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Removal of the Natural Organic Matter in the Different Stages of the Drinking Water Treatment Process



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ABSTRACT

Surface waters in Finland contain usually a high amount of natural organic matter (NOM). Incomplete removal of NOM in the drinking water treatment has an adverse effect on the water quality. Hence, it is desirable to reduce the concentration of the NOM from the drinking water. The quantification and characterization of the NOM in the different stages of the purification process is important in order to improve and optimise various drinking water treatment processes. In this study, the high-performance size-exclusion chromatography (HPSEC) fractionation with UV₂₅₄ detection, and a number of conventional water quality analyses were used to measure the organic matter content and characteristics in water, and the transformation of the organic matter during the purification process.

In this study, the removal of the NOM was monitored in three full-scale water treatment processes. Besides the conventional unit operations (coagulation/flotation/sedimentation), the enhancement of NOM removal by activated carbon (AC) filtration and ozonation, followed by AC filtration, were evaluated. Moreover, two pilot-scale studies for the enhanced NOM removal were conducted; nanofiltration (NF) as a refining phase after conventional treatment, as well as ozonation followed by AC filtration.

The conventional treatment processes (coagulation/flotation/sedimentation) removed the high molar mass (HMM) organic matter almost completely (over 94%). The intermediate molar mass (IMM) matter was more difficult to be removed; 12-55% removal was obtained. Still, the hardest fraction to be removed was the low molar mass (LMM) organic matter, which were removed only by 3-14% from chemically coagulated water. The optimisation of the coagulation/flotation process by selection of the proper coagulant improved the NOM removal. The process modification by replacing the aluminium sulphate with ferric sulphate enhanced the NOM removal 10%. The greatest difference between the two coagulants occurred in the removal of the NOM that has molar mass of 1000-4000 g/mol (IMM). These IMM compounds were removed 25% more effectively with iron-based than with aluminium-based coagulant.

The AC filtration enhanced the removal of NOM. The HMM substances were not removed any further on the AC filtration, but 30% more of IMM matter was removed. The LMM matter was also reduced slightly. However, occasionally the smallest fractions of NOM even increased in the AC filtration. Regeneration of the AC filters had a significant effect on NOM removal. Immediately after regeneration the efficiency of the filter increased about 50%. However, the NOM removal efficiency was reverted to the approximate same level as before regeneration, after few months of operation.

The ozonation on the full-scale process removed primarily the smaller molar mass fractions of NOM. Removal rates of 23% and 32% were observed, regarding IMM and LMM matter, respectively. Thus, it was concluded that the NOM was degraded to the really LMM compounds, with little or non UV-absorption capacity, thus not showing in HPSEC-UV₂₅₄ measurement. According to the pilot-scale ozonation study, the amount of assimilable organic carbon, AOC, increased with increasing ozone dose, hence implicating that NOM was degraded. Nevertheless, the AC filtration after ozonation was effective in the removal of produced AOC.

The nanofiltration (NF), as a refining phase after conventional treatment, removed the HMM matter completely and the reduction of the IMM matter was 52-100%, depending on the type

of the membrane studied. The enhancement of the reduction of the LMM matter ranged between 43-79%. The NF membranes studied removed generally over 60% of the remaining organic matter, measured as DOC and sum of peak heights in HPSEC, from the water after conventional treatment process. From the organic matter removal processes studied the water with lowest organic matter were obtained by NF.

TIIVISTELMÄ

Suomen pintavesissä esiintyy runsaasti luonnosta peräisin olevia eli eloperäisiä orgaanisia aineita. Humus muodostaa suurimman osan eloperäisistä orgaanisista aineista. Humus aiheuttaa monia laatuongelmia juomaveteen, ja vaikeuttaa vedenpuhdistusprosesseja vesilaitoksilla. Se aiheuttaa veteen mm. makua, hajua ja ruskeaa väriä sekä reagoi desinfioinnissa käytettyjen aineiden, lähinnä kloorin, kanssa muodostaen karsinogeenisia sivutuotteita. Näiden ongelmien vuoksi humuksen ja muiden eloperäisten orgaanisten aineiden vähentäminen juomavedestä on eräs tärkeimmistä asioista erityisesti pintavesien puhdistuksessa. Niiden poistumista voidaan tehostaa puhdistusprosesseja kehittämällä ja optimoimalla. Tähän kuitenkin tarvitaan lisää tietoa orgaanisten aineiden määrästä ja laadusta puhdistusprosessien eri vaiheissa. Tässä tutkimuksessa orgaanisten aineiden poistumista ja rakenteiden muuttumista vedenpuhdistusprosessin eri vaiheissa seurattiin molekyylikokojakauman muutoksena. Molekyylikokojakauman muutoksia tutkittiin käyttämällä nestekromatografista määrittystä, HPSEC-UV₂₅₄ (high-performance size-exclusion chromatography, UV₂₅₄ detektorilla). HPSEC-UV₂₅₄ tuloksia vertailtiin perinteisesti käytettävillä orgaanisen aineen kokonaispitoisuuksia mittaavilla menetelmillä saatuihin tuloksiin.

Tässä tutkimuksessa seurattiin eloperäisten orgaanisten aineiden määrää ja rakennetta kolmen täyden mittakaavan vedenpuhdistusprosessin eri vaiheissa. Perinteisen puhdistuksen eli saostuksen ja selkeytyksen lisäksi tutkittiin otsonoinnin ja aktiivihiilisuodattimien merkitystä orgaanisten aineiden poistamisessa. Lisäksi tutkittiin pienemmässä mittakaavassa, pilot-laitteistoilla, perinteisestä puhdistuksesta jäljelle jäävien orgaanisten aineiden poiston tehostamista; otsonointia ja sen jälkeistä aktiivihiilisuodatusta sekä nanosuodatusta pintavedenkäsittelyn viimeistelevänä vaiheena.

Perinteinen puhdistusprosessi eli kemiallinen saostus ja sen jälkeinen selkeytys poisti tehokkaasti molekyyylimassaltaan suuria yhdisteitä (yli 94% poistuu). Molekyyylimassaltaan keskisuuret yhdisteet poistuivat kohtalaisesti (12-55%) mutta molekyyylimassaltaan pienet yhdisteet eivät juurikaan poistuneet. Kemiallisella esikäsitteilyllä saatiin poistettua vain 3-14% pienen molekyyylimassan omaavia yhdisteitä. Optimoimalla saostusprosessia voitiin orgaanisten aineiden poistoa kuitenkin tehostaa. Saostuskemikaalin vaihto alumiinisulfaattista rautasulfaattiin lisäsi orgaanisten aineiden poistotehokkuutta 10%. Saostuskemikaalin vaihto vaikutti eniten keskisuurten molekyylien poistoon. Keskisuuret (1000-4000 g/mol) molekyylit poistuivat 25% tehokkaammin rautasulfaattisaostuksella verrattuna alumiinisulfaatti saostukseen.

Aktiivihiilisuodatus tehosti orgaanisten aineiden poistoa. Se ei parantanut suurikokoisten molekyylien poistoa, mutta keskisuurten yhdisteiden poistoa se tehosti noin 30%. Molekyyylimassaltaan pienten yhdisteiden poisto oli hankalampaa. Itse asiassa kaikkein pienin molekyylikokofraktio suureni aika ajoin aktiivihiilisuodatuksen yhteydessä. Aktiivihiilien regenerointi tutkimuksen aikana paransi sen tehoa huomattavasti. Välitön tehon paraneminen oli 50%, mutta tehokkuus tasaantui muutaman käyttökuukauden jälkeen lähes ennalleen.

Täyden mittakaavan vedenpuhdistusprosessissa otsonoinnilla saatiin poistettua lähinnä molekyyylimassaltaan pienempiä orgaanisia yhdisteitä. Keskisuurten yhdisteiden poistuma oli 23% ja pienien 32%. Orgaaninen aines oli todennäköisesti hajonnut hyvin pieniksi yhdisteiksi. Hyvin pienet orgaaniset yhdisteet eivät näy UV₂₅₄ mittauksessa, jota käytettiin HPSEC menetelmän detektorina. Pilot-mittakaavan kokeissa huomattiin että bakteereille

käyttökelpoinen hiili, AOC (assimilable organic carbon), lisääntyi otsoniannosta lisättäessä. Tämä viittaisi siihen että orgaaninen aines on hajonnut pienemmiksi yhdisteiksi. Vaikka AOC lisääntyi voimakkaasti otsonoitaessa, otsonoinnin jälkeinen aktiivihiihli-suodatus poisti syntyneen AOC määrän tehokkaasti.

Nanosuodatus pintavedenkäsittelyn viimeistelevänä vaiheena poisti molekyyli-massaltaan suuret yhdisteet lähes kokonaan ja keskisuuriakin huomattavasti, 52-100% riippuen tutkittavan kalvon laadusta. Pienen molekyylikoon yhdisteiden poistuma vaihteli 43-79%. Yleisesti, kemiallisesti esikäsiteltyyn veteen jääneiden eloperäisten orgaanisten aineiden poistuma kaikilla tutkimuksessa olleilla nanosuodatuskalvoilla oli keskimäärin yli 60%. Verrattuna muihin vedenpuhdistusprosesseihin, nanosuodatus poisti parhaiten eloperäiset orgaaniset aineet tutkituista vesistä.

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TABLE OF CONTENTS

1 INTRODUCTION	1
1.1 Background	1
1.2 Research problem and objective	2
1.3 Research methods	3
2 THE CHARACTERISTICS OF NATURAL ORGANIC MATTER IN WATER	4
2.1 Natural organic matter	4
2.2 Structures of humic substances	5
2.3 Molecular sizes of humic substances	8
3 NOM IN THE WATER PURIFICATION PROCESS	9
3.1 Coagulation	9
3.2 Sorption on solid surfaces	10
3.2.1 Activated carbon (AC) filtration	10
3.2.2 Biologically activated carbon (BAC) filtration	11
3.2.3 Ion exchange resin filtration	11
3.3 Disinfection and oxidation	12
3.3.1 Chlorine-based disinfectants	12
3.3.2 Ozonation	13
3.3.3 Advanced oxidation processes (AOPs)	14
3.4 Membrane filtration	14
3.5 Summary of different processes for removal of NOM	15
4 DIFFERENT METHODS FOR CHARACTERIZATION OF AQUATIC NOM	17
4.1 General parameters	17
4.2 Biological tests	17
4.3 Isolation and concentration	17
4.4 Fractionation of NOM	17
4.4.1 Resin fractionation	17
4.4.2 High-performance size-exclusion chromatography (HPSEC)	18
4.4.3 Ultrafiltration (UF)	20
4.5 Other analytical methods	21
5 AIMS OF THE STUDY	22
6 MATERIALS AND METHODS	23
6.1 Tampere Waterworks; Rusko Water Treatment Plant	23
6.1.1 AC filtration in the Rusko Water Treatment Plant	23
6.2 Oulu Waterworks; Hintta and Kurkelanranta Water Treatment Plants	24
6.2.1 Ozonation in Hintta and Kurkelanranta Water Treatment Plants	24

6.2.2 AC filtration in Hintta and Kurkelanranta Water Treatment Plants	24
6.2.3 Pilot-scale ozonation	25
6.3 Other waterworks	26
6.3.1 Pilot-scale nanofiltration (NF)	27
6.4 Analysis	27
6.4.1 Sampling procedure	27
6.4.2 Basic water analysis at Rusko Water Treatment Plant	28
6.4.3 Basic water analysis at Hintta and Kurkelanranta Water Treatment Plants	28
6.4.4 HPSEC measurements	28
7 RESULTS AND DISCUSSION	30
7.1 Water quality in the Water Treatment Plants	30
7.1.1 Rusko Water Treatment Plant	30
7.1.2 Hintta and Kurkelanranta Water Treatment Plants	31
7.2 NOM removal at different stages in the treatment process based on DOC and other conventional quality parameters; A_{254} and turbidity	32
7.3 NOM characterization and removal at different stages in the treatment process based on HPSEC-UV ₂₅₄ measurements	32
7.3.1 The MSD of NOM in the raw water	32
7.3.2 The effect of chemical coagulation on the MSD of NOM	33
7.3.3. The effect of ozonation on the MSD of NOM	35
7.3.4 The effect of AC filtration on the MSD of NOM	36
7.3.5 The removal of NOM during the entire treatment process	37
7.4 The effect of ozonation and AC filtration on NOM according to the pilot-scale study	38
7.4.1 DOC and other conventional quality parameters	38
7.4.2 AOC concentrations	38
7.4.3 HPSEC results	39
7.5 The effect of NF on the removal of NOM according to pilot-scale study	39
7.6. Evaluation of the performance of HPSEC-UV ₂₅₄ in the measurement of NOM during water treatment process	41
8 CONCLUSIONS	42
9 REFERENCES	44
APPENDIX 1	
APPENDIX 2	
ORIGINAL PAPERS	

LIST OF ORIGINAL PAPERS

This thesis is based on the following original papers referred in the text by their Roman numerals (Paper I-V):

- I Matilainen, A., Lindqvist, N., Korhonen, S. and Tuhkanen, T. 2002. Removal of NOM in the different stages of the water treatment process. *Environment International*. 28:457-465.
- II Matilainen, A., Vieno, N. and Tuhkanen, T. 2006. Efficiency of the activated carbon filtration in the natural organic matter removal. *Environment International*. 32:324-331
- III Matilainen, A., Lindqvist, N. and Tuhkanen, T. 2005. Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process. *Environmental Technology*. 26:867-857.
- IV Matilainen, A., Iivari, P., Sallanko, J., Heiska, E. and Tuhkanen, T. 2006. The role of ozonation and activated carbon filtration in the natural organic matter removal from drinking water. *Environmental Technology*. 27:1171-1180
- V Matilainen, A., Liikanen, R., Nyström, M., Lindqvist, N. and Tuhkanen, T. 2004. Enhancement of the natural organic matter removal from drinking water by nanofiltration. *Environmental Technology*. 25:283-291.

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ABBREVIATIONS

AC	Activated carbon
AMM	Apparent molar mass
AOC	Assimilable organic carbon
AOP	Advanced oxidation processes
AOX	Adsorbable organic halogen
BAC	Biologically activated carbon
BDOC	Biodegradable dissolved organic carbon
ClO ₂	Chlorine dioxide
DBP	Disinfection by-products
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
ESR	Electron spin resonance
FFF	Field flow fractionation
GC-MS	Gas chromatography-mass spectrometry
HMM	High molar mass
HPLC	High-performance liquid chromatography
HPSEC	High-performance size-exclusion chromatography
IMM	Intermediate molar mass
IR	Infrared
LMM	Low molar mass
MALS	Multi-angle light scattering
MF	Microfiltration
MIEX	Magnetic ion exchange resin
MM	Molar mass
MSD	Molecular size distribution
MWCO	Molecular weight cut-off
NF	Nanofiltration
NMWCO	Nominal molecular weight cut-off
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
PSS	Polystyrene sulphonate
RI	Refractive index
RO	Reverse osmosis
SEC	Size-exclusion chromatography
SOPH	Sum of peak heights
THM	Trihalomethanes
THMFP	Trihalomethanes forming potential
TOC	Total organic carbon
UC	Ultracentrifugation
UF	Ultrafiltration
UV ₂₅₄	Ultraviolet absorbance at wavelength of 254 nm
VPO	Vapor pressure osmometry

1. INTRODUCTION

1.1 Background

In the Northern hemisphere the amount of dissolved natural organic matter (NOM) in soil and surface water is high due to the relatively thin soil cover and due to the climate. More than half of the dry matter weight in the water in this region may be due to NOM. It is responsible for giving the water a distinct yellow-brown colour (Nordtest 2003). It has been noticed that the colour and to a lesser extend the dissolved organic carbon (DOC) in surface water in Northern European countries have increased considerably during the past 1 1/2 decades (Eikebrokk et al. 2004). There is apparently an increase in the use of groundwater and artificial groundwater in Finland. Consequently the share of surface water is declining. Still, about 40% of the drinking water produced in Finland is from surface water sources, and all larger water treatment facilities use surface water as a raw water source (Ympäristökeskus 2004).

NOM causes problems in the production of drinking water. It has an adverse effect on the aesthetic water quality and may result in biofouling of pipelines with negative hygienic consequences (Nordtest 2003). It has also been demonstrated that the NOM is the basis for the production of potentially hazardous disinfection by-products (DBPs) (Singer 1999). Thus, it has to be removed from drinking water more efficiently. The most obvious solution to the enhanced removal of NOM from raw waters would be the improvement of the performance of existing processes; coagulation, flocculation and filtration. However, if the existing water treatment process is considered insufficient, there are still unit operations for the removal of the residual organic matter and possible micro-pollutants from water; membrane techniques and oxidization of organic matter followed by assimilation by micro-organisms. In general, the quality of the drinking water, supplied by the water treatment facilities in Finland, meets the standards (Ympäristökeskus 2004). Nevertheless, some improvements in the technical and aesthetic qualities of drinking water are still required. More data is needed for the risk assesment and selection of proper treatment technologies.

NOM can be removed from water by a number of different treatment processes (Jacangelo et al. 1995). The most common and economically feasible processes to remove NOM are coagulation and flocculation followed by sedimentation/flotation and sand filtration. NOM with high molar mass (HMM) is removed effectively from water in the chemical coagulation process (Ratnaweera et al. 1999a, Vik et al. 1985). However, a part of the organic matter is passing through when this method is used. This part consists predominantly of intermediate molar mass (IMM) and low molar mass (LMM) organic compounds. The NOM remaining after coagulation can be further removed by advanced treatment processes, such as activated carbon (AC) filtration, biologically activated carbon (BAC) filtration and membrane filtration (Jacangelo et al. 1995). The intermediate molar mass (IMM) organic compounds and a part of the low molar mass (LMM) organic matter can be removed quite efficiently in the AC filtration process (McCreary and Snoeyink 1980). However, a part of the LMM organic matter fraction does not adsorb onto AC (Swietlik et al. 2002). Membrane filtration achieves the highest removal capacity of NOM, especially as a last step of treatment after conventional processes (Liikanen 2006). The costs of the membrane filtration processes, however, have been relatively high and its use, therefore, is restricted to special cases (Jacangelo et al. 1995, Liikanen 2006).

Disinfection of water with chlorine can lead to the formation of disinfection by-products, DBPs. Thus there is an increasing interest in using ozone as disinfectant. Ozone has also other positive effects on the NOM removal besides disinfection (Amy et al. 1991, Owen et al. 1995). Still, the ozonation of NOM in water is not very well understood, because of the variable structures and the different chemical groups attached to the NOM (Langlais et al. 1991, Ho et al. 2002). Ozonation, combined with AC filtration, can enhance the removal of NOM due to increasing biodegradation of NOM and hence an increased assimilation to AC (Langlais et al. 1991).

The amount of organic matter in water is determined usually by total organic carbon (TOC), dissolved organic carbon (DOC), UV-abs and colour measurements. However, in order to evaluate the impact of the different treatment-steps on the quality of the organic matter, high-performance size-exclusion chromatography (HPSEC) has proved to be very useful (Peuravuori and Pihlaja 1997, Nissinen et al. 2001, Myllykangas et al. 2002). It should be kept in mind, however, that the HPSEC method has its own limitations, particularly due to the fact that UV₂₅₄ is often used as a detector. Small aliphatic compounds, do not for example, absorb UV light and are thus not indicated by the UV₂₅₄ measurements. Still, the method has been extensively used since the 80's for the measurements of molecular size distribution (MSD) of NOM in water with good results (Miles and Brezonik 1983, Kronberg et al. 1985, Vartiainen et al. 1987, Knuutinen et al. 1988, Peuravuori and Pihlaja 1997, Miettinen et al. 1998, Vuorio et al. 1998, Nissinen et al. 2001, Myllykangas et al. 2002, Hurst et al. 2004, Goslan et al. 2006).

1.2 Research problem and objective

Pure drinking water is essential for any society. Due to the water quality problems and stricter regulations for drinking water quality, more efficient and still economical methods for the purification are needed. The need for more efficient removal of NOM necessitates more knowledge of the matter. In Finland, there have been studies about NOM removal in drinking water processes (Tuhkanen et al. 1994, Kainulainen et al. 1995, Vuorio et al. 1998, Nissinen et al. 2001, Myllykangas et al. 2002), about the formation of the DBPs during the drinking water treatment process (Nissinen et al. 2002, Myllykangas et al. 2005) as well as microbial growth in drinking waters (Miettinen et al. 1999, Lehtola et al. 2001, Lehtola et al. 2002). However, the knowledge of the NOM quality and quantity in the actual drinking water treatment train, and how is it removed during the process, needed to be studied more in long term investigation.

The main objective was to monitor the drinking water purification process on full-scale at the water treatment plant. In long-term follow-up the behaviour of NOM in all seasons with various raw water supplies was studied. Besides the conventional treatment methods, the advanced treatment techniques, and especially how they are operating in Finnish conditions, was of interest; the enhancement of the NOM removal by the nanofiltration (NF) process as a refining surface water treatment phase and the effects of ozonation of NOM with ozone, followed by filtration with AC. The quantity of NOM is not the only parameter affecting the treatment efficiency. Thus, the removal of the different molar mass (MM) fractions of NOM in the different purification processes was especially worth studying further.

The nature of organic matter is very complex and there is a need for a simple and rapid method to characterize NOM. One of the most common innovative method to characterize NOM is the determination of the molecular size and molar mass distribution (MSD) of NOM

by high-performance size-exclusion chromatography (HPSEC). Thus, the use of HPSEC-UV₂₅₄ method in the routine monitoring of the purification process needed to be evaluated. We also wanted to determine whether the HPSEC-UV₂₅₄ method could yield any information on the process beyond what could be gained by basic water quality measurements.

1.3 Research methods

The removal of NOM was monitored in full-scale drinking water treatment facilities, using lake water as well as river water as water supplies. In addition, an advanced purification process, NF as a refining treatment process after conventional purification, was studied in pilot scale. The use of ozonation, in combination with AC filtration, and its effects on NOM removal was also investigated in pilot-scale as well as full-scale.

2. THE CHARACTERISTICS OF NATURAL ORGANIC MATTER IN WATER

2.1. Natural organic matter

Natural organic matter (NOM) in aquatic environments can be derived from both the external sources (allochthonous) and from sources within the aquatic ecosystem (autochthonous). The main source of aquatic humic substances is however from the terrestrial vegetation and soils in the watershed (McKnight and Aiken 1998). Climatic factors, such as precipitation and temperature are important factors regulating the soil organic matter pool and carbon fluxes, including NOM dynamics (Aiken and Cotsaris 1995, Gjessing 2003).

Organic matter in natural waters can be divided into dissolved and particulate organic carbon. No natural cutoff exists between these two fractions and the distinction is operational. Filtration through a 0.45 µm filter has been arbitrarily established as the standard procedure for separating dissolved and particulate components (Danielsson 1982). Research of NOM in the water has been almost exclusively concerned with dissolved fraction. Dissolved organic carbon can be divided into six fractions: hydrophobic acids, bases and neutrals; and hydrophilic acids, bases and neutrals (Leenher 1981). NOM can be also divided into humic and non-humic fractions. The humic fraction is more hydrophobic in character and comprises humic acids and fulvic acids. The nonhumic fraction is less hydrophobic in character and comprises hydrophilic acids, proteins, amino acids and carbohydrates (Owen et al. 1995). Monomeric species such as simple sugars and amino acids may also be present in surface water, but they are less abundant because they are subject to relatively rapid biodegradation (Croue et al. 2000). Non-humic substances can be bound covalently to humic substances, thus making the separation of these two groups difficult (Peuravuori 1992). Different fractions and the chemical groups involved are shown in Table 2.1.

Table 2.1 NOM fractions and chemical groups (in Edzwald 1993).

FRACTION	CHEMICAL GROUP
HYDROPHOBIC	
acids	
<i>strong</i>	humic and fulvic acids HMM alkyl monocarboxylic and dicarboxylic acids, aromatic acids
<i>weak</i>	phenols, tannins IMM alkyl monocarboxylic and dicarboxylic acids
bases	proteins, aromatic amines, HMM alkyl amines
neutrals	hydrocarbons, aldehydes, HMM methyl ketones and alkyl alcohols, ethers, furans, pyrrole
HYDROPHILIC	
acids	hydroxy acids, sugars, sulfonics, LMM alkyl monocarboxylic and dicarboxylic acids
bases	amino acids, purines, pyridines, LMM alkyl amines
neutrals	polysaccharides, LMM alkyl alcohols, aldehydes and ketones

Humic substances are a complex mixture of both aliphatic and aromatic molecules with a wide variety of chemical compositions and molecular sizes. The classification is therefore based on an operational chemical characterization, which is often referenced to a solubility scheme originally developed by soil scientists (Oden 1919). The soil science terminology was carried over into the aquatic field at an early stage of the study of NOM and the terms are now commonly used (Aiken and Cotsaris 1995). The basic definitions of humic substances are based on the procedure used for their isolation. Humic substances are defined in terms of their solubilities in aqueous acids and bases – regardless of sources of samples. The insoluble organic matter remaining after alkaline extraction is termed humin. The soluble fraction is treated with acid to low pH, and the material that precipitates is termed humic acid, while the organic material remaining in solution is called fulvic acid (Figure 2.1) (Stevenson 1982).

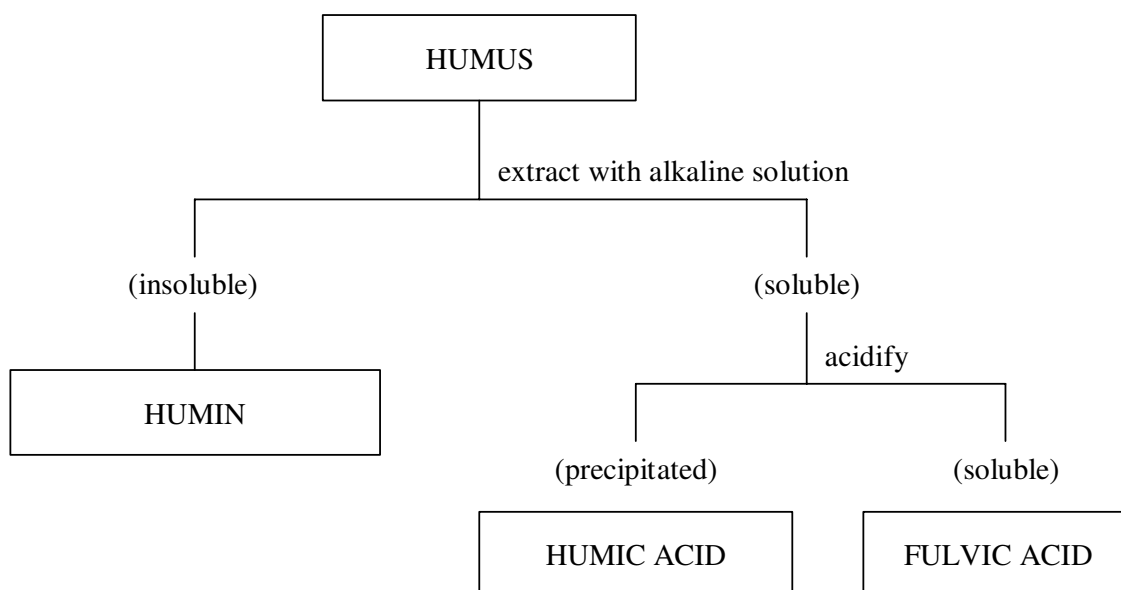


Figure 2.1. Scheme for the extraction of humic substances (adapted from Stevenson 1982).

Regardless of the isolation or definition scheme, humic and fulvic acids constitute a major fraction of any aquatic NOM sample. They account for widely varying proportions of NOM, generally one-third to one-half of the DOC in water (Thurman and Malcolm 1981). Fulvic acids are probably more representative than humic acids, especially in the dissolved fraction (Malcolm 1985). In general, fulvic acids are more soluble, smaller in average molecular weight, less aromatic and more highly charged than humic acids. Fulvic acids typically also have higher oxygen content, with higher carboxylic acid (COOH) and lower aromatic hydroxyl (ArOH) content than humic acids (Hayes et al. 1989b). At pH values typical of natural waters, a fulvic acid molecule has a net negative charge (Amy et al. 1992).

2.2 Structures of humic substances

Unlike synthetic polymers and many biological polymers, humic molecules are not comprised of unique, highly reproducible monomeric building blocks. In many humic molecules, the group of similar building blocks are probably present, but the sequence and frequency of occurrence of the blocks differ. The exact structure of the regions between adjacent building

blocks is probably different in every humic molecule (Croue et al. 2000). Several hypothetical structures have been proposed to account for the chemical composition and behaviour of humic substances. The assumption that lignin is essential in humification processes is common to most structural formulas. The proposed structural formulas consist mainly of highly condensed aromatic rings substituted with carboxylic, phenolic and methoxy groups (Hatcher and Spiker 1988, Peuravuori 1992, Amy et al. 1992). In general, two types of structures have been proposed. First type has random aggregates of highly substituted aromatic and phenolic acids held together by weak interactions, such as hydrogen bonds. This type of structure has been proposed chiefly for fulvic acids. The other type consists of highly cross-linked networks of mainly aromatic and aliphatic structural components and this is applied generally to humic acids (Hayes et al. 1989a, Peuravuori 1992). Figure 2.2 illustrates an example of proposed structure for humic acid. Structure suggested for fulvic acid molecule is in Figure 2.3.

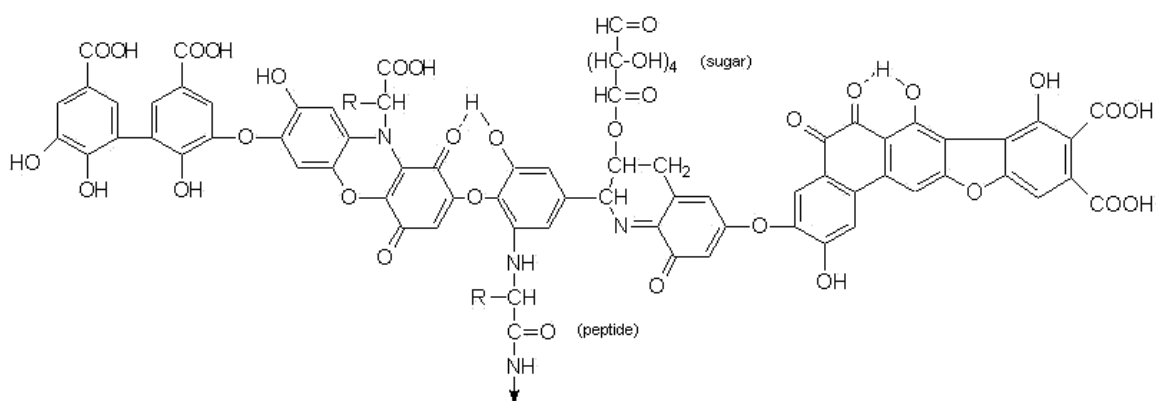


Figure 2.2 Example of proposed structure for humic acid in aqueous environment after Stevenson, 1982.

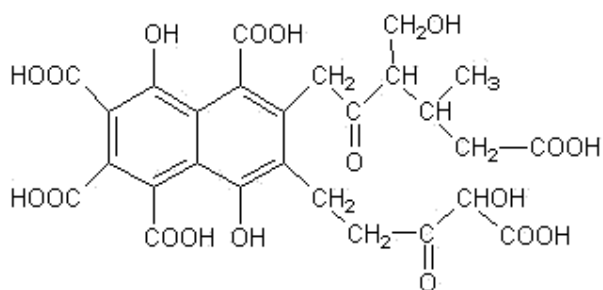


Figure 2.3 Average structure for fulvic acid after Buffle (1977) (in Peuravuori 1992).

Although there is some discussion about the most appropriate molecular model for the conformation of humic substances in solution, the random coil model is more likely to accommodate the apparent irregularity of chemical structure and apparent lack of internal bonding and crosslinking (Swift 1989). Humic substances are polyelectrolytes and therefore carry a substantial electrostatic charge in aqueous solution (Swift 1989, Peuravuori 1992). Ghosh and Schnitzer (1980) proposed a theory for the modelling of polyelectrolyte structure of humic substances. This structure is based on molecular coiling and uncoiling in response to change in solution pH, ionic strength and organic solution concentration. According to this theory, NOM exists as a flexible linear macromolecule at very low ionic strength, high pH and low solution concentration, when intramolecular charge repulsion is high and repulsive (Figure 2.4 A). At high ionic strength, low pH and high solution concentration NOM exist as a rigid, compact, spherocolloidal macromolecule (Figure 2.4 B) (Ghosh and Schnitzer 1980, Braghetta et al. 1997). This approach has been questioned in recent studies (Piccolo et al. 1996, Conte and Piccolo 1999a and 1999b). Conte and Piccolo (1999a) suggested, based on studies with HPSEC and cross-polarization magic angle spinning ^{13}C NMR spectroscopy, that aquatic humic substances are loosely bound self-association of relatively small molecules rather than having a macromolecule random coil structure. The predominant binding forces in the structure are intermolecular hydrophobic interactions, which are affected by the ionic strength and pH (Piccolo et al. 1996, Conte and Piccolo 1999a).

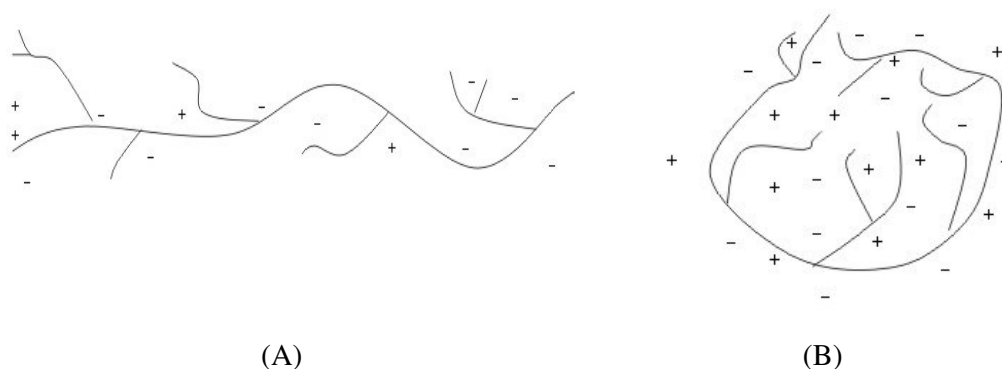


Figure 2.4 Conceptual sketch of hypothetical macromolecular endpoints from polyelectrolyte solution theory: A) high pH, low ionic strength, low solute concentration; B) low pH, high ionic strength, high solute concentration (Adapted from Braghetta et al. 1997).

The third approach, without chemical structural formula, for identification of the nature of humic substances is the utilization of different concepts of molecular conformations, which also has caused contradictory reactions (Varga et al. 2000). Wershaw (1993) has proposed that humic molecules are amphiphilic, containing hydrophilic carboxylate or carbohydrate end and the hydrophobic part from the relatively unaltered plant polymer segments. These amphiphilic molecules interact with soil mineral grains and formate a membrane-like coating to the hydrous oxide surface of these grains. The hydrophobic interiors of the membranes and micelles can serve as hydrophobic phases into which nonpolar compounds partition. Similarly the charged exterior surfaces of the membranes and micelles act as separate ion exchange phases that interact with charged species (Wershaw 1993, Piccolo 1997, Wandruszka 1998).

2.3 Molecular sizes of humic substances

A number of analytical techniques have been used for measuring the molecular size distribution (MSD) of aquatic organic colloids and humic substances. These include high-performance size-exclusion chromatography (HPSEC) (Chin and Gschwend 1991, Pelekani et al. 1999), ultra membrane filtration (UF) (Aiken 1984), ultracentrifugation (UC) (Reid et al. 1990), field flow fractionation (FFF) (Beckett et al. 1987, Pelekani et al. 1999), diffusivimetry (Egeberg et al. 2002), vapor pressure osmometry (VPO) (Aiken and Malcolm 1997) and low angle X-ray scattering (Wershaw 1989). Reported molecular sizes for humic and fulvic acids determined by these methodologies range from 500 to 1 000 000 g/mol. These reported MM may or may not reflect the true size of the colloid because the sizing of these substances is subject to nuances unique to each method (Chin and Gschwend 1991). One reason for the very large MM sometimes reported is the possibility that humic substances may aggregate even to the extent of forming micelle-like structures (Beckett et al. 1987, Wershaw 1993, De Paolis and Kukkonen 1997). MM of humic and fulvic acids are a topic of major disagreement in the literature. Recent data has shown that MM of less than 10 000 g/mol is most abundant in aquatic environments (Amy et al. 1992, Peuravuori and Pihlaja 1997, Pelekani et al. 1999).

The size of the humic substances will affect nearly all environmental aspects of these compounds. The molecular size of various humic substance samples has been related to disinfection by-product formation (El-Rehaili and Weber 1987, Reckhow et al. 1990), coagulation efficiency and removal by commonly employed water treatment processes (Collins et al. 1986, El-Rehaili and Weber 1987), complexation of trace metals (Weber 1988, Pettersson 1992), adsorption of humic substances onto minerals and activated carbon (McCreary and Snoeyink 1980) and partitioning of organic pollutants (Chin et al. 1997).

3. NOM IN THE WATER PURIFICATION PROCESS

3.1 Coagulation

Coagulation is a process, where the repulsive potential of electrical double layer of colloids is reduced so that micro-flocs can be produced. These micro-flocs collide with each other and form larger structures (flocs) in flocculation process (Gregor et al. 1997). Chemical coagulation is achieved by addition of inorganic coagulants such as aluminium- or iron salts. Although coagulation is effective in precipitation of soluble NOM, it has also an important objective of removing other particles and pathogens. Pathogen removal is far more important from a public health point of view compared to NOM, so the removal of NOM should not, therefore be done at the expense of particle- and pathogen removal (Edzwald and Tobiason 1999). The coagulation process is optimized in order to add as little coagulants as possible and at the same time remove maximum amount of NOM and other particles (Ratnaweera et al. 1999b).

The effectiveness of coagulation to remove NOM and particles depends on several factors including type and dosage of coagulant, pH, temperature, particle and NOM properties, such as size and hydrophobicity (Vrijenhoek et al. 1998, Jarvis et al. 2004). NOM is removed through a combination of charge neutralization, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates. Further agglomeration of these micro-particles leads to the formation of flocs (Randtke 1988, Jarvis et al. 2004). The hydrophobic fraction of NOM is removed in the coagulation process more efficiently than hydrophilic fraction of NOM (Collins et al. 1986, Aiken and Cotsaris 1995, Kim and Yu 2005, Kim et al. 2005, Sharp et al. 2006a and 2006b). HMM matter is probably more aromatic (consisting mostly humic acid) than IMM and LMM matter (consisting more fulvic acid), therefore rendering HMM fraction more hydrophobic. Thus, the HMM organic matter is easier to remove by coagulation processes than the LMM matter (Randtke 1988, Sharp et al. 2006a). LMM compounds possess a higher carboxylic acidity, and therefore these molecules with the highest content of acidic functional groups are the most difficult to destabilize by coagulation (Collins et al. 1986). According to the study of Lindqvist (2001), the LMM fraction was not removed properly even when the coagulation process was optimised with respect to organic matter removal. Optimisation of the coagulation process was noticed to influence primarily the removal of the IMM part of the organic matter (Hooper 1996, Lindqvist 2001). However, in the study by Lindqvist et al. (2004), almost 40 % removal of the smallest MM fraction was observed if anionic polyelectrolytes were used as coagulation aids in the process. Cationic polymers were not observed to have any significant improvements in removal rates of NOM during coagulation (Lindqvist et al. 2002, Jarvis et al. 2006).

The most widely used coagulant in drinking water production is aluminium sulphate (Amirtharajah and O'Melia 1990) but recently the use of ferric salts has become more common. Many jar-test studies have been made to compare the effectiveness of one coagulant with another (Crozes et al. 1995, Lovins et al. 2003, Budd et al. 2004, Lidqvist et al. 2004, Tuhkanen et al. 2004). According to these studies ferric-based coagulants have been noticed to remove NOM, measured by DOC or UV-absorbance, more effectively than aluminium-based ones. In the studies made by Lindqvist et al. (2004) and Tuhkanen et al. (2004) the IMM fraction of NOM was removed approximately 15% more efficiently with ferric coagulants than with aluminium ones. Lovins et al. (2003), however, noticed in their investigation, that the aluminium-based coagulants generally provided higher colour removal.

The ferric coagulants are suggested to perform more efficiently at higher doses, especially in treating elevated levels of organics, whereas aluminium coagulants are thought to be more selective (Budd et al. 2004, Kastl et al. 2004, Jarvis et al. 2006). The removal mechanisms of ferric and aluminium coagulants are suggested to be different. Ferric-based coagulants are reported to present roughly twice the number of active positive charges per dry weight unit of coagulant compared to aluminium-based (Grozes et al. 1995). Thus, because of its high charge density, ferric coagulants may better be able to precipitate especially the IMM molecules (MM range of 1000-4000 g/mol) which consist primarily from fulvic acids (Lindqvist et al. 2002). Moreover, the flocs formed during ferric coagulation, are noticed to be both larger and more numerous than those formed during aluminium coagulation, therefore increasing the likelihood of collisions and subsequent removal (Ratnaweera et al. 1999, Lindqvist 2001).

3.2 Sorption on solid surfaces

NOM can be bound in porous solid materials to a certain extent. Therefore, porous solid materials are used in technical sorption systems for drinking water treatment. However, sometimes removal of inorganic and organic pollutants, as well as taste- and odour-causing substances, is the main task. Effects of competitive sorption with NOM may then play an important role. Sorption of dissolved substances from the aqueous phase in solid surfaces occurs in a variety of natural systems as a result of attractive interactions, mostly due to van der Waals forces, hydrogen bonding and electrostatic forces (Fettig 1999). Many different applications are applied in practice or have at least been investigated in pilot scale. These applications include activated carbon (AC) filtration, anion exchange resins, carbonaceous resins and metal oxides (Heijman et al. 1999, Fettig 1999).

3.2.1 Activated carbon (AC) filtration

AC adsorption is an effective adsorbent used widely in the removal of both man-made and natural micropollutants such as pesticides, industrial chemicals, tastes and odours and algal toxins (Newcombe 1999). AC is a relatively expensive water treatment process, but the operating costs can be reduced by replacing the sand with AC in already existing rapid gravity filter basins (Hyde et al. 1987). The AC filtration has only quite recently been taken into use at Finnish water treatment plants. It wasn't until the middle of the 1980's, when the replacement of sand filters with AC became more common in water purification in Finland (Vahala 1995).

NOM competes for adsorption sites on AC, decreasing the removal of other micropollutants. However, AC can also be considered as an additional treatment for the removal of NOM (Newcombe 1999). Different MM fractions of NOM adsorb on AC to different extents, the HMM fractions being least adsorbable (El-Rehaili and Weber 1987). The lower MM compounds are more adsorbable on AC because more surface area is accessible for these substances (McCreary and Snoeyink 1980). Also, because they are smaller in size, they are able to enter nanopores that would exclude macromolecules. This suggests that there is a relationship between MSD of NOM, carbon pore size distribution and the effectiveness of adsorption for removal of NOM (El-Rehaili and Weber 1987). As the result of IMM and LMM matter removal, AC is effective in reducing DBP precursor compounds (Newcombe 1999).

All adsorbents have a limited capacity and have to be replaced or recharged. In European practice of drinking water treatment AC is reactivated and reused several times (Boere 1992). The most common regeneration method for AC is thermal reactivation at temperatures above 700°C (Boere 1992, Cannon et al. 1993). According to the study by Hyde et al. (1987) there was no evidence of a change in particle size as a result of regeneration. But still, when AC has been in use for several years and AC has been subjected to numerous regenerations, a degradation of AC particles has been found to occur (Hyde et al. 1987). Metals, like aluminium, calcium, iron and manganese, can accumulate into the AC. These metals appear naturally in waters or they may be added during chemical treatment (Cannon et al. 1993). These metals can be removed from AC only by acid washing. Calcium inside the used AC may influence the AC pore size during regeneration. Still, if regeneration is performed under proper conditions, its virgin pore characteristics can be restored (Cannon et al. 1993). However, because change or regeneration of AC are the most expensive steps in the AC filtration process, various alternatives have been investigated to expand the lifetime of carbon, e.g. preozonation (Langlais et al. 1991, Kainulainen et al. 1995).

3.2.2 Biologically activated carbon (BAC) filtration

Microbial re-growth in the distribution system has always been a major concern for water utilities. The extent of re-growth depends on the substrate availability and the presence of residual disinfectants. One method of re-growth control is to limit nutrient concentration (Miettinen et al. 1999, Lehtola et al. 2002). These nutrients are naturally occurring or are produced during oxidation processes like ozonation. Allowing some processes in the treatment plant to become biologically active has been found to reduce the biodegradable organic matter in water (Langlais et al. 1991, Miltner et al. 1992). AC colonized by a heterotrophic biomass reduces the proportion of easily assimilated and biodegradable elements, which are mainly LMM organic molecules (Boualam et al. 2003). The highest amount of microbial growth is found on the surface and top layer of AC filter (Kainulainen et al. 1995). Preozonation has been shown to increase the biodegradability (and hence assimilable organic carbon, AOC content) of organic matter (Langlais et al. 1991, Miettinen et al. 1998). The increased AOC content enhances the biological activity in the filter, and thus enhances the removal of NOM (Langlais et al. 1991, Van der Hoek et al. 1999). Most ozonation/biofiltration plants in the world use AC as biofilter medium, thus combining adsorption and biofiltration (Odegaard et al. 1999). The effect of carbon regeneration on biological activity of AC, and the removal efficiency of DOC and AOC, have been noticed to be negligible (Van der Hoek et al. 1999). Thus, enhanced biological activity with preozonation prolongs the running time of AC filters and reduces the costs of regeneration of the carbon (Langlais et al. 1991, Boere 1992, Van der Hoek et al. 1999).

3.2.3 Ion exchange resin filtration

Ion exchange is an effective method for removing NOM from drinking water. Since a large fraction of NOM can be characterized as anionic polyelectrolytes, macroporous ion exchange resins are well-suited for NOM removal (Fettig 1999). Resins of open structure and high water content are very efficient at removal of any charged material, including NOM, and especially LMM NOM (Bolto et al. 2002a). Ion exchange resins are more homogeneous with respect to the binding of NOM, compared to activated carbon (Fettig 1999). Ion exchange resins can also be regenerated as much as 50 times, so the costs of the DOC removal are very low compared to AC (Heijman et al. 1999).

Magnetic ion exchange resin, the MIEX® process, is quite recently developed in Australia (Orica Australia Pty, Ltd). The method is based on traditional ion exchange process. In comparison with traditional process, MIEX® is microsize, having smaller sized resin particles (mean particle size 150 µm) than traditional resins. Moreover, the resin beads in the MIEX® process are dispersed as a slurry, in a stirred contactor with treated water, allowing for maximum surface area for adsorption (Drikas et al. 2004, Fearing et al. 2004). The magnetic properties of the resin promote aggregation of the resin particles, facilitating resin recovery (Drikas et al. 2004). This strong-base resin was developed for reversible removal of negatively charged organic ions, and specifically for the removal of DOC to minimize the formation of DBPs in drinking water supplies (Hammann et al. 2004, Drikas et al. 2004). Especially the IMM and LMM NOM are efficiently removed, thus reducing the DBPs forming potential of treated waters (Hammann et al. 2004). The negatively charged DOC is removed from water by exchanging it with a chloride ion on active sites on the resin surface (Hammann et al. 2004). High NOM removals (85-90%) can be achieved with 10 to 20 minutes contact times (Drikas et al. 2004). Moreover, MIEX® resin has been reported to achieve high NOM removal (46-87% and 53-100% for DOC and UV, respectively) as a result of pre-treatment process before coagulation (Singer and Bilyk 2002, Fearing et al. 2004). This is because coagulants and ion exchangers are noticed to remove different kind of NOM compounds. The preference of the coagulants are for larger molecules, and of the resins for the smaller, highly charged compounds (Bolto et al. 2002b).

3.3 Disinfection and oxidation

The primary purpose for disinfection of drinking water is to destroy and eliminate pathogenic organisms responsible for waterborne diseases. Commonly used disinfectants are chlorine, chlorine dioxide, chloramine and ozone. Also ultraviolet (UV) radiation and sodium hypochlorite have been used in water disinfection. No single disinfection method alone is right for all circumstances. Water treatment facilities may use a variety of methods to meet overall disinfection goals at treatment plants and to provide residual protection throughout the whole distribution system. (CCC 2003)

3.3.1 Chlorine-based disinfectants

Although ozone was first recognized to disinfect polluted water in the late 19th century, after World War I the use of chlorine became more popular (Langlais et al. 1991). Up until the late 1970's, chlorine was virtually the only disinfectant used to treat drinking water. Even today, chlorine is the most commonly used disinfectant, based on its proven characteristics; effectiveness against pathogens, ease to apply, control and monitor and reasonable cost (CCC 2003). However, humic substances react with chlorine to produce a number of different halogenated organics, such as trihalomethanes (THMs). Several of these compounds have been shown to cause cancers in laboratory animals (Singer 1999). The MM fractions <40 000 g/mol are predominantly responsible for THM production during chlorination (El-Rehaili and Weber 1987). In Finland, high concentrations of chlorinated organic matter and high mutagenic activity were measured in the drinking water in the 1980s. The mutagenicity decreased markedly from 1985 to 1994 in Finnish waterworks. This was due to that particularly prechlorination of drinking waters stopped and post-chlorination decreased in water purification facilities. Waterworks have also improved their NOM removal processes (coagulation, AC filtration), and thus the amount of organic precursors for THM production has decreased (Nissinen et al. 2002).

Many drinking water utilities are changing from chlorine to alternative disinfectants such as chlorine dioxide and chloramines. Substitution of chlorine by any other disinfectants has been noticed to decrease the mutagenicity and the concentration of THMs (Backlund 1990). Chloramine disinfection has been found to be one of the best treatment options for reducing mutagenicity and the DBPs formation (Nissinen 2002). However chloramines are relatively weak as a disinfectant and almost never used as a primary disinfectant (CCC 2003). Chlorine dioxide is a strong disinfectant and a selective oxidant (CCC 2003). However, the disinfection with chlorine dioxide also generates by-products. These by-products are mainly inorganic (chlorites and chlorates), but also organic by-products formation are reported (Dabrowska et al. 2003). Thus, alternative disinfectants result in new problems. Source of raw water conditions can affect the levels and types of DBP species formed, and a new type of DBPs is evolving (Richardson et al. 2002).

3.3.2 Ozonation

The disinfectant ability of ozone was recognized as early as in the late 19th century. However, it was not until after World War II, when ozonation became more common (Langlais et al. 1991). Nowadays, ozonation is widely used in the drinking water treatment for disinfection, bleaching and taste and odor removal. Ozonation also results in decolorisation, as well as turbidity removal (Langlais et al. 1991). It has been reported of a 45 % and 43 % colour and turbidity removals, respectively, after ozonation (Tuhkanen et al. 1994). Ozonation reaction products are far more biodegradable than the original humic substances themselves (Odegaard et al. 1999). Thus, it is used also to enhance the removal of residual organic carbon by increasing the biodegradability of recalcitrant NOM prior to biofilter medium, such as AC (Owen et al. 1995).

The ozonation of NOM in water is still not well understood as NOM consists of a diverse range of compounds with very different chemical properties (Ho et al. 2002). According to literature (Owen et al. 1995), ozonation does not result as much in NOM destruction, but rather in transformation. It has been reported (Amy et al. 1992, Owen et al. 1995, Miettinen et al. 1998, Kim et al. 2005) that ozonation could convert NOM from higher to lower MM fractions as well as alter the hydrophobic compounds to more hydrophilic. In several studies, ozonation has been noticed to have a great impact on the different MM fractions of NOM, but it virtually has had no effects on the TOC content of the different waters studied (Langlais et al. 1991, Tuhkanen et al. 1994, Kainulainen et al. 1995, Nissinen et al. 2001, Myllykangas et al. 2002, Myllykangas et al. 2005). Slight decrease in HMM compounds fraction of NOM has been detected, while LMM matter fraction has been noticed to increase. The organic compounds of the IMM fraction developed either way, depending on ozone dose and general conditions. Moreover, strong degradation of colour and UV absorbance has been noticed to occur (Langlais et al. 1991, Amy et al. 1992). Ozonation is also noticed to be very effective method for reducing the amount of DBPs (Kainulainen et al. 1995, Nissinen et al. 2002, Kim et al. 2005, Chin et al. 2005).

Oxidation of NOM with ozone results in the formation of several by-products, including aldehydes and carboxylic acids (Kim et al. 2005, Kasprzyk-Hordern et al. 2005). These by-products contribute to a large extent to the amount of biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC), which are easily used by microbes (Miettinen et al. 1998, Miettinen et al. 1999). That is the reason why ozonation is usually followed by biofiltration in order to remove BDOC and AOC from water. The removal of NOM by ozonation followed by AC is attributed more to the biodegradation than adsorption by so

called biologically activated carbon (BAC) (Langlais et al. 1991, Odegaard et al. 1991). By this way the bacteria growth in the distribution system, as well as high disinfectant demand, can be prevented (Kasprzyk-Hordern et al. 2005).

3.3.3 Advanced oxidation processes (AOPs)

An alternative group of technologies that can be used to remove the NOM from drinking water and minimize the formation of DBPs are advanced oxidation processes (AOPs). AOPs are defined as near-ambient temperature processes that involve the generation of highly reactive radical intermediates, especially the hydroxyl radicals (Glaze et al. 1987 and 1992). The hydroxyl radical has been reported to oxidise a range of organic compounds highly efficiently (Tuhkanen et al. 1994). AOPs involve many different disinfectants used in combination with others, e. g. O_3/H_2O_2 , UV/H_2O_2 , and O_3/UV . Also Fenton's and photo-Fenton processes have been studied (Murray and Parsons 2004, Goslan et al. 2006). These methods have been used for the removal of pesticides, pharmaceuticals etc. from polluted water. Many studies have been made to evaluate these AOPs for control of NOM in drinking waters (Glaze et al. 1992, Tuhkanen et al. 1994, Wang et al. 2000, Murray and Parsons 2004, Chin and Bérubé 2005, Goslan et al. 2006). The formation of the DBPs and mutagenicity is usually lower than that found after the use of individual disinfectants. The titanium dioxide-based photocatalytic degradation is also one of the studied processes (Li et al. 2002). It is reported (Li et al. 2002) that photocatalytic oxidation is effective process for the mineralization of NOM, even up to CO_2 , H_2O and in-organic constituents.

3.4 Membrane filtration

Membranes used for NOM removal have relatively recently been taken into use to a greater extent, although the technology has been available for several decades (Jacangelo et al. 1995). Pressure driven membrane processes include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) (Jacangelo et al. 1995). MF will remove turbidity (particulates and bacteria), but no dissolved compounds unless associated with colloids. UF will, depending on the molecular weight cut off (MWCO) of the membrane, remove NOM partially and viruses. NF will remove NOM and hardness almost completely (Schäfer et al. 2001). NF has proven to be reliable for the removal of organic and inorganic compounds (Amy et al. 1990, Thorsen et al. 1999, Siddiqui et al. 2000, Liikanen 2006), with lower operating pressures than RO and lower MWCO than UF (Her et al. 2000). Organic and inorganic compounds are removed by steric exclusion, electrostatic repulsion and hydrophobic interaction. Matter with MM larger than the membrane cut off is removed mainly by a sieving mechanism, and molecules with MM lower than the membrane cut off by diffusion and charge repulsion based mechanism. Molecule polarity, charge, hydrophobicity and configuration may also affect the retention (Cho et al. 1999, Van der Bruggen et al. 1999, Chellam 2000). Polyhydroxy aromatics (hydrophobic acids) such as humic substances are believed to be rejected by negatively charged NF membranes (Her et al. 2000).

Much of the research has focused on a greater understanding of the membrane fouling potential of surface water constituents (Maartens et al. 1998, Fan et al. 2001, Park et al. 2006) and better pre-treatment techniques (Vickers et al. 1995, Lin et al. 1999, Lin et al. 2000). The fouling of membranes and the decline of flux have been reported to be some of the main problems related to membrane techniques. The extent of membrane fouling is dependent on water quality, membrane properties and operational conditions (Her et al. 2000, Liikanen 2006). Several studies indicate that NOM play an important role in membrane fouling.

Especially the hydrophobic and HMM fractions of NOM have shown to be responsible for this membrane fouling (Childress and Elimelech 1996, Nilson and DiGiano 1996, Hong and Elimelech 1997, Schäfer et al. 1998, Her et al. 2000). The NOM fouling of polymer membranes has been noticed to increase in the presence of divalent captions, at low pH and at high ion content (Childress and Elimelech 1996, Braghetta et al. 1997, Hong and Elimelech 1997, Schäfer et al. 1998, Her et al. 2000, Zander and Curry 2001). It should be borne in mind that fouling changes the membrane properties as well as the characteristics of the foulants in the fouling layer, and thus also affects membrane retention (Yoon et al. 1998, Cho et al. 1999, Schäfer et al. 2000).

NF process, as a refining step in surface water treatment, enhance the removal of residual organic matter and bacteria to levels, which restrict the need for post-chlorination and limits consequent DBP formation and bacteria growth in distribution network (Liikanen et al. 2003). Still, very small LMM organic molecules pass through the NF membranes more easily than higher MM organics, and some post-chlorination is required to suppress microbial growth in distribution systems (Liikanen et al. 2003). However, in applications not requiring notably improved organic matter or ion removals, simpler and less costly process options, like AC filtration and UF or coagulation and UF or MF may be more suitable process options than NF (Liikanen 2006). Consequently, membrane filtration has become a more common method to remove organic matter from drinking water. In the future, membrane filtration most probably will increase its share in the water treatment industry with soft and coloured surface raw waters, due to good and stable water quality obtained by this process (Thorsen 1999, Gorenflo et al. 2002).

3.5 Summary of different processes for removal of NOM

The interest in NOM removal is increasing among water treatment facilities because of more stringent regulations of drinking water quality, and moreover, because of a significant increase in the amount of NOM observed in Nordic countries (Nordtest 2003). The most common processes for NOM removal in Finland are coagulation and AC filtration or ozonation combined with AC filtration. Recently developed processes are membrane (mostly NF) filtration and MIEX®, which are not in full-scale use in Finland, atleast not yet. There have been few investigations about these novel techniques in Finnish conditions (Toivanen and Härmä 2004, Sallanko and Merisalo 2005, Liikanen 2006).

Enhanced NOM removal can be achieved by optimising the coagulation processes, but this results in higher costs because of increased coagulant doses and greater amount of sludge. Also the removal of the lowest MM organic compounds is not improved even when coagulation is optimised (Lindqvist 2001). Advanced purification processes are usually expensive and demand some process modifications. Still, if the NOM amount, and especially the LMM matter or DBP forming potential in treated water, needs to be reduced, the advanced treatment techniques such as AC, NF and MIEX® have to be considered (Jacangelo et al. 1995, Hooper et al 1996, Drikas et al. 2004, Liikanen 2006). NF process has been observed to be superior as the refining phase after conventional treatment. Especially, the removal of residual LMM organic matter has been improved (Liikanen 2006). MIEX® process has given very promising results on the removal of NOM. Combined with coagulation it can result in high NOM removal with reduced costs by lowering the demand for coagulation agent, as well as other chemicals, thus reducing the amount of sludge and enhancing the performance of other unit operations (Toivanen and Härmä 2004). In spite of the excellent NOM removal capacity of these processes, they may include some problems;

e.g. the problems in the use of NF in surface water treatment include membrane fouling, low process yields in comparison with conventional processes, high energy consumption, need for retentate and cleaning solution disposal, as well as overall costs and adverse environmental impact (Liikanen 2006). Process costs and efficiencies for NOM removal are always site specific; e.g. raw water quality varies from area to area . Moreover, small and medium size waterworks doesn't usually have resources to invest in the best available drinking water treatment techniques, and hence it is important to find the best possible solution for particular cases. However, some basic trends and comparisons of the different treatment processes can be made. The various processes for NOM removal are summarized in Table 3.1.

Table 3.1 Qualitative summary of selected aspects of various technologies used for removal of NOM.

Treatment process	NOM removal efficiency	Process complexity	Reference
coagulation MIEX®	fair - good excellent	low - medium medium	Jacangelo et al. 1995 Toivanen and Härmä 2004, Drikas 2004, Fearing 2004
AC filtration	very good	medium - high	Jacangelo et al. 1995
ozonation/AC	very good	medium-high	Van der Hoek et al. 1999, Iivari 2006
nanofiltration	excellent	medium	Liikanen 2006 Jacangelo et al. 1995

4. DIFFERENT METHODS FOR CHARACTERIZATION OF AQUATIC NOM

4.1 General parameters

In practice the concentration of NOM is usually characterized by sum parameters like TOC, DOC, UV-absorbance and COD (Chemical Oxygen Demand; oxidizability by K_2CrO_4 or $KMnO_4$). NOM has also a major contribution to the amount of colour in water. These tests are fast and they can be automated. Still, these tests do not give any information about the quality of NOM. They only measure the quantity of organic matter present.

4.2 Biological tests

Several biological tests have been developed to assess the level of biodegradable organic matter in water. These bioassays are based on two concepts: (1) the assimilable organic carbon (AOC), that measures the growth of bacterial inoculum in response to the amount of nutrients in the water and (2) the biodegradable dissolved organic carbon (BDOC) that measures the fraction of DOC assimilated and mineralised by heterotrophic microbes (Huck 1990, Miettinen et al. 1999, Escobar and Randall 2001).

4.3 Isolation and concentration

The diversity of molecules that constitute NOM and the relative low concentration of NOM in drinking water sources poses some major difficulties in the characterization of NOM. Methods are needed that can either characterize NOM in dilute solutions or that can isolate NOM without altering its properties (Croue et al. 2000). Usually isolation and concentration of aquatic NOM begin by separating the sample into dissolved and particulate fractions (Danielsson 1982). A widely accepted method is the filtration through a $0.45\ \mu m$ filter. Hence, numerous isolation and concentration methods are available. The most commonly used are vacuum distillation, freeze-drying and some sorption methods (Aiken 1985).

4.4 Fractionation of NOM

NOM molecules are all unique while also sharing many common properties. Fractionation of NOM selects a sub-group of molecules from the mixture, that share a narrower range of properties, than the entire aggregate does (Croue et al. 2000). One of the major analytical difficulties in the characterization of aqueous NOM is the lack of any fractionation procedure which will yield pure components which can be subsequently characterized by standard techniques. Fractionation procedures cannot be clearly distinguished from isolation procedures, because some of the isolation methods (e.g. adsorption chromatography) partly also fractionate aquatic NOM (Leenher 1985). Commonly used chemical fractionation methods are precipitation, solvent extraction, and adsorption chromatography. Moreover, the physical fractionation methods available are electrophoresis, ultrafiltration (UF), size exclusion chromatography (SEC) and ultracentrifugation (UC) (Leenher 1985).

4.4.1 Resin fractionation

The most common approach for distinguishing between hydrophobic and hydrophilic dissolved NOM is to define them as the organic matter that is adsorbable and non-adsorbable, respectively, on XAD resins. A method developed by Thurman and Malcolm (1981) for the concentration and fractionation of NOM used a two-column adsorption technique. The

columns contained XAD-8 and XAD-4 Amberlite non-functional resins and the method allowed for the isolation and separation of both the hydrophobic acid fraction and the hydrophilic acid fraction. The two-column method and its variations are widely used in NOM characterization studies (Malcolm and MacCarthy 1992, Krasner et al. 1996, Martin-Mousset et al. 1997, Goslan et al. 2001, Maurice et al. 2002, Goslan et al. 2004, Sharp et al. 2006a, b and c).

Adsorptive methods, like XAD-resin adsorption, usually do not isolate 100% of dissolved organic matter and subject the NOM to extreme pH levels. It is not known how the extreme changes in pH during isolation and fractionation procedures alter the structure and natural reactivity of NOM (Crum et al. 1996). Resin fractionation is also quite time-consuming and creates considerable amounts of hazardous waste. Still the preparative NOM fractionation and its modifications can be used as a basis for quantitative and qualitative organic analysis of water. Fractionation procedures generate specific organic solute fractions, which can be then used for chemical and biological testing (Leenher 1981).

4.4.2 High-performance size-exclusion chromatography (HPSEC)

The fractionation of NOM by size exclusion chromatography (SEC), using particularly Sephadex gels, was introduced in the 1960's (Ferrari and Dell'Agnola 1963, Posner 1963, Gjessing 1965). The exclusion theory in SEC is primarily based on differences in molecular size. When a sample is applied to the SEC column the components are eluted in order of decreasing molecular sizes (Nobili et al. 1989). However, these soft gels had some major disadvantages (Swift and Posner 1971, Gjessing 1973, Hine and Bursill 1984). The separation was time consuming and resolution was poor. Thus, more modern techniques were developed (Fukano et al. 1978, Saito and Hayano 1979). The characterization of NOM by high-performance liquid chromatography (HPLC) applied with SEC column became possible with introduction of rigid, silica or polymer based hydrophilic stationary phases (Fukano et al. 1978, Saito and Hayano 1979, Miles and Brezonik 1983, Becher et al. 1985). High-performance size-exclusion chromatography (HPSEC) method is non-destructive, relatively fast and requires no sample pre-treatment. It also utilizes only small amounts of sample (Rausa et al. 1991). Thus, the most extensively used method during the last decade for molecular size distribution (MSD) determination of NOM from different sources is apparently HPSEC (Becher et al. 1985, Kronberg et al. 1985, Vartiainen et al. 1987, Knuutinen et al. 1988, Rausa et al. 1991, Hongve et al. 1996, Peuravuori and Pihlaja 1997, Miettinen et al. 1998, Pelekani et al. 1999, Conte and Piccolo 1999a and 1999b, Nissinen et al. 2001, Myllykangas et al. 2002, Hurst et al. 2004, Murray and Parsons 2004, Sharp et al. 2006a, Goslan et al. 2006).

In earlier years the HPSEC measurements were criticized because there were undesirable effects due to solute-gel interactions (Miles and Brezonik 1983). Nowadays column materials have developed and bonded silica and polymeric gels have as few reactive sites as possible. Thus HPSEC has become more reliable for MSD analysis (Conte and Piccolo 1999b, Pelekani et al. 1999). However, the HPSEC column gels might still have some charge repulsion effects (Chin and Gschwend 1991, Peuravuori and Pihlaja 1997) as well as adsorption interactions with the organic compounds (Chin and Gschwend 1991, Myllykangas et al. 2002). Different silica-based and polymer-based columns are used in HPSEC measurements and MSD determinations of aquatic NOM. These include columns like TSK (Becher et al. 1985, Vartiainen et al. 1987, Hongve et al. 1996, Peuravuori and Pihlaja 1997, Her et al. 2002, Wu et al. 2003), Biosep (Conte and Piccolo 1999b), Shodex (Rausa et al. 1991, Hongve et al.

1996), and Waters-Protein-Pak 125 (Chin et al. 1994, Pelekani et al. 1999, Zhou et al. 2000, Her et al. 2002).

The most critical step in studying aquatic organic matter solutes using HPSEC is the choice of the eluent. The surface charge characteristics of the gel, the NOM charge and structure, and the NOM-gel interactions are affected by the eluent (Miles and Brezonik 1983, Gloor et al. 1981, Knuutinen et al. 1988, Chin and Gschwend 1991, Pelekani et al. 1999). The column manufacturers recommend distilled water as a mobile phase for separating non-ionic compounds. However, distilled water as a mobile phase is not very suitable for NOM substances, which are repelled by ionic sites on the support because of their negative charge in aqueous solutions (Hongve et al. 1996, Knuutinen et al. 1988). When ionic strength of the mobile phase is increased by addition of neutral salts or a pH buffer, ionic repulsion is reduced (Hongve et al. 1996). Many different eluents are used as a mobile phase in the investigations of NOM characterization by HPSEC (Kronberg et al. 1985, Knuutinen et al. 1988, Rausa et al. 1991, Chin and Gschwend 1991, Hongve et al. 1996). In the study of Peuravuori and Pihlaja (1997), it was obtained that resolution of Finnish natural lake humic water solutes is poor with phosphate buffer eluents. However, the use of 10 mmol sodium acetate solution as the mobile phase gives a fairly good resolution and each water sample shows its own elution profile. This kind of information is very difficult to attain by using any other eluent composition (Kronberg et al. 1985, Vartiainen et al. 1986, Peuravuori and Pihlaja 1997).

Several detectors have been used with HPSEC, including multi-angle light scattering (MALS), refractive index (RI) (Wagoner and Christman 1999), on-line DOC analysers (Gloor et al. 1981, Her et al. 2002, Amy 2004) and excitation emission matrix fluorescence detection (Wu et al. 2003). However, variable wavelength UV-vis detectors are among the most commonly used with HPSEC measurements. UV-Vis detectors are simple and rapid to use and widely available in the majority of laboratories. Limitations of UV-vis detectors are that they only respond to or detect analytes that absorb at the wavelength at which they are operating. Because the structures of NOM contain a range of chromophores with varying molar absorptivities, the MM calculated for HPSEC chromatograms may be biased by the wavelength setting of the detector (O'Loughin and Chin 2001). Moreover, small aliphatic compounds do not adsorb UV light due to the lack of conjugated double bonds, thus giving too small response for LMM matter of NOM. Anyhow, any wavelength from 230 to 280 is appropriate for NOM measurements, although small differences may occur. Still, the most useful wavelength in NOM measurements is 254 nm and it is thus widely used (Zhou et al. 2000). Fluorescence detection at specific excitation/emission (Ex/Em) wavelengths has been employed in HPLC separation and characterization of NOM (Wu et al. 2003). However, limited information and poor separation resolution as compared to UV absorbance detection, has been provided with fluorescence, particularly in the larger MM range. Recently, a more sensitive and fast spectrofluorometer, which can be used as an on-line detector for HPLC has been developed (Wu et al. 2003). Results with HPSEC-fluorescence method indicated that there existed a strong relationship between MM, fluorescence pattern and polarity (Wu et al. 2003). The DOC analyzer detects virtually all of the organic carbon in the sample (Her et al. 2002). Still, UV detector needs much less sample volume than DOC analyser. The eluent composition and flow rate must be optimized carefully, while using DOC analyser as a detector. Thus, commercially available on-line DOC analysers are under further development (Her et al. 2002, Her et al. 2003). The use of HPSEC with sequential UV and DOC detectors overcomes the limitations of both methods along. The relative difference between two detectors also provide additional qualitative information (Her et al. 2002). Moreover, Her et al.

(2003 and 2004) have analyzed organic matter samples with HPSEC-UV-fluorescence-DOC combination, which detects highly efficiently different insights of NOM in the sample. However, this combination of detectors might not be economically possible in majority of research laboratories.

MM of the organic matter fractions observed from the chromatogram can be determined using standards or ultrafiltration (UF) measurements (Pelekani et al. 1999, Ratnaweera et al. 1999a, Amy et al. 1987). The selection of the proper standards to characterize the MM of NOM fractions is determined by their hypothesized structure (Chin et al. 1994). A number of investigators (Nissinen et al. 2001, Peuravuori and Pihlaja 1997, Vartiainen et al. 1987) have used globular proteins as standards. However, it has been reported (Chin and Gschwend 1991, Reid et al. 1990, Beckett et al. 1987) that the proteins tend to over-predict the MM of NOM fractions by a factor of 5 or more. The use of random coil structure standards such as polystyrene sulphonates (PSS) has lately been used in MM determinations (Swietlik et al. 2002, O'Loughlin and Chin 2001, Zhou et al. 2000, Pelekani et al. 1999, Hongve et al. 1996). Although the NOM molecules may be random coil-like in shape, they may also be more branched and cross-linked than PSS (Chin and Gschwend 1991). Still, the MM of NOM fractions measured by HPSEC under appropriate conditions are noticed to be comparable with the values determined by established methods such as vapor pressure osmometry (VPO) and field flow fractionation (FFF) (Pelekani et al. 1999, Chin et al. 1994)

4.4.3. Ultrafiltration (UF)

UF is a convenient procedure for fractionation of materials into different size ranges. NOM can be separated into different nominal MM fractions and the separated fractions can be characterized by other methods, e.g. TOC, UV or HPSEC (Gjessing 1973, Amy et al. 1987, Logan and Jiang 1990, Pelekani et al. 1999). UF is a membrane separation process used for concentration and purification of macromolecular solutes and colloids. The solution is caused to flow under pressure across a membrane surface. Solutes and colloids are rejected at the semi-permeable membrane barrier while solvents and micro solutes below the molecular weight cut-off (MWCO) pass through the membrane (Dickenson 1987). Migration of molecules through membranes is generally accomplished by a combination of advective flow and molecular diffusion. The diffusivity of a molecule is primarily a function of molecular size and secondarily of molecular shape. Smaller molecules diffuse more rapidly than larger ones and spherical molecules more rapidly than linear ones of similar MM (Amy et al. 1987). In addition to molecular size, there are other factors that influence the diffusive and advective transport of organics through ultrafiltration membranes. These include membrane pore size distribution, water temperature, cell filtration pressure, solution pH and ionic strength, as well as molecule shape and affinity for the different membrane materials (Amy et al. 1987, Logan and Jiang 1990, Ludwig et al. 1997). Membranes used are usually made of regenerated cellulose or polyethenesulfone (Logan and Jiang 1990, Collins et al. 1986, Cai 1999). Each membrane has a characteristic nominal molecular weight cut-off (NMWCO) level, which is operationally defined as the mass of a molecule whose retention is 90% on this membrane (Kuchler and Miekeley 1994). Commercial UF membranes are available with different NMWCO, for example 500 g/mol, 1000 g/mol, 10 000 g/mol and 100 000 g/mol. The large NMWCO membranes (> 3000 g/mol) are usually calibrated with proteins, while sugars and polysaccharides are used in calibrating lower NMWCO membranes. As a result of different structures between NOM constituents and the standards used, the true size range for organic compounds in NOM is not necessarily obtained (Pelekani et al. 1999). The choice of membrane can seriously affect the results. UF may yield results comparable with results

obtained by other methods, provided there is a proper choice of membrane (Egeberg et al. 2002). A problem associated with the UF is that macromolecules can adhere to the sides of the membrane pores and markedly affect membrane permeability. An even more important factor is a flow restriction called concentration polarization. This is the deposition of macromolecules on the membrane surface, which results in a gel layer that becomes the dominant resistance to flow (Amy et al. 1987).

4.5 Other analytical methods

The different characteristics of NOM can be measured by a number of methods (Croue et al. 2000). Elemental analysis provide general compositional information about NOM. The average composition of the molecules can be determined by combustion or pyrolysis followed by final measurement e.g. pyrolysis/GC-MS (Huffman and Stuber 1985, Schulten 1999). The functional group composition and some other structural features can be determined in several ways; potentiometric titration (Perdue 1985), solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Mikita et al. 1981) and other spectroscopic methods like fluorescence, infrared (IR) and electron spin resonance (ESR) spectroscopy (MacCarthy and Rice 1985).

The “NOM-typing project” in Norway is screening a large number of methods for analysing and characterizing the properties of NOM in order to develop a protocol for the typing of NOM (Gjessing et al. 1999, Abbt-Braun and Frimmel 1999, Frimmel and Abbt-Braun 1999, Gjessing et al. 1998).

Another approach for determining the properties of NOM are to investigate the potential of NOM for DBP formation e.g. trihalomethane forming potential (THMFP) (Krasner et al. 1996) or binding of NOM into the inorganic and organic micro-pollutants (Weber 1998, De Paolis and Kukkonen 1997, Mohan et al. 2000, Gjessing et al. 2007).

5. AIMS OF THE STUDY

The aim of the study was to monitor the drinking water purification process on full-scale at the water treatment plants, as well as on pilot-scale. The purpose was to enhance the knowledge of removal of NOM in the different stages of the drinking water treatment train in order to optimize and develop these processes. Particular attention was paid to the removal of different molecular size fractions of NOM (HMM, IMM and LMM fractions) by conventional and advanced drinking water treatment methods. The efficient removal of NOM, and especially the removal of IMM and LMM fractions of NOM, require either optimisation of the existing processes or investment in the additional advanced treatment units. In this study the enhanced coagulation, ozonation, activated carbon (AC) filtration and membrane techniques were studied to improve NOM removal efficiency. Especially the various treatment techniques performance and optimisation in Finnish conditions, with high NOM content and temperature variation (0°-25°) was of interest. The characterisation of NOM helps in the selection of proper treatment technologies.

The removal of NOM was determined with various methods. Besides the conventional characterisation methods, like TOC, the aim of the study was to use HPSEC in routine monitoring of the performance of the different treatment processes and also to determine whether the HPSEC method, with UV₂₅₄ detection, yielded any information on the process beyond what could be gained by traditional analytical methods. The specific aims covered in the present work are:

1. To study coagulation process in the NOM removal and how the removal can be enhanced by optimised coagulation and selection of the proper coagulant (Papers I and III)
2. To study AC filtration and the effect of seasonal variation and time of regeneration on its efficiency (Paper II and IV).
3. To study ozonation and its effects on the efficiency of AC to remove NOM in the purification process (Paper IV). Also to study biologically activated carbon (BAC) on the NOM removal at the pilot-scale (Paper IV).
4. To study nanofiltration (NF) as the last removal stage of NOM after conventional treatment to obtain the enhancement of the removal of the residual LMM organic matter in the treated water (Paper V).

6. MATERIALS AND METHODS

6.1 Tampere Waterworks; Rusko Water Treatment Plant

The Rusko Water Treatment Plant pumps its raw water from Lake Roine, seven kilometers southeast of the plant and produces 68% of the drinking water for the city of Tampere, Finland. The plant has a maximum treatment capacity of 55 000 m³/d and an average water flow of about 1 400 m³/h.

The treatment process consists of lime and coagulant addition, flocculation and clarification with sedimentation (before modification) and flotation, chlorine dioxide disinfection, sand filtration (after modification), AC filtration, and post-chlorination. The coagulant agent was changed from aluminium sulphate to ferric sulphate during research period. Diagrams of Rusko Water Treatment Plant can be seen in Appendix 1 in Figures 1 and 2. More detailed information about the water purification processes during the studies can be found in Papers I, II and III.

6.1.1 AC filtration in the Rusko Water Treatment Plant

Rusko Water Treatment Plant has 14 AC filters, which are conventional one-layer filters. Each filter has a surface area of 30 m² and a bed depth of about 115 cm. All similar in structure, the filters are so-called sand replacement filters, in which AC replaces sand. AC is regenerated every two years and changed after about three regenerations. In the first study (Paper I), one filter from sedimentation line (AC-A) and one from flotation line (AC-B) were studied.

Because enhanced NOM removal was detected in the first study, some further investigations were carried out with AC filters. In the second study (Paper II) the age and regeneration frequency of the filters in respect to NOM removal was monitored. Four of the AC filters were selected for the research. Table 1 in Paper II characterizes the filters used in this study. Filter A was of the type Aqva Sorb BG-09 and was regenerated twice. The type of the carbons in filters B and C were Filtrasorb TL 820 and in filter D Filtrasorb 200. Carbons in filters B and D were changed to new ones before the study. Carbon in filter C was regenerated twice and third regeneration was done during the study in May 2001 (Figure 6.1).

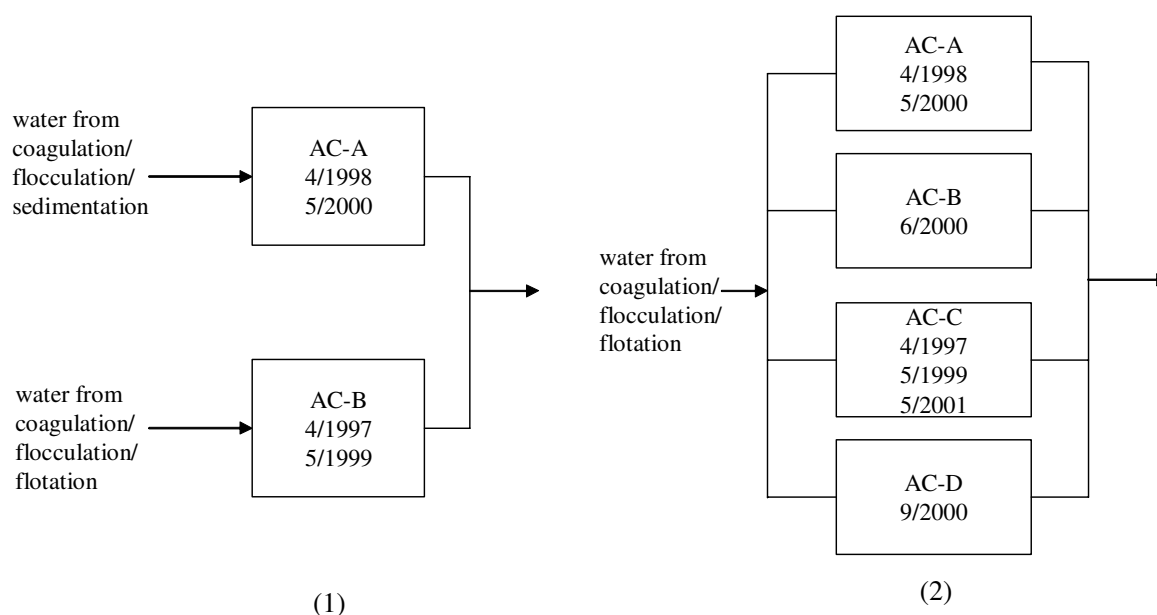


Figure 6.1 AC filters in Tampere Waterworks, Rusko Water Treatment Plant in (1) 8/1999-5/2000 and (2) 9/2000-9/2001 investigations, respectively. Time of AC replacement or regeneration is illustrated in the figure.

6.2 Oulu Waterworks; Hintta and Kurkelanranta Water Treatment Plants

Waterworks of Oulu, consisting of Hintta and Kurkelanranta Water Treatment Plants, were observed in the study concerning ozonation and AC filtration efficiency on NOM removal (Paper IV). The two plants produce drinking water for the city of Oulu, Finland. Raw water is taken from River Oulu from about 4 meters depth and the two Water Treatment Plants are situated on the opposite strands of the river. The capacities of the Treatment Plants are 900 and 1200 m³/h for Kurkelanranta and Hintta, respectively. Treatment processes consist of coagulation with ferric sulphate, flocculation and flotation, sand filtration, ozonation, activated carbon filtration and disinfection (Kurkelanranta treatment process is illustrated in Appendix 1, Figure 3).

6.2.1 Ozonation in Hintta and Kurkelanranta Water Treatment Plants

The ozone dose in the full-scale treatment varied between 0.4 to 1.5 mg/l. Ozone feed was higher in the summer (0.9-1.5 mg/l) than in the winter (0.4-0.7 mg/l). Ozonation was performed primarily to enhance the biodegradability of NOM before AC filtration, but also to reduce the odour and taste problems as well as enhance possible pathogen removal.

6.2.2 AC filtration in Hintta and Kurkelanranta Water Treatment Plants

The performances of all four AC filters, in both Treatment Plants, were studied. The filters in Kurkelanranta Treatment Plant were called AC-K1, AC-K2, AC-K3 and AC-K4. The filters were in-line and water from the filter AC-K1 was filtered through AC-K2 and the water from the filter AC-K3 was filtered also through AC-K4 (Figure 6.1, see also Figure 3 in Appendix 1). The first filter in-line was designed to act more as a biologically active AC filter (BAC)

and second as normal adsorption based AC process. The history of the carbons in the filters was as follows: new carbon was placed on AC-K2 in November 2003 and the old carbon from filter AC-K2 was moved to AC-K1. Also during the study, in July 2005, carbon in filter AC-K2 was changed to new one and the old carbon was again moved to AC-K1. Regenerated carbon was changed on AC-K4 in July 2004, before the study was started, and the old carbon from filter AC-K4 was moved to AC-K3.

The filters in Hintta Treatment Plant were called AC-H1, AC-H2, AC-H3 and AC-H4 (Figure 6.2). The filters were parallel and they were last regenerated or AC was changed to new as follows: AC-H1 was changed in October 2000, AC-H2 was regenerated in July 2004, AC-H3 was changed in September 2003 and AC-H4 was regenerated in September 2004.

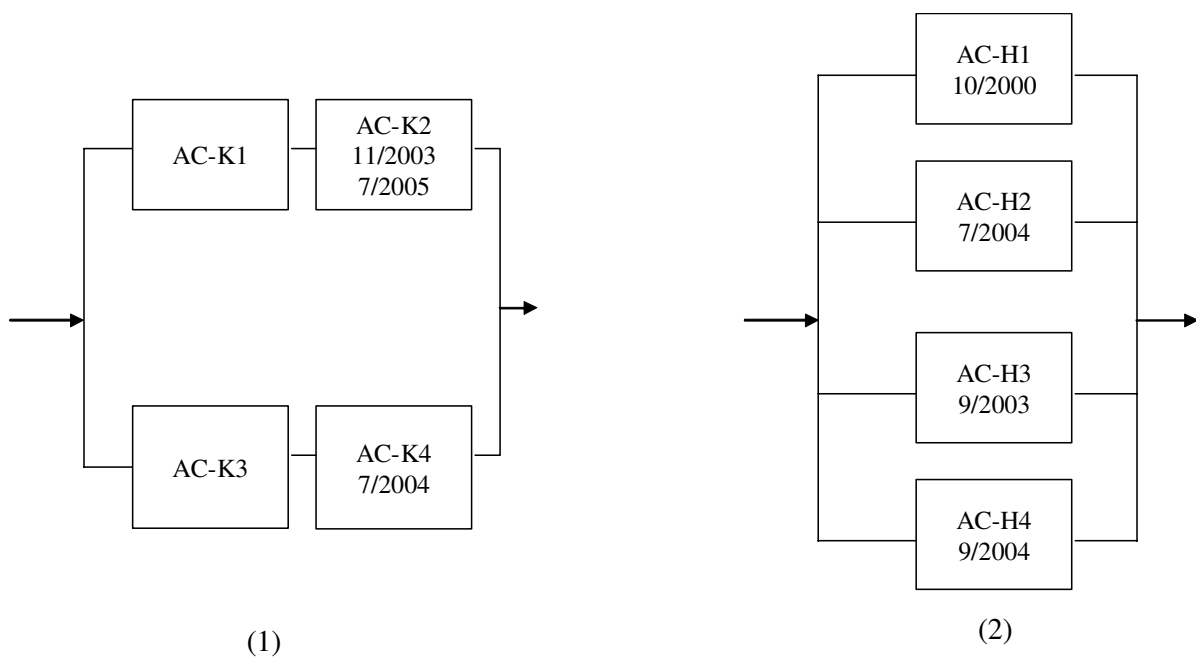


Figure 6.2 AC filters in Oulu Waterworks, (1) Kurkelanranta and (2) Hintta Water Treatment Plants. The time of AC replacement or last regeneration is illustrated in the figure.

6.2.3 Pilot-scale ozonation

The pilot-scale experiments were performed at the Kurkelanranta Water Treatment Plant. The ozonation apparatus comprised ozone generator (Herrmann-laboratory-ozonator LO-50-1), continuous flow column (total volume 45 l; i.d. 0.17 m; height 2 m) and two AC filtration columns (i.d. 0.25 m, height 1.5 m, carbon from the full-scale process from filters AC-K1 and AC-K2) (Figure 6.3). The AC columns were placed in-line as in the full-scale process at Kurkelanranta Water Treatment Plant. The batch-test was conducted in a different column (total volume 10 l; i.d. 0.09 m; height 1.7 m). The water to the pilot was taken after chemical coagulation and flotation and sand filtration from the full-scale process (see Figure 3 in Appendix 1). Ozone containing gas was added at the bottom of the columns through a

ceramic diffuser. Ozone concentration in water varied between 0.3-1.2 mg O₃/mg TOC (ozone feeding dose 2-7.5 mg O₃/min).

The first phase of tests was conducted in a batch mode (volume of the column 10 l) with different ozone doses. Other tests were carried out in continuous flow mode (volume 45 l) and the water was lead through the system at 120-130 l/h. The contact time in ozonation was 18 minutes and empty bed contact time (EBCT) of AC filters about 14 minutes per filter, overall residence time being 28 minutes. Water samples were taken from feed water, ozonated water and after the second AC filter.

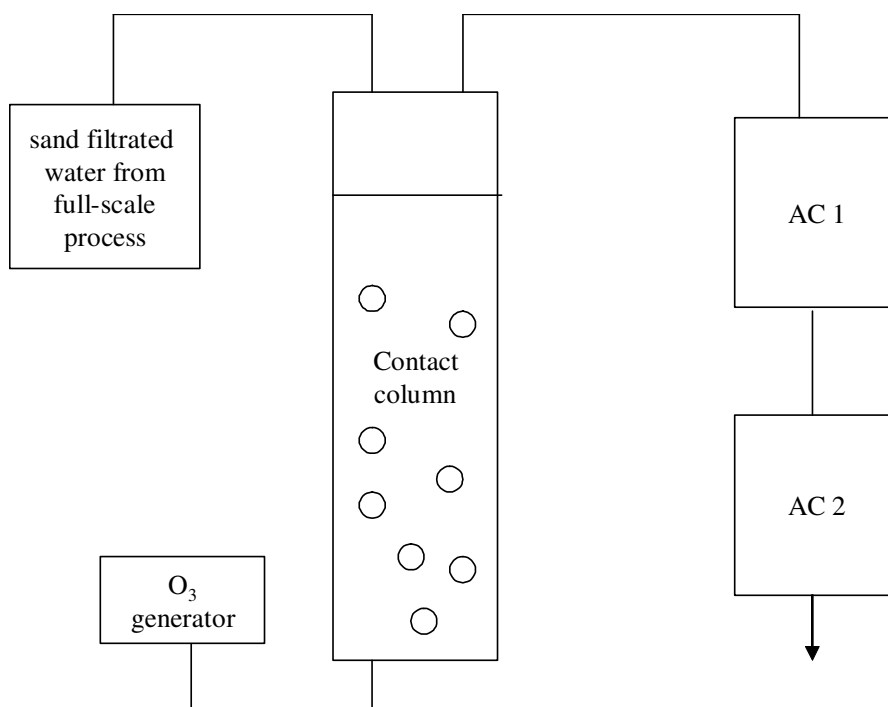


Figure 6.3 A schematic picture of the pilot-scale ozonation apparatus

6.3 Other waterworks

Water samples from five different surface water treatment plants and one artificial ground water treatment plant were collected in the NF study (Paper V). The surface water treatment facilities studied were Espoo, Tampere, Turku, Raisio-Naantali and Pietarsaari Waterworks and the artificial ground water treatment plant studied was Kotka Waterworks. Samples were collected after a conventional water treatment train (coagulation/flotation and AC/sand filtration), but before post-treatment (alkalization and disinfection). Ninety litres of each sample was delivered to Lappeenranta University of Technology in filtration. The details of the treatment process in each studied water treatment plant are summarised in Table 2. in Paper V.

6.3.1 Pilot-scale nanofiltration (NF)

The study was carried out using a laboratory scale membrane filtration unit (Figure 6.4). Three cross-flow flat-sheet modules were run parallel with the same feed water. The membrane area in each module was 46.0 cm². The membranes studied in the parallel membrane modules were Desal-5 DL, NF255 and NF270. The representative characteristics of the membranes are presented in Table 1 in Paper V. All membranes were supplied as dry, rolled sheets and were stored as received at room temperature. More detailed information about the operation of NF process is given in Paper V.

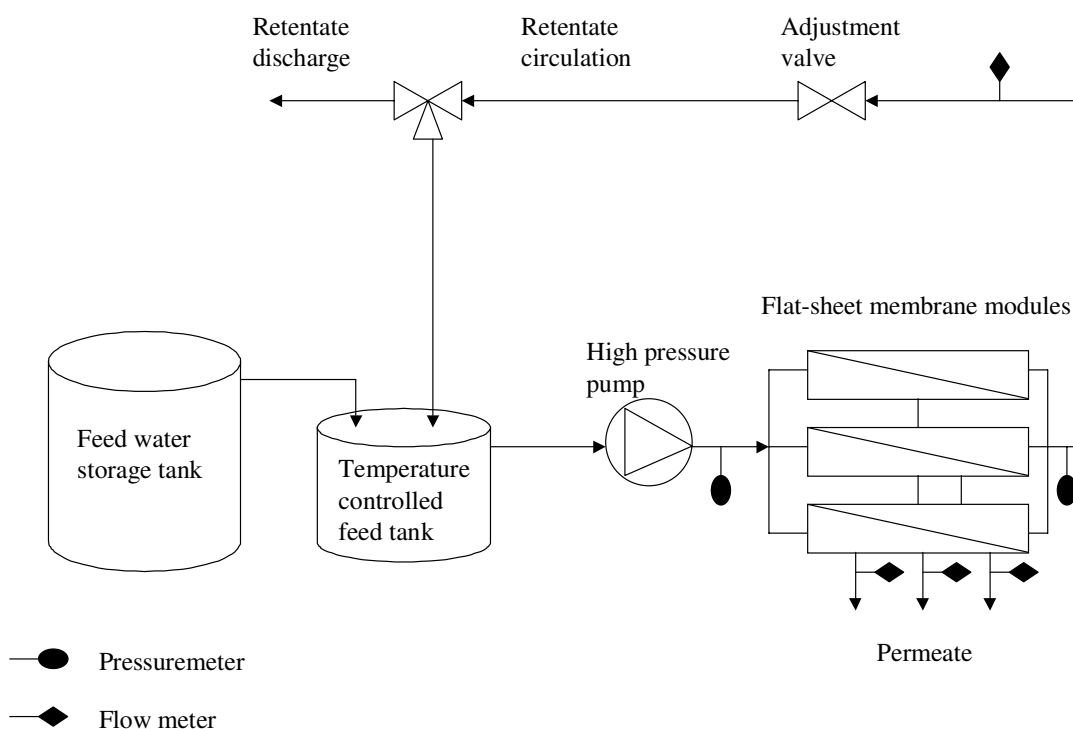


Figure 6.4 A schematic picture of the pilot-scale nanofiltration apparatus

6.4 Analysis

6.4.1 Sampling procedure

Samples were taken from the following stages of the treatment sequence: 1) raw water, 2) water after coagulation/flotation 3) water after different AC filters and 4) combined pure water from all AC filters before it was pumped in to the distribution system (Papers I, II, III and IV). In Hintta and Kurkelanranta Water Treatment Plants samples were taken also after ozonation. Basic water analyses were done at the same day as sampling. The 10 ml samples were collected and frozen until analysed with HPSEC and UV₂₅₄.

6.4.2 Basic water analysis at Rusko Water Treatment Plant

UV₂₅₄ absorbance was measured with a spectrophotometer. The raw water sample and the samples after flotation and sedimentation were centrifuged before UV measurement. TOC samples were filtered through 0.45 µm membrane and they were measured as DOC according to the SFS-EN 1484 standard and by using a Shimadzu TOC-5000A with a high sensitivity catalyst. The total organic material was measured by the KMnO₄ oxidation method according to the Finnish Society of Food Science and Technology guidelines. Hardness, alkalinity, turbidity and colour were measured according to the SFS 3003/-87, SFS 3005/-81, SFS-EN ISO 7027/-00 and SFS-EN 7887/part 4/-95 standards, respectively.

6.4.3 Basic water analysis at Hintta and Kurkelanranta Water Treatment Plants

The basic water quality parameters were measured in the laboratory of the Oulu Waterworks, at Hintta Water Treatment Plant. TOC samples were measured according to the Finnish Standard SFS-EN 1484/-97 and by using a Shimadzu TOC-Vcph. Total organic material was measured by the KMnO₄ oxidation method according to the Finnish Standard SFS 3036/-81. Turbidity and colour were measured according to the Finnish Standards SFS-EN ISO 7027/-00 and SFS-EN ISO 7887/-95, respectively.

The content of assimilable organic carbon (AOC) was measured in National Public Health Institute, Kuopio, according to the modified method (Miettinen et al. 1999) of the standard by APHA et al. (1992). In the AOC analyses maximum growth of *Pseudomonas fluorescens* P17 and *Aquaspirillum NOX* in the water samples were transformed into the amount of AOC. Inorganic nutrients were added into the samples (N, P, K, etc.) to ensure that microbial growth in water samples was not limited by inorganic nutrients.

6.4.4 HPSEC measurements

The HPSEC samples were first filtered through a Gelman 0.45 µm membrane and then size-exclusion fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector ($\lambda=254$) and a TSKgel G3000SW 7.5mm(ID) x 30 cm column. Pre-column was not used. Sodium acetate (0.01 M) was used as an eluent at a flow rate of 1 ml/min. Injection volume was 30 µl. The method was selected on the basis of results from earlier investigations (Kronberg et al. 1985, Vartiainen et al. 1987, Peuravuori and Pihlaja 1997, Vuorio et al. 1998, Nissinen et al. 2001).

Heights of the peaks in the HPSEC chromatogram were used in the data analysis. The height of the peak refers to the amount of NOM in a specific molecular size fraction with a peak having the lowest retention time referring to the highest MM fraction of NOM and peak having the highest retention time to the lowest MM fraction of NOM. The sum of all peak heights (SOPH) represents the total amount of NOM in the sample.

The HPSEC method was evaluated by ultrafiltration. Stirred cell (Amicon, model 8400) was used in UF experiments with membranes characterized by NMWCO of 500, 1000, 3000, 5000, 10 000 and 30 000 g/mol (membranes YC05, PLAC, PLBC, PLCC, PLGC and PLTK; Millipore). Conductivity, TOC, UV₂₅₄ and HPSEC of the fractions obtained from the process were measured. Apparent molar masses (AMM) of the peak fractions in the HPSEC chromatogram were roughly estimated using UF (Ratnaweera et al. 1999a). The membrane rejection in this study was considered using a method presented by Logan and Jiang (1990).

Figure 6.5 shows the remaining NOM after various UF membranes measured as the reduction of the heights of the peaks in the HPSEC chromatogram. The retention of the molecules in UF depends on the pore size distribution of the membranes as well as the characteristics of the molecules, mainly the molecular volumes. Thus, the retention of the molecules on the membrane is not sharp but, for instance, the membrane with NMWCO value of 30 000 g/mol retains molecules from all size ranges as can be seen in Fig. 6.5. The membrane cutoff values are usually defined as the mass of a molecule whose retention is 90% on this membrane. When this retention value of 90% is applied to different peaks in the HPSEC chromatogram, the following approximate AMMs for the different peaks can be presented 5 500 g/mol, 4 000 g/mol, 3 500 g/mol, 2 000 g/mol and 500 g/mol for peaks I, II, III, IV and V, respectively. Because the individual peaks in the chromatogram do not present sharply just molecules having one definite size, the more accurate way is to present the AMM ranges rather than the specific MM. The ranges are >5 000 g/mol, 4 000-5 000 g/mol, 3 000-4 000 g/mol, 1 000-3000 g/mol and 500-1 000 g/mol for peaks I, II, III, IV and V, respectively.

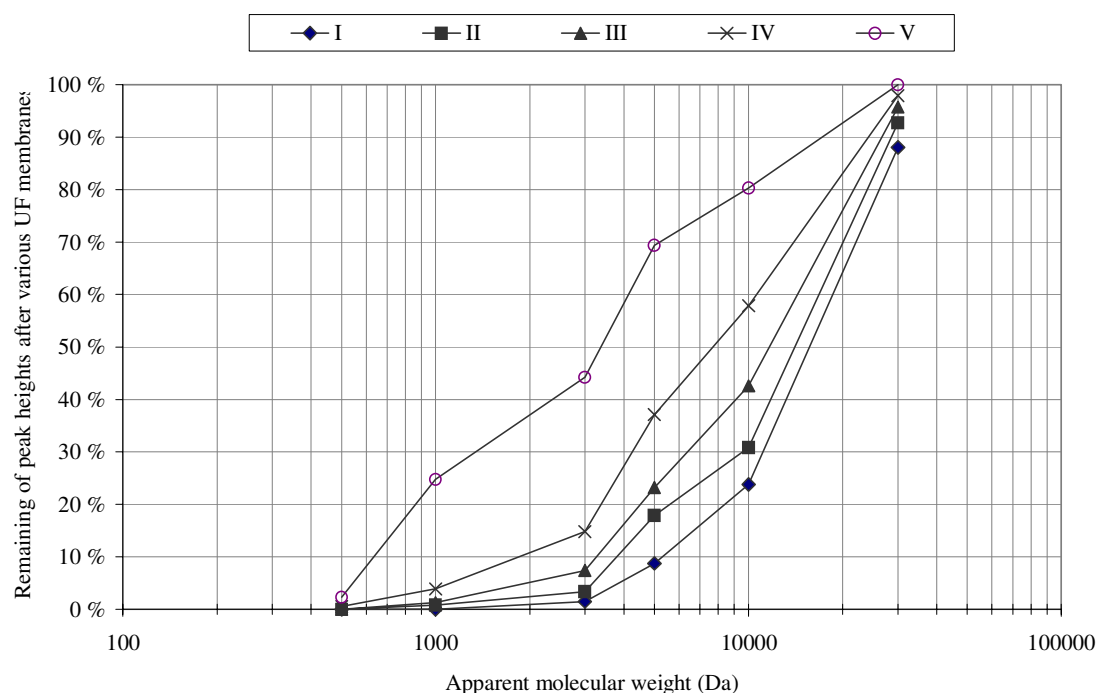


Figure 6.5 The remainder of NOM after various UF membranes measured as the reduction of the heights of the peaks (I, II, III, IV and V) in HPSEC chromatogram.

7. RESULTS AND DISCUSSION

7.1 Water quality in the Water Treatment Plants

7.1.1 Rusko Water Treatment Plant

The water quality at Rusko Water Treatment Plant was monitored at their laboratory during the studies and the results are shown in Table 7.1 (see also Table I in Paper I, Table 2 in Paper II and Table 1 in Paper III). The raw water is typical Finnish lake water having low alkalinity (about 0.25 mmol/l) and quite a low turbidity (about 2 FTU). Organic carbon content is also fairly low (about 5 mg/l) compared to typical Finnish surface waters. Much higher values were obtained in investigations of Vartiainen et al. (1987) and Knuutinen et al. (1988), 9-17 mg/l and 12-83 mg/l, respectively, with other Finnish lake water sources. Lake Roine is a good water source, since it is an oligotrophic lake with very low seasonal fluctuation of quality.

The treated water has a TOC value of about 2.8 mg/l. This is quite a typical amount in the conventional water treatment facilities with AC filtration (Nissinen 2002). The average TOC value in Finnish drinking waters distributed by surface water treatment plants is 2.7 mg/l (Ympäristökeskus 2004). Other average values of treated water quality measured at Finnish surface water treatment plants are 5.6 mg/l, 0.3 FTU, and 3.1 mg Pt/l, respectively, for KMnO_4 , turbidity and colour (Ympäristökeskus 2004). As can be seen in table 7.1, Rusko produces good quality of drinking water. On average, the treatment process removed 70, 50, 95 and >84% of the NOM measured as KMnO_4 , TOC, turbidity and colour, respectively. The NOM content of the raw water from Lake Roine was already quite low, so the purification percentages were not so high. Still, the absolute values of finished water were really low, and in accordance with regulatory values in Finland and the EU (STM 2000). Recommendations for KMnO_4 and turbidity are 20 mg/l, and under 1 NTU, respectively. In the study made by Nissinen (2002) among Finnish water treatment facilities, reduction of 78% and 59% of organic matter were measured as KMnO_4 and TOC, respectively, after conventional treatment with AC filtration. Removal of colour by 98% is also reported (Kainulainen et al. 1994).

Table 7.1. Water quality parameters at Rusko Water Treatment Plant (August 1999 – April 2003). The treatment consisted of coagulation/flocculation (aluminium sulphate/ferric sulphate), flotation/sedimentation, AC-filtration and chlorination (Papers I, II and III, Figure 1 and 2 in Appendix 1).

	raw water			treated water		
	average	min	max	average	min	max
Alkalinity (mmol/l)	0.25	0.23	0.30	0.73	0.57	0.85
Hardness (dH)	1.1	0.96	1.8	3.3	3.0	3.5
Colour, Pt (mg/l)	16	10	30	<2.5	<2.5	2.5
Turbidity (FTU)	2.2	0.16	12.0	0.12	0.01	0.36
pH	7.1	6.4	7.6	8.5	7.8	9.0
TOC (mg/l)	5.6	4.3	8.1	2.8	1.7	3.4
KMnO_4 (mg/l)	17	14	19	5.1	3.2	7.8

In this study no significant seasonal variations were noticed in measured values at the different stages of the treatment process. Minor variation was observed in the study (Paper II) conducted on the performance of AC filters. Detailed information about the seasonal variation of UV₂₅₄, TOC, KMnO₄ and HPSEC results in Rusko Water Treatment Plant is presented in Figure 2. a-f in Paper I.

7.1.2 Hintta and Kurkelanranta Water Treatment Plants

The chemical characteristics of the raw and treated water at Hintta and Kurkelanranta Water Treatment Plants during the study are presented in Table 7.2. The purification process in Oulu removed NOM measured as TOC efficiently; the removal of TOC was 84%. KMnO₄, turbidity and colour were reduced by approximately 70%, 94% and >84%, respectively. The raw water temperature was very low in wintertime (0 °C) compared to summer (about 19 °C).

Table 7.2. Water quality at Hintta and Kurkelanranta Water Treatment Plants (December 2004-August 2005). The treatment consisted of coagulation/flocculation (ferric sulphate), flotation, sand filtration, ozonation, AC-filtration and disinfection (Paper IV, Figure 3 in Appendix 1).

		Raw Water			Treated Water	
		Average	min	max	Average	Average
					HINTTA	KURKELANRANTA
Temperature	°C	8	0	19		
Colour	mg/l Pt	87	60	140	<5	<5
pH		6.8	6.3	7.0	8.5	8.4
KMnO ₄	mg/l	51	42	74	3,9	3,2
TOC	mg/l	12.2	10.0	17.2	2.0	2.1
Abs. 254nm*	1/m	49.7	38.6	70.9	1.8	1.8
Turbidity	NTU	2.37	0.56	7.70	0.17	0.15

* measured 1.1.-30.6.2005

Even as the TOC value in raw water of Oulu (12.2 mg/l) was twice as high than in Tampere (5.6 mg/l), the finished water in Oulu had lower TOC concentration than Tampere; 2.0 mg/l vs. 2.8 mg/l, respectively.

At Hintta and Kurkelanranta Water Treatment Plants, the quality of raw water from River Oulu fluctuated during the seasons. The highest values of the quality parameters were measured in the spring, (during April and May), when the river was flooding and the lowest during the wintertime (Table 7.2). The catchment area of River Oulu is large (22 900 km²) (Wikipedia 2006). This causes increase in flow and an increase in organic matter concentration during snow melting and heavy rains. Moreover, the catchment area of River Oulu is rich with peatland and agriculture, thus increasing the amount of NOM in water (Wikipedia 2006). The increase in organic matter and turbidity may be controlled by adjusting the coagulant dose. Both Water Treatment Plants in Oulu produce high quality drinking water, which meets Finnish and European standards for distributed drinking water (STM 2000). According to literature (Sharp et al. 2006b) a number of UK and US water utilities

have reported about the same problems connected with the increased DOC levels during autumn and winter periods, which results in a higher coagulant demands.

7.2 NOM removal at different stages in the treatment process based on DOC and other conventional quality parameters; A_{254nm} and turbidity

At Rusko Water Treatment Plant, the organic matter, measured as DOC, was removed with approximately 51-59% efficiency (Papers I, II and III) after the entire treatment train. It was shown that DOC reduced more efficiently with ferric sulphate compared to that with aluminium sulphate as a coagulation agent (Paper III, Table 2). Enhancement of removal was 13% after the flotation and 9% after the entire treatment process. According to the literature (Lovins et al. 2003) the iron-based coagulants have been shown to remove approximately 10-15% more DOC than the aluminium-based coagulants, with maximum DOC removal values reaching 77% for ferric and 65% for aluminium sulphate. Our results are in agreement with these results. The removal of NOM, based on DOC, was about 20% lower than measured as A_{254nm} (and HPSEC). This indicates that the NOM that contains structures capable of adsorbing UV light, i.e. large aromatic compounds, was removed effectively. Smaller aliphatic compounds which do not absorb UV light due to the lack of conjugated double bonds are not properly shown by the UV_{254} measurements.

Turbidity, on the other hand, was removed about 7% more efficiently with aluminium sulphate than with ferric sulphate, considering the entire treatment process; 93% and 86% respectively. Aluminium sulphate is reported to be more efficient in turbidity removal than ferric sulphate also in the jar-test study by Tuhkanen et al. (2004). The turbidity of the Rusko raw water was the lowest in the winter, 0.2 NTU, but turbidity was found to increase in the coagulation/flotation process in the wintertime (Figure 5 in Paper III). However, the increase in turbidity was compensated by the effective removal of turbidity in the sand filtration stage following the flotation stage in the full-scale process. According to literature (Budd et al. 2004), a shift to a higher optimum pH for turbidity removal was reported to occur in cold water period. Because of this shift, the effective removal of both turbidity and DOC are harder to gain (Budd et al. 2004). After several jar-test studies (Morris and Knocke 1984, Haarhoff and Cleasby 1988), ferric coagulants have been found to be less sensitive to low temperatures than aluminium in regard of turbidity removal, although the flocs formed during cold temperature conditions are smaller than those produced in higher temperatures also with ferric coagulants (Hurst et al. 2004). This was, however, not confirmed by the jar-test study of Tuhkanen et al. (2004). They found that aluminium sulphate was performing better than ferric sulphate in cold water, which is also in agreement with our present study. The reason for the similar observations might be that the results were obtained by using the water from Lake Roine, as in the full-scale process studied in this thesis.

7.3 NOM characterization and removal at different stages in the treatment process based on HPSEC- UV_{254} measurements

7.3.1 The MSD of NOM in the raw water

Five to seven different peaks were found in the HPSEC chromatograms of the raw waters studied as can be seen in Figure 7.1 (see also Figure 3 in Paper I, Figure 2 in Paper II, Figure 2 in Paper III and Figure 2 in Paper IV). Similar patterns of peaks of raw waters were observed also in other studies concerning Finnish surface waters (Vartiainen et al. 1987, Kainulainen et al. 1994, Vuorio et al. 1998, Nissinen et al. 2001). According to our study, the

SEC profile was dominated by highest MM fractions in both raw water supplies (Figure 7.1). However, in River Oulu HMM (>4000 g/mol) and IMM (4000-1000 g/mol) matter were more abundant and the concentration of NOM as sum of peak heights (SOPH) was higher than in Lake Roine (on average 33.6 mAU vs. 10.7 mAU). Thus there is a significant difference between river and lake water as raw water supplies. The amount of NOM is much higher in river water. Nissinen et al. (2001) noticed the same phenomenon in their study, and suggested that sedimentation of the large molecules within lakes might be one explanation for this. The water flow in rivers probably prevents the sedimentation of large molecules. Moreover, the catchment area of River Oulu is rich with peatland, thus increasing the load of NOM in River Oulu water (Wikipedia 2006).

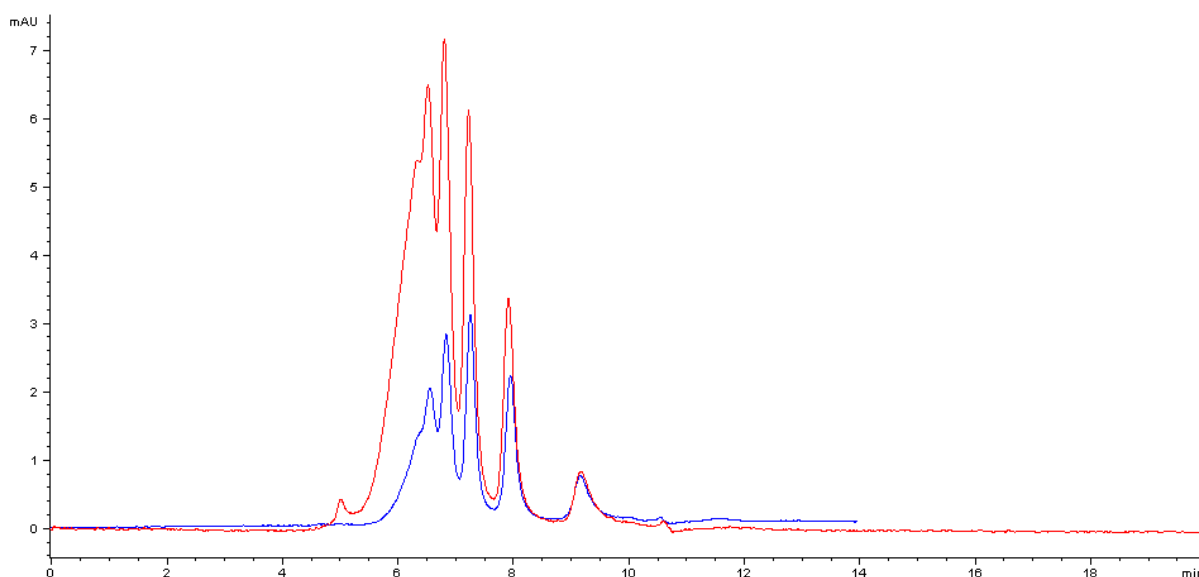


Figure 7.1. HPSEC chromatograms of the raw water from Lake Roine (blue) and River Oulu (red).

7.3.2 The effect of chemical coagulation on the MSD of NOM

Studies at Rusko Water Treatment Plant (Papers I, II, III) indicated that chemical treatment followed by flotation or sedimentation removed the MM fraction >5000 g/mol completely and the MM fraction 4000-5000 g/mol almost completely (over 90%). Thus the organic matter at the size range of >4000 g/mol (HMM) was effectively removed. Flotation seemed to be somewhat more efficient than sedimentation especially in the removal of HMM matter. Also at Hintta and Kurkelanranta Water Treatment Plants, almost all of the HMM matter was removed during coagulation with ferric sulphate followed by flotation (Paper IV). HMM matter removal was 98% in coagulation/flotation. No further removal was noticed in the following process stages. It has been noticed in several investigations that high removal rates of HMM compounds occur during coagulation (Vuorio et al. 1998, Chow et al. 1999, Nissinen et al. 2001, Parsons et al. 2002, Tuhkanen et al. 2004, Sharp et al. 2006a).

Change of coagulant from aluminium to ferric sulphate in the full-scale process at Rusko Water Treatment Plant had a significant effect on the removal of the NOM on size fraction of 3000-4000 g/mol (Figure 7.2) (Paper III). The long-term investigation (August 1999-May

2002) show that 55-50% of NOM of this size fraction was removed from water in coagulation/flotation process when aluminium was used as coagulant (Papers I, II and III). Ferric sulphate coagulation removed 83% of MM fraction of 3000-4000 g/mol. Thus, this fraction was removed 28% more efficiently with ferric sulphate than with aluminium sulphate. Ferric sulphate coagulation removed MM fraction of 1000-3000 g/mol about 20% more efficiently. Hence the overall removal of the IMM matter (size range 1000-4000 g/mol) was 65% with ferric sulphate as coagulant, which is about 25% more efficient than with aluminium sulphate. According to several studies (Crozes et al. 1995, Bell-Ajy et al. 2000, Lindqvist et al. 2002, Lindqvist et al. 2004, Tuhkanen et al. 2004), the selection of coagulant particularly affected the removal of the IMM of NOM; Ferric salts were noticed to be on average 15% more effective than aluminium salts especially in removing the NOM fraction with MM less than 4000 g/mol.

Most of the IMM compounds were removed in Kurkelanranta and Hintta during coagulation, especially the MM fraction 3000-4000 g/mol, of which 90% was removed during coagulation/flotation. After all purification steps in the treatment plant the removal of this size fraction (3000-4000 g/mol) was 94%. The MM fraction 1000-3000 g/mol was not removed as effectively by coagulation. Only 55% of this fraction was removed after coagulation/flotation. The overall removal percent of this IMM fraction (1000-4000 g/mol) in treated water was 80%. Although the removal percentages of NOM in Oulu were higher than in Rusko during coagulation, the organic matter content measured as sum of peak heights (SOPH) was nearly equal after coagulation at both plants, especially with ferric sulphate as a coagulant agent. It can be concluded that even though Oulu had more organic matter in the raw water, both plants were able to remove the NOM to equal level.

In Rusko, the removal of the LMM matter (< 1000 g/mol) was very poor with both aluminium and ferric sulphate. Only about 10% of the LMM matter was removed from water after the coagulation process with both coagulants (Figure 7.2). In Oulu, the removal of LMM compounds was also marginal, only 6-13% was removed in coagulation/flotation. The remaining organic matter after coagulation in the water is observed to be of LMM ranging about 500-700 g/mol also by Chow et al. (1999). This LMM fraction is very hard to remove by coagulation. Parsons et al. (2002) has demonstrated that LMM fraction of NOM consists primarily of hydrophilic molecules, which were hard to remove (16% removal). Hydrophobic fraction of NOM was effectively removed. According to the jar-tests of Lindqvist et al. (2002), Tuhkanen et al. (2004) and Lindqvist et al. (2004) the LMM fraction was not removed any better even when the process was optimised in regard to NOM removal. However, in the study made by Lindqvist et al. (2004), almost 40% removal of the smallest MM fraction was obtained when polyelectrolytes were used as coagulation aids.

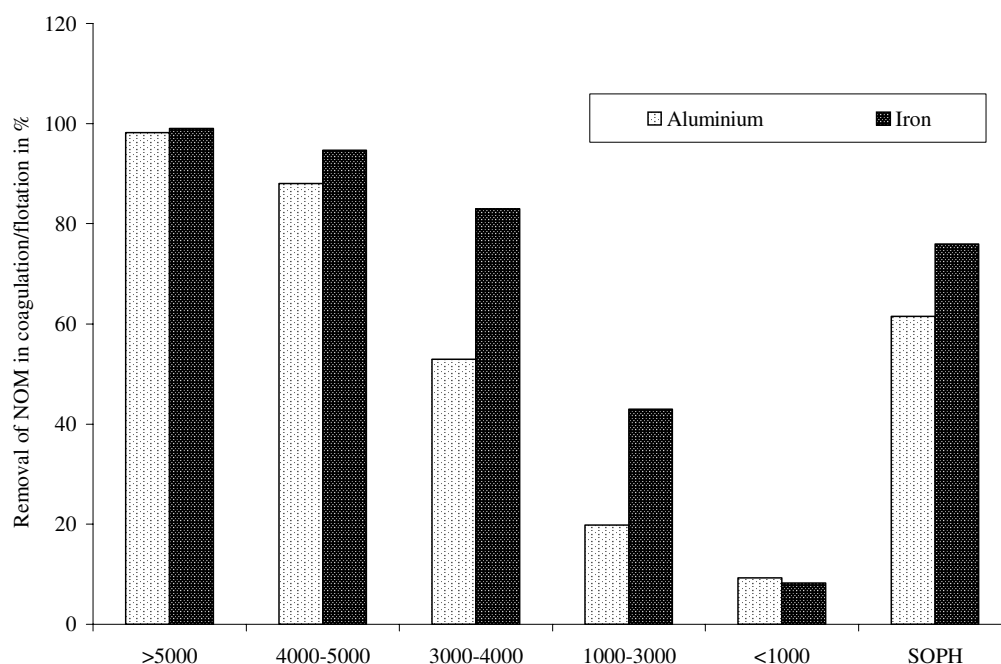


Figure 7.2. Different MM fractions of NOM (according to the HPSEC measurements) removed after coagulation/flotation process with aluminium sulphate (May 2001-May 2002) and ferric sulphate (June 2002-April 2003) as the coagulation agent at the Rusko Water Treatment Plant. Results are in percentages compared to the raw water results, and calculated as averages.

7.3.3 The effect of ozonation on the MSD of NOM

The ozone dose feed in the full-scale treatment at Oulu Waterworks, Hintta and Kurkelanranta Water Treatment Plants, varied between 0.4 to 1.5 mg/l. Ozone feed was higher in the summer (0.9-1.5 mg/l) than in the winter (0.4-0.7 mg/l). The HMM matter and the molecules larger than 3000 g/mol were not affected by ozonation, although in some cases the ozonation was observed to increase the amount of HMM fraction. This fraction increased particularly in winter and spring. This might be explained by polymerization of organic molecules during ozonation while using lower ozone doses. The same phenomenon was observed also in the pilot-scale studies (see chapter 7.5). Nevertheless, ozonation removed particularly the lowest MM compounds. The removal of the IMM matter fractions with size range of 3000-4000 g/mol and 1000-3000 g/mol, respectively, enhanced from 89% to 93% and from 52% to 75%; total NOM removal after coagulation/flotation vs. after ozonation. The sand filtration after coagulation/flotation did not improve the removal of NOM, but sometimes even increased the amount of especially HMM NOM. The ozonation was obtained to remove effectively especially the IMM NOM at full-scale treatment process by the study of Vuorio et al. (1998) in Helsinki Waterworks. However, in Oulu Waterworks, the LMM compounds were removed the most effectively, from only 7-16% removed after coagulation/flotation to 38-49% removal during ozonation. Thus, the removal of NOM was more effective in the LMM fraction than in the HMM fraction. Still, this might be because the ozonated water included low amounts of HMM matter left to be degraded, while IMM and LMM matter was more abundant after coagulation/flotation.

The better removal of LMM NOM in comparison with HMM matter is contradictory to literature, since ozone is said to remove primarily HMM substances and convert them to the LMM compounds (Langlais et al. 1999). However, a strong decrease in UV absorption has been noticed to occur in earlier studies (Kainulainen et al. 1995, Miettinen et al. 1998, Myllykangas et al. 2002, Myllykangas et al. 2003). This indicates that NOM is degraded into small MM compounds, which do not have any chromophores capable of UV absorption at 254 nm; the same as used as detection wavelength in our HPSEC measurements. According to the study by Kasprzyk-Hondern et al. (2005), the chromatograms of ozonated NOM recorded at 220 nm indicate an increase in UV₂₂₀ absorbance of molecules with MM lower than 200 g/mol (LMM). This can be connected with the decomposition of the HMM fractions of NOM and also to the subsequent formation of LMM by-products. Moreover, in previous studies made by Miettinen et al. (1998) and Lehtola et al. (2001), ozonation caused a major increase in the content of assimilable organic carbon (AOC), which indicates also that organic matter has been converted into smaller compounds. In full-scale process at Hintta and Kurkelanranta the AOC was noticed to rise during ozonation to little over 100 µg/l to as high as over 250 µg/l. Still, the AOC was removed efficiently in the AC filtration following pre-ozonation (Iivari 2006). Similar results were observed in the study of Lehtola et al. (2001), where ozonation was noticed to increase the AOC concentration in the various full-scale processes studied to the level of over 200 µg/l and in one case almost to 400 µg/l. In the same study by Lehtola et al (2001), it was noticed that ozonation did not change the concentration of TOC in full-scale treatment with ozone dose of 1.0-2.0 mg O₃/l. The greatest decrease which was noticed was 0.2 mg/l TOC, which is in good agreement with our results (measured TOC values were 2.3 mg/l and 2.0 mg/l, respectively, before ozonation and at treated water).

7.3.4 The effect of AC filtration on the MSD of NOM

In the water treatment train of Rusko Water Treatment Plant, AC filtration could not remove any more of the HMM substances but was feasible in reducing the amount of the IMM and the LMM matter (Tables 2 and 3 in Paper I, Figures 3 and 5 in Paper II). The removal of NOM after the coagulation/flocculation followed by AC filtration was over 90% for the HMM matter. The total removal percentages for different MM fractions were about 68%, 41-53%, and 38-51% for fractions 3000-4000 g/mol, 1000-3000 g/mol and 500-1000 g/mol, respectively, after AC. Similar removal percentages were achieved in the study of Nissinen et al. (2001). Swietlik et al. (2002) noticed that a part of the NOM present in the raw water was affected by ClO₂ oxidation. The oxidation may have caused a break up of the larger molecules to smaller ones (Swietlik et al. 2004). These LMM molecules were more polar in nature, and thus did not adsorb well on AC. This might explain the poor removal of the MM fractions <500 g/mol also in this study. Moreover, the LMM fraction of NOM was noticed to occasionally increase in Rusko, especially during summer months. In some cases, the lowest MM peak fraction emerged only after AC filtration (Paper II). It was concluded that this increase might be the decomposition or metabolic products of the bacteria living in the filters (Vuorio et al. 1998, Boulam et al. 2003).

The NOM removal capacity of the AC filters is reduced with the aging. This was shown also in the study of Vahala (1995). In our study it was observed that the regeneration of the AC filters improves the efficiency considerably, nearly 50%. Table 7.3 shows the removal capacity improvement of regenerated filters at Rusko Water Treatment Plant. After about three months operation the NOM removal capacity of the filters reverted almost to the same level as before regeneration. Other studies have indicated that the efficiency after reactivation

is equal to or superior to virgin AC (Hyde et al. 1987, Oxenford and Lykins 1991). The removal of different MM fractions after regeneration varied slightly.

Table 7.3. Enhancement of the capacity of filters AC-A in Paper I and filter AC-C in Paper II to remove different MM fractions of NOM. Values are calculated comparing the average of the HPSEC values measured two months before and right after the regeneration.

filters	MM fractions g/mol					
	>5000	4000-5000	3000-4000	1000-3000	500-1000	<500
AC-A	0	50	56	65	67	
AC-C	0	38	64	61	49	14

At both Hintta and Kurkelanranta Water Treatment Plants there is an ozonation stage prior to AC filtration. In Kurkelanranta, the AC filters were in-line, so that the first filter in-line was designed to act as a biological filter and the second one as adsorption filter (Paper IV). The NOM removal in AC filtrations at Hintta and Kurkelanranta Water Treatment Plants was also dependent on the prior use of the different AC filters. The AC regeneration interval was about 2-3 years.

In Hintta and Kurkelanranta Water Treatment Plants, the best removal rates with regard to AC were observed on the MM ranges of 1000-3000 g/mol, and <1000 g/mol (LMM). The NOM removal capacity of the filters with well used AC were on average 6%, 4% and 9% for the HMM, IMM and LMM matter, respectively, compared to the values after ozonation. The total removal after AC was 99%, 87% and 55%, respectively. One filter (AC-K2) was regenerated during the study and its removal efficiency was improved dramatically right after regeneration. The removal percentages, compared to ozonation, were 68%, 76% and 83% for HMM, IMM and LMM matter, respectively; total removal being 100%, 97% and 93%, respectively. According to literature (McCreary and Snoeyink 1980), the LMM matter was noticed to be more amenable for adsorption than the HMM organic matter due to the size exclusion effect, which was seen also in this study. On the other hand, ozonation before AC filtration also increases the biodegradability of NOM and hence the removal of NOM by AC might be explained more by biodegradation than adsorption (Langlais et al. 1991). The removal capacity was slightly higher during summer months, and especially on LMM fraction of NOM, thus indicating some biological activity on the filters. This finding is supported also by the pilot-scale experiments conducted (Paper IV). The results of pilot-scale experiments are summarized in chapter 7.4. There was an increase in AOC after ozonation, depending on the dose. Also in the full-scale process at Hintta and Kurkelanranta, the AOC was noticed to increase during ozonation (Iivari 2006). Still the AC filtration at both plants was effective in removal of the formed AOC concentrations.

7.3.5 The removal of NOM during the entire treatment process

A summary of the percentage removal of the different MM fractions during the treatment processes at Rusko, Hintta and Kurkelanranta Water Treatment Plants are shown in Tables 1, 2 and 3, respectively, in Appendix 2. The HMM matter was removed from the water in purification processes by over 95%. This was the case at all Water Treatment Plants studied. The treated water contained some IMM (4000-1000 g/mol) organic matter. Average removal of 46-68% and 87% was detected in Rusko and Oulu, respectively. However, the most difficult to remove was the LMM (<1000 g/mol) organic matter; 38-46% and 60% at Rusko and Oulu, respectively, were removed. It is noteworthy that the substantially higher removal

efficiency of NOM in Oulu Waterworks is explained by the two times higher initial DOC concentration of raw water; 5.6 mg/l vs. 12.2 mg/l. However, the amount of NOM in treated water measured as DOC was higher at Rusko than in Oulu, 2.8 mg/l and 2.0 mg/l, respectively. Likewise, the sum of peak height (SOPH) of treated water was slightly higher in Rusko, thus implicating that the treatment process in Oulu is more efficient in regard of NOM removal. In comparison to Rusko, the removal of NOM was more efficient during the ozonation followed by AC filtration, as in Oulu, than during AC filtration alone. One explanation for the lower DOC and SOPH values of treated water in Oulu, than in Tampere, might be this difference in treatment processes.

7.4 The effect of ozonation and AC filtration on NOM according to the pilot-scale study

7.4.1 TOC and other conventional quality parameters

Pilot-scale ozonation and AC filtration experiments were conducted at Kurkelanranta Water Treatment Plant. The water to the pilot came from full-scale process after chemical coagulation/flotation and sand filtration, where practically all the HMM matter and most of the IMM matter were already removed. More information on the test is given in the Paper IV. The addition of ozone was done in a continuous flow reactor with four different ozone doses and with two stages AC filtration. The ozone doses in different test runs were 0.5 mg/l, 1.4 mg/l, 2.9 mg/l and 4.0 mg/l. Samples were collected from the feed water, the ozonated water and the AC filtered water after the second AC filter. The contact time with ozone in the column was 18 minutes and EBCT 14 min in both AC filters; total of 28 min.

During the test, UV_{254} absorbance was clearly decreased, as the ozone dose was increased. AC filtration after the ozonation removed UV absorbing compounds even further and the greatest reduction after AC (56%) was noticed with the highest ozone dose, which was 4.0 mg/l; over twice as high as in full-scale treatment (1.5 mg/l). The total amount of NOM, measured as the SOPH in HPSEC, was reduced by 45%.

The reduction of TOC in the pilot-scale ozonation experiment was small. In the feed water the amount of TOC varied from 2.3 mg/l to 2.5 mg/l. After the ozonation the TOC value was 2.3 mg/l and after the activated carbon filtration about 2.0 mg/l, the same as in treated water after full-scale treatment. Thus, the approximate TOC reduction in ozonation was 4% and in AC filtration 13%.

7.4.2 AOC concentrations

The AOC concentration determines the assimilable carbon content available for microbes. AOC was observed to increase as the ozone dose was increased. With the smallest ozone dose (0.5 mg/l), two-fold AOC values were measured. The maximum AOC (0.36 mg/l) was achieved with a very high ozone dose of 4.0 mg/l (2.4 mg O_3 /mg TOC). The amount of AOC was ten times higher than in the original feed water sample (0.038 mg/l) (Figure 7 in Paper IV). The higher AOC concentrations were obtained with *Aquaspirillum NOX* than with *Pseudomonas Fluorescence P17*. Similar observation has been made also in other studies (Langlais et al. 1991). However, according to Langlais et al. (1991), the maximum AOC production was reached by a specific amount of ozone, after which no more increase in AOC occurred (suggestion for the limit of AOC production was 1.5-2.0 mg O_3 /mg TOC). Nevertheless, the increase of AOC in ozonation depends not only on the TOC concentration,

but also on the raw water quality and especially the character of organic matter present in water (Langlais et al. 1991).

Although the amount of AOC was high after the ozonation, the AC filtration removed the AOC content very efficiently. About 74% of the AOC was removed by AC filter with the lower ozone doses and 88% with the highest ozone dose (Figure 7 in Paper IV). According to the study by Lehtola et al. (2002) the AC filtration removed 23% of TOC and 85% of AOC concentration in water.

7.4.3 HPSEC results

The first ozonation test was conducted as a batch test (Ozone feeding 0.34 mgO₃/min, 1.36 mgO₃/min and 3.9 mgO₃/min; sampling with time intervals of 2min, 5min, 10 min and 20 min). The amount of NOM was reduced in nearly all of the MM fractions when ozone dose was increased, but moreover when ozone contact time with studied water was increased. However, quite opposite phenomena occurred in the fraction of 4000-5000 g/mol (HMM fraction) (Figure 5 in Paper IV). The HMM matter was noticed to increase from time to time; especially with the lowest ozone doses (values were compared to the feed water). This can be explained by polymerization of organic matter during ozonation. Hence, some by-products with higher UV absorption capacity might have been produced during ozonation. Certain molecules are resistant to the action of ozone or they may be transformed into products that remain nonbiodegradable (Langlais et al. 1991). In other earlier studies (Ho et al. 2002, Bose et al. 1994) it has been noticed that the amount of HMM (measured as TOC and UV-absorbance) also increased in some cases.

In the second part of the test, the addition of ozone was done in a continuous flow reactor with four different ozone doses (0.5 mg/l, 1.4 mg/l, 2.9 mg/l and 4.0 mg/l) and with two stages AC filtration. With the lowest ozone dose of 0.5 mg/l, the reduction of NOM was lower, but the following AC filtration was more effective, especially when the removal of the LMM fraction was considered (Figure 6 in Paper IV). The higher ozone doses (1.4 mg/l-4.0 mg/l) resulted in higher removal of NOM on every MM fraction. However, the AC was not able to remove the NOM any further (Figure 6 in Paper IV). The ozonation with higher ozone doses might have converted the NOM to the compounds with higher polarity and solubility. Hence they are unable to adsorb on to the AC and the removal of NOM by AC is reduced (Chang et al. 1995). Moreover, the HMM fraction increased slightly after the ozonation with the lowest ozone doses, indicating possible polymerization of organic matter. Same phenomenon was also observed in the full-scale process, with ozone doses 0.4 mg/l - 0.7 mg/l (wintertime), as well as in the batch test.

7.5 The effect of NF on the removal of NOM according to the pilot-scale study

The efficiency of different nanofiltration (NF) membranes to remove various water components, including NOM, from chemically pre-treated water samples, was studied in pilot-scale (Paper V). The membranes studied were *Desal-5 DL*, *NF255* and *NF270*. Six different feed waters from five surface water treatment plants and one artificial ground water treatment plant were collected. Samples were taken after conventional water treatment train, but before post-treatment (alkalinization and disinfection). In general, considering all the different membranes studied, 49-100% removal of the remaining organic matter after conventional treatment was obtained. The removal was in the most cases above 60%. Removal of the different molecular size fractions varied between 56-100%, 54-100% and 19-

88%, regarding the HMM, the IMM and the LMM organic matter, respectively. The best removal capacity was performed with “*Desal-5 DL*” membrane. Figure 7.3 summarizes the NOM removal capacities of the different NF filters studied. The NOM removal efficiency of the NF process according to the HPSEC measurements in detail can be seen in Table 4 in Paper V.

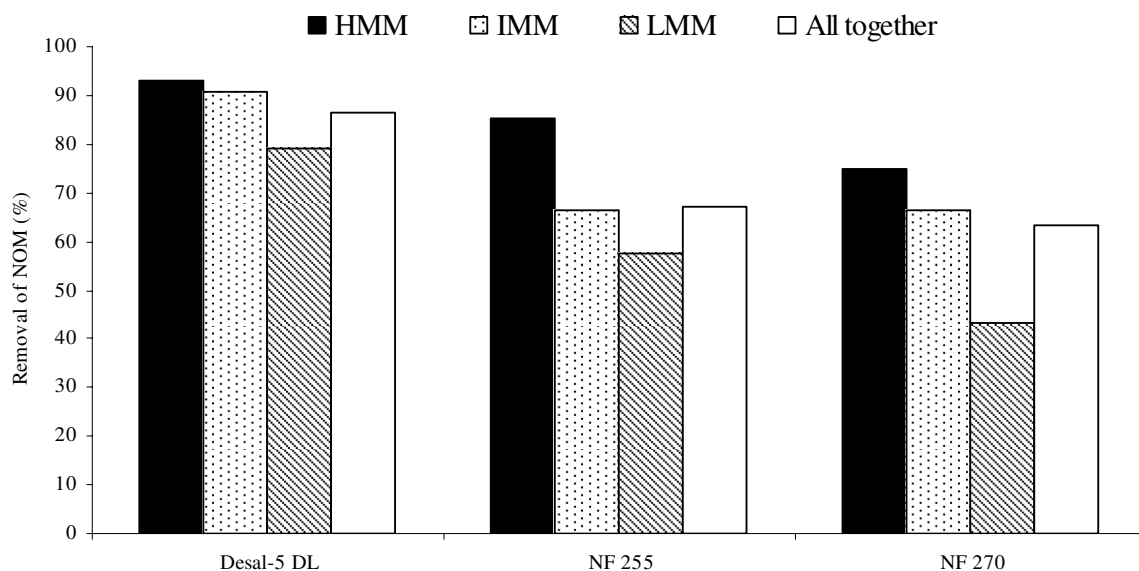


Figure 7.3. Removal of the different MM fractions of NOM during NF filtration with various membrane types studied. Values are averages from results on all the water treatment facilities (Espoo, Tampere, Turku, Kotka, Raisio-Naantali, and Pietarsaari).

The removal efficiencies of organic matter as DOC and UV_{254} by different NF membranes were in general 47-100% (see Table 5 in Paper V) of the remaining organic matter in chemically pretreated waters. Several studies indicate that the NF is very effective in removal of organic matter from a variety of feed waters: DOC removals of 60-95%, UV_{254} removals of 60-99% and DBP precursor removals of 41-100% have been reported (Amy et al. 1990, Chellam 2000, Schäfer et al. 2000, Siddiqui et al. 2000, Liikanen 2006). The NF was also found, by the study of Tuhkanen et al (1994), to be a highly effective method to remove precursors of adsorbable organic halogens (AOX), mutagenicity as well as organic matter, colour and turbidity; the removal was 88%, 85%, 68%, 90% and 68%, respectively. It was noticed in the study by Liikanen et al. (2003) that although NF performed high bacteria and organic matter removals, remarkable potential for microbial growth was showed in NF permeate waters. Thus, post-chlorination with minor chlorine dosages is needed to suppress microbial growth in distribution systems (Liikanen et al. 2003).

When considering the performance of an NF membrane one should bear in mind that the aim is to achieve the required drinking water quality with the lowest possible costs. Accordingly, the membrane with the highest NOM removal capacity may not always be the best choice, as other membrane may result in sufficiently high water quality at a lower cost due to a higher productivity (Liikanen 2006).

7.6 Evaluation of the performance of HPSEC-UV₂₅₄ in the measurement of NOM during water treatment process

The sizes of different chemical fractions of NOM are found to influence various aspects of NOM behaviour in water treatment. While NOM contains different molecular sizes, the HPSEC-UV₂₅₄ method was able to clearly separate up to seven MM fractions present in Finnish surface water samples, hence giving the samples a “fingerprint” of organic matter. The HPSEC-UV₂₅₄ method proved to be highly informative in measuring the transformation of molecular size distribution (MSD) of NOM during the different water treatment processes. The reduction and increase of these fractions during water treatment clearly demonstrates the treatment process performance efficiency, with regard of apparent sizes of NOM fractions. The bulk parameters, like TOC or UV-absorbance, can give information about the total concentration of NOM, but not any specific knowledge of different fractions of NOM. However, if these, and other basic water quality parameters (like colour or KMnO₄), are used in combination with the HPSEC-UV₂₅₄ method, the performance of unit operations could be effectively monitored. Moreover, HPSEC-UV₂₅₄ is a method which effectively characterizes aquatic NOM samples with no prior concentration or fractionation, thus leaving the sample unaltered. Also, the HPLC apparatus, and especially with UV detector, is relatively common in research and water quality laboratories, thus lowering the costs involved in using this method.

With HPSEC analysis, the compounds present in water sample can be roughly identified to different MM size ranges but the different charged groups of NOM can not be separated. Charge load originating from each fraction of NOM has been shown to vary and the majority of the charge load has been noticed to come from the hydrophobic fraction of NOM (Sharp et al. 2006c). The hydrophilic and hydrophobic fractions of NOM, as well as humic and fulvic acid fractions, can be roughly separated by resin fractionation, although the method is quite time consuming and labourous. On the contrary, by the separation with SEC, the fraction with HMM includes humic acids, as well as other HMM compounds. Likewise, LMM fraction, can conclude fulvic acids, as well as other LMM organic compounds. Hence, there are also other rapid methods under investigation for characterization of NOM, e.g. fluorescence spectroscopy (Goslan et al. 2004).

The limitations of the HPSEC method include the use of UV₂₅₄ absorption as detection method, thus under estimating the amounts of LMM organic matter with less UV-absorptive chromophores. Still, the UV₂₅₄ is widely used and accepted for the measurements of NOM. Moreover, the charge repulsion and adsorption of column material with organic compounds studied are possible. In spite of these limitations, the column used in this study (TSK G30000SW), was able to separate efficiently different molecular size fractions from aquatic NOM samples. A similar column and other measurement parameters, as in our study, have been used for several years with good results. It has been reported to highlight the changes of aquatic NOM in a highly visual manner (Kronberg et al. 1985, Vartiainen et al. 1987, Kainulainen et al. 1994, Peuravuori and Pihlaja 1997, Vuorio et al. 1998, Miettinen et al. 1998, Nissinen et al. 2001, Myllykangas et al. 2002, Hurst et al. 2004). Especially the Finnish researchers have used this method in various water quality investigations. Thus, the comparison of results, gained from various studies, is possible, hence giving valuable information for Finnish water treatment facilities.

8. CONCLUSIONS

During the last two decades there have been huge investments in the improvement of drinking water quality. Still there is a pressure to further improve the quality and safety of drinking water. The most obvious solution would be the enhancement of the performance of the existing processes; coagulation, flocculation and filtration. There are also unit operations for the enhanced removal of NOM and possible micro-pollutants from water; membrane techniques as well as ozonation of organic matter followed by assimilation by micro-organisms. If the NOM in the raw water cannot be removed by conventional unit operations, the use of additional advanced and/or innovative processes are unavoidable. However, particularly the small waterworks don't have resources to invest in additional unit operations for NOM removal. Thus, the enhancement of NOM removal and stable drinking water quality should be obtained also by process optimization and raw water source selection and protection.

The full-scale study of NOM removal during water treatment included three surface water treatment plants; Rusko Water Treatment Plant in Tampere (Papers I, II and III) and Hintta and Kurkelanranta Water Treatment Plants in Oulu (Paper IV). All of the studied plants produced high quality drinking water, although the amount of raw water NOM in Oulu, measured as TOC and SOPH, was twice as high as in Tampere. Waterworks of Oulu used river water (River Oulu) as raw water source, while in Tampere raw water source was Lake Roine.

In the treatment processes studied, the removal efficiencies of the different molecular size fractions of NOM varied significantly. The removal of the HMM matter was sufficient, almost 100%. The IMM and the LMM NOM were more difficult to remove than the HMM matter (Papers I, II, III and IV).

The coagulation was effective in the removal of the HMM matter and reasonably effective in the IMM matter removal. However, in the removal of the smallest molecular size fractions of NOM, the coagulation was ineffective, only about 3-25% of this fraction was removed. The selection of a proper coagulant for a particular raw water used was very important. The replacement of alum coagulant with a ferric coagulant at Rusko Water Treatment Plant enhanced the removal of NOM by 10%. Especially the removal of the IMM fraction was improved; as much as by 25% (Paper III).

The AC filtration improved the reduction of the NOM most effectively in the IMM organic matter fraction. The IMM NOM removal was enhanced by about 30% (Papers II and III). The reduction of the HMM matter was insignificant. LMM matter was removed poorly, depending on the particular AC. On the contrary, the LMM matter was noticed to even increase from time to time, especially during summer months (Paper II). This increase might be due to microbiological activity and release of metabolites from the filter bed. The effectiveness of the AC filtration to remove NOM depended primarily on the regeneration history of the particular filter (Papers I, II, III and IV). On average, the highest removal rates were observed for the NOM molecules in the size range of < 3000 g/mol, especially when the AC was new or recently regenerated. In Oulu Waterworks, there was an ozonation step prior to AC filtration, thus altering the NOM to more biodegradable form. The AC filters in Oulu were more effective in removing LMM matter during summer, thus indicating that there might have been some biological activity on the filters (Paper IV).

Ozonation in the full-scale treatment in Oulu Waterworks (Paper IV) removed primarily the lower molar mass compounds. The IMM fraction of size range 1000-3000 g/mol and the LMM matter of size range > 1000 g/mol were further decreased by 23% and 32%, respectively, during ozonation. The HMM matter was either unaltered or increased. The reason for the increase was suggested to be the polymerization of NOM and by-products produced during ozonation. This phenomenon was observed primarily in wintertime when ozonation dose was lower. Same was noticed to occur also during pilot-scale study with low doses of ozone. Moreover, ozonation removed primarily the LMM matter also in the pilot-scale studies. The amount of HMM compounds were almost constant, while the amount of IMM and LMM matter was decreased. This is contradictory to previous studies, where ozonation is said to remove primarily the HMM matter and degrade it to the LMM compounds. Nevertheless, according to the AOC measurements, the available assimilable organic matter to microbes increased from 0.030 mg AOC /l to 0.1-0.3 mg AOC /l when the ozone dose was increased. Hence, the NOM was degraded into smaller compounds. It can be concluded that in the ozonation, the NOM was degraded into very small compounds, with no or little conjugated double bonds and, thus, not showing in the HPSEC-UV₂₅₄ measurements. In spite of the high AOC concentration produced in the ozonation, the AC filtration after the ozonation efficiently removed the AOC from water. The amount of TOC was reduced only slightly during the ozonation, even with the highest ozone doses. TOC was reduced from 2.3 mg/l to 2.0 mg/l; being almost equal in full-scale as in pilot-scale investigations.

NF removed residual NOM highly effectively (Paper V). High removal percentages after traditional pre-cleaning gave very high quality drinking water. The residual HMM NOM was almost completely removed and IMM matter diminished considerably. Also the LMM matter removal was improved. The membrane quality: “Desal-5 DL” membrane gave the best results. The removal of NOM measured as both TOC and UV₂₅₄ was also improved.

In spite of its limitations, HPSEC-UV₂₅₄ proved to be a very informative method in the monitoring of the performance of the different treatment processes. It provided useful information on the MSD of NOM in the water sample fast and relatively easily. Compared to traditional methods like TOC, it yielded additional information about the removal and especially about the transformation of the MSD of NOM during the treatment train. TOC measurements could not give information about the quality of NOM, only about quantity, and for example the amount of the biodegradable fraction which comprises mainly LMM organic matter was difficult to predict in finished drinking water. The HPSEC-UV₂₅₄ method produced especially valuable information of the performance of advanced techniques to remove the residual, IMM and LMM organic matter. Hence, the HPSEC-UV₂₅₄ can be used as a routine analysis method in combination with the basic water quality measurements in water treatment plants in the follow-up of the performance and optimization of unit operations.

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APPENDIX 1

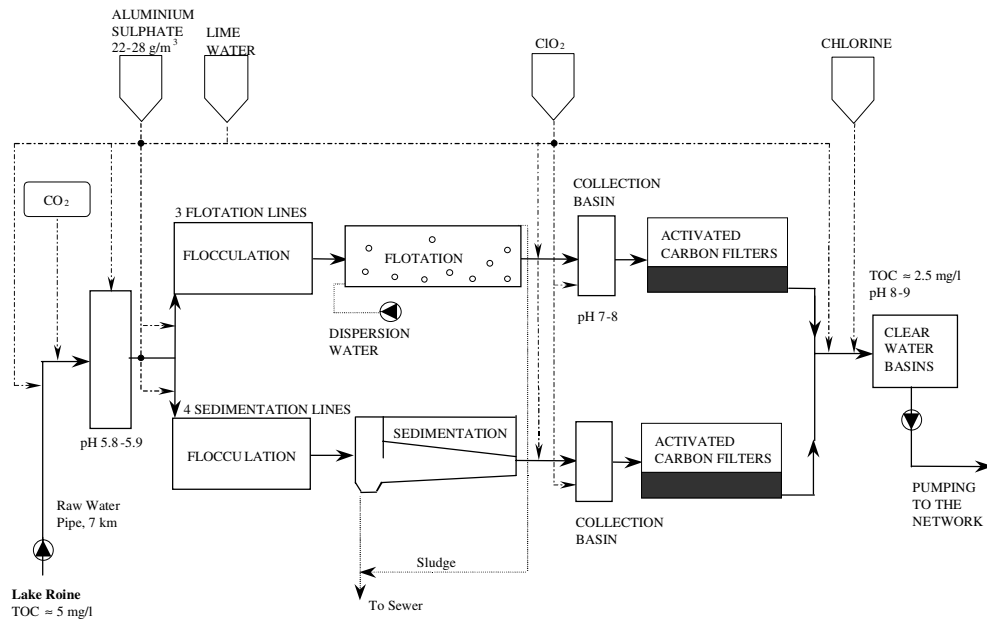


Figure 1. Schematic picture of the Rusko Waterworks in year 1999

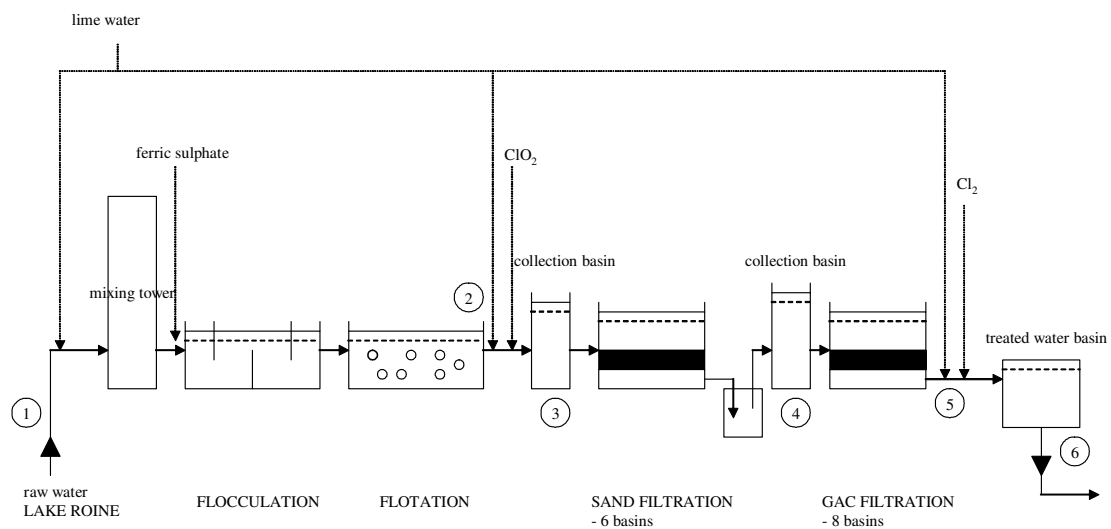


Figure 2. Schematic picture of the Rusko Waterworks in year 2002

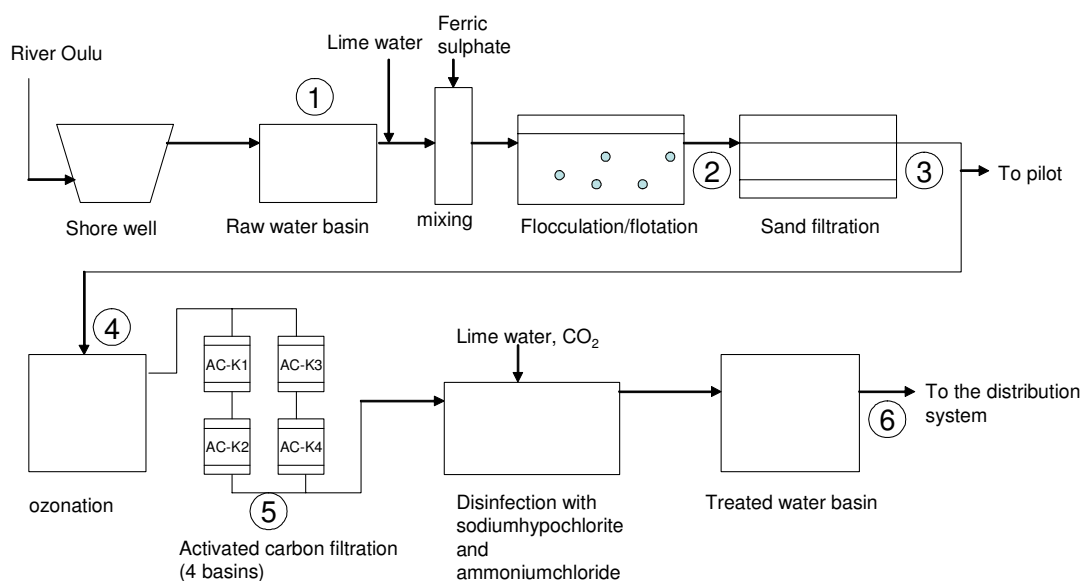


Figure 3. Diagram of the Kurkelanranta Water Treatment Plant. In Kurkelanranta AC filters were paired so that two of them were in-line and pairs were parallel. In Hintta all AC filters were parallel. Sampling points are illustrated in the figure by numbers 1-6.

APPENDIX 2.

Table 1. The removal percentages of different MM fractions of NOM during the water treatment process at Rusko Water Treatment Plant. Results are averages from studies on Papers I and II (sedimentation n=12; AC-B, AC-D n=51, flotation, AC-A, AC-C n=63).

	MM fractions g/mol				
	>4000	3000-4000	1000-3000	<1000	<500
Sedimentation	95	48	12	3	
Flotation	96	55	20	14	19
AC-A	95	65	41	39	21
AC-B	94	68	48	43	26
AC-C	95	66	44	38	38
AC-D	95	70	53	51	21
Treated water	96	68	46	46	38

Table 2. The removal percentages of different MM fractions of NOM during the water treatment process at Hintta Water Treatment Plant.

	MM fractions g/mol				
	>4000	3000-4000	1000-3000	<1000	SOPH
Flotation	98	90	54	6	90
Sand filtration	98	88	50	7	89
Ozonation	98	92	72	38	93
AC-H1	98	93	75	43	94
AC-H2	98	94	81	62	96
AC-H3	98	93	76	49	94
AC-H4	99	95	74	65	97
Treated water	98	94	80	57	95

Table 3. The removal percentages of different MM fractions of NOM during the water treatment process at Kurkelanranta Water Treatment Plant.

	MM fractions g/mol				
	>4000	3000-4000	1000-3000	<1000	SOPH
Flotation	98	90	55	13	90
Sand filtration	98	89	54	16	90
Ozonation	98	93	77	49	94
AC-K1	98	93	77	48	94
AC-K2	99	95	82	64	96
AC-K3	98	93	76	48	94
AC-K4	98	94	79	57	95
Treated water	98	94	82	63	95

I

Removal of NOM in the different stages of the water treatment process.

Matilainen, A., Lindqvist, N., Korhonen, S. and Tuhkanen, T.

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Removal of NOM in the different stages of the water treatment process

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Abstract

Natural organic matter (NOM) is abundant in natural waters in Finland and in many ways affects the unit operations in water purification. In this study, the organic matter content in water in different stages of a full-scale treatment process over 1 year was measured. The full-scale treatment sequence, studied at the Rusko water treatment plant in Tampere, Finland, consisted of coagulation, flocculation, clarification by sedimentation or flotation, activated carbon (AC) filtration, and disinfection. High-performance size exclusion chromatography (HPSEC) was used for separation to determine changes in the humic substances content during the purification process. In addition, total organic carbon (TOC), KMnO_4 -number, and UV-absorbance at wavelength 254 nm (UV_{254}) were measured. High molecular weight (HMW) matter was clearly easier to remove in coagulation and clarification than low molecular weight (LMW) matter. Furthermore, depending on the regeneration of the activated carbon filters, activated carbon filtration was effective to a degree but did not remove most of the lowest molecular weight compounds. Significant correlation was established among HPSEC, KMnO_4 , UV_{254} absorbance, and TOC. HPSEC proved to be a fast and relatively easy method to estimate NOM content in water and, in fact, gave more information than traditional methods on the type of NOM in a water sample. It also helped the process performance follow-up.

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Keywords: High-performance size exclusion chromatography (HPSEC); Natural organic matter (NOM); Drinking water; Water purification

1. Introduction

Natural organic matter (NOM), defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment, including the performance of unit processes (i.e., oxidation, coagulation, and adsorption), application of disinfectants, and biological stability. As a result, NOM acts upon potable water quality by contributing to disinfection by-products (DBP), biological regrowth in the distribution system, colour, taste, and odour (Owen et al., 1995). Various water treatment processes can either directly or indirectly and, to varying degrees, remove aquatic organic matter from raw water, depending on their operational conditions and the specific characteristics of the NOM such as molecular weight distribution (MWD), carboxylic acidity, and humic substances content (Collins et al., 1985). High molecular weight (HMW) NOM is more amenable to removal than low molecular weight (LMW) NOM, particularly the fraction with an

MW of < 500 Dalton (Da). NOM with the highest carboxylic acidity and hence the highest charge density are generally difficult to remove by conventional treatment (Collins et al., 1986). Water source with HMW (5000–10000 Da) humic acids is a good candidate for chemical coagulation (Amy et al., 1992). The LMW species are more adsorbable presumably because more surface area is accessible to these substances (McCreary and Snoeyink, 1980).

High-performance size exclusion chromatography (HPSEC) has been widely used to determine the MWD of aquatic humic substances (Pelekani et al., 1999; Conte and Piccola, 1999; Rausa et al., 1991; Knuutinen et al., 1988; Amy et al., 1987; El-Rehaili and Weber, 1987; Miles and Brezonik, 1983). In HPSEC analysis, humic molecules are separated primarily on the basis of differing molecular size so that the largest molecules are eluted first in the column, while the smallest molecules are eluted last (Potschka, 1993). Other factors such as charge, molecular structure, steric effects, and hydrophobicity may also influence the result (Wershaw and Aiken, 1985).

The objective of this study was to monitor the purification process on full scale at a water treatment plant and to evaluate the quality of the water with HPSEC in the different stages of the process. A further aim was to use HPSEC

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to monitor the performance of the treatment process and to determine if the method yielded any information on the process beyond what could be gained by traditional methods such as total organic carbon (TOC) measurement.

2. Materials and methods

2.1. Rusko waterworks

The Rusko waterworks pumps its raw water from Lake Roine, 7 km southeast of the plant and produces 68% of the distributed drinking water for the city of Tampere, Finland. The plant has a maximum treatment capacity of 55 000 m³/day and an average water flow of about 1400 m³/h. Raw water is typical Finnish lake water having low alkalinity (about 0.25 mmol/l) and quite a low turbidity (about 2 FTU). Organic carbon content is fairly low (about 5 mg/l) compared to typical Finnish surface waters. The treated water has a TOC value of about 2.5 mg/l.

As shown in Fig. 1, the treatment process at Rusko consists of chemical addition, coagulation and clarification, disinfection, activated carbon filtration, and post-chlorination. After coagulant addition ($\text{Al}_2(\text{SO}_4)_3$), the process is branched into two separate lines, the older employing sedimentation for clarification and the newer flotation. Sedimentation line has four sedimentation basins and its total

Table 1

Results on water quality at Rusko water treatment plant (August 1999–August 2000)

	Raw water			Pure water		
	Average	Min	Max	Average	Min	Max
Alkalinity (mmol/l)	0.25	0.24	0.25	0.73	0.68	0.80
Hardness (dH)	1.1	1.1	1.2	3.3	3.0	3.5
Colour, Pt (mg/l)	16	10	30	<2.5	<2.5	<2.5
Turbidity (FTU)	2.3	0.58	5.5	0.13	0.06	0.36
pH	7.1	6.8	7.3	8.5	7.8	8.9
TOC (mg/l)	5.5	5.4	5.6	2.9	2.2	3.1
KMnO ₄ (mg/l)	17	14	19	5.0	3.8	6.4

design capacity is 28 000 m³/day. The flotation line has three basins with total capacity of 24 000–32 000 m³/day. After clarification, the water passes through collection basins and onto activated carbon filters. The activated carbon (AC) filters are ordinary one-layer filters, 14 in all with 8 in the sedimentation line and 6 in the flotation line. Each filter has a surface area of 30 m² and a bed depth of about 115 cm. The filters are flushed with water and air after about 40 h of use, and the AC is regenerated every 2 years. Disinfection with chlorine dioxide (ClO_2) takes place in the collection basins, and post-chlorination is done with chlorine gas to yield a 0.3 mg/l free chlorine residual in the purified water before it is pumped into the distribution system.

One filter from both clarification lines was used to study the efficiency of AC filters to remove organic matter. AC-A

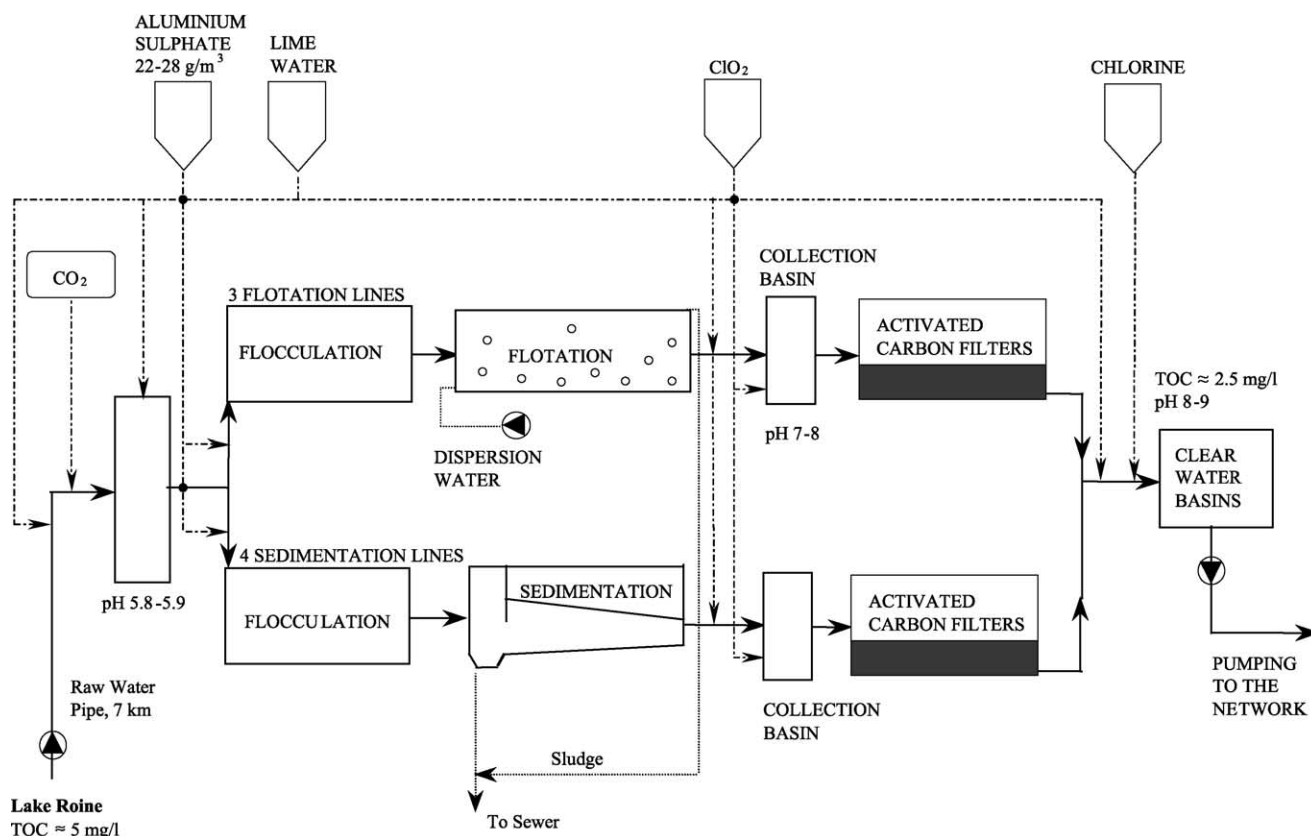


Fig. 1. Diagram of Rusko drinking water treatment plant.

(brand name Aqva Sorb BG-09) was taken in use in sedimentation line in July 1995. It was manufactured in China and made of bitumic coal. It was regenerated in April 1998 and May 2000. AC-B (brand name Filtrasorb TL820) was in flotation line and it was taken in use in December 1994. It was manufactured in Belgium, made also of bitumic coal and regenerated in April 1997 and May 1999.

2.2. Analysis

Water samples were taken from the following stages of the treatment sequence once a month between the beginning of August 1999 and the end of May 2000: raw water, after sedimentation and flotation, after two different AC filters

(AC-A in the sedimentation line and AC-B in the flotation line), and pure drinking water. These samples ($V=10$ ml) were frozen and analysed with HPSEC in the summer 2000. The other parameters were measured on site upon sampling (in Rusko waterworks laboratory). UV₂₅₄ absorbance was measured with a spectrophotometer. The raw water sample and the samples after flotation and sedimentation were centrifuged before UV measurement. TOC samples were filtered through 0.45- μ m membrane and they were measured as dissolved organic carbon (DOC) according to the SFS-EN 1484 standard and by using a Shimadzu TOC-5000A with a high sensitivity catalyst. Total organic material was measured by the KMnO_4 oxidation method according to the Finnish Society of Food Science and Technology guidelines.

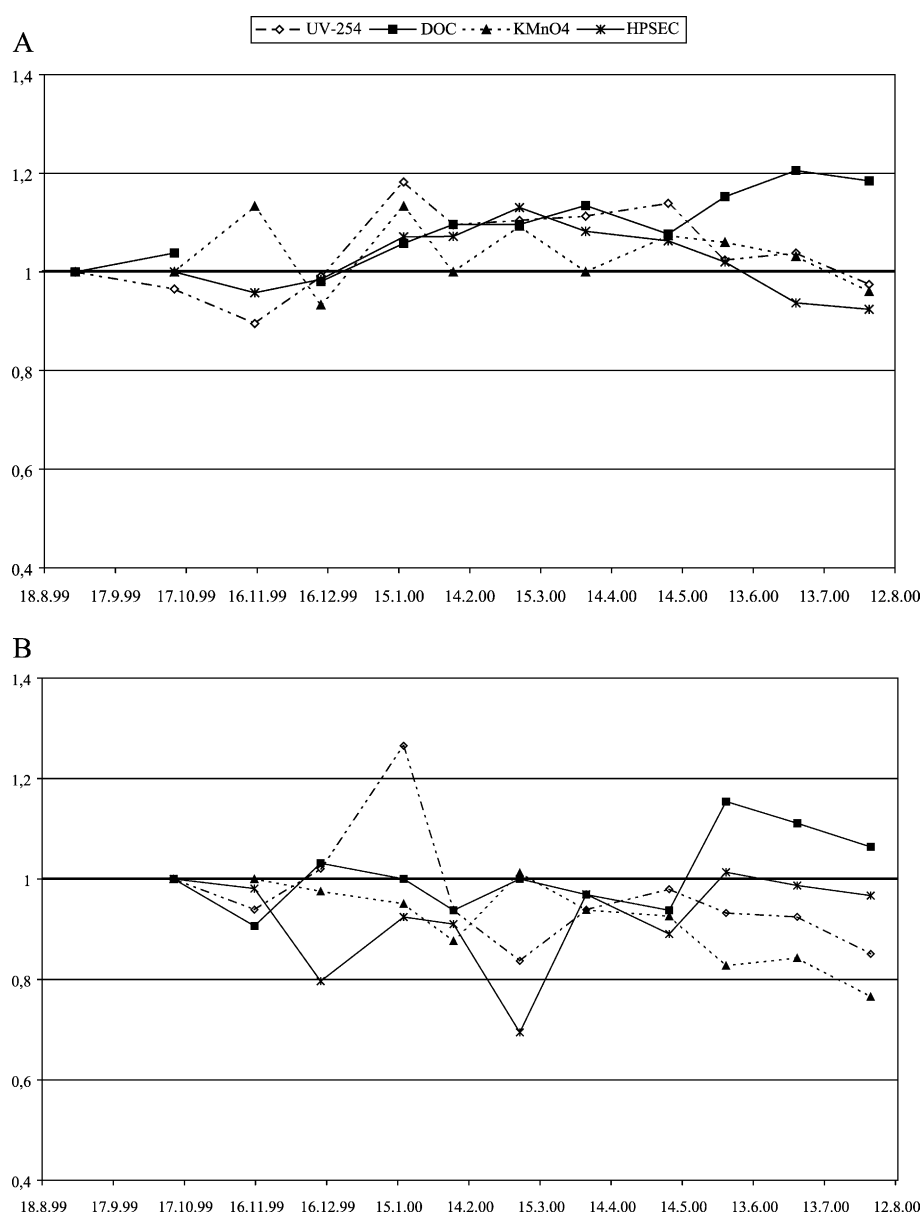


Fig. 2. (A–F) Seasonal variation in organic matter content according to different measuring techniques. Results are relative amounts of organic matter compared to the first value of measurement. (A) Raw water, (B) flotation, (C) sedimentation, (D) AC-A, (E) AC-B, (F) treated water.

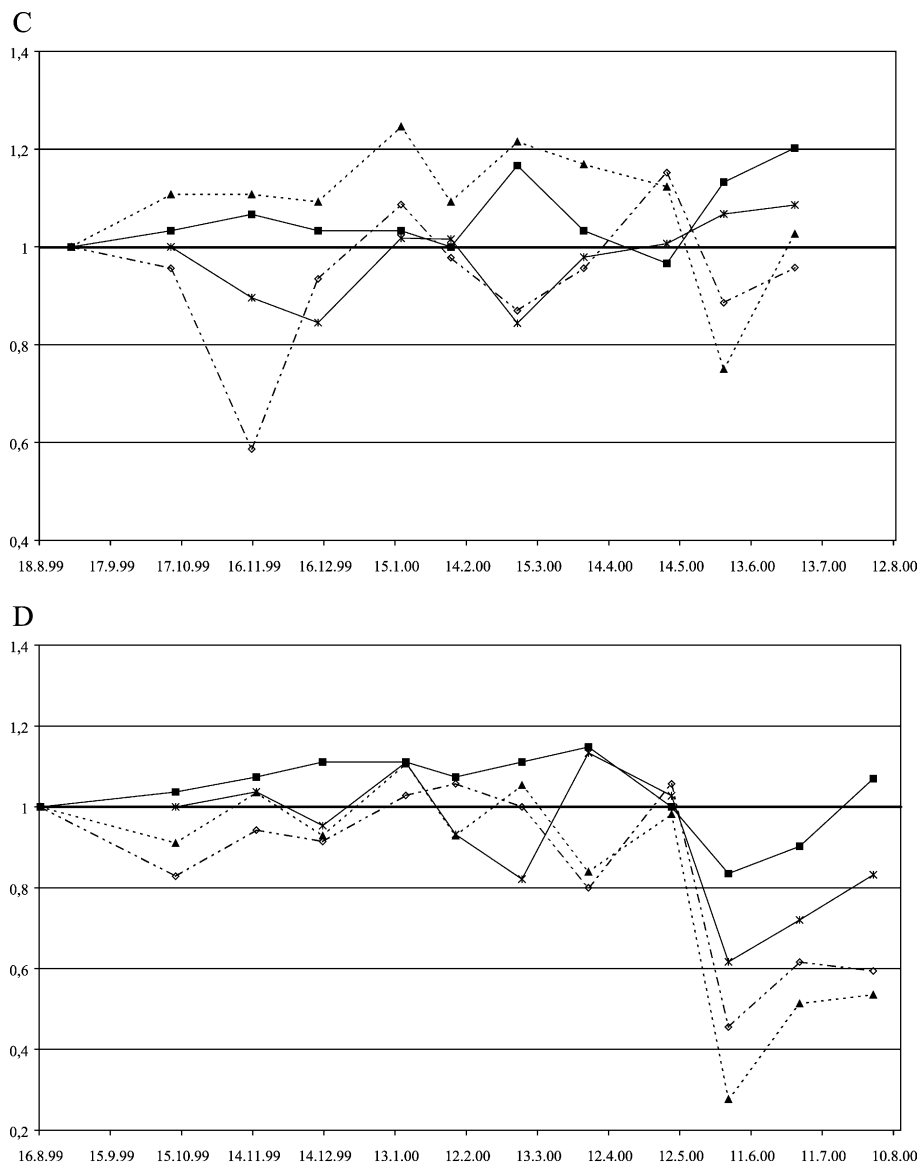


Fig. 2 (continued).

Hardness was measured according to the SFS 3003/-87, alkalinity by the SFS 3005/-81, turbidity according to the SFS-EN ISO 7027/-00, and colour according to the SFS-EN 7887/part 4/-95 standard.

From the beginning of June to the end of August 2000, samples were taken every other week and measured at Tampere University of Technology laboratories. UV₂₅₄ absorption was measured with a Shimadzu UV-1601, UV–VIS spectrophotometer. Before measurement, the raw water sample and the samples after flotation and sedimentation were filtered through a Gelman 0.45- μ m membrane. TOC and KMnO₄ were determined as described above. Samples were filtered through 0.45- μ m membrane.

HPSEC measurements were done on the frozen samples in June and July 2000 and on those taken in the summer upon sampling. The samples were first filtered through a Gelman 0.45- μ m membrane and then HPSEC fractionated with a

Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector ($\lambda=254$) and a TSKgel G3000SW 7.5 mm(ID) \times 30 cm column. Pre-column was not used. Sodium acetate (0.01 M) was used as eluent at a flow rate of 1 ml/min. Injection volume was 30 μ l. Method was selected based on results from earlier investigations (Becher et al., 1985; Vartiainen et al., 1987; Vuorio et al., 1998).

3. Results and discussion

3.1. Effect of freezing on the HPSEC samples

The effect of freezing was tested with raw water samples. Samples were analysed after different times of freezing. According to our study, results showed less than 8% relative

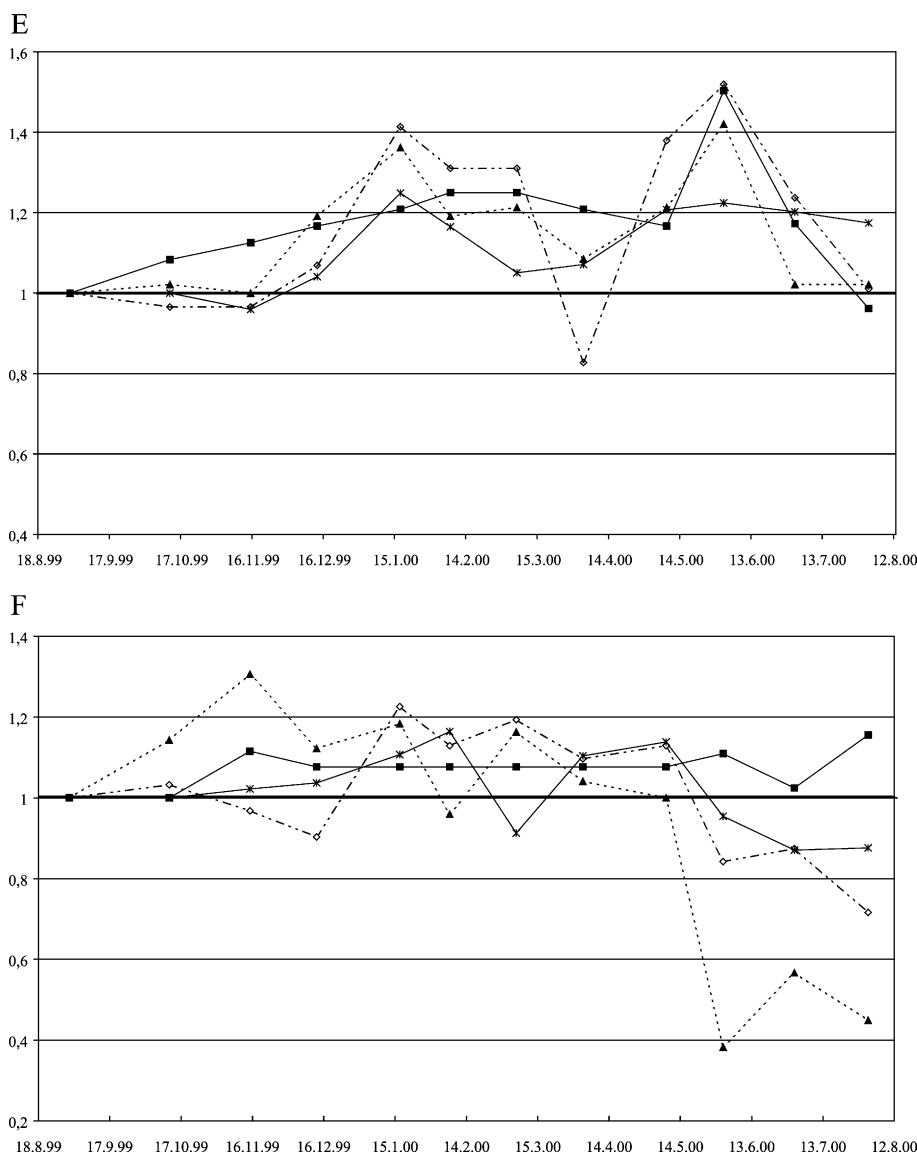


Fig. 2 (continued).

standard deviation. It could be seen on the results that this was due more from process uncertainty than freezing. The reliability of the method is affected by the adsorption interactions and charge exclusion between the humic compounds and the HPSEC gel as well as the ionic strength and pH of the eluent and sample (Miles and Brezonik, 1983; Becher et al., 1985; Nissinen et al., 2001).

3.2. Seasonal variation of raw water and results of purification

The results on the water quality in the Rusko water treatment plant measured at their laboratory are shown in Table 1. On average, the treatment process removed >84%, 95%, 47%, and 70% of NOM measured as colour, turbidity, TOC, and KMnO_4 , respectively.

More detailed UV_{254} , TOC, KMnO_4 , and HPSEC results are presented in Fig. 2A–F. HPSEC values were calculated as height of the peaks. The height of the peak in the HPSEC chromatogram refers to the amount of NOM in specific molecular size fraction. The sum of all the peak heights in the chromatogram represents the total amount of NOM in the sample, with peak having the lowest retention time referring to the highest MW, and peak having the highest retention time to the lowest MW NOM. The heights of the peaks in the HPSEC chromatogram were summed together and this sum was then compared with the results obtained by UV_{254} , TOC, and KMnO_4 .

In the raw water, UV_{254} absorbance varied between 0.136 and 0.103. Highest values were obtained in winter and spring (from January to May). TOC was lowest in December then rising towards the summer, varying between 5.1 and 6.3 mg/l.

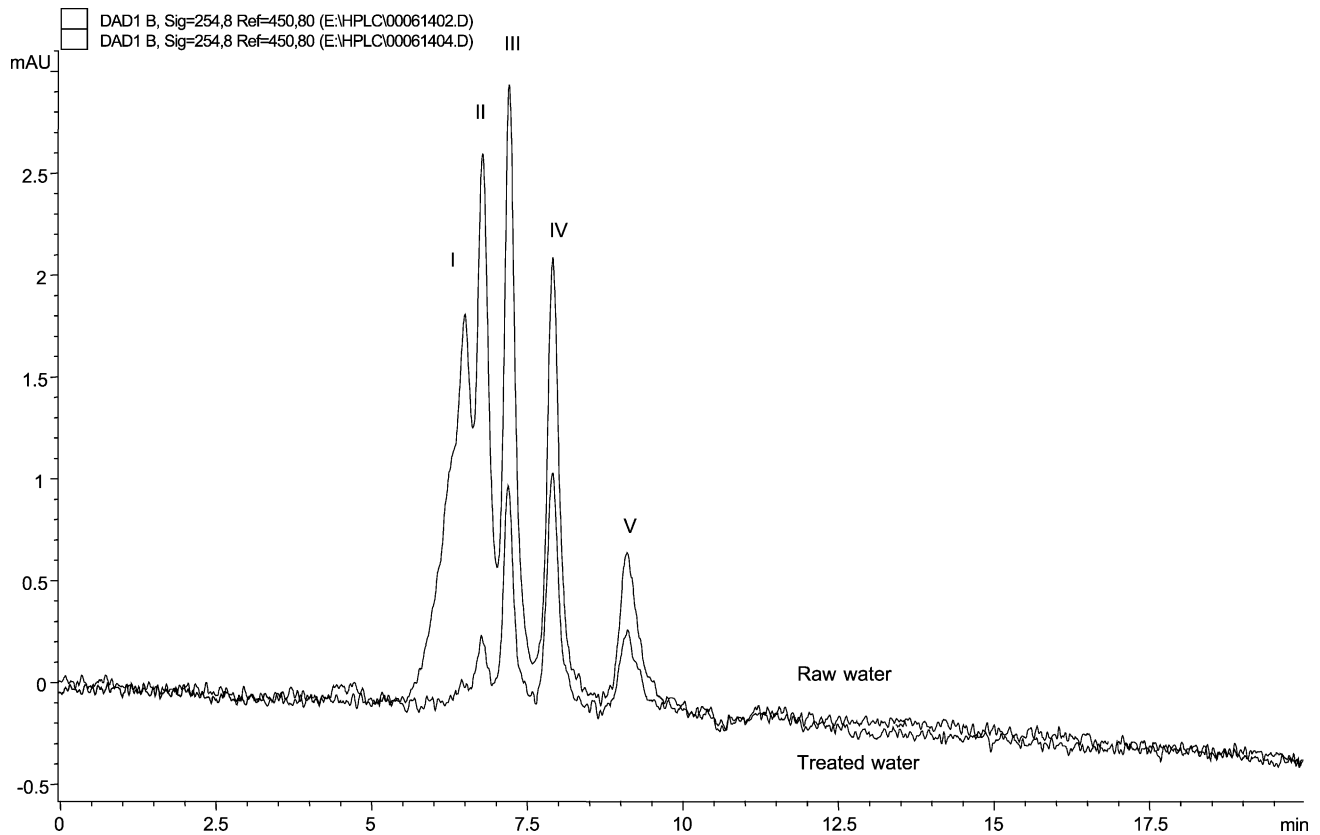


Fig. 3. HPSEC chromatogram of raw (above) and treated (below) water from Lake Roine.

KMnO₄ varied between 14 and 17 mg/l in raw water without a clear pattern. The highest values of HPSEC analysis in the raw water occurred in spring and the lowest in summer. According to the above results by different measurement techniques, there was a slight increase in winter with all raw water results, except those with TOC, which seemed to

increase during the investigation. Compared to the values in the beginning of the measurements, the values in the fall 2000 were about 20% higher.

Results measured after sedimentation and flotation did not show clear seasonal variation. KmnO₄-number values were higher in winter at flotation, while other results were constant.

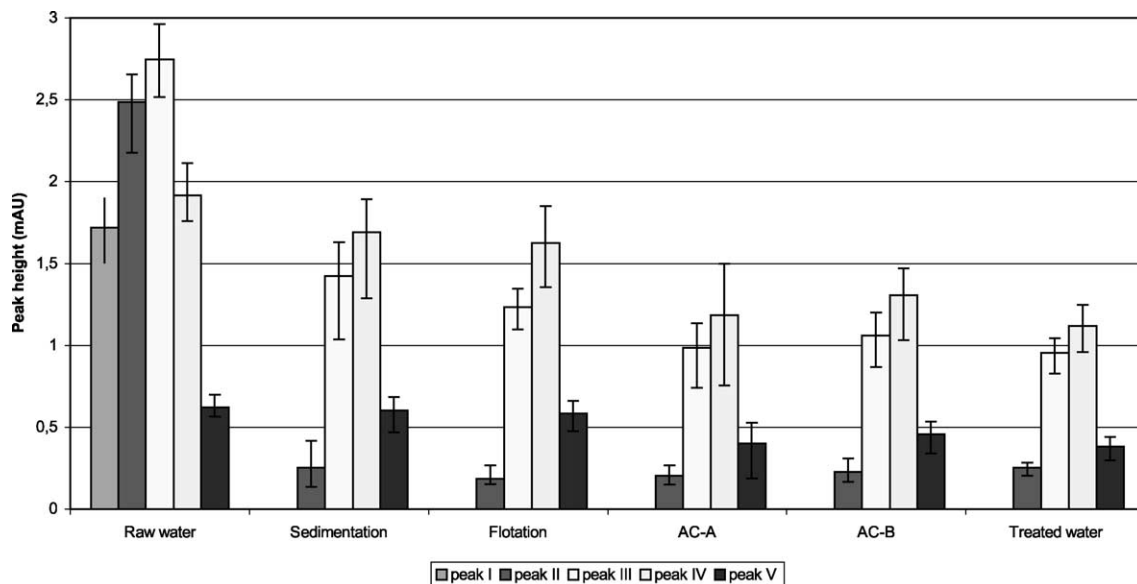


Fig. 4. Absolute peak heights in different stages of purification process. Results of period August 1999–August 2000 ($n=12$) in averages with variations.

AC-B has strong peak in May when all the results were higher than usual. Also, in winter, results are slightly elevated. From May onwards, the NOM removal efficiency of AC-A in the sedimentation line was higher than the efficiency of AC-B in the flotation line because the former had been regenerated in the spring. The results were lower than the results from treated water. AC-A removal efficiency, measured as UV₂₅₄, TOC, KMnO₄, and HPSEC, improved by 15%, 10%, 24%, and 12%, respectively, compared to the situation before regeneration. Compared to AC-B, the removal efficiency was better by 24%, 22%, 32%, and 17%, respectively. Thus, the regeneration of AC-A improved its capacity to remove NOM significantly.

3.3. Effect of the purification process on HPSEC chromatograms

Five different peaks in the raw water were found (Fig. 3). Peaks I and II are referred to HMW, peaks III and IV to intermediate molecular weight (IMW), and peak V to LMW organic matter. Further studies will determine the corresponding molecular size for each fraction. Now, the method is only a rough “fingerprint method”. Other researchers have found five to seven peaks in Finnish surface water samples (Nissinen et al., 2001; Vuorio et al., 1998; Kainulainen et al., 1994; Vartiainen et al., 1987). The chromatograms are always specific for different surface waters because the nature of NOM is greatly affected by the environment of the site. According to the chromatogram (Fig. 3), the raw water consisted mostly of HMW and IMW NOM. Fig. 3 shows also the chromatogram for the treated water, in which HMW and partially the IMW NOM have decreased after purification.

LMW fraction seems to be more difficult to remove. LMW fraction consists mostly from fulvic acids (Hayes et al., 1989). Fulvic acids are more soluble, smaller in average molecular weight, and more highly charged than humic acids. Fulvic acids also typically have higher oxygen content, with higher carboxylic acid (COOH) and lower aromatic hydroxyl (ArOH) content than humic acids (Hayes et al., 1989). They are therefore more difficult to destabilize by aluminium coagulation dosages commonly employed in water treatment

Table 2

Organic matter in different molecular size fractions removed from raw water after each purification step compared to raw water results (yearly average)

	Peak number				
	I	II	III	IV	V
Sedimentation	100	90	48	12	3
Flotation	100	93	55	15	6
AC-A	100	92	64	38	36
AC-B	100	91	61	32	27
Treated water	100	90	65	42	38

Results are in percentage compared to the raw water results.

Table 3

Organic matter removal efficiency of activated carbon filters in 4 months period, calculated in percentages compared to the values after clarification processes

		Peak number				
		I	II	III	IV	V
AC-A	April	0	0	9	17	29
	May	0	2	13	17	14
	June	0	3	29	55	75
	July	0	1	21	42	59
AC-B	April	0	0	8	17	31
	May	0	0	3	15	25
	June	0	0	6	40	49
	July	0	0	7	15	20

(Collins et al., 1986). Fig. 4 shows the relative changes in the different molecular size fractions during treatment.

The average removal efficiencies of NOM are shown in percentages in Table 2. Coagulation with aluminium sulphate decreased the NOM content effectively and led to the total disappearance of the first peak, i.e., the largest MW NOM. After sedimentation, the heights of the second and third peaks were reduced by 90% and 48% and after flotation by 93% and 55%, respectively, with flotation slightly more effective in removing NOM. Flotation seemed somewhat more efficient than sedimentation especially in the removal of HMW matter. The reduction in the sum of the peak heights was 71% and in terms of TOC 51%. The results coincide with those of Vuorio et al. (1998), who found that chemical treatment with subsequent sand filtration decreased NOM effectively and removed the largest MW NOM. No significant changes were observed in their study in the amount of the lowest MW NOM. Vuorio et al. (1998) observed that the sum of peak heights decreased by 66%, while the TOC measurement indicated only a 52% removal of NOM.

3.4. Effect of activated carbon filtration on the MWD of NOM

Activated carbon filtration could remove no more of the high molecular weight substances, but was instrumental in reducing the amount of IMW and LMW matter. AC-A reduced the height of the third, fourth, and fifth peak by about 16%, 26%, and 33% and AC-B by about 6%, 17%, and 21%, respectively. When AC-A was regenerated in the spring (May 25, 2000), the two filters differed in performance immediately after the event (Table 3).

Table 4

Pearson correlation coefficients between different NOM measurements ($n = 106$)

	KMnO ₄	UV ₂₅₄	TOC
SEC (sum of peak heights)	0.961	0.986	0.959
KMnO ₄		0.972	0.943
UV ₂₅₄			0.965

As shown in Table 3, AC-A was more efficient than AC-B in the removal of NOM when calculated as the height of the third, fourth, and fifth peak by 23%, 15%, and 26%, respectively, right after regeneration. In July, the efficiencies were a little lower, but still the AC-A was better than AC-B. In general, AC was the most important factor in removing IMW and LMW organic matter.

3.5. Correlation between different techniques of NOM measurement

The Pearson correlation coefficients among the different NOM measurement techniques are shown in Table 4. As expected, HPSEC and UV₂₅₄ correlated best, and though TOC yielded higher values than the other techniques, they yet correlated well with each other. In general, TOC gave higher results than the other techniques evidently because UV₂₅₄ absorbance cannot detect all compounds present in the smallest molecular weight fractions. This may lead to an underestimation of the NOM content measured as UV₂₅₄ in samples where LMW organic matter is prominent. In turn, as the TOC analyzer may not be able to oxidize large molecules, TOC concentration may be underestimated in raw water.

Good correlation was also achieved in other studies (Vuorio et al., 1998; Kainulainen et al., 1994; Vartiainen et al., 1987), where TOC, KMnO₄, and UV absorbance showed the strongest correlation with the mid-sized fractions of NOM.

4. Conclusions

Even though little seasonal variation was detected in the NOM content in raw water with different measurement techniques, the treatment process is not affected by the quality of raw water, and the quality of the treated water remains fairly stable. Raw water sources in Finland are large and residence times are long. They do not react to seasonal variations so easily than river sources or small water systems. Purified water is affected more by the functioning of the treatment process than the quality of raw water.

LMW matter is more difficult to remove than HMW and IMW NOM, which can be easily removed by coagulation. However, the removal of the smallest molecular size fractions can be enhanced by optimising the water treatment process, e.g., by conditioning the AC filters. By enhancing the LMW matter removal, the quality of water will improve relating to, e.g., DBP formation and microbial regrowth in the distribution line.

Size exclusion chromatography is a fast and relatively easy method and provides useful information about the type of NOM in the water sample. In comparison with traditional methods like TOC, it yields additional information about the removal and transformation of NOM and can hence be used as a tool for routine analysis in water

treatment plants especially in determining the function of AC filters.

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II

Efficiency of the activated carbon filtration in the natural organic matter removal.

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Efficiency of the activated carbon filtration in the natural organic matter removal

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Abstract

The removal and transformation of natural organic matter were monitored in the different stages of the drinking water treatment train. Several methods to measure the quantity and quality of organic matter were used. The full-scale treatment sequence consisted of coagulation, flocculation, clarification by flotation, disinfection with chlorine dioxide, activated carbon filtration and post-chlorination. High-performance size-exclusion chromatography separation was used to determine the changes in the humic substances content during the purification process; in addition, a UV absorbance at wavelength 254 nm and total organic carbon amount were measured. A special aim was to study the performance and the capacity of the activated carbon filtration in the natural organic matter removal. Four of the activated carbon filters were monitored over the period of 1 year. Depending on the regeneration of the activated carbon filters, filtration was effective to a degree but did not significantly remove the smallest molar mass organic matter fraction. Activated carbon filtration was most effective in the removal of intermediate molar mass compounds (range 1000–4000 g/mol). Regeneration of the carbon improved the removal capacity considerably, but efficiency was returned to a normal level after few months.

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Keywords: High-performance size-exclusion chromatography (HPSEC); Natural organic matter (NOM); Water purification; Activated carbon (AC) filtration

1. Introduction

Diverse organic compounds generated by the biological processes both in a water body and in a surrounding watershed are found in all surface waters. These compounds are referred to as the natural organic matter (NOM). One common approach for characterizing NOM is to divide the mixture into the hydrophilic and hydrophobic fractions. The hydrophilic fraction includes, e.g. carboxylic acids, carbohydrates and proteins, while the hydrophobic fraction includes so-called humic substances (HS) (Croue et al., 2000). HS is a term referring to a broad class of interrelated compounds, including, for example, humic and fulvic acids. Compositions of HS vary from source to source with respect

to, e.g. solubility and reactivity (Aiken et al., 1985; McCreary and Snoeyink, 1980).

NOM is important in a water treatment process due to its role as precursor to the formation of chlorination by-products as well as its role in the concentration and transport of inorganic and organic pollutants (Collins et al., 1986). NOM can be removed from water by traditional treatment processes such as chemical coagulation, or by advanced techniques like activated carbon adsorption and nanofiltration (NF) (Owen et al., 1995). The high molar mass (HMM) matter is proved to be more amenable to removal in the coagulation/flocculation process than the low molar mass (LMM) material, particularly that fraction with an apparent molar mass (AMM) of <500 g/mol (Matilainen et al., 2002; Collins et al., 1986). Coagulation prior to the granular activated carbon (GAC) filtration removes particles that might clog the GAC filter. Coagulation also removes NOM, which reduces the loading on the GAC filters (Jacangelo et al., 1995). Previous studies

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have shown that coagulation can significantly increase both bed life and the adsorptive capacity of NOM on GAC (Semmens et al., 1986; Hooper et al., 1996).

GAC is an effective adsorbent used widely for drinking water treatment. Its main use is the removal of micro-pollutants such as pesticides, industrial chemicals, tastes and odors and algal toxins (Newcombe, 1999). The adsorption of compounds to the GAC is influenced by the structural and the chemical characteristics of the carbon surface (Newcombe, 1999; Karanfil et al., 1999). GAC adsorbs NOM to some degree (Jacangelo et al., 1995). The adsorption behaviour of NOM is particularly difficult to understand due to its heterogeneous nature (Newcombe, 1999). McCreary and Snoeyink (1980) noticed that the extent of adsorption of the HS decreased with increasing total carboxyl groups. In many studies the LMM matter was noticed to be more amenable for adsorption than the HMM organic matter mainly due to size exclusion effect (McCreary and Snoeyink, 1980; Karanfil et al., 1999; Newcombe et al., 2002). According to study by Newcombe et al. (2002) the adsorption of NOM is controlled predominantly by the relationship between the molecular size distribution (MSD) of NOM and the pore size distribution of the carbon. The lifetime of the GAC filters can be expanded by reactivation of the carbons (Hyde et al., 1987). However, the thermal reactivation can result in an enlargement of the macropores in the carbon because of burn-off effects and increase the removal of the HMM organics and decrease the LMM matter removal (Boere, 1992).

Chlorine dioxide (ClO_2) is used in the water treatment train mainly as preoxidant and disinfectant. The application of GAC adsorption subsequent to water preoxidation by ClO_2 may lead to the formation of organic by-products due to interactions between GAC, NOM and ClO_2 (Swietlik et al., 2002). Swietlik et al. (2004) noticed that ClO_2 caused a break-up of the large molecules and altered the MSD of NOM towards smaller molecules. On the contrary, oxidation with small doses of ClO_2 can increase the molar masses (MM) of some organic matter molecules (Swietlik et al., 2002). Swietlik et al. (2002) also demonstrated that even a small dose of ClO_2 may significantly influence the adsorptivity of the NOM onto GAC. They concluded that after ClO_2 oxidation the HMM NOM adsorbed on the GAC filter to the higher level in comparison with the unoxidized NOM. The adsorption of the LMM (<500 g/mol) NOM was decreased after ClO_2 oxidation. Their explanation was that part of the LMM NOM was insignificantly affected by the oxidant. Therefore this fraction was relatively polar and did not absorb onto the carbon surface.

The aim of this study was to measure the organic matter content and its transformation in the water treatment train. The high-performance size-exclusion chromatography (HPSEC) fractionation was used as the measuring technique. In addition to HPSEC, also some conventional methods were used. Special attention was paid to the monitoring of the efficiency of the GAC filtration to remove NOM, and

the influence of the age and regeneration of the filters on the NOM removal capacity.

2. Materials and methods

2.1. Rusko Water Treatment Plant

The raw water for the treatment plant is pumped from the Lake Roine, 7 km southeast of the plant. Lake Roine is approximately 52 m² wide and 25–35 m in depth. The raw water intake pipe goes to the depth of 4–5 m, 200 m from the shore. The Rusko Water Treatment Plant produces 65% of the distributed drinking water for the city of Tampere, Finland. The maximum treatment capacity is 55 000 m³/day and an average water flow is about 1400 m³/h. The raw water source is fairly typical surface water source in Finland: alkalinity is low (about 0.25 mmol/l), turbidity is fairly low (about 2 FTU) and the NOM content measured as total organic carbon (TOC) is approximately 5 mg/l. The treated water has a TOC value of about 2.5 mg/l.

The treatment process at Rusko consists of chemical addition ($\text{Al}_2(\text{SO}_4)_3$), which was added 25–33 g/m³, followed by flocculation and clarification with flotation, chlorine dioxide (ClO_2) disinfection, GAC filtration, and post-chlorination (Fig. 1). The purpose of the ClO_2 addition is to disinfect the water and to control taste and odor problems and it was added 0.2 g/m³. Chlorine gas is used in post-chlorination to yield a free chlorine residual of 0.3 mg/l in the purified water.

2.2. GAC filters

The 14 GAC filters are ordinary one-layer filters and each of them has a surface area of 30 m² and a bed depth of about 115 cm. All similar in structure, the filters are so-called sand replacement filters, in which the GAC replaces the sand to mechanically filter and remove odor and taste from water. The filter contact time with water is 15 min (1600 m³/h). The filters are flushed with water and air after about 40 h of use and the GAC is regenerated every couple of years. Carbons are changed after about three regenerations because the aluminum accumulates into the filter and cannot be removed in regeneration.

In this research four of the filters (characterized in Table 1) were studied. The types of the filters B and C were Filtrasorb TL 820 and filter D Filtrasorb 200. Carbons in filters B and D were changed before the start of the study. Filter C was regenerated twice before the study and during the study in May 2001. Filter A was Aqva Sorb BG-09 and regenerated twice before the study.

2.3. Sampling procedure

Water samples were taken once a week between the middle of September 2000 and the end of September 2001, a total of 12 months. Samples were taken from the following stages of the treatment sequence: (1) raw water, (2) water after the flotation, prior to ClO_2 addition, (3) water after four parallel AC filters (AC-A, AC-B, AC-C and AC-D) before chlorination, and (4) combined purified water from all 14 GAC filters (see Fig. 1). Basic water analyses were done at the day of the sampling. The 10 ml samples were collected and frozen until analysed with HPSEC and UV₂₅₄ during the year 2001.

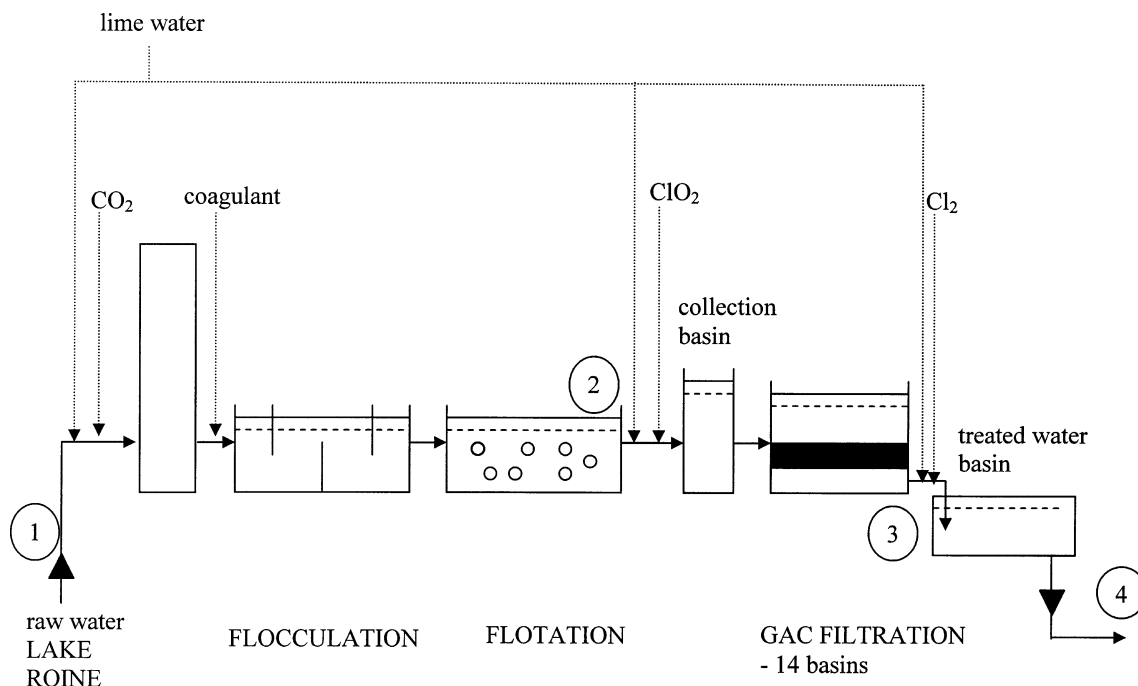


Fig. 1. Diagram of the Rusko Water Treatment Plant.

2.4. Analysis

The basic water quality parameters were measured in the laboratory of the Rusko Water Treatment Plant. TOC samples were measured according to the SFS-EN 1484 (2001) standard and by using a Shimadzu TOC-5000A with a high sensitivity catalyst. Total organic material was measured by the KMnO_4 oxidation method according to the Finnish Society of Food Science and Technology guidelines. Hardness, alkalinity, turbidity and colour were measured according to the SFS 3003 (1987), SFS 3005 (1981), SFS-EN ISO 7027 (2000) and SFS-EN ISO 7887/part 4 (1995) standards, respectively.

UV_{254} and HPSEC measurements were done on the frozen samples during the year 2001 at the laboratory of the Tampere University of Technology. UV_{254} absorption was measured with a Shimadzu UV-1601, UV-VIS spectrophotometer. Before the measurement, the raw water samples and the samples after flotation were filtered through a Gelman 0.45 μm membrane. HPSEC samples were first filtered through a Gelman 0.45 μm membrane and then size-exclusion fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector ($\lambda=254$) and a TSKgel G3000SW 7.5 mm(ID) \times 30 cm column. Pre-column was not used. Sodium acetate (0.01 M) was used as

eluent at a flow rate of 1 ml/min. Injection volume was 30 μl . Method was selected and performed based on results from earlier studies (Vartiainen et al., 1987; Peuravuori and Pihlaja, 1997).

Heights of the peaks in the chromatogram were used in data analysis (Peuravuori and Pihlaja, 1997; Vartiainen et al., 1987). The height of the peak in the HPSEC chromatogram refers to the amount of the NOM in the specific molecular size fraction. The sum of all the peak heights (SOPH) in the chromatogram represents the total amount of the NOM capable of UV adsorption in the sample, with the peak having the lowest retention time referring to the highest MM and the peak having the highest retention time to the lowest MM NOM. Determination of the AMM for the different peak fractions is illustrated in Matilainen et al. (2001). Determination was done with the ultrafiltration (UF) fractionation. The values were calculated according to the method reported by Logan and Jiang (1990). AMM for the different peak fractions are defined roughly as >5000 g/mol, 4000–5000 g/mol, 3000–4000 g/mol, 1000–3000 g/mol, 500–1000 g/mol and <500 g/mol for the peaks I, II, III, IV, V and VI, respectively. The peaks I and II are here referred to the HMM organic matter with the AMM >4000 g/mol, the peaks III and IV to the intermediate molar mass (IMM) organic matter with the AMM range of 4000–1000 g/mol

Table 1

The type and regeneration conditions of the GAC filters studied in the Rusko Water Treatment Plant

	AC-A	AC-B	AC-C	AC-D
Name	Aqua Sorb BG-09	Filtrisorb TL 820	Filtrisorb TL 820	Filtrisorb 200
Manufactured in	China	Belgium	Belgium	Belgium
Raw material	Bitumic coal	Bitumic coal	Bitumic coal	Bitumic coal
Iodine value	950 mg/g	900 mg/g	900 mg/g	850 mg/g
Granular size	90%, 0.4–1.4 mm	>91%, 0.9–2.0 mm	>91%, 0.9–2.0 mm	0.6–0.7 mm
Taken in use	13.7.1995	13.6.2000	1.12.1994	29.9.2000
Regenerated	4.4.1998 25.5.2000		12.4.1997 15.5.1999 11.5.2001	

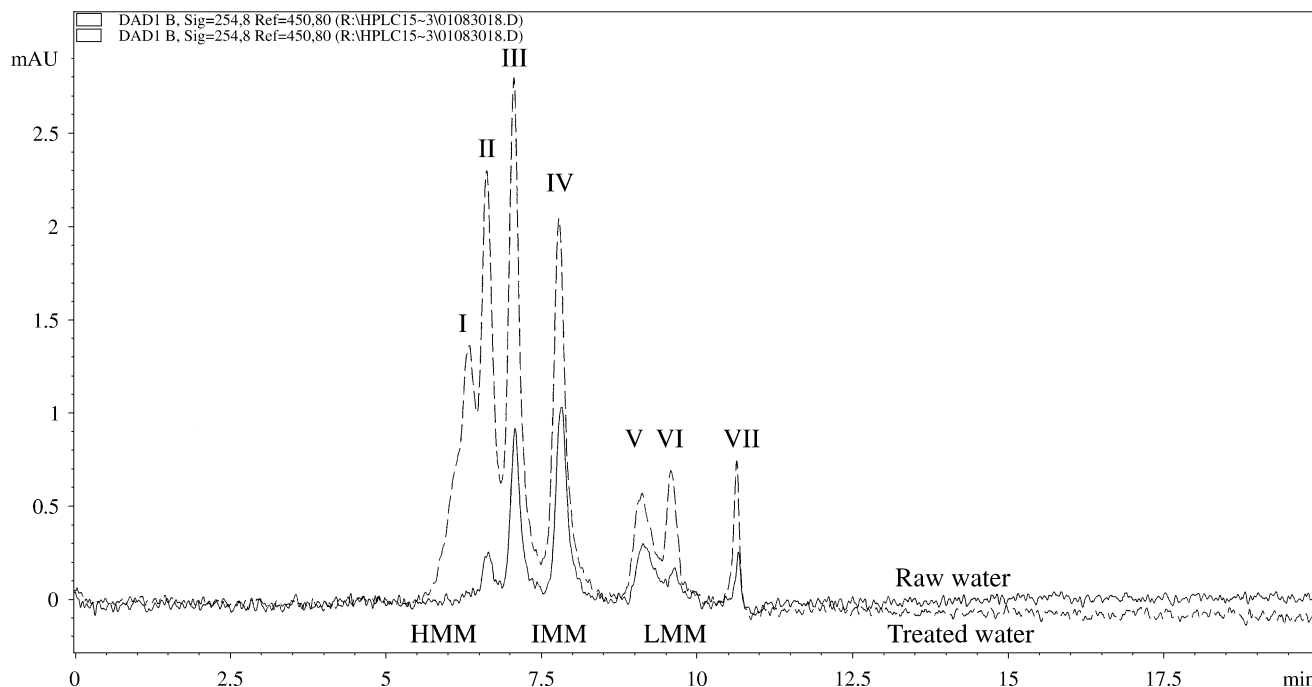


Fig. 2. HPSEC chromatogram of the raw and the treated water samples from the Rusko Water Treatment Plant. The components are eluted in order of decreasing molecular sizes, the small molecules are the last to elute from the column (high molar mass (HMM) matter represents peaks I and II, intermediate molar mass (IMM) peaks III and IV and low molar mass (LMM) peaks V–VII).

and the peak V to VII to the LMM organic matter with the AMM <1000 g/mol (see Fig. 2).

3. Results and discussion

3.1. NOM removal in the treatment train

On average, the treatment process removed 69%, 53%, 77%, 95% and 84% of NOM measured as KMnO_4 , TOC, UV_{254} , turbidity and colour, respectively (Table 2). In the HPSEC measurements, five to seven peaks were found in the raw water samples (Fig. 2). Other researchers have obtained similar patterns on the Finnish surface water samples (Mylykangas et al., 2002; Nissinen et al., 2001; Vuorio et al., 1998; Vartiainen et al., 1987). However, it must be emphasized that the HPSEC column gels might have charge repulsion effects (Peuravuori and Pihlaja, 1997), as well as adsorption interactions with the humic compounds (Mylykangas et al., 2002), which can affect the measurement of the NOM with the HPSEC. When using UV adsorption as a detection method, one should also remember that small aliphatic compounds do not adsorb UV light due to the lack of conjugated double bonds, and thus are not indicated by the UV_{254} measurements. Still, the similar TSK columns as ours have been used for NOM measurements for more than 17 years and the method has proved to be highly informative in studying changes in the MSD of NOM (Mylykangas et al., 2002; Nissinen et al., 2001; Vuorio et al., 1998; Peuravuori and Pihlaja, 1997; Vartiainen et al., 1987).

Calculated as the sum of the peak heights (SOPH) on the chromatogram, the total removal of the NOM was 75% at the treatment process when the yearly average results of the raw and treated water were compared (Fig. 3). The raw water consisted mostly of the HMM and the IMM NOM (Fig. 2). The treated water

had very small amount of HMM matter left and also the IMM matter was diminished considerably. The removal of the LMM compounds was the most inefficient (Fig. 3).

3.2. NOM removal on the coagulation

Coagulation/flocculation followed by flotation removed efficiently the HMM organic matter. The highest MM fraction (>5000 g/mol) was completely removed and the second highest (4000–5000 g/mol) by over 90%. About 60% of the IMM matter remained

Table 2

Average results of water quality parameters measured at the Rusko Water Treatment Plant laboratory (19.9.2000–27.9.2001)

		Raw water			Treated water		
		Average	Min	Max	Average	Min	Max
KMnO_4	mg/l	17	15	19	5.2	3.2	7.8
(n=49)							
DOC (n=13)	mg/l	5.4	4.6	5.8	2.7	2.1	3.1
TOC (n=248)	mg/l	5.5	4.3	7.6	2.6	1.7	3.4
UV_{254}	cm^{-1}	0.13	0.11	0.15	0.03	0.02	0.04
(n=15)							
pH (n=253)		7.1	6.7	7.4	8.4	7.8	9.0
Alkalinity	mmol/l	0.25	0.23	0.30	0.73	0.57	0.85
(n=253)							
Conductivity	mS/m	6.5	6.1	7.1	14	13	16
(n=55)							
Turbidity	FTU	2.1	0.16	5.5	0.10	0.01	0.23
(n=253)							
Colour (n=50)	mg Pt/l	16	10	25	<2.5	<2.5	2.5
Hardness	$^{\circ}\text{dH}$	1.1	0.96	1.8	3.3	3.0	3.5
(n=54)							

n = maximum amount of measurements.

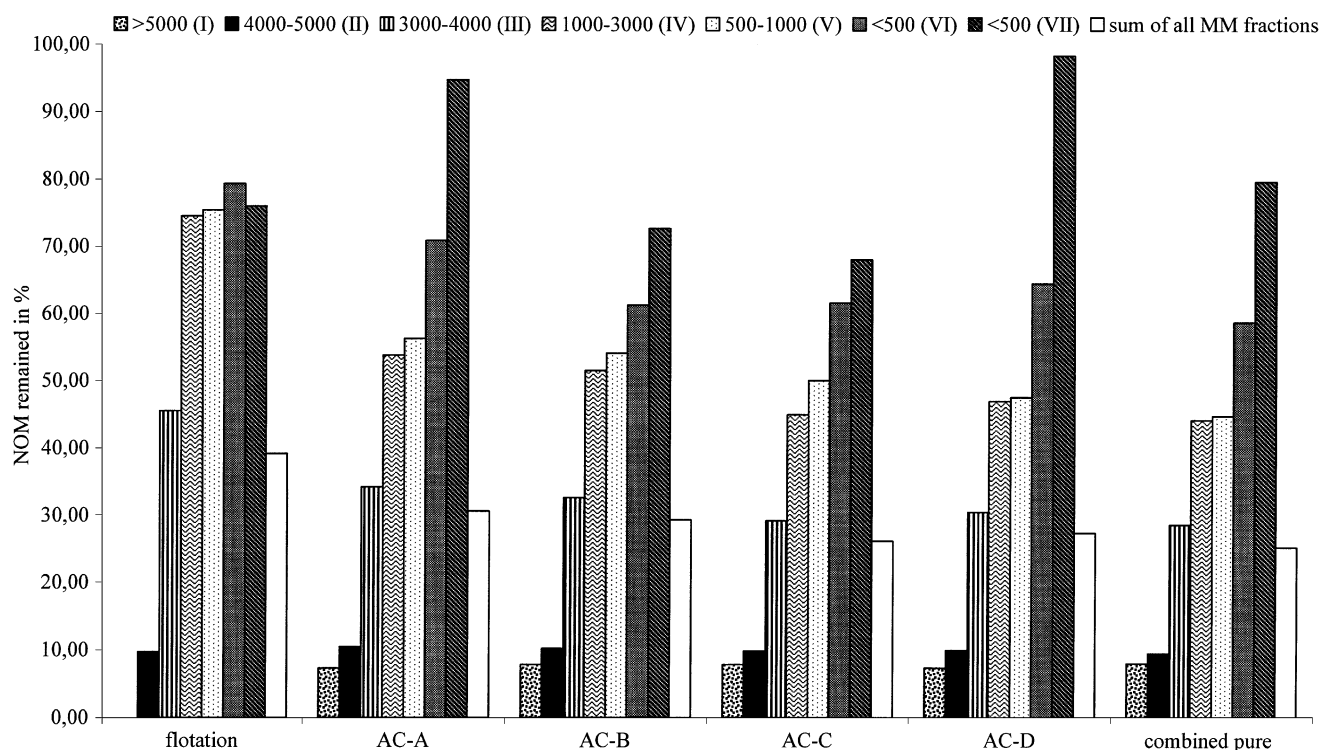


Fig. 3. Different MM fractions of NOM remained (according to the HPSEC results) after each purification process (in % compared to the raw water results) calculated as an average during the investigation 19.9.2000–27.9.2001 ($n=53$).

in water on the coagulation/flocculation and flotation. The removal of the LMM matter was more complicated. About 80% of the LMM matter was still present in water after the coagulation process (Fig. 3). According to the literature, the removal of the LMM fraction in coagulation is difficult because it consists mostly of fulvic acids, which are difficult to destabilize by the aluminum coagulation dosages commonly employed in the water treatment (Collins et al., 1986).

3.3. NOM removal on the GAC filtration

The HMM substances, which were easily removed in the coagulation, reappeared in the GAC filtered water and in the combined purified water from time to time. The overall increase compared to the situation after the coagulation/flotation was nearly 10%. This may be due to the polymerisation of the organic matter in the ClO_2 oxidation before the GAC filtration. It has been reported that small doses of ClO_2 oxidant could increase the molecular weight of some NOM molecules (Swietlik et al., 2002). When compared to the sample collected after the coagulation/flotation, the enhancement of the removal of the IMM fraction in the GAC filtration was in general about 20%. The amount of the LMM matter diminished slightly in the GAC filtration, except of the smallest fraction, which increased occasionally.

The overall efficiency of the parallel GAC filters to remove the different MM fractions of NOM is shown in Fig. 4. The removal or reappearance of the MM fractions in the GAC filtration is compared to the values measured after the coagulation/flotation but prior the ClO_2 oxidation. The highest MM fraction (peak I, >5000 g/mol) disappeared after the flotation. During the study, it reappeared few times in samples taken after the GAC filtration. This happened in every filter in January and February and again in

the summertime. This phenomenon may be due to the polymerisation in the ClO_2 oxidation that was mentioned earlier or breakthrough of the components from the filter bed. The height of the peak II (4000–5000 g/mol) increased and decreased without a clear pattern. Thus, the GAC filtration did not cause any further purification of the HMM (>4000 g/mol) fraction of the NOM. Compared to the situation after the coagulation/flotation, the removal of the NOM represented by the peaks III, IV and V (MM 500–4000 g/mol) was further enhanced in every GAC filter studied. On average, the removal rates were 27%, 30%, 36% and 36% on the filters A, B, C and D, respectively. Swietlik et al. (2002) noticed in their study that the GAC filtered water previously treated with ClO_2 contained exclusively the LMM fraction of NOM with the AMM <500 g/mol compared to the untreated water. This means that after the ClO_2 oxidation the HMM and the IMM fraction of the NOM adsorbed better on the GAC filter. According to our study, the reduction of the LMM matter was complicated. As mentioned before, the small molecules are less visible in the HPSEC measurements because of their weak UV_{254} response resulting from the scarcity of the aromatic structures (Nissinen et al., 2001). Still, in our study, the MM fraction of <500 g/mol (peaks VI and VII) was observed to increase occasionally in the filtered water. Especially in the spring and the summer few large increases in the amount of this MM fraction were noticed. In some cases, the peak VII emerged only on the GAC filtered water. The increase in the amount of the NOM in the MM fraction of <500 g/mol may be due to the breakthrough of the molecules that may have been the decomposition or metabolic products of the bacteria living in the filters (Boualam et al., 2003; Vuorio et al., 1998). The overall poor removal values of the MM fraction of <500 g/mol may also be due to the oxidation of the NOM with ClO_2 just before the GAC filtration. The oxidation may have caused the large

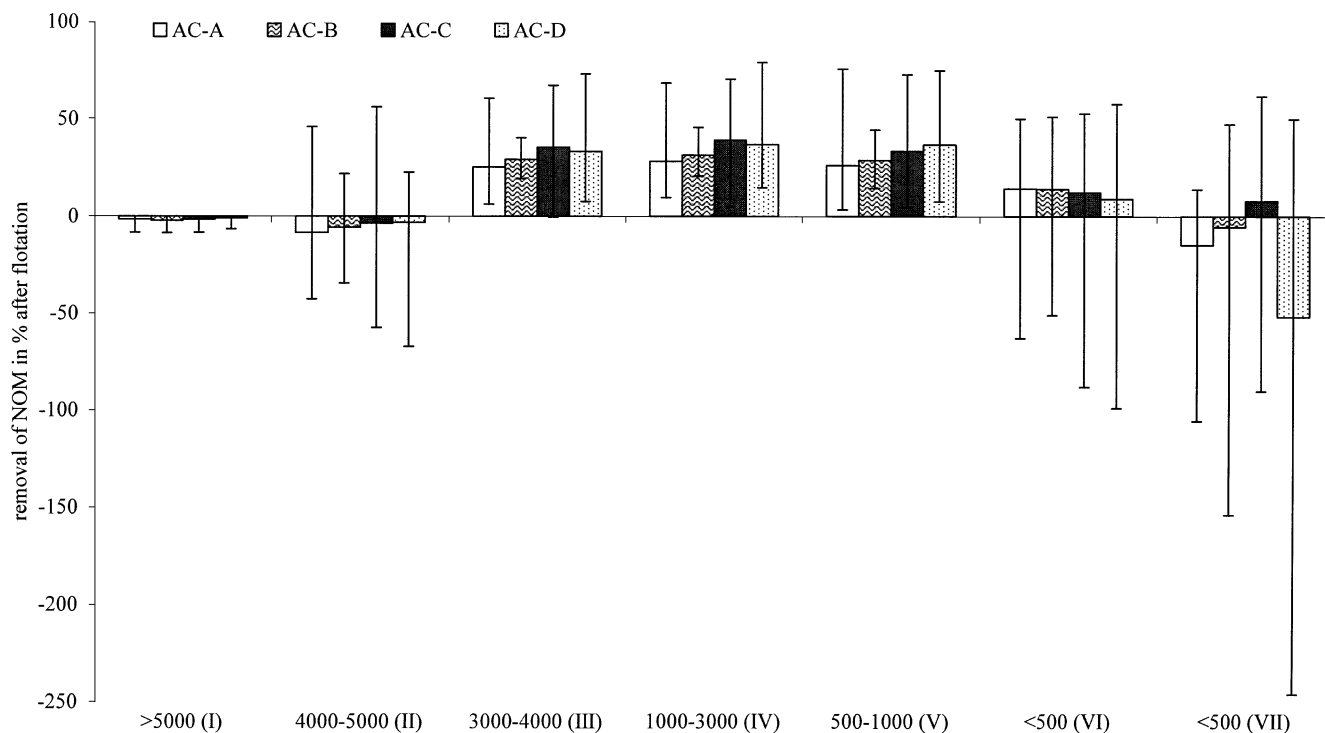


Fig. 4. The efficiency of the GAC filtration to remove the residual MM fractions of NOM remained after coagulation/flotation in percentages with variation bars ($n=53$).

molecules to break-up into the smaller ones (Swietlik et al., 2004). These small molecules do not adsorb well in to the GAC because of their high polarity (Swietlik et al., 2002).

One of the filters was regenerated during the study. Filter AC-C was regenerated for the third time in May 2001. In general, the regeneration significantly enhanced the removal of the NOM, and

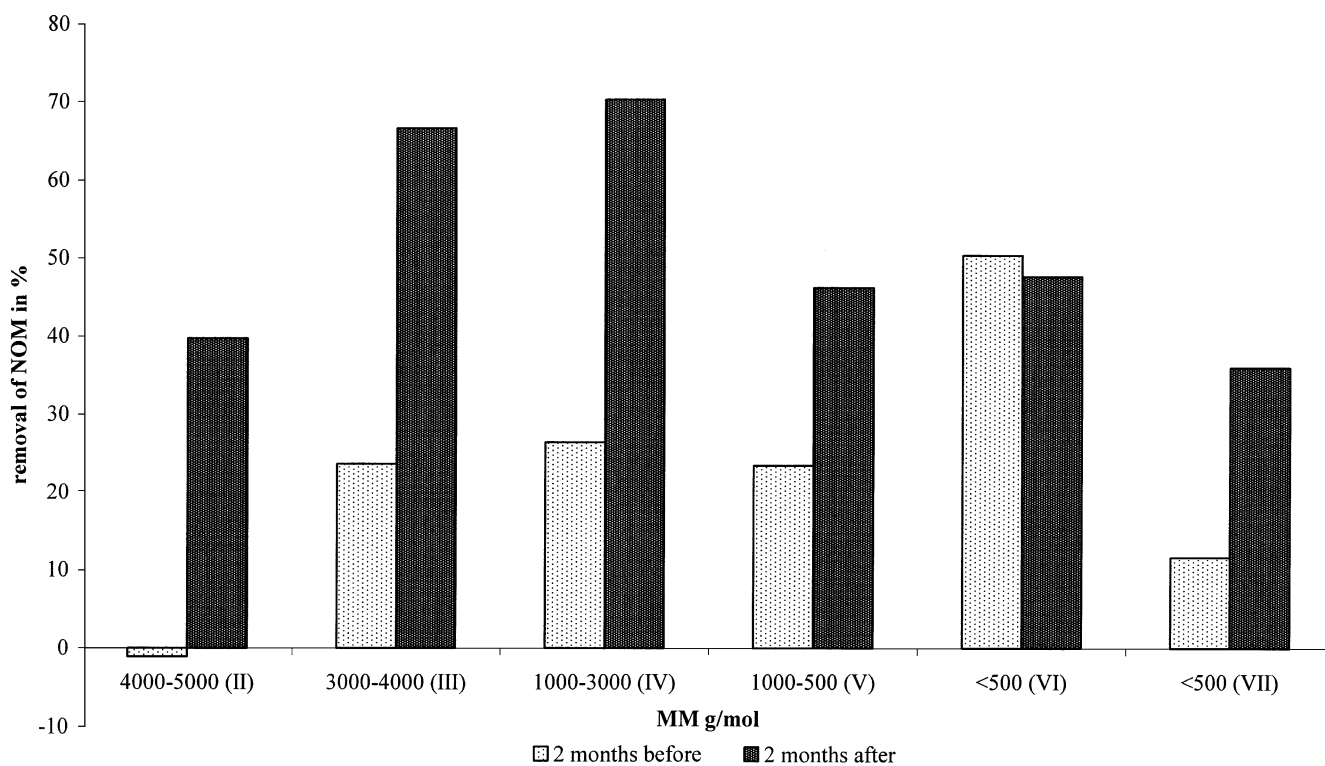


Fig. 5. Influence of the regeneration to the capacity of filter AC-C to remove different MM fractions of NOM after coagulation/flotation. Values are calculated on the average of the percentage removal values 2 months prior to the regeneration to the averages of values 2 months after regeneration.

especially the IMM matter removal (Fig. 5). The IMM matter removal efficiency was approximately 45% higher right after the regeneration. The HMM matter (mainly fraction 4000–5000 g/mol) removal rate increased to about 40% and the increase in the removal rates of the part of the LMM matter was about 30%. However, the removal of this LMM fraction was on average very irregular. Boere (1992) noticed in his study that the removal of the HMM matter organics was constant or increasing after the reactivation and the content of the LMM matter was constant or decreasing. The carbon in AC-D was changed to a new one in the beginning of the study, in October 2000, and same improvement was detected especially in the IMM matter removal, as with regeneration of the filter AC-C. However, the efficiency seemed to be reverted to the same level as before regeneration and change of carbon within few months.

4. Conclusions

The treatment process at the Rusko Water Treatment Plant removed 53–95% of the NOM from the raw water according to different measurement techniques. Measured with HPSEC, the HMM matter was removed almost completely and the IMM matter reduced considerably but the LMM matter was hard to remove in the process.

The capacity of the GAC filtration to remove the organic matter was influenced by the age and the regeneration of the carbons on the filters. In general, different MM fractions remained in water after the coagulation/flotation process was removed in GAC filtration dissimilarly. The amount of the HMM matter did not reduce any further. The GAC filtration was the most effective in the IMM organic matter removal. The LMM organic matter was hard to remove even in the GAC filtration. On the contrary, the LMM organic fraction increased occasionally. This might be due to bacteria living on the filter and release of metabolites from the filter bed. The ClO₂ oxidation prior the GAC filtration most probably decreased the adsorption of the LMM fraction of NOM. Regeneration or change of the carbon enhanced the NOM removal considerably, but within few months efficiency reverted to the level before the operation.

HPSEC was very useful tool for monitoring the organic matter quantity and quality during the water treatment process. Particularly, to the monitoring of the condition of an individual GAC filter, HPSEC can provide the information about the removal efficiency quickly and relatively easily. Hence, the saturation and decrease of efficiency of the filters to remove NOM are noticed immediately.

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III

Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process.

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COMPARISON OF THE EFFICIENCY OF ALUMINIUM AND FERRIC SULPHATE IN THE REMOVAL OF NATURAL ORGANIC MATTER DURING DRINKING WATER TREATMENT PROCESS

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ABSTRACT

The removal of natural organic matter by coagulation in the drinking water treatment train was studied for a period of two years. In the middle of the study, the coagulation/flotation process was modified by replacing the aluminium sulphate by ferric sulphate. At the same time, the filtration unit was enhanced by adding a sand filter unit before the activated carbon filtration and by changing new carbons on to the activated carbon filters. A special aim was to compare the efficiency of the aluminium and ferric coagulants in the organic matter removal by several methods, including high-performance size-exclusion chromatography. A comparison of quantity and characteristics of organic matter in treated water before and after treatment process modification provided an insight into process performance. Approximately 95% of high molar mass organic substances were removed in the process with both coagulation agents. The greatest difference between the coagulants occurred in the removal of organic matter having molar masses of 1000-4000 g mol⁻¹. These intermediate molar mass organic compounds were removed 25 % more efficiently with iron-based coagulant than with aluminium-based. Low molar mass material was poorly removed regardless of the coagulant. On average, only 10 % of this fraction was removed. According to different measuring techniques used in the study, the ferric sulphate coagulation was 10 % more efficient in the overall organic matter removal compared to the aluminium sulphate coagulation. Turbidity removal was more efficient with aluminium than with ferric sulphate. Turbidity even increased during winter in ferric sulphate coagulation. However, turbidity was effectively removed in filtrations.

Keywords: High-performance size-exclusion chromatography (HPSEC), natural organic matter (NOM), water purification, coagulation

INTRODUCTION

Natural organic matter (NOM) is found in varying concentrations in all natural water sources. NOM consists of a range of compounds, from largely aliphatic to highly coloured and aromatic, as well as highly charged to uncharged and has molecular masses (MM) of several hundred to 10 000 or larger. In natural water, NOM carries weakly acidic functional groups such as carboxylic and phenolic groups [1]. NOM causes several problems in the water treatment process. It forms disinfection by-products, causes biological regrowth in the distribution system, contributes to annoying colour, taste and odour problems and acts as a carrier of metals and hydrophobic organic chemicals [2].

The more efficient removal of NOM can be achieved by enhancing the traditional treatment processes such as chemical coagulation, or by providing advanced techniques

like activated carbon (AC) adsorption and nanofiltration [3, 4, 5]. Coagulation can be used prior to AC filtration to remove particles and NOM, thus reducing the loading on the AC filters [2]. Historically coagulation has been employed in water treatment practise to decrease turbidity. However, optimum conditions for turbidity removal are not always the same as those for NOM removal [6, 7]. The effectiveness of coagulation to remove NOM and particles depends on several factors, including coagulant type and dosage, pH, particle and NOM properties, such as size and hydrophobicity, temperature and presence of divalent cations [8]. The major coagulation mechanisms involve charge neutralization of colloidal NOM, precipitation as humates or fulvates and coprecipitation by adsorption on the metal hydroxide [9]. Usually, NOM removal is accomplished by several of these mechanisms at the same time [7].

In order to enhance the removal of NOM, the best way

is to optimise coagulation conditions in regard to pH and coagulant dose [7, 10]. Coagulation pH is reported to be the determinant factor for the removal of NOM [5, 9, 10]. In most studies the optimum values were between 5.2 and 5.8 for aluminium sulphate and from 4.5 to 5.0 for ferric sulphate [10, 11, 12, 13]. The coagulant dose optimising is important because the coagulant overdosing produces extra amount of sludge. Thus, because the metal coagulant addition leads to pH reduction, the addition of alkaline chemicals is needed in order to maintain the coagulation pH within an effective range [6, 14]. On the other hand, under-dosing normally results in excess residual metal in treated water [14] and can cause an increase in processed water turbidity [7]. Moreover, the removal can be enhanced by a choice of a proper coagulant. The most widely used coagulant in drinking water production is aluminium sulphate [15]. Ferric salts have become more common coagulants because of many reasons, including health concerns about the unconfirmed link between aluminium and Alzheimer disease [16, 17]. Many jar-test and pilot studies comparing the effectiveness of one coagulant with another are being undertaken [5, 6, 11, 12, 13, 17, 18]. One coagulant may be significantly more effective than another for a given water, but effectiveness is related also to other factors. According to several studies [5, 10, 11, 13, 18] ferric-based coagulants have been noticed to remove NOM more effectively than aluminium-based ones. Especially the intermediate molecular mass (IMM) fraction of NOM is removed approximately 15 % more efficiently with ferric than with aluminium sulphate [11, 18]. Ferric salts have also been reported to remove NOM more efficiently in low temperature, especially in cold water ($< 3^{\circ}\text{C}$), and low turbidity waters [17, 18]. On the other hand, alum-based coagulants have been shown to remove color more efficiently [13].

Coagulation preferentially removes organic contaminants that are of high molar mass (HMM), naturally hydrophobic and those that possess functional groups able to adsorb to the floc particles [9]. Aluminium sulphate coagulation has been reported to remove HMM organic matter almost completely ($> 95\%$) while IMM matter is only partly removed (approximately 35 %) [19]. The low molar mass (LMM) organic material, particularly the fraction with an apparent molar mass (AMM) of less than 500 g mol^{-1} , is poorly removed [19, 20]. Fulvic acids ($\text{MM} < 2000\text{ g mol}^{-1}$) possess a high carboxylic acidity causing high anionic charge densities and hence are the most difficult to destabilize by coagulant doses commonly employed in water treatment [20, 21].

Ferric salts have proved to be effective in NOM removal in several laboratory tests but their performance in full-scale treatment train has not been reported. The aim of this study was to investigate the organic matter content and its transformation in the water treatment train and especially to study the effect of change of coagulation agent from aluminium sulphate to iron sulphate in NOM and turbidity removal. Aluminium sulphate coagulation data from several years was compared to the data from a one-year period of

iron coagulation in full-scale purification process covering all the seasons. The studied full-scale treatment sequence consisted of coagulation, flocculation, clarification by flotation, disinfection with chlorine dioxide, activated carbon filtration and post-chlorination. The high-performance size-exclusion chromatography (HPSEC) fractionation was used as the measuring technique. In addition to HPSEC, NOM content was determined also with UV_{254} , KMnO_4 and total organic carbon (TOC) methods.

MATERIALS AND METHODS

Rusko Water Treatment Plant

The study was made in the Water Work of Tampere, Rusko Water Treatment Plant. The plant produces drinking water for the city of Tampere, Finland. The raw water is pumped from the Lake Roine, seven kilometers southeast of the plant. The maximum treatment capacity is $55\,000\text{ m}^3\text{d}^{-1}$ and an average water flow is about $1\,400\text{ m}^3\text{h}^{-1}$.

The treatment process consists of lime and coagulant addition, flocculation and clarification with flotation, chlorine dioxide (ClO_2) disinfection, sand filtration (after modification), granular activated carbon (GAC) filtration, and post-chlorination (Fig. 1). The purpose of the ClO_2 addition is mainly to control taste and odor problems but also to disinfect the water. Chlorine gas is used in post-chlorination to yield a free chlorine residual of 0.3 mg l^{-1} in the purified water.

In the beginning of the study (May 2001), all 14 filters were ordinary one-layer GAC filters, operating as parallel filters. Six of the GAC filters were changed to sand filters during the study, in May 2002. After that in-line two-fold filtration was carried out, where water from coagulation/flotation was first filtered through sand filters (6 parallel filters) followed by GAC filtration (8 parallel filters) (Fig. 1). At the same time, the coagulant agent was changed from aluminium sulphate to ferric sulphate.

In this research four of the filters were studied. In the middle of the study (June 2002 forward) two of the four GAC filters were changed to sand filters (S1 and S2). The sand filters consisted of one meter of quartz sand and were designed to mechanically remove some of the TOC and nearly all of the turbidity and residual iron flocs.

In the first half of the study (May 2001 till May 2002) the filters S1 and S2 were GAC filters. S1 was GAC filter of type Filtrasorb TL 820. The carbon in the filter S1 was regenerated in the beginning of the study, May 2001. Filter S2 was GAC filter of type Filtrasorb 200 and the carbon in the filter S2 was changed to a new one in September 2000. Two of the GAC filters (AC1 and AC2) were followed through the investigation. The type of the filter AC1 was Aqua Sorb BG-09. Carbon in the filter AC1 was changed to a new one during the study in June 2002. AC2 was of type Filtrasorb TL 820 and new carbon was changed also during the study in September 2002. All of the GAC filters had a surface area of 30 m^2 and a bed depth of about 115 cm. The contact time with water was

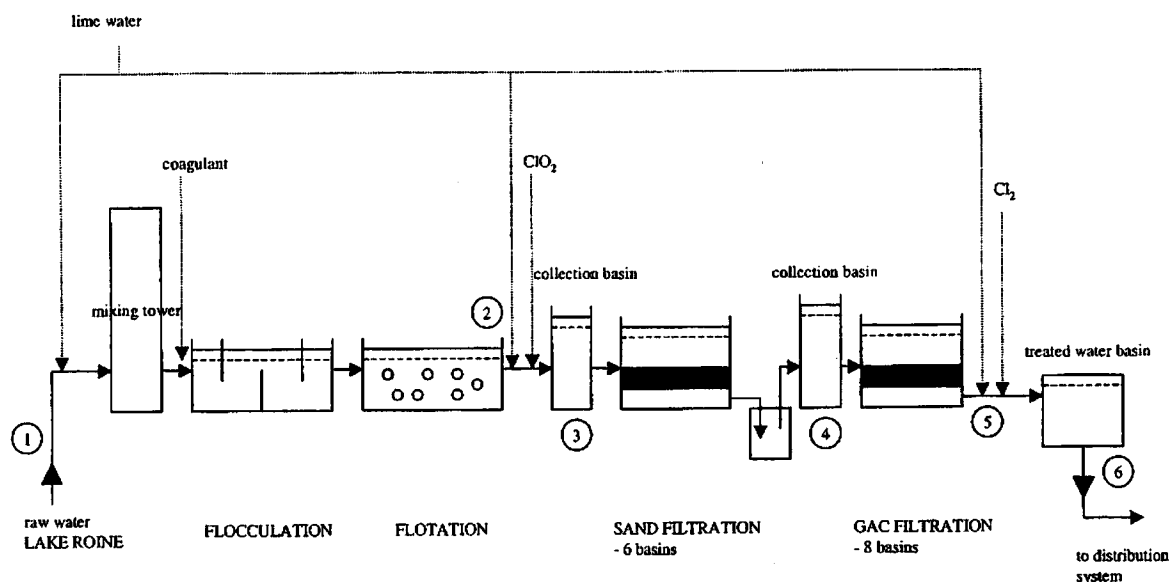


Figure 1. Diagram of the Rusko Water Treatment Plant after the modification. Sampling points are marked with numbers 1-6.

15 min ($1\,600\text{ m}^3\text{h}^{-1}$). The main aim of the filters was to filter and remove residual turbidity as well as odor and taste from water.

Coagulants and Coagulation/Flotation Conditions

The coagulation process was modified during the study. The process modification was made to primarily enhance the removal of NOM. Operating conditions in the coagulation/flotation process in the first half of the study (from May 2001 to May 2002) were as follows: coagulant agent was aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), pH was adjusted to approximately 6, and coagulant doses were around $20\text{--}25\text{ g m}^{-3}$. Coagulant agent was changed to ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) in the middle of the study (May 2002). Iron coagulant type was PIX-322, the pH range in the process was around 5 and coagulant doses were an average $55\text{--}65\text{ g m}^{-3}$.

Sampling Procedure

Water samples were taken once a week between May 2001 and April 2003, a total of two years. Samples were taken from the following stages of the treatment sequence: 1) raw water, 2) water after the coagulation/flotation, prior to ClO_2 addition, 3) water after the coagulation/flotation, after ClO_2 addition, 4) water after the filters S1 and S2, 5) water after two parallel activated carbon filters (AC1 and AC2), and 6) combined purified water from all AC filters (See Fig. 1). Basic water analyses were done on the day of sampling. The 10 ml samples were collected and frozen until analysed with HPSEC.

Analysis

The basic water quality parameters were measured in

the laboratory of the Rusko Water Treatment Plant. TOC samples were filtered through $0.45\text{ }\mu\text{m}$ membrane and they were measured as dissolved organic carbon (DOC) according to the SFS-EN 1484 standard and by using a Shimadzu TOC-5000A with a high sensitivity catalyst. Total organic material was measured by the KMnO_4 oxidation method according to the Finnish Society of Food Science and Technology guidelines. Turbidity was measured according to the SFS-EN ISO 7027/-00 standard. UV_{254} absorbance was measured with a spectrophotometer. The raw water samples and samples after the flotation were centrifuged before UV measurement.

HPSEC measurements were done on the frozen samples at the laboratory of the Tampere University of Technology. HPSEC samples were first filtered through a Gelman $0.45\text{ }\mu\text{m}$ membrane and then size-exclusion fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector ($\lambda=254$) and a TSKgel G3000SW $7.5\text{mm}(\text{ID}) \times 30\text{ cm}$ column. Sodium acetate (0.01 M) was used as eluent at a flow rate of 1 ml min^{-1} . Analysis was performed by the method used in earlier studies [12, 19, 22, 23, 24].

Heights of the peaks in the chromatogram were used in the data analysis. The height of the peak in the HPSEC chromatogram refers to the amount of NOM in the specific molecular size fraction. The sum of all the peak heights (SOPH) in the chromatogram represents the total amount of NOM in the sample with the peak having the lowest retention time corresponding to the highest MM and the peak having the highest retention time to the lowest MM fraction of NOM. Determination of the apparent molar mass (AMM) for the different peak fractions was done by Matilainen et al. [25] and the results are illustrated elsewhere. Determination was done with the ultrafiltration fractionation by the method developed by Logan and Jiang [26]. AMM for the different peak fractions are defined roughly as $> 5000\text{ g mol}^{-1}$, $4000\text{--}5000\text{ g mol}^{-1}$,

3000-4000 g mol⁻¹, 1000-3000 g mol⁻¹, 500-1000 g mol⁻¹ and < 500 g mol⁻¹ for the peaks I, II, III, IV, V and VI, respectively. The peaks I and II are here referred to as the HMM organic matter with the AMM >4000 g mol⁻¹, the peaks III and IV as the IMM organic matter with the AMM ranging 4000-1000 g mol⁻¹ and the peak V to VII as the LMM organic matter with the AMM < 1000 g mol⁻¹.

RESULTS AND DISCUSSION

Water Quality in the Rusko Water Treatment Plant

The chemical characteristics of the raw and treated water in the Rusko Water Treatment Plant during the study are presented in Table 1. The raw water source is a fairly typical surface water source in Finland: alkalinity is low (about 0.25 mmol l⁻¹), turbidity is fairly low (about 2 FTU) and the NOM content measured as DOC is approximately 6 mg l⁻¹. Finnish raw waters are generally soft, with low levels of turbidity, alkalinity and DOC. Rusko produces very high quality treated water, which meets the standards for distributed drinking water in Finland and EU.

In HPSEC analysis, five to seven peaks were found in the raw water as shown in Fig. 2. Other researchers have obtained similar patterns in the Finnish surface water samples in their studies [22, 24, 27.]. The chromatograms are always specific for the different surface waters because the nature of NOM is greatly affected by the surroundings. Raw water consisted mostly of the HMM and the IMM NOM (Fig. 2). Treated water had only a small amount of HMM matter left and also the amount of the IMM matter had decreased considerably. The removal of the LMM compounds was the most inefficient.

NOM Removal According to the HPSEC Results

NOM removal in the coagulation/flotation process

Coagulation/flotation removed the highest MM fraction completely (>5000 g mol⁻¹) and the second highest (4000-5000 g mol⁻¹) over 90 % regardless of the coagulant (Fig. 3). Thus, the HMM matter was effectively removed.

According to our earlier study and the literature [19, 28], coagulation with coagulant doses commonly employed in the water treatment is found to remove primarily HMM and low charge density humic acids.

Change of coagulant from aluminium to ferric sulphate affected the most on the NOM fraction of MM 3000-4000 g mol⁻¹ (Figs. 2 and 3). Roughly 50 % of the organic matter in this fraction remained in the water after the coagulation with aluminium sulphate. In the earlier study made by the authors [19] in the Rusko Water Treatment Plant (August 1999-August 2000), the aluminium coagulation was noticed to remove 55 % of NOM of this size. Thus according to the long-term investigation, 45-50 % of NOM of this size was found to remain in the process. In this study, ferric sulphate coagulation removed 83% of MM fraction of 3000-4000 g mol⁻¹, i.e. only 17 % of this fraction remained in the water after flotation. Thus, this fraction was removed 28 % more efficiently with ferric sulphate than with aluminium sulphate. MM fraction of 1000-3000 g mol⁻¹ was removed about 20 % more efficiently with ferric, thus the overall removal of the IMM matter was about 25 % more efficient with ferric than with aluminium sulphate. According to several studies [5, 10, 11, 12, 18], coagulation jar-tests with diverse coagulants particularly affected the removal of the IMM NOM. Ferric salts were noticed to be an average 15 % more effective than aluminium salts in removing especially the NOM fraction with MM less than 4000 g mol⁻¹.

In our study, the removal of the LMM matter was very poor with both aluminium and ferric sulphate. Nearly 90 % of the LMM matter was still present in water after the coagulation process with both of the coagulants (Fig. 3). LMM fraction is very hard to remove in the coagulation. This was also noticed in the earlier study of the authors [19] where only 6 % of the LMM NOM was removed in the aluminium sulphate coagulation. According to the jar-test studies [11, 12, 18] the LMM fraction was not removed any better even when the process was optimised in regard to NOM removal. However, in the study by Lindqvist et al. [11], almost 40 % removal of the smallest MM fraction was observed if polyelectrolytes were used as coagulation aids in the process.

Table 1. Water quality at Rusko Water Treatment Plant during the study (May 2001-April 2003: Al coagulation from May 2001 until May 2002, Fe coagulation from June 2002 until April 2003).

		Raw Water			Aluminium coagulation			Iron coagulation		
		average	min	max	average	min	max	average	min	max
Temp.	°C				8	1	23	9	1	23
pH		7.1	6.4	7.6	8.3	7.7	9.0	8.4	7.7	9.1
KMnO ₄	mg l ⁻¹	18.5	15.6	31.0	5.7	2.3	8.4	4.2	1.1	6.8
TOC	mg l ⁻¹	5.9	5.2	8.1	2.7	1.2	3.7	2.0	1.0	2.8
Abs.	254 nm	0.140	0.110	0.187	0.032	0.015	0.043	0.023	0.005	0.062
Turbidity	NTU	2.11	0.20	12.00	0.11	0.01	0.35	0.13	0.06	0.36

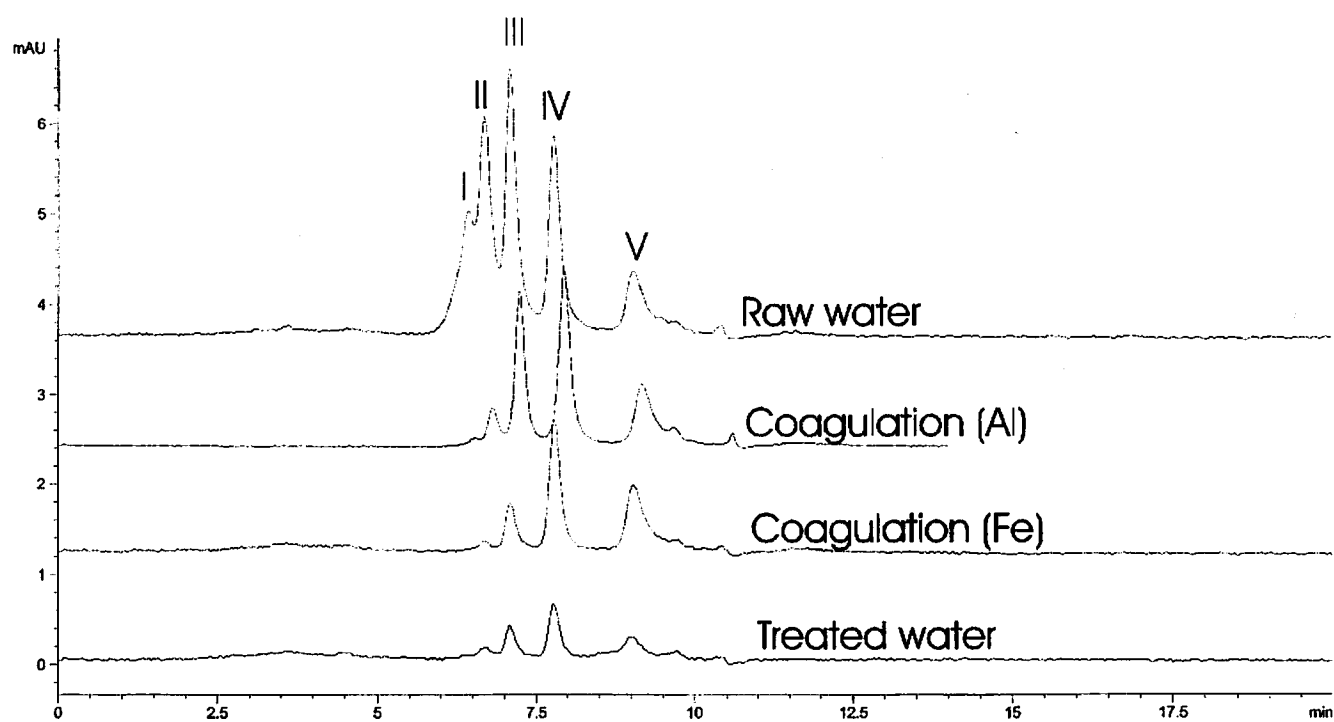


Figure 2. HPSEC chromatograms of raw (above), aluminium sulphate coagulated, ferric sulphate coagulated and treated (below) water samples from Rusko Water Treatment Plant.

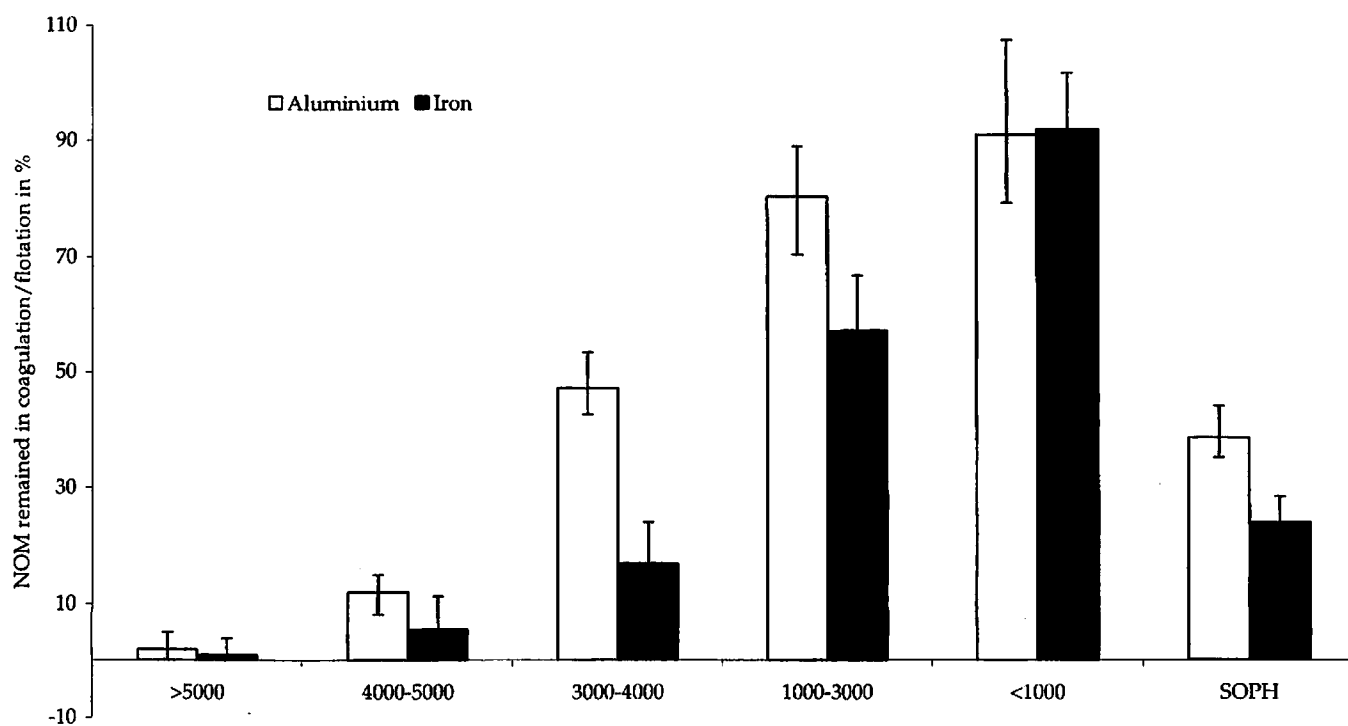


Figure 3. Different MM fractions of NOM (according to the HPSEC measurements) remaining after coagulation/flotation process with aluminium sulphate (May 2001-May 2002) and ferric sulphate (June 2002-April 2003) as the coagulation agent (in % compared to the raw water results) in averages with variation bars.

NOM removal in the overall purification process

In the entire purification process, NOM was removed (compared to the raw water), by 84 % with ferric sulphate as the coagulant and 75 % with aluminium sulphate as the coagulant (Fig. 4). Hence, ferric sulphate was a more efficient coagulant than aluminium sulphate. According to the literature [11, 18] ferric salts resulted in an average 10 % higher NOM removal than aluminium sulphate in the jar-test study.

In our study, HPSEC results measured from samples after the coagulation/flotation, showed that the NOM as sum of peak heights (SOPH) was removed 14 % more efficiently with ferric compared to aluminium sulphate as the coagulation agent. Temperature variations during the year did not affect the NOM removal rates measured as HPSEC.

During the aluminium sulphate coagulation, only the GAC filtration followed the flotation process. Two of the studied GAC filters (S1 and S2) were changed to sand filters in the middle of the study, at the same time as the coagulant agent was changed to ferric sulphate. In this way the age and efficiency of the rest of the GAC filters were increased and filtration costs were decreased. The GAC filter S1 was regenerated in the beginning of the study (May 2001). NOM removal rate in the GAC filter S1 was high during the period May 2001-May 2002. Especially the removal of the IMM and the LMM NOM was generally much higher with this filter

than with other GAC filters studied during the Al-coagulation period (Fig. 4). The efficiency decreased gradually after the regeneration. However, calculated as SOPH, the NOM removal was on average 7 % more efficient than with other GAC filters, which were last regenerated or changed to new ones in spring and fall 2000. During the period of ferric sulphate coagulation (June 2002-April 2003), the carbons in the GAC filters AC1 and AC2 were changed to new ones in June 2002 and in September 2002, respectively. The removal capacities were noticed to increase quite dramatically immediately after the change. However, within a few months the capacities returned to the levels before the change. This was also noticed in the earlier study made by Matilainen et al. [29] in the Rusko Water Treatment Plant. In that study, it was also noticed that the GAC filtration enhanced the removal of the IMM matter of NOM most effectively. In contrast, GAC filtration did not enhance the removal of HMM or LMM matter fractions any further.

In the ClO_2 oxidation, the amount of the IMM and the LMM NOM was slightly decreased (Fig. 4). It is reported that the reaction of ClO_2 with humic fraction of NOM proceeds mainly on an aromatic part of the molecules and generates significant amounts of biodegradable by-products [30]. Hence, the amount of IMM NOM may decrease during ClO_2 oxidation, as can be seen in our results. On the other hand, the NOM oxidation by-products with smaller molecular sizes are

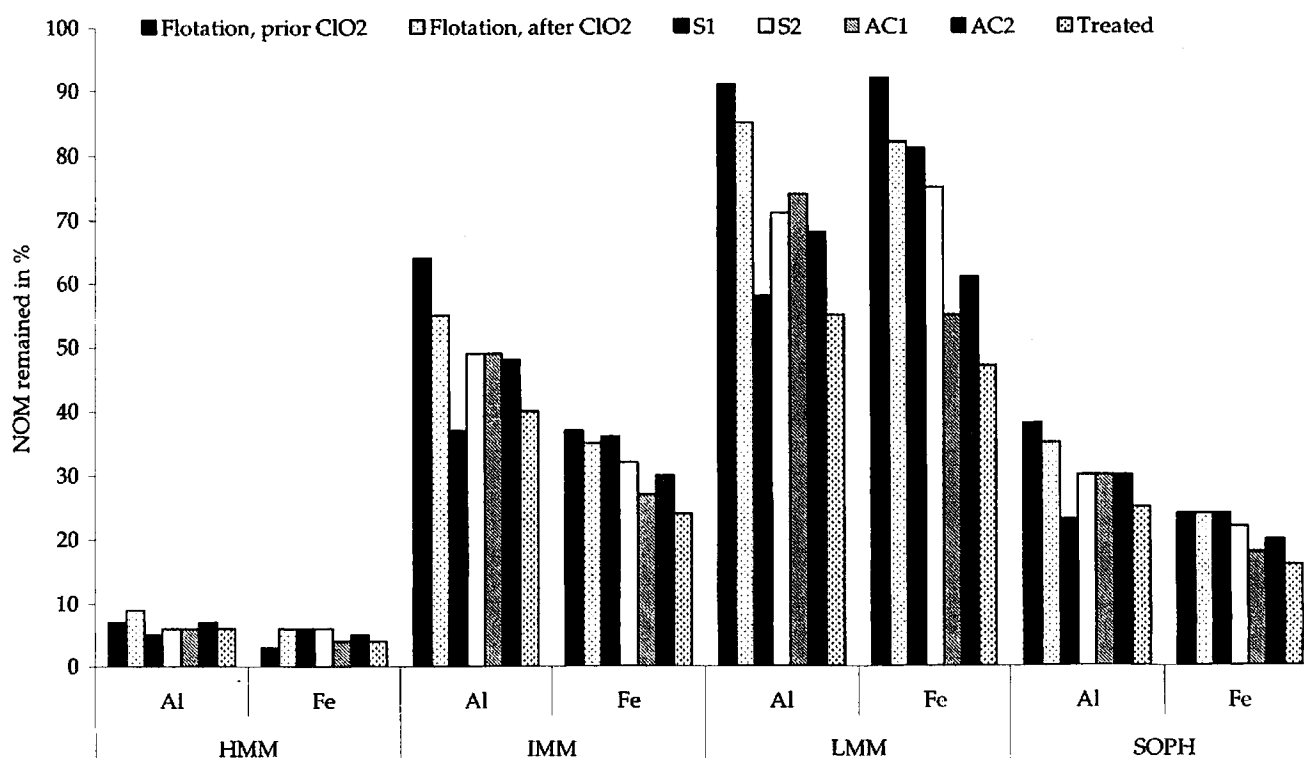


Figure 4. Different MM fractions of NOM remaining (according to the HPSEC results) after the each purification step (in % compared to the raw water results), calculated as an average (Al: May 2001-May 2002 and Fe: June 2002-April 2003). S1 and S2 were GAC filters during the Al-period and changed to sand filters at the beginning of the Fe-period.

less visible with HPSEC method because of their weak UV₂₅₄ response resulting from the scarcity of aromatic structures [27].

NOM and Particle Removal According to DOC, UV₂₅₄, KMnO₄ and Turbidity Measurements

Organic matter was removed approximately 13 % more efficiently after the flotation and 9 % more efficiently after all the purification steps with ferric than with aluminium sulphate as a coagulation agent (Table 2.). According to the literature [13] the iron-based coagulants have been noticed to remove approximately 10-15 % more DOC than the aluminium-based coagulants, with maximum DOC removal values reaching 77 % for ferric and 65 % for aluminium

sulphate. Our results are in agreement with these results. The removal rates measured as DOC were about 20 % lower than measured by UV₂₅₄ (and HPSEC). This indicates that the NOM that contains structures capable of adsorbing UV light, i.e. large aromatic compounds, was preferably removed. Small aliphatic compounds do not absorb UV light due to the lack of conjugated double bonds, and thus are not indicated by the UV₂₅₄ measurements.

Turbidity was removed in the entire treatment train by 93 % when aluminium sulphate was used in the coagulation/flotation process. In contrast, during the ferric sulphate coagulation, turbidity was removed by 86 % in the entire purification process. Aluminium sulphate is also reported to be more efficient at turbidity removal than ferric sulphate in the jar-test study by Tuhkanen et al. [18]. The

Table 2. Organic matter remaining (in % compared to raw water results) after coagulation/flotation and after the entire treatment train using either Al- or Fe-coagulation. The values are calculated as averages (Al: May 2001-May 2002, Fe: June 2002-April 2003).

	After flotation			Treated water		
	KMnO ₄	TOC	UV ₂₅₄	KMnO ₄	TOC	UV ₂₅₄
Aluminium	47	59	nm	30	45	22
Iron	34	46	27	21	33	16

nm= not measured

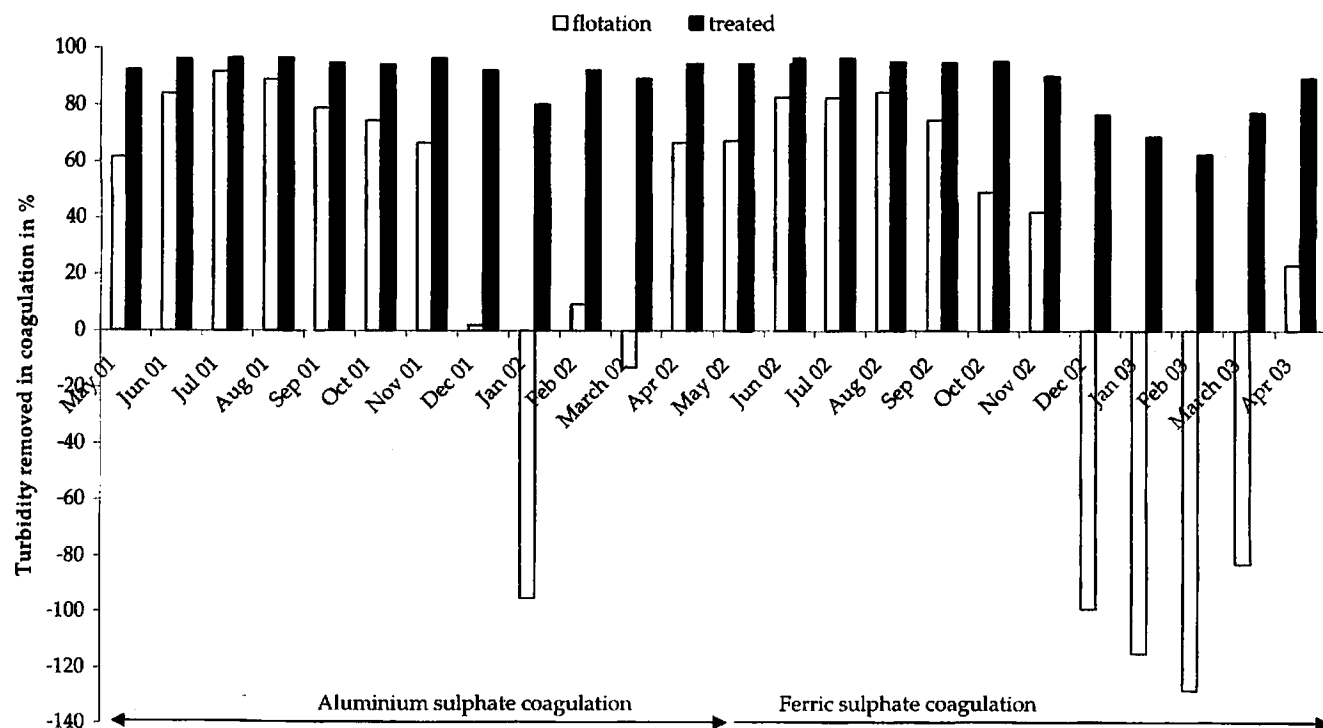


Figure 5. Turbidity removed in the coagulation/flotation and in the entire purification process (in % compared to raw water results). From May 2001 until May 2002 coagulation agent was aluminium sulphate and from June 2002 until April 2003 the coagulation agent was ferric sulphate.

turbidity of the Rusko raw water was the lowest in winter, but turbidity was found to increase in the coagulation/flotation process in the wintertime. Every once in awhile, turbidity of the coagulated water was twice the turbidity of the raw water (Fig. 5) In the literature [6], a shift to a higher optimum pH for turbidity removal was noticed to occur in a cold water period. This shift separated the regions of effective turbidity and DOC removal [6]. Variation in the coagulation pH can cause high turbidity values after the coagulation, because pH affects both the composition of the NOM and the formation of different coagulant-hydrolysis species [6]. Also the flocs formed during the cold water period have been noticed to be smaller than those formed in room temperature, thus impacting on high turbidity values [31]. In Rusko Water Treatment Plant, turbidity is removed effectively by filtrations, especially by sand filtration. However, this excess matter burdens the filters and increases the need for washing. After several jar-test studies [17, 31], ferric coagulants have been found to be less sensitive to low temperatures than alum in regard to turbidity removal because larger and more settleable flocs are formed. In contrast, according to the jar-test study by Tuhkanen et al. [18], aluminium sulphate was performing better than ferric sulphate in cold water, which is in agreement with our study.

CONCLUSIONS

On average, the treatment process in the Rusko Water Treatment Plant removed 74, 61, 81, and 80% of NOM measured as KMnO_4 , DOC, UV_{254} and HPSEC, respectively.

The HMM matter was removed almost completely and the amount of the IMM matter was considerably reduced. The LMM matter was hard to remove in the process and considerable levels were still measured in treated water.

Coagulation with the ferric sulphate was noticed to remove about 10 % more NOM than aluminium sulphate coagulation according to different measuring techniques. Especially the removal of the middle size fraction of NOM was enhanced. It was removed approximately 25 % more efficiently with ferric sulphate than with aluminium sulphate as a coagulant. On average, aluminium coagulation removed 6 % more turbidity than did iron. Turbidity removal was affected by the temperature variations between summer and winter. In wintertime, when water temperature was low, turbidity removal was reduced dramatically and turbidity even increased in the coagulation process, especially with ferric sulphate coagulation. The excess turbidity was, however, effectively removed by sand/GAC filtrations.

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IV

The role of ozonation and activated carbon filtration in the natural organic matter removal from drinking water.

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THE ROLE OF OZONATION AND ACTIVATED CARBON FILTRATION IN THE NATURAL ORGANIC MATTER REMOVAL FROM DRINKING WATER

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ABSTRACT

Aquatic natural organic matter is one of the most important problems in the drinking water treatment process design and development. In this study, the removal of the natural organic matter was followed both in the full-scale drinking water treatment process and in the pilot-scale studies. The full-scale process consisted of coagulation, flocculation and flotation, sand filtration, ozonation, activated carbon filtration and disinfection. The aim of the pilot study was to investigate the influence of the dose and contact time of ozonation, and also the impact of activated carbon filtration, on the removal efficiency of organic matter. Several methods, including high-performance size-exclusion chromatography, total organic carbon content and assimilable organic carbon content measurements were used to characterize the behaviour of organic matter and its removal efficiency. On the full-scale process, total organic carbon was removed by over 90 %. According to size-exclusion measurements, chemical coagulation removed the high molar mass organic matter with an efficiency of 98 %. The ozonation further removed the smaller molar mass fraction compounds by about 27%, while residual higher molar mass matter remained quite unaltered. Activated carbon filtration removed primarily intermediate and low molar mass organic matter. In the pilot-tests, conducted with sand filtered water from the full-scale process, it was noticed, that the ozonation removed primarily smaller organic compounds. The amount of assimilable organic carbon increased with increasing ozone dose, up to 0.4 mg l⁻¹ with the highest ozone dose of 4.0 mg l⁻¹. The activated carbon filtration removed the assimilable organic carbon. Total organic carbon content was not reduced in ozonation.

Keywords: Ozone, activated carbon (AC) filtration, natural organic matter (NOM), drinking water treatment, high-performance size-exclusion chromatography (HPSEC)

INTRODUCTION

Natural organic matter (NOM) is one of the key water quality parameters that affect drinking water treatment processes. It is responsible for the formation of disinfection by-products (DBPs), causes biological regrowth in the distribution system, contributes to annoying colour, taste and odor problems, as well as the transport of inorganic and organic pollutants [1]. NOM can be removed from water by traditional treatment processes such as chemical coagulation [2]. Because of the formation of DBPs, more advanced technologies including oxidation, adsorption and membrane filtration are introduced to remove NOM prior to the disinfection process [3].

Ozonation has been widely used in the treatment of drinking water for disinfection and taste and odor removal. It is used also to enhance the removal of residual organic carbon by increasing the biodegradability of recalcitrant NOM prior

to activated carbon (AC) filtration [2]. The ozonation of NOM in water is still not well understood as NOM consists of a diverse range of compounds with very different chemical properties [4]. According to the literature [2], ozonation results in NOM transformation rather than destruction. It has been reported [2, 5] that ozonation could convert NOM from higher to lower molar mass (MM) fractions or from humic to non-humic compounds. Based on earlier studies [5, 6], the action of ozone on aquatic humic substances leads primarily to a slight abatement of total organic carbon (TOC) content, and a strong degradation of colour and UV-absorbance. Also a slight decrease in the fraction of high molar mass (HMM) compounds of NOM was detected, while low molar mass (LMM) matter fraction was slightly increased. The organic compounds of intermediate molar mass (IMM) fraction develop either way, depending on ozonation dose and conditions.

In the post-ozonation process, ozone is added after the coagulation process and prior to the AC filtration. The HMM

organic matter may be difficult to treat by AC adsorption because large molecules are unable to enter the smaller pores of AC. Still, the NOM of IMM molecules ($1000\text{--}5000\text{ g mol}^{-1}$) can be effectively treated by adsorption. On the other hand, the LMM fulvic acids are relatively hydrophilic and are not amenable to removal by adsorption [5]. Ozonation can convert compounds to enhance the adsorption capacity of the AC [7]. On the other hand, ozonation increases the biodegradability of NOM and hence the removal of NOM by AC is increasingly attributed to the biodegradation rather than adsorption by so called biologically activated carbon [6]. Conversely, the end products of post-ozonation with higher polarity and solubility also reduce the adsorption efficiency of the AC [8].

In this study, the ozonation and AC filtration efficiency to remove NOM after chemical coagulation were investigated, both in full-scale treatment process on two water treatment plants and in pilot-scale experiments. The aim of the pilot-scale experiments was to investigate the influence of the ozone dose and contact time, as well as the AC filtration, on the transformation of NOM and on the removal of NOM. The transformation of the molecular size distribution (MSD) of NOM was investigated with the high-performance size-exclusion chromatography (HPSEC).

MATERIALS AND METHODS

Oulu Water Works

The study was made in the Water Works of Oulu, Kurkelanranta and Hintta Water Treatment Plants. The plants produce drinking water for the city of Oulu, Finland. Raw water is taken from the River Oulu at a depth of 4 meters and the two Water Treatment Plants are situated on opposite

strands of the river. The capacity of the water works are 900 and $1200\text{ m}^3\text{ h}^{-1}$ for Kurkelanranta and Hintta Treatment Plants, respectively. Treatment processes consist of coagulation with ferric sulphate, flocculation and flotation, sand filtration (in Hintta 8 basins and in Kurkelanranta 6 basins), ozonation, AC filtration and disinfection with sodium hypochlorite and ammonium chloride (Kurkelanranta treatment process is in Figure 1).

The ozone dose in the full-scale treatment varies between 0.4 to 1.5 g dm^{-3} . Ozone feed is higher in summer ($0.9\text{--}1.5\text{ g dm}^{-3}$) than in winter time ($0.4\text{--}0.7\text{ g dm}^{-3}$). Ozonation is meant primarily to enhance the biodegradability of NOM before AC filtration, but also to reduce the odor and taste problems as well as enhance possible pathogen removal.

The performances of all four AC filters, in both Treatment Plants, were studied. The filters in Kurkelanranta Treatment Plant are called AC-K1, AC-K2, AC-K3 and AC-K4. The filters were in-line so that water from the filter AC-K1 were filtered through AC-K2 and the water from the filter AC-K3 were filtered also through AC-K4 (see Figure 1). The history of filters: new carbon was placed on AC-K2 in November 2003 and the old carbon from the filter AC-K2 was moved to AC-K1. During the study, in July 2005, carbon in the filter AC-K2 was changed to a new one and the old carbon was moved to AC-K1. In July 2004, before we started our study, regenerated carbon was changed to AC-K4 and the old carbon was moved to AC-K3.

The filters in the Hintta Treatment Plant are referred to as AC-H1, AC-H2, AC-H3 and AC-H4. The filters were parallel and they were last regenerated or a new carbon was changed to the filter as follows: AC-H1 was changed in October 2000, AC-H2 was regenerated in July 2004, AC-H3 was changed in September 2003 and AC-H4 was regenerated in September 2004.

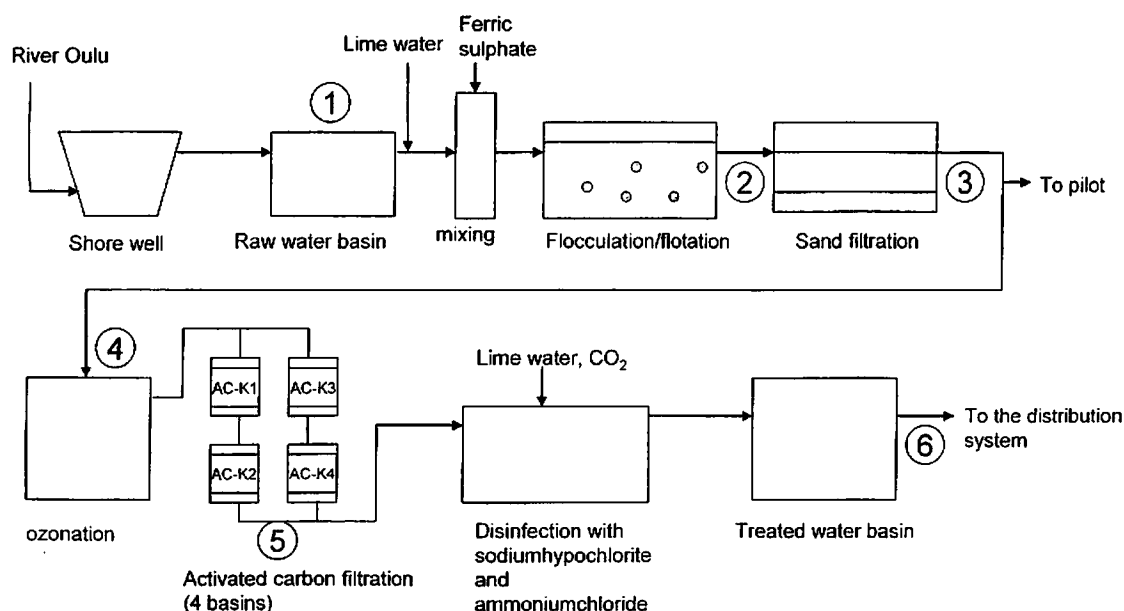


Figure 1. Diagram of the Kurkelanranta Water Treatment Plant. In Kurkelanranta AC filters were paired so that two of them were in-line and pairs were parallel. In Hintta all AC filters were parallel. Sampling points are illustrated in the figure by numbers 1-6.

Pilot-scale Ozonation

The pilot-scale experiments were done on the Kurkelanranta Water Treatment Plant. The ozonation apparatus included ozone generator (Herrmann-laboratory-ozonator LO-50-1), continuous flow column (total volume 45 l; i.d. 0.17 m; height 2 m) and two AC filtration columns (i.d. 0.25 m, height 1.5 m, carbon from the full-scale process from filters AC-K1 and AC-K2). The AC columns were placed in-line as in full-scale process in Kurkelanranta. The batch-test was conducted in a different column (total volume 10 l; i.d. 0.09 m; height 1.7 m).

The water to the pilot was taken after chemical coagulation and flotation and sand filtration from the full-scale process (see Figure 1). Ozone-containing gas was added at the bottom of the columns through a ceramic diffuser. Ozone concentration in water varied between 0.3 and 1.2 mg O₃ mg⁻¹ TOC (ozone feeding dose 2-7.5 mg O₃ min⁻¹).

The first phase of tests was conducted in a batch mode (volume of the column 10 l) with different ozone doses. Other tests were done in continuous flow mode (volume 45 l) and the water was led through the system at 120-130 l h⁻¹. The contact time in ozonation was 18 minutes and empty bed contact time (EBCT) of AC filters about 14 minutes per filter, overall residence time being 28 minutes. Water samples were taken from feed water, ozonated water and after the second AC filter.

Sampling Procedure on Full-scale Process

Water samples were taken once a month between December 2004 and August 2005. Samples were taken from the following stages of the treatment sequence: 1) raw water, 2) water after the coagulation/flotation 3) water after the sand filters 4) water after ozonation, 5) water after four AC filters, and 6) combined purified water from all AC filters (See Figure 1). Basic water analyses were done at the day of sampling. The 10 ml samples were collected and frozen until analysed with HPSEC.

Analysis

The basic water quality parameters were measured in the laboratory of the Oulu Water Works, Hintta Water Treatment Plant. TOC samples were measured according to the Finnish Standard SFS-EN 1484/-97 [9] and by using a Shimadzu TOC-Vcph. Total organic material was measured by the KMnO₄ oxidation method according to the Finnish Standard SFS 3036/-81 [10]. Turbidity and colour was measured according to the Finnish Standards SFS-EN ISO 7027/-00 [11] and SFS-EN ISO 7887/-95 [12], respectively.

Content of assimilable organic carbon (AOC) was measured in National Public Health Institute, Kuopio, according to the modified method [13] of the standard by APHA et al. [14]. In the AOC analyses maximum growth of

Pseudomonas fluorescens P17 and *Aquaspirillum* NOX in the water samples were transformed into the amount of AOC. Inorganic nutrients were added into the samples (N, P, K, etc.) to ensure that microbial growth in water samples was not limited by inorganic nutrients

HPSEC measurements were done on the fresh or frozen samples at the laboratory of the Tampere University of Technology. HPSEC samples were first filtered through a Gelman 0.45 µm membrane and then size-exclusion fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector (λ = 254 nm) and a TSKgel G3000SW 7.5mm(ID) x 30 cm column. Sodium acetate (0.01 M) was used as eluent at a flow rate of 1 ml min⁻¹. Analysis was performed by the method used in earlier studies [15, 16, 17, 18, 19].

Heights of the peaks in the chromatogram were used in the data analysis [16]. The height of the peak in the HPSEC chromatogram refers to the amount of NOM in the specific molecular size fraction. The sum of all the peak heights (SOPH) in the chromatogram represents the total amount of NOM in the sample. The peak having the lowest retention time refers to the highest MM and the peak having the highest retention time to the lowest MM fraction of NOM. Determination of the apparent molar mass (AMM) for the different peak fractions was done by Matilainen et al. [17]. Determination was done with the ultrafiltration fractionation by the method developed by Logan and Jiang [20]. AMM for the different peak fractions are defined roughly as > 5000 g mol⁻¹, 4000-5000 g mol⁻¹, 3000-4000 g mol⁻¹, 1000-3000 g mol⁻¹ and 500-1000 g mol⁻¹ for the peaks I to III, IV, V, VI and VII, respectively. The peaks I to IV are here referred as the HMM organic matter with the AMM >4000 g mol⁻¹, the peaks V and VI as the IMM organic matter with the AMM ranging from 4000-1000 g mol⁻¹ and the peak VII as the LMM organic matter with the AMM < 1000 g mol⁻¹.

RESULTS AND DISCUSSION

Water Quality in the Kurkelanranta and Hintta Water Treatment Plants

The chemical characteristics of the raw and treated water in the Water Treatment Plants during the study are presented in Table 1. The raw water source is fairly typical river water source in Finland: alkalinity is low (about 0.19 mmol l⁻¹), turbidity is fairly low (about 2 FTU) and the NOM content measured as TOC is approximately 12 mg l⁻¹. The amount of NOM measured as TOC is slightly higher than in lake water sources in Finland [19, 21]. The raw water temperature is very low in wintertime (0 °C) compared to summer (about 19 °C).

The raw water quality had a distinct seasonal variation. The highest values of the quality parameters were measured in the spring (April and May), when the river was flooding, and the lowest values were recorded during wintertime

Table 1. Water quality at Kurkelanranta and Hintta Water Treatment Plants during the study.

		Raw Water			Treated Water	
		Average	min	max	Average HINTTA	Average KURKELANRANTA
Temperature	°C	8	0	19		
Colour	mg l ⁻¹ Pt ⁻¹	87	60	140	<5	<5
pH		6.8	6.3	7.0	8.5	8.4
KMnO ₄	mg l ⁻¹	51	42	74	3.9	3.2
TOC	mg l ⁻¹	12.2	10.0	17.2	2.0	2.1
Abs. 254nm*	l m ⁻¹	49.7	38.6	70.9	1.8	1.8
Turbidity	NTU	2.37	0.56	7.70	0.17	0.15

* measured 1.1.-30.6.2005

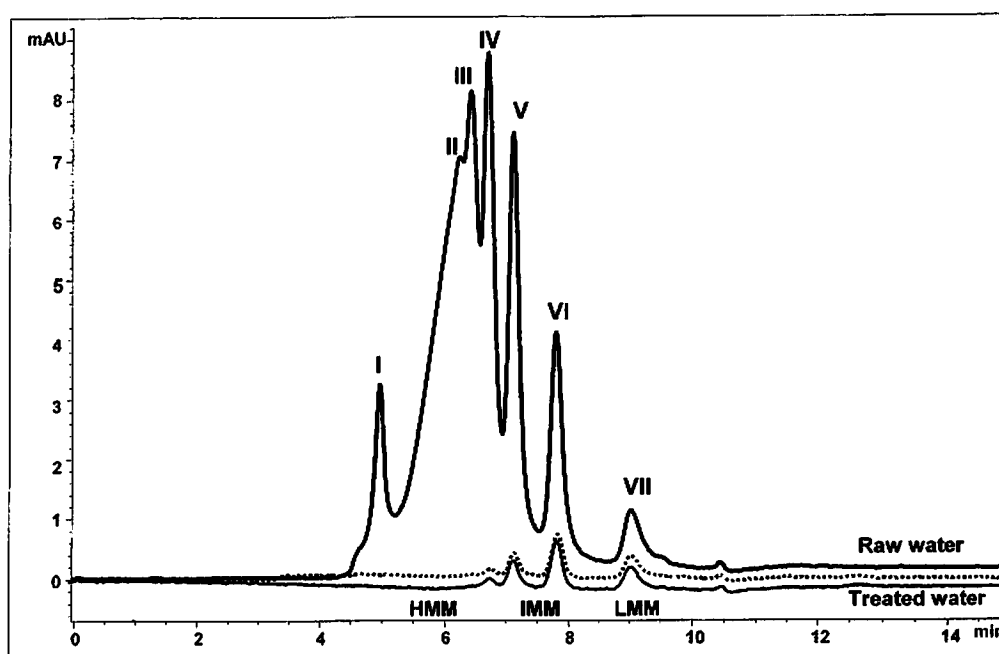


Figure 2. HPSEC chromatograms of the raw water from River Oulu (above) and treated waters from the Hintta (middle) and Kurkelanranta (below) Water Treatment Plants.

(Table 1). Due to a large catchment area of River Oulu, snow melting and heavy rains cause increase in the river flow rate and the amount of organic matter. In the water treatment plants, the increase in the organic matter and the turbidity is controlled by adjusting the coagulant dose. Both plants in Oulu produce very high quality treated water, which meets the standards for distributed drinking water in Finland and the EU.

In the HPSEC analysis, six to seven peaks were found in the raw water as shown in Figure 2. Other researchers have obtained similar patterns on the Finnish surface water samples [15, 21, 22]. When using UV adsorption as a detection method, one should remember that small aliphatic compounds do not adsorb UV-light due to the lack of conjugated double bonds, and thus are not indicated by the UV₂₅₄ measurements. Still, the method has proved to be highly informative in studying changes in the MSD of NOM [15, 16, 18, 19, 21, 22].

Raw water consisted mostly of the HMM and the IMM

NOM (Figure 2). Compared to the typical Finnish lake water sources, the Oulu river water contains more HMM compounds [18, 19] than lake water. In earlier studies with lake water, the peaks I and II were not present in the chromatograms and conversely lake water had an extra group of smaller MM peaks than river water [18, 19]. In Oulu, the treated water had only a small amount of the HMM matter left in water. The amount of the IMM matter had decreased considerably whereas the removal of the LMM compounds was fairly inefficient.

NOM Removal in the Water Treatment Train

NOM removal in the overall process

The purification processes in Hintta and in Kurkelanranta were very efficient concerning the removal of the organic matter. Only about 2 mg l⁻¹ of TOC remained in the treated water, resulting in the TOC removal of about 90 %. According to the HPSEC measurements, the total amount

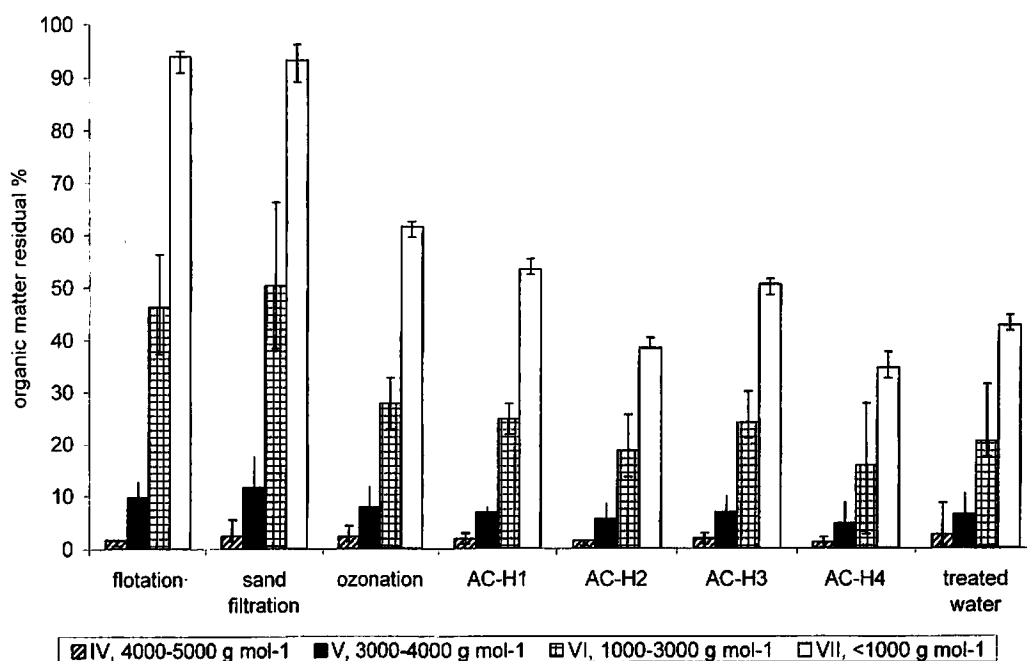


Figure 3. Organic matter remaining, according to the HPSEC measurements, in different MM fractions after each purification step (in percent compared to the raw water results) in Hintta Water Treatment Plant. All AC filters were parallel. Percents are averages from December 2004 to August 2005 with variation bars.

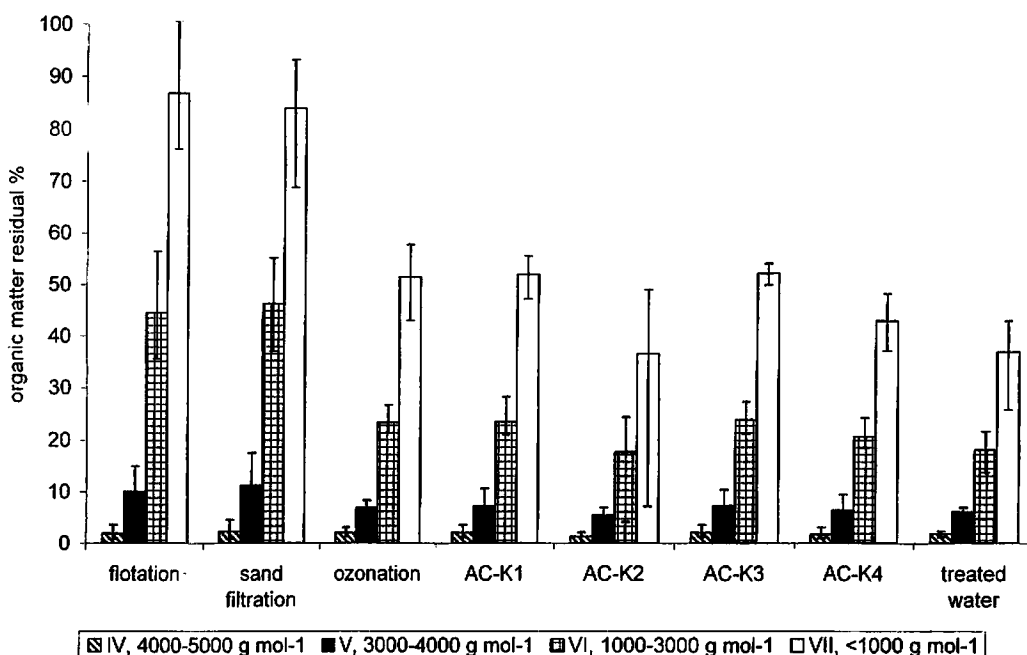


Figure 4. Organic matter remaining, according to the HPSEC measurements, in different MM fractions after each purification step (in percent compared to the raw water results) in Kurkelanranta Water Treatment Plant. AC filters were in pairs: AC-K1 and AC-K2, as well as AC-K3 and AC-K4 were in-line. Percents are averages from December 2004 to August 2005 with variation bars.

of NOM (determined as the sum of peak heights = SOPH) removed in the process was about 95 %. The most abundant NOM molecules in the raw water were the HMM compounds, which were also the most efficiently removed in the treatment

process. In the raw water, 68% of all the NOM was characterized to belong to a HMM fraction. This fraction was almost entirely removed in the process (peak fractions I, II and III were totally removed, and fraction IV considerably),

and only about 2% was remained in the treated water (Figures 3 and 4). The IMM matter accounted for 30 % of all the NOM in the raw water and it was removed with about 87 % efficiency. Only 2 % of the NOM was characterized as being LMM compounds. With an average removal of 60 % this fraction was the hardest to remove in the treatment process applied by the plants.

NOM removal during coagulation/flotation

Almost all of the HMM matter was removed during the coagulation/flotation. The removal rate of 98 % accounted for the entire removal of the HMM matter in the treatment train, i.e. HMM matter was no further removed in the following unit operations. Most of the IMM compounds were removed during this stage, especially the MM fraction of 3000-4000 g mol⁻¹ (peak V), where 90 % was removed during the coagulation/flotation (94 % after all the purification steps). The MM fraction of 1000-3000 g mol⁻¹ (peak VI) was not as effectively removed. About 54 % were removed in the coagulation/flotation. The overall removal rate in the treatment process was 80 %. Only a minimal removal (6-13 %) in the coagulation/flotation was noticed for the LMM compounds. According to the literature [1, 18, 23], coagulation with coagulant doses commonly employed in the water treatment is found to primarily remove the HMM and low charge density humic acids. The LMM matter is harder to remove, because fulvic acids (MM < 2000 g mol⁻¹) possess a high carboxylic acidity, causing high anionic charge densities, and hence are the most difficult to destabilize by coagulant doses commonly employed in water treatment.

NOM removal during ozonation

The ozone feed in the full-scale treatment varied between 0.4 and 1.5 g dm⁻³. Ozone feed was greater in the summer (0.9-1.5 g dm⁻³) than in winter time (0.4-0.7 g dm⁻³). Ozonation seemed to remove primarily the lowest MM compounds (< 3000 g mol⁻¹) (see Figures 3 and 4). The amount of HMM molecules and the larger MM part of the IMM molecules (> 3000 g mol⁻¹) were quite unaltered. In the ozonation, the MM fractions 3000-4000 g mol⁻¹ (peak V) and 1000-3000 g mol⁻¹ (peak VI) were diminished from about 12 % remaining after coagulation/flotation to 8 % and from about 48 % remaining after the coagulation/flotation to 25 %, respectively. The LMM compounds were removed the most effectively in the ozonation. In coagulation/flotation the NOM remaining was 84-93 %, but the amount of NOM was diminished to 51-62 % during ozonation. The removal of NOM was higher in the LMM fraction, than in HMM, which is contradictory to the literature, where ozone is said to remove primarily HMM substances and convert them in to the LMM compounds [6]. However, a strong diminishing in UV-absorption was noticed also in earlier studies, which can mean that NOM was degraded into the lower MM compounds, which do not have any chromophores capable of UV absorption at the wavelength of 254 nm, as is required in our HPSEC measurements.

NOM removal in AC filtration

The NOM removal in the AC filtrations in Hintta and Kurkelanranta was dependent on the regeneration history of the particular AC filters. In Oulu, the AC regeneration frequency is about 2-3 years. The reactivation frequency varies depending on the raw water characteristics, pre-treatment and the water quality criteria set by the management [24]. In Hintta and Kurkelanranta, the residual HMM matter after coagulation/flotation and ozonation was not reduced in the AC filtration. Also the largest molecules in the IMM part were negligibly adsorbed on to the carbon. The highest removal rates were observed for the lower MM part of the IMM matter (1000-3000 g mol⁻¹, peak fraction V) and the LMM compounds (<1000 g mol⁻¹). In the literature [19, 25], the LMM matter has been noticed to be more amenable for adsorption than the HMM organic matter due to size exclusion effect. On the other hand, ozonation prior to AC filtration increases the biodegradability of the NOM and hence the NOM removal by the AC might be attributed to the biodegradation rather than adsorption [6].

In Hintta the filters were parallel and filters AC-H1 and AC-H3 were last regenerated in the years 2000 and 2003, respectively. Their capacities to remove NOM were nearly identical with minor variation during the research period. As expected, the oldest filter AC-H1 had slightly lower removal rates of NOM. Compared to the ozonated water, the further removal of the residual organic matter by the AC was around 3 %, concerning the IMM part (peak fraction VI, 1000-3000 g mol⁻¹) and 9 % for the LMM fraction (<1000 g mol⁻¹), respectively. The capacity was slightly higher during summer months (from June to August) which might indicate some biological activity in the filter. This is supported by the observation that especially the lowest MM NOM was better removed by the AC in the summer.

The filters AC-H2 and AC-H4 were regenerated in the year 2004, just before the research period. In both of the filters, and especially in AC-H4, which was last regenerated, a downward trend in removal capacity was noticed. Good removal capacity was observed in the beginning of the study, but the removal rate of the NOM decreased gradually (see Figure 3, variation in error bars).

In Kurkelanranta the filters were in-line, i.e. water from the filter AC-K1 was further filtered through the filter AC-K2, and water from the filter AC-K3 through the filter AC-K4 (see Figure 1). The old carbon from the second filter in-line was always transferred in to the first one during regeneration or carbon change in the second filters. Hence, the efficiencies of the filters AC-K1 and AC-K3 were slightly lower than the other two filters (average removal percentages were 6 %, 4 % and 9 % for the HMM, IMM and LMM matter, respectively). The filter AC-K4 was regenerated in June 2004. A similar downward trend in NOM removal was seen with this filter than in Hintta filters AC-H2 and AC-H4. The carbon in the filter AC-K2 was changed, in 2003 and the carbon was changed again to a new one during the research, in June 2005. Before the change, the efficiency was similar to the filters AC-

K1 and AC-K3. The removal efficiencies improved quite dramatically after the carbon change. The removal rates were -14 %, 5 % and 15 % for HMM, IMM and LMM matter before the change and 68 %, 76 % and 83 % after the change, respectively. This can also be seen on variation bars in Figure 4.

The Effects of Ozonation on NOM in the Pilot-scale Treatment

HPSEC

The first ozonation test was conducted as a batch test. The effect of the amount and the contact time of ozone to the MSD of the NOM were studied. The tests were done with the ozone feeding dose of $0.34 \text{ mg O}_3 \text{ min}^{-1}$ (test series 1), $1.36 \text{ mg O}_3 \text{ min}^{-1}$ (test series 2) and $3.9 \text{ mg O}_3 \text{ min}^{-1}$ (test series 3). The samples were collected after 2 minutes (1.1, 2.1 and 3.1), 5 min (1.2, 2.2 and 3.2), 10 min (1.3, 2.3 and 3.3) and 20 minutes (1.4, 2.4 and 3.4) intervals (for example test run 2.3 was conducted with ozone feeding dose $1.36 \text{ mg O}_3 \text{ min}^{-1}$ with contact time 10 minutes). The amount of NOM was reduced in all the MM fractions except in the fraction of $4000\text{--}5000 \text{ g mol}^{-1}$ (Figure 5), where an increase was noticed from time to time (values were compared to the feed water). This can be explained by polymerization especially with the lowest ozone doses. In earlier studies [4, 26] it has been noticed that the amount of HMM NOM content (measured as TOC and UV-absorbance) increased in some cases. The conclusion of the dose test was, that the feeding dose of ozone might not be as critical as the contact time with ozone.

In the second part of the test, the ozonation was done in continuous flow reactor with four different ozone doses and with two stage AC filtration. The ozone dose in different test

runs were 0.5 mg l^{-1} , 1.4 mg l^{-1} , 2.9 mg l^{-1} and 4.0 mg l^{-1} . Samples were collected from the feed water, the ozonated water and the AC filtered water after the second AC-filter. The contact time with ozone was 18 minutes and EBCT 14 min/AC filter. With the lowest ozone dose of 0.5 mg l^{-1} , the reduction of NOM was lower, but the following AC filtration was more effective, especially when the removal of the LMM fraction was considered (Figure 6). The higher ozone doses (1.4 mg l^{-1}) resulted in higher removal of NOM on every MM fraction. However, the AC was not able to remove the NOM any further. This was evident also with the higher ozone doses of 2.9 mg l^{-1} and 4.0 mg l^{-1} (Figure 6). The HMM fraction increased slightly after the ozonation, as in the full-scale process. The reduced AC adsorption at higher ozone doses might be because the higher ozone doses ($>1.4 \text{ mg l}^{-1}$) converted the NOM to the compounds with higher polarity and solubility, unable to adsorb on to the AC [8].

UV-absorption and TOC

In the ozonation, UV_{254} -absorbance was clearly diminished, as the ozone dose was increased. AC filtration after the ozonation removed UV-absorbing compounds even further and the greatest reduction (56 %) was noticed with the largest ozone dose. The total amount of NOM measured as HPSEC was reduced by 45 %.

The reduction of TOC was minimal. In the feed water the amount of TOC varied from 2.3 mg l^{-1} to 2.5 mg l^{-1} . After the ozonation the TOC value was 2.3 mg l^{-1} and after the activated carbon filtration about 2.0 mg l^{-1} . Thus, the approximate TOC reduction in ozonation was 4 % and in AC filtration 13 %. According to the literature [27], ozonation did not change the concentration of TOC in full-scale treatment

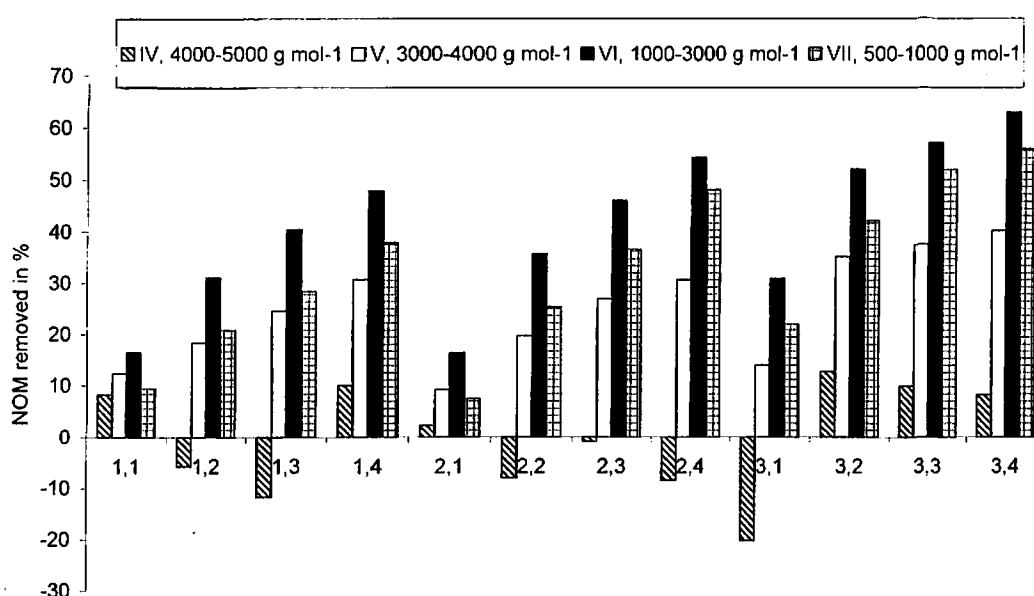


Figure 5. Ozone dose experiment, the removal of NOM by ozonation measured with HPSEC. The first ozone dose was 0.34 mg min^{-1} (1.1-1.4), second 1.36 mg min^{-1} (2.1-2.4) and third 3.9 mg min^{-1} (3.1-3.4). The contact time with ozone was (1.1, 2.1 and 3.1) 2 minutes, (1.2, 2.2 and 3.2) 5 min, (1.3, 2.3 and 3.3) 10 min and (1.4, 2.4 and 3.4) 20 minutes.

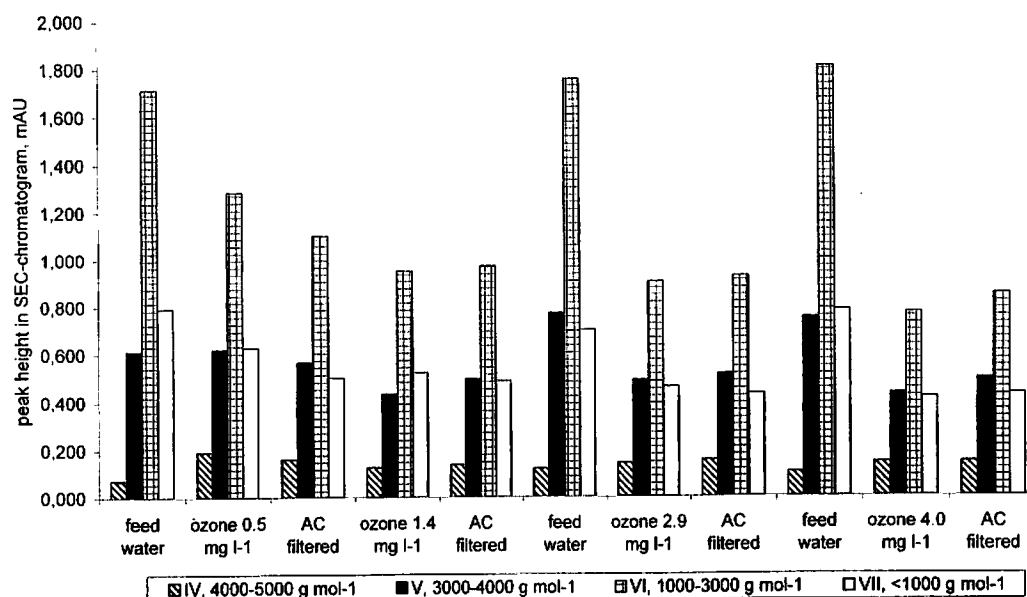


Figure 6. Continuous flow test, with 120-130 l h⁻¹, contact time 18 minutes and EBCT of AC filters 14 minutes per filter. The ozone feeding doses were 0.5 mg l⁻¹, 1.4 mg l⁻¹, 2.9 mg l⁻¹ and 4.0 mg l⁻¹.

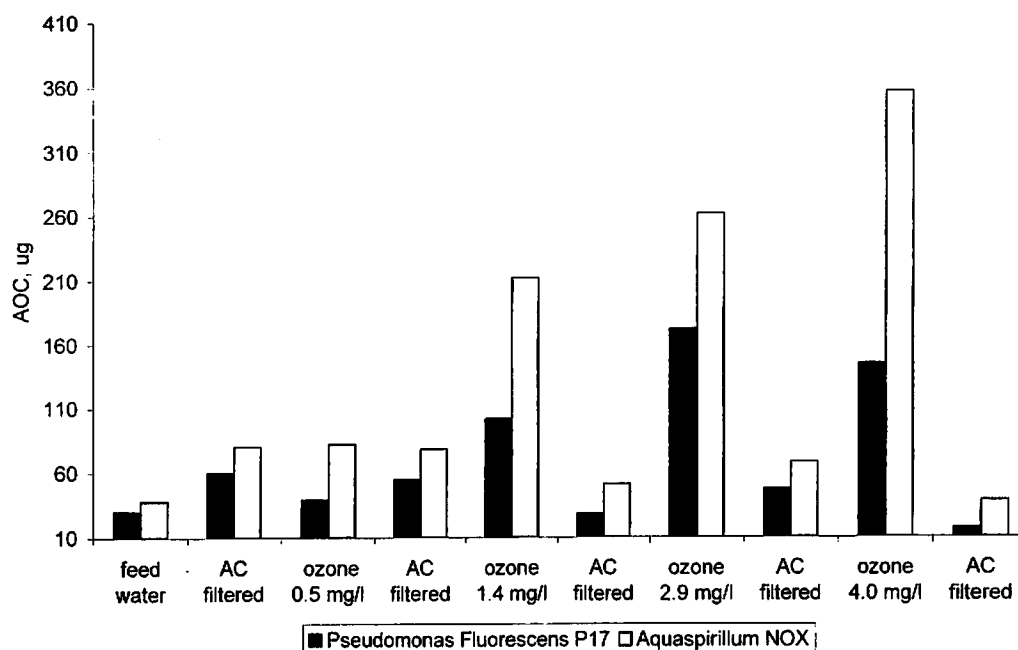


Figure 7. The amount of AOC (μg AOC l⁻¹) on the pilot tests with different ozone doses. AOC was determined with two different series, using either *Pseudomonas Fluorescens* P17 or *Aquaspirillum* NOX.

with ozone dose of 1.0-2.0 mg O₃ l⁻¹. The greatest decrease which was noticed was 0.2 mg l⁻¹ TOC, which is in good agreement with our results.

AOC concentrations

The AOC was determined to investigate the influence of ozone on to the assimilated carbon content available for microbes. AOC was noticed to increase when the ozone dose

was increased. With the smallest ozone dose, two-fold AOC values were measured. The maximum AOC (0.36 mg l⁻¹) was achieved with very high ozone dose of 4.0 mg O₃ l⁻¹ (2.4 mg O₃ mg⁻¹ TOC). The amount of AOC was nine times greater than in the original feed water sample (Fig. 7). However, according to the literature [6], the maximum AOC production was reached at the dose 2 mg O₃ l⁻¹ (or 1.5-2.0 mg O₃ mg⁻¹ TOC), after which no more increase in AOC occurred. According to

the literature [27] the AOC content increased on average by 157 % in ozonation (ozonation dose 1.0-2.0 mg O₃ l⁻¹) in the full-scale process. In the full-scale process in Hintta and Kurkealanranta, the ozone dose is between 0.4-1.5 mg O₃ l⁻¹.

Although the amount of AOC was high after the ozonation, the AC filtration removed the AOC content highly efficiently. Roughly 74 % of the AOC was removed by AC filter with the lower ozone doses and 88 % with the highest ozone dose (Figure 7). According to the literature [28] the AC filtration removed 23 % of TOC and 85 % of AOC concentration in water.

CONCLUSIONS

The river water, as raw water source, contains a significantly higher amount of HMM matter than typical Finnish lake raw water source, and the variation in NOM content between seasons was greater. Nevertheless, the full-scale purification process was effective and almost all of the HMM matter (98 %) was removed from the water during the purification. Only a minor amount of IMM matter (14 %) was remaining in the water. The LMM matter was hardest to remove with 40 % remaining in the distributed water.

The HMM matter and most of the IMM matter were removed during coagulation/floitation. Ozonation removed primarily the lower molar mass compounds. The lowest MM fraction of the IMM matter was further decreased by 23% and the LMM matter by 32 % in ozonation, respectively. The HMM matter was either increased or unaltered. The effectiveness of the AC filtration to remove NOM depended primarily on the regeneration history of the particular filter.

On average, the highest removal rates were recorded for the NOM molecules in the size range of < 3000 g mol⁻¹, especially when the AC was recently changed or regenerated and in some cases during the summer months.

In the pilot-scale studies, ozonation diminished primarily the LMM matter also. According to the AOC measurements, the available assimilable organic matter to microbes increased from 0.030 mg AOC l⁻¹ to 0.1-0.3 mg AOC l⁻¹ while the ozone dose was increased. Hence, the NOM was degraded to the smaller compounds. Nevertheless, in the HPSEC measurements, the amounts of higher molar mass compounds were constant and the amount of smaller molar mass matter was decreased. It can be concluded that in the ozonation, the NOM was degraded on to the very small compounds, with no conjugated double bonds. The AC filtration after the ozonation efficiently removed the AOC from water. The amount of TOC reduced only slightly, even when the amount of ozone was increased.

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V

**Enhancement of the natural organic matter removal from drinking water by
nanofiltration.**

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ENHANCEMENT OF THE NATURAL ORGANIC MATTER REMOVAL FROM DRINKING WATER BY NANOFILTRATION

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ABSTRACT

Finnish surface waters are abundant in natural organic matter. Natural organic matter can be removed from drinking water in a water treatment process by coagulation and filtration. The standard treatment operations are not able to remove the smallest molar mass fraction of organic matter and the intermediate molar mass matter is only partly removed. The removal of residual natural organic matter from drinking water by nanofiltration was evaluated in this study. Three different nanofiltration membranes were compared in filtering six pre-treated surface waters. The total organic carbon content of the feed waters varied from 2.0 to 4.2 mg l⁻¹. Other water quality parameters measured were conductivity, alkalinity, hardness, UV-absorbance, SUVA, E₂/E₃ value and molecular size distribution by high-performance size-exclusion chromatography. The natural organic matter removal efficiencies of the membranes were good and varied between 100% and 49%, and between 85% and 47% according to molecular size distribution and total organic carbon measurements, respectively. Removal of different molecular size fractions varied from 100% to 56%, 100% to 54% and 88% to 19%, regarding high molar mass, intermediate molar mass and low molar mass organic matter, respectively. The Desal-5 DL membrane produced the highest natural organic matter removals.

Keywords: Nanofiltration, natural organic matter (NOM), water treatment, high-performance size -xclusion chromatography (HPSEC), water quality

INTRODUCTION

Water sources used for drinking water purposes generally contain dissolved natural organic matter (NOM). The character and properties of NOM in water of different origin differ considerably [1]. Particularly in boreal areas the humic substances are ubiquitous in all surface waters. NOM can be removed from drinking water by conventional treatment processes such as coagulant addition, flocculation, sedimentation/flotation and filtration. However, low molar mass (LMM) and intermediate molar mass (IMM) organic compounds are removed only partially [2]. NOM can cause several problems in drinking water quality and distribution. In addition to forming disinfection by-products (DBPs) with chlorine, NOM has a potential to transport metals and hydrophobic organic chemicals. NOM also contributes to bacterial regrowth, corrosion and slime growths in

distribution systems, as well as to annoying taste and odour problems [3]. Due to these water quality problems and stricter regulations for drinking water quality, there is a need for more efficient and still economical methods for the removal of the residual organic matter.

Membrane processes are a relatively new innovation for NOM removal from waters [3]. Nanofiltration (NF) has proven to be reliable for the removal of organic and inorganic compounds [4, 5, 6]. Foulants with molar masses bigger than the membrane cut off are removed mainly by a sieving mechanism, and molecules with molar masses smaller than the membrane cut off by diffusion and charge repulsion based mechanisms. Molecule polarity, hydrophobicity and configuration also affect the retention [7, 8, 9]. However, most studies have concentrated on the NOM removal from natural surface waters, ground waters or model waters, and little is known about the NOM removal from rather pure chemically

pre-treated surface waters.

Several studies have focused on a greater understanding of the membrane fouling potential of surface water constituents [10, 11, 12] and better pre-treatment techniques [13, 14]. The membrane fouling is seen as a decline of flux and has been reported to be one of the main problems related to NF. Several studies indicate that NOM has an important role in membrane fouling, especially the high molar mass (HMM) and hydrophobic fraction of NOM seem to be responsible for membrane fouling [15, 16, 17]. The NOM fouling of polymer membranes has been noticed to increase in the presence of divalent cations, at low pH and at high ion content [11, 12, 15, 16, 18]. It should be borne in mind that fouling changes the membrane properties as well as the characteristics of the fouling layer, and thus it also affects membrane retention [7, 11, 19].

The need for more efficient removal of NOM necessitates more knowledge of the matter. The nature of organic matter is very complex and there is a need for a simple and rapid method to characterize NOM. The most extensively used method for molecular size and molar mass distribution determination is apparently high-performance size-exclusion chromatography (HPSEC) [20]. It has been reported to be a simple and rapid method for the characterization of the behaviour of the organic matter in drinking water treatment [2, 20, 21, 22].

The aim of this work was to evaluate the efficiency of NF membranes to remove different water components and molecular size fractions of NOM from chemically pre-treated surface waters. Three different NF membranes were

compared in treating six different feed waters. HPSEC was used as the measuring technique to demonstrate the molecular size distribution (MSD) alterations during the process. The results concerning the hydraulic performance and fouling of the membranes during the study are published elsewhere [23].

MATERIALS AND METHODS

NF Pilot Process and Feed Waters

The study was carried out using a laboratory-scale membrane filtration unit (Fig. 1). Three cross-flow flat-sheet modules were run parallel with the same feed water. The membrane area in each module was 46.0 cm². The membranes studied in the parallel membrane modules were Desal-5 DL, NF255 and NF270. The representative characteristics of the membranes are presented in Table 1. All membranes were supplied as dry, rolled sheets and were stored as received at room temperature.

Six different feed waters were collected from five surface water treatment plants and from one artificial ground water treatment plant for the pilot process. Samples were collected after a traditional water treatment train, but before post-treatment. Ninety litres of each sample was delivered to Lappeenranta University of Technology. The details of the treatment process in each water treatment plant studied are summarised in Table 2.

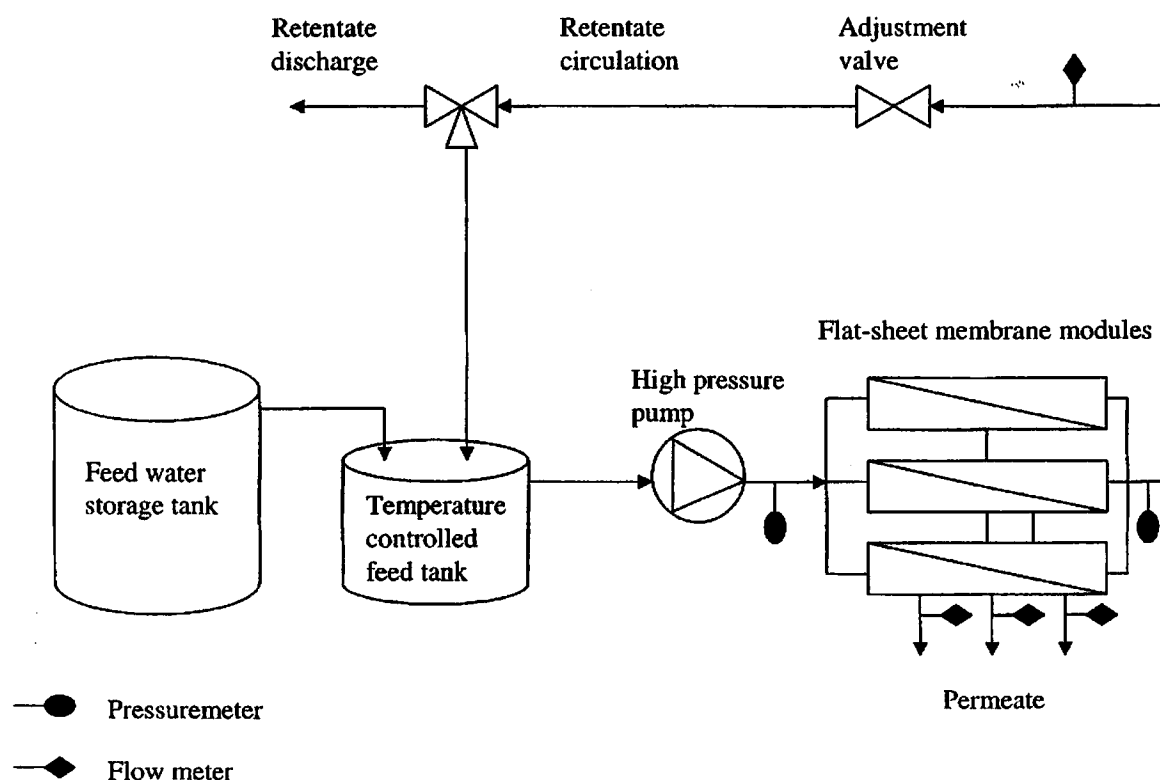


Figure 1. Schematic picture of the laboratory-scale membrane filtration unit.

Table 1. The tested membranes and their characteristics. Information provided by manufacturers.

Membrane	Manufacturer	Material	Cut off g mol ⁻¹	Operating pH range	CaCl ₂ rejection %	MgSO ₄ rejection %
NF270	Filmtec	PPZ	300	3-10	40-60	>97
NF255	Filmtec	PPZ	300	3-10	>50	
Desal-5 DL	Osmonics	PPZ	150-300	2-11		96

PPZ = Polypiperazine amide

Table 2. Pre-treatment trains of the studied feed waters.

Feed water	Pre-treatment train
Espoo	Coagulation with ferric sulphide, coagulation pH adjusted with lime, flocculation, flotation, sand filtration
Tampere	Alkalinity adjustment with CO ₂ and pH adjustment with lime, coagulation with alum, flocculation, flotation, disinfection with ClO ₂ , activated carbon filtration
Turku	Alkalinity adjustment with CO ₂ and pH adjustment with lime, coagulation with ferric chloride sulphite, flocculation, sedimentation, addition of powdered activated carbon and lime, coagulation with ferric chloride sulphite, coagulation pH adjusted with NaOH, cationic coagulation aid, flocculation, flotation, disinfection with a combination of Cl ₂ , ClO ₂ , and NaClO ₂ , sand filtration
Kotka	Artificial ground water
Raisio-Naantali	Coagulation with polyaluminium chloride, coagulation pH adjusted with lime, cationic coagulation aid, flocculation, sedimentation, pH adjustment with lime, sand filtration
Pietarsaari	Coagulation with ferric chloride sulphite, coagulation pH adjusted with lime, flocculation, flotation, pH adjustment with lime, sand filtration

Operation of the NF Process

Virgin membranes were rinsed with reverse osmosis filtered and ion-exchanged water (RO-water). Then the membranes were pressurised at 20 bar for 15 minutes to wet them thoroughly. After that the membranes were conditioned by pre-cleaning with 0.1% Ultrasil 10 cleaning solution for 30 minutes (20 minutes hydraulically enhanced cleaning with high cross-flow velocity (CFV) (1.5 m s⁻¹) and low net driving pressure (NDP) (<1.4 bar), and 10 minutes soaking period). The cleaned membranes were rinsed with RO-water.

The pilot process was operated in a retentate circulation mode until 60 litres of permeate were produced as a sum of all modules. Fresh feed water was added to the feed stream to compensate the permeate removal and to keep the amount of feed water in the process constant. The temperature of the feed water was kept constant at 20°C. CFV was constant at 0.65 m s⁻¹ and NDP was 10 bar for all the membrane modules.

Water Analysis

The feed and permeate waters were characterised by pH, hardness, conductivity, alkalinity, TOC, UV spectrum and MSD of organic matter. TOC was measured according to the national standard SFS-EN 1484 by a Shimadzu TOC-5000A

analysator using a combustion - non dispersive infrared gas analysis method. The UV spectrum was done according to the APHA (1995) standard [24] with the exception that absorption was measured at all wavelengths between 200 to 400 nm instead of only at 254 nm. Hardness and alkalinity were measured according to Finnish standards SFS 3003/-87 and SFS 3005/-81, respectively. The organic matter hydrophobicity was evaluated by the SUVA (Specific ultraviolet absorbance) value. SUVA is defined as the UV absorbance of a given sample determined at 254 nm and divided by the TOC concentration of the solution. A SUVA value > 4 indicates mainly hydrophobic and especially aromatic material whilst a SUVA value < 3 indicates mainly hydrophilic material [25]. Absorbance values at wavelengths 250 (E₂) and 356 nm (E₃) were measured and the quotient E₂/E₃ was calculated. The quotient E₂/E₃ correlates with the molecular size and aromaticity of aquatic humic solutes. The E₂/E₃ value is high when aromaticity and molecular size of aquatic humic solutes are low [20].

HPSEC was used to determine the MSD of NOM. The relative apparent sizes of the molecules in the feed water and permeate were measured after four-hour run. The samples were filtered through a Gelman 0.45 µm membrane and then size-exclusion fractionated with a Hewlett-Packard HPLC 1100-series system, equipped with a diode array UV detector

($\lambda = 254$) and TSKgel G3000SW 7.5mm(ID) x 30 cm column. A pre-column was not used. Sodium acetate (0.01 M) was used as eluent at a flow rate of 1 ml min⁻¹. The injection volume was 30 μ l. The method used was based on earlier investigations [2, 20, 21, 22].

HPSEC values were calculated as the height of the chromatograms peaks. This height refers to the amount of NOM in a specific molecular size fraction with a peak having the lowest retention time referring to the highest molar mass and a peak having the highest retention time to the lowest molar mass NOM. The sum of all peak heights represents the total amount of NOM in the sample. The most critical step in studying aquatic humic solutes using HPSEC is the choice of the eluent. The use of 10 mmol sodium acetate solution as the mobile phase gave fairly good resolution and each water sample showed its own elution profile [20]. The chromatograms shown in Fig. 2 provide illustrative information about the nature of dissolved organic matter in different feed waters that is very difficult to attain using

HPSEC with any other eluent composition than sodium acetate [20]. Apparent molar masses (AMM) for different peak fractions were defined roughly as > 5000 g mol⁻¹, 4000-5000 g mol⁻¹, 3000-4000 g mol⁻¹, 1000-3000 g mol⁻¹, 500-1000 g mol⁻¹ and <500 g mol⁻¹ for peaks I, II, III, IV, V and VI, respectively. Determinations of AMM for different peak fractions were done with the ultra filtration (UF) fraction. AMM determinations are demonstrated elsewhere [26]. Peaks I and II are referred to HMM organic matter with AMM >4000 g mol⁻¹, peaks III and IV to IMM organic matter with AMM 4000-1000 g mol⁻¹ and peaks V, VI and VII to LMM organic matter with AMM <1000 g mol⁻¹.

RESULTS AND DISCUSSION

Feed Water Quality

The qualities of the feed waters during the test runs are shown in Table 3. TOC increases approximately threefold

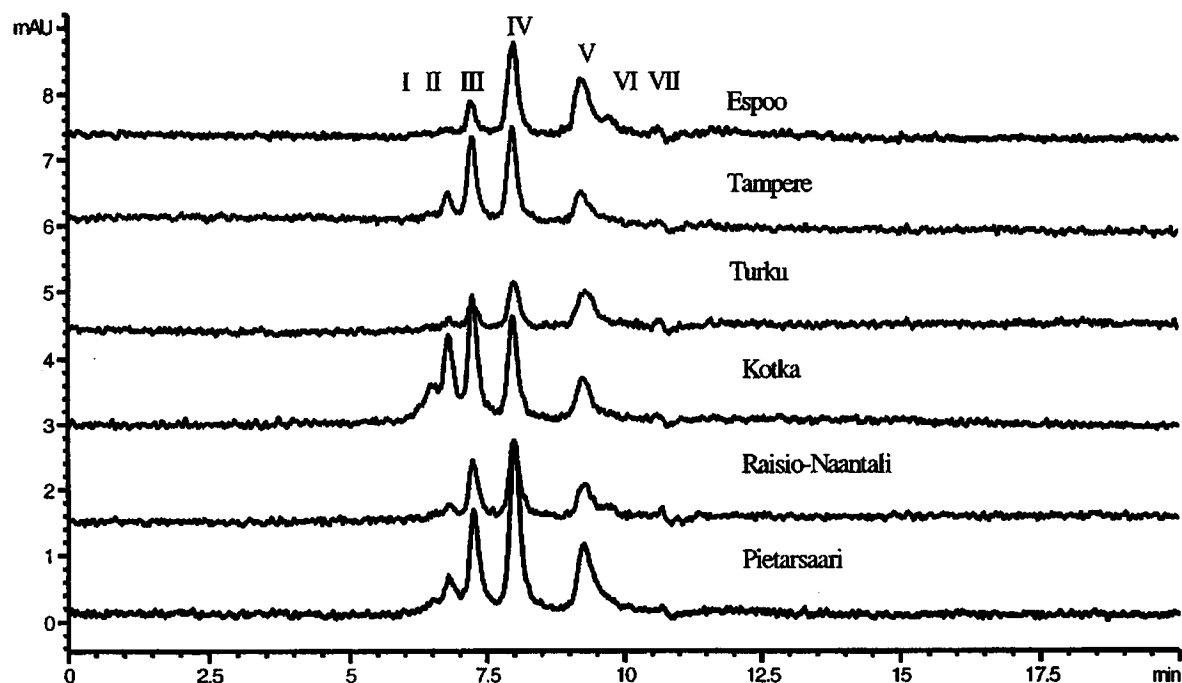


Figure 2. HPSEC chromatograms on the different feed waters studied. Peaks as mAU min⁻¹.

Table 3. The feed water characteristics in the beginning and in the end of the run.

		Espoo 0h→48h	Tampere 0h→48h	Turku 0h→48h	Kotka 0h→48h	Raisio-Naantali 0h→48h	Pietarsaari 0h→48h
TOC	mg l ⁻¹	2.2→7.3	2.9→8.9	2.0→7.6	3.4→9.3	3.2→8.2	4.2→11.5
UV-254		0.043→0.115	0.040→0.122	0.023→0.060	0.058→0.160	0.049→0.137	0.068→0.189
pH		5.7→6.6	7.6→7.9	7.9→8.2	6.8→7.5	7.1→7.8	9.3→9.1
Conductivity	μ S cm ⁻¹	155→284	141→314	243→491	92→191	174→299	205→421
Alkalinity	mmol l ⁻¹	0.10→0.11	0.66→1.33	0.62→1.25	0.38→0.80	0.48→0.98	0.45→0.90
Hardness	mmol l ⁻¹	0.49→1.42	0.55→1.30	0.91→2.15	0.33→0.74	0.58→1.14	0.77→1.82
SUVA	l mg m ⁻¹	2.0→1.6	1.4→1.4	1.1→0.8	1.7→1.7	1.5→1.7	1.6→1.6
E ₂ /E ₃		4.8→10.9	14.0→13.9	6.0→10.8	8.4→9.2	13.0→8.4	8.9→8.5

and conductivity doubles during the run. The TOC values are quite low in all feed waters, indicating that the pre-treatment has been efficient. The lowest TOC values were in the Turku and the highest in the Pietarsaari waters. The UV_{254} values coincide with the TOC measurements. Conductivity was the highest in Turku and the lowest in Kotka feed waters and alkalinity the highest in Tampere and the lowest in Espoo feed waters. Hardness was low in every feed water studied. The SUVA values below 2 indicate that the organic matter consisted mostly of LMM material with low hydrophobicity and aromaticity [25]. This is expected since the water pre-treatment process removes most of the HMM matter from the waters. The quotient E_2/E_3 values are high in the Raisio-Naantali and the Tampere waters indicating that these waters had the lowest aromaticity and molar mass of the organic matter. The Espoo feed water had the highest aromaticity with the lowest E_2/E_3 value.

HPSEC Characterization of Feed Waters

Four to seven different HPSEC peaks were found in the feed waters (Fig. 2). Other investigators have also found 4-6 peaks in the purified surface waters in Finland [2, 21, 22]. It has been noticed [2] that drinking waters usually have almost

undetectable peaks for the largest fractions (peaks I and II) and the most dominant peaks are the smaller molecular size fractions (IV, V and VI). The results coincide with our findings. The LMM fraction is more difficult to remove because it contains highly charged fulvic acids that are difficult to destabilise by coagulation dosages commonly employed in water treatment [27]. In an earlier study [28] coagulation and activated carbon filtration treatment removed >95% of the HMM, about 50 % of the IMM and about 40 % of the LMM organic matter fraction from the raw water. The reduction in the sum of peak heights (total organic matter) was 71 %.

Molar mass fractions are presented as percentages and the total amounts of organic matter as a sum of peak heights in the chromatogram (mAU) in Fig. 3. The Espoo, Tampere, Kotka, Raisio-Naantali and Pietarsaari feed waters contained mainly IMM organic matter (over 55%). The Turku feed water had more LMM (45 %) matter than others, almost equivalent to IMM (46 %). The HMM fraction was, as expected, small in all feed waters. The Kotka feed water, which was the only artificial ground water tested, contained most HMM matter in relation to the other waters. In the Kotka feed water the total amount of the organic matter was the highest according to the HPSEC analysis.

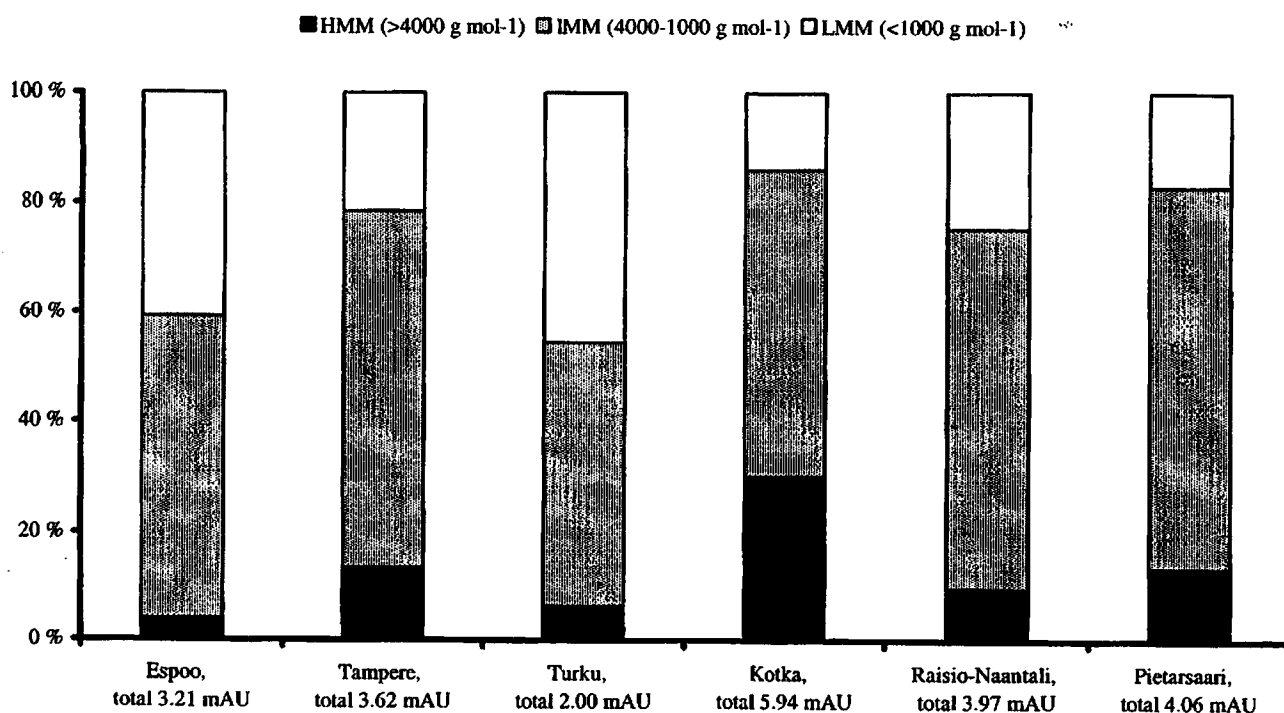


Figure 3. Molar mass fractions as percentages of the total amount of organic matter (sum of peak heights in the chromatogram, mAU).

NF Membrane Performance on NOM Removal

The organic matter removal efficiency of the tested NF membranes from the different feed waters during the first four hours of the run is summed as different molar mass fractions removals in Table 4. The TOC and UV₂₅₄ removals are shown in Table 5. In general, all the membranes removed 100-47% of the remaining organic matter, in most cases over 60%, which is a very good result. Several other studies also indicate that NF is very effective in removing organic matter from a variety of feed waters: DOC removals of 95-60%, UV₂₅₄ removals of 99-60% and DBP precursor removals of 100-41% have been reported [4, 6, 9, 19].

On the basis of the HPSEC, TOC and UV₂₅₄

measurements the Desal-5 DL membrane seemed to be the most efficient in removing organic matter. The Desal-5 DL performed extremely high removals with all the feed waters except with the Raisio-Naantali feed water. The Raisio-Naantali feed water did not show any major differences in comparison to other feed waters and the removal efficiency of the other tested membranes was not reduced remarkably when filtering the Raisio-Naantali feed water.

Peaks VI and VII were not found in the Pietarsaari feed water and peak VII in the Kotka feed water but they appeared in the NF255 (Pietarsaari) and NF270 (Pietarsaari and Kotka) permeates. This might be due to uncertainty in the HPSEC chromatogram integrations, because the peaks were really small.

Table 4. Removal (%) of the different molar mass fractions of the feed water organic matter in NF according to the HPSEC measurements.

Desal-5 DL	HMM	IMM	LMM	Total
Espoo		93	90	92
Tampere	100	100	100	100
Turku	100	100	52	78
Kotka	100	100	100	100
Raisio-Naantali	66	52	34	49
Pietarsaari	100	100	100	100
NF255				
Espoo		83	83	84
Tampere	100	69	80	75
Turku	100	61	53	60
Kotka	69	65	45	63
Raisio-Naantali	57	54	66	57
Pietarsaari	100	66	19	63
NF270				
Espoo		74	86	80
Tampere	69	65	34	59
Turku	100	59	60	62
Kotka	79	77	31	71
Raisio-Naantali	56	57	27	50
Pietarsaari	71	67	21	59

Table 5. TOC and UV₂₅₄ removals as percentage (%) in NF during the run.

	TOC			UV ₂₅₄		
	Desal-5 DL	NF 255	NF 270	Desal-5 DL	NF 255	NF 270
	4h→48h	4h→48h	4h→48h	4h→48h	4h→48h	4h→48h
Espoo	76→91	65→80	77→90	93→99	82→95	80→89
Tampere	71→93	66→79	62→80	93→100	76→92	78→93
Turku	64→88	48→61	46→73	84→95	64→64	72→81
Kotka	81→90	76→66	70→83	95→98	61→65	77→90
Raisio-Naantali	47→57	56→51	57→62	60→63	59→60	64→70
Pietarsaari	85→92	57→64	59→72	100→98	69→83	77→88

According to the HPSEC results the HMM fraction was removed almost completely (average removal with Desal-5 DL 93 %, NF255 85% and NF270 75%) with every membrane from all the feed waters studied, except from the Raisio-Naantali water. The IMM fraction removal was not as effective, ranging from 100% to 52% (average removal with Desal-5 DL 80 %, NF255 66% and NF270 67%). These fractions should not be able to pass through the NF membranes because they are bigger than the membrane cut off values. Their breakthrough is an indication of the fact that NOM rejection is not controlled only by molar mass, but molecular charge, hydrophobicity, conformation and polarity also affect the rejection [7, 8, 29]. The LMM fraction rejection was also the best with the Desal-5 DL membrane (average 79%), the second efficient was the NF255 membrane (average 58%), and the worst the NF270 membrane (average 43%). Other authors have also noticed that the NF membranes reject the high and moderate molar mass fraction of organic matter efficiently, while the low molar mass organics are generally removed only slightly [4, 6, 8, 9, 27, 29]

According to TOC and UV₂₅₄ results (Table 5.) the organic matter removal improved on average by 12% during the run. A similar phenomenon was noticed also by Schäfer et al. [17]. This is most probably due to the fact that organic matter removal is mainly controlled by sieving, and a concentration increase at the feed side of the membrane cannot force more material through the small membrane pores.

Correlation between Measurement Techniques

The organic matter removal efficiencies were slightly smaller according to TOC than HPSEC and UV₂₅₄ measurements. In general, this is due to the fact that UV₂₅₄ requires aromatic double bonds or similar chromophores for sample detection, and therefore, cannot detect all compounds in the smallest fraction, thus giving too good removal percentages for the LMM fraction. Anyhow, the Pearson correlation coefficients between the measurement techniques were fairly good, as can be seen in Table 6. HPSEC and UV₂₅₄

Table 6. Correlation coefficients between the different NOM measurements (n=23).

	TOC	HPSEC	HMM	IMM	LMM
TOC		0.902	0.629	0.933	0.728
UV ₂₅₄	0.960	0.940	0.670	0.969	0.752

correlation was expected to be good, since they both have a similar detection of organic compounds (UV light at the wavelength 254 nm). However, also TOC correlates well with

both HPSEC and UV₂₅₄. Good correlation values have been achieved also in other studies [21, 22, 30].

When comparing the different molar mass fractions of the HPSEC analysis to other techniques, UV₂₅₄ and TOC correlated best with the IMM fraction of NOM. The Turku feed water had the lowest amount of organic matter according to all analysis methods. According to the SUVA value, the organic matter in the Turku feed water contained mostly LMM material, which is in accordance with HPSEC. SUVA values did not correlate well with the other organic matter measurements: the correlation coefficient was 0.66 with the UV₂₅₄ and HPSEC values and 0.46 with the TOC values.

NF in Inorganics Removal

The removal efficiencies of the other feed water parameters by the NF membranes are presented in Table 7. The Desal-5 DL membrane seemed to be the most efficient in inorganics removal, too: it removed conductivity, alkalinity and hardness on average by 80%, 67% and 82%, respectively.

Table 7. Removal of conductivity, alkalinity and hardness in NF as percentages. Values after 4 h and 48 h runs.

	Conductivity	Alkalinity	Hardness
	4h→48h	4h→48h	4h→48h
Espoo			
Desal-5 DL	81→77	33→36	74→90
NF255	73→74	44→36	70→86
NF270	73→70	33→36	76→83
Tampere			
Desal-5 DL	83→79	73→65	83→81
NF255	62→68	61→57	69→71
NF270	63→59	51→40	59→62
Turku			
Desal-5 DL	76→74	74→72	81→83
NF255	54→53	50→nm	59→60
NF270	52→50	50→50	56→63
Kotka			
Desal-5 DL	77→73	75→69	92→80
NF255	50→47	47→42	58→52
NF270	57→56	50→51	61→63
Raisio-Naantali			
Desal-5 DL	45→43	46→48	50→50
NF255	47→41	50→nm	54→45
NF270	41→36	46→41	47→41
Pietarsaari			
Desal-5 DL	83→78	80→nm	80→83
NF255	58→62	52→57	58→69
NF270	59→62	50→51	62→67

nm=not measured

The average removals of conductivity, alkalinity and hardness were 57%, 51% and 61% with NF255 and 58%, 47% and 60% with NF270, respectively. Again the inorganic material removals from the Raisio-Naantali water were considerably lower than with the other feed waters, with the Desal-5 DL membrane especially.

Inorganics removal efficiency did not improve during the run as it did with the organic matter removal. The explanation for this is a different removal mechanism. Inorganics removal is mainly determined by the diffusion through the membrane and by the electroneutrality rule. Thus increased concentration at the feed side of the membrane leads to a higher transport of inorganic material through the membrane.

CONCLUSIONS

NF removed NOM effectively from pre-treated surface waters. The residual HMM organic matter disappeared almost completely and IMM organic matter diminished considerably. Also the LMM organic matter removal was improved. High removal percentages after traditional surface water treatment resulted in drinking water of a very high quality. The removal of organic matter improved during the run of membranes, most probably due to the formation of a fouling layer on the membrane surfaces. Of the tested membranes Desal-5 DL gave the best results in organics removal.

When considering the performance of a NF membrane

one should bear in mind that the aim is to achieve the required drinking water quality at the lowest possible costs. Accordingly, the membrane with the highest NOM removal capacity may not always be the best choice, as some other membrane may produce a high enough water quality at a lower cost due to higher productivity.

In Finland the quality of drinking water produced from surface waters is generally high already without NF and the need for NF is restricted to special cases. Still, especially the LMM fraction of NOM, which is hard to remove by other means, can be further removed by NF. This fraction is easily used by microbes, and thus its enhanced removal is desirable for improved quality of drinking water.

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