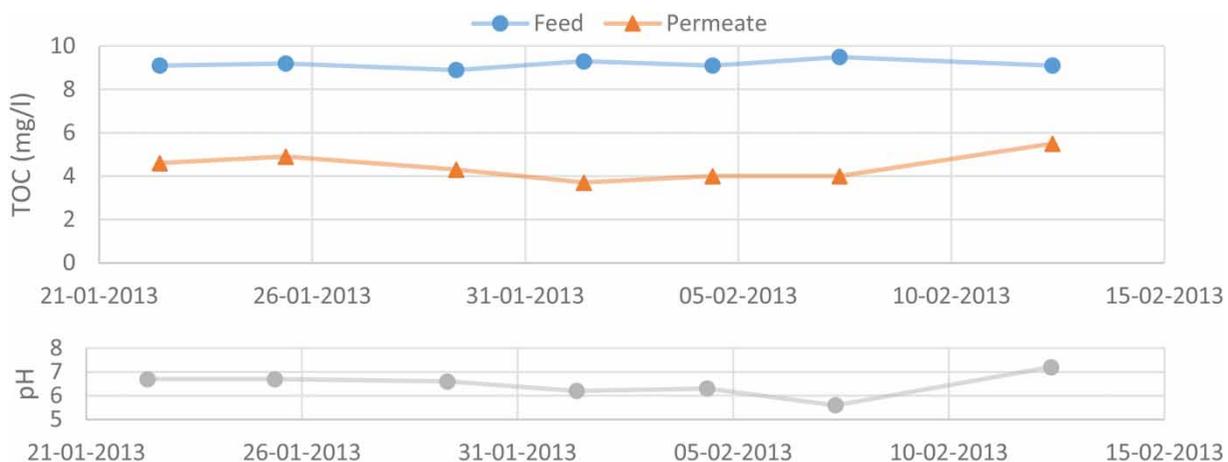

Figure 6 | TOC in the feed and the permeate, as well as pH in the feed for the same occasion, Stångån, HFUF and PACl. Initial flux: 45 L/(m^{2}h); January 21–22: 60 l/(m^{2}h); January 22 and forward: 75 l/m^{2}h (normalized: 125 l/m^{2}h).

The level of the coagulant dose was varied between 4 and 6 ppm Al. Since the effects from these changes were minor, the dosing is not shown in Figure 6.

Ferric chloride (FeCl) proved to entail problems for the HFUF-process, impeding the Stångån trial. The iron in combination with the soft water made it hard to operate the process; pH was fluctuating between pH 3 and 6 and the pressure increased with a quick, but varying, rate. TOC was reduced to 5.1 mg/L and the UVA to 0.1. These results are in the same range, but not as successful as the trial with PACl. However, the samples were too scarce and the conditions too unstable to conclude any superiority of PACl regarding water quality.

At Ringsjö WTP, the available coagulant, alum, gave good results for water from Lake Bolmen, but the operation settings were difficult to optimize. The dose and pH were adjusted at several occasions to find an optimum setting for this situation. A dose higher than 3.5 mg Al/L could not improve the retention of UVA and TOC, and a pH range of 5.9–6.2 gave the best results. The TOC retention was better than for Stångån, with a concentration of 3.3 mg/L in the permeate samples, while the UVA in the permeate was the same at $0.08\ cm^{-1}$. The better results with alum were not expected, since other coagulants have shown better organic removals, especially ferric coagulants. In this trial, the raw water source was different from when the other coagulants were used, which is the evident explanation to why the difference is rather large (for TOC retention), although characterizations of the organic species would help to further explain what causes the difference.

The coagulant was added into the feed tank that was equipped with a mechanical mixer. The retention time in the feed tank was 20 min for a flux of 75 L/(m²h) and up to 30 min for the lower fluxes. Acid and base were dosed into the feed tank, while the pH meter was located just before the inflow to the membrane. This distance between the dosing point and the pH meter was accounted for by a delay between the dosing and the next measurement for next adjustment. This time delay was set to 1–3 min to find an optional one. However, this distance led to a lag in the pH-adjustment which probably affected its implementation.

Similar results of pH dependence have been seen in Poland (Kabsch-Korbutowicz 2005), where a TOC removal of 59% was achieved with the best removal around pH

5. TOC concentration of the raw water was about the same, but HFUF had a MWCO of 30 kDa. Another study (Wang et al. 2012), again a HFUF with an MWCO of 30 kDa, has shown that the removal of fulvic acid decreases from pH 6 to 5, which indicates that the humic compounds are predominantly targeted at lower pH, which confirms an earlier study from the same team (Wang et al. 2011). Further evaluation of the NOM fractions targeted is completed in a collaboration with Köhler and Lavonen (Lavonen 2015).

Comparison between the two membrane modules

Two of the water sources were treated by both membrane modules in the same pilot. This makes it possible to compare the different modules for varying conditions. Also, there are data for an additional water source for the HFNF (Ringsjön).

Table 5 summarizes the average permeate water quality for all the trials in this work, and from this, a favoring of species with a high UVA is evident for both modules. Regarding the HFUF, the reduction of UVA is significantly higher than of the TOC concentrations. However, while the reduction of the TOC concentrations is high for the HFNF, the lower limit for the analyzing method used was 1.0 mg/L, and all concentrations below this were assumed to 0.9 mg/L (the lab analysis gives results with one decimal accuracy). Thus, the actual TOC retention might be better than what has been possible to show. Nevertheless, although the TOC retention was lower than what has been found from spiral-wound NF, which generally gives values below 0.5 mg/L in the permeate (Reiss et al. 1999), the HFNF would significantly increase the TOC reduction compared to conventional treatment.

Table 5 further illustrates the superiority in NOM removal of HFNF compared to direct-filtration by HFUF. Yet, the HFUF achieves a reduction that is of the same magnitude as the chemical treatment of today, with the advantage that it is a more time and space efficient method. Before the conclusion can be drawn that the choice of an HFNF is always favorable to an HFUF, further studies should evaluate the operational aspects, and what costs and environmental impact the two different membrane processes entails.

Based on these results, the HFNF is the obvious choice for a better drinking water quality, except from one perspective; the HFNF shows a reduction in hardness. Although a

Table 5 │ Average results of water quality in the different permeates, and retention as percentage removed from feed

	UVA (cm^{-1})	TOC (mg/L)	Hardness (mg/L)	Ca (mg/L)
HFNF				
Bolmen	0.013 ($\pm$ 0.002)	<1.0[a] ($\pm$ 0.12)	14.4 ($\pm$ 1.9)	4.2 ($\pm$ 0.5)
(n = 34)	97%	91%	38%	37%
Ringsjön	0.024 ($\pm$ 0.003)	1.15[a] ($\pm$ 0.17)	79.7 ($\pm$ 8.0)	27.8 ($\pm$ 2.9)
(n = 25)	90%	86%	18%	19%
Stångån	0.021 ($\pm$ 0.013)	1.3[a] ($\pm$ 0.5)	31.0 ($\pm$ 3.0)	9.9 ($\pm$ 1.0)
(n = 26)	91%	87%	35%	34%
HFUF				
Bolmen (alum)	0.08 ($\pm$ 0.01)	3.3 ($\pm$ 0.3)	23.9 ($\pm$ 1.5)	7.0 ($\pm$ 0.3)
(n = 22)	77%	65%	0%	0%
Stångån (FeCl)	0.10 ($\pm$ 0.05)	5.1 ($\pm$ 0.8)	42.8 ($\pm$ 0)[b]	13.5 ($\pm$ 0)[b]
(n = 4)	67%	46%	4%	10%
Stångån (PaCl)	0.07 ($\pm$ 0.01)	4.3 ($\pm$ 0.4)	42.8 ($\pm$ 1.5)	13.8 ($\pm$ 0.3)
(n = 7)	77%	54%	4%	8%

[a]In calculations <1.0 has been replaced with 0.9.
[b]Only one sampling occasion.

reduction in ion content is expected from NF, this membrane module was developed to limit this reduction. Compared to spiral-wound NF, the hardness reduction is lower by the HFNF, but for Lake Bolmen and Stångån, with low hardness in the feed, any small reduction is proportionately high (Table 5). Spiral-wound NF may cause ion retentions as high as 99% (Thanuttamavong *et al.* 2002) or more commonly around 50% (Ericsson *et al.* 1996). Nonetheless, since the hardness in the raw waters is already low, the resulting effect from a hardness reduction in the treatment process would be small, which means that the increase in lime addition would be negligible.

Comparing the results from the NOM removal with the existing WTP, there is a difference between the two WTPs included in this paper. Although the average results for the TOC retention by the HFUF is about the same as for the conventional chemical treatment, the UVA retention is lower. UVA values for HFUF permeate samples for Lake Bolmen are higher than for rapid sand filtrate at Ringsjö WTP, which is around 0.04 cm^{-1}. Hence, while the UVA retention is favored before the more general TOC retention, it is lower than what is desirable. However, the coagulant in the pilot study was another one used at Ringsjö WTP, which is ferric chloride, and this might explain the difference, since

ferric chloride has shown better NOM removal when combined with HFUF than aluminum based coagulants (Koncieczny *et al.* 2007). Results from Stångån do not give the same indication, since the HFUF achieved about the same retention for UVA and TOC as the existing chemical treatment process. Furthermore, comparing the HFNF to the conventional treatments, it is obvious that the NOM retention is better by the HFNF for all three water sources, with lower values for both TOC concentrations and UVA in the permeate than the outgoing water from the full scale plants.

Considering the high occurrences of DBPs found in the drinking water from Ringsjö WTP by Lavonen *et al.* (2013), a decreased concentration of humic substances and other NOM species should be a goal for drinking water producers. When chlorination is only performed in the end of the treatment process, less NOM in the treated water means a lower risk for DBPs.

CONCLUSIONS

In summary, the membranes show potential for improving drinking water treatment in Sweden. The trials with

membranes of commercial size show great potential for a full-scale application. Significantly, the HFNF has obvious advantages to the HFUF regarding the content of NOM in the produced permeate. On the other hand, the HFUF is a more space efficient alternative to conventional chemical treatment, achieving about the same level of NOM retention as existing chemical treatments.

Regardless of the raw water quality, both of the membrane modules showed similar NOM-retentions for all three sources included in this paper. Although other factors could have affected the results, it has been shown that membrane filtration was especially efficacious for water from Lake Bolmen, which could be due to the local water chemistry.

ACKNOWLEDGEMENTS

REFERENCES

Camper, A. K. 2004 Involvement of humic substances in regrowth. Int. J. Food Microbiol. 92, 355–364.

Cho, J., Amy, G. & Pellegrino, J. 1999 Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. Water Res. 33, 2517–2526.

De La Rubia, Á., Rodríguez, M., León, V. M. & Prats, D. 2008 Removal of natural organic matter and THM formation potential by ultra- and nanofiltration of surface water. Water Res. 42, 714–722.

Eikebrokk, B. 1999 Coagulation-direct filtration of soft, low alkalinity humic waters. Water Sci. Technol. 40, 55–62.

Ericsson, B., Hallberg, M. & Wachenfeldt, J. 1996 Nanofiltration of highly colored raw water for drinking water production. Desalination 108, 129–141.

Evans, C. D., Monteith, D. T. & Cooper, D. M. 2005 Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. Environ. Pollut. 137, 55–71.

Evans, C. D., Chapman, P. J., Clark, J. M., Monteith, D. T. & Cresser, M. S. 2006 Alternative explanations for rising dissolved organic carbon export from organic soils. Global Change Biol. 12, 2044–2053.

Frank, M., Bargeman, G., Zwijnenburg, A. & Wessling, M. 2001 Capillary hollow fiber nanofiltration membranes. Separ. Purif. Technol. 22–23, 499–506.

Friberg, N., Rebsdrof, A. & Larsen, S. 1998 Effects of afforestation on acidity and invertebrates in Danish streams and implications for freshwater communities in Denmark. Water Air Soil Pollut. 101, 235–256.

Futselaar, H., Schonewille, H. & Meer, W. V. D. 2002 Direct filtration nanofiltration – a new high-grade purification concept. Desalination 145, 75–80.

Guigui, C., Rouch, J. C., Durand-Bourlier, L., Bonnelye, V. & Aptel, P. 2002 Impact of coagulation conditions on the in-line coagulation/UF process for drinking water production. Desalination 147, 95–100.

Hijnen, W. A. M., Beerendonk, E. F. & Medema, G. J. 2006 Inactivation credit of UV radiation for viruses, bacteria and protozoan (oo)cysts in water: a review. Water Res. 40, 3–22.

Hongve, D., Riise, G. & Kristiansen, J. 2004 Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? Aqua. Sci. 66, 231–238.

Hrudey, S. E. 2009 Chlorination disinfectant by-products, public health risk tradeoffs and me. Water Res. 43, 2057–2092.

Kabsch-Korbutowicz, M. 2005 Effect of Al coagulant type on natural organic matter removal efficiency in coagulation/ ultrafiltration process. Desalination 185, 327–333.

Kabsch-Korbutowicz, M. 2006 Removal of natural organic matter from water by in-line coagulation/ultrafiltration process. Desalination 200, 421–423.

Koncieczny, K., Bodzek, M., Kopeć, A. & Szczepanek, A. 2007 Coagulation – submerged membrane system for NOM removal from water. Polish J. Environ. Stud. 16, 563–569.

Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H. & Laudon, H. 2009 Dynamics of stream water TOC concentrations in a boreal headwater catchment: controlling factors and implications for climate scenarios. J. Hydrol. 373, 44–56.

Lavonen, E. 2015 Tracking Changes in Dissolved Natural Organic Matter Composition – Evaluating Drinking Water Production using Optical and Molecular Level Tools. PhD thesis, Swedish University of Agricultural Sciences. www.slu.se. (Last accessed 11 September 2015.)

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-Kopplin, P. & Kohler, S. J. 2013 Selective chlorination of natural organic matter: identification of previously unknown disinfection byproducts. Environ. Sci. Technol. 47, 2264–2271.

Ledesma, J. L. J., Köhler, S. J. & Futter, M. N. 2012 Long-term dynamics of dissolved organic carbon: implications for drinking water supply. Sci. Total Environ. 432, 1–11.

Lee, S., Kwon, B., Sun, M. & Cho, J. 2005 Characterizations of NOM included in NF and UF membrane permeates. Desalination 173, 131–142.

Matilainen, A., Vepsäläinen, M. & Sillanpää, M. 2010 Natural organic matter removal by coagulation during drinking water treatment: a review. *Adv. Colloid Interface Sci.* **159**, 189–197.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T. & Andersen, D. T. 2001 Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanograph.* **46**, 38–48.

Mijatović, I., Matošić, M., Hajduk Černeha, B. & Bratulić, D. 2004 Removal of natural organic matter by ultrafiltration and nanofiltration for drinking water production. *Desalination* **169**, 223–230.

Monteith, D. T., Stoddard, J. L., Evans, C. D., De Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J. & Vesely, J. 2007 Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **450**, 537–540.

Nikolaou, A., Golfinopoulos, S., Lekkas, T. & Kostopoulou, M. 2004 DBP Levels in chlorinated drinking water: effect of humic substances. *Environ. Monit. Assess.* **93**, 301–319.

Ødegaard, H., Eikebrokk, B. & Storhaug, R. 1999 Processes for the removal of humic substances from water – an overview based on Norwegian experiences. *Water Sci. Technol.* **40**, 37–46.

Park, N., Kwon, B., Sun, M., Ahn, H., Kim, C., Kwoak, C., Lee, D., Chae, S., Hyung, H. & Cho, J. 2005 Application of various membranes to remove NOM typically occurring in Korea with respect to DBP, AOC and transport parameters. *Desalination* **178**, 161–169.

Pentair 2015 *Pentair X-flow* [Online]. http://www.x-flow.com. (Last accessed 11 September 2015.)

Reiss, C. R., Taylor, J. S. & Robert, C. 1999 Surface water treatment using nanofiltration – pilot testing results and design considerations. *Desalination* **125**, 97–112.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R. & Demarini, D. M. 2007 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-product in drinking water: a review and roadmap for research. *Mutat. Res.* **636**, 178–242.

Salehi, F., Wintgens, T. & Melin, T. 2006 Ultrafiltration with pre-coagulation in drinking water production – survey on operational strategies. Techneau. www.techneau.org. (Last accessed 11 September 2015.)

Thanuttamavong, M., Yamamoto, K., Ik Oh, J., Ho Choo, K. & June Choi, S. 2002 Rejection characteristics of organic and inorganic pollutants by ultra low-pressure nanofiltration of surface water for drinking water treatment. *Desalination* **145**, 257–264.

Veríssimo, S., Peinemann, K.-V. & Bordado, J. 2005 New composite hollow fiber membrane for nanofiltration. *Desalination* **184**, 1–11.

Wang, Q., Gao, B., Wang, Y., Yang, Z., Xu, W. & Yue, Q. 2011 Effect on pH on humic acid removal performance in coagulation-ultrafiltration process and the subsequent effects on chlorine decay. *Separ. Purif. Technol.* **80**, 549–555.

Wang, Y., Mao, R., Wang, Q., Yang, Z., Gao, B. & Zhao, Y. 2012 Fulvic acid removal performance and control of disinfection by-products formation potential in coagulation-ultrafiltration process. *Desalination* **302**, 55–64.

Worrall, F., Harriman, R., Evans, C., Watts, C., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P., Nisbet, T., Reynolds, B. & Stevens, P. 2004 Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry* **70**, 369–402.