THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Applications of natural organic matter optical properties for assessing drinking water disinfection and distribution

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Cover:
Left: Fluorescence excitation-emission matrix of drinking water
Top right: Yellow-brown colour of lake water
Bottom right: Tap water
Photos: Masoumeh Heibati

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Abstract

The task of providing safe drinking water requires proper monitoring of water quality and treatment performance from source to tap. Accordingly, the demand for online monitoring is increasing both at treatment plants and within distribution networks. Some of the available techniques use correlations between the optical properties of dissolved organic matter (DOM), mainly absorbance, and other water quality parameters. Fluorescence spectroscopy is significantly more sensitive than absorbance spectroscopy and gives comprehensive information about the composition and concentration of organic matter, so it has a strong potential for online monitoring applications. In this thesis, the application of fluorescence spectroscopy was investigated for two locations in the drinking water treatment system: the ultraviolet (UV) disinfection chambers and the distribution network. With respect to UV_{254} disinfection, fluorescence spectroscopy was investigated as a proxy of potential unwanted by-products (assimilable organic carbon (AOC) and disinfection by-products (DBPs)), in addition to the administered UV dose. The UV_{254} irradiation increased assimilable organic carbon (AOC) concentration, with the estimated AOC production induced by UV_{254} irradiation at a dose of 40 mJ cm^{-2} being 0.4 % of the dissolved organic carbon. The concentration of adsorbable organic chlorine (AOCl), a subset of adsorbable organic halogens (AOX), generally increased following UV_{254} irradiation at the typical disinfection dose. Weak but statistically-significant correlations were found between the UV-induced fluorescence reduction and increases in both AOC and AOCl concentrations. Compared to absorbance, greater reductions were observed in fluorescence intensity following sequential UV irradiation and chlorination and these correlated more strongly with AOCl production. Following UV_{254} disinfection, a linear relationship was observed between UV_{254} dose and changes in long-wavelength fluorescence (> 400 nm) intensities at doses up to 200 mJ cm^{-2}. However, the application of fluorescence as a proxy of the UV_{254} dose is limited due to the relatively small and unpredictable direction of change of fluorescence intensity. In the distribution network, the sensitivity of fluorescence to detect contamination caused by entrainment was compared to the sensitivity of other common water quality parameters including several trace elements and microbial indicator species abundances. Of these, fluorescence was the most sensitive tracer for distinguishing contamination from natural variation, followed by absorbance. The relationship between fluorescence and microbial regrowth was also examined; however, no correlation was observed. The results of this thesis imply that although fluorescence might not always correlate with the chemical and microbial water parameters, its prompt response to treatment-induced modifications and fluctuations, together with high analytical precision and sensitivity of fluorescence measurements, make it a useful parameter for real-time monitoring of water quality changes in drinking water treatment plants and distribution systems.

Keywords: Optical properties, drinking water, UV disinfection, dissolved organic matter, distribution network, disinfection by-products, assimilable organic carbon.

LIST OF PUBLICATIONS

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I. Heibati, M., Stedmon, C.A, Stenroth, K., Rauch, S, Toljander, J, Säve-Söderbergh, M. and Murphy, K.R. Assessment of drinking water quality at the tap using fluorescence spectroscopy. *Water Research*, 2017, 125, 1-10.
II. Heibati, M., Stedmon, C.A, Bergstedt, O. and Murphy, K.R. Organic matter fluorescence tracks UV disinfection dose during drinking water treatment. Submitted manuscript. 2019.
III. Heibati, M., Halle, C., Stedmon, C.A, Bergstedt, O., Wünsch, U. and Murphy, K.R. Ultraviolet disinfection effects on microbial growth potential in drinking water. Submitted manuscript. 2019.
IV. Heibati, M., Croué, J.P., Stedmon, C.A, Bergstedt, O. and Murphy, K.R. UV irradiation enhances the formation of chlorinated disinfection by-products. Manuscript.

The author of this thesis has made the following contributions:
Paper I: Contributed to the sample collection from the distribution network, performed the DOM measurements (absorbance, fluorescence and DOC), carried out the data analysis, wrote the first draft of the paper, critically revised the manuscript until publication.

Paper II: Contributed to the sample collection from the DWTPs, designed the experiments, prepared the experimental set-up, ran the experiments and DOM measurements, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript until submission.

Paper III: Contributed to the sample collection from the DWTPs, designed the experiments, prepared the experimental set-up, ran the experiments, assisted with measurements of DOM, HPSEC and AOC, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript until submission.

Paper IV: Contributed to design of the experiment, prepared the experimental set-up, ran the experiments, performed the DOM measurements, AOX and GC-MS analyses, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript.

ACRONYMS AND ABBREVIATIONS:

AOC	Assimilable organic carbon
AOBr	Adsorbable organic bromine
AOCl	Adsorbable organic chlorine
AOX	Adsorbable organic halogen
BAN	Bromoacetonitrile
BCAN	Bromochloroacetonitrile
BDCM	Bromodichloromethane
BDOC	Biodegradable dissolved organic carbon
CAN	Chloroacetonitrile
CDOM	Chromophoric or coloured dissolved organic matter
DBAN	Dibromoacetonitrile
DCAN	Dichloroacetonitrile
DBCM	Dibromochloromethane
DBP	Disinfection by-product
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWTP	Drinking water treatment plant
EEM	Excitation and emission matrix
FDOM	Fluorescent dissolved organic matter
FI	Fluorescence index
HAN	Haloacetonitrile
HPSEC	High performance size exclusion chromatography
NOM	Natural organic matter
NPOC	Non-purgeable organic carbon
SUVA	Specific UV absorbance
TBM	Tribromomethane
TCAN	Trichloroacetonitrile
TCM	Trichloromethane
THM	Trihalomethane
TOC	Total organic carbon
TOX	Total organic halogen
UV	Ultraviolet

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Table of Contents

1. Introduction

The increasing concentration of dissolved organic matter (DOM) in surface water in northern Europe, including Sweden, and North America during the last decades (Ledesma et al. 2012, SOU 2007:60) imposes challenges for drinking water suppliers. The increasing spatial and temporal fluctuations in DOM composition and concentration in the raw water constrain water suppliers to control the efficiency of the treatment processes and quality of the finished water received by the consumers using the current monitoring techniques. The typical water quality parameters that are monitored by water utilities through source protection, treatment processes and distribution systems include online turbidity, dissolved oxygen, chlorine, pH and ultraviolet (UV) absorbance. Additional parameters such as total organic carbon (TOC) and disinfection by-products are measured off-line, with some analysed less frequently than the others. Although these analyses inform an overall assessment of the water quality, they deliver limited resolution of DOM composition (Storey et al. 2011, van der Gaag et al. 2008).

Additional online monitoring techniques can deliver early warning systems for monitoring water quality (Storey et al. 2011) and the performance of treatment processes (Hargesheimer et al. 2002). Some of these techniques use the correlation between physical properties, in particular the optical properties (mainly absorbance) of organic matter, and other water quality parameters, such as biochemical oxygen demand (BOD), TOC and turbidity (Storey et al. 2011). The potential of fluorescence spectroscopy as an online monitoring tool for water quality has been investigated in previous studies (Ahmad and Reynolds 1999, Baker et al. 2015, Hambly et al. 2010, Shutova et al. 2014). As fluorescence is significantly more sensitive than absorbance, there is great interest in fluorescence spectroscopy for monitoring drinking water treatment systems and distribution networks. However, before implementing fluorescence as a proxy for any other water quality parameter, its sensitivity and reproducibility must be understood.

Disinfection by UV irradiation and chlorination are implemented in the final stages of drinking water treatment. After water has been treated to remove organic and inorganic matter (suspended or dissolved) and microorganisms, typically by coagulation/flocculation, sedimentation and filtration, disinfection is applied to inactivate any remaining pathogenic microorganisms. UV disinfection is often considered the primary disinfection method due to its higher efficacy against *Giardia lamblia* cysts and *Cryptosporidium* oocysts compared to chlorination (Hijnen et al. 2006). UV irradiation can modify the structure of the organic matter pool in drinking water (Frimmel 1998), leading to direct or indirect disinfection by-products and formation of assimilable organic matter. However, the composition and concentration of organic matter varies among source waters, affecting the degree of organic matter modification due to UV irradiation. In addition, the source and dose of the applied UV light are important factors defining the extent to which UV disinfection alters the structure of organic matter. The compliance between the microbiological risks promoted by insufficient UV disinfection and the chemical and microbial side effects rendered by excessive UV irradiation must be considered when optimizing a disinfection process (Bridgeman et al. 2011). Although some studies reported an effect of UV irradiation on organic matter composition at UV doses applied during drinking water disinfection (Liu et al. 2002, Magnuson et al. 2002), the relationship between UV dose and organic matter properties is poorly understood. A better understanding of this relationship may not only assist us in predicting the effectiveness of UV disinfection by its impact rate on organic matter, but may also help us to assess the associated risks with the UV-induced changes in organic matter, particularly the production of assimilable organic carbon and disinfection by-products.

After leaving the treatment plant, drinking water enters the distribution network and resides there until it is delivered to the consumers' tap. Water quality can quickly deteriorate within the distribution network due to e.g. microbial regrowth, corrosion or entrainment of untreated water through damaged pipes, leading to serious health risks to consumers (WHO 2014). High organic matter concentrations can provoke excessive regrowth, resulting in declining water quality including poor odour, taste, and turbidity (Van Der Kooij 2000). Changes to water quality within distribution networks need to be detected before the water reaches the customer. Fast and sensitive monitoring methods are needed that can distinguish unsafe conditions from natural variation.

1.1. Research hypothesis and the scope of this thesis

The overall aim of this thesis is to assess the application of the dissolved organic matter optical properties, in particular fluorescence, as a proxy for the ultraviolent disinfection efficacy and water quality parameters during the final stages of the drinking water system: disinfection and distribution. The following aims were investigated:

1. What is the fluorescence composition of treated drinking water? [paper I, II, III and IV]
2. How do the DOM properties modify following UV disinfection?
   2.1. The impact of UV disinfection on the DOM optical properties including fluorescence and absorbance was studied in paper II, III and IV.
      - The relationship between the UV dose and DOM fluorescence intensity was investigated in paper II.
   2.2. The impact of UV irradiation on the DOM molecular weight distribution was assessed in paper III.
   2.3. The changes in the formation of by-products induced by UV disinfection were examined in paper III and IV.
      - The impact of UV irradiation on the production of assimilable organic carbon (AOC): paper III.
      - The impact of UV irradiation on the production of disinfection by-products (DBPs): paper IV.
3. How is the sensitivity of fluorescence for monitoring water quality in comparison to other parameters?
      - The sensitivity of fluorescence intensity to track the UV dose during UV disinfection was assessed in paper II.
      - Absorbance and fluorescence were compared as a proxy for DBPs formation in paper IV.
      - The sensitivity of fluorescence was compared with the other microbial and chemical parameters measured in distribution network in paper I.

2. Background

2.1. Dissolved organic matter (DOM)

Natural organic matter (NOM) is a complex, heterogeneous mixture of organic compounds presence in all natural surface- and groundwater. It is composed of a continuum of sizes between two operationally-defined groups: dissolved and particulate DOM. DOM is defined as the fraction of organic substances which passes through a filter (typically 0.45 - 1.0 µm) whereas the particulate fraction does not (Hansell and Carlson 2002). DOM derives from a range of origins including terrestrial (exogenous) or aquatic (autochthonous, in situ) sources and is one of the largest reservoirs of organic matter in natural waters. The DOM pool constitutes both the hydrophobic compounds rich in aromatic carbon and conjugated bonds, and also the hydrophilic compounds consisting of aliphatic carbon. The dominant fraction of DOM comprises of humic substances (humic and fulvic acids), which contains chromophoric compounds that absorb light and display a yellow-brown colour. Among the other fractions of DOM, there are carbohydrates, amino acids, proteins and phenols with various molecular sizes and properties (Hassett 2006, Thurman 2012).

DOM in natural water plays multiple functions in photo-induced, chemical, microbial and geochemical processes (Corin et al. 1996, Ogawa and Tanoue 2003). For example, it interacts with metal ions and controls their speciation and bioavailability (Cuss and Gueguen 2014, Yamashita and Jaffe 2008). By absorbing light irradiation, DOM has a substantial impact upon the amount of light available to aquatic microorganisms for photosynthesis (Del Vecchio and Blough 2004). Through photochemical reactions, the bioavailability of DOM is altered and photochemistry may destroy or generate substrates for microorganisms (Mopper and Kieber 2002, Rodriguez-Zuniga et al. 2008).

The chemical characterization of DOM components is hampered by their chemical complexity. In fact, the bulk physiochemical properties used to characterize DOM represent the averaged parameters for the mixture of components (Hur and Schlautman 2003). DOM is often quantified only as total organic carbon (TOC) or dissolved organic carbon (DOC) which constitute the overall quantity of organic matter in the particulate and dissolved pools (Hansell and Carlson 2002, Matilainen et al. 2011). To study the composition and sources of additional DOM pools in water, various analytical technologies and methods have emerged that are predominately laboratory based such as biological assays; e.g. assimilable organic carbon (AOC) (Escobar and Randall 2001), fractionation techniques (Croué 2004) such as size exclusion chromatography, and elemental composition characterization using nuclear magnetic resonance and Fourier transform infrared. In some studies, the links between DOM chemical composition acquired from some of these sophisticated analytical methods such as ultrahigh resolution mass spectrometry or high performance size exclusion chromatography (HPSEC) and the optical properties have been investigated (Her et al. 2003, Wünsch et al. 2018).

Measuring the spectroscopic properties of the optically-active fraction of DOM, including UV- visible spectra and fluorescence spectra, is one of the most important developments in water science for gaining information about the concentration, composition, and source of DOM (Coble et al. 2014, Li and Hur 2017). Advantages of these spectroscopic approaches include high sensitivity and simplicity of their techniques. They also provide rapid and non-invasive methods using a small sample volume with little need for preparation prior to analyses. Moreover, they benefit from having the potential for online monitoring application (Bridgeman et al. 2011).

2.2. Optical properties of dissolved organic matter

2.2.1. Absorbance

The optically-active fraction of DOM, called chromophoric or coloured dissolved organic matter (CDOM), determines the optical properties of DOM (Green and Blough 1994, Stedmon et al. 2000). CDOM consists of a mixture of components which have different optical properties. They absorb light in visible wavelengths and also ultraviolet UV-A (315 - 400 nm), UV-B (280 - 315 nm), UV-C (200 - 280 nm) and producing the yellow to brown colour of natural waters (Blough and Del Vecchio 2002). CDOM light absorption decreases in an approximately exponential fashion with increasing irradiation wavelength across the visible-UV spectrum (Figure 1) (Coble 2007) (eq. 1).

$$a(\lambda) = a(\lambda_0)\, e^{-S(\lambda - \lambda_0)} \quad \text{eq. 1}$$

where, $a(\lambda)$ and $a(\lambda_0)$ are the absorption coefficient at wavelength λ and reference wavelength λ_0, respectively and S is the spectral slope parameter. The absorption coefficient, a, is calculated using eq. 2:

$$a = 2.303\, A/l \quad \text{eq. 2}$$

where, l is the path length and A is absorbance, calculated as:

$$A = \log(I_0/I) \quad \text{eq. 3}$$

where, I and I_0 are the incident and transmitted light, respectively.

According to the Beer-Lambert law, the absorbent molecules act independently and do not interact with each other, so that the absorption spectrum of a mixture of DOM components is a simple superposition of the spectra from the individual chromophores (Coble et al. 2014). However, some researchers believe that interactions between molecules commonly influence the shape of absorbance spectra in DOM mixtures, especially at longer wavelengths (Del Vecchio and Blough 2004).

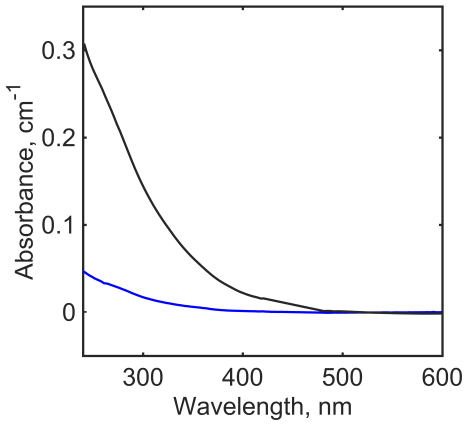

Figure 1. UV- visible absorption spectra of a drinking water sample at the tap (blue) and an untreated water sample from treatment plant (black) [paper II]

2.2.2. Fluorescence

A subset of CDOM compounds emit some absorbed light as fluorescence and belong to a pool known as fluorescent dissolved organic matter (FDOM). Fluorescence is the phenomenon that occurs after light absorption by fluorophores (Figure 2). The electron of the fluorophore molecule is excited to a higher energy level after absorbing the light (photon). This is followed by vibrational relaxation to the lowest level of the excited state. Finally, the electron returns to the ground state by emitting the energy as fluorescence. Sir G. G. Stokes first explained that

the energy of light emitted by a fluorophore is always less than the energy of absorption (i.e. longer wavelength) because of the loss of energy at the vibrational state. This phenomenon is called the Stokes shift (Lakowicz 1983) (Figure 3).
The intensity and the wavelengths at which each fluorophore fluoresces is controlled by its molecular structure. For instance, aromatic molecules containing freely rotating functional groups lose energy through these functional groups, thus aromatic molecules with functional groups fluoresce less intensely compared to those without. Conjugated molecules fluoresce at longer energy wavelengths (lower energy) due to the small energy gaps between the excited and ground levels. The emission spectra of CDOM are broad and featureless. By increasing the excitation wavelength, the emission spectra of CDOM shift to longer wavelengths (red shift) and decrease in intensity (Coble et al. 2014). Figure 3 shows the absorption (excitation) and emission spectra of a FDOM component identified in Paper II of this study.

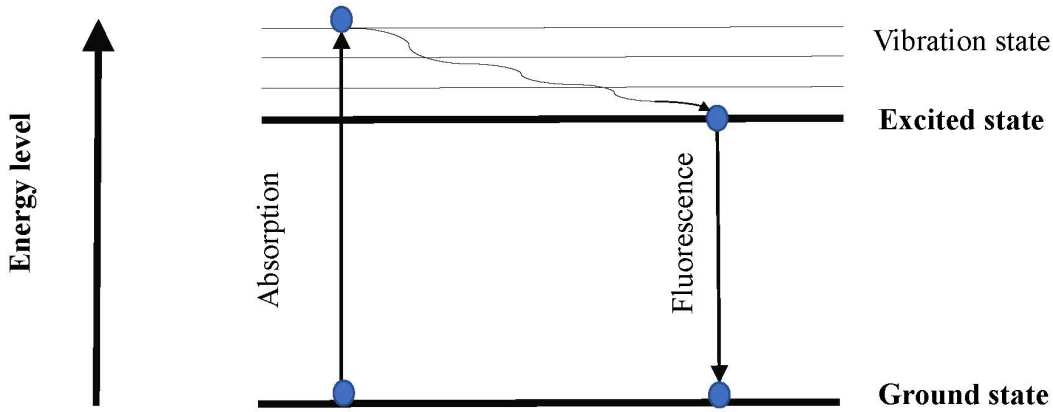

Figure 2. Simplified Jablonski diagram describing the fluorescence phenomenon.

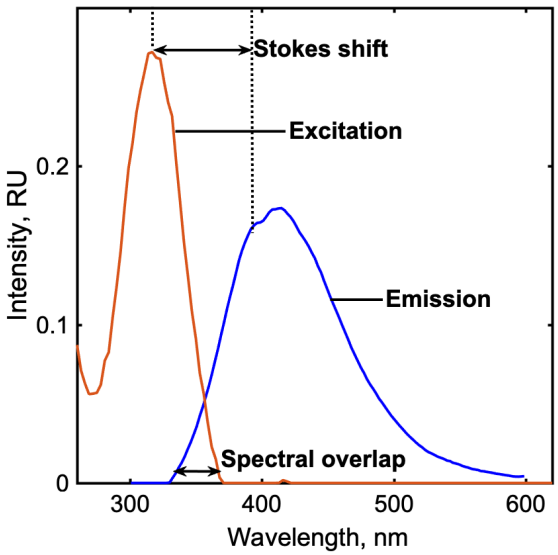

Figure 3. Excitation and emission spectra of a FDOM component, identified using parallel factor analysis in Paper II.

DOM fluorescence can be collected using different approaches, the simplest being to measure the fluorescence intensity at a single excitation-emission wavelength pair. A commonly-used parameter is the so-called fluorescence index (FI), which is the ratio of fluorescence intensity measured at 470 to 520 nm at excitation wavelength of 370 nm (McKnight et al. 2001). The FI

is sometimes used to estimate the relative contribution of microbial and terrestrially derived FDOM in DOM pool, although its sensitivity for this purpose has been questioned (Lavonen et al. 2015, Murphy et al. 2008). Another parameter in frequent use is the freshness index (emission intensity at 380 nm divided by the maximum intensity between 420 and 435 nm at 310 nm excitation) which is used to estimate DOM age (Lavonen et al. 2015). Another method to collect the fluorescence data is measuring the emission spectra at one excitation wavelength or measuring the excitation spectra at one emission wavelength.

The most comprehensive method of measuring FDOM is to measure fluorescence emission over a range of excitation wavelengths, which produces excitation-emission matrices (EEMs, Figure 4) (Baker 2001, Coble et al. 2014). The EEMs can be collected together in a 3-dimensional dataset of fluorescence intensities for different samples and excitation-emission pairs. EEMs can provide considerable information about the DOM pool. For instance, protein-like fluorescence (tryptophan- and tyrosine-like) is attributed to proteins or aromatic amino acids; it is therefore used as a proxy for biological activity (Determann et al. 1998, Sorensen et al. 2015) .

Previously-reported fluorescence components extracted from EEM datasets, and their reported sources, are listed in Table 1 (Coble 2007, Ishii and Boyer 2012, Murphy et al. 2008). The fluorescence components that have been observed in drinking water samples are similar to those observed in diverse aquatic samples. They include humic-like components with either a terrestrial or autochthonous origin, and protein-like components containing tyrosine-like or tryptophan-like fluorophores.

Table 1. Fluorescence properties of reoccurring CDOM components

Component	Peak name (Ref. 1, Ref. 2, Ref. 3)[1]	Peak position (Ex/Em)[2]	Possible source
Tyrosine-like, protein-like	C1[1], B[2]	270/300	Autochthonous
Tryptophan-like, protein-like	C6[1], T[2]	275/328 (340)	Autochthonous
UVC humic-like	C3[1], C8[1], A[2], C1[3]	260/400-460	Terrestrial, allochthonous
UVA humic-like	C3[1], C8[1], C[2]	320-360/420-460	Terrestrial, anthropogenic
Marine humic-like	C2[1], M[2]	290-310/370-410	Terrestrial, agriculture
UVA humic-like + UVA humic-like	C2[3], C2[5]	<240-275(295-380)/375-450	Terrestrial, anthropogenic[1]

[1] Ref. 1 (Murphy et.al. 2008); Ref. 2 (Coble 2007); Ref. 3 (Ishii and Boyer 2012)
[2] Wavelength given in parenthesis represents the secondary peak.

2.2.3. Parallel factor analysis (PARAFAC)

If the Beer-Lambert law applies, then fluorescence EEMs datasets can be separated into chemically and mathematically independent fluorescence components using parallel factor analysis (PARAFAC). PARAFAC decomposes the multi-way data of EEMs (sample x excitation x emission) into independently-varying components using an alternating least squares algorithm.

The results of a PARAFAC model are represented as the excitation and emission spectra of the identified independent fluorescence signals termed ‘components’ and the calculated relative intensity of each component in each sample termed ‘score’ (Bro 1997). The trilinear terms and residual array of a PARAFAC model are presented as:

$$x_{ijk} = \sum_{f=1}^{F} a_{if}\, b_{jf}\, c_{kf} + e_{ijk} \quad \text{eq. 4}$$

In eq. 4, x_{ijk} is the fluorescence data of the i^{th} sample at the j^{th} and k^{th} excitation and emission wavelengths, respectively. f represents the number of underlying components and e_{ijk} is the residual of data which is not explained by the model.

Figure 4 illustrates the decomposition of drinking water EEMs into underlying fluorescence components using PARAFAC.

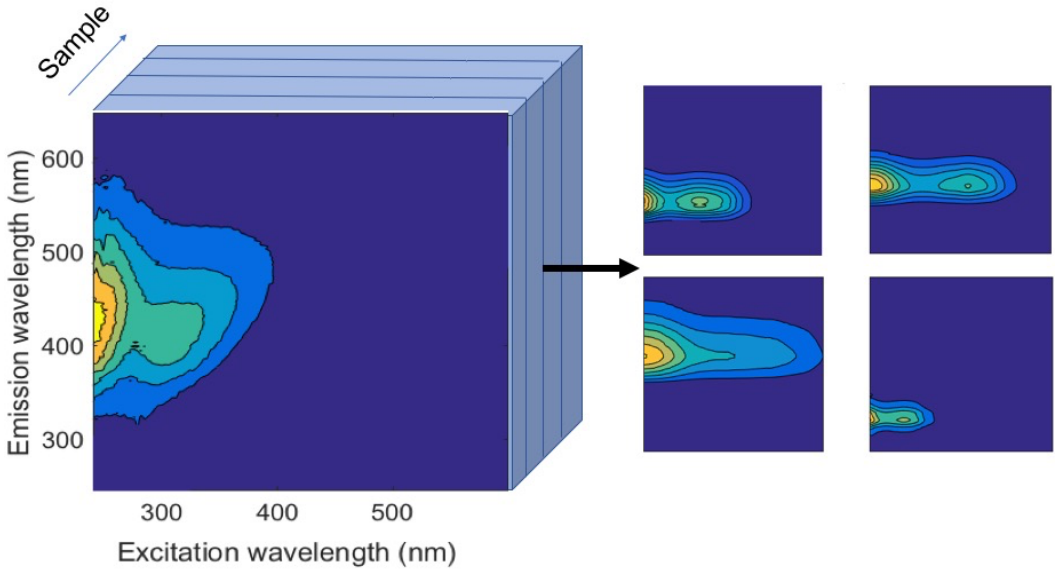

Figure 4. A drinking water EEM dataset can be decomposed into underlying fluorescence components using PARAFAC [paper I]

2.3. Applications of fluorescence in aquatic systems

In the past 60 years, fluorescence spectroscopy has been used to characterise DOM in various aquatic systems (Coble et al. 2014). The large quantity of carbon in oceanic DOM gives it an important role in balancing the global carbon budget. Extensive studies have been made of marine ecosystems, using DOM fluorescence to characterize composition, concentration and dynamic of DOM derived from different sources (Coble 1996, Jaffe et al. 2004, Murphy et al. 2008, Stedmon et al. 2005, Yamashita and Tanoue 2003). Fluorescence spectroscopy has also been extensively used to study the DOM distribution in marine systems due to its significant role in the microbial loop and in determining nutrient fluxes to microorganisms.

In rivers and lakes, to lesser extent than in marine systems, fluorescence spectroscopy has been used to characterize DOM composition and source (Hautala et al. 2000, Her et al. 2003, Newson et al. 2001). The spatial changes of humic-like and tryptophan-like DOM fluorescence has been used to trace the source of DOM in upstream and downstream waters (Baker 2002, Galapate et al. 1998). DOM fluorescence has also been used to identify the pollutants in urban catchments affected by agriculture (Baker et al. 2004, Graeber et al. 2015). A strong correlation between protein-like fluorescence and biodegradable DOM is reported for freshwater ecosystems. Fluorescence has therefore been used to evaluate biological activity in rivers and lakes (Fellman et al. 2010).

In wastewater systems, fluorescence spectroscopy has been used for monitoring treatment processes and water quality (Ahmad and Reynolds 1999, Carstea et al. 2016). Due to the strong fluorescence signals in sewage-derived DOM, fluorescence has been investigated as a surrogate for various water quality parameters commonly used to monitor river pollution (Goldman et al. 2012) and wastewater treatment. Strong correlations have been found between tryptophan-like fluorescence intensity and phosphate (PO_4^{3-}) and nitrate (NO_3^-) in the catchment area of the

river water (Baker and Inverarity 2004). Correlations between bulk organic matter parameters including TOC, DOC and chemical oxygen demand (COD) and fluorescence are inconsistent between studies. However, when sewage-derived DOM components are at high concentrations, the correlation between COD and fluorescence is improved (Baker and Inverarity 2004, Wu et al. 2006). There are positive correlations between tryptophan-like fluorescence and biochemical oxygen demand (BOD) in settled sewage (Ahmad and Reynolds 1999). Protein-like fluorescence has been used as an indicator of the presence/absence of faecal coliforms (Sorensen et al. 2015).

2.3.1. Fluorescence spectroscopy in drinking water

DOM optical properties, mainly involving UV absorbance, have been used to monitor water quality and assess treatment performance in drinking water systems (Bridgeman et al. 2011). The most common approach to extract information about DOM using absorbance spectroscopy is to measure the absorbance at a single wavelength, most commonly at 254 nm and sometimes at 272 nm, which are used as a surrogate for the aromaticity and the humification of DOM (Korshin et al. 2002, Roccaro et al. 2008). Additionally, the carbon specific UV absorbance, SUVA (Abs_{254} normalised by DOC concentration) has been used as a surrogate for water quality during various treatment processes such as coagulation and filtration (Archer and Singer 2006b). In drinking water, SUVA correlates positively with aromaticity, hydrophobicity and the molecular weight of organic matter (Ates et al. 2007, Weishaar et al. 2003). SUVA and Abs_{254} are also useful for estimating the formation of disinfection by-products (DBPs) (Ates et al. 2007). In addition to the single wavelength measurement, the spectral slopes can be extracted if the absorbance spectrum is scanned within the UV-vis wavelengths range. Helms et al. (2008) found correlation between the spectral slopes' ratios and the molecular weight, however, only in freshwater and marine samples.

Fluorescence spectroscopy has greater sensitivity than absorbance (UV-vis) spectroscopy (Coble 1996), in addition to being more informative. Useful information about the physiochemical properties of DOM such as source (allochthonous or autochthonous), reactivity, degree of hydrophobicity and aromaticity can be extracted from DOM fluorescence properties. However, fluorescence has been used in drinking water systems to a lesser extent than absorbance due to higher instrument costs, and difficulties related to artefacts caused by light scattering by particles and calibration (Guilbault 1990).

The application of fluorescence spectroscopy to drinking water system has been mainly focused on monitoring water quality. DOM fluorescence can be used as surrogate parameter for other water quality parameters such as DOC and *E-Coli* (Baghoth et al. 2011a, Baker et al. 2015). Strong correlations have been observed between tryptophan-like fluorescence and the abundance of coliforms (Sorensen et al. 2015), the biopolymer fraction (Baghoth et al. 2011b) and bacteria extracted from drinking water, such as *Xenophilus* sp and *Rhodococcus* sp (Bridgeman et al. 2015).

Fluorescence spectroscopy has also been used to monitor the performance of drinking water treatment processes such as coagulation, granular activated carbon, and membrane filtration (Baghoth et al. 2011b, Bieroza et al. 2009a, Bieroza et al. 2009b, Lavonen 2015, Moona et al. 2018, Shutova et al. 2014). A few studies used fluorescence to assess the performance of TOC removal during the treatment processes (Bieroza et al. 2009a, Bieroza et al. 2010), but the main application has been to predict the formation of disinfection by-products (DBPs) during chlor(am)ination processes (Beggs et al. 2009, Johnstone and Miller 2009, Roccaro et al. 2009). Given its high sensitivity and ability to provide information about the activated aromatics, fluorescence has also been used to study the reactivity of organic matter with disinfectants (Korshin et al. 1999, Świetlik and Sikorska 2004).

Fluorescence could potentially be used to trace contamination in drinking water distribution networks, as attempted in Paper I of this dissertation. Fluorescence is expected to fluctuate when the intrusion of untreated water or microbial regrowth happens within the network and causes probable changes in the CDOM composition or concentration. A high organic matter concentration is a risk factor for microbial regrowth since it provides a source of nutrients and energy for microorganisms. Strong correlations have been reported between humic-like fluorescence (Ex/Em: 300-360/400-480 nm) and DOC concentration of the water samples at taps connected to drinking water network using in-situ fluorometers (Bridgeman et al. 2015). However, the low sensitivity of portable fluorometers makes it difficult to detect small changes in fluorescence due to low-level contamination. In Paper I of this thesis, a benchtop fluorometer is used to examine the limits of fluorescence intensity for detecting contaminated drinking water at the tap. In addition, due to the reported positive correlations between *E. coli* concentrations and tryptophan-like fluorescence in environmental samples (Baker et al. 2015), the correlation between fluorescence intensity and abundance of microbial indicators was assessed.

2.4. DOM in drinking water system

2.4.1. The scheme of drinking water treatment processes

Among the drinking water treatment plants (DWTP) in Sweden (n ≈1750), around 10% use surface water from lake or streams supplying water mainly in the big cities, which together serve half of the population, while the remaining 90% use infiltrated (artificial) groundwater or groundwater, operating at a smaller scale with fewer treatment processes. The typical treatment steps implemented particularly to treat surface water in a Swedish DWTP include: i) pH adjustment and coarse prefiltration to remove big objects such as plant branches; ii) coagulation/flocculation to remove colour, turbidity, organic material, microorganisms, taste and odour, by adding coagulant to the raw water to form flocs which can be settled in the sedimentation basins. The flocculation process can be supplemented by another reagent as flocculant; iii) the remaining flocs are filtered through a rapid sand filter; iv) a filtration process such as a slow sand filter, activated carbon filter or membrane (microfiltration, nanofiltration and ultrafiltration) as microbial barrier and organic matter removal; v) disinfection using either a chemical disinfectant (chlorine, hypochlorite or chlorine dioxide) and/or UV irradiation to inactivate the remaining pathogens and to maintain the chlorine residual within distribution network (Svenskt Vatten 2016, WHO 2011).

2.4.2. The role and fate of DOM during drinking water treatment

In drinking water systems, DOM plays a substantial role and affects the performance of most treatment processes. DOM is responsible for undesirable taste and odour of water, fouling of filtration membranes, interfering with pollutant removal, transportation of heavy metals and pollutants, increasing chlorine demand, formation of carcinogenic disinfection by-products (DBPs), shielding microorganisms during UV disinfection, and triggering microbial regrowth in distribution system (Frimmel and Huber 1996, Ødegaard et al. 2010, WHO 2011).
During the treatment processes, the DOM concentration and composition change drastically. Due to coagulation, a great amount of DOM is removed, with removal efficiency dependant on the DOM reactivity with the coagulant, as well as operational parameters (temperature, coagulant dose, pH, etc.). Generally, the hydrophobic and high molecular weight fractions of DOM are removed more efficiently during coagulation (Matilainen et al. 2010). Following coagulation, membrane filtration might be used to also remove different fractions of DOM depending on the pore size (Ødegaard et al. 2010).

After DOM removal and achieving an acceptable DOC concentration, the final stages of the treatment processes comprise merely of microbial barriers such as UV irradiation, ultrafiltration and chlorination in which the targeted bacterial log-reduction is the main parameter to assess efficacy. Eventually, after the treated water enters the distribution network, microbial regrowth is a major concern for water quality with the DOC concentration remaining essentially unchanged. However, even though the concentration of DOM is not prone to changing during these stages, its composition is modified. The impact upon DOM of two final stages (UV irradiation and distribution), which are the main focuses of this dissertation are explained in the following sections.

2.5. Ultraviolet disinfection

After the discovery of the germicidal properties of sunlight by Downing et al. (1878), UV disinfection technology began with the development of mercury lamps and the use of quartz as the transiting material. The first application of UV light for drinking water disinfection dates back to 1910 in Marseilles, France (Henry 1910). However, due to the high cost and the operational problems of the early UV disinfection equipment, chlorination surpassed UV technology as the main technology to inactivate the pathogens. Since 1955, UV technology has gained more attention, being implemented in some DWTPs in Austria and Switzerland to control the contamination of groundwater and heterotrophic plate counts. After discovery of the disinfection by-products associated with chlorination, other countries such as the Netherlands and Norway installed UV disinfectors in their DWTPs (Kruithof 1990, US EPA 2006). In Sweden, UV disinfection has been in use in the drinking water industry since the 1990s (SVU 2009). According to a survey conducted in 2014, more than half of the Swedish DWTPs use UV as the primary disinfection process, and some in combination with hypochlorite (Svenskt Vatten 2015).

Market breakthrough of the UV applications resulted from the discovery of its high efficacy against *Giardia* lamblia cysts and *Cryptosporidium* oocysts, which are resistant to chemical disinfectants (Hijnen et al. 2006). The UV disinfection process occurs due to light absorption (UV-C: 200-280 nm and UV-B: 280-315 nm) by the cells of microorganisms. When the irradiant UV light is absorbed by a microorganism, its genetic material gets damaged, making it less likely to grow or reproduce (Hijnen et al. 2006). Water utilities apply UV disinfection using either low-pressure (monochromatic at 254 nm) lamps or medium-pressure (polychromatic: 240-280 nm) lamps (Bukhari et al. 1999). Despite the high efficiency of the UV disinfection to inactivate the resistant pathogens, there are some downsides associated with the technology.

To achieve the desirable log-reduction, delivery of a sufficient UV dose by the microorganisms must be ensured. In a continuous flow UV system, the hydraulics and the complex trajectory of the reactor cause the inhomogeneous reception of the UV light by microorganisms. The dose distribution of the light inside the UV rector can be estimated using mathematical modelling such as computational fluid mechanics (CFD) or light intensity distribution (LID), which can be verified using biodosimetry method applying the established laboratory-based dose-response (US EPA 2006). However, the technical difficulties of the biodosimetry implementation and its inability to determine the dose distribution delivered by the UV reactor rendered the emergence of alternative methods such as actinometric dyed microspheres, which is based on using fluorescent chemicals sensitive to the UV light (Blatchley III et al. 2008, Shen et al. 2009). In paper II of this dissertation, the possibility of using CDOM as a natural “actinometer” to validate the dose delivered by a UV reactor was investigated. Since CDOM is ubiquitously present in all waters and absorbs the UV light, if its response to the UV doses applied for

disinfection can be quantified using sensitive and rapid methods such as fluorescence spectroscopy, it might be possible to use it to monitor the administered UV dose in real-time.

2.6. Impact of UV irradiation on DOM

The impact of solar and UV irradiation on DOM in aquatic systems has been investigated extensively (Corin et al. 1996, Del Vecchio and Blough 2002, Helms et al. 2013, Kouassi and Zika 1990, Lepane et al. 2003, Loiselle et al. 2012). Upon absorption of UV light by CDOM molecules, a combination of photophysical and/or photochemical processes occur. When the light energy is absorbed, fundamental chemical modifications can arise due to either direct photolysis, which is rendered by long-lived triplets or indirect photochemical reactions initiated by photosensitized intermediate reactive species formed by CDOM and other compounds (Miller 1998). Such structural modifications lead to changes in DOM properties such as bioavailability, molecular size distribution, aromaticity, reactivity and ultimately changes in the chromophoric and fluorescent fraction of dissolved organic matter (CDOM and FDOM); referred to as photobleaching (Del Vecchio and Blough 2002, Helms et al. 2014, Moran et al. 2000). The schematic UV-induced alternation in the DOM properties is presented in Figure 5.
Fluorescence intensity (Moran et al. 2000, Waiser and Robarts 2004) and UV-absorbance (Ferrari et al. 1996) by CDOM both decrease as a result of solar and UV irradiation, referred to as photobleaching. The loss rates of various DOM fractions (DOC, CDOM and FDOM) are different following irradiation. The photodegradation rate of DOC is lower than for CDOM photobleaching, and the reduction of FDOM outpaces the removal of CDOM (Moran et al. 2000, Spencer et al. 2009).
In a drinking water context, during the UV disinfection process, not only are the microorganisms exposed to UV irradiation, but also the DOM molecules. The light dose employed for disinfection under normal operating conditions is often considered to be too low to alter DOM structure or change its optical properties. However, in paper II of this thesis, UV_{254} irradiation of drinking water is shown to produce measurable changes to DOM fluorescence. Consequently, these UV-induced modifications might lead into formation of new molecules that are more assimilable (digestible) for the microorganisms [paper III] or more reactive towards chlorination [paper IV].

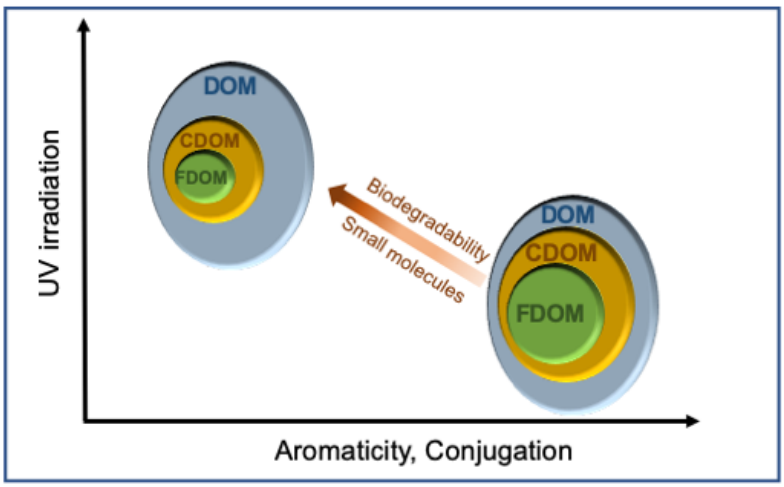

Figure 5. The schematic alteration of the dissolved organic matter (DOM), chromophoric dissolved organic matter (CDOM) and fluorescence dissolved organic matter (FDOM). Upon UV irradiation the FDOM reduces more than CDOM followed by DOM. Overall, the degree of aromaticity, conjugation, molecular size decrease, and biodegradability increase.

2.6.1. Assimilable organic carbon

Through the exposure of DOM compounds to UV light, molecular bonds may break so that large molecules split into small molecules that are more accessible by microorganisms (Buchanan et al. 2004, Frimmel 1998). The increased biodegradability results in greater risk of microbial regrowth and biofilm formation in the drinking water distribution system, deteriorating the aesthetical properties of water (taste and odour), damaging the piping system, multiplying the opportunistic bacteria and increasing the risk of water-borne diseases (van der Kooij 1990). In drinking water systems, biodegradable organic matter is typically quantified using two approaches: biodegradable dissolved organic carbon (BDOC) or assimilable organic carbon (AOC). BDOC methods measure the dissolved organic carbon consumed by a natural bacterial community (Joret and Levi 1986, Servais et al. 1987), and are mainly used to determine the biologically labile products formed during chlorination or ozonation. Meanwhile, AOC methods quantify the growth of indicator strains and, using the growth yield, estimate the initial concentrations of assimilable organic nutrients (LeChevallier et al. 1993) that are often used to indicate the microbial regrowth within the distribution network.
The impact of UV irradiation on the AOC concentration has been investigated in several studies, the majority of them reporting no significant change in AOC concentration in drinking water following UV irradiation at the disinfection dose (Långmark et al. 2007, Malley et al. 1996, Shaw et al. 2000, Sun et al. 2012). However, the low precision of the AOC bioassay is the main hurdle preventing the detection of the potentially slight change in AOC under the relatively low dose of UV light applied for disinfection. Paper III of this dissertation quantifies the impact of UV irradiation on AOC production by applying high UV doses on treated drinking waters and scaling the produced AOC to a normal disinfection level under an assumed linear dose-response relationship.

2.6.2. Impact of UV irradiation on disinfection by-products formation

The key factors affecting DBP formation are the concentration and composition of the DOM present in water, chlorine dose and reaction time (WHO 2011). One of the significant advantages of UV disinfection is to provide primary inactivation of the pathogens to minimize the required chlorine concentration in the following stage, thus reducing DBP formation. However, despite efficiently reducing one of the agents, UV disinfection might enhance the reactivity of another, i.e. DOM compounds, resulting in greater formation of halogenated by-products compared to when not preceded by UV irradiation (Magnuson et al. 2002).
The majority of the studies investigating the impact of UV disinfection on DBP formation used conventional analytical methods to quantify the individual DBPs and focused on regulated species or groups, such as trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Choi and Choi 2010, Liu et al. 2006, Lyon et al. 2014). However, more than 50% of the halogenated DBPs formed during chlorination are still unknown, possibly with higher toxicity compared to known and regulated compounds (Richardson et al. 2007). In paper IV of this dissertation, the impact of UV irradiation on the formation of halogenated DBPs was quantified by measuring adsorbable organic halogens (AOX), a subset of total halogenated halogens (TOX). This includes a wider range of compounds than just HANs, HAAs and THMs, thus providing a more holistic estimation of halogenated DBPs (Langsa et al. 2017).

3. Material and methods

3.1. Ultraviolet irradiation experiments

3.1.1. Paper II

The effect of UV_{254} irradiation on DOM fluorescence of drinking water was studied using both field and laboratory experiments. In the field experiment, the UV disinfection system at nine drinking water treatment plants were studied. The samples were collected from the sampling ports located before and after the UV disinfection chamber. The applied UV dose at the DWTPs ranged between 35-100 mJ cm^{-2}. The aim was to determine whether the UV disinfection process at the dose applied in treatment plant has a residual on DOM fluorescence or not.
In the laboratory experiments, water samples were subjected to UV_{254} irradiation at the low range of UV_{254} doses corresponding to UV disinfection (< 200 mJ cm^{-2}), while DOM fluorescence was measured continuously. The aim was to investigate the relationship between radiant UV_{254} dose and DOM fluorescence intensities. The irradiation experiments in the lab were conducted using a customized flow-through system (Figure 6). During each experiment, the sample was circulated using a peristaltic pump from the sample vial to the irradiation cell where it was exposed to the UV_{254} irradiation. From the irradiation cell, the sample flowed to the fluorescence cell placed in the spectrofluorometer where the fluorescence/absorbance were measured and then recirculated back to the samples vial. The sample temperature during measurements was set at 20°C using a water bath circulated past the fluorescence cell.

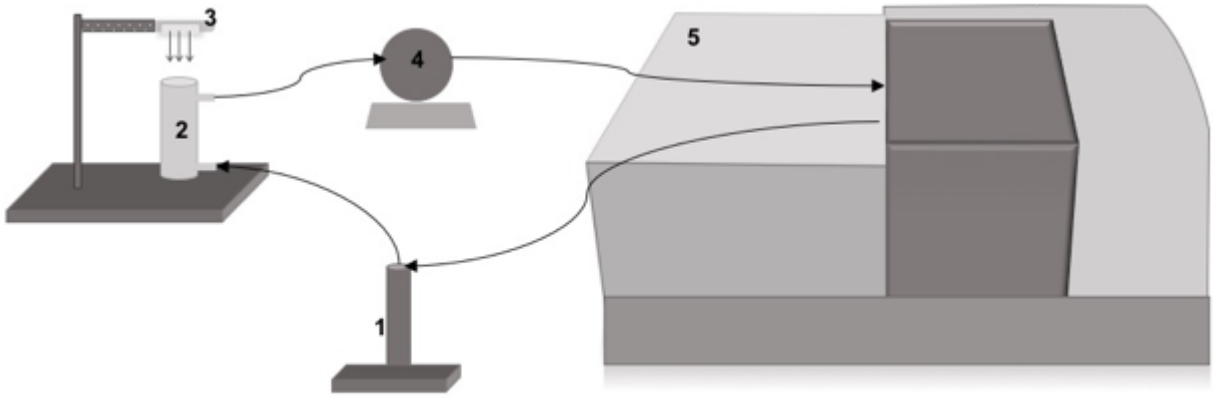

Figure 6. Irradiation experimental set up. 1) sample vial; 2) irradiation cell; 3) UV light source; 4) peristaltic pump; 5) Horiba Aqualog fluorometer. [paper II]

3.1.2. Paper III

The effect of UV_{254} irradiation on assimilable organic carbon in treated drinking water was investigated in the laboratory. Samples from seven Swedish DWTPs were collected on location prior to the disinfection process. The irradiation experiments and unirradiated control samples were replicated. To run the UV_{254} irradiation, the samples were transferred to a 200 ml irradiation vial placed on an agitator to facilitate homogenous distribution of UV_{254} light through the sample. The pre-washed UV_{254} lamp was submerged inside the irradiation vial, which was covered with aluminium foil, with the entire apparatus surrounded by a black box to avoid scattering the light. Samples were irradiated under various UV_{254} doses, inversely proportional to their initial absorbance (Abs_{254}) in order to deliver a greater UV_{254} dose to the samples containing less light-absorbing CDOM.

3.1.3. Paper IV

The impact of pre-irradiation on the formation of halogenated disinfection by-products (DBPs) in the chlorinated samples (NaOCl: 1.8 ± 0.2 mg initial Cl_2 per mg of DOC; 24 h) was investigated in paper IV using four different DOM samples. A series of irradiation experiments were carried out for each sample under two or three irradiation doses (40, 200 and 1000 mJ cm^{-2}), which were immediately followed by chlorination. To perform the irradiation experiments, samples were retained in a 250-mL Pyrex dish placed on a stirrer. The UV_{254} lamp was located at short distance (2 cm) from the irradiation vial parallel to the sample surface.

3.2. Ultraviolet light source

The UV light source used in all the irradiation experiments was a mercury Pen-Ray lamp (UVP, Cambridge, UK) with the primary radiant wavelength at 254 nm (Figure 7) with a nominal light intensity of 40 W m^{-2} at a 2 cm distance. The irradiation dose was calculated according to eq. 5:

UV dose (J m^{-2}) = UV intensity (W m^{-2}) x Exposure time (s) eq. 5

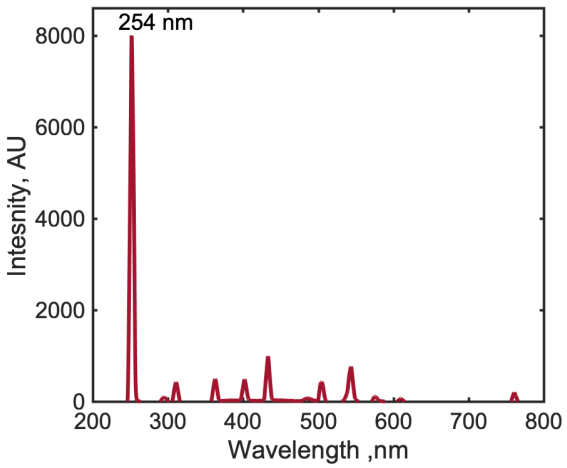

Figure 7. Emission spectrum of the UV_{254} light source used in this study.

Prior to each irradiation experiment, the light intensity was measured using a radiometer (J-225 light meter in paper II&III). To obtain accurate UV intensity measurements received by the sample in each irradiation set-up, iodide/iodate actinometry (Rahn 1997) was carried out. The iodide/iodate actinometry was performed by making a stock solution comprising of an acidometer (0.6 M iodide), an electron scavenger (0.1 M iodate) and a borax buffer (0.01 M). The solution was prepared by mixing 4.98 g of potassium iodide (KI; CAS No.: 7681-11-0, Alfa Aesar), 1.07 g of potassium iodate (KIO3, CAS No.:7758-05-6, Alfa Aesar) and 0.19 g of borax buffer ($B_4Na_2O_7$ .10 H_2O; CAS No: 1303-96-4, Sigma-Aldrich) in 50 ml of Milli-Q water. To conduct an individual test, the actinometry solution was transferred to the irradiation cell. Prior to exposure, the absorbance spectrum of the solution was scanned within the wavelength range of 290-380 nm. The molar concentration of iodide (C_{KI}) in the solution was determined using the absorbance at 300 nm according to the following equation:

$$C_{kI}\ (M) = \frac{Abs_{300}\ cm^{-1}}{1.061\ M^{-1}\ cm^{-1}} \quad \text{eq. 6}$$

The actinometer solution was exposed to UV_{254} by turning on the UV lamp. The absorbance spectra of the actinometer were scanned during (or after) the course of irradiation (Figure 8).

Upon irradiation of the iodide/iodate mixture, triiodide is produced which can be measured by the absorbance at 352 nm according to eq. 7:

$$Triiodide\ (mol) = \frac{(Abs_{352,post} - Abs_{352,pre})\ \mathrm{cm}^{-1}\ (V_{Sol})\ L}{\varepsilon\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}} \quad \text{eq. 7}$$

where, ε is the molar absorption coefficient equal to 26400 M^{-1} cm^{-1} and V_{sol} is the volume of the actinometry solution in litres. The quantum yield of the actinometer (number of triiodide moles formed per mole of photons absorbed) depends on the temperature of the solution, with iodide concentration calculated using eq. 8:

$$\phi\ (\mathrm{mol}\ /\ \mathrm{einstein}) = 0.75\ [\ 1 + 0.02\ (\ T_{sol} - 20.7)] * [1 + 0.23\ (C_{kI} - 0.577)\ ] \quad \text{eq. 8}$$

Finally, the UV dose ($Dose_{act}$) received by the actinometer (mJ cm^{-2}) is calculated as:

$$Dose_{act} = \frac{(4.72 * 10^8)(Abs_{352,post} - Abs_{352,pre})\ (V_{Sol})}{\varepsilon\ \phi\ A_{Sol}} \quad \text{eq. 9}$$

In eq. 9, 4.72×10^8 is the number of milijoules per einstein of photons absorbed at 254 nm. A_{sol} is the cross-sectional area of actinometry solution exposed to UV light ($\pi \times (1.1\ \mathrm{cm})^2$).

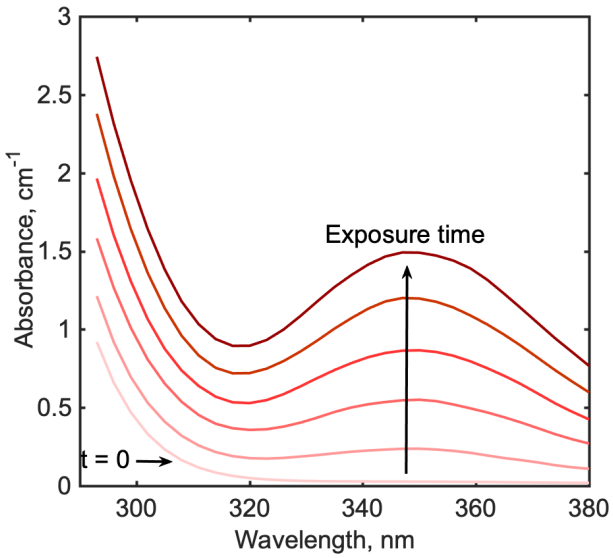

Figure 8. Absorbance spectra of actinometer solution before UV exposure (black line) and at intervals during UV exposure.

3.3. Analyses

3.3.1. DOM Optical properties

DOM fluorescence and absorbance were measured using an Aqualog spectrofluorometer (Horiba Scientific) in a 1-cm quartz cuvette (Paper I & III) or a 1-cm quartz through-flow cell [paper II]. Excitation and emission matrices (EEMs) were obtained at 20°C with 2-3 s integration time. The emission wavelengths spanned from 240 to 800 nm at 2.33 nm increments, and the excitation wavelengths spanned from 220 or 240 to 600 or 700 nm at 3 nm increments. In paper IV, fluorescence EEMs were measured using a Varian Cary Eclipse spectrophotometer in a 1-cm cell at 1200 nm min^{-1} with 5-nm slit widths on excitation and emission. Excitation wavelengths spanned 250-400 nm at 3-snm intervals and emission wavelengths spanned 240-600 nm at 5-nm intervals. Blank EEMs were obtained from ultra-pure water sealed in a quartz fluorometer cell. In paper III and IV, absorbance spectra were measured in a 1-cm cell using a Shimadzu spectrophotometer, UV-1800 (2 s integration time) and Cary 60 UV-vis spectrophotometer (600 nm min^{-1}), respectively.

The measured EEMs were imported into MATLAB for post-processing. Fluorescence intensities were converted to Raman unit (RU) by dividing to the Raman area of the blank within the emission wavelength of 378 - 424 nm at excitation wavelength of 350 nm (Lawaetz and Stedmon 2009, Murphy et al. 2010). Prior to modelling, the scatter bands (Raman and Rayleigh) were removed and data were corrected for concentration biases (inner filter effects) (Andersen and Bro 2003, Lakowicz 1983).
PARAFAC modelling was implemented using the *N-way* and drEEM toolboxes for MATLAB (Andersson and Bro 2000, Murphy et al. 2013). The results of the PARAFAC modelling are presented as the maximum fluorescence intensity (F_{max}) for each component which were calculated by multiplying the maximum loadings of excitation and emission for each component by its score (Murphy et al. 2013).

3.3.2. Dissolved organic carbon (DOC)

DOC was measured using a Shimadzu TOC-V_{CPH} carbon analyser, using the non-purgeable organic carbon (NPOC) method (EN 1484: 1997). Samples were acidified to pH = 2 using HCl (37% v/v) prior to the analysis. The dissolved inorganic carbon was converted to carbon dioxide after sparging the sample for five minutes with purified air before injection into the analyser.

3.3.3. Apparent molecular weight distribution

The apparent molecular weight distribution of the CDOM was measured using high performance size exclusion chromatography (HPSEC) equipped with UV-254 nm absorbance detection. The standard solution (polyethylene glycol) was used to obtain the retention time against the molecular weight within the range between 0.4-10 kDa. The integrated area under the chromatograms were calculated within three ranges: total area (0-4-10 kDa), low molecular weight (< 1 kDa) and high molecular weight (> 1 kDa) [paper III].

3.3.4. Assimilable organic carbon (AOC)

Assimilable organic matter bioassays were carried out using the protocol established by (LeChevallier et al. 1993). In summary, the AOC was determined from the growth of two strains, *Pseudomonas fluorescens* (P-17) and *Spirillum* (NOX), which were added to the pasteurized samples (Escobar and Randall 2000) and incubated at 20°C for three days. The formed P-17 and NOX colonies were counted visually after three days, converted to colony forming units per ml (CFU/ml), and then AOC concentrations were calculated using previously-derived empirical yield values for P-17 (4.1×10^6 CFU P-17/µg acetate-C) and NOX (2.9×10^6 CFU NOX/µg oxalate-C) according to the eq. 10 [paper III]:

$$\mu g\ AOC/l = [(\text{mean P} - 17\ \text{CFU/ml})\ (\mu g\ \text{acetate} - C/4.1 \times 10^6\ \text{CFU}) + (\text{mean NOX CFU/ml})\ (\mu g\ \text{oxalate} - C/2.9 \times 10^6\ \text{CFU})] \times (1000\ \text{ml/l}) \quad \text{eq.10}$$

3.3.5. Disinfection by-products

The disinfection by-products were analysed using two methods: gas chromatography-mass spectrometry (GC-MS) and adsorbable organic halogens (AOX). The concentrations of four trihalomethanes, THM4 (trichloromethane, bromodichloromethane, dibromochloromethane and bromoform) and six haloacetonitriles, HAN6 (chloroacetonitrile, dichloroacetonitrile, trichloroacetonitrile, bromoacetonitrile, bromochloroacetonitrile and dibromoacetonitrile) were quantified using headspace GC-MS with the solid-phase microextraction as the extraction method (Allard et al. 2012).
To measure the concentration of the total chlorinated and brominated disinfection by-products, AOX analysis was performed according to the established method (Langsa et al. 2017). Briefly, the acidified samples were absorbed onto activated carbon microcolumns and combusted at

1000°C. The produced halogenated gases were collected in a gas absorption unit, and then injected to ion chromatography system. The concentrations of adsorbable organic chlorine (AOCl) and adsorbable organic bromine (AOBr) as two subsets of AOX were measured using a conductivity detector as chloride (Cl^-) and bromide (Br^-) [paper IV].

3.4. Distribution network [paper I]

Drinking water samples were collected at 87 locations (taps of houses and public buildings) connected to the municipal drinking water distribution network in Gävle, Sweden in December, 2015. The sampling locations were chosen to encompass the entire range of water residence time (0.5-50 h) within the network.

Concentrations of trace metals (Al, Cu, Fe) were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Scientific iCAP Q spectrometer. Microbial analyses were performed according to standard methods for quantifying culturable microorganisms (pour plate technique, incubation at 22°C for 3 days) and slow-growing bacteria (incubation at 22°C for 7 days).

To compare the precision of measured variables in the distribution network study, relative standard deviations (RSD = standard deviation/mean) of the replicate samples were determined for each of the chemical and microbial parameters. The averaged measurements of the replicate samples were used in all further analyses.

To determine the threshold at which a significant elevation in the chemical and microbial parameters could be diagnosed, trigger thresholds (TT) were calculated according to eq. 11:

$$TT = \bar{x} + 3s \qquad \text{eq. 11}$$

where, $\bar{x}$ and s are the average and standard deviation of measurements from samples collected across the whole network.

4. Results and discussion

The main aim of this dissertation was to investigate the link between changes in DOM character as assessed by fluorescence and absorbance and the major water quality parameters in the treated water following UV disinfection, chlorination and distribution. Although CDOM is not a main concern for the water quality per se, they might correlate with the other parameters, thus potentially be useful as indicators. Here, three processes that might alter the CDOM characterization in the final stages of the drinking water system were studied: a) absorption of UV light by CDOM upon UV disinfection; b) the reaction between chlorine and CDOM during chlorination; c) the fluctuation in CDOM characterization within the distribution network. In each of these processes, one major chemical or microbial water quality parameter was also analysed and linked to the CDOM optical properties (Figure 9).

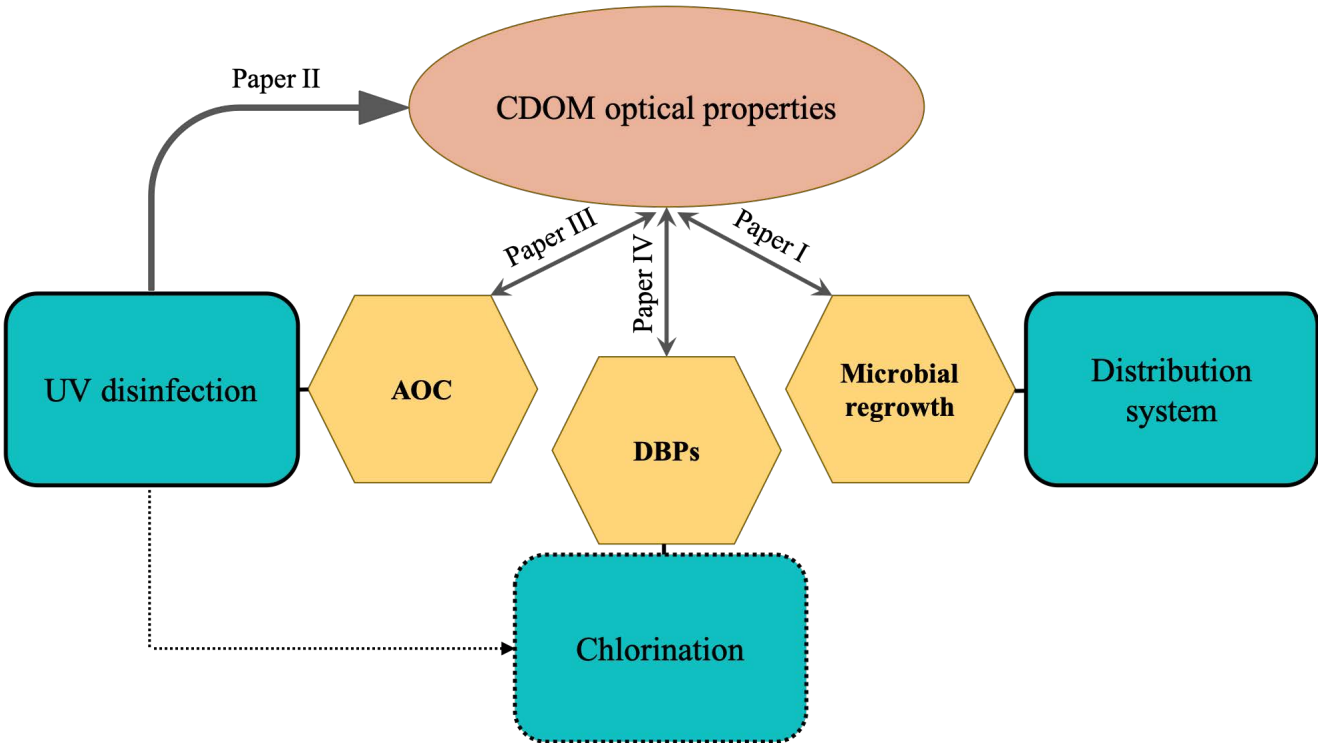

Figure 9. Schematic of the processes (green) and parameters (orange) investigated in this thesis.

4.1. Optical properties of CDOM in treated drinking water

4.1.1. Fluorescence

The fluorescence fingerprint of dissolved organic matter was collected by either scanning the excitation-emission matrixes (EEMs) or the emission spectra at selected excitation wavelengths. Additional to the inspection of the collected raw fluorescence EEMs, the PARAFAC modelling was carried out with one of the following aims: i) to use the calculated PARAFAC components as the fluorescence-based parameters for further analysis combined with the other parameters [paper I and III]; ii) to select the ranges of the excitation/emission pairs changing the most upon UV_{254} irradiation [paper II]; iii) to replace the raw fluorescence EEMs containing high measurement noises with the modelled EEMs to generate less noisy dataset for the peak-picking method [paper IV].

Four- or five- component models were calculated in each study with two of the components being similar in all the models (C_1, C_4), mainly with respect to their emission spectra. The short-wavelength component, C_5, generally referred to as "protein-like" was also identified in all the models, however with slightly different spectra. All of the other five components are referred to as "humic-like" compounds in literatures. Due to the controversial dispute on the real origin of these compounds, the typical humic-like and protein-like terms are avoided in this dissertation and instead, are referred to by the components' numbers. The list of the components and their corresponding excitation/emission wavelengths are presented in Table 2.

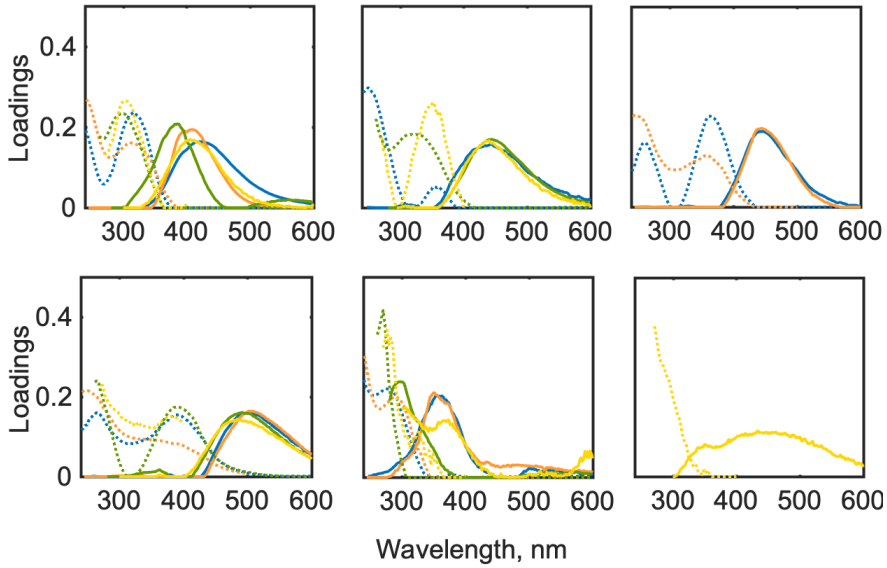

Figure 10. The loadings of the PARAFAC models obtained in four studies. Paper I: orange; Paper II: green; Paper III: blue; Paper IV: yellow.

Table 2. Fluorescence components in the PARAFAC models derived in each of the four studies. The datasets underlying each model were collected from: the distribution system, Gävle, Sweden [paper I]; treated water from eight DWTPs in Sweden [paper II and III], DOM isolates of treated river waters from the U.S. and France, and coagulated/filtered river water from Australia [paper IV].

Component	Peak position Ex/Em	Paper I	Paper II	Paper III	Paper IV
C_1	298-317 / 385-422	+	+	+	+
C_2	<280 (325-360) / 440	–	+	+	+
C_3	<280 (360) / 445	+	–	+	–
C_4	<280 (380-390) / 480-500	+	+	+	+
C_5	<280 / 300-370	+	+	+	+
C_6	<280 / 440	–	–	–	+

4.1.2. Absorbance

Ultraviolet and visible absorbance are widely used in drinking water industry for DOM characterization and process optimization (Matilainen et al. 2011). The most common absorbance-based parameter are the absorbance at 254 nm (Abs_{254}), which is an indicator of the DOM aromaticity and reactivity (Korshin et al. 2009) and it's corresponding carbon specific value (SUVA: Abs_{254}/DOC) (Archer and Singer 2006a). In this dissertation, besides fluorescence spectroscopy, UV-vis absorption spectroscopy was used in all studies to characterize the dissolved organic matter, mainly in attempt to compare its sensitivity and applicability with fluorescence. The absorbance spectra of all DOM samples decreased monotonically with increasing wavelength (Figure 14a).

4.2. The impact of UV_{254} irradiation on dissolved organic matter's optical properties

The impact of UV_{254} irradiation on the dissolved organic matter fluorescence in the treated water was examined in paper II and IV, in which relatively low doses of UV_{254} (<=200 mJ cm^{-2}) were applied both at lab scale [paper II and IV] and full scale [paper II]. Measurable changes were detected in the DOM fluorescence intensity in all the examined waters. To determine which regions of the fluorescence EEMs were more susceptible to the UV irradiation, the raw fluorescence EEMs of the post-UV waters were subtracted by that of the pre-UV waters (Figure 11). The alteration of the full fluorescence EEMs against increasing UV dose was examined in one sample in Paper II (Mölndal) and in four samples in Paper IV. The impact of UV was mainly observed at the longer emission wavelengths (> 400 nm), which is typically associated with the "humic-like" fluorescence components. However, at the longer excitation wavelengths (~400 nm), the fluorescence intensity increased in Mölndal sample.

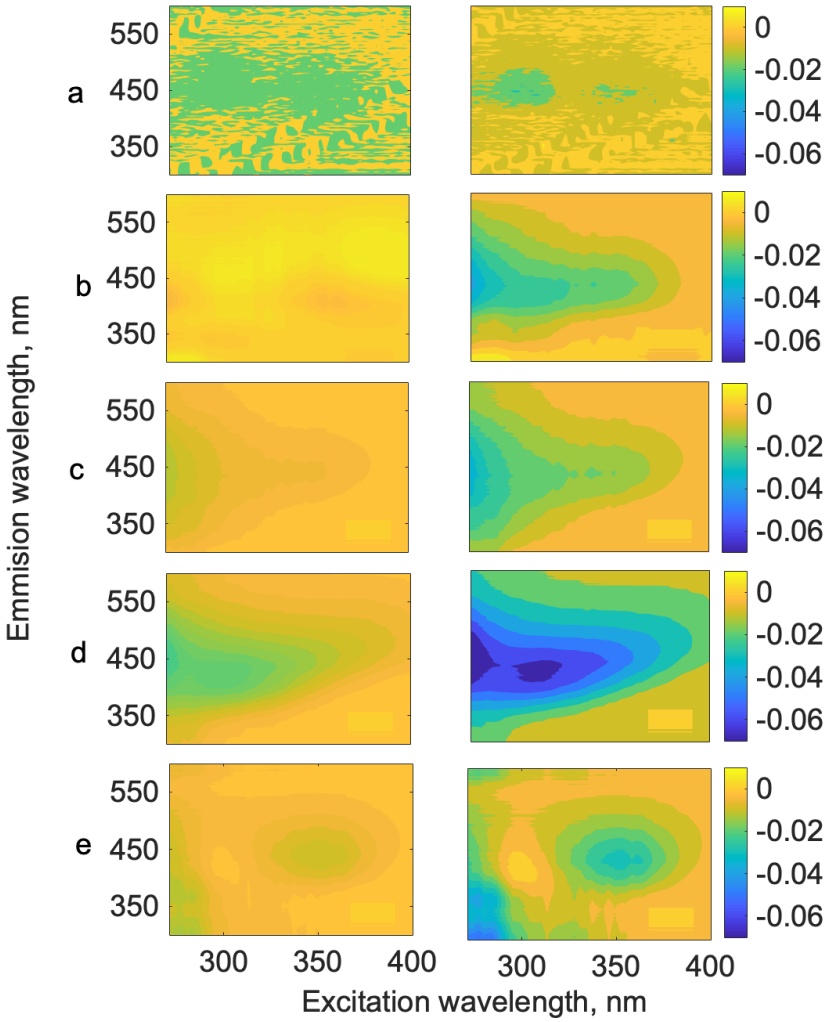

Figure 11. The differential EEMs between the pre- and post-UV samples (ΔEEM = $EEM_{post\text{-}UV}$ - $EEM_{pre\text{-}UV}$) at low (left column) and medium (right column) UV doses. a) Mölndal (80 and 160 mJ cm^{-2}); b) Denmark Rr (40 and 200 mJ cm^{-2}); c) Col Rr (40 and 200 mJ cm^{-2}); d) Daon Rr (40 and 200 mJ cm^{-2}); e) Sth Platte Rr (40 and 200 mJ cm^{-2}).

Not only were the UV-induced fluorescence changes detectable in lab-scale irradiation experiments, but also at full-scale in nine DWTPs when routine disinfection UV doses (35-100 mJ cm^{-2}) were applied. The differential fluorescence EEMs between the water samples leaving and entering the UV chamber of one of the treatment plants (Lilla Edet, Sweden) is shown in the Figure 12. Although the scale of changes in the fluorescence intensity was similar between the lab- and full-scale irradiated waters, the directions of changes were the opposite at the lower excitation wavelengths (<400 nm). At seven of nine treatment plants, water leaving the UV chamber had higher fluorescence intensity (Ex/Em: 320/420 nm) compared to the water entering the chamber, while at the remaining two treatment plants it had slightly lower fluorescence intensity versus the entering water. The higher fluorescence intensity of the irradiated water at the full-scale might be partly related to the fluorescence dark recovery caused by the time delay between the sampling at the treatment plant and the fluorescence measurement at the laboratory (2-14 days), a phenomenon that was investigated in Paper II. Briefly, fluorescence intensity of irradiated water increased slightly in the dark, possibly due to short-term changes in the DOM fluorescence efficiency (Sharpless and Blough 2014) or

alterations in the macromolecular conformation of the humic substances (Patel-Sorrentino et al. 2004).

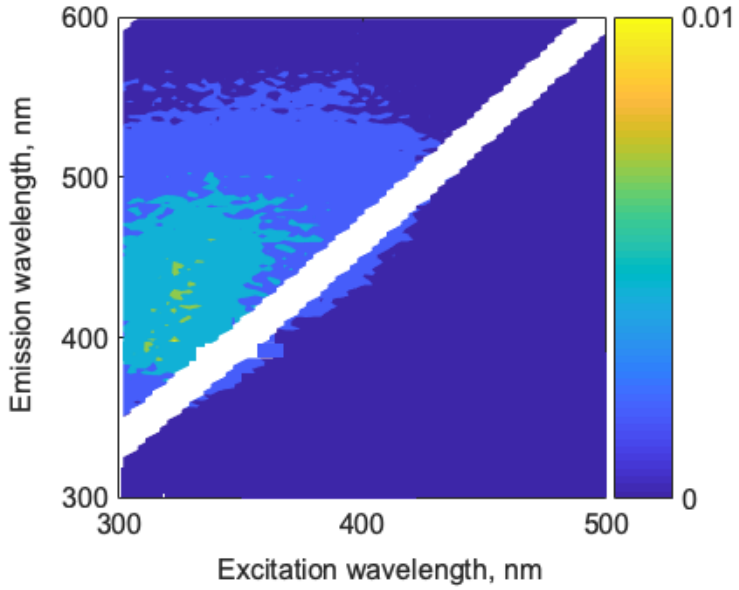

Figure 12. The differential fluorescence EEM (ΔEEM = $EEM_{post\text{-}UV}$ - $EEM_{pre\text{-}UV}$) during normal UV operation (35 mJ cm^{-2}) at the drinking water treatment plant (Lilla Edet DWTP, Sweden; Paper II)

The changes in the fluorescence intensity induced by applying low UV doses under laboratory and full-scale conditions prompted an investigation into whether there is a consistent and predictable relationship between the UV dose (UV intensity × irradiation time) and changes in fluorescence intensity [paper II]. To begin, the photobleaching kinetics of the fluorescence signals were determined by rapid measurement of the fluorescence emission spectra at single excitation wavelengths (Ex=320 and 400 nm; corresponding to C_2 and C_4, respectively) at different irradiation times under a constant UV intensity (0.32 mW cm^{-2}) for each water. The measured emission spectra and the maximum fluorescence intensity of one of the samples (Alelyckan, Paper II) against the irradiation dose are illustrated in Figure 13. This shows that C_2 and C_4 decreased and increased, respectively, in linear proportion to the UV_{254} dose.

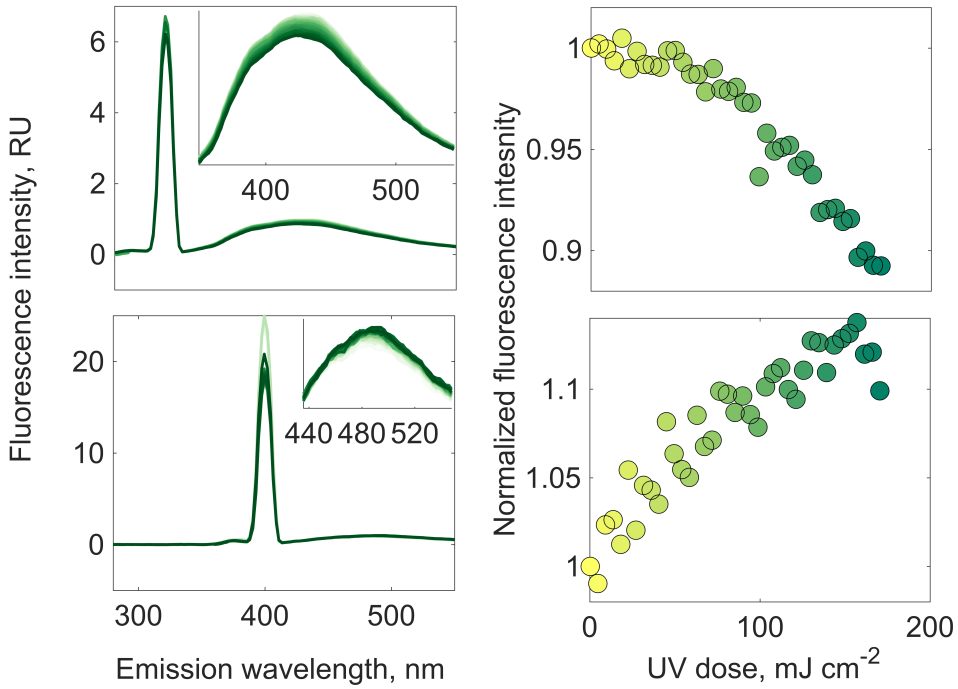

Figure 13. Changes in fluorescence intensity versus UV dose at two excitation wavelengths (320 and 400 nm) for Alelyckan water [paper II]. a) Emission spectra at Ex= 320 nm. The insert shows zoomed in spectra between 350-550 nm; b) Fluorescence intensity at the peak maximum (Ex/Em: 320/420) against the UV dose, normalized by the initial value; c) Emission spectra at Ex= 400 nm. The insert shows zoomed in spectra between 440-550 nm; d) Fluorescence intensity at the maximum peak of the spectra (Ex/Em: 400/500) against the UV dose, normalized by the initial value.

4.2.1. Absorbance

Generally, UV_{254} irradiation reduced the CDOM absorbance at the wavelengths below 280 nm, with the maximum reduction occurring at wavelengths close to UV lamp output (254 nm). Loss of absorbance at 254 nm (Abs_{254}) and its specific value ($SUVA_{254}$) indicate the degradation of aromatic and conjugated organic matter moieties (Traina et al. 1990, Weishaar et al. 2003). Sometimes, the absorbance at longer wavelengths (> 280 nm) increased. The differential absorbance spectra between the pre- and post-UV waters under different UV doses are illustrated in Figure 14. As expected, increasing the UV dose caused greater reduction in the absorbance at 254 nm (Abs_{254}). However, the loss of CDOM absorbance also depended on the water sample, and various waters responded differently to similar UV doses. For instance, although Col Rr and Denmark Rr waters [paper IV] were irradiated with similar UV doses (40 and 200 mJ cm^{-2}), their absorbance reduction differed at each UV dose, and they each responded differently to increasing the UV dose.

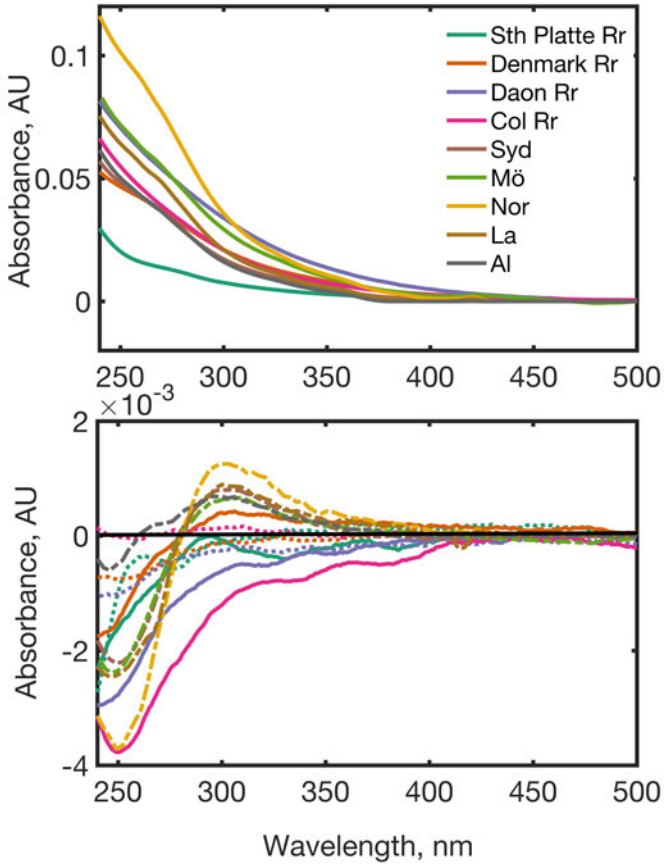

Figure 14. The initial absorbance (top) and the differential absorbance spectra (bottom) of nine DOM samples [paper II and IV].

In addition to absorbance at 254 nm, several concentration-independent spectral parameters that have previously been related to CDOM chemistry (such as molecular size, aromaticity) were calculated. The spectral slopes; S_{275_295}, S_{350_400} and their ratio S_R were calculated using the pre- and post- irradiation absorbance spectra in Paper III. Both the spectral slopes decreased following UV irradiation, while their ratio either increased or decreased. No significant changes in dissolved organic carbon (DOC) concentration were detected in any of the studies, resulting in reduced carbon specific UV_{254} absorbance ($SUVA_{254}$) following irradiation (Paper III and Paper IV).

4.3. Impact of UV on the CDOM molecular weight

The impact of UV_{254} on the molecular size distribution of samples from seven DWTPs was studied in paper III. The total area under the HPSEC chromatograms decreased following UV_{254} irradiation in all samples. To assess which fraction of the CDOM molecular weight changed the most under UV_{254} irradiation, the area under the chromatogram was calculated for two different segments along the measured molecular size range: below 1 kD, and above 1 kD, referred to as low molecular weight (LMW) and high molecular weight (HMW) fractions respectively, then compared between the pre- and post- UV samples. No consistent trend was found; while the LMW fraction was preferentially removed in some samples, the HMW fraction was preferentially removed in others.

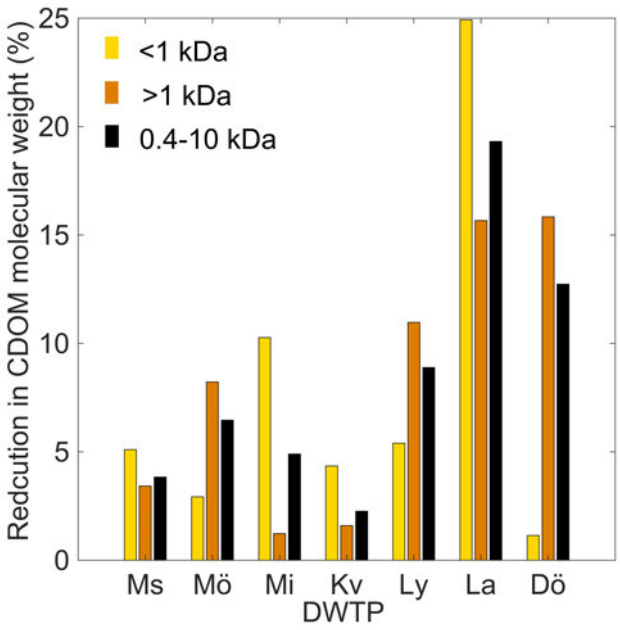

Figure 15. The percent reduction of three fractions of CDOM molecular weight in seven DWTPs in paper III: (post-UV - pre-UV/pre-UV)× 100. Black: 0.4-10 kDa; Yellow: 0.4-1 kDa; Orange: 1-10 kDa. DWTPs are ordered along x axis by ascending UV dose.

4.4. Impact of UV on assimilable organic carbon

The impact of UV irradiation on the DOM bioavailability was investigated in paper III by measuring assimilable organic carbon (AOC), in addition to analysing the changes in the molecular weight distribution of CDOM and fluorescence/absorbance properties. Generally, the concentration of AOC increased after UV irradiation, with a greater increase observed in samples exposed to higher UV doses. A significant positive linear relationship was found between the production of the carbon-specific AOC and the UV dose (solid black line in Figure 16; $R^2 = 0.57$, p-value= 0.02). Therefore, in order to scale the AOC production to a typical disinfection dose (40 mJ cm^{-2}), a linear relationship was assumed for each individual water. The estimated average increase in carbon specific AOC concentration at UV dose of 40 mJ cm^{-2} was 4.0 ± 1.3 µg mg^{-1}; i.e. on average 0.4 % of the dissolved organic matter would be expected to convert to assimilable organic carbon under normal UV disinfection conditions.

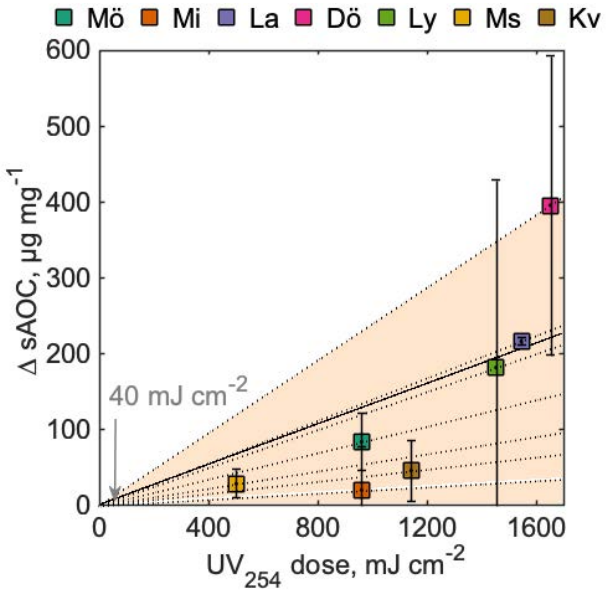

Figure 16. The impact of UV_{254} irradiation on AOC produced per unit of DOC (sAOC = AOC/DOC). Solid line: the general linear fit between UV dose and Δ sAOC of seven sampling sites. Dashed lines: individual linear fit between each data point and the origin. Impact of UV irradiation on the DBPs.

4.5. Impact of UV irradiation on the disinfection by-products (DBPs)

Another consequence of the UV-induced modifications of DOM molecular structure is the altered organic matter reactivity towards disinfectants such as chlorine that might be added to the treated water after UV disinfection in order to maintain the chlorine residual within distribution system. This may change the concentration and speciation of the DBPs formed during the chemical reactions between DOM as the main precursor species and the chlorine. The impact of UV irradiation on the formation of DBPs in the irradiated DOM samples followed by chlorination was investigated [paper IV].

Generally, the concentration of total chlorinated by-products increased proportionally with increasing the UV dose. Upon irradiation under the typical disinfection dose (40 mJ cm^{-2}), the concentration of adsorbable organic chlorine (AOCl) increased by 10-15% in four DOM samples, implying that even under low UV dose irradiation, the reactivity of the CDOM increased, which led to the greater formation of chlorinated organic by-products (Figure 17). Among the measured AOCl concentrations in different samples, three appeared as outliers in the observed behaviuor, (Figure 17: Denmark Rr @ 200 mJ cm^{-2}; Col Rr @ 0 mJ cm^{-2} and Sth Platte @ 40 mJ cm^{-2}). These samples had greater inter-replicate variations compared to the other samples, suggesting measurement error was the possible source of deviation from the observed increasing behaviuor of AOC against UV dose. Contrary to AOCl, generally, no significant change was detected in the adsorbable organic bromine (AOBr) concentration due to UV irradiation. The individual DBPs did not respond to the UV irradiation under low and medium doses (40 and 200 mJ cm^{-2}). Only when a high UV dose (1000 mJ cm^{-2}) was applied for two of the DOM samples (Daon Rr and Sth Platte Rr), significant increases were observed in the concentration of trichloromethane (TCM) in both samples, while the concentration of dibromochloromethane and bromodichloromethane increased only in Daon Rr (300 % and 50%, respectively). None of the HAN6 compounds increased in samples irradiated at UV dose of 1000 mJ cm^{-2}.

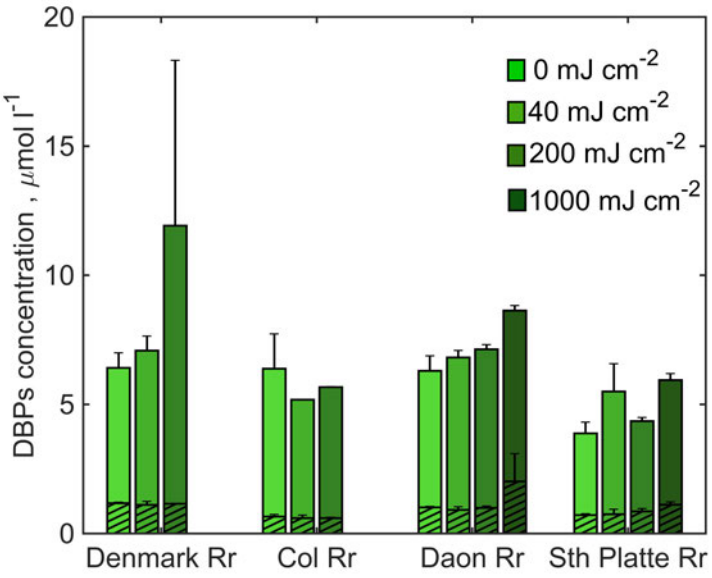

Figure 17. Concentration of disinfection by-products in four chlorinated waters preceded by different UV dose irradiation. Green bars: AOCl concentration; Hatched area: THM4+HAN6.

4.6. The link between dissolved organic matter fluorescence and other parameters

4.6.1. Fluorescence as a proxy for the applied UV dose

The efficiency of UV disinfection to inactivate pathogens mainly depends on the received UV dose. While under-dosing causes insufficient log-reduction of the microorganism leading to increased microbial risk, excessive UV irradiation renders direct or indirect formation of organic and inorganic by-products exposing potential risks to human health and the integrity of the piping system (Choi and Choi 2010, Frimmel 1998, Lehtola et al. 2003). The CDOM fluorescence can be used as a proxy for the applied UV dose if it responds sensitively to the UV irradiation, and if the scale and direction of the changes are predictable. According to the findings of the paper II, despite the different direction of changes (increase, decrease or unchanged) of two fluorescence peaks (corresponding to C_2 and C_4), their ratios (C_2/C_4) always decreased linearly against the UV dose, with the slopes significantly different from zero (p-value < 10^{-5}).

The application of CDOM fluorescence to predict the administrated UV dose, however, was hindered by two factors. Primarily, the scale of change was small in all waters (< 5 %), except two in which a 10% and 25% reduction in the fluorescence ratio occurred. This hampers the detection of fluorescence changes when real-time monitoring is to be implemented using online fluorometers typically using LED lamps as light sources. Compared to the laboratory fluorometers, the online sensors are less sensitive due to their power output, thus may not be able to detect the slight variation in the fluorescence of outgoing water from the UV chamber, which is caused by slight fluctuation in the UV dose. Moreover, the scale of changes in DOM individual fluorescence signals (C_2 and C_4) could not be predicted from the measured initial water parameters including: the source type (groundwater vs surface water), pH, DOC concentration and initial fluorescence- and absorbance-based parameters (humification index, biological freshness index, fluorescence index and Abs_{254}). This implies that the fluorescence dose-response curve should be established locally and temporally for each treatment plant.

4.6.2. Fluorescence as a proxy for assimilable organic carbon production

In previous studies, the increase in biodegradability of organic matter was related to the loss of aromaticity, using a linear relationship between reduction in Abs_{254} and increase of AOC or BDOC (Buchanan et al. 2004, van der Kooij et al. 1989), suggesting that CDOM optical properties may be a potential indicator for AOC concentration. In paper III, in addition to absorbance, the relationship between the fluorescence reduction and AOC production was investigated by applying various UV doses on seven different waters. A weak correlation was found between the percent reduction of the long-wavelength PARAFAC component and the produced carbon specific AOC (R^2= 0.55; p-value=0.06). The weak correlation between the data is partly attributed to the differences between the examined waters and their corresponding fluorescence and AOC responses to the UV irradiation. The high variability between the AOC replicates also weakened the correlation.

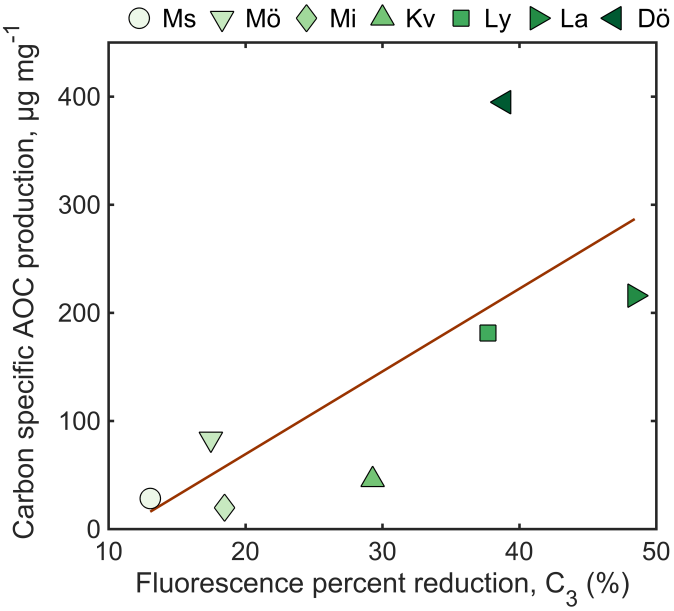

Figure 18. Relationship between the carbon specific AOC (sAOC: AOC/DOC) production and percent reduction in the fluorescence intensity of PARAFAC component (C_3); samples were from seven DWTPs and were exposed to different UV doses. Marker shading indicates UV irradiation intensity.

4.6.3. Fluorescence as a proxy for disinfection by-products

The combined impact of UV irradiation and chlorination on CDOM fluorescence and disinfection by-product formation was examined in paper IV. The relationship between fluorescence and AOCl was examined for DOM samples irradiated at different UV doses. Figure 19 shows AOCl concentration plotted against fluorescence reduction following UV irradiation and chlorination. Samples treated with a higher UV dose almost always produced greater AOCl and had a greater reduction in fluorescence intensity, with an exception in one of the "Col Rr" experiments. Both AOCl formation and fluorescence reduction were greater in "Col Rr" sample when unirradiated (0 mJ cm^{-2}) compared to when it was preceded with the UV irradiation, although still following a linear relationship. Due to the relatively high measurement error between the AOCl replicates of this sample (Figure 17) it is difficult to draw conclusions with respect to its contradictory behaviour.

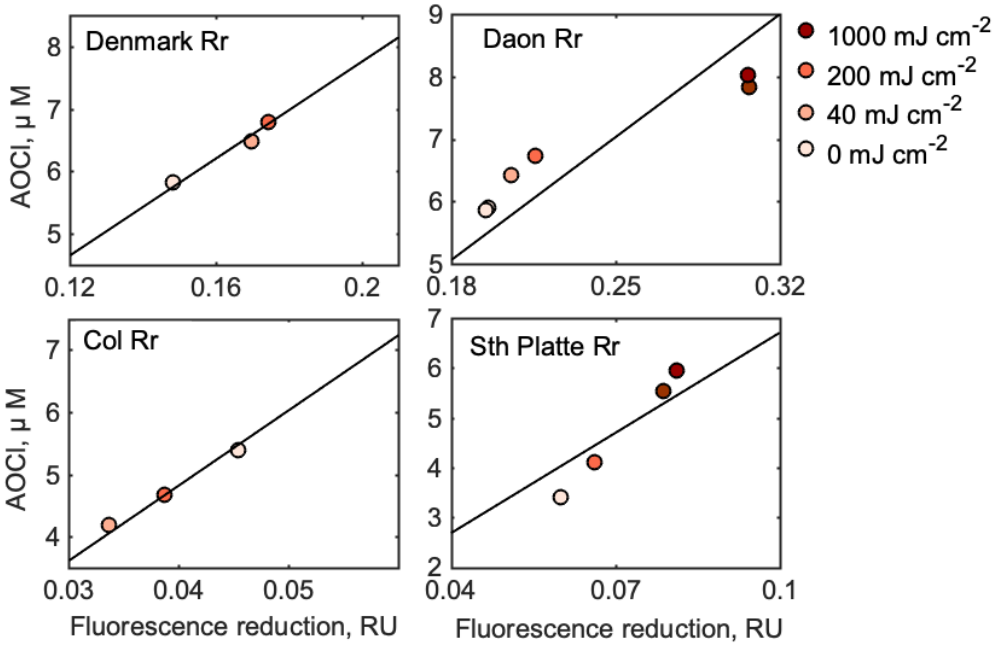

Figure 19. Correlations between AOCl production and fluorescence reduction in four chlorinated samples preceded by various doses. Regression lines pass through the origin.

4.6.4. Fluorescence as a proxy for water quality at the tap

Microbial quality of drinking water within distribution networks is predisposed to deteriorate due to many factors including microbial regrowth, intrusion of untreated water through damaged pipes, and decaying chlorine residuals. The general lack of accurate and inexpensive real-time monitoring techniques to detect deviations in microbial water quality within distribution networks increases the challenges for water suppliers. Microbial analyses needed to examine the quality of water are performed in a laboratory and yield results long after water has been delivered to the consumers. In recent years, online analytical methods have been developed that target microorganisms using flow cytometry (Prest et al. 2013) and adenosine triphosphate (ATP) (Vang et al. 2014). However, these methods are not chemical-free and demand extensive equipment maintenance (Højris et al. 2016). Optical online bacteria detectors have also been tested in the context of detecting contamination in tap water; this is based on counts of bacteria and abiotic particles, with the latter being more sensitive and capable of detecting a 15-20 % of deviation from average values (Højris et al. 2016).

Stability is a requisite criterion for a water quality tracer if it is to be used to distinguish significant deviations from natural variation. As discussed in paper I, the more stable the concentration of a water quality tracer within a distribution network, the easier it is to detect contamination caused by entrainment of untreated water or caused by microbial regrowth. To estimate the threshold at which each parameter is able to distinguish potential contamination from natural variation, trigger thresholds (TT) can be used (eq. 11). The lower the value of TTrel (TT divided by the mean) the higher the sensitivity of a parameter for detecting contamination.

Natural variability affects the sensitivity of trigger thresholds by defining the extent of the deviation in the concentration of each parameter compared to the network mean. The relative standard deviation (RSD) of slow growing bacteria abundances was 100 %, due to the relatively low precision of heterotrophic plate counts. Different trace metals had relative standard deviations ranging between 14% and 170%. In contrast, fluorescence intensities were stable across the network compared to other parameters (Figure 20). The lowest variability (RSD = 4%) occurred at the long excitation and emission wavelengths (C_1, C_3 and

C_4 in Table 2). Absorbance was more variable than long-wavelength fluorescence (RSD = 10% for A_{254}) and almost as variable as short-wavelength fluorescence (RSD = 11%) (Table 3).

Measurement error also affects the sensitivity of trigger thresholds by its amplifying effect on experimental variance. The lower the variability among the concentrations of replicate samples, the smaller the fraction of the standard deviation in eq. 11 (*s*) that is devoted to measurement variance, and the lower the trigger threshold. Fluorescence intensities of the long-wavelength components varied less than other parameters in replicate samples due to very high measurement precision (Table 3).

Fluorescence was the most sensitive tracer for detecting contamination among the parameters measured in Gävle. This sensitivity improved further when copper was taken into account [paper I]. The low variability in fluorescence intensities (standard deviation = 4 - 11%) across the network and its high measurement precision (averaged standard deviation between replicates = 1 - 4%) made it the most sensitive tracer among all measured parameters. Absorbance was the second-most sensitive tracer. A 20% increase in absorbance at 254 nm (Abs_{254}) relative to the system average would be needed to trigger an outlier, compared to a 10% increase needed for fluorescence.

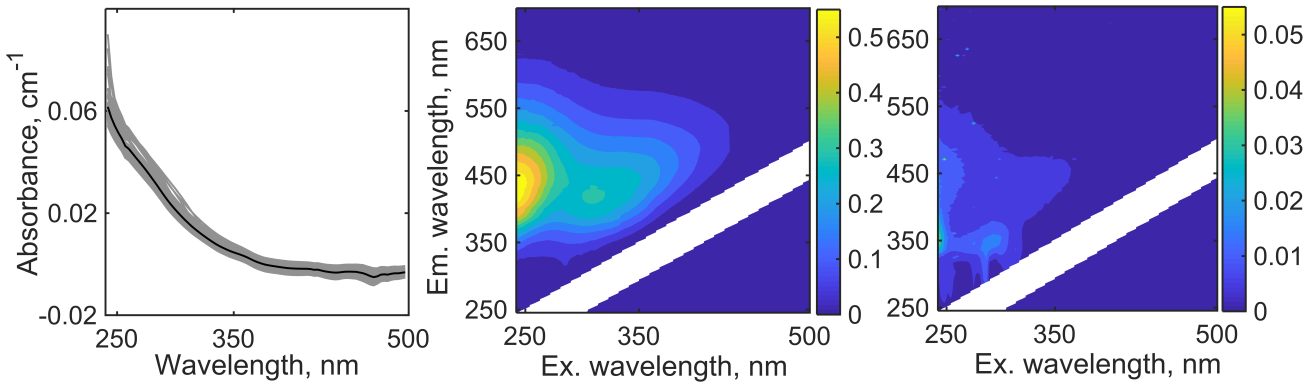

Figure 20. Variation in optical properties across the distribution network. (a) Absorbance spectra (grey lines) compared to the average spectrum (black line); (b) Average fluorescence; (c) standard deviation of fluorescence. [paper I]

Table 3. Water quality parameters measured in households connected to the Gävle drinking water distribution network (modified from Paper I). Analytical limits of detection (LoD) were determined from procedural blanks. Trigger thresholds were determined using uncorrected (un) and corrected (c) data.

Parameter	Min	Max	Median	RSD across sites (%)	RSD between replicates (%)		LoD	*TT*	TT_{rel} (*TT*/mean)
					Median	Max			
Fe (ppb)	1	20	4	75	7	17	0.74	17.7	3.3
Al (ppb)	0.50	8	2	47	14	79	1.72	6.7	2.4
Cu (ppb)	10	500	50	87	3	14	0.07	253	3.7
F 2 (RU)	0.25	0.31	0.29	4	1	1.4	0.01	0.32 [uc.] 0.35 [c.]	1.1 [uc.] 1.06 [c.]
F 4 (RU)	0.13	0.23	0.14	11	4	14	1.2	0.19	1.3
DOC (ppm)	2.5	8.9	3.5	41	8	13	0.16	10.34	2.25
A_{254} (cm^{-1})	0.04	0.08	0.05	10	2	19	0.001	0.06	1.20
Slow-growing bacteria (cfu/ml)	< 1	110	17	100	25	94	1	120.3	3.9

5. Conclusions

- Similar underlying fluorescent organic matter components were identified in drinking water or isolated DOM of treated water collected from sources in Sweden, Australia, the U.S., and France.
- Fluorescence spectroscopy was sensitive enough to detect small changes in organic matter fluorescence intensities due to UV_{254} irradiation (35-100 mJ cm^{-2}) during full-scale drinking water disinfection.
- Fluorescence intensity of drinking water samples generally decreased linearly in proportion to UV_{254} dose, however sometimes increased at longer excitation wavelengths (>400 nm). The ratio of two fluorescence peaks (Ex/Em: 320/420 and 400/500) always responded linearly to UV_{254} dose.
- Due to slight changes in DOM fluorescence upon UV_{254} irradiation at disinfection doses and unpredictable scale/direction of changes, fluorescence spectroscopy would not be a suitable proxy for tracking the administered UV_{254} dose during UV_{254} disinfection of drinking water in most situations.
- Upon UV irradiation at the typical disinfection dose (40 mJ cm^{-2}), 0.4 % of the dissolved organic matter is estimated to convert to assimilable organic carbon (AOC).
- Carbon-specific AOC (AOC/DOC) production varied between water samples and could not be predicted using the measured initial water parameters such as fluorescence, absorbance and molecular weight distribution. However, a weak correlation was found between changes in fluorescence and AOC production.
- The concertation of adsorbable organic chlorine (AOCl) in the chlorinated DOM samples (whole-water and isolates) was greater when samples preceded by UV irradiation compared to when unirradiated.
- The AOCl production correlated more strongly with fluorescence loss compared to absorbance loss.
- Compared to slow growing bacteria, trace metals, DOC and absorbance, CDOM fluorescence measurements in a healthy drinking water distribution network showed higher measurement precision and lower variability across the network.
- CDOM fluorescence could be a sensitive tracer of contamination caused by entrainment in healthy distribution network. An outlier would be triggered when the fluorescence intensity of humic-like components (emission at visible light wavelengths) exceeds the network average by 10%.

6. Summary and future research

The main focus of this dissertation was to investigate how optical properties can be used to detect changes in drinking water DOM and to link these changes to other water quality parameters. Optical properties were measured in the laboratory using a bench-top spectrofluorometer, which is generally more sensitive than using online sensors. One of the main directions for future research is to assess whether fluorescence spectroscopy can be applied to track water quality changes in real-time at treatment plants or within distribution networks using commercially-available online sensors. In this regard, the sensitivity of in-situ fluorometers for detecting small changes in fluorescence intensities during UV disinfection or due to entrainments in distribution networks should be investigated.

A single distribution network was studied in this thesis (Paper I). Further studies of additional networks are needed to assess the sensitivity of optical approaches for monitoring different finished waters with varying fluorescence and microbial quality backgrounds. The study should be expanded to include less-reliable distribution networks in which there is higher risk of contamination intrusion, for instance during pipe repairs and leakages. At the laboratory scale, the trigger threshold of various water quality parameters, e.g. fluorescence, absorbance, heterotrophic bacteria and bacterial cell counts, might be further investigated by spiking drinking water with wastewater.

In papers III and IV, potential side effects of UV irradiation including impacts on AOC and DBP concentrations, were investigated at lab-scale. In future studies, it is suggested to investigate the impact of UV disinfection at full-scale to determine whether the increasing impact of UV irradiation on AOC and AOX concentrations is observed in drinking water plants. To validate the results in this thesis, it is important that the reported linkage between optical properties and disinfection byproducts (AOC and AOX) is also demonstrated at drinking water plants under real operational conditions.

Finally, this dissertation focused on a single, widely used disinfection scheme i.e. UV irradiation using low pressure lamp (paper II and III) followed by chlorination (paper IV). At other treatment plants, different schemes might be implemented, such as using medium pressure UV lamps or using chloramine as a chemical disinfectant instead of chlorine. Moreover, the order of treatment steps can vary between treatment plants; i.e. the chlor(am)ination may take place prior to UV irradiation and in some plants, may be implemented more than once. These scenarios could result in different impacts on DOM optical properties and should be investigated in future studies.

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