



Tracking changes in the optical properties and molecular composition of dissolved organic matter during drinking water production



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ABSTRACT

Absorbance, 3D fluorescence and ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) were used to explain patterns in the removal of chromophoric and fluorescent dissolved organic matter (CDOM and FDOM) at the molecular level during drinking water production at four large drinking water treatment plants in Sweden. When dissolved organic carbon (DOC) removal was low, shifts in the dissolved organic matter (DOM) composition could not be detected with commonly used DOC-normalized parameters (e.g. specific UV₂₅₄ absorbance – SUVA), but was clearly observed by using differential absorbance and fluorescence or ESI-FT-ICR-MS. In addition, we took a novel approach by identifying how optical parameters were correlated to the elemental composition of DOM by using rank correlation to connect optical properties to chemical formulas assigned to mass peaks from FT-ICR-MS analyses. Coagulation treatment selectively removed FDOM at longer emission wavelengths (450–600 nm), which significantly correlated with chemical formulas containing oxidized carbon (average carbon oxidation state ≥ 0), low hydrogen to carbon ratios (H/C: average \pm SD = 0.83 ± 0.13), and abundant oxygen-containing functional groups (O/C = 0.62 ± 0.10). Slow sand filtration was less efficient in removing DOM, yet selectively targeted FDOM at shorter emission wavelengths (between 300 and 450 nm), which commonly represents algal rather than terrestrial sources. This shorter wavelength FDOM correlated with chemical formulas containing reduced carbon (average carbon oxidation state ≤ 0), with relatively few carbon-carbon double bonds (H/C = 1.32 ± 0.16) and less oxygen per carbon (O/C = 0.43 ± 0.10) than those removed during coagulation. By coupling optical approaches with FT-ICR-MS to characterize DOM, we were for the first time able to confirm the molecular composition of absorbing and fluorescing DOM selectively targeted during drinking water treatment.

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1. Introduction

Dissolved organic matter (DOM) in inland waters is a complex, heterogeneous mixture of natural organic compounds of both terrigenous and aquatic origin. These compounds vary in size, hydrophobicity, age, bioavailability and reactivity (Steinberg et al.,

2008; Thurman, 1985). In Sweden, as in several other countries in Northern Europe and North America, dissolved organic carbon (DOC) concentrations, commonly used as a proxy for DOM abundance, are currently increasing in surface waters (Evans et al., 2005; Freeman et al., 2001; Ledesma et al., 2012; Roulet and Moore, 2006). Because colored DOM in particular has been found to increase (Hongve et al., 2004), this is often referred to as browning of inland waters (Roulet and Moore, 2006). It is presently unclear whether DOC concentrations will stabilize or continue to increase in the future, and which changes in its composition may occur.

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Surface water is a major source of drinking water. Because the increasing DOM levels were not considered when many water treatment plants (WTPs) were constructed, the industry is currently struggling to manage sufficient DOM removal in order to maintain a high drinking water quality. Rising DOC concentrations in raw waters increase the demand on treatment and becomes costly due to the need for higher doses of chemical coagulants (Eikebrokk et al., 2004), and more frequent regeneration of active carbon filters and cleaning of membrane surfaces. Residual DOM results in the consumption of disinfectants (such as chlorine chemicals and UV) and leads to production of disinfection by-products (Richardson, 2011; Richardson et al., 2007) as well as fouling of costly membranes and active carbon filters (Kaiya et al., 1996; Summers et al., 1989). Besides the obvious economic implications, disinfection by-products may pose health risks (Richardson, 2011; Richardson et al., 2007). Recently, many (so far structurally unknown) disinfection by-product components have been identified (Gonsior et al., 2014; Lavonen et al., 2013; Zhang et al., 2012a, 2012b), which may also contribute to negative health effects. Low DOC concentration in drinking water is further desirable to avoid potential regrowth of microorganisms in the distribution system (Camper, 2004; Huck, 1990), as well as for esthetic reasons (color, odor and taste).

WTPs use a range of treatment techniques to remove DOM, including chemical coagulation and slow sand filtration. Coagulant dosing is optimized with respect to a number of parameters such as turbidity, color or DOC removal and residual iron or aluminum. The DOC removal efficiency may vary greatly between WTPs even when their treatment processes are similar. The range of removal efficiencies has been reported to occur due to differences in DOM quality (e.g. (Matilainen et al., 2010; Ødegaard et al., 2010)). Yet, detailed information regarding selective DOM removal is sparse, and highly needed to improve our ability to predict treatability of different raw waters and to develop more efficient treatment strategies. Only a few studies have addressed the selective removal of DOM caused by coagulation at the molecular level (Gonsior et al., 2014; Zhang et al., 2012a).

Because DOM removal is costly, there is an increasing demand for online monitoring techniques to track temporal changes in DOM quality of relevance to the operation of WTPs. Many WTPs depend solely on the DOC-normalized value of absorbance at 254 nm (specific UV absorbance – SUVA) to assess DOM quality. SUVA is an indicator of carbon aromaticity (Weishaar et al., 2003) and has been shown to be useful to assess the removal efficiency of DOM with coagulation (Matilainen et al., 2011). SUVA provides an estimate of the average aromatic content for all DOM compounds present in solution (Traina et al., 1990; Weishaar et al., 2003). However, samples with the same SUVA may differ in their distribution around this average value (Shutova et al., 2014), and consequently in their reactivity. Due to the complexity of DOM, more detailed and sensitive analytical approaches are likely to provide more insight regarding DOM reactivity. Fluorescence spectroscopy is a promising alternative because it is a rapid and straightforward analytical technique, and still provides detailed information. When applied in 3D mode, it generates an emission-excitation matrix (EEM), providing a fingerprint of the fluorescent DOM (FDOM) in a sample, which can supply substantial information about DOM quality. The method therefore holds strong advantages for more detailed offline or online monitoring. A key limitation of fluorescence is the lack of molecular level information. Hence, combining fluorescence spectroscopy with a method that provides detailed molecular level information is needed to identify how optical properties are related to the molecular characteristics. Changes in measured fluorescence EEMs and calculated indices during treatment processes used in drinking

water production are commonly small. Differential fluorescence may however capture these small changes and has previously been applied to investigate e.g. the formation of several DBPs (at a single excitation wavelength) (Roccaro et al., 2009), removal of PARAFAC components during coagulation (Sanchez et al., 2013), as well as removal of different fluorophores during ozonation of a wastewater effluent (Liu et al., 2015). In this study, we used differential fluorescence of full EEMs in order to identify potential patterns in the removal of FDOM during conventional drinking water treatment and develop a novel index related to FDOM reactivity.

ESI-FT-ICR-MS provides ultrahigh mass resolution and has a mass accuracy below 1 ppm and is therefore able to differentiate between DOM components having small differences in molecular mass. To date, only a few studies have coupled results from FT-ICR-MS analysis with fluorescence spectra (Gonsior et al., 2013; Herzsprung et al., 2012; Kellerman et al., 2014; Stubbins et al., 2014) and none during drinking water production. We aimed to investigate the molecular composition of FDOM and CDOM that is targeted during conventional drinking water treatment processes by correlating conventional and novel optical indices with individual DOM components from FT-ICR-MS analyses. Through this approach, we evaluate the usefulness of commonly used optical indices to describe selective DOM removal and couple DOM reactivity to specific chemical properties.

2. Methods

2.1. Sampling

Water samples were collected from four Swedish WTPs; Lovö, Lackarebäck, Ringsjö, and Kvarnagården (Fig. A1) on a monthly to bi-monthly basis between May and December 2011. Lovö WTP was sampled between all the main treatment process steps, namely alum ($\text{Al}_2(\text{SO}_4)_3$) coagulation, slow sand filtration, and disinfection with UV and monochloramine (NH_2Cl). The three additional WTPs were sampled at the raw water intake and the outgoing treated drinking water. Ringsjö WTP applies FeCl_3 coagulation, slow sand filtration and sodium hypochlorite (NaOCl) disinfection. Lackarebäck WTP uses pre-chlorination (Cl_2), $\text{Al}_2(\text{SO}_4)_3$ coagulation, active carbon filtration, and disinfection with Cl_2 and ClO_2 . At Kvarnagården WTP only rapid sand filtration is applied to reduce the water turbidity before disinfection using NH_2Cl and UV (Fig. A2).

All samples were analyzed for DOC, UV-Vis absorbance, and 3D fluorescence. Prior to these analyses, samples were filtered (within 24 hrs after sampling) using pre-rinsed (Milli-Q, $18.2 \Omega \text{ cm}^{-1}$) 0.45 μm cellulose acetate filters (Minisart, Sartorius). During one sampling event (October 17–18, 2011) samples were also collected for FT-ICR-MS analyses.

2.2. Analyses and data processing

2.2.1. DOC and UV-Vis absorbance

Filtered samples were acidified to pH 2 with 2 M HCl and analyzed for DOC, after purging of inorganic carbon with CO_2 -free air, using a Shimadzu TOC- V_{CPH} carbon analyzer. Absorbance spectra were recorded between 240 and 600 nm in a spectrophotometer (Perkin-Lambda 40) in a 1 cm quartz cuvette for samples at ambient pH. For further details see Lavonen et al., 2013. Specific absorbance (SUVA) was calculated using the absorbance at 254 nm normalized to the DOC concentration and is reported in the unit liter per milligram carbon and meter ($\text{L mg}^{-1} \text{ m}^{-1}$) (Weishaar et al., 2003). Differential absorbance spectra were calculated by subtracting the measured absorbance after a

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