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Research article

Natural organic matter fractions and their removal in full-scale drinking water treatment under cold climate conditions in Nordic capitals

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ABSTRACT

Drinking water treatment plants (DWTPs) designed to remove natural organic matter (NOM) are challenged as concentrations of NOM in raw waters are increasing. Here, we assess seasonal differences in NOM quality and quantity, from raw waters to the distribution network, at three large DWTPs in Oslo, Stockholm and Helsinki. Samples, collected during stable stratification in both winter and summer and during the autumnal turnover, were analysed for NOM concentrations and composition. The NOM was characterized by common routine parameters, size and content (TFF, LC-OCD, fluorescence) and biodegradability. The NOM concentration decreased to 2.5 mg/L (55%), 4.0 mg/L (48%) and 5.7 mg/L (76%) at the respective DWTPs in Oslo, Stockholm and Helsinki. The NOM in raw waters were predominantly in the largest size fraction (> 50 kDa), in particular from Oslo. High MW fractions > 50 kDa and humics remained the largest fractions with minimum 30% and maximum 80% of the total NOM. The BDOC in treated water < 0.3 mg/L and the conditions in the distribution network imply low probability for bacteria regrowth.

The multi-step treatment consisting of coagulation/flocculation, sedimentation, rapid sand filtration, ozonation and biological activated carbon filtration (BAC) was most effective in removing NOM. Coagulation/flocculation followed by sedimentation and sand filtration were critical, especially for the removal of biopolymers and humics, and somewhat for building blocks. The sand filtration provided up to 25% additional removal of biopolymers and below 7% removal of other fractions. The ozonation and BAC was more effective and removed 11% of biopolymers, and about 35% of building blocks and LMW neutrals.

1. Introduction

In Fennoscandia, surface waters are the main sources for drinking water production. In recent decades increasing concentrations of dissolved natural organic matter (NOM) have been observed (de Wit et al., 2007, 2016). Most of the NOM in northern surface waters is of terrestrial origin and subject to biological, chemical and physical processes that determine its fate along the aquatic continuum (Dillon and Molot, 1997; Neff and Asner, 2001; Catalán et al., 2016). The primary drivers of browning surface waters typically considered are reduced sulfate

deposition (Monteith et al., 2007) and climate change (de Wit et al., 2016), suggesting that current browning trends will continue into the future. Water colour has shown larger increases than dissolved organic carbon (DOC) concentrations (Haaland et al., 2010), suggesting a change in NOM composition from lower to higher molecular weight and increasing aromaticity. Removal of increasing concentrations of NOM to reach compliance with drinking water quality regulations is a challenge for many drinking water treatment plants (DWTPs) in Fennoscandia (Ledesma et al., 2012). Particularly for many DWTPs that waterworks have had sufficient raw water qualities (Norwegian

Abbreviations: BAC, biologically activated carbon filtration; BDOC, biodegradable dissolved organic carbon; Cl-N, chloramine disinfection; Da, Dalton; DBP, disinfection by-products; DMF, dual media filtration; DOC, dissolved organic carbon; DOM, dissolved organic matter; DWTP, drinking water treatment plant; HMW, high molecular weight; LC-OCD, liquid chromatography - organic carbon detection; LMW, low molecular weight; MW, molecular weight; MWCO, molecular weight cut-off; N.M., not measured; NOM, natural organic matter; O₃, ozonation; PAX, polyaluminium chloride; RSF, rapid sand filtration; SSF, slow sand filtration; SUVA, specific UV absorbance; SHA, slightly hydrophobic acids; TFF, tangential flow filtration; TOC, total organic carbon; UV, ultraviolet disinfection; UV₂₅₄, UV-absorbance at 254 nm; VHA, very hydrophobic acids

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guidelines: TOC < 5 mg C/L and colour < 20 mg Pt/L), implying that implementation of advanced treatment to remove NOM was not required when initially designed. Consequently, DWTPs will probably need to invest in NOM removal and to adapt treatment procedures (Tryland et al., 2011) in accordance with high levels of NOM, and possibly even higher levels in the future. This in turn may increase both the complexity and costs of the drinking water production.

Other cases in Fennoscandia show that decreasing NOM concentrations to an acceptable level during treatment results in increased consumption of chemicals (mainly coagulants) (Anderson et al., 2017), shorter filter run times resulting in higher consumption of filter backwash water and production of more sludge, and consequently in decreased treatment capacity and increased operational costs (Eikebrokk et al., 2004). Not only the quantity, but also the composition of NOM has implications for challenges regarding the removal of NOM. If particular fractions of dissolved natural organic matter are not sufficiently removed, elevated concentrations in the treated water may potentially bring about problems with taste and odour, a higher risk for bacterial regrowth, pipe corrosion and higher concentrations of disinfection by-products (DBP) after disinfection with chlorine (Vreeburg et al., 2005; Sun et al., 2014; Prest et al., 2016). Hydrophobic and high-molecular weight NOM fractions typically responsible for the formation of DBPs are far more easily removed by coagulation (Eikebrokk et al., 2006) than hydrophilic and low-molecular weight fractions which typically are associated with bacterial regrowth in the distribution network. Moreover, biodegradable dissolved organic carbon (BDOC), or assimilable organic carbon (AOC) (Uhl, 2008), is of importance with regard to the biological stability of the finished drinking water entering a distribution system (Zappia et al., 2008), as NOM in the distribution network promotes the development of biofilms (Prest et al., 2016). Production and processing of NOM in catchments and aquatic pathways are sensitive to seasonal and short-term variations in temperature and precipitation, and thus to hydrology and in the longer term, climate change (de Wit et al., 2016). Thus, knowledge on seasonal variability of raw water, seasonal changes in NOM fractions composition and effects on NOM treatability is relevant for the assessment of short-term and longer-term challenges for drinking water treatment with changing quantity and quality of NOM. Until now, the removal of NOM fractions during different stages at full-scale drinking water treatment plants is not thoroughly explored (Matilainen et al., 2002; Vasyukova et al., 2013; Papageorgiou et al., 2016).

The objectives of the presented work was to (1) assess seasonal variability of raw water and changes in NOM fractions, (2) assess changes in composition and behaviour of NOM during treatment in full-scale DWTPs, (3) evaluate the removal effectiveness of different NOM fractions by different treatment processes during drinking water treatment, and (4) to assess the level of biodegradable organic matter in and estimate biological stability of raw and treated water coming from DWTPs by means of BDOC test.

2. Material and methods

2.1. Study sites and sampling

This study investigated three drinking water reservoirs located in Fennoscandia, namely Lake Maridalen (Berge et al., 2011), Lake Mälaren (Johansson et al., 2010; Köhler et al., 2013) and Lake Päijänne (Castrén et al., 2014; Forsius et al., 2017), (Fig. 1a), and three full-scale DWTPs that provided drinking water to capitals in Norway (Oslo), Sweden (Stockholm) and Finland (Helsinki) (Fig. 1b). The treatment train of the three DWTPs consists of chemical precipitation, sedimentation, filtration and disinfection processes. In addition, a slow sand filtration is employed to further clean the raw water prior to disinfection in the Stockholm DWTP. At the Helsinki DWTP the effluent of the filtration process is treated with ozonation and activated carbon filtration.

The DWTPs were sampled in winter (as a reference), summer (with good stratification) and autumn (during the circulation period when the lake was turning over) in 2015 to consider seasonal differences. The samples were collected at the DWTPs from the inlet at the same depths as the intakes, after selected treatment processes, and at the outlet after disinfection. For the intermediate stage, samples were collected at different points in the treatment train (Fig. 1b) to assess the effect of the particular treatment processes that were expected to mostly impact the NOM concentration. These processes were coagulation-flocculation and sedimentation (coagulation/sedimentation) in Stockholm DWTP and coagulation-flocculation, sedimentation and media filtration (coagulation/sedimentation/filtration) in Oslo and Helsinki DWTPs. In Oslo DWTP, the media filtration stage process was dual media filtration consisting of filterlite (1.50 m depth, 1.5–2.5 mm grain size) and quartz sand (0.5 m depth, 0.4–0.8 mm grain size), operated with typical filtration velocity of 15 m/h. In Helsinki DWTP, it was rapid sand filtration with quartz sand (1 m depth, 0.5–1.0 mm grain size, 7 m/h filtration velocity). The rapid sand filtration in Stockholm DWTP consists of single quartz sand layer (1.1 m depth, 0.95 mm effective grain size, 3 m/h filtration velocity). Polyaluminium chloride (PAX) and aluminium sulfate are used for coagulation/flocculation at the Stockholm DWTP (coagulant dosage of 3.0–4.2 mgAl/L and pH of 6.6–7.0) and Oslo DWTP (coagulant dosage of 1.8–2.4 mgAl/L and pH of 6.2–6.5). Ferric sulfate is used for coagulation/flocculation in the Helsinki DWTP (coagulant dosage of 6.25–7.5 mgFe/L and pH of 4.8–4.9). Detailed description of the DWTPs is provided elsewhere (Vuorio et al., 1998; Venkatesh and Brattebø, 2012; Lavonen et al., 2013, 2015; Laurrell et al., 2014; Tryland et al., 2015), whereas details of the associated catchment areas and drinking water reservoirs are provided in Table 1.

Raw waters, water after selected treatment processes and finished treated water samples were collected for the analyses. Grab samples were collected in HDPE plastic containers pre-washed with ultrapure water and collected sample, and in DOC-free amber glass bottles for liquid chromatography - organic carbon detection (LC-OCD) analysis, and immediately transported or shipped to the analytical labs for analyses. Each campaign included routine water quality analyses; total organic carbon (TOC), dissolved organic carbon (DOC), pH, turbidity, ultraviolet absorbance at a wavelength of 254 nm (UV₂₅₄) and colour, as well as BDOC and LC-OCD. Samples from the winter, summer and partially the autumn campaign were also subjected to membrane size fractionation.

2.2. Routine analyses

The routine water quality measurements were conducted in accordance with the procedures described in Norwegian Standard Methods: colour and UV-absorbance at wavelength of 254 nm (UV₂₅₄) with ManTech analyse robot and Perkin Elmer Lambda 40P UV/VIS spectrophotometer, respectively (NS-EN ISO 7887:2011), pH (NS-EN ISO 10523:2012), alkalinity (NS-EN ISO 9963-1:1996), turbidity with ManTech analyse robot (NS-EN ISO 7027:2000), aluminium and iron with Agilent 7700x ICP-MS (NS EN ISO 17294-1:2007; NS-EN ISO 17294-2:2005) and TOC and DOC with Phoenix 8000 TOC-TC analyser (NS-EN ISO 1484; 1:1997).

Prior to DOC, colour, UV₂₅₄ and LC-OCD analyses, the samples were filtered using pre-combusted (muffled at 450 °C for 4 h) and pre-washed (200 mL of MilliQ water) glass fiber filters with a nominal pore size of 0.7 µm (Whatman GF/F). Only pre-combusted glassware was used to decrease the risk of contamination of the samples. In case the samples were stored for more than a day prior to DOC analysis, the samples were acidified for preservation by addition of 1 mL of 4M H₂SO₄ to 100 mL. The specific UV absorbance (SUVA) (Edzwald and Tobiasson, 1999) was calculated by dividing the UV₂₅₄ by the corresponding DOC concentration.

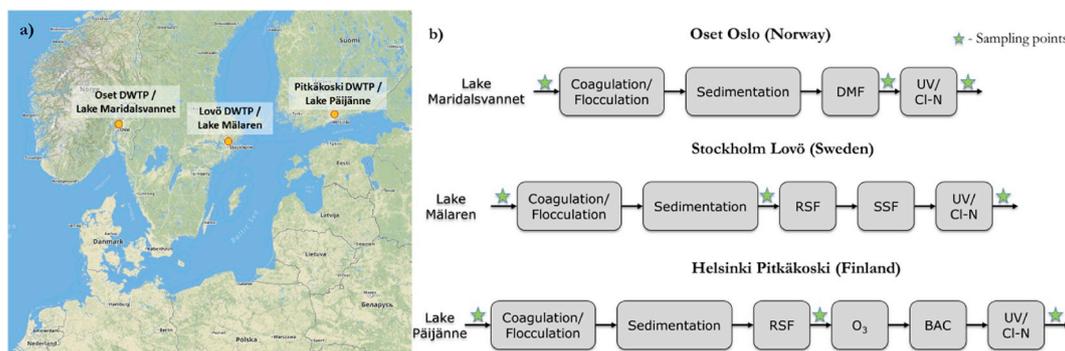


Fig. 1. (a) Location of sampling sites and (b) associated treatment scheme with location of sampling points. BAC – biologically activated carbon filtration; Cl – chlorine disinfection; Cl-N – chloramine disinfection; DMF – dual media filtration; O₃ – ozonation; RSF – rapid sand filtration; SSF – slow sand filtration; UV – ultraviolet disinfection.

2.3. Size exclusion chromatography fractionation

Samples for LC-OCD analysis were collected in dedicated 100 mL oven-burned DOC-free amber glass bottles and immediately sent for analysis. Quantitative analysis of NOM fractions was performed by a modified version of the LC-OCD-8 model; SC2000 system (Postnova analytics, Landsberg, Germany) together with an OCD (DOC-Labor Huber), UV-detector PN3211 (Postnova analytics) and a SEC column filled with Toyopearl HW-50S (30 μm , dimensions 250 \times 20 mm). The detection limit was not checked; however, it is assumed to be in the low ppb range about 1.5 $\mu\text{g/L}$ according to the LC-OCD instrument producer (Huber and Frimmel, 1991; Huber et al., 2011). In the LC-OCD, DOC was divided into hydrophobic organic carbon (HOC) and hydrophilic organic carbon (CDOC). The hydrophilic organic carbon was further fractionated into five fractions based on the interactions with the gel and their apparent molecular size: biopolymers (e.g. polysaccharides, proteins and amino sugars, > 20 000 g/mol), humic substances (e.g. fulvic and humic acids, 350–10 000 g/mol), building blocks (hydrolysates of humic substances, 300–500 g/mol), low molecular weight (LMW, < 350 g/mol) acids and LMW neutrals (< 350 g/mol) (Huber et al., 2011; Slavik et al., 2012). Data interpretation was carried out with the evaluation software ChromCALC.

2.4. Membrane filtration size fractionation

A custom-made bench scale membrane unit, operated in tangential (crossflow) flow filtration (TFF) mode, was used for the size fractionation of the collected samples applying a standardized protocol. A detailed description of the installation can be found elsewhere (Krzeminski et al., 2017). Each fractionation was carried out with a new membrane, cut from commercially available flat sheet and spiral wound membranes. The effective membrane area was 99.4 cm². The flat-sheet membranes used had a molecular weight cut-off (MWCO) of 50 kDa (Alfa Laval GR51PP), 10 kDa (GE PW) and 0.3 kDa (GE DL).

Table 1

Description of drinking water treatment plants (DWTPs) catchment area.

DWTP name and location	Catchment size, lake area, lake retention time	Raw water source	Sampling times
Oset, Oslo, Norway	252 km ² , 3.7 km ² , 0.31–0.38 year (115–140 days ^a)	Lake Maridalen (Maridalsvannet)	2 March 2015 17 August 2015 19 November 2015
Lovö, Stockholm, Sweden	22 063 km ² , 1096 km ² , 2.8 year (948 days ^a)	Lake Mälaren	6 March 2015 24 August 2015 27 November 2015
Pitkääkoski, Helsinki, Finland	26 459 km ² , 1081 km ² , 2.5 years	Lake Päijänne	2 March 2015 20 August 2015 27 November 2015

^a www.lakepedia.com.

Fractionation experiments were carried out in the concentration mode, i.e. the concentrate was returned to the feed tank, while the permeate was collected separately, except from initial 15–30 min phase when both streams were wasted. Serial fractionation with the permeates filtered subsequently through the next membranes was applied (Fig. 2). A series of filtration steps was used to minimize concentration polarization effects as suggested by Gang et al. (2003) and Wei et al. (2008). According to the multi-stage filtration method, the high-molecular-weight molecules are removed first. In addition, to decrease the risk of contamination, samples were fractionated in the following order: (1) treated water, (2) selected intermediate step, and (3) raw water.

All of the experiments were performed at ambient temperature of 21–22 °C and at pressure representative for each membrane type. Permeate collected within the first 30 min was discarded. The experiments were carried out until a desired volume of permeate was obtained. The mass balance of DOC was used to evaluate the potential contamination or loss of organic carbon during fractionation. The membrane fractionation resulted in different size fraction samples based on their molecular weight.

2.5. Biodegradable dissolved organic matter

The biodegradability of the organic matter was assessed using the BDOC method in which bacteria attached to sand is used as inoculum (Joret and Levi, 1986). The procedure used is based on shaker acclimated-sand method developed by Joret et al. (1988) and described by Vasukova et al. (2013). Cleaned and sterilized at 240 °C filter sand was inoculated with naturally occurring sessile bacteria in similar origin and DOC-rich water and incubated a period of three weeks for bacterial enrichment and depletion of the original DOC. At the end of the incubation, one litre glass bottle containing 100 mL sand was filled up with a sample and incubated in the dark at ambient temperature of 22 \pm 1 °C for 14 days. BDOC concentrations were derived from the difference between an initial DOC concentration (after inoculation) and

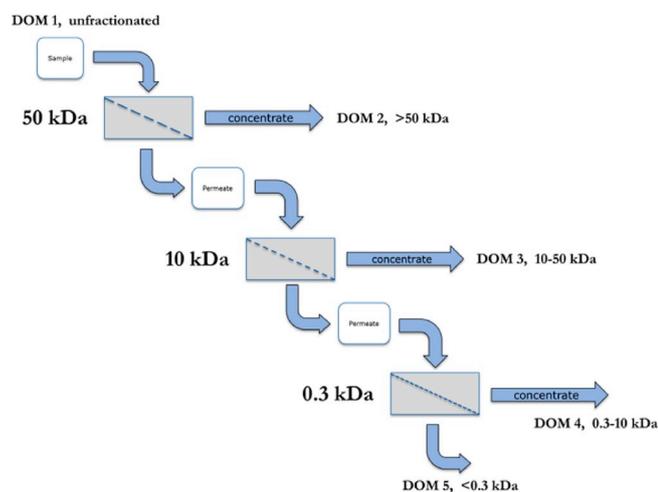


Fig. 2. Schematic representation of the multi-stage filtration (membrane size fractionation).

the DOC concentration after 14 days of incubation. The accuracy of the DOC-analysis test is about 1% when the DOC is around 1.5 mg/L and 15% when DOC is around 0.5 mg/L. The level of detection (LoD) of the TOC analysis method used was 0.1 mg/L. The BDOC data were evaluated statistically and interpreted using confidence intervals, at a confidence levels of 0.33.

2.6. Fluorescence analysis

To assess the optical properties of the dissolved organic matter, selected samples from the summer campaign were analysed for fluorescence following the procedure described by Lavonen et al. (2015). Three optical indices were calculated from the corrected excitation-emission matrices (EEMs): Humification index HIX (Ohno, 2002), fluorescence index FI (Cory and McKnight, 2005) and freshness index $\beta:\alpha$ (Parlant et al., 2000). Explanations of how they are defined and have been interpreted can be found in Table 2. The results are displayed in the Supplementary Material.

3. Results and discussion

3.1. Physicochemical characteristics of water samples

The concentrations of dissolved organic matter in the raw waters varied between 4.2 mg/L in Oslo and 7.9 mg/L in Stockholm, respectively. It is worthy to note that, the Stockholm reservoir, lake Mälaren, is open for public use and significantly impacted by runoff from surrounding agricultural activities. The Helsinki reservoir, lake Päijänne, is also open for public, but considerably less impacted by agriculture runoff (Forsius et al., 2017). The Oslo reservoir, lake Maridalen, is closed to the public and different agriculture activities have a much lower impact, although not necessarily when its relatively small size is taken into account. Based on Edzwald and Tobiason (1999), the analysis of available SUVA data (2.7–3.9 L/mgC/m) indicates that the raw

waters are mostly a mixture of aquatic humics and other NOMs, hydrophobic and hydrophilic NOM and high and low molecular mass matter (Matilainen et al., 2010). A SUVA in the range of 2–4 indicates fair to good treatability of raw water by coagulation with removal rates between 25 and 50% for aluminium- and somewhat better for iron-based coagulants (Edzwald and Tobiason, 1999). The coagulation pH was in range of 6.2–7.0 for the DWTPs in Oslo and Stockholm, utilizing aluminium-based coagulants. The Helsinki DWTP was operating their coagulation at pH 4.8–4.9, using iron-based coagulants. The pH is an important parameter with respect to removal of organic matter by coagulation. Even though the relationships are complex, generally, lowering pH improves NOM removal (Edwards, 1997) as organics are protonated and adsorb better to the iron or aluminium hydroxide flocs. Thus, at acidic pH, higher removal can be achieved, or lower coagulant doses can be realized (Crozes et al., 1995). The optimal pH is in the range of pH 5–6, which is slightly dependent on the chemical composition of the water and type of the coagulant. However, the pH at which coagulation can be carried out is governed by other factors as well. For example, the tolerance of the construction material of filter basins to acidic conditions might limit the feasibility of operation at lower pH.

The detailed physicochemical characteristics of the collected water samples of raw waters, effluents from selected treatment processes and final treated water during different seasons are given in the Supplementary Material (Table S1).

Additional information on DOM quality from fluorescence analysis of the samples confirms the importance of SUVA for characterising raw and treated waters. The lower freshness index, β/α , of the raw water in Oslo (0.5) compared to the raw waters in Helsinki and Stockholm (0.6) indicates larger contribution of more freshly in-lake produced autochthonous DOM in the larger catchments. The good correlation between SUVA and β/α ($R^2 = 0.92$) coincides with earlier studies across a gradient in lake Mälaren where β/α increased while SUVA decreased, which is interpreted to be an effect of DOC processing during the 2.8 years retention time in the lake (Köhler et al., 2013, 2016). The high precision of β/α (1%) compared to SUVA (between 5 and 15% depending on DOC and UV) is advantageous for the quality of prediction. In addition to its higher precision, it is based on a single measurement instead of two (DOC and absorbance). More detailed information can be found in Table S2, Fig. S1 and Fig. S2.

3.2. NOM fractions distribution in raw water: spatial and seasonal differences

Two different fractionation methods were used, i.e. LC-OCD fractionation and TFF membrane fractionation. The LC-OCD was performed on all water samples except April, while the TFF characterization was complete only for the Oslo samples, and only done in summer and winter for the other two DWTPs. The LC-OCD method separates the bulk DOC compounds in specific classes of compounds based on their hydrophobicity, molecular weight and charge: biopolymers, humic substances, building blocks, LMW acids, LMW neutrals, and hydrophobic organic carbon (section 2.3). All but the latter are considered hydrophilic compounds (i.e. they are not retained by the hydrophobic polymethacrylate resin) using LC-OCD fractionation nomenclature. The TFF method separates the NOM into fractions of different molecular

Table 2

Definition and interpretation of previously established optical indices used in this study. A = area under the curve. Em = Emission. Ex = Excitation.

Index	Definition [No. in nm (if not other indicated)]	Interpretation
HIX	Em: $A(345-480)/[A(300-345) + A(435-480)]$ Ex: 254	Degree of humification; high HIX = more humified material
FI	Em: 470/520 Ex: 370	Source; gradient from higher FI = more of microbial origin to smaller FI = more of terrestrial origin
$\beta:\alpha$	Em: $380/\max(420-435)$ Ex: 310	Age; higher $\beta:\alpha$ = larger contribution of more freshly produced DOC

weight sizes by means of membranes with different molecular weight cut-off ranges.

The LC-OCD fractionation showed that the main NOM fraction (82–92% of DOC) in all three reservoirs was of hydrophilic nature. This is inconsistent with the typical observations done when using XAD resin fractionation, where a similarly high fraction is indicated to be very hydrophobic acids (VHA) and slightly hydrophobic acids (SHA) (Fabris et al., 2008; Eikebrokk et al., 2018). However, both LC-OCD and XAD have experimentally derived definitions of what is hydrophobic and hydrophilic (i.e., defined by the different resins used). Also, the LC-OCD and TFF methods gave contrasting results. By membrane fractionation the majority (> 55%) of the NOM is classified as > 50 kDa, whereas the LC-OCD data indicated that significant portion (44–86%) of the total DOC is also classified as fraction < 1 kDa. This is likely due to the fact that these fractions or size classes are operationally defined for each method (for example by the membrane cut-off for the TFF method or available space within the resin) and are most probably somewhat dynamic. Besides, they are complex mixture of compounds that may behave very different, including possible entangling, aggregation or interactions of already adsorbed compounds on the membrane/in the resin. This may partially explain the differences in the identified fractions by the TFF method compared to the LC-OCD method. It is also possible that the TFF method is closer to the quantification limit for DOC than the LC-OCD method, which is considered to have higher measuring sensitivity. Hence, the above aspects should be considered when interpreting the results and indicate the need for inter-comparison and correlation of the different fractionation methods used for NOM fractionation.

In all reservoirs, the humic substances were the dominant fraction in raw water, between 58% and 73% of all DOC (Fig. 3a). The building blocks were in the range of 10–18%, LMW neutrals in the range of 5–8%, and LMW acids in range of 0–0.6%. For detailed results of the LC-OCD fractionation the reader is referred to Table S4 and Table S5 in the Supplementary Material.

The size distribution obtained by membrane size fractionation of NOM fractions in raw water indicated that in all locations the largest fraction (> 50 kDa) dominated (between 55% and 95% of all DOC; Fig. 3b). The 50–10 kDa and 10–0.3 kDa fractions each contained between 5 and 25% of all DOC, whereas the smallest fraction (< 0.3 kDa), had less than 3% of all DOC. Interestingly, raw water samples from Oslo DWTP had a different size distribution than the other two reservoirs, i.e. more DOC in the largest fraction (> 50 kDa) and less in the middle-sized fraction (50–0.3 kDa). These contrasts in size may be related to the differences in retention times (i.e. 2.5–2.8 years in Stockholm and Helsinki reservoirs, circa 0.4 years in Oslo) (Table 1). A smaller catchment size and lower water residence time may leave less time for degradation of NOM, which could result in a larger size NOM as found in the Oslo reservoir. Other evidence to support the relationship between retention time and the NOM size is from the long-term monitoring station in Langtjern, Norway, with a very small catchment area of 4.69 km² and retention time of 0.2 years (de Wit et al., 2018). At Langtjern, after 0.2 µm prefiltration, the NOM fraction > 100 kDa was in the range of 86–95% while the > 10 kDa fraction contained usually above 96% of all DOC (Francés, 2017). Concluding, there appeared to be correlation between the raw water NOM size and lake retention time.

Raw water DOC samples showed little seasonal differences, except for the Oslo reservoir which had higher DOC in the autumn (Table S1). The low seasonal differences might be related to the large residence times for the Helsinki and Stockholm reservoirs, levelling out seasonal differences in catchment DOC inputs. By contrast, seasonal differences were found for several NOM quality indicators. For instance, SUVA was clearly lowest in the autumn in all reservoirs (Fig. S4), with the most variation found in the Oslo reservoir. For all three DWTPs, the hydrophobic fraction was largest during the autumn (Fig. 3a). The increase of the hydrophobic fraction was at the expense of the hydrophilic humic

substances fraction.

Compared to the LC-OCD, the TFF fractionation indicated that size distribution depended on season in all DWTPs. In Oslo raw water samples, the > 50 kDa fraction was largest in winter (97% of all DOC) compared to summer (85% of all DOC). The high molecular weight fractions contribute most to the colour of the water (Ødegaard et al., 2000), with about one third coming from > 50 kDa fraction (Ratnaweera et al., 1999). There is a shift from the largest > 50 kDa fraction to smaller fractions between the winter and summer season, which could be evidence of in-lake processing resulting in smaller NOM fractions, of in-lake production of smaller-sized NOM or of differences in NOM inputs in winter and summer (Fig. 3b). The middle fractions (50–10 kDa and 10–0.3 kDa) were largest in the summer (8% and 5% of all DOC, respectively) and smallest in winter (both 2% of all DOC). In Stockholm raw water samples, the > 50 kDa fraction was larger in winter whereas the 50–10 kDa fraction was larger in summer (Fig. 3b), potentially indicating a small shift in NOM from larger to smaller fraction between winter and summer period. The Helsinki raw water samples had > 50 kDa fraction significantly larger in the summer compared to the winter season (Fig. 3b). The 50–10 kDa fraction was comparable between the two seasons, whereas two smaller fractions, namely 10–0.3 kDa and < 0.3 kDa, were present at a lower degree in the summer.

3.3. NOM and NOM fractions removal during drinking water production

3.3.1. NOM removal by coagulation/sedimentation and filtration

The observed removal of NOM varied between the DWTPs and was in general correlated with the treatment processes applied. Overall, according to the LC-OCD analyses, 40–44% of initial NOM was removed during the coagulation/sedimentation process in Stockholm DWTP, whereas 52–61% and 64–68% during the coagulation/sedimentation/filtration processes in Oslo and Helsinki DWTPs, respectively. Typically 10–60% of the NOM removal is achieved in the coagulation-flocculation process alone (Sharp et al., 2006), however, removal can vary between 10 and 90% depending on the treatment process, raw water quality and coagulation conditions (Volk et al., 2000). For example, high molecular weight (MW), hydrophobic NOM fractions may be removed more efficiently than low molecular weight hydrophilic fractions by coagulation (Eikebrokk et al., 2006). Thus, considering rather hydrophilic raw waters with a SUVA of 2–4, less effective removal was expected in coagulation.

The removal rates of different NOM fractions also varied between the treatment processes applied in different DWTPs (Fig. 4). The details on the removal of different NOM fractions during the investigated treatment processes in the three full-scale DWTPs are presented in Table S6, Table S7 and Table S8.

The coagulation-flocculation, sedimentation and dual media filtration evaluated in Oslo DWTP, removed primarily the > 50 kDa fraction (47–67%), which typically is well removed during the coagulation-flocculation process (Slavik et al., 2012). Less effective removal of the high MW fraction correlated with the lower SUVA of 3.7 in the summer period. Interestingly, an increase in percentage distribution of the 50–0.3 kDa and 10–0.3 kDa fractions was measured after coagulation/sedimentation/filtration. This can potentially indicate that the > 50 kDa fraction was broken down into smaller fractions. Biopolymers were removed by 64–79%, humic substances by 70–79%, building blocks up to 13%, and LMW neutrals by 14–22%.

The coagulation-flocculation process, investigated in Stockholm DWTP, partially removed all fractions, but the efficiency varied between the summer and winter period. In the summer, fractions predominantly smaller than 50 kDa were removed by 49–83%, whereas in winter only fractions larger than 10 kDa were removed by 31–40%. In winter, the 10% increase of 10–0.3 kDa fraction during the coagulation-flocculation may also indicate that the > 50 kDa fraction was probably broken down to smaller fractions. But there may be also other potential

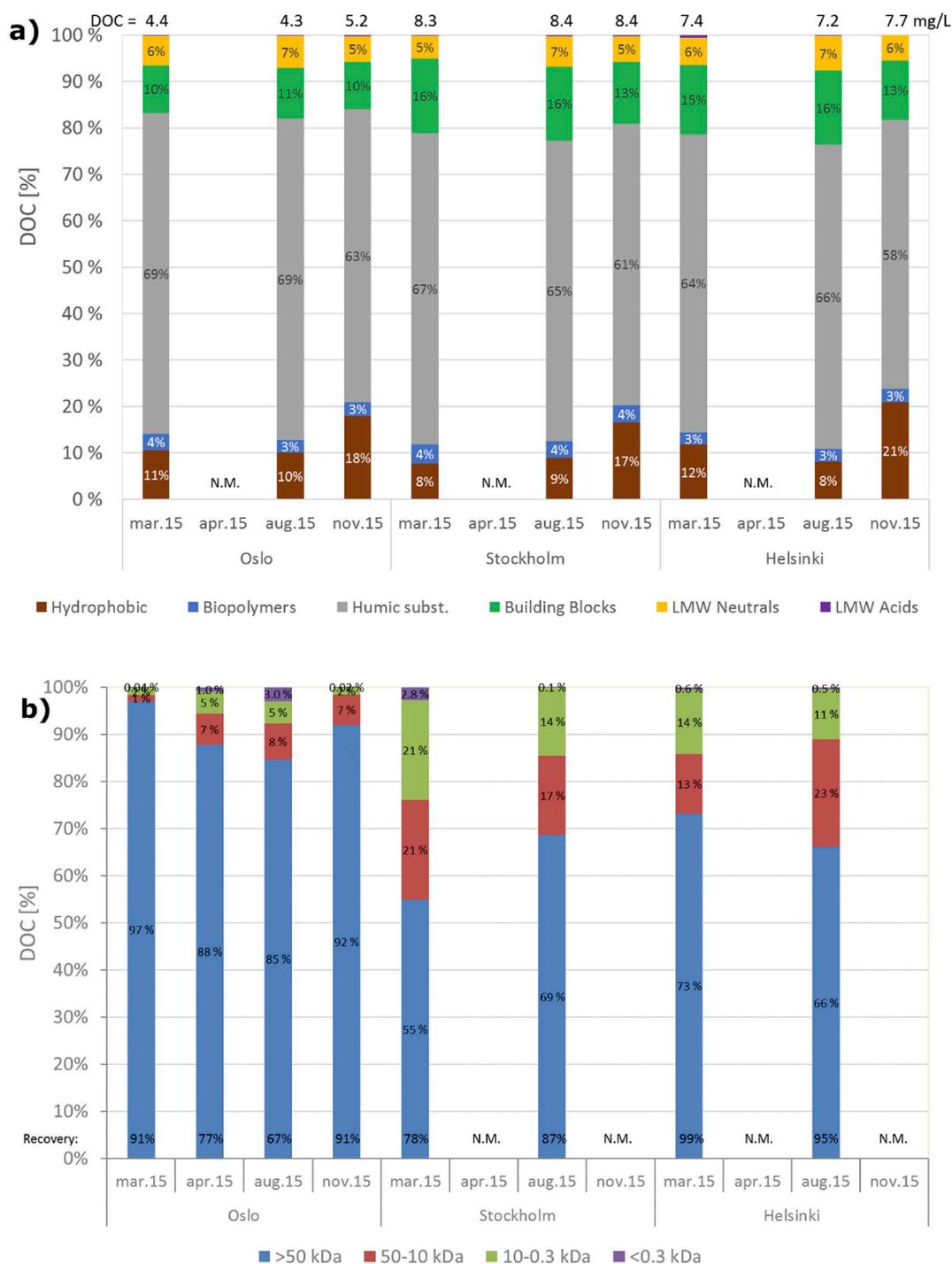


Fig. 3. Average size distributions of raw water NOM fractions in Oslo Oset, Stockholm Lovö, and Helsinki Pitkäkoski DWTPs during different seasons: a) LC-OCD and b) TFF. N.M. - not measured.

causes for this increase, such as uncertainties related to sampling, sample preparation and analysis. In summer, the > 50 kDa fraction was not well removed as indicated by the increase in the percentage share of the > 50 kDa fraction. In addition, NOM removal was less effective in the summer when higher DOC concentrations were observed in the raw water. Coagulation alone, compared to coagulation-flocculation and dual media filtration process in Oslo, underachieved with regard to biopolymers (removal in range of 32–50%) and humic substances (44–51%), in comparison to achieving better removal rates with regard to building blocks (37–57%) and LMW neutrals (9–21%). Nevertheless, despite higher removal rates in Stockholm, the concentrations of both

building blocks and LMW neutrals were still higher than in Oslo finished water. Humic substances in particular were poorly removed in Stockholm coagulation-flocculation process. Despite higher removal per mg/L (2.5 mg/L vs. 2.2 mg/L for Oslo), elevated concentrations of humics exceeding 2.5 mg/L were still measured, possibly indicating some optimization potential available for coagulation-flocculation process. The poorer DOC removal during flocculation in Stockholm is a result of the in-lake processing, due to microbial mineralization, flocculation or photolytic processing, that has been earlier documented (Köhler et al., 2013; de Wit et al., 2018).

The coagulation-flocculation, sedimentation and rapid sand

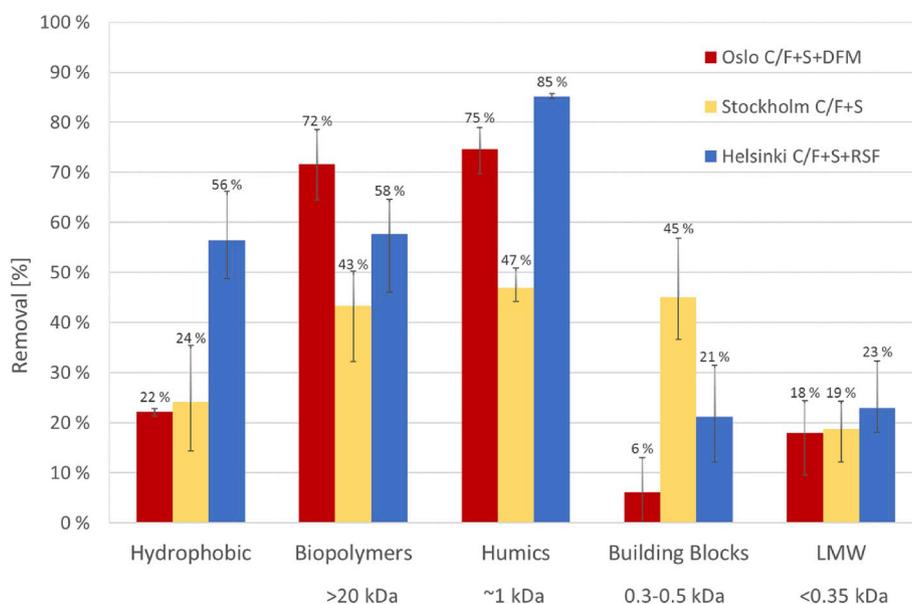


Fig. 4. Average removal of NOM fractions based on three sampling seasons during (a) investigated coagulation/sedimentation or coagulation/sedimentation/filtration process in Oslo, Stockholm and Helsinki DWTPs. Error bars shows the maximum and minimum removal.

filtration process in Helsinki, provided good removal in range of 45–84% through the investigated seasons for most of the fractions, except for the smallest < 0.3 kDa fraction. The removal of < 0.3 kDa fraction varied between 79% in the winter and 0% in the summer. Biopolymers were decreased by 46–65%, humic substances by 85–86%, building blocks by 12–32%, and LMW neutrals by 20–26%. The NOM removal of the investigated processes was generally more effective in the winter period compared to the summer period. Improved organic matter removal observed in Helsinki DWTP may be attributed to the type of coagulants used. The ferric salts tend to be more effective in removing NOM, especially the middle size fractions, compared to aluminium based coagulants (Müller and Uhl, 2009; Matilainen et al., 2010), which were used in the other two locations. The improved effectiveness of iron based coagulants is often attributed to a more complex flocs structure, i.e. larger flocs and smaller floc density, of the iron hydroxide flocs. However, the positive effect of iron based coagulant could be counter balanced by the fact that Helsinki treatment process was designed to treat water which is more hydrophobic than hydrophilic, which is not necessarily the case according to the LC-OCD results.

3.3.2. NOM removal in subsequent treatment stages

The treatment processes following the coagulation/sedimentation/filtration step provided between 0% and 11% of additional DOC removal.

As expected, little to no removal was observed in post coagulation/sedimentation/filtration treatment step in Oslo consisting of UV/Cl disinfection process. The UV/Cl disinfection did not further remove biopolymers or humic substances and in some cases removed a maximum 4% of the buildings blocks and 6% of LMW neutrals. Despite observed removal of LMW acids, the actual removal is difficult to quantify due to concentrations in treated water below or close to the levels of quantification. In addition, the observed process performance varied between the seasons, being less effective with higher DOC concentrations in the raw water.

In Stockholm, the post coagulation/sedimentation step treatment processes, namely rapid and slow sand filtration followed by UV/Cl disinfection, removed additional 0.47 mg/L (6%) of the bulk DOC. Again, the NOM removal effect of UV/Cl disinfection is considered negligible and therefore attributed mostly to the sand filtration processes (Collins et al., 1992). The reduction of DOC observed during sand

filtration is within the range reported in the literature (Matilainen, 2007; Sohn et al., 2007). Sand filtration contributed to the NOM-fractions removal by removing different fractions fairly equally: up to 30% of > 50 kDa fraction, up to 20% of 50–10 kDa fraction, up to 30% of 10–0.3 kDa fraction and up to 35% of < 0.3 kDa fraction. On average, additional 26% of biopolymers, 4% of humic substances, 3% of building blocks and 7% of LMW neutrals were removed. In addition, LMW acids concentrations were removed below levels of quantification.

In Helsinki, the ozonation, activated carbon filtration and UV/Cl disinfection processes removed an additional 0.68 mg/L (11%) of the bulk DOC. As observed in case of Oslo DWTP, UV/Cl disinfection does not contribute significantly to the NOM removal. Since ozonation does not provide significant removal of the NOM (Sohn et al., 2007; Ødegaard et al., 2010; Zhang et al., 2015), any removal can be attributed to the activated carbon filtration processes. The biological activated carbon filtration is reportedly effective in reducing the low and intermittent size fractions of the NOM (Matilainen et al., 2002). This was partially confirmed by both fractionation methods used in this study. Additional 25–35% reduction of building blocks and 50–10 kDa fraction (i.e. intermittent size fractions), LMW neutrals and < 0.3 kDa fraction (i.e., low size fractions), and below 10% reduction of the other fractions. On the other hand, the 10–0.3 kDa fraction was not further removed significantly (2%). The LMW acids removal was inconsistent and varied, likely due to concentrations close to levels of quantification.

3.3.3. NOM removal by the entire treatment process of the DWTPs

In all DWTPs, finished water met standards for safe drinking water production removing colour below the recommended 20 mgPt/L in Norway (Drikkevannsforskriften, 2016), 15 mgPt/L in Sweden (Livsmedelsverket, 2001), and to acceptable levels by customers in Finland. On average, 2.5 mg/L, 4.0 mg/L and 5.7 mg/L of NOM was removed, which respectively accounted for 55%, 48% and 76% of DOC removed in Oslo, Stockholm and Helsinki waterworks. The non-removed NOM represented on average 2.1 mg/L, 4.3 mg/L and 1.8 mg/L in Oslo, Stockholm and Helsinki waterworks, respectively. The remaining NOM was predominantly a high molecular weight fraction of > 50 kDa size with 55–80% share, consisting mainly of humics (33–62%), building blocks (14–30%) and LMW neutrals (7–17%). The details on the removed and remaining NOM is presented in Table S9 in the Supplementary Materials.

When the DOC and SUVA measured during different seasons after

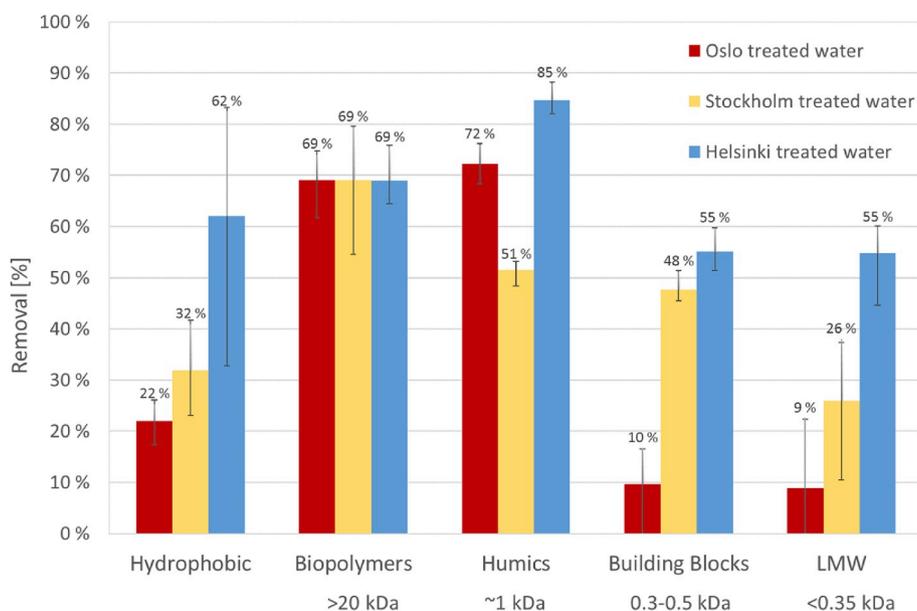


Fig. 5. Average removal of NOM fractions based on three sampling seasons during complete treatment process in Oslo, Stockholm and Helsinki DWTPs. Error bars show the maximum and minimum values.

the selected treatment stages were normalized to raw water, slight differences between different seasons were observed for each of the DWTPs. The removal effectivity of DOC and SUVA was little affected by the seasonal changes at the three investigated DWTPs allowing to pool the results from the three seasons together (Fig. S4).

The removal rates of different NOM fractions varied between the treatment processes applied in different DWTPs with an interesting exception that, all DWTPs achieved on average 69% removal of biopolymers (Fig. 5).

The complete treatment process consisting of coagulation and dual media filtration, primarily removed humic substances, biopolymers, largest (> 50 kDa) and smallest (< 0.3 kDa) fractions, with effectiveness in range of 55–76%. In addition, middle size fractions in the range of 50–0.3 kDa have increased during the treatment process.

The complete treatment process consisting of coagulation, rapid and slow sand filtration achieved partial removal in the range of 45–85% for most of the fractions (i.e., > 50, 50–10 kDa, humic substances, building blocks, biopolymers and < 0.3 kDa), yet was not effective in removing 10–0.3 kDa fraction and LMW neutrals. Noteworthy, although individual fractions were generally removed at higher percentage compared to coagulation and dual media filtration treatment train, the total NOM removal was less effective. This was mainly due to the fact that, despite higher removal per mg/L (2.8 mg/L vs. 2.2 mg/L for Oslo), elevated concentrations of humics in range of 2.5 mg/L were measured in the finished drinking water. The humic substances concentration did not exceed 1.0 mg/L in the other two DWTPs.

The most advanced treatment process, combining coagulation, sand filtration, ozonation and activated carbon filtration partially removed all fractions. As expected, the removal rates were highest typically exceeding 60% for > 50–0.3 kDa fractions, humics and biopolymers, and varied between 30% and 95% for < 0.3 kDa fraction, building blocks and LMW neutrals. The removal of different NOM fractions during the entire treatment process is presented in Table 3 and Table 4.

3.3.4. Seasonal differences in NOM fractions removal

Considering the effectiveness of treatment processes to remove NOM during different seasons of the year, differences were identified between the DWTPs. Again, the differences may be linked to the differences in the retention times of the water reservoirs. There is a rather stable removal of different fractions throughout the year, although

there is a reduction in removal during autumnal turnover, which was observed in Stockholm and Helsinki DWTPs. Little seasonal differences in NOM treatment previously reported in the literature were attributed to large lakes with long residence times (Matilainen et al., 2002). By contrast, when residence time in the drinking water reservoirs is much lower (Oslo), variable removal of different fractions were observed throughout the year. During the summer period, the treatment process at Oslo DWTP was most effective for high molecular weight fractions and least effective for low molecular weight fractions, such as building blocks and LMW neutrals. The Stockholm treatment system was most effective in the summer for biopolymers and in autumn for biopolymers and LMW neutrals, and less effective in the winter for biopolymers and LMW neutrals. In Helsinki, biopolymers were most effectively removed in the autumn, whereas other fractions were most effectively removed in the summer, except for the 50–10 kDa fraction. The generally higher NOM removal in summer period corroborates with the findings of Sohn et al. (2007) who attributed higher NOM removal in the summer with beneficial input of higher temperatures on the biologically active systems such as sand filtration and activated carbon filtration.

3.4. NOM fractions distribution in finished treated water

The applied treatment processes have changed the distribution of NOM fractions and consequently resulted in finished treated water with generally lower proportions of humic substances, higher, or comparable at Stockholm DWTP, for building blocks and higher for LMW neutrals (Table 5). Nevertheless, the largest fraction > 50 kDa remained to be a dominant fraction with above 55% and up to 80% (Table 6). Despite reduction in concentrations, the observed changes in biopolymers and LMW acids distributions were inconclusive and too small to properly assess. On the other hand, high molecular weight fractions of DOM, such as biopolymers, are reportedly well removed during the coagulation process (Slavik et al., 2012), which was also observed in this study.

The raw water had a different size distribution of NOM than the treated water, which was season-dependent in the Oslo reservoir. First, treated water had a higher proportion of smaller NOM fractions and second, during winter this shift towards smaller NOM fractions was less prominent. The seasonal changes in size distribution of treated water could not be properly assessed for the other reservoirs due to insufficient amount of data.

Table 3
Percentage removal range of NOM size fractions during investigated treatment stages at the Oslo, Stockholm and Helsinki DWTPs.

Treatment process	DWTP location	Size fractions [%] according to membrane (TFF) fractionation method			
		>50 kDa	50–10 kDa	10–0.3 kDa	<0.3 kDa
C+DMF	Oslo	55–69	-	-	-64
C+RSF+SSF	Stockholm	48–49	44–54	0–30	67–84
C+RSF+O ₃ +AC	Helsinki	72–84	72–93	60–72	32–95

Legend: C - coagulation-flocculation-sedimentation; DMF - dual media filtration; RSF - rapid sand filtration; SSF - slow sand filtration; O₃ - ozonation; AC - activated carbon filtration; Orange colour indicates removal in range of 0–30%, blue in 30–70%, and green in 70–100%.

Table 4
Removal range in mg/L of the LC-OCD investigated NOM size fractions during drinking water production process at the Oslo, Stockholm and Helsinki DWTPs.

Treatment process	DWTP location	Hydrophobic fraction	Size fractions according to LC-OCD fractionation method [mg/L]				
			Biopolymers > 20 kDa	Humics ~ 1 kDa	Building blocks 0.3–0.5 kDa	LMW neutrals < 0.35 kDa	LMW acids < 0.35 kDa
C + DMF	Oslo	0.10–0.16	0.08–0.12	2.08–2.32	– 0.02–0.08	– 0.02–0.08	N.Q.
C + RSF + SSF	Stockholm	0.17–0.58	0.19–0.24	2.46–2.94	0.52–0.69	0.03–0.15	N.Q.
C + RSF + O ₃ +AC	Helsinki	0.19–1.34	0.13–0.17	3.67–4.18	0.53–0.69	0.20–0.36	N.Q.

Legend: N.Q. – not quantified.

Table 5
NOM fractions (determined by LC-OCD) of the treated water.

Location	DOC _{LC-OCD} [mg/L]	Hydrophobic DOC	Size fractions [%]				
			Hydrophilic DOC				
			Biopolymers > 20 kDa	Humics ~ 1 kDa	Building blocks 0.3–0.5 kDa	LMW neutrals < 0.35 kDa	LMW acids < 0.35 kDa
Oslo	1.9–2.4	18–32	1.8–2.4	38–50	18–26	10–17	0–0.3
Stockholm	4.2–4.4	10–18	1.4–3.7	59–62	14–17	7–9	0
Helsinki	1.7–1.8	14–23	2.9–4.1	33–44	25–30	10–12	0.6–2.3

Table 6
NOM molecular weight fractions of the treated water.

Location	DOC concentration [mg/L]	Size fractions [%]			
		> 50 kDa	50–10 kDa	10–0.3 kDa	< 0.3 kDa
Oslo	1.7–1.9	58–80	8–17	8–23	0.04–1.8
Stockholm	4.0–4.2	63–66	10–23	14–24	0.1–0.3
Helsinki	1.3–1.7	55–60	6–24	20–34	0.3–0.6

3.5. Biodegradability and biological stability of water

The biodegradable dissolved organic matter in the raw water varied between 0.8 and 1.55 mgC/L and appeared to be moderate to high, representing 13%, 17% and 24% of the bulk DOC in Helsinki, Stockholm and Oslo, respectively (Fig. 6a). The raw water BDOC concentration was either comparable between the seasons as in the case of the Oslo DWTP or decreased during the year with the lowest concentrations in autumn, as in the cases of the Stockholm and Helsinki DWTPs. The higher BDOC

in winter raw waters could be an indication of a lower biodegradation in the drinking water reservoirs during the winter period, resulting in more biodegradable NOM when the water is brought into the DWTPs.

BDOC expressed as a percentage of raw water DOC, indicated that winter raw water samples were more biodegradable than in other seasons and in range of 22–26% for Oslo raw water, 15–20% for Stockholm raw water and 12–16% for Helsinki raw water. The more biodegradable DOC in Oslo raw water, suggests that the raw water DOC in the Oslo reservoir is possibly less processed than in the other two reservoirs. The percentage contribution of BDOC to the DOC in raw waters decreased slightly during the year for all locations.

The BDOC was removed efficiently and above 70% at all sites. However, complete BDOC removal was not achieved. BDOC removal followed the ‘advancement’ of the treatment process, with the following trend: C/F + S + DMF < C/F + S + SSF + RSF < C/F + S + SF + O₃+BAC (Fig. 6b). The coagulation/sedimentation/filtration process removes most of the BDOC, whereas further treatment slightly decreases BDOC (results not showed). As expected, BAC filtration process contributed to decrease of the BDOC (Uhl, 2008) in Helsinki. The BAC step seems to be designed properly, as the BDOC

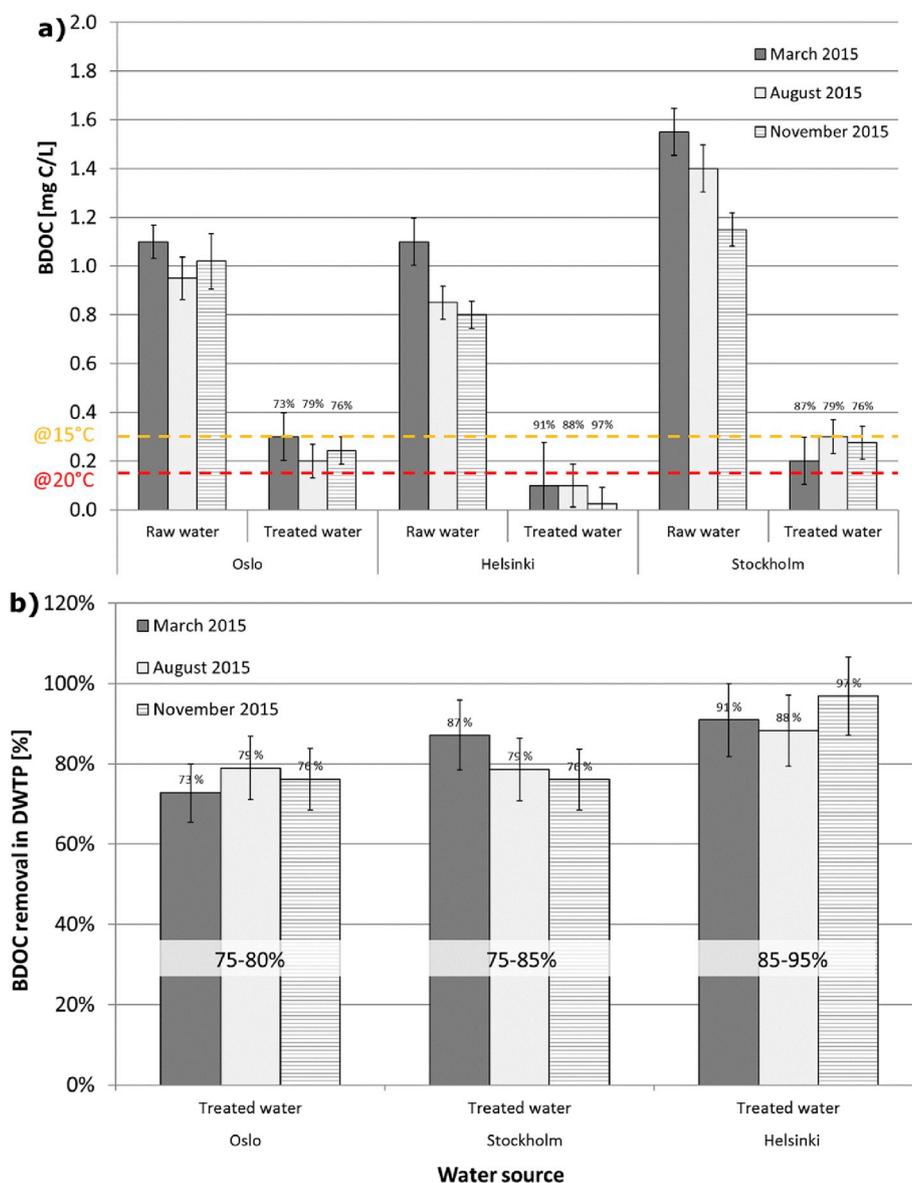


Fig. 6. BDOC a) concentrations in raw and treated water and b) removal in Oslo, Stockholm and Helsinki DWTPs during winter, summer and autumn period. Error bars shows the confidence interval (67% confidence level) of the test.

produced during the ozonation process from non-biodegradable DOC was removed in the subsequent BAC. The removal rates of the BDOC fraction were comparable between seasons, considering the confidence interval of the analytical methods. Non-biodegradable DOC, defined as a difference between initial DOC and BDOC, was primarily removed during coagulation/sedimentation or coagulation/sedimentation/filtration processes, with little to no further removal in the subsequent treatment processes (results not shown).

The treated water BDOC was statistically at a comparable level during the year at each of the individual DWTPs but with some differences between the sites (Fig. 6a). The finished water with BDOC below the 0.15–0.30 mg/L level was appropriate, as to avoid regrowth in the distribution system (Joret et al., 1994; Volk et al., 1994; Servais et al., 1995; Volk and LeChevallier, 2000; Niquette et al., 2001). Finished treated water from the Helsinki DWTP had smaller regrowth potential with BDOC concentrations below the 0.15 mg/L threshold, when compared with the higher regrowth potential in Oslo and Stockholm DWTPs, with treated water BDOC at or below the 0.30 mg/L threshold (Fig. 6a). However, since the temperature in the distribution network in Oslo was below 15 °C and the residence time for major parts of Oslo is below 24 h,

under these criteria, the probability for regrowth in treated water was considered low. In Helsinki, the residence time may be up to 48 h in some parts of the distribution network, but typically the highest temperature in the distribution network does not exceed 9 °C. On the other hand, as the residence time may vary significantly depending on the location and to some degree consumption, certain parts of the Oslo area may occasionally have residence time exceeding 24 h. The combination of exceptionally warm summers and raw water temperatures above 20 °C may increase the probability of bacteria regrowth in raw water the distribution network, as previously reported (Uhl and Schaule, 2004). Besides water temperature and residence time also hydraulic conditions, pipe material, and disinfectant residual decay may influence biological stability in the distribution network (Prest et al., 2016).

4. Conclusions

From the current study of seasonal differences in NOM composition and the removal of respective fractions in full-scale drinking water treatment plants in three Nordic capital cities, the following conclusions are drawn:

- Raw water NOM was dominated by humic substances and large compounds with molecular weights above 50 kDa. Seasonal differences in NOM fractions removal throughout the year were more pronounced for DWTPs treating water from the lakes with the shorter residence time.
- Coagulation/flocculation followed by sedimentation and a filtration processes roughly remove 40–70% of NOM, predominantly removing the humic matter, biopolymer and high molecular weight fractions over the hydrophobics and the low molecular weight fractions. Additional NOM removal following coagulation/flocculation, may be provided by the biological processes such as slow sand filtration and activated carbon filtration.
- The most effective process train for removal of NOM appeared to be the multi-step treatment train, consisting of C + SF + O₃ + AC, applied in the Helsinki DWTP. The ozonation-biofiltration process, compared to coagulation-sedimentation-filtration, enables increased removal of hydrophobic fraction, LMW fractions, and BDOC.
- Remaining NOM consists of the HMW (> 50 kDa) fraction and humics, building blocks and LMW compounds.
- BDOC represented less than one fourth of the bulk DOC in raw waters of the respective DWTPs, with higher concentrations in winter. BDOC removal improved when sand filtration or ozonation and activated carbon filtration followed the chemical precipitation process. The concentration of BDOC in treated water (< 0.3 mg/L) results in a low probability for bacteria regrowth when considering the conditions in the distribution network in the Nordic capitals (temperature below 15 °C and HRT below 24 h).

Further studies on possible implications of climate change on NOM are needed to answer whether the DWTPs are sufficiently equipped to deal with the expected changes in NOM quantity and quality and how to adapt to possible future water quality. Moreover, an inter-comparison and correlation of the different NOM fractionation methods is needed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2019.02.024>.

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