Tracking Changes in Dissolved Natural Organic Matter Composition

Evaluating Drinking Water Production using Optical and Molecular Level Tools

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Cover: Ekoln, Lake Mälaren
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Abstract

During the last decades, the abundance of dissolved organic matter (DOM), a complex heterogeneous mixture of organic compounds, has increased in many surface waters in Northern Europe and North America. Surface waters are widely used as raw water sources for drinking water production. Increasing DOM is problematic for water treatment plants (WTPs) due to e.g. increased coagulant demand and because its constituents act as precursors for potentially harmful disinfection by-products. Many WTPs employing conventional treatment are currently struggling to maintain sufficient DOM removal, and are considering additional novel techniques.

In this thesis, changes in the DOM composition were investigated during i) conventional water treatment and disinfection practices, ii) pilot scale studies of novel processes (nanofiltration and ion exchange), and iii) transport in a large Swedish boreal lake. Analytical techniques used include common spectroscopic methods (absorbance and fluorescence), and more advanced molecular level techniques (ultra-high resolution mass spectrometry). Results show that coagulation was highly selective towards oxidized DOM components, and that the removed fraction resembled terrestrial endmembers. Meanwhile, DOM with microbial endmember characteristics, which correlated with chemically reduced DOM components, was especially reactive during slow sand filtration. After disinfection, 499 different chlorine-containing by-products were identified, of which many had not been reported in the literature earlier. Both nanofiltration and ion exchange removed more DOM than coagulation, and components with a wider range of chemical properties. Both techniques were, however, most efficiently removing terrestrial DOM.

In the studied large boreal lake, terrestrial, aromatic compounds were lost over time, while no significant net in-lake production occurred. Decreasing components overlapped largely with those removed during coagulation treatment at WTPs, indicating that coagulation had contributed significantly to DOM removal within the lake, especially considering a concurrent loss of dissolved iron.

Keywords: dissolved organic matter, drinking water, absorbance, fluorescence, FT-ICR-MS, coagulation, nanofiltration, in-lake processing, selective removal

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Dedication

To Mom & Dad, for always believing in me.

"The scientist doesn't study nature because it is useful; he studies it because he delights in it, and he delights in it because it is beautiful."
    Henri Poincaré

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Lavonen, E.E., Gonsior, M., Tranvik, L.J., Schmitt-Kopplin, P., Köhler, S.J. (2013). Selective chlorination of natural organic matter: Identification of previously unknown disinfection by-products. *Environmental Science & Technology* 47(5), 2264-2271.
http://pubs.acs.org/doi/abs/10.1021/es304669p

II Lavonen, E.E., Kothawala, D., Tranvik, L.J., Gonsior, M., Schmitt-Kopplin, P., Köhler, S.J. Ultra-high resolution mass spectrometry explains changes in the optical properties of dissolved organic matter during drinking water production. (manuscript in review for Water Research)

III Köhler, S.J., Lavonen, E.E, Keucken, A., Schmitt-Kopplin, P., Spanjer, T., Persson, K.M. Upgrading coagulation with hollow-fibre nanofiltration for improved organic matter removal during surface water treatment. (manuscript)

IV Lavonen, E.E, Hertkorn, N., Schmitt-Kopplin, P., Harir, M., Köhler, S.J. How turnover time affects dissolved organic matter composition – tracking lake organic carbon processing with optical and molecular level tools. (manuscript)

Paper I is reproduced with the permission of the publishers.

The contribution of Elin Lavonen to the papers included in this thesis was as follows:

I   Planned the study together with the co-authors and had the main responsibility for sample preparation and DOC measurements. Had the main responsibility for data processing and interpretation, as well as writing the paper, with assistance from the co-authors.

II   Planned the study together with the co-authors and had the main responsibility for sample preparation and DOC measurements. Had the main responsibility for data processing and interpretation, as well as writing the paper, with assistance from the co-authors.

III   Was responsible for DOC, absorbance and fluorescence analyses as well as preparation of samples intended for mass spectrometry (MS) analyses. Had the main responsibility of data processing and interpretation of fluorescence and MS data. Was responsible for writing specific sections based on this data, and assisted the writing of the rest of the paper.

IV   Planned the study together with the co-authors and had the main responsibility for sample preparation, as well as measurements of dissolved organic carbon, absorbance, and fluorescence. Had the main responsibility for data processing and interpretation, as well as writing the paper, with assistance from the co-authors.

Abbreviations

$\overline{C_{OS}}$	Average carbon oxidation state
$\overline{C_{OS,w}}$	Weighted mean value of the average carbon oxidation state
CDOM	Chromophoric dissolved organic matter
Da	Dalton
DBE/C	Double bond equivalency per carbon
DBP	Disinfection by-product
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EEM	Excitation emission matrix
ESI	Electrospray ionization
FDOM	Fluorescent dissolved organic matter
Fe_{diss}	Dissolved iron
FI	Fluorescence index
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
GAC	Granular active carbon
H/C	Hydrogen to carbon ratio
HIX	Humification index
MIEX®	Magnetic ion exchange
NF	Nanofiltration
NMR	Nuclear magnetic resonance
O/C	Oxygen to carbon ratio
SA420	Specific colour (DOC-normalized absorbance at 420 nm)
SUVA	Specific UV absorbance (DOC-normalized absorbance at 254 nm)
TOC	Total organic carbon
UV-Vis	Ultraviolet-visual
WTP	Water treatment plant
β:α	Freshness index

1 Introduction

Carbon is the 4th most abundant element in the universe and is formed in stars through helium fusion (Killops & Killops, 2009). On Earth, carbon is present in all life forms as organic compounds as well as in the lithosphere and atmosphere as e.g. carbonates, fossilized organisms, soil organic matter, methane and carbon dioxide. In the hydrosphere, carbon occurs in its inorganic form, carbonate - the main contributor to alkalinity, and as particulate and dissolved organic carbon (POC and DOC). Inland waters have traditionally not been attributed any particular role in the global carbon cycle, but has rather been viewed as inactive transporters of carbon from terrestrial sources to the oceans (Meybeck, 1982; Schlesinger & Melack, 1981), probably due to their small contribution to Earth's surface area. More recent studies have, however, estimated that out of the approximately 1.9-2.9 Pg C inland waters annually receive on a global scale, only about 0.9 Pg C y^{-1} reach the oceans while roughly 0.2-0.6 Pg C y^{-1} are buried in sediments, and 0.8-1.4 Pg C y^{-1} is lost to the atmosphere through outgassing (Tranvik *et al.*, 2009; Cole *et al.*, 2007). During transport in freshwater systems, the composition of organic matter can be affected by photoreactions, flocculation, microbial degradation and in-lake production of new organic matter. This demonstrates that inland waters actively participate in the global carbon cycle and, in relation to their size, have a major impact on the amount and composition of organic matter reaching the ocean.

1.1 What is dissolved organic matter (DOM)?

The term "dissolved", when it comes to natural organic matter, is an operational definition where material not retained by a 0.45 μm filter is considered to be in solution, as opposed to in the particulate phase. In spite of

this, much of the DOM is not truly dissolved but is rather present as smaller colloids in suspension.

DOM in freshwater systems is a complex heterogeneous mixture of organic compounds with both terrestrial and aquatic origins, so called allochthonous and autochthonous organic material respectively. The material is usually divided into humic and non-humic substances where the former represent residual degradation products, largely from decomposition and solubilisation of soil organic matter and the latter more well-known biomolecular classes such as lipids, carbohydrates and amino acids.

1.1.1 Formation of DOM from soil organic matter

Organic matter in soil pore water consist of soluble compounds, such as low molecular weight organic acids, proteins and carbohydrates (mainly cellulose), as well as solubilisation products of more hydrophobic molecules from structural plant and animal residues (Kleber & Johnson, 2010; Killops & Killops, 2009). The latter originate from decomposition of soil organic matter, during which hydrophobic organic material is oxidized and acquire oxygen functional groups (e.g. hydroxyl (-OH) and carboxyl (-COOH) groups), resulting in more polar and consequently, more soluble compounds (Kleber & Johnson, 2010). Once the terrestrial organic matter is dissolved, it can be transported from soils to inland water bodies. However, further degradation and consumption by microorganisms occur prior in the soil, leading to shifts in the chemical composition of soil-derived DOM. An aqueous environment is a prerequisite for microbial uptake and studies have shown that CO_2 production from soil samples coincides with a decrease in the water-extractable fraction of organic carbon (Marschner & Bredow, 2002; Marschner & Noble, 2000). Carbohydrates is seemingly the preferred substrate for microorganisms leading to enrichment of lignin-derived aromatic compounds in the aqueous phase (Kalbitz *et al.*, 2003). Additional abiotic processes also regulate the composition and concentration of soil DOM including i) adsorption/desorption, ii) precipitation/dissolution, iii) diffusion, iv) complexation/decomplexation, and v) protonation/deprotonation. These processes are in turn controlled by e.g. soil quality (presence of iron and aluminium oxides or hydroxides and clay minerals as well as their surface area), conductivity (competition for ion exchange or adsorption) and pH (protonation/deprotonation) (Kalbitz *et al.*, 2000).

1.1.2 DOM in lakes

Solubilized soil organic matter is transported to inland water bodies with runoff. Humic substances typically constitute half of the DOM in an average river (Thurman, 1985). However, the variation may be large and depends on climate variables and the catchment characteristics. Terrestrially derived organic matter has a relatively high abundance of aromatic carbon as well as phenolic and carboxyl acid moieties (Kleber & Johnson, 2010; Fabris *et al.*, 2008). The aromaticity of DOM is commonly measured with specific (DOC normalized) UV absorbance at 254 nm (SUVA), which strongly correlates with the aromatic carbon content measured by ^{13}C-NMR (Weishaar *et al.*, 2003). Humic components are further attributed the majority of DOM absorbance of visible light, as well as the fluorescence of lake and river samples (Leenheer & Croué, 2003). Absorption of visible light by DOM is of ecological importance because it can restrict phytoplankton primary production (Karlsson *et al.*, 2009), but also protect plankton and benthic organisms against harmful UV environments (Morris *et al.*, 1995). DOM fluorescence in the shorter emission wavelength range has been related to protein-like and freshly produced DOM (Parlanti *et al.*, 2000; Coble *et al.*, 1990), demonstrating the usefulness of fluorescence spectroscopy to identify a wide range of DOM components. Because fluorescence spectroscopy is at least twice as sensitive as UV absorbance (Leenheer & Croué, 2003), it has great potential for monitoring DOM quality, in spite of less than 1% of the aromatic moieties emitting light as fluorophores (Lapen & Seitz, 1982). Autochthonous DOM that is produced within lakes originates from phytoplankton and bacteria biomass (cells) or extracellular release, has higher nitrogen content (C:N<10) than terrestrial organic matter (C:N>20) (Leenheer, 2009) and more aliphatic carbon. This has been demonstrated for isolates of DOM from lakes in Antarctica, where no higher plants are present, as lower SUVA and higher hydrogen to carbon ratios as well as larger abundance of nitrogen-containing components compared to isolates from sources with a higher influence from vascular plants (D'Andrilli *et al.*, 2013; Weishaar *et al.*, 2003; McKnight *et al.*, 1991).

The composition of DOM in lakes change as a function of the water residence time (Kothawala *et al.*, 2014; Algesten *et al.*, 2004). Reported losses of DOC and colour as well as decreasing SUVA with increasing water residence time are indicative of a selective removal of terrestrial DOM. Shifts in DOM composition can be attributed to several processes, including i) photochemical transformations (Gonsior *et al.*, 2009; Bertilsson & Tranvik, 2000; Zhou & Mopper, 1997), ii) production of DOM by plankton (Cole *et al.*, 1982), iii) biodegradation and mineralization of DOM by microorganisms (Søndergaard & Middelboe, 1995), and iv) flocculation of allochthonous DOM

(von Wachenfeldt & Tranvik, 2008) mediated by e.g. Fe(III) (Köhler *et al.*, 2013; Stumm & Morgan, 1996) or microbial activity (von Wachenfeldt *et al.*, 2009).

1.1.3 Traditional vs. modern view of humic substances

Traditionally, humic substances have been regarded as large, complex macromolecules with high molecular weight, usually referred to as the polymer model (Ghosh & Schnitzer, 1980), with an inherent recalcitrance to further degradation. For example, (Cameron *et al.*, 1972) reported mass-weighted average molecular masses of 20000-50000 Dalton (Da) and e.g. (Piret *et al.*, 1960) suggested sizes up to several hundred thousand Da. The humic substances supposedly consisted of isolated aromatic rings, covalently linked by aliphatic chains (Schulten *et al.*, 1991). More recent studies are, however, not consistent with the polymer model and indicate that humic substances are comprised of small primary molecules (100-2000 Da, with a majority <800 Da). The primary molecules obtain macromolecular characteristics as aggregates formed through weak interactions (hydrogen bonds or hydrophobic interactions), further increasing their complexity (Sutton & Sposito, 2005; Leenheer & Croué, 2003; Piccolo, 2001; Wershaw, 1986). Aggregates have been proposed to be able to form pseudo-micelles or micelle-like micro-particles where hydrophobic regions are separated from the aqueous solution by exterior hydrophilic layers (Sutton & Sposito, 2005; Kerner *et al.*, 2003; Piccolo, 2001; Conte & Piccolo, 1999). Biomolecular fragments derived from e.g. proteins, lipids and carbohydrates that traditionally are classified separately from humic substances are suggested to be associated and even covalently bonded with humics, which may protect them from microbial degradation (Sutton & Sposito, 2005).

1.2 DOM is increasing

DOM has been found to increase in many surface waters in northern Europe and North America during the last decades (Ledesma *et al.*, 2012; Roulet & Moore, 2006; Evans *et al.*, 2005; Skjelkvåle, 2003; Freeman *et al.*, 2001). The increase has been particularly pronounced for the coloured fraction (Eikebrokk *et al.*, 2004; Hongve *et al.*, 2004; Weyhenmeyer *et al.*, 2004) and is therefore called browning of inland waters.

Several theories have been brought forth to explain the increasing trend of DOM including i) increased precipitation and run-off leading a larger export of organic material from terrestrial systems (Hudson *et al.*, 2003) as well as less degradation due to decreased water retention times, ii) increased annual mean

temperature resulting in higher rate of photosynthesis and primary production (Forsberg, 1992), and in case of higher soil temperatures a general increase in the rate of SOM decomposition (Chapman & Thurlow, 1998), resulting in higher DOC concentrations in soils (Clark *et al.*, 2005), iii) changes in land use, e.g. increased agriculture (Chen & Driscoll, 2009; Chow *et al.*, 2007) and forest harvesting (Laudon *et al.*, 2009; Nieminen, 2004), and iv) declining acid deposition affecting the solubility of organic carbon through changes in pH and ionic strength (Evans *et al.*, 2006; Evans *et al.*, 2005).

It is presently unknown whether DOM will continue to increase or if the trend will level off in the future. It should further be noted that the increase, on a longer time scale, has been suggested to represent a return to historical DOC concentrations (Valinia *et al.*, 2015; Cunningham *et al.*, 2011).

1.3   How is DOM measured?

Because DOM is such a complex mixture of different organic components, analysing it is a great challenge and to date there are no techniques that can determine its complete structural molecular composition. There is a multitude of analytical methods used to characterize DOM on different levels, of which a selection is presented below.

DOC concentration is commonly used as a proxy for DOM, however, giving no information regarding its composition. Optical spectroscopic techniques, namely absorbance and fluorescence have been widely applied for DOM characterization due to the relatively low cost of analysis, small sample size needed and low demands on sample preparation (only filtration is needed). Different optically active fractions have been connected to e.g. the source, age, size, redox state, biological and photochemical reactivity, and the degree of humification of DOM (Helms *et al.*, 2008; Miller *et al.*, 2006; Cory & McKnight, 2005; McKnight *et al.*, 2001; Parlanti *et al.*, 2000; Zsolnay *et al.*, 1999; Coble *et al.*, 1990).

DOM can be fractionated according to specific chemical properties. Different resins, commonly including Amberlite XAD, have been applied to divide DOM according to hydrophobic, hydrophilic and transphilic acid, base or neutral fractions (Chow *et al.*, 2004; Croué, 2004; Leenheer, 1981). Limitations with the technique include the need of relatively large sample volumes as well as uncertainties due to possible chemical alteration due to the use of extreme pH levels, resin bleeding causing contamination, irreversible binding of DOM components to the resins, and different operational conditions (Song *et al.*, 2009; Town & Powell, 1993; Malcolm, 1991).

High-pressure liquid chromatography systems with size exclusion columns (HPSEC) have also been widely used to separate DOM into size fractions, especially for studies of DOM removal in drinking water treatment plants (Matilainen *et al.*, 2011). UV-Vis absorbance is the most common detection method used, but systems with e.g. fluorescence as well as organic carbon, nitrogen and multi-detectors are also applied (Wu *et al.*, 2003; Her *et al.*, 2002; Huber & Frimmel, 1992). Due to lack of proper DOM standards poly-styrene sulphonate (PSS) has been one of the most used standards for calibration of HPSEC (Peuravuori & Pihlaja, 1997). Therefore, and because it is not known to which degree aggregates or individual molecules are being measured, results are approximations and reported as apparent molecular weight of DOM. Results may be further impaired from the eluent where ionic strength and pH can affect the configuration of DOM components (Specht & Frimmel, 2000).

Ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has revolutionized the analysis of DOM during the past decade. FT-ICR-MS analysis typically results in the identification of thousands of mass peaks for one single sample of isolated DOM, usually in the size range 200-1000 Da. This is due to a high mass accuracy (<1ppm) that allows differentiation between DOM components having small differences in molecular mass. The ultrahigh resolution allows unambiguous assignment of molecular formulas up to approximately 600 Da. However, structural information cannot be obtained, due to the high number of possible isomers. Interpreting this kind of complex data is challenging but the use of e.g. van Krevelen diagrams (Wu *et al.*, 2004; Kim *et al.*, 2003) where elemental ratios of H/C and O/C are plotted against each other allows a synoptic visualization of FT-ICR-MS data. Recent studies have coupled components from FT-ICR-MS analysis to optical and structural information, further evolving detailed knowledge regarding DOM (Kellerman *et al.*, 2014; Stubbins *et al.*, 2014; Gonsior *et al.*, 2013; Herzsprung *et al.*, 2012).

1.4 Drinking water production and the role of DOM

In this section the most common current treatment processes in drinking water production will be described, along with effects from DOM during treatment. The coagulation/flocculation process will then be described in more detail as it is widely applied at WTPs and is responsible for the large majority of the DOC removal when conventional treatment is used. I will then give a short introduction to two more novel treatment processes, namely membrane filtration and ion exchange, which were both investigated in pilot scale experiments under the course of my PhD project.

1.4.1 General water treatment scheme

Surface waters are widely used as raw water sources for drinking water production. For example, in Sweden, 50% of all drinking water that is being produced originates from lakes and rivers. Conventional treatment for production of drinking water from surface waters is usually performed in three main steps: a chemical, a mechanical and a biological. In the chemical step a coagulant is added to the raw water which forms flocs together with small particles and different dissolved compounds. After passing sedimentation basins where most flocs settle and form sludge at the bottom, residual flocs are removed in a mechanical step, most commonly rapid sand filtration. In the following biological treatment, which takes place in large outdoor sand basins (so called slow sand filtration) or activated carbon filters, organic compounds causing unwanted odour and taste are removed. Activated carbon filters can also function as a chemical barrier removing micro-pollutants. Before the drinking water enters the distributions system it is disinfected with chlorine-based chemicals (chlorine, hypochlorite or chlorine dioxide) or UV radiation, so called primary disinfection. Monochloramine is commonly used as secondary disinfectant where the purpose is to provide a longer-lasting protection in the distribution network. In addition to removal of particles and dissolved compounds, some of the processes also constitute microbiological barriers. These processes include coagulation with following filtration, slow sand filtration and primary disinfection.

1.4.2 Effects from DOM during drinking water production

The presence of DOM causes several problems for drinking water production such as i) unwanted taste, colour and odour, ii) fouling of membranes (Kaiya *et al.*, 1996) and activated carbon filters (Summers *et al.*, 1989), iii) co-transportation of heavy metals (Frimmel & Huber, 1996) and organic pollutants (Murphy *et al.*, 1990), iv) formation of a variety of disinfection by-products (DBPs) (Gonsior *et al.*, 2014; Lavonen *et al.*, 2013; Richardson, 2011; Rook, 1974) which may have negative health effects for humans (Richardson *et al.*, 2007; Dodds *et al.*, 1999; Waller *et al.*, 1998; Cantor, 1997; Morris *et al.*, 1992), and v) increased risk of biological regrowth in the distribution network (Camper, 2004; Huck, 1990) (Figure 1). The observed increasing DOC concentrations have further led to, e.g. a higher demand of higher chemical doses during conventional coagulation treatment (Eikebrokk *et al.*, 2004).
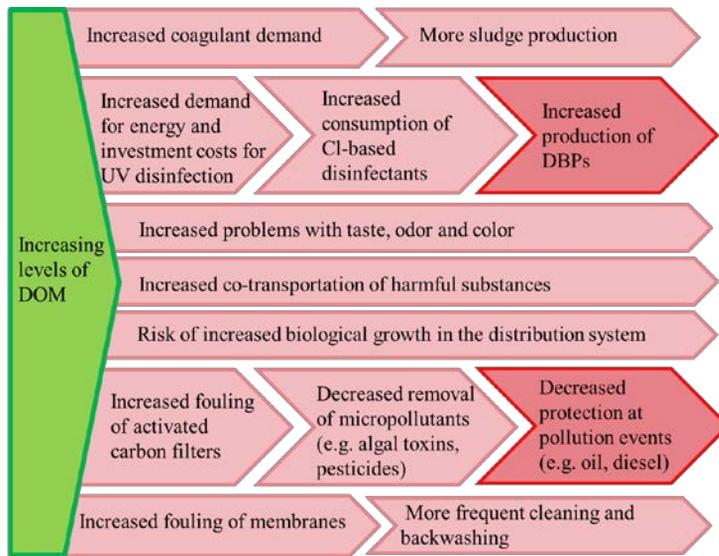
Figure 1. Summary of negative effects from dissolved natural organic matter during drinking water production from surface waters.

1.4.3 Chemical coagulation

Coagulation/flocculation treatment is one of the most common processes used in drinking water production for removal of DOM, but also to reduce turbidity. It is an economically feasible technique and generally removes a considerable amount of DOM (Matilainen *et al.*, 2010). In order to remove DOM and inorganic particles causing turbidity, aggregation and thereby particle density needs to be enhanced in order to increase the sedimentation rate, which can be done through coagulation. The most commonly used coagulants are metal salts from aluminum or iron but other options such as polymers are also available (Matilainen *et al.*, 2010). Other products such as activated silicic acid, produced from water glass (sodium silicate, Na_2Si_3) and ammonium sulphate $((NH_4)_2SO_4)$, can be used to enhance the treatment. Silicic acid aids both the coagulation and flocculation processes, the former by substituting hydroxide ions in the formed flocs and the latter by binding flocs together, leading to the formation of larger aggregates. The most important feature of a coagulant is high positive charge since its primary task is to reduce the repulsive forces between negatively charged DOM species and inorganic particulates to allow them to aggregate. Highly charged complexes of up to thirteen aluminum ions are formed in aqueous solution through hydrolysis of water molecules and polymerization of complex hydrated aluminum hydroxides when the coagulant

is added to the untreated water. The repulsive forces dominate in a stabile suspension leading to very limited aggregation (Machenbach, 2007). Coagulants destabilize a suspension through i) *sweep coagulation* – a process in which DOM is adsorbed to the solid metal hydroxide and particulate material is removed when it is trapped within the growing precipitation or ii) *charge neutralization*, where the cationic metal adsorbs to anionic DOM, thereby reducing the repulsive forces, which leads to the formation of insoluble charge neutral products. Surface deposition of one particle on another may also lead to charge neutralization, which is also called hetero-coagulation (Machenbach, 2007; Chow *et al.*, 2004). There is an established relationship between DOM removal with coagulation/flocculation and SUVA where, using aluminum sulphate, >50% of the DOC is removed from waters with SUVA >4, and less than 25% removal when SUVA is low (<2). DOC removal is generally somewhat higher using ferric chloride compared to aluminum sulphate (Matilainen *et al.*, 2010; Machenbach, 2007; Edzwald, 1993).

1.4.4 Membrane filtration

Membrane treatment is a technique of growing interest for the drinking water industry. Through membrane filtration, particulate and dissolved organic matter, colloids as well as bacteria and viruses can be removed with size exclusion. Removal is dependent on the pore size, dividing membrane treatment into three categories: microfiltration, ultrafiltration and nanofiltration. For significant removal of DOM, nanofiltration is needed. Ultrafiltration can, however be used as filtration after coagulation, so called direct filtration, which can enhance the DOM removal compared to conventional treatment. Removal with microfiltration is limited to bacteria and larger microorganisms (Machenbach, 2007). Membranes with a pore size below 0.1 μm (ultra- and nanofilter) are considered as microbiological barriers.

1.4.5 Ion exchange

Ion exchange can be used to remove charged DOM, commonly by using conventional polymeric anion exchange resins or a magnetic ion exchange (MIEX®) resin. Conventional resins are used in fixed-beds through which water is filtered, and a gradual decrease in the DOC removal will occur between regeneration cycles. MIEX® is applied in a continuous treatment process, where the resin is kept in suspension, resulting in more stable outgoing DOC concentrations. The MIEX® resin beads, with an average size of 150-180 μm, are smaller compared to conventional resins, which increase the external surface area where the initial exchange occurs (Slunjski *et al.*, 1999). The resin has a magnetic core which aids in aggregation and separation

of the beads from the treated water. During treatment, stirring keeps the resin in suspension by creating hydraulic forces that exceed the magnetic attraction between the resin beads. There are two different types of reactors used for the continuous MIEX® process: i) "High rate configuration", where untreated water is pumped into the bottom of the reactor holding MIEX® resin. In order to keep the resin suspended a continuous flow is applied. Treated water is taken out from the top of the reactor where the flow rate is sufficiently low for the MIEX® resin beads to aggregate and settle back to the reactor; and ii) "Dual stage configuration", where ion exchange and resin separation takes place separately.

For both types of reactor systems the majority of the MIEX® resin is kept in, or pumped back to, the ion exchange reactor, while a small amount is continuously removed and replaced with an equal amount of regenerated resin. The removed resin is recovered and usually regenerated off-line in batches (Slunjski *et al.*, 2000).

2 Objectives

The overall aim of this thesis was to investigate the composition of DOM in natural and engineered systems using multiple analytical tools. The specific objectives were to:

1. Evaluate the removal of DOM from surface water with conventional and novel drinking water treatment techniques using various analytical methods (II, III)

2. Investigate the formation of chlorine-containing disinfection by-products during drinking water disinfection using non-target analysis (I)

3. Identify optical parameters sensitive enough to capture small shifts in DOM composition (II-IV)

4. Connect optical properties of DOM to structural and molecular level information (II, IV)

5. Study in-lake processing of DOM and how it affects drinking water production (IV)

3 Background, Materials and Methods

3.1 Projects

The work presented in this thesis was conducted within two projects: Color of Water (CoW) and GenoMembran.

CoW is a strong research environment funded by the Swedish research council FORMAS. The project is a collaboration between three universities: Uppsala University; Swedish University of Agricultural Sciences; and Linköping University, as well as two drinking water producers (Stockholm Water and Norrvatten). There are five subgroups within the project, all connected by DOC, working with i) DOC monitoring through a) fluorescence spectroscopy and b) remote sensing, ii) DOC removal from drinking water, iii) the role of DOC in the regional carbon cycle, and iv) modelling of DOC quantity and quality. The project aims to provide results of importance for i) safe drinking water production in Sweden and other boreal areas with similar climate development, and ii) correct estimations of the role of inland waters for the carbon cycle. In this project I have worked with DOC removal from drinking water (subgroup ii defined above), investigating existing and novel treatment processes with a variety of analytical tools.

GenoMembran ("through membranes"), funded by the Swedish Water & Wastewater Association. is a collaboration between Lund University, Swedish University of Agricultural Sciences, the Norwegian research centre SINTEF and four drinking water producers: Norrvatten (Görväln WTP, Stockholm), VIVAB (Kvarnagården WTP, Varberg), Tekniska Verken (Råberga WTP, Linköping) and Sydvatten (Ringsjö WTP, Skåne). The project aims to investigate ultra- and nanofiltration membranes for improved DOC removal during drinking water production. My role in the project has been to perform characterization of DOM before and after pilot scale membrane filtration and compare results to the full scale treatment at the studied WTPs.

3.2 Study sites and sampling

3.2.1 Water treatment plants with conventional processes (paper I and II)

In paper I and II samples from four large WTPs in Sweden were used; Lovö, Lackarebäck, Ringsjö and Kvarnagården (Figure 2 and 3). Samples were collected monthly or bi-monthly between May and December 2011 and analysed for DOC and optical characteristics. Lovö WTP was studied most thoroughly with samples taken between all treatment steps while raw water and drinking water was collected from the three other WTPs. For one sampling occasion, ultra-high resolution mass spectrometry was used to obtain DOM molecular level information. Additional data from two other WTPs, Råberga and Görväln was used to confirm results from paper I and II.

Figure 2. Map (Google Maps) of middle and southern Sweden showing the location of the six water treatment plants (WTPs) that were sampled within this PhD project. Note that the locations for Görväln and Lovö WTPs are not resolved at this scale.

Lovö is one of the three WTPs supplying drinking water to Sweden's capital Stockholm, which has 1.4 million inhabitants. Lake Mälaren, the third largest lake in Sweden, is used as raw water source. The WTP was constructed 1933 with coagulation using aluminium sulphate as the main treatment process, followed by rapid sand filtration to remove flocs that have remained after sedimentation. In 1938 slow sand filtration, in large outdoor basins, was added in the treatment train in order to manage problems with unwanted taste and odour. Slow sand filtration only has a small effect on the DOC concentration but a minor fraction is removed through bacterial consumption. In 1959 an expansion of the WTP was done to increase its capacity, but the main treatment has remained. Before the water enters the distribution network it is disinfected with UV-light and monochloramine to avoid bacterial regrowth. The average water production at Lovö WTP is 150000 m^3 per day.

Ringsjö WTP is situated in the

south of Sweden and supplies drinking water for the Skåne County. The production averages approximately 110000 m^3 per day. When built, in 1963, the lake Ringsjön was used as raw water source but after construction of an 80 km long tunnel, that was finished in 1987, the WTP started to use Lake Bolmen instead. Ringsjö WTP also applies conventional treatment with chemical coagulation with iron chloride followed by rapid sand filtration. The water thereafter passes through slow sand filtration basins and is then disinfected with sodium hypochlorite before pumped to the distribution network.

One of the two treatment plants producing drinking water for Gothenburg, Sweden's second largest city, is Lackarebäck WTP. The raw water intake for Lackarebäck is situated in the Delsjö lakes. These lakes work as reservoirs and approximately 1000 L s^{-1} is pumped into the lakes from the large river Göta Älv through an intake at Lärjeholm. When the water quality in Göta Älv is insufficient the water intake at Lärjeholm is closed, which occurs up to 100 days per year. At the treatment plant, the raw water is pre-chlorinated before coagulation treatment with aluminium sulphate is applied. After filtration with active carbon, the water is disinfected with chlorine dioxide and chlorine. Lackarebäck WTP is currently being upgraded with an additional treatment step, ultrafiltration membranes to introduce and additional microbial barrier. The pore size of the membranes is, however, too large to remove DOM. Together with the other Gothenburg WTP, Alelyckan, Lackarebäck produces 170000 m^3 drinking water per day. In addition to the new ultrafiltration step, the active carbon filters at Lackarebäck are also being expanded and after completion, the treatment plant will alone have a maximum production capacity of 186000 m^3 per day.
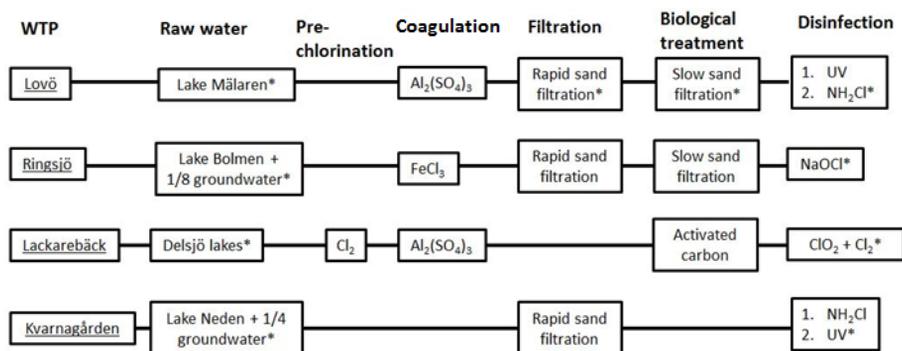

Figure 3. Overview of treatment processes used at the four drinking water treatment plants studied in paper I and II. Sampling points are marked with asterisks.

At Kvarnagården WTP, located in Varberg commune in western Sweden, the raw water consists of a mixture of Lake Neden and approximately 15-20% groundwater. This raw water contains considerable less DOC compared to the three other studied treatment plants. Therefore, the treatment (during the studied time period) only consisted of a rapid sand filter for removal of particles, followed by disinfection with monochloramine and UV radiation. Even if the DOC concentration in Lake Neden is still relatively low, the water colour (as mg Pt L^{-1}) doubled between 1997 and 2011 and to counteract the increasing browning and furthermore introduce another microbial barrier, ultrafiltration with direct coagulation is currently being added as an additional treatment step.

Råberga WTP was sampled within the GenoMembran project. The WTP was built in 1920 but has been reconstructed and expanded continuously since then. Today, approximately 10000 m^3 of drinking water is being produced each day which will be increased to 45000 m^3 per day through a current reconstruction of the treatment plant. The WTP employs coagulation treatment with aluminium sulphate followed by rapid sand filtration, slow sand filtration and disinfection with sodium hypochlorite. The rapid sand filters will in the future be substituted by granular activated carbon (GAC) filters to increase the removal of compounds causing unwanted taste and odour. Furthermore, UV disinfection will be added after the slow sand filters as an additional microbial barrier.

Görväln WTP was built in the late 1920's and is one of three large surface water treatment plants in Stockholm, providing drinking water to the northern areas of the capital. The eastern part of Lake Mälaren is used as raw water source, and the treatment processes are similar to those at Lovö WTP, however, with GAC filters instead of slow sand filters. The daily production of drinking water at Görväln WTP is approximately 120000 m^3.

3.2.2 Pilot study of magnetic ion exchange (MIEX®) (unpublished)

At Lovö WTP a pilot the MIEX® process was studied, using a pilot scale high rate contactor, between October 2013 and April 2014. One of the main aims was to lower the DOC concentration to below 2 mg C L^{-1} in order to decrease the formation of DBPs and the risk of biological regrowth in the distribution system. The MIEX® pilot was fed with untreated raw water and was connected to an existing pilot plant downstream where coagulation and slow sand filtration was applied. From December 2013 to the end of March 2014 a constant treatment of approximately 900 bed volumes (mL treated water/mL settled MIEX resin) was applied in the MIEX® pilot. Meanwhile, the coagulant dose in the pilot plant was successively lowered from equivalent to

the full scale dose down to 15% of the full scale dose in March. In April, a coagulant dose equivalent to the full scale treatment was used, while the treated bed volumes in the MIEX® pilot was gradually lowered from 900 to approximately 720.

3.2.3 Pilot study of a novel hollow fibre nanofiltration membrane (paper III)

In June 2012, a pilot study using a novel hollow fibre nanofiltration (NF) membrane was initiated at Görväln WTP. The used membrane was HFW 1000, a capillary, hollow-fibre nanofiltration membrane developed by Pentair X-Flow for high removal of DOM and low retention of hardness. The membrane fibres are permanently hydrophilic and have a molecular weight cut-off of 500-1000 Da. The motivation behind the study at Görväln WTP was to i) increase the removal of DOM (with less than 20% increase in salt removal), and ii) investigate if the performance of downstream GAC filters could be improved. Görväln WTP aims to use the GAC filters as a chemical barrier that can remove micro-contaminants or protect the drinking water in case of oil or diesel pollution events in the raw water source. The presence of DOM, however, leads to the GAC filters being saturated within approximately 2 months after regeneration and thereafter only work as bio-filters. The NF membrane pilot was fed with coagulated water from the full scale treatment and the NF permeate was treated with a pilot scale GAC filter. As a reference to the full scale treatment, an additional pilot scale GAC column was fed directly with coagulated water. This experimental set-up was used until May 2014 during which samples were collected monthly. Some initial problems with swelling of the membrane pores during chemical cleaning resulted in three test periods with slightly different, and with time improved, membrane elements. In this thesis the focus has been on the last, and most successful, trial period which lasted from August 2013 to May 2014 during which no regeneration of the GAC occurred.

3.2.4 Lake Mälaren (paper IV)

Lake Mälaren is Sweden's third largest lake and is situated west of the capital Stockholm. It has a surface area of 1140 km^2 and spans 120 km from west to east. The lake is divided into 6 basins as a function of its specific shape and a large abundance of islands (Wallin & Andersson, 2000) (Figure 4). A majority of the water, approximately 70% enters the lake in the most western basin A, while 11% is added in basin D, in the northeast part of the lake (Wallin & Andersson, 2000). These two water masses meet and mix in the eastern basin E where the average water age is 2.8 years (Liungman *et al.*, 2010). Lake Mälaren is widely used for recreational purposes and is also the raw water

source for the three surface water treatment plants in Stockholm, all with raw water intakes in the eastern part of the lake.

For paper IV, the sampling was performed in August 2013 concurrently with the regular monitoring of Lake Mälaren. 11 lake sites were sampled for surface water (Figure 4) and three of them additionally for deep water. Samples were also collected from the two rivers contributing with the largest amount of water to basin A and D, Arboga River and Fyris River.
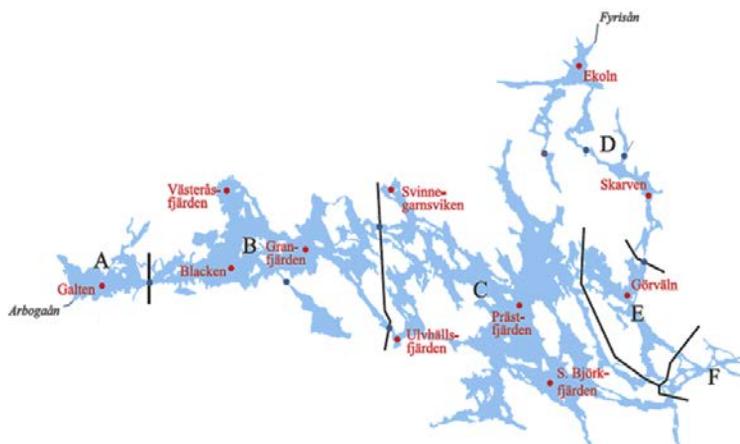

Figure 4. Map of Lake Mälaren with the 11 sampling points for paper IV marked in red. The 6 basins of the lake are denoted A-F. The figure is modified from (Wallin & Andersson, 2000)

3.3 Chemical analyses and data processing

In this section a shorter summary of the analytical methods used in this thesis is given. Detailed information can be found in the respective papers.

3.3.1 DOC and dissolved iron

Filtered (0.45 μm) samples were analysed for DOC using a Shimadzu TOC-V_{CPH} carbon analyser with a measurement error of ± 0.4 mg C L^{-1}. Dissolved iron (Fe_{diss}) was measured using ICP-AES for the samples intended for paper IV. Analyses were performed at the accredited laboratory at the Department for Aquatic Sciences and Assessment, SLU, Uppsala according to SS-EN ISO 11885:2009.

3.3.2 Absorbance and 3D fluorescence

Three different instruments were used for the samples in this thesis. For paper I and II, absorbance was collected using a Perkin-Elmer Lambda 40 spectrophotometer while fluorescence was measured with a Flouromax-2 spectrofluorometer (Horiba Jobin Yvon). For the second half of this PhD project a new instrument (Aqualog, Horiba Jobin Yvon), capable of collecting absorbance and fluorescence simultaneously, was purchased which was used to measure samples for paper III and IV. The sample fluorescence signal (S) was corrected with a lamp reference signal (R), to obtain S/R, both for measurements done with the Fluoromax-2 and the Aqualog. Further corrections included: i) conversion of the S/R signal to S_c/R_c according to spectral biases which are instrument specific and provided from the manufacturers, ii) removal of the water Raman peak though blank subtraction using Milli-Q water (18.2 Ω cm^{-1}) for samples measured with Fluoromax-2 and Starna Raman Ultra-Pure Water (Certified reference material 3/Q/10/WATER, Starna Scientific), iii) nullification of areas of Rayleigh scatter, and iv) inner filter effects correction (primary and secondary) using measured absorbance. The corrected fluorescence signals were converter from counts per second (cps) to water Raman units (RU) using the area under the water Raman peak (excitation: 350 nm, emission: 380-420 nm) which was measured in the beginning of every day analyses were performed.

Absorbance data was used to calculate the specific UV and visual absorbance, SUVA and SA420, by dividing the absorbance (in m^{-1}), at 254 and 420 nm respectively, with the DOC concentration. SUVA is related to carbon aromaticity as measured with ^{13}C-NMR (Weishaar *et al.*, 2003) while SA420 was used as a measure for water colour per DOC. When dissolved iron concentrations were significant (paper IV), values of SUVA and colour were corrected (Köhler *et al.*, 2013; Weishaar *et al.*, 2003) because iron has been found to significantly contribute to absorbance, especially in the visual spectrum.

Previously established indices were calculated from the fluorescence data, namely humification index (HIX = the ratio of areas under the emission spectra at 435-480 nm and the sum at 300 to 345 nm and 435 to 480 nm at an excitation wavelength of 254 nm) (Ohno, 2002; Zsolnay *et al.*, 1999), fluorescence index (FI = ratio of emission intensity at 470 nm and 520 nm at 370 nm excitation) (Cory & McKnight, 2005; McKnight *et al.*, 2001) and freshness index (β:α = emission intensity at 380 nm divided with the maximum intensity between 420 and 435 nm at 310 nm excitation) (Parlanti *et al.*, 2000). HIX has been coupled to degree of humification defined as a positive correlation with condensation (decreased H/C) (Zsolnay *et al.*, 1999), FI is an

indicator of DOM source on a range from terrestrial (FI ≈ 1.3) to microbial (FI ≈ 1.8) (Cory *et al.*, 2007) and β:α is related to DOM age with a higher value indicative of a larger contribution of freshly produced DOM (Parlanti *et al.*, 2000).

Differential fluorescence and absorbance spectra (ΔEEMs, ΔAbs) were calculated by subtracting the measured signal intensities from a sample downstream in a process train or natural gradient from an upstream sample (paper II-IV). Differential spectra were also used to plot the percent removed FDOM and CDOM.

3.3.3 FT-ICR-MS

Solid phase extracted samples were analysed at the Helmholtz Centre for Environmental Health in Munich, Germany, using a Bruker Solarix 12 Tesla FT-ICR mass spectrometer with electrospray ionization (ESI). ESI-FI-ICR-MS is considered a qualitative method because ESI is a competitive ionization process where compounds that are more prone to ionize will suppress less ionizable ones and ionization efficiency can also be affected by the sample matrix. However, it can be used semi-quantitatively when comparing samples with similar matrices to look at differences in the relative abundance of mass peaks and their assigned formulas e.g. along a natural gradient or from consecutive treatment processes in a WTP. Van Krevelen bubble plots (y = H/C, x = O/C), where bubble size represents the relative abundance in a sample, or the change in relative abundance during a treatment process or along a natural gradient were used in all papers to illustrate shifts in DOM composition with respect to H/C and O/C ratios. Values of H/C, O/C, double bond equivalency per carbon (DBE/C), and the average carbon oxidation state for components with C, H and O only ($\overline{C_{OS,CHO}}$) (paper I-IV) were calculated for single mass peaks and for whole samples as mean values weighted against the relative abundance of each component.

3.3.4 ^{1}H-NMR

Proton detected NMR spectra (paper IV) were acquired with a Bruker Avance III NMR spectrometer. ^{1}H-NMR section integrals were derived from AMIX-based bucket analysis (normalized to total ^{1}H NMR integral = 100%) in the chemical shift range $\delta_H = 0.4 – 10.0$ ppm, with the exclusion of resonance from methanol ($\delta_H = 3.20 – 3.40$ ppm) and residual water ($\delta_H = 4.85 – 5.26$ ppm). Key structural units related to the different ranges of chemical shifts are listed in Table 1.

Table 1. *List of chemical shift ranges and associated key structural units for proton NMR.*

δ(^{1}H) (ppm)	Key structural units
10.0-7.3	N-heterocycles in 6-membered rings, polycyclic aromatics, (poly) carboxylic acids
7.3-7.0	Single aromatic rings with neutral substituents
7.0-6.5	$C_{ar}\underline{\mathbf{H}}$ with oxygenated substituents (OH, OR) in ortho and para positions; five membered heterocycles (O, N, S)
6.5-6.0	Conjugated double bonds, =C-C=C$\underline{\mathbf{H}}$, five membered ring heterocycles (O, N, S)
6.0-5.3	Isolated double bonds, =C$\underline{\mathbf{H}}$; O_2C$\underline{\mathbf{H}}$
5.3-5.26	Isolated double bonds, =C$\underline{\mathbf{H}}$; O_2C$\underline{\mathbf{H}}$
4.9-3.1	OC$\underline{\mathbf{H}},$ oxygenated aliphatics
3.1-2.1	OCC$\underline{\mathbf{H}}$, carboxylic-rich alicyclic materials (CRAM) and other functionalized aliphatics
2.1-1.9	OCCC$\underline{\mathbf{H}}$
1.9-1.35	OCCC$\underline{\mathbf{H}},$ branched aliphatics, condensed alicyclic rings
1.35-1.25	(C$\underline{\mathbf{H}}_2$)$_n$ polymethylene; certain branched aliphatics
1.25-0.4	CCCC$\underline{\mathbf{H}}$, C$\underline{\mathbf{H}}_3$ groups

3.3.5 Rank correlation

In paper II and IV rank correlation was used, according to Herzsprung *et al.* 2012, in order to couple optical (absorbance and fluorescence indices) (paper II and IV) and structural (^{1}H-NMR) (paper IV) information to chemical formulas assigned to mass peaks from FT-ICR-MS analyses. The Spearman's rank correlation coefficient was calculated between each mass peak and the optical and structural parameters. The p-value for each correlation was determined according to commonly used critical values. All correlations with $p<0.05$ were considered significant.

4 Results and Discussion

4.1 Correlating optical and structural properties of DOM with molecular level information (paper II and IV)

Ultrahigh-resolution mass spectrometry, e.g. FT-ICR-MS, provide detailed molecular level information for DOM, and can be used to identify chemical properties related to DOM reactivity in natural and engineered systems. FT-ICR-MS analyses are, however, too time-consuming and expensive to be used at WTPs. Optical analyses, namely absorbance and fluorescence techniques, are considerably faster and cheaper and can be used to obtain real-time monitoring of DOM quality through online sensors. By using rank correlation to relate absorbance and fluorescence measurements with individual components obtained from FT-ICR-MS analyses we aimed to identify how optical properties are related to the molecular characteristics of DOM.

The optical parameters selected for the rank correlations have, by others, previously been related to specific DOM characteristics as well as the removal of DOC during drinking water production. In both paper II and IV optical indices indicative of a terrestrial (allochthonous) origin and prevalence of aromatic carbon (HIX and SUVA (Weishaar *et al.*, 2003; Zsolnay *et al.*, 1999)), together with FDOM with emission at longer wavelengths (%FDOM$_{450\text{-}600}$) correlated positively with oxidized CHO components ($\overline{C_{OS}}$ ≥ 0) with relatively high DBE/C (Figure 5) and O/C. High SUVA and FDOM with emission at relatively long wavelengths are related to DOM being readily removed during chemical coagulation at WTPs (paper II) (Shutova *et al.*, 2014; Sanchez *et al.*, 2013; Baghoth *et al.*, 2011; Edzwald, 1993), as are components with high O/C (paper II) (Gonsior *et al.*, 2014; Zhang *et al.*, 2012). Indices connected to freshly produced DOM (β:α) of microbial origin (FI) (McKnight *et al.*, 2001; Parlanti *et al.*, 2000) and FDOM with emission at shorter

wavelengths (%FDOM$_{300-450}$) were positively correlated to CHO components with reduced carbon ($\overline{C_{OS}} \leq 0$) and relatively low DBE/C (Figure 5).

In paper IV, data from analyses of ^{1}H-NMR were also included in the rank correlation where resonance related to hydrogen associated with aromatic rings with neutral and oxygenated (-OH, -OR) substituents (δ_H = 7.3-7.0 and 7.0-6.5 ppm respectively), conjugated double bonds (δ_H = 6.5-6.0 ppm) and oxygenated aliphatics correlated with similar components as HIX, SUVA and %FDOM$_{450-600}$. This could be expected due to the prevalence of aromatic moieties and methoxy functional groups in lignin-derived, terrestrial DOM (Kleber & Johnson, 2010; Kalbitz *et al.*, 2003; Ralph *et al.*, 1999). NMR resonance related to aliphatic groups ("pure" aliphatics, methyl groups (0.4-1.25 ppm), methylene groups, branched aliphatics, alicyclic rings (1.35-1.25 ppm, 1.9-1.35 ppm), as well as functionalized aliphatics (3.1-2.1 ppm) such as carboxyl-rich alicyclic materials (CRAM) showed similar correlations as β:α, FI and %FDOM$_{300-450}$. More simple aliphatic structures are connected with algal matter (Zhang *et al.*, 2014; Mash *et al.*, 2004) while functionalized aliphatics are expected to increase with in-lake bacterial processing of algal matter leading to the formation of a more complex mixture of compounds, such as CRAM (Hertkorn *et al.*, 2013; Hertkorn *et al.*, 2006).

The most important finding was that $\overline{C_{OS}}$ clearly divided components that correlated with optical parameters connected to allochthonous and autochthonous DOM along the zero line into two groups of oxidized and reduced components respectively (Figure 5). Clearly, the average oxidation state of carbon could be connected both to selective removal during commonly used drinking water treatment techniques (paper II) as well as changes occurring with increasing residence time in a large boreal lake (paper IV) as will be further discussed in the following sections.
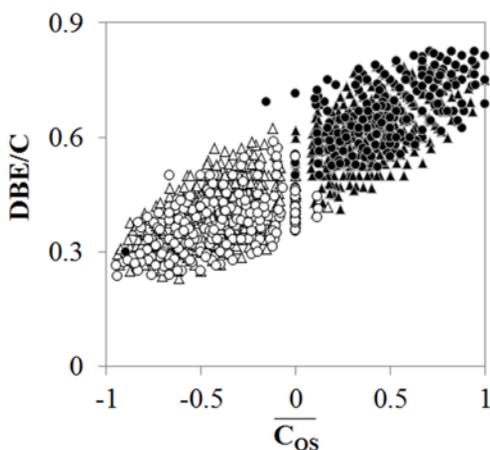

Figure 5. Double bond equivalency per carbon and the average carbon oxidation state for allochthonous (black markers) and autochthonous DOM (white markers) in paper II (triangles) paper IV (circles).

4.2 Selective removal of DOM during drinking water production with conventional and novel treatment processes (paper I-III)

In paper (II) the main focus was on selective removal of DOM with different optical properties during conventional drinking water treatment and disinfection and how these changes related to the removal of specific DOM components detected with FT-ICR-MS analyses. In order to validate results from paper (II), which were mainly based on data from one treatment plant, I add here additional unpublished data from several other WTPs, together with data from the full scale treatment measured during the course of the pilot scale membrane experiment at Görväln WTP (paper III). Two pilot scale studies of more novel treatment techniques, i.e. magnetic ion exchange (MIEX®) (unpublished) and hollow fibre nanofiltration (paper III) that were conducted at Lovö and Görväln WTPs respectively will thereafter be presented and compared.

4.2.1 Coagulation

During coagulation treatment, close to 50% of the raw water DOC was removed from Lovö and Görväln WTPs (Table 2). This is in line with what can be expected from their respective raw water SUVA (Table 3) as the removal efficiency has been reported to be 25-50% from waters with SUVA from 2 to 4 (Matilainen *et al.*, 2010; Edzwald, 1993).

Table 2. *Changes occurring during coagulation treatment using aluminium sulphate ($Al_2(SO_4)_3$) (Lovö, Görväln, Lackarebäck and Råberga water treatment plants (WTPs) and iron chloride ($FeCl_3$) (Ringsjö WTP). ΔDOC = % removed dissolved organic carbon, ΔFI, ΔHIX, and Δβ:α = fluorescence index, humification index and freshness index from differential excitation emission matrices, ΔH=% removed humic-like fluorescence, and ΔP=% removed protein-like fluorescence.*

WTP	Samples (n)	ΔDOC (%)	ΔFI	ΔHIX	Δβ:α	ΔH (%)	ΔP (%)	Source
Lovö 1	8	43 ± 3	1.27 ± 0.03	0.93 ± 0.01	0.47 ± 0.02	58 ± 2	30 ± 6	Paper II
Lovö 2	18	49 ± 2	1.34 ± 0.01	0.93 ± 0.01	0.48 ± 0.01	63 ± 1	37 ± 2	Unpublished
Görväln	22	49 ± 4	1.36 ± 0.02	0.94 ± 0.01	0.47 ± 0.01	64 ± 4	33 ± 11	Paper III
Ringsjö	12	72 ± 2	1.32 ± 0.01	0.94 ± 0.01	0.43 ± 0.01	82 ± 2	60 ± 6	Unpublished
Lackarebäck	3	47 ± 1	1.22 ± 0.02	0.90 ± 0.00	0.49 ± 0.00	62 ± 1	40 ± 2	Unpublished
Råberga	6	47 ± 4	1.34 ± 0.01	0.94 ± 0.01	0.48 ± 0.02	65 ± 3	39 ± 9	Unpublished

Additional data from Lackarebäck and Råberga WTPs further support this (Table 2 and 3). The significantly higher DOC reduction at Ringsjö WTP (Table 1) likely resulted from a combination of the use of iron chloride as coagulant, which is more effective than aluminium sulphate and the higher raw water SUVA (Table 3). During treatment, SUVA decreased (Table 3), as commonly reported (Matilainen *et al.*, 2010), indicating that aromatic, terrestrially derived DOM (Weishaar *et al.*, 2003) was preferentially removed. Fluorescence indices support this as shown by decreased HIX (selective removal of humic, terrestrial FDOM) as well as increased FI and β:α (poor removal of microbial, freshly produced FDOM) (Table 3). The optical indices, however, only show which type of DOM that is easiest to remove. In paper II we demonstrated that plotting the percentage removed FDOM gives a more complete view of the range of removal efficiencies (Figure 6). For Lovö WTP removal during coagulation treatment ranged from approximately 30% for shorter emission wavelength protein-like FDOM (excitation = 276 nm, emission = 320 nm) to almost 60% for longer emission wavelength humic FDOM (excitation = 350 nm, emission = 550 nm) (Table 2). Still, FI calculated from differential EEMs (ΔFI) was approximately 1.30-1.35 (Table 2), which is close to reported values for terrestrial endmember samples (typically 1.3) (Cory *et al.*, 2007; Cory & McKnight, 2005), demonstrating the high selectivity towards removal of terrestrial DOM during coagulation treatment.
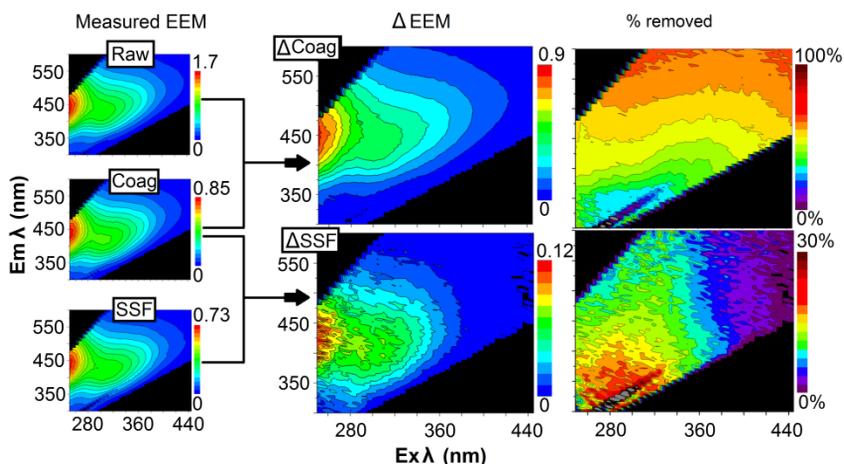
Figure 6. Calculation scheme for differential excitation emission matrices (ΔEEMs) as exemplified by coagulation (Coag) and slow sand filtration (SSF) at Lovö water treatment plant. The differential EEMs are divided by the sample before treatment in order to calculate the % removed fluorescing dissolved organic matter. Em λ = emission wavelength, Ex λ = excitation wavelength. Signal intensities of measured and ΔEEMs are given in Raman units. The figure is modified from paper II.

This is further supported by the high HIX and low β:α for the differential EEMs (ΔHIX and Δβ:α, Table 2) compared to values in the respective raw waters (Table 3) showing that the removed FDOM is relatively old and humified (Ohno, 2002; Parlanti *et al.*, 2000; Zsolnay *et al.*, 1999).

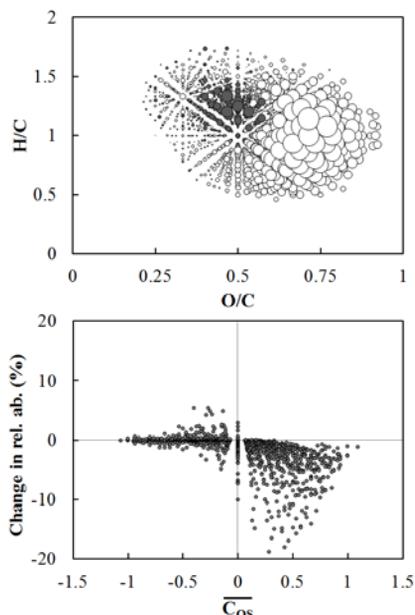*Figure 7.* Change in relative abundance of chemical formulas containing C, H and O that was present both before and after coagulation treatment at Lovö WTP. Above = van Krevelen diagram where the y-axis shows the hydrogen to carbon ratio (H/C) and the x-axis the oxygen to carbon ratio (O/C). Bubble size represents the change in relative abundance during coagulation (gray bubble = increase, white bubble = decrease). Below = change in relative abundance of individual components as a function of the average carbon oxidation state ($\overline{C_{OS}}$). The figure is modified from paper II.

On the molecular level, we found that for components that decreased in relative abundance with more than 2% during the coagulation treatment at Lovö WTP (paper II), the majority (58%) correlated with terrestrial optical indicators and a smaller amount (6%) with parameters related to in-lake produced DOM, in line with the results from differential EEMs. Among the decreasing components, 99% of those that correlated with SUVA in the rank correlation (see section 4.1) were represented, demonstrating the usefulness of the parameter for assessing the treatability of DOM during coagulation. The decreasing components had, in general, high O/C and low H/C (Figure 7), in line with Gonsior *et al.*, 2014 and Zhang *et al.*, 2012, which is indicative of a high abundance of carbon-carbon double bonds, likely conjugated or present in aromatic moieties, and oxygen functional groups, as can be expected for DOM of terrestrial origin (Kleber & Johnson, 2010). Carbon oxidation was particularly related to DOM removal by coagulation as every single component

with positive C_{OS} decreased during treatment (Figure 7). The components that decreased during coagulation with more than 2% were compared to equivalent ones from other sampling events of Lovö and Görväln WTPs. Among these components approximately 80% were reoccurring during the three sampling events demonstrating that i) there were no large differences in the DOM composition between the sampled years and seasons (October 2011, September 2013, and January 2014), or the different geographical locations of the two

treatment plants' raw water intakes in Lake Mälaren, and ii) coagulation is a robust process that repeatedly removes similar DOM components.

Differential absorbance curves were used to plot the % removed CDOM which demonstrated that at most WTPs there was constant removal from 240-275 nm, followed by a gradual increase of approximately 10% up to 340 nm (Figure 8). At Lackarebäck WTP there was a small deviation from the gradual increase, as absorbance around 260-270 nm appeared to be particularly efficiently removed. We, and others, have found that absorbance in this range is especially reactive during chlorination and chloramination (paper II) (Roccaro & Vagliasindi, 2009; Korshin, 2002) (see section 4.2.4 on disinfection practices).
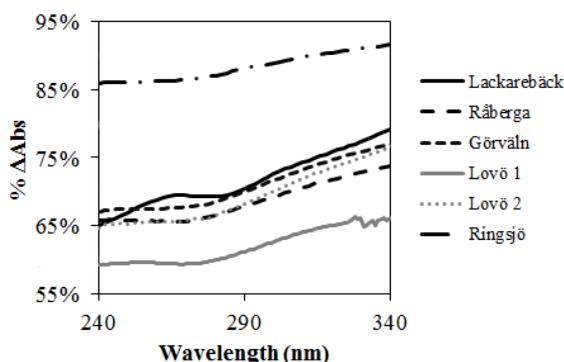

Figure 8. The percent removed absorbance during coagulation treatment (average values) at five large Swedish water treatment plants (WTPs). The two sampling campaigns at Lovö WTP are plotted separately (Lovö 1 = 2011, paper II, Lovö 2 = 2013-2014, unpublished).

During chlorination, reduced DOM components are likely to be responsible for the majority of the disinfectant consumption through oxidation reactions (paper I, paper II) (Zhang *et al.*, 2012; Rice & Gomez-Taylor, 1986). These reactions should therefore be connected to the removal of absorbance around 260-270 nm, which occurs simultaneously. If the deviating differential absorbance at Lackarebäck WTP is purely an effect of CDOM reacting with chlorine or if the coagulation treatment has been enhanced cannot be determined from our data. But because components with positive $\overline{C_{OS}}$ were particularly reactive during coagulation, reduced CDOM components that were oxidized during the pre-chlorination could have been subsequently removed during coagulation. Previous studies of pre-oxidation with various oxidants have shown both positive and negative effects on coagulation efficiency. Positive effects have been proposed to be attributed to formation of smaller molecules with increased hydrophobic affinity, a polymerization effect or formation of oxygenated functional groups (Camel & Bermond, 1998; Moyers & Wu, 1985), while negative effects are hypothesized to arise mainly from formation of smaller, more bioavailable compounds from humic substances (Ji *et al.*, 2008; Becker & O'Melia, 1996; Moyers & Wu, 1985).

Table 3. *Dissolved organic carbon concentration (DOC), specific UV absorbance (SUVA), humification index (HIX), fluorescence index (FI) and freshness index (β:α) for samples from full and pilot scale treatments. Raw = raw water, RSF = rapid sand filtrate (sample taken after coagulation treatment), SSF = slow sand filtrate, DW = drinking water (sample taken after disinfection, MIEX = sample taken after MIEX treatment of raw water, RSF-P = pilot rapid sand filtrate, SSF-P = pilot slow sand filtrate, GAC = granular activated carbon filtrate, NFperm = nanofiltration permeate, GAC2 = pilot granular activated carbon filtrate (downstream from the NF treatment), GAC4 = pilot reference granular activated carbon (fed with coagulated water, as in the full scale treatment), DEK = decanted water, taken after coagulation treatment (when rapid sand filtration is not applied).*

		DOC (mg L^{-1})	SUVA (mg^{-1} L m^{-1})	HIX	FI	β:α
Lovö 1	Raw	8.9 ± 0.4	2.7 ± 0.1	0.90 ± 0.01	1.41 ± 0.02	0.61 ± 0.01
	RSF	5.1 ± 0.3	1.9 ± 0.1	0.87 ± 0.02	1.58 ± 0.03	0.74 ± 0.01
	SSF	4.7 ± 0.3	1.8 ± 0.1	0.87 ± 0.02	1.57 ± 0.01	0.72 ± 0.01
	DW	4.4 ± 0.3	1.8 ± 0.1	0.88 ± 0.02	1.56 ± 0.01	0.72 ± 0.01
Lovö 2	Raw	9.8 ± 0.9	2.7 ± 0.1	0.91 ± 0.00	1.47 ± 0.01	0.61 ± 0.00
	RSF	4.9 ± 0.4	1.8 ± 0.1	0.88 ± 0.00	1.67 ± 0.01	0.76 ± 0.01
	SSF	4.4 ± 0.2	1.8 ± 0.1	0.89 ± 0.00	1.67 ± 0.01	0.74 ± 0.01
	DW	4.4 ± 0.2	1.8 ± 0.1	0.88 ± 0.00	1.68 ± 0.01	0.74 ± 0.01
Lovö pilot	MIEX	3.1 ± 0.5	1.3 ± 0.1	0.81 ± 0.02	1.82 ± 0.03	0.88 ± 0.04
	RSF-P	2.6 ± 0.4	1.3 ± 0.1	0.82 ± 0.01	1.84 ± 0.03	0.92 ± 0.03
	SSF-P	2.5 ± 0.4	1.3 ± 0.1	0.83 ± 0.01	1.85 ± 0.03	0.91 ± 0.04
Görväln	Raw	9.4 ± 1.0	2.9 ± 0.2	0.92 ± 0.01	1.48 ± 0.01	0.60 ± 0.02
	RSF	4.8 ± 0.3	1.9 ± 0.1	0.88 ± 0.01	1.68 ± 0.01	0.76 ± 0.02
	GAC	4.7 ± 0.3	1.9 ± 0.1	0.88 ± 0.01	1.68 ± 0.03	0.75 ± 0.01
	DW	4.7 ± 0.3	1.8 ± 0.1	0.89 ± 0.01	1.66 ± 0.02	0.75 ± 0.01
Görväln pilot	NFperm	1.0 ± 0.3	1.2 ± 0.2	0.83 ± 0.01	1.84 ± 0.03	0.95 ± 0.04
	GAC2	0.7 ± 0.3	0.9 ± 0.3	0.83 ± 0.01	1.74 ± 0.04	0.80 ± 0.02
	GAC4	4.1 ± 1.2	1.9 ± 0.2	0.88 ± 0.00	1.65 ± 0.02	0.71 ± 0.02
Ringsjö	Raw	10.2 ± 1.1	3.9 ± 0.2	0.93 ± 0.01	1.40 ± 0.01	0.50 ± 0.01
	RSF	2.9 ± 0.2	1.9 ± 0.2	0.88 ± 0.01	1.71 ± 0.02	0.72 ± 0.01
	SSF	2.7 ± 0.3	1.8 ± 0.2	0.87 ± 0.01	1.69 ± 0.02	0.70 ± 0.01
	DW	2.6 ± 0.2	1.6 ± 0.2	0.89 ± 0.01	1.73 ± 0.02	0.71 ± 0.01
Lackarebäck	Raw	4.9 ± 0.1	2.5 ± 0.1	0.86 ± 0.01	1.42 ± 0.01	0.64 ± 0.00
	DEK	2.6 ± 0.1	1.5 ± 0.2	0.81 ± 0.02	1.69 ± 0.01	0.81 ± 0.01
	GAC	2.3 ± 0.1	1.4 ± 0.2	0.80 ± 0.03	1.61 ± 0.03	0.75 ± 0.00
	DW	2.3 ± 0.1	1.3 ± 0.2	0.77 ± 0.03	1.75 ± 0.02	0.86 ± 0.03
Råberga	Raw	9.3 ± 0.3	2.9 ± 0.1	0.92 ± 0.01	1.47 ± 0.01	0.61 ± 0.01
	RSF	5.0 ± 0.3	1.8 ± 0.1	0.88 ± 0.01	1.67 ± 0.01	0.76 ± 0.01
	SSF	4.2 ± 0.3	1.8 ± 0.1	0.90 ± 0.03	1.67 ± 0.03	0.73 ± 0.00
	DW	4.4 ± 0.3	1.6 ± 0.1	0.91 ± 0.03	1.68 ± 0.02	0.74 ± 0.01

4.2.2 Slow sand filtration

DOC removal in slow sand filters was small (7-15%) or insignificant (Table 4). Using fluorescence analysis a clear pattern was revealed, where DOM emitting fluorescence with relatively short emission wavelengths had been especially reactive, opposite to coagulation (Figure 6). In fact, removal of protein-like FDOM exceeded that of humic-like material in all studied WTPs (Table 4). ΔFI (Table 4) show that the removed FDOM resembled that of microbial endmember samples (paper II), which have values of approximately 1.8 (Cory *et al.*, 2007; Cory & McKnight, 2005; McKnight *et al.*, 2001). Meanwhile, ΔHIX was considerably lower and Δβ:α significantly higher (Table 3) compared to material removed during coagulation (Table 2), demonstrating that freshly produced, autochthonous DOM was primarily removed. Differential absorbance data show that the shoulder at 260-270 nm was especially susceptible to slow sand filtration (paper II, supported by unpublished data) (Figure 9). Absorbance in this wavelength range overlaps with that from the amino acids tyrosine, tryptophan and phenylalanine (Lakowicz, 2007), which are also considered to be responsible for protein-like fluorescence (Coble, 1996; Coble *et al.*, 1990). In spite of slow sand filtration mainly removing protein-like material, the difference in DOC removal between the WTPs could not be unambiguously connected to any of the quality measures. For example, none of the fluorescence indices, SUVA, or the DOC concentration differed between the rapid sand filtrates (slow sand filtration feed) at Lovö and Råberga WTPs (Table 3) and still, DOC removal was approximately the double at Råberga. However, at Ringsjö, where no significant DOC reduction occurred across the slow sand filters, DOC concentration in the feed was significantly lower. It is therefore likely to contribute with less carbon substrate, especially because the DOM composition was of more humic, terrestrial character (Table 3).
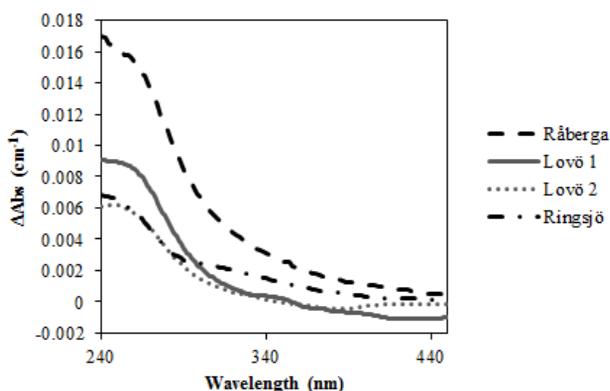

Figure 9. Average differential absorbance (ΔAbs) during slow sand filtration at Råberga, Lovö, and Ringsjö water treatment plants. The figure is modified from paper II.

Table 4. *Changes in dissolved organic carbon quantity and quality during slow sand filtration. ΔDOC = percent removed dissolved organic carbon, ΔFI, ΔHIX, and Δβ:α = fluorescence index, humification index and freshness index calculated from differential excitation emission matrices, ΔH = percent removed humic-like fluorescence, and ΔP = percent removed protein-like fluorescence.*

WTP	Samples (n)	ΔDOC (%)	ΔFI	ΔHIX	Δβ:α	ΔH (%)	ΔP (%)	Source
Lovö 1	8	8 ± 3	1.71 ± 0.10	0.82 ± 0.02	0.99 ± 0.10	6 ± 2	13 ± 5	Paper (II)
Lovö 2	7	7 ± 3	NS[a]	0.73 ± 0.05	1.24 ± 0.21	2 ± 2	11 ± 3	Unpublished
Ringsjö	12	NS	1.97 ± 0.11	0.84 ± 0.03	0.97 ± 0.09	8 ± 2	11 ± 5	Unpublished
Råberga	6	15 ± 5	1.72 ± 0.08	0.80 ± 0.04	0.95 ± 0.09	11 ± 3	24 ± 16	Unpublished

NS = not significant, [a]removal at an excitation wavelength of 370 nm was not quantifiable

Clearly, removal of DOM in biological filters is more complex than that of coagulation which can easily be related to the composition of the organic matter. Except for DOM composition, it is likely that DOC concentration, temperature, water chemistry, potential microbial production of DOM, and the composition of the microbial community in the filters have affected the DOC removal efficiency to different extents. It is also possible that the removal efficiency differs between compounds within the protein-like, autochthonous DOM fraction, further contributing to differences in the DOC reduction.

4.2.3 Granular activated carbon (GAC) filters

GAC may affect the DOC concentration and composition through i) adsorption and ii) biodegradation by microorganisms attached to the filters. There was no significant decrease in DOC at either Görväln (unpublished) or Lackarebäck WTPs (Table 3). FDOM, however, was affected, and at Görväln 15 ± 11 % of protein-like material was removed compared to only 4 ± 3 % of humic-like fluorescence indicating that the GAC mainly acted as a biofilter, as protein-like material is generally more bioavailable than humic material (Cammack *et al.*, 2004). At Lackarebäck on the other hand, there was no significant difference between removal of humic- and protein-like FDOM (32 ± 5% and 29 ± 8% respectively), showing that the GAC had more remaining adsorptive function, as humic substances would primarily be removed through adsorption (Velten *et al.*, 2011).

4.2.4 Disinfection

Using FT-ICR-MS analyses, we found a diversity of chlorine-containing disinfection by products (DBPs) at four studied WTPs using monochloramine (Lovö and Kvarnagården), sodium hypochlorite (Ringsjö), or a combination of chlorine and chlorine dioxide (Lackarebäck) as disinfectants (paper I). In total 499 DBPs with 1 and 2 Cl where identified, of which 230 had not been reported earlier. Chlorine chemicals can form DBPs with DOM through oxidation, addition to unsaturated bonds or electrophilic substitution. The two latter lead to the formation of organochlorine compounds, however, addition reactions are proposed to proceed too slowly to be significant under the conditions applied in drinking water disinfection. Therefore, electrophilic substitution is the most likely reaction for formation of Cl-DBPs (Deborde & Gunten, 2008). Because O/C and DBE/C are not affected during electrophilic substitution but were higher for the Cl-DBPs compared to the bulk DOM components, we concluded that selective chlorination of components with a high abundance of oxygen and carbon-carbon double bonds had occurred at all WTPs.

In paper II we showed that CDOM with absorbance around 260-270 nm was especially reactive during UV/monochloramine disinfection. Here, we can further confirm this with data from four additional WTPs, using different chlorine chemicals (Figure 10). This is in line with previous studies where mainly absorbance at 272 nm decreased during chlorination (Roccaro & Vagliasindi, 2009; Korshin *et al.*, 2002). These studies focused on connecting the loss of absorbance to the formation of different chlorinated DBPs. With FT-ICR-MS analyses, we found that the most pronounced shift in DOM composition was from reduced to oxidized components (paper I, paper II), and similarly Zhang *et al.*, 2012 concluded that components with low O/C were especially reactive during chlorination, as can be expected due to the larger energy gain for oxidation of the most reduced molecules. Therefore, it is most likely that the majority of the decrease in absorbance represents oxidation of chemically reduced DOM components. The reduced components should be connected to autochthonous DOM, as established with rank correlation (section 4.1, paper II, paper IV). By measuring absorbance for a MilliQ water extract from an algae mixture dominated by cyanobacteria (*Pseudanabaena sp.*) we found a signal maximum around 260 nm (Figure 10). Hence, algae-derived DOM was likely the most reactive material during chlorination and chloramination, and should therefore have been responsible for the majority of the unwanted disinfectant consumption.
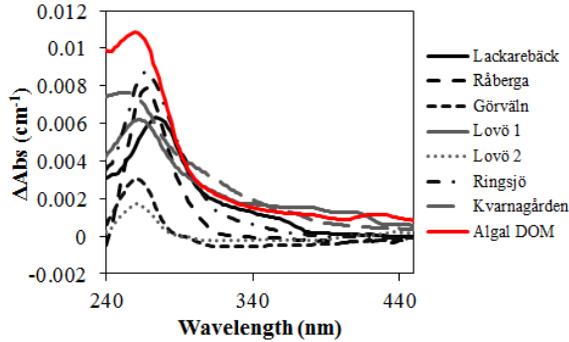
Figure 10. Differential absorbance (ΔAbs) during disinfection with monochloramine (Lovö, Görväln and Kvarnagården water treatment plants (WTPs)), sodium hypochlorite (Råberga and Ringsjö WTPs) as well as chlorine and chlorine dioxide (Lackarebäck WTP). The red line representing algal DOM shows the measured absorbance of a MilliQ water extract from an algae mixture dominated by cyanobacteria. The figure is modified from paper II

4.2.5 Pilot studies of nanofiltration and ion exchange

The novel nanofiltration membrane that was investigated in pilot scale at Görväln WTP led to a significant reduction in DOC with an additional $79 \pm 7\%$ removal from the, in full scale, coagulated feed (Table 3) (paper III). At Lovö WTP, MIEX® treatment reduced the raw water DOC concentration more than the full scale coagulation, however, applying subsequent coagulation in pilot scale only increased removal with 0.5 ± 0.1 mg C L^{-1} (Table 3), even though the coagulant dose was incrementally increased up to the same as used in the full scale treatment. Differential fluorescence EEMs demonstrate a similar pattern between coagulation, nanofiltration and MIEX® treatment with FDOM removal increasing with emission wavelength (Figure 11, compare to Figure 6), however, the two latter were able to remove larger amounts of FDOM as
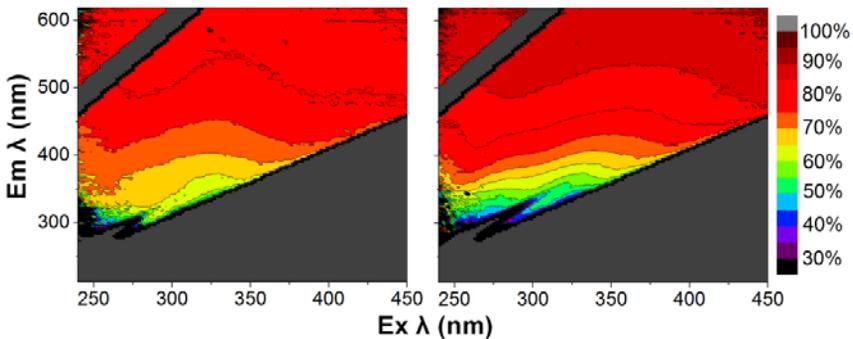

Figure 11. Percentage of removed fluorescing dissolved organic matter during pilot scale nanofiltration of the coagulated feed at Görväln water treatment plant (WTP) (left) as well as using magnetic ion exchange (MIEX®) on untreated raw water at Lovö WTP (right). Em λ = emission wavelength, Ex λ = excitation wavelength.

well as DOC (Table 3). Therefore, there was little gain in applying coagulation treatment after MIEX®. One can hypothesize that the effect would have been similar if the two treatments at Görväln WTP had been reversed.

FT-ICR-MS analyses of samples from Görväln WTP revealed that even if there were similarities in which components that were removed during coagulation and nanofiltration, as indicated by fluorescence analyses, there were also pronounced differences between the treatments. The coagulation treatment was highly selective towards oxidized components (as described in section 4.2.1) while nanofiltration removed a wider range of both reduced and oxidized components. Almost 90% of the components that decreased with more than 2 % during coagulation continued to decrease with nanofiltration. This demonstrates the higher efficiency of the membrane treatment, in line with the fluorescence results. Furthermore, approximately 50% of the components that decreased in relative abundance with more than 2% during nanofiltration were not removed with coagulation, which enhances the wider ability for DOM removal with nanofiltration. Components that were not removed with nanofiltration all had m/z below 400 Da, which indicates that they do not aggregate significantly and can pass through the membrane that has a molecular weight cut-off of 500-1000 Da.

The reference GAC filter in the pilot plant at Görväln WTP, which was fed with coagulated water from the full scale treatment, initially lowered the incoming DOC concentration from the coagulated feed significantly, with 75%. The removal was, however, significantly reduced already after one month's use, to 11%. After two months there was practically no difference in the performance of the pilot filter compared to the full scale GAC. The pilot GAC filter that was fed with permeate from the nanofiltration membrane was more challenging to evaluate due to the low DOC concentration in the feed (on average 1.0 mg C L^{-1}), and subsequently in the GAC filtrate (0.7 ± 0.3 mg C L^{-1}) (Table 3), keeping in mind an approximate measurement error of ± 0.4 mg C L^{-1}. There were however, indications of a similar behaviour as the reference GAC with 72% DOC removal when the activated carbon was new and significantly reduced performance the following months down to $13 \pm 5\%$ removal during the last 6 months of the trail period. Fluorescence data confirms that the initial high removal of DOM in the reference GAC filter rapidly decreased during the first two months of operation. Thereafter, no significant difference in the removal of protein-like FDOM was seen compared to the full scale treatment (Figure 11). There was, however, a slightly higher reduction of humic-like FDOM ($8 \pm 4\%$ compared to $3 \pm 1\%$ for full scale GAC) that maintained during the last 7 months of the experiment, indicating that some of the adsorptive properties of the activated carbon had not been

exhausted. During the final 6 months, the removal efficiency of protein-like material was significantly higher than that of humic-like FDOM across the reference GAC filter (10 ± 2% and 6 ± 2% respectively), implying that the activated carbon mainly had functioned as a biofilter during this time. The removal of humic-like FDOM with the GAC filter fed with nanofiltration permeate was close to 100% during the first two months (Figure 12) and only 30-40% of protein-like FDOM remained in the filtrate. It is clear that the adsorptive function of this filter also decreased over time, as the removal of all FDOM was successively lowered, and the difference in removal efficiencies between humic-like and protein-like FDOM decreased (Figure 12).
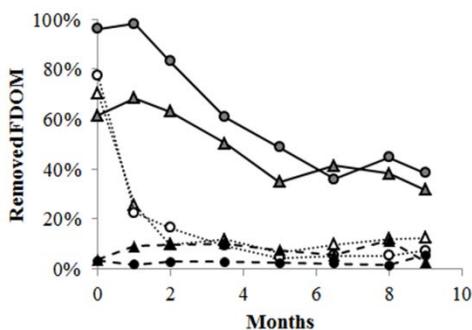

Figure 12. Removal of protein-like (triangles) and humic-like (circles) fluorescing dissolved organic matter across granulated activated carbon (GAC) filters in the full scale treatment (black symbols), as well as the pilot plant reference (white symbols), and downstream from the nanofiltration membrane (grey symbols).

Both pilot GAC filters could only remove approximately 0.1 mg C L^{-1} from their respective feeds during the last 6 months of the experiment and, hence, showed no significant improvement in DOC removal compared to the full scale GAC. Whether the two filters had experienced an equal reduction in the adsorptive properties or not is not entirely clear as no tests for e.g. their ability to remove oil or diesel were performed in the end of the trial period. However, we can conclude that in spite of the large DOC removal with nanofiltration, fouling of downstream GAC still occurred.

The slow sand filter placed downstream from the pilot scale MIEX® and coagulation treatment at Lovö WTP did not remove additional carbon from the feed, in spite of the DOM composition resembling a microbial endmember with FI of approximately 1.8 (Table 3). This further confirms that other factors than the DOC quality are of importance for the removal efficiency, as discussed in section 4.2.2.

In summary, the combined process MIEX®/coagulation/slow sand filtration reduced raw water DOC in the Lovö pilot water treatment plant with 72 ± 4%. The highest removal of 80% was achieved when the coagulant dose in the pilot plant was equivalent to the full scale treatment while the volume ratio of treated water to MIEX resin was the lowest (720 bed volumes). This resulted in a DOC concentration of 1.6 mg C L^{-1} in the pilot slow sand filtrate.

Meanwhile, full scale coagulation followed by membrane nanofiltration and GAC filtration in pilot scale at Görväln WTP removed $93 \pm 2\%$ of the raw water DOC resulting in a treated water with DOC < 1 mg C L^{-1}. Hence, the investigated nanofiltration membrane was more efficient to remove DOC compared to treatment with MIEX® under all experimental conditions applied in these two studies.

4.3   Processing of DOM within a large boreal lake (paper IV)

Lake Mälaren is ideal for studies of in-lake processing of DOM as the majority of the water mass enters in the most western basin and is transported during approximately 2.8 years to the outlet in the eastern part of the lake (Liungman *et al.*, 2010) with only small contributions from other tributaries along the flow pathway (Wallin & Andersson, 2000), allowing the substitution of space for time. In paper IV, we studied in-lake processing of DOM with optical and molecular level tools. We aimed to determine how changes in DOM composition may affect the downstream positioned WTPs in Stockholm. SUVA and the DOC-normalized water colour (specific absorbance at 420 nm, SA420) decreased linearly from west to east. However, there was a concurrent rapid loss of dissolved iron (Fe_{diss}), and because iron can significantly contribute to absorbance, especially in the visual range of the spectra, values of SUVA and SA420 were corrected accordingly (Köhler *et al.*, 2013; Weishaar *et al.*, 2003). While the trend for SUVA still remained after correction, demonstrating a loss of aromatic carbon across the lake, we could show that iron had been mainly responsible for the loss in SA420 during this sampling event. DOC also decreased across the lake, showing that removal exceeded in-lake production. We estimated the autochthonous fraction of DOC with an equation from Köhler *et al* 2013 and found that there was no significant change occurring across the lake. Therefore, the net loss in DOC should mainly have been connected to removal of allochthonous organic matter. This was supported by shift in the distribution of NMR chemical shifts with a decreasing contribution from protons connected to terrestrial DOM (see section 4.1) along the west-east flow pathway. The DOM quality measure that varied the most was the carbon oxidation state as the weighted mean value of $\overline{C_{OS}}$ ($\overline{C_{OS,w}}$) had a relative standard deviation of 72 % across the lake, which was by far more than any of the other fluorescence, absorbance, NMR and FT-ICR-MS parameters. $\overline{C_{OS,w}}$ was also strongly positively correlated to DOC concentration ($r^2 = 0.77$, p<0.0001) showing that the loss in DOC had been more pronounced for oxidized components. We found that all components with a positive $\overline{C_{OS}}$ decreased from west to east, a similar pattern as occurred

during the coagulation process at several WTPs (see section 4.2.1). In fact, 72% of the components that decreased more than 2% in relative abundance across Lake Mälaren also decreased < 2% during coagulation treatment at Lovö WTP, which has the raw water intake in the eastern part of the lake (paper II). Hence, coagulation may have significantly contributed to the DOC removal in Lake Mälaren, especially considering the concurrent loss of Fe_{diss}. DOM processing across the west-east flow pathway in Lake Mälaren occurring during our sampling event should have been favourable for the WTPs because i) DOC concentration decreased, ii) DOM with a terrestrial fingerprint was removed which should have decreased the coagulant demand and sludge production, and iii) there was no significant net production of autochthonous DOM which is more challenging to remove during drinking water production with conventional treatment techniques.

5 Summary, Conclusions and Future Perspectives

In this thesis, common optical analytical techniques have been combined with more advanced structural and molecular level tools to investigate selective removal of DOM with conventional and novel drinking water treatment processes, as well as during transport in a large Swedish boreal lake upstream of three major water treatment plants. Figure 13 provides a visual summary of relationships between DOM origin, chemical properties and reactivity during drinking water production.

The results demonstrate that the average carbon oxidation state is related to DOM source as well as to reactivity in natural and engineered systems. Chemical components that correlated with optical indices indicative of allochthonous DOM all had $\overline{C_{OS}} \geq 0$ while those correlating with indices connected to autochthonous DOM had $\overline{C_{OS}} \leq 0$. During drinking water production, the coagulation process was highly selective towards oxidized, allochthonous chemical components. Additional novel treatment techniques (nanofiltration and ion exchange with MIEX®), that were investigated in pilot scale experiments, improved DOM removal. Hence, although also selective towards terrestrial DOM, they i) enhanced removal of DOM molecules that were susceptible to coagulation, and ii) removed additional components with $\overline{C_{OS}} \leq 0$ that were insensitive to coagulation treatment.

Differential absorbance and fluorescence spectra were useful in order to i) capture small changes in DOM composition and ii) visualize removal over a range of excitation and emission wavelengths, representing different characteristics of the DOM. Fluorescence indices calculated from differential EEMs demonstrated that coagulation treatment removed DOM with characteristics typical of terrestrial end-member samples while material with microbial end-member characteristics was reactive during slow sand filtration.

By studying the large Swedish boreal lake Mälaren we found that DOM with similar optical and molecular properties as material removed during coagulation treatment in WTPs was removed over time along the main flow pathway of the lake. This implies that coagulation could have been responsible for the observed loss in DOC in the lake, especially considering the concurrent decrease in dissolved iron. We found no significant net in-lake production of DOM. The lake may therefore be considered as a "free" WTP, reducing DOC concentration by removal of material that is also lost during coagulation treatment. It is worth noting that if the net in-lake production of DOM would be significant, e.g. as could occur during an algal bloom, the sum of processing across the lake may not be of gain for WTPs. Even if the total concentration of DOC would decrease, the typically lower removal efficiency of autochthonous DOM in the WTP may result in more inefficient overall removal.

In summary, I used straightforward optical methods as well as ultra-high resolution analytical tools to demonstrate important constraints and regulating factors for the production of safe drinking water using a range of Swedish surface waters as raw water sources. In addition, I show that in-lake processing upstream of a WTP can provide valuable "free" pre-treatment. These studies gave rise to several new questions and avenues in future research towards improved drinking water treatment. For example, we found a large number of previously unidentified DBPs which deserve attention regarding potential health effects as well as to identify their reaction pathways. Also, we could establish that DOM of microbial endmember character was removed in slow sand filters, however, because the incoming raw water quality could not be related to the removal efficiency further studies of biological filter performance are needed. Both investigated novel techniques, ion exchange and nanofiltration, improved the DOM removal significantly. If these techniques would be implemented in the full scale treatments several questions remain to be addressed. This includes what effects a lowered DOC concentration, with a composition differing from the present drinking water, would have on biofilms in the distribution network, that provide protection against corrosion of the pipes. A lowered drinking water DOC concentration also opens up possibilities to use more potent disinfectants than monochloramine, including chorine and hypochlorite, hopefully decreasing the DBP formation and disinfectant consumption while increasing the disinfectant stability. In addition, we found that the performance of WTPs is highly dependent on characteristics of the raw water, that in turn are expected to change with climate change (e.g water shortening water retention time in a wetter future climate). This calls for efforts to combine studies of WTP performance and design with predictions of future changes in climate and hydrology.
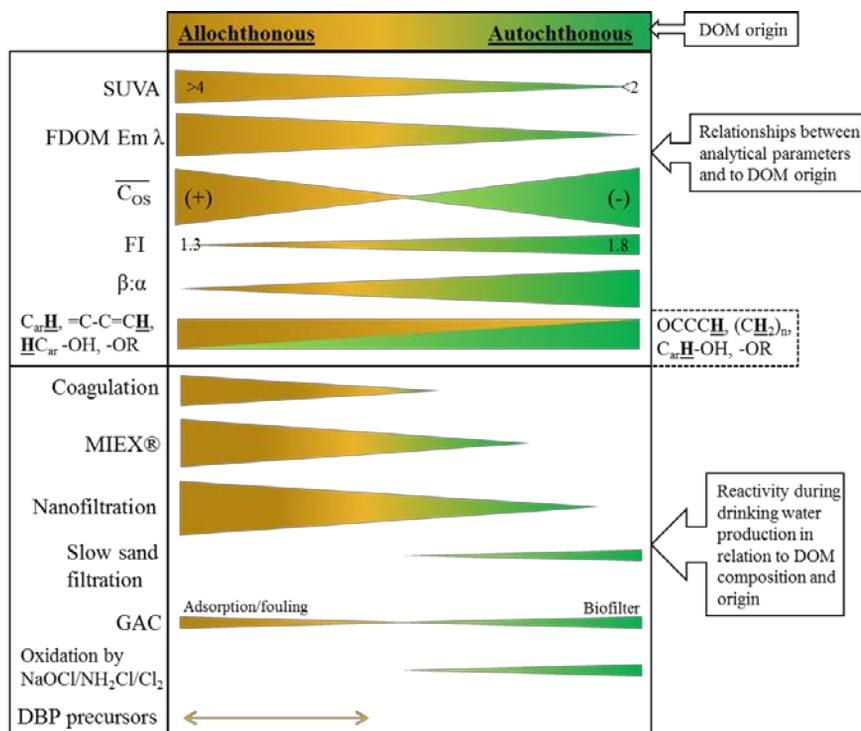
Figure 13. Summary of relationships between dissolved organic matter origin, chemical properties, and reactivity during conventional and novel drinking water treatment. $\underline{SUVA}$ = specific UV absorbance at 254 nm, FDOM Em λ = fluorescence emission wavelength, $\overline{C_{OS}}$ = average carbon oxidation state, FI = fluorescence index, β:α = freshness index, $C_{ar}\underline{\mathbf{H}}$ = hydrogen associated with aromatic carbon, =C-C=C$\underline{\mathbf{H}}$ = hydrogen bound to carbon having conjugated double bonds, $\underline{\mathbf{H}}C_{ar}$ -OH, -OR = hydrogen associated with aromatic carbon with oxygenated substituents, OCCC$\underline{\mathbf{H}}$ = hydrogen in branched aliphatics and condensed alicyclic rings, and $(C\underline{\mathbf{H}}_2)_n$ = hydrogen in polymethylene and certain branched aliphatics. The colour bars indicate the direction of change in values (thick = high values, thin = low values) as well as magnitude of variation/sensitivity (thickness of the bars) for analytical parameters and the relative reactivity (thickness of the bars) and approximate range (length of the bars) of reactive DOM components during the different drinking water processes. The number-specified ranges for SUVA and FI are based on values from Matilainen *et al.* 2010 and Cory *et al.* 2007.

References

Algesten, G., Sobek, S., Bergström, A.K., Ågren, A., Tranvik, L.J. & Jansson, M. (2004). Role of lakes for organic carbon cycling in the boreal zone. *Global Change biology,* 10(1), pp. 141-147.

Baghoth, S., Sharma, S. & Amy, G. (2011). Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation–emission matrices and PARAFAC. *Water Research,* 45(2), pp. 797-809.

Becker, W.C. & O'Melia, C.R. (1996). Ozone, Oxalic Acid, and Organic Matter Molecular Weight–Effects on Coagulation.

Bertilsson, S. & Tranvik, L.J. (2000). Photochemical transformation of dissolved organic matter in lakes. *Limnology and Oceanography,* 45(4), pp. 753-762.

Camel, V. & Bermond, A. (1998). The use of ozone and associated oxidation processes in drinking water treatment. *Water Research,* 32(11), pp. 3208-3222.

Cameron, R., Thornton, B., Swift, R. & Posner, A. (1972). Molecular weight and shape of humic acid from sedimentation and diffusion measurements on fractionated extracts. *Journal of Soil Science,* 23(4), pp. 394-408.

Cammack, W., Kalff, J., Prairie, Y.T. & Smith, E.M. (2004). Fluorescent dissolved organic matter in lakes: Relationships with heterotrophic metabolism. *Limnology and Oceanography,* 49(6), pp. 2034-2045.

Camper, A.K. (2004). Involvement of humic substances in regrowth. *International Journal of Food Microbiology,* 92(3), pp. 355-364.

Cantor, K.P. (1997). Drinking water and cancer. *Cancer Causes & Control,* 8(3), pp. 292-308.

Chapman, S. & Thurlow, M. (1998). Peat respiration at low temperatures. *Soil Biology and Biochemistry,* 30(8), pp. 1013-1021.

Chen, X. & Driscoll, C.T. (2009). Watershed land use controls on chemical inputs to Lake Ontario embayments. *Journal of Environmental Quality,* 38(5), pp. 2084-2095.

Chow, A.T., Dahlgren, R.A. & Harrison, J.A. (2007). Watershed sources of disinfection byproduct precursors in the Sacramento and San Joaquin

Rivers, California. *Environmental Science & Technology,* 41(22), pp. 7645-7652.

Chow, C., Fabris, R. & Drikas, M. (2004). A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *Aqua,* 53, pp. 85-92.

Clark, J.M., Chapman, P.J., Adamson, J.K. & Lane, S.N. (2005). Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change biology,* 11(5), pp. 791-809.

Coble, P.G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. *Marine Chemistry,* 51(4), pp. 325-346.

Coble, P.G., Green, S.A., Blough, N.V. & Gagosian, R.B. (1990). Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy.

Cole, J.J., Likens, G.E. & Strayer, D.L. (1982). Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria1. *Limnology and Oceanography,* 27(6), pp. 1080-1090.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A. & Middelburg, J.J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems,* 10(1), pp. 172-185.

Conte, P. & Piccolo, A. (1999). Conformational arrangement of dissolved humic substances. Influence of solution composition on association of humic molecules. *Environmental Science & Technology,* 33(10), pp. 1682-1690.

Cory, R.M. & McKnight, D.M. (2005). Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environmental Science & Technology,* 39(21), pp. 8142-8149.

Cory, R.M., McKnight, D.M., Chin, Y.P., Miller, P. & Jaros, C.L. (2007). Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations. *Journal of Geophysical Research: Biogeosciences (2005–2012),* 112(G4).

Croué, J.-P. (2004). Isolation of humic and non-humic NOM fractions: structural characterization. *Environmental Monitoring and Assessment,* 92(1-3), pp. 193-207.

Cunningham, L., Bishop, K., Mettävainio, E. & Rosén, P. (2011). Paleoecological evidence of major declines in total organic carbon concentrations since the nineteenth century in four nemoboreal lakes. *Journal of Paleolimnology,* 45(4), pp. 507-518.

D'Andrilli, J., Foreman, C.M., Marshall, A.G. & McKnight, D.M. (2013). Characterization of IHSS Pony Lake fulvic acid dissolved organic matter by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry and fluorescence spectroscopy. *Organic Geochemistry*.

Deborde, M. & Gunten, U.v. (2008). Reactions of Chlorine with Inorganic and Organic Compounds during Water Treatment - Kinetics and Mechanisms: A critical review. *Water Research,* 42, pp. 13-51.

Dodds, L., King, W., Woolcott, C. & Pole, J. (1999). Trihalomethanes in public water supplies and adverse birth outcomes. *Epidemiology,* 10(3), pp. 233-237.

Edzwald, J. (1993). Coagulation in drinking water treatment: Particles, organics and coagulants. *Water Science and Technology,* 27(11), pp. 21-35.

Eikebrokk, B., Vogt, R.D. & Liltved, H. (2004). NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Science and Technology,* 4(4), pp. 47-54.

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T. & Cresser, M.S. (2006). Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change biology,* 12, pp. 2044-2053.

Evans, C.D., Monteith, D.T. & Cooper, D.M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution,* 137, pp. 55-71.

Fabris, R., Chow, C.W., Drikas, M. & Eikebrokk, B. (2008). Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Research,* 42(15), pp. 4188-4196.

Forsberg, C. (1992). Will an increased greenhouse impact in Fennoscandia give rise to more humic and coloured lakes? In: *Dissolved Organic Matter in Lacustrine Ecosystems* Springer, pp. 51-58.

Freeman, C., Evans, C.D. & Monteith, D.T. (2001). Export of organic carbon from peat soils. *Nature,* 412, p. 785.

Frimmel, F.H. & Huber, L. (1996). Influence of humic substances on the aquatic adsorption of heavy metals on defined mineral phases. *Environment International,* 22(5), pp. 507-517.

Ghosh, K. & Schnitzer, M. (1980). Macromolecular structures of humic substances. *Soil science,* 129(5), pp. 266-276.

Gonsior, M., Peake, B.M., Cooper, W.T., Podgorski, D., D'Andrilli, J. & Cooper, W.J. (2009). Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry. *Environmental Science & Technology,* 43(3), pp. 698-703.

Gonsior, M., Schmitt-Kopplin, P. & Bastviken, D. (2013). Depth-dependent molecular composition and photo-reactivity of dissolved organic matter in a boreal lake under winter and summer conditions. *Biogeosciences,* 10(11), pp. 6945-6956.

Gonsior, M., Schmitt-Kopplin, P., Stavklint, H., Richardson, S.D., Hertkorn, N. & Bastviken, D. (2014). Changes in Dissolved Organic Matter during the Treatment Processes of a Drinking Water Plant in Sweden and Formation of Previously Unknown Disinfection Byproducts. *Environmental Science & Technology,* 48(21), pp. 12714-12722.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J. & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography,* 53(3), p. 955.

Her, N., Amy, G., Foss, D., Cho, J., Yoon, Y. & Kosenka, P. (2002). Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection. *Environmental Science & Technology,* 36(5), pp. 1069-1076.

Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A. & Hedges, J.I. (2006). Characterization of a major refractory component of marine dissolved organic matter. *Geochimica Et Cosmochimica Acta,* 70(12), pp. 2990-3010.

Hertkorn, N., Harir, M., Koch, B., Michalke, B. & Schmitt-Kopplin, P. (2013). High-field NMR spectroscopy and FTICR mass spectrometry: powerful discovery tools for the molecular level characterization of marine dissolved organic matter. *Biogeosciences,* 10, pp. 1583-1624.

Herzsprung, P., von Tumpling, W., Hertkorn, N., Harir, M., Buttner, O., Bravidor, J., Friese, K. & Schmitt-Kopplin, P. (2012). Variations of DOM Quality in Inflows of a Drinking Water Reservoir: Linking of van Krevelen Diagrams with EEMF Spectra by Rank Correlation. *Environmental Science & Technology,* 46(10), pp. 5511-5518.

Hongve, D., Riise, G. & Kristiansen, J.F. (2004). Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water–a result of increased precipitation? *Aquatic Sciences,* 66(2), pp. 231-238.

Huber, S. & Frimmel, F. (1992). A new method for the characterization of organic carbon in aquatic systems. *International journal of environmental analytical chemistry,* 49(1-2), pp. 49-57.

Huck, P.M. (1990). Measurement of Biodegradable Organic Matter and Bacterial Growth Potential in Drinking Water. *Journal American Water Works Association,* 82(7), pp. 78-86.

Hudson, J.J., Dillon, P.J. & Somers, K.M. (2003). Long-term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. *Hydrology and Earth System Sciences Discussions,* 7(3), pp. 390-398.

Ji, Q., Liu, H., Hu, C., Qu, J., Wang, D. & Li, J. (2008). Removal of disinfection by-products precursors by polyaluminum chloride coagulation coupled with chlorination. *Separation and Purification Technology,* 62(2), pp. 464-469.

Kaiya, Y., Itoh, Y., Fujita, K. & Takizawa, S. (1996). Study on fouling materials in the membrane treatment process for potable water. *Desalination,* 106(1-3), pp. 71-77.

Kalbitz, K., Schwesig, D., Schmerwitz, J., Kaiser, K., Haumaier, L., Glaser, B., Ellerbrock, R. & Leinweber, P. (2003). Changes in properties of soil-derived dissolved organic matter induced by biodegradation. *Soil Biology and Biochemistry,* 35(8), pp. 1129-1142.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. & Matzner, E. (2000). Controls on the dynamics of dissolved organic matter in soils: a review. *Soil science,* 165(4), pp. 277-304.

Karlsson, J., Byström, P., Ask, J., Ask, P., Persson, L. & Jansson, M. (2009). Light limitation of nutrient-poor lake ecosystems. *Nature,* 460(7254), pp. 506-509.

Kellerman, A.M., Dittmar, T., Kothawala, D.N. & Tranvik, L.J. (2014). Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. *Nature communications,* 5.

Kerner, M., Hohenberg, H., Ertl, S., Reckermann, M. & Spitzy, A. (2003). Self-organization of dissolved organic matter to micelle-like microparticles in river water. *Nature,* 422(6928), pp. 150-154.

Killops, S.D. & Killops, V.J. (2009). *Introduction to organic geochemistry*: John Wiley & Sons.

Kim, S., Kramer, R.W. & Hatcher, P.G. (2003). Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram. *Analytical Chemistry,* 75(20), pp. 5336-5344.

Kleber, M. & Johnson, M.G. (2010). Advances in understanding the molecular structure of soil organic matter: implications for interactions in the environment. *Advances in agronomy,* 106, pp. 77-142.

Korshin, G.V. (2002). *Development of Differential UV Spectroscopy for DBP Monitoring*: American Water Works Association.

Korshin, G.V., Wu, W.W., Benjamin, M.M. & Hemingway, O. (2002). Correlations between differential absorbance and the formation of individual DBPs. *Water Research,* 36(13), pp. 3273-3282.

Kothawala, D.N., Stedmon, C.A., Müller, R.A., Weyhenmeyer, G.A., Köhler, S.J. & Tranvik, L.J. (2014). Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey. *Global Change biology,* 20(4), pp. 1101-1114.

Köhler, S.J., Kothawala, D., Futter, M.N., Liungman, O. & Tranvik, L. (2013). In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes. *PloS one,* 8(8), p. e70598.

Lakowicz, J.R. (2007). *Principles of fluorescence spectroscopy*: Springer.

Lapen, A.J. & Seitz, W.R. (1982). Fluorescence polarization studies of the conformation of soil fulvic acid. *Analytica Chimica Acta,* 134, pp. 31-38.

Laudon, H., Hedtjärn, J., Schelker, J., Bishop, K., Sørensen, R. & Ågren, A. (2009). Response of dissolved organic carbon following forest harvesting in a boreal forest. *AMBIO: A Journal of the Human Environment,* 38(7), pp. 381-386.

Lavonen, E.E., Gonsior, M., Tranvik, L.J., Schmitt-Kopplin, P. & Köhler, S.J. (2013). Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts. *Environmental Science & Technology,* 47(5), pp. 2264-2271.

Ledesma, J.L., Köhler, S.J. & Futter, M.N. (2012). Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Science of the total Environment,* 432, pp. 1-11.

Leenheer, J.A. (1981). Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science & Technology,* 15(5), pp. 578-587.

Leenheer, J.A. (2009). Systematic approaches to comprehensive analyses of natural organic matter. *Annals of Environmental Science,* 3, pp. 1-130.

Leenheer, J.A. & Croué, J.P. (2003). Characterizing aquatic dissolved organic matter. *Environmental Science & Technology,* 37(1), pp. 18A-26A.

Liungman, O., Borell Lövstedt, C. & Moreno-Arancibia, P. (2010). Hydrodynamisk modellstudie av Mälaren in Swedish. *Project report*, p. 51.

Machenbach, I. (2007). *Drinking Water Production by Coagulation and Membrane Filtration.* Diss.: Norwegian University of Science and Technology.

Malcolm, R.L. (1991). Factors to be considered in the isolation and characterization of aquatic humic substances. In: *Humic substances in the aquatic and terrestrial environment* Springer, pp. 7-36.

Marschner, B. & Bredow, A. (2002). Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilised and biologically active soil samples. *Soil Biology and Biochemistry,* 34(4), pp. 459-466.

Marschner, B. & Noble, A.D. (2000). Chemical and biological processes leading to the neutralisation of acidity in soil incubated with litter materials. *Soil Biology and Biochemistry,* 32(6), pp. 805-813.

Mash, H., Westerhoff, P.K., Baker, L.A., Nieman, R.A. & Nguyen, M.-L. (2004). Dissolved organic matter in Arizona reservoirs: Assessment of carbonaceous sources. *Organic Geochemistry,* 35(7), pp. 831-843.

Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A. & Sillanpaa, M. (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere,* 83(11), pp. 1431-1442.

Matilainen, A., Vepsalainen, M. & Sillanpaa, M. (2010). Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science,* 159(2), pp. 189-197.

McKnight, D.M., Aiken, G.R. & Smith, R.L. (1991). AQUATIC FULVIC-ACIDS IN MICROBIALLY BASED ECOSYSTEMS - RESULTS FROM 2 DESERT LAKES IN ANTARCTICA. *Limnology and Oceanography,* 36(5), pp. 998-1006.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T. & Andersen, D.T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography,* 46(1), pp. 38-48.

Meybeck, M. (1982). Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci,* 282(4), pp. 401-450.

Miller, M.P., McKnight, D.M., Cory, R.M., Williams, M.W. & Runkel, R.L. (2006). Hyporheic exchange and fulvic acid redox reactions in an alpine stream/wetland ecosystem, Colorado Front Range. *Environmental Science & Technology,* 40(19), pp. 5943-5949.

Morris, D.P., Zagarese, H., Williamson, C.E., Balseiro, E.G., Hargreaves, B.R., Modenutti, B., Moeller, R. & Queimalinos, C. (1995). The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnology and Oceanography,* 40(8), pp. 1381-1391.

Morris, R.D., Audet, A.-M., Angelillo, I.F., Chalmers, T.C. & Mosteller, F. (1992). Chlorination, chlorination by-products, and cancer: a meta-analysis. *American journal of public health,* 82(7), pp. 955-963.

Moyers, B. & Wu, J.S. (1985). Removal of organic precursors by permanganate oxidation and alum coagulation. *Water Research,* 19(3), pp. 309-314.

Murphy, E.M., Zachara, J.M. & Smith, S.C. (1990). Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds. *Environmental Science & Technology,* 24(10), pp. 1507-1516.

Nieminen, M. (2004). Export of dissolved organic carbon, nitrogen and phosphorus following clear-cutting of three Norway spruce forests growing on drained peatlands in southern Finland. *Silva Fennica,* 38(2), pp. 123-132.

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science & Technology,* 36(4), pp. 742-746.

Parlanti, E., Wörz, K., Geoffroy, L. & Lamotte, M. (2000). Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Organic Geochemistry,* 31(12), pp. 1765-1781.

Peuravuori, J. & Pihlaja, K. (1997). Molecular size distribution and spectroscopic properties of aquatic humic substances. *Analytica Chimica Acta,* 337(2), pp. 133-149.

Piccolo, A. (2001). The supramolecular structure of humic substances. *Soil science,* 166(11), pp. 810-832.

Piret, E., White, R. & Walther Jr, H. Some physico-chemical properties of peat humic acids. In: *Proceedings of Scientific Proceedings of the Royal Dublin Society, Series A*1960, pp. 69-79.

Ralph, J., Marita, J.M., Ralph, S.A., Hatfield, R.D., Lu, F., Ede, R.M., Peng, J., Quideau, S., Helm, R.F. & Grabber, J.H. (1999). Solution-state NMR of lignins. *Advances in lignocellulosics characterization*, pp. 55-108.

Rice, R.G. & Gomez-Taylor, M. (1986). Occurrence of By-Products of Strong Oxidants Reacting With Drinking Water Contaminants - Scope of the Problem. *Environmental Health Perspectives,* 69, pp. 31-44.

Richardson, S.D. (2011). Disinfection By-Products: Formation and Occurrence in Drinking Water. *Chapter 2, J.O. Nriagu (ed.), Encyclopedia of Environmental Health. Elsevier Science Inc., Burlington, MA,*, pp. 2:110-136.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R. & DeMarini, D.M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research-Reviews in Mutation Research,* 636(1-3), pp. 178-242.

Roccaro, P. & Vagliasindi, F.G. (2009). Differential vs. absolute UV absorbance approaches in studying NOM reactivity in DBPs formation: Comparison and applicability. *Water Research,* 43(3), pp. 744-750.

Rook, J.J. (1974). Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.,* 23, pp. 234-243.

Roulet, N. & Moore, T.R. (2006). Browning the waters. *Nature,* 444, pp. 283-284.

Sanchez, N.P., Skeriotis, A.T. & Miller, C.M. (2013). Assessment of dissolved organic matter fluorescence PARAFAC components before and after

coagulation–filtration in a full scale water treatment plant. *Water Research,* 47(4), pp. 1679-1690.

Schlesinger, W.H. & Melack, J.M. (1981). Transport of organic carbon in the world's rivers. *Tellus,* 33(2), pp. 172-187.

Schulten, H.-R., Plage, B. & Schnitzer, M. (1991). A chemical structure for humic substances. *Naturwissenschaften,* 78(7), pp. 311-312.

Shutova, Y., Baker, A., Bridgeman, J. & Henderson, R.K. (2014). Spectroscopic characterisation of dissolved organic matter changes in drinking water treatment: From PARAFAC analysis to online monitoring wavelengths. *Water Research,* 54(0), pp. 159-169.

Skjelkvåle, B.L. (2003). *The 15-year report: Assessment and monitoring of surface waters in Europe and North America acidification and recovery, dynamic modelling and heavy metals*: Norsk institutt for vannforskning.

Slunjski, M., Bourke, M., Nguyen, H., Ballard, M., Morran, J. & Bursill, D. MIEX® DOC Process–A new ion exchange process. In: *Proceedings of 18th Federal AU Water Association Convention Adelaide, Australia*1999.

Slunjski, M., Cadee, K. & Tattersall, J. (2000). MIEX resin water treatment process. *Proceedings of Aquatech*, pp. 26-29.

Song, H., Orr, O., Hong, Y. & Karanfil, T. (2009). Isolation and fractionation of natural organic matter: evaluation of reverse osmosis performance and impact of fractionation parameters. *Environmental Monitoring and Assessment,* 153(1-4), pp. 307-321.

Specht, C.H. & Frimmel, F.H. (2000). Specific interactions of organic substances in size-exclusion chromatography. *Environmental Science & Technology,* 34(11), pp. 2361-2366.

Stubbins, A., Lapierre, J.-F., Berggren, M., Prairie, Y., Dittmar, T. & del Giorgio, P. (2014). What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environmental Science & Technology*.

Stumm, W. & Morgan, J. (1996). Aquatic chemistry: Chemical equilibria and rates in natural waters, JohnWiley & Sons. *Inc., New York*, p. 1022.

Summers, R.S., Haist, B., Koehler, J., Ritz, J., Zimmer, G. & Sontheimer, H. (1989). The influence of background organic matter on GAC adsorption. *American Water Works Association Journal,* 81(5), pp. 66-74.

Sutton, R. & Sposito, G. (2005). Molecular structure in soil humic substances: the new view. *Environmental Science & Technology,* 39(23), pp. 9009-9015.

Søndergaard, M. & Middelboe, M. (1995). A cross-system analysis of labile dissolved organic carbon. *Marine ecology progress series. Oldendorf,* 118(1), pp. 283-294.

Thurman, E.M. (1985). *Organic geochemistry of natural waters*2): Springer.

Town, R.M. & Powell, H.K.J. (1993). Limitations of XAD resins for isolation of the non-colloidal humic fraction in soil extracts and aquatic samples. *Analytica Chimica Acta,* 271(2), pp. 195-202.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K. & Knoll, L.B. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography,* 54(6), pp. 2298-2314.

Valinia, S., Futter, M.N., Cosby, B.J., Rosén, P. & Fölster, J. (2015). Simple models to estimate historical and recent changes of total organic carbon concentrations in lakes. *Environmental Science & Technology*.

Waller, K., Swan, S.H., DeLorenze, G. & Hopkins, B. (1998). Trihalomethanes in drinking water and spontaneous abortion. *Epidemiology,* 9(2), pp. 134-140.

Wallin, M. & Andersson, B. (2000). *Mälaren: miljötillstånd och utveckling 1965-98*: Sveriges lantbruksuniv.(SLU).

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R. & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology,* 37(20), pp. 4702-4708.

Velten, S., Knappe, D.R., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M. & Meylan, S. (2011). Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Research,* 45(13), pp. 3951-3959.

Wershaw, R.L. (1986). A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems. *Journal of Contaminant Hydrology,* 1(1), pp. 29-45.

Weyhenmeyer, G.A., Willén, E. & Sonesten, L. (2004). Effects of an extreme precipitation event on water chemistry and phytoplankton in the Swedish Lake Mälaren. *Boreal Environment Research,* 9(5), pp. 409-420.

von Wachenfeldt, E., Bastviken, D. & Tranvik, L.J. (2009). Microbially induced flocculation of allochthonous dissolved organic carbon in lakes. *Limnol Oceanogr,* 54, pp. 1811-1818.

von Wachenfeldt, E. & Tranvik, L.J. (2008). Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems,* 11(5), pp. 803-814.

Wu, F., Evans, R. & Dillon, P. (2003). Separation and characterization of NOM by high-performance liquid chromatography and on-line three-dimensional excitation emission matrix fluorescence detection. *Environmental Science & Technology,* 37(16), pp. 3687-3693.

Wu, Z.G., Rodgers, R.P. & Marshall, A.G. (2004). Two- and three-dimensional van Krevelen diagrams: A graphical analysis complementary to the Kendrick mass plot for sorting elemental compositions of complex organic mixtures based on ultrahigh-resolution broadband Fourier transform ion cyclotron resonance mass measurements. *Analytical Chemistry,* 76(9), pp. 2511-2516.

Zhang, F., Harir, M., Moritz, F., Zhang, J., Witting, M., Wu, Y., Schmitt-Kopplin, P., Fekete, A., Gaspar, A. & Hertkorn, N. (2014). Molecular and structural characterization of dissolved organic matter during and post cyanobacterial bloom in Taihu by combination of NMR spectroscopy and FTICR mass spectrometry. *Water Research,* 57, pp. 280-294.

Zhang, H., Zhang, Y., Shi, Q., Ren, S., Yu, J., Ji, F., Lou, W. & Yang, M. (2012). Characterization of low molecular weight dissolved natural organic matter along the treatment trait of a waterworks using Fourier transform ion cyclotron resonance mass spectrometry. *Water Research*, pp. 5197-5204.

Zhou, X. & Mopper, K. (1997). Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange. *Marine Chemistry,* 56(3), pp. 201-213.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B. & Saccomandi, F. (1999). Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere,* 38(1), pp. 45-50.

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