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Optical sensors in drinking water production

Towards automated process control in relation to natural organic matter

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Abstract

Access to safe and clean drinking water is a basic human right (A/RES/64/292). In Sweden, large drinking water treatment plants use mainly surface water as water source. The long-term trend of increasing natural organic matter (NOM) in boreal and north European surface waters negatively affects the overall performance of the treatment processes. To address this issue, sensors are increasingly used as a tool for real-time analysis of water quality providing early warning of potential contamination and decision support for process control.

In this thesis, absorbance- and fluorescence-based sensors were used to estimate dissolved organic matter (DOM) concentrations in two Swedish rivers prior to managed aquifer recharge (MAR) and their accuracy was compared (Paper I and IV). The possibility of coupling a coagulation treatment with MAR was explored at laboratory-scale. Two pilot-scale experiments using granular activated carbon filtration were carried out to optimise DOM removal (Paper II). A recent method for molecular DOM analysis was tested to investigate the effect of ozone on low molecular weight compounds. An open-source Python toolbox called "AbspectroscoPY" was developed to pre-process the large amount of absorbance-based sensor data and compute a range of spectral metrics from the time-series data. This allowed a preliminary identification of variability in the spectrophotometric profiles of treated water as a step forward toward automated early warning systems (Paper III). An algorithm for turbidity compensation of the raw absorbance spectra was added (Paper IV). This thesis contributes to an increased knowledge on NOM removal in water treatment using high frequency sensor data from optical sensors.

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Optiska sensorer i dricksvattenproduktion – vägen till automatiserad processtyrning av halten naturligt organiskt material.

Sammanfattning

Tillgång till säkert och rent dricksvatten är en grundläggande mänsklig rättighet (A/RES/64/292). I Sverige använder stora dricksvattenreningsverk huvudsakligen ytvatten som vattenkälla. Den långvariga trenden av ökande naturligt organiskt material (NOM) i borealt och nordeuropeiskt ytvatten påverkar den totala prestandan hos reningsprocesserna negativt. För att ta itu med detta problem används sensorer i allt större utsträckning som ett verktyg för realtidsanalys av vattenkvaliteten, vilket i sin tur ger kan ge tidig varning om potentiell kontaminering och agera som beslutsstöd för processtyrningen.

I denna avhandling användes absorbans- och fluorescensbaserade sensorer för att uppskatta koncentrationer av löst organiskt material (DOM, engelska: *dissolved organic matter*) i två svenska älvar före konstgjord grundvattenbildning (MAR, engelska: *managed aquifer recharge*), och deras noggrannhet jämfördes (artikel I och IV). Möjligheten att kombinera flockulering med MAR undersöktes i laboratorieskala. Två experiment i pilotskala med filtering genom granulerat aktivt kol utfördes för att optimera DOM-borttagningen (artikel II). En ny metod för molekylär DOM-analys testades för att undersöka effekten av ozon på föreningar med låg molekylvikt. En Python-verktygslåda med öppen källkod, "AbspectroscoPY", utvecklades för att förbehandla den stora mängden absorbansbaserad sensordata och för att beräkna ett antal spektrala parametrar från tidsseriedata. Detta möjliggjorde en preliminär identifiering av variationer i de spektrofotometriska profilerna för behandlat vatten, vilket utgör ett steg framåt mot automatiserade tidiga varningssystem (artikel III). En algoritm för turbiditetskompensation för obearbetade absorbansspektra adderades (artikel IV). Denna avhandling bidrar till ökad kunskap om NOM-borttagning vid dricksvattenvattenproduktion med användandet av högfrekvent sensordata från optiska sensorer.

Nyckelord: automatiserad rening, digitalisering av vattenreningsverk, python, löst organiskt material, löst organiskt kol, UV-Vis-spektroskopi, absorbans, fluorescens, proton-överföringsreaktion masspektrometri, lutningskvot.

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Dedication

Ai miei genitori, per fare sempre il tifo per me.

To my parents, for always cheering for me.

Contents

List of publications

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

I.   Hoffmeister, S., Murphy, K.R., **Cascone, C.**, Ledesma, J.L.J. & Köhler, S.J. (2020). Evaluating the accuracy of two in situ optical sensors to estimate DOC concentrations for drinking water production. *Environmental Science: Water Research & Technology,* 6(10), 2891-2901.

II.   Golovko, O., de Brito Anton, L., **Cascone, C.**, Ahrens, L., Lavonen, E. & Köhler, S.J. (2020). Sorption Characteristics and Removal Efficiency of Organic Micropollutants in Drinking Water Using Granular Activated Carbon (GAC) in Pilot-Scale and Full-Scale Tests. *Water,* 12(7), 2053.

III. **Cascone, C.**, Murphy, K.R., Markensten, H., Kern, J.S., Schleich, C., Keucken, A. & Köhler, S.J. . AbspectroscoPY, a Python toolbox for absorbance-based sensor data in water quality monitoring (manuscript).

IV.   **Cascone, C.**, Murphy, K.R., Markensten, H., Stenroth, K. & Köhler, S.J. . Optical sensors in turbid waters: exploring opportunities and limitations (manuscript).

Abbreviations

β:α	freshness index
BBs	building blocks
BPs	biopolymers
BVs	bed volumes
c.u.	colour units
CDOC	chromophoric DOC
CDOM	coloured or chromophoric dissolved organic matter
DEC	sedimentation
DOC	dissolved organic carbon
DOM	dissolved organic matter
DWTP	drinking water treatment plant
EBCT	empty bed contact time
EEM	excitation – emission matrix
EM	emission
EX	excitation
fDOM	fluorescent dissolved organic matter
FA	fulvic acids
FI	fluorescence index
FNU	formazin nephelometric unit
GAC	granular activated carbon
GW	groundwater
HA	humic acids
HIX	humification index

HMW	high molecular weight
HOC	hydrophobic organic carbon
HSs	humic substances
IFE	inner filter effect
IQR	interquartile range
LC-OCD	liquid chromatography – organic carbon detection
LMW	low molecular weight
LMW-A	low molecular weight acids
LMW-N	low molecular weight neutrals
MAR	managed aquifer recharge
MW	molecular weight
nC	number of carbon atoms per molecule
NOM	natural organic matter
NTU	nephelometric turbidity units
OMPs	organic micropollutants
OSc	mean oxidative state of carbon
PLS	partial least squares regression
ppbv	parts per billion by volume
pptv	parts per trillion by volume
PTR-MS	proton transfer reaction – mass spectrometry
PTR-TOF-MS	proton-transfer-reaction time-of-flight mass
RMSE	root-mean-square error
RSF	rapid sand filtration
S_R	slope ratio
SUVA	specific ultraviolet absorbance
SW	surface water
TD	thermal desorption
TOC	total organic carbon
TOF	time-of-flight
UF	ultrafiltration
UV-Vis	UV and visible light

1 Introduction

"The extraordinary greatness of the Roman Empire manifests itself above all in three things: the aqueducts, the paved roads, and the construction of the drains." (Dionysius of Halicarnassus). Ancient Rome's aqueducts are one of the first examples of the use of groundwater to support a population of over a million by the early Imperial era, although some of the aqueducts were fed by surface water (Deming 2020).

Access to safe and clean drinking-water is a basic human right and a component of effective policy for health protection, as the United Nations (UN) General Assembly declared in 2010 (A/RES/64/292).

The World Health Organization (WHO) published the Guidelines for drinking-water quality with the primary goal to protect public health associated with drinking-water quality. Key topics of the fourth edition (2011) included microbial hazards, climate change and its implications for water quality and scarcity, chemical contaminants not considered previously or responsible for large-scale health effects and the important roles of many different stakeholders in ensuring drinking-water safety. More recently, to improve the quality of drinking water and provide greater access and information to citizens, the European Commission has adopted in February 2018 a proposal to revise the Drinking Water Directive (Council Directive 98/83/EC).

On 16 December 2020, the European Parliament formally adopted it (DIRECTIVE (EU) 2020/2184). As stated in Article 7, one of the key features of the Directive is to intervene at the source to reduce pollution, as introduced by the "risk based approach" based on an in-depth analysis of the whole water cycle, from source to distribution. In response to growing public concern about the effect of emerging compounds, including endocrine-disrupting compounds, pharmaceuticals and microplastics, the Directive

points out the need for introducing a watch list mechanism. This would allow to follow up on new knowledge about the most appropriate monitoring approaches and methodologies. As stated in Annex II, "monitoring programmes shall also include an operational monitoring programme that provides rapid insight into operational performance and water quality problems and that allows rapid pre-planned remedial action". Among the parameters to include in the monitoring programme at the water supply plant, turbidity is mentioned in order to "regularly control the efficacy of physical removal by filtration processes". Concerning the frequency of sampling and analysis, if volumes of water distributed or produced each day within a supply zone above 10 000 m^3, the frequency of sampling and analysis needs to be continuous. For these supplies, also the total organic carbon (TOC), a measurement for natural organic matter (NOM) concentration, needs to be measured. The measurement uncertainty should be estimated at the level of 1.0 nephelometric turbidity units (NTU) and 3 mg·L^{-1} of the total organic carbon.

To comply with these regulations and provide continuous measurements, automation plays an essential role in drinking water treatment plants (DWTPs). Many process operation decisions, both in manual and automated systems, are based on data acquired from online sensors. Sensors are used in drinking water production as a tool for real-time analysis of water quality for early warning of presence of contaminants or water quality anomalies in surface water and to provide decision support for process control (Bartrand 2017). Artificial intelligence (AI) or "machine learning" plays a crucial role in the analysis of big data for pattern identification. Or as the American computer scientist Andrew Ng put it: "AI is the New Electricity. Just as electricity transformed industry after industry 100 years ago, I think AI will now do the same".

Section 1 is a discussion on the importance of monitoring natural organic matter in drinking water production, as well as an in depth review of its composition. Section 2 and 3 give background information on the DWTPs involved in the PhD project and an overview of the aims defined by the DWTPs. Section 4 is a discussion to address these aims.

1.1 Drinking water treatment in relation to NOM removal

In the Nordic countries, drinking water is mostly provided by waterworks. The water source differs from country to country: Denmark and Norway mainly use groundwater and surface water, respectively, while Sweden and Finland mainly use surface water for large DWTPs and groundwater for medium- and small-sized DWTPs (Guzman-Herrador *et al.* 2015). When using surface water as water source, different treatment trains can be used in order to supply the consumers with delivered water that respects the targets defined by law. Examples include conventional water treatment, direct- and in-line filtration and membrane filtration treatment.

In case of high turbidity (larger than 20 NTU), high colour (larger than 20 c.u.) or high TOC (larger than 4 mg·L^{-1}), a conventional water treatment can be used, including different chemical, mechanical and biological steps. Briefly, the treatment starts with a coagulation-flocculation process, during which coagulant is added to the surface water to form flocs with small particles and dissolved compounds which mostly settle in the sedimentation basins, producing sludge. The residual flocs undergo granular media filtration (rapid sand filtration, followed by slow sand filtration or active carbon filtration) with the aim of removing organic compounds causing undesired odour and taste as well as micropollutants (e.g. algal toxins and contaminants of emerging concern). Before the water enters the distribution system, it is subjected to a primary disinfection with chlorine-based chemicals, ozone or UV radiation and additionally to a secondary disinfectant, such as monochloramine, to get a longer-lasting protection. Ozone can also be used to increase the biodegradability of the residual organic carbon prior to biofilter medium (Owen *et al.* 1995; Crittenden 2005).

In case of low turbidity (lower than 10 NTU), moderate to low color (lower than 10 c.u.) and TOC (lower than 4 mg·L^{-1}), a membrane filtration process train is often selected. It includes a screening system (cartridge filters or microscreens, together with coarse screens at the raw water if needed), low-pressure membranes configured in modules and disinfection. The membrane filtration process train can also be used for surface waters with lower water quality if it is combined with the processes that precede the granular filters in the conventional water treatment (Crittenden 2005).

Over the past decades, boreal and northern European surface waters have experienced significantly increased concentrations and fluctuations of

natural organic matter (NOM), most likely as an effect of climate variation, reduced acid rain and increased primary production/standing biomass (Forsberg & Petersen 1990; Lepistö *et al.* 2008).

High concentrations of NOM can affect the taste and odour of the produced water, promote regrowth of bacteria, viruses and parasites, promote the formation of carcinogenic disinfection by-products, increase the solubility of metals and affect the treatment processes. Therefore, the NOM increase potentially represents a severe economic and environmental challenge for the DWTPs, in terms of process control systems and operation performance of water treatment and distribution systems.

Among the available treatments for NOM removal, the following paragraphs summarise the main treatments investigated in this thesis, with a short definition of aim of the process and of the main concepts used in the thesis.

1.1.1 Managed aquifer recharge (MAR)

Managed aquifer recharge (MAR) technology is a combination of natural and engineered treatment solutions, whose primary ecosystem service consists in water quality enhancement and is a common technique to recharge the groundwater. MAR is conducted via "planned use of injection wells, and infiltration basins and galleries for rainwater, storm water, reclaimed water, mains water and water from other aquifers that is subsequently recovered for all types of uses" (Zawadzka *et al.* 2019). Different processes contribute to the dissolved organic carbon (DOC) removal, including the DOC decomposition, adsorption on mineral matter and dilution due to mixing with groundwater (Kortelainen & Karhu 2006).

Despite the good results achieved using MAR, the introduction of a high DOC load and turbidity for an extended period of time might compromise its functionality. Exceeding the esker's natural removal capacity might lead to clogging-induced permeability reductions and ultimately a deterioration of water quality (Baveye *et al.* 1998; Martin 2013; Bekele *et al.* 2018; Page *et al.* 2018). Therefore, in most of the cases, the water is pre-treated before infiltration and a post treatment is performed (Heviánková *et al.* 2016).

1.1.2 Coagulation-flocculation

Coagulation-flocculation treatment is a technology used to decrease turbidity, reduce the amount of dissolved organic matter (DOM) and pathogens in the water. The process is based on reducing the repulsive potential of electrical double layers of colloids to produce micro-particles, which collide with each other and produce larger structures (flocs), enhancing their sedimentation. Chemical coagulation is commonly performed using inorganic coagulants, including aluminium and iron salts, but other options such as polymers are available (Matilainen *et al.* 2010).

Higher concentrations in NOM require an increase in the coagulant dose that leads to more sludge that needs to be disposed. In order to optimise coagulation in relation to NOM removal, different coagulant doses and pH conditions can be tested, starting from performing jar-tester experiments (Jarvis *et al.* 2005).

1.1.3 Granular activated carbon (GAC) filtration

GAC filtration is commonly used to control taste and odour of drinking water, as well as to remove specific organics including DOM and organic micropollutants (OMPs). GAC can be manufactured from different carbon based materials that give it specific properties. Typically, GAC materials are identified by the manufacturer's code (e.g. Norit® 830W). The common feature of all varieties is that, once activated, the material has a large surface area with a porous structure consisting of interconnected micropores, mesopores and macropores with a large number of adsorptive sites.

NOM present in the water competes with OMPs for adsorption and therefore diminishes the GAC performance. In the thesis, repeated reference is made to the terms empty bed contact time (EBCT) and GAC breakthrough. The EBCT is the water residence time in the GAC given by the ratio of the bed volume (BV) to the flow rate. The breakthrough percentage is an indicator of the GAC saturation and is computed as the ratio of target compound concentration after filtration to the incoming concentration. High values indicate that the GAC needs to be reactivated or replaced.

1.1.4 Membrane filtration

Membrane filtration is a separation mechanism based on differences in permeability of the water components. Permeable components (permeate) pass through the membrane while impermeable components (retentate) are

retained. The membranes are classified according to their retention rating which is a measure of the size of particles that are retained by a given membrane. In the case of ultrafiltration (UF) membranes, the retention rating is called the molecular weight cutoff (unit: dalton) where lower cutoff values imply increased retention and better water quality at the cost of higher energy consumption in the filtration process.

NOM has a negative effect on the efficiency of membrane filtration since it contributes to its fouling, i.e. the accumulation of dissolved or suspended substances on the surface and/or pores of the membrane, that requires backwashing or even chemical cleaning.

To conclude Table 1 includes a summary of the negative impacts of NOM on the treatment processes.

Table 1. Effects of natural organic matter (NOM) on drinking water treatment processes (adapted from (Crittenden 2012).

Treatment process	NOM effect
Coagulation	NOM reacts with coagulants, decreasing the amount of coagulants available for turbidity removal → increased coagulant dose → increased sludge production
Adsorption	NOM adsorbs to activated carbon, decreasing its adsorption capacity → decreased removal of micropollutants and reduced protection to pollution events (e.g. oil spills) → more frequent replacement or regeneration of the carbon
Membranes	NOM adsorbs to membranes, increasing their clogging and fouling and therefore causing a decrease in flux through the membrane → more frequent physical and chemical cleaning cycles
Disinfection	NOM reacts with disinfectants → increased disinfectant dose
Distribution	NOM can be biodegradable, leading to corrosion and slime growth in the distribution system

1.2 NOM sources, composition and analysis

Besides the NOM concentration, it is relevant to investigate its composition when selecting a suitable treatment technology and optimizing the operational performance of treatment plants.

1.2.1 Sources and composition

NOM is considered a complex matrix of heterogeneous mixture of organic compounds such as humic substances, polysaccharides, amino sugars, proteins, peptides, lipids, small hydrophilic acids. Its composition can be extremely variable depending on its source and level of degradation (Bhatnagar & Sillanpää 2017).

NOM is ubiquitous in soils, waters and sediments. In natural waters it exists in dissolved, colloidal and particulate states: DOM is the most studied fraction. It is the result of hydrological, biological and geological interactions. We distinguish an "autochthonous NOM", generated through biological activity, mainly algal and microbial, and an "allochthonous NOM", if the substances derived from the breakdown of terrestrial organisms are transported to the water body via drainage within watersheds (Sillanpää *et al.* 2018). The percentage of autochthonous and allochthonous NOM depends on the location and environmental conditions of the water body. Human activities alter DOM composition by increasing production of autochthonous DOM and the processing of allochthonous DOM inputs according to the levels of nutrients introduced, human land use, and human population density in a watershed (Williams *et al.* 2016).

NOM present in waters consists of both hydrophobic and hydrophilic components. The hydrophobic part is rich in aromatic carbon, characterized by phenolic structures and conjugated double bonds, while the hydrophilic part contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates and proteins, sugars and amino acids (Thurman 1985). The allochthonous NOM, which shows a highly variable composition, mainly contains humic substances, while the autochthonous NOM includes soluble extracellular and intracellular macromolecules such as carbohydrates, amino acids, peptides, enzymes and toxins (Sillanpää *et al.* 2018). Hydrophobic acids represent more than half of the DOC in water (Swietlik et al. 2004). Figure 1 displays the molecular structure of theoretical humic (HA) and fulvic (FA) acids (Aiken 1985).
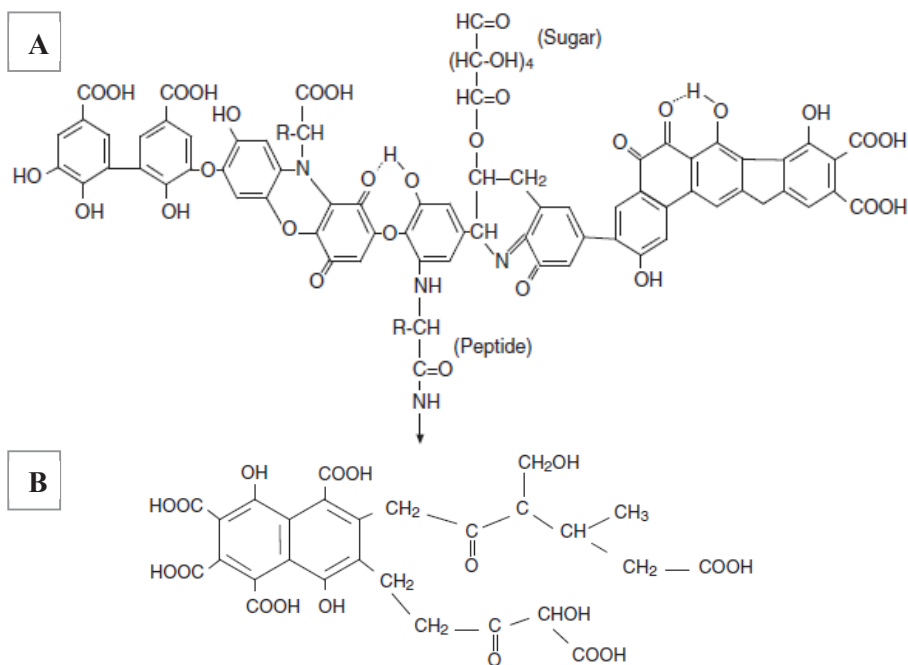
Figure 1. Molecular structure of theoretical humic and fulvic acids (Stevenson, 1982 and Buffle, 1977, cited in Aiken 1985).

The factors that influence the fate of NOM in aquatic environments include its biochemical composition, pH, temperature and the biological processes occurring in the water body. Therefore, the amount and composition of NOM is site-specific and can substantially vary seasonally in response to floods, droughts, and rainfalls (Sillanpää *et al.* 2018).

1.2.2 NOM analysis

Among the available methods used to characterize NOM, this thesis focuses on the following:

- Bulk parameters: total organic carbon, dissolved organic carbon
- Spectroscopy: UV and visible (UV-vis) absorbance, fluorescence
- Chromatography: liquid chromatography – organic carbon detection (LC-OCD)
- Mass spectrometry: proton transfer reaction – mass spectrometry (PTR-MS)

For a detailed survey of other common methods for NOM analysis in drinking water treatment see Matilainen *et al.* (2011).

TOC and DOC

TOC is the sum of particulate organic carbon (POC) and DOC in a water sample. To quantify the organic carbon, the sample is acidified and purged with carbon-free air or nitrogen prior to the measurement to remove the inorganic fraction and then oxidized to CO_2, which is measured by non-dispersive infrared spectroscopy. To measure DOC, the sample is initially filtrated through a 0.45 µm filter. Pre-combusted glass-fiber filters (0.7 µm GF/F, Whatman, UK), coupled with a glass filtration set, are often preferred, since they are binder-free and do not contaminate the sample (Avagyan *et al.* 2014).

Popular tools to characterize DOM are UV-Vis and/or fluorescence spectroscopy since they are easy to use and relatively cheap, they give fast results and have high sensitivity. They are mainly used to investigate DOM aromaticity, sources and reactivity. Conjugated double bonds (polyenes) in the coloured or chromophoric DOM (CDOM) allow for the absorption of UV-Vis light while aromatic rings in the fluorescent DOM (fDOM) emit light when excited by photons with specific energy. However, inside the total DOM pool, the fraction characterized by monomeric and polymeric aliphatic compounds, such as carbohydrates, lipids, and aliphatic amino acids, does not absorb UV-Vis light (Stedmon & Alvarez-Salgado 2011).

UV-Vis absorbance

Light absorbance in water samples is due to CDOM, as well as pure water, inorganic salts, phytoplankton pigments, non-algal particulate matter and Fe colloids. These interferences, except for Fe colloids, can be removed by using blank water as reference or filtration (Köhler *et al.* 2013).

Table 2 indicates how absorbance, using one or more wavelengths, can be used to predict DOC concentrations, as well as specific fraction of DOM. However, up to four-fold spatial and seasonal variations need to be taken into account (Li & Hur 2017).

Absorbance at a specific wavelength or a combination of them is also used to investigate DOM character. Among the available methods used to characterize NOM, this thesis focuses on the following:

- Specific ultraviolet absorbance, SUVA

The absorbance at 254 nm is often normalized for DOC concentration ($mg \cdot C \cdot L^{-1}$) to obtain the specific ultraviolet absorbance, $SUVA_{254}$. $SUVA_{254}$

Table 2. Models to predict total and dissolved organic carbon (TOC, DOC) concentrations based on absorbance spectra for different water samples, using one or more wavelengths (adapted from Li and Hur, 2017).

Wavelengths (nm)	Algorithms	Sources
Single: **254 – 440**	DOC = α a(λ) + β	Lake, river (Giancoli Barreto *et al.* 2003)
Double: **250, 364**	TOC = 0.492 a (250) – 1.23 a (364) + 1.83	Lake (Erlandsson *et al.* 2012)
Three: **275, 295, 365**	DOC = α + β a (275) + γ a (295) + δ a (365)	Lake (Jiang *et al.* 2012)
Four: **260, 265, 280, 285**	TOC = 1.476 + 207.534(a 260) – 236.472(a 265) - 199.004(a 280) + 112.074(a 285)	River with high DOC and low suspended solids (Kim *et al.* 2016)

is a good indicator of the humic fraction of DOC and therefore is used as surrogate measurement for aromaticity and hydrophobicity of organic carbon (McKnight *et al.* 2001; Weishaar *et al.* 2003).

Since the coagulation process is efficient in removing the humic fraction, this parameter also indicates raw water treatability by coagulation. Table 3 reports the NOM removal expected for different SUVA ranges showing that the different NOM fractions exhibit a different treatability potential by coagulation. High molecular weight (HMW) and hydrophobic NOM fractions show high removal efficiencies by coagulation, while low molecular weight (LMW) hydrophilic fractions are not removed.

- Absorbance ratios and slope ratio

In order to investigate the sources and molecular properties of CDOM, a well-known metric is the ratio of absorbance at two specific wavelengths ($A_{λ1}/A_{λ2}$). They can be used to investigate the CDOM quality, such as the humification degree, aromaticity, hydrophobicity and the molecular weight (MW), since organic molecules with different MW absorb light at different wavelengths.

Table 3. NOM removal efficiency by coagulation according to specific ultraviolet absorbance at 254 nm (SUVA$_{254}$) values, related to its chemical characteristics (Ghernaout *et al.* 2009).

SUVA$_{254}$	NOM removal (%)	NOM characteristics
> 4	> 50	High molecular weight (HMW), hydrophobic HA fractions
2-4	25 - 50	a mixture of hydrophobic and hydrophilic fractions of different MW, HA and FA, as well as other NOM (e.g. algae and algae residues)
< 2	< 25	mostly non-humic, LMW and low hydrophobicity compounds

- Slope ratio and spectral curve

The slope ratio (S$_R$) is the ratio of the slope at shorter wavelengths (S$_{275-295}$) to the slope at longer wavelengths (S$_{350-400}$). It is not a simple ratio between absorbance at two wavelengths, but between slope values computed using linear regression of the natural log transformed absorbance spectra. S$_R$ was shown to negatively correlate with CDOM MW and S$_{275-295}$ is sometimes used to estimate the effect of photodegradation (Helms *et al.* 2008).

The spectral curve (S$_\lambda$) is the distribution of the spectral slope across the wavelengths. Similarly to S$_R$, the algorithm computes the slopes from the linear regression of the logarithm of the absorbance spectra over a sliding window (width 21 nm) applied to the wavelengths 220-697.5 nm at 1 nm resolution (Loiselle *et al.* 2009). The advantage of using the spectral curve analysis to compare different dates in comparison to the analysis of absolute changes of absorbance is that the wavelength regions with the greatest variability are more easily identified.

This information can be used to investigate the biogeochemical process on CDOM and its sources. For example, Müller explained that in Lake Tämnaren, a shallow humic lake in Sweden, the largest increase in absorption spectral slopes (15 to 20 %) and CDOM loss occurs during summer at a wavelength of 295 nm, most probably due to radiation-induced decomposition (Müller *et al.* 2014).

For a more detailed survey of common methods for absorbance analysis of NOM see Li and Hur (2017).

Fluorescence

Fluorescence spectroscopy provides information about molecular size, aromaticity or aliphatic properties. It is based on the systematic evaluation of intensity of emitted light quality (Em) as a function of the excitation light at a specific wavelength (Ex). Compounds that, in addition to absorbing light ("chromophores"), also re-emit it, are named "fluorophores". In natural waters, humic substances and amino acids in proteins and peptides provide particularly well suited for fluorescence measurements. Table 4 summarises the nomenclature coined by Coble (1996) and the nomenclature based on fluorophore type, where the suffix "-like" indicates that the fluorescence is measured in the same optical area where their standards are measured (Coble 1996; Hudson *et al.* 2007). The protein-like components are used as indicators of biologic activity and DOM bioavailability.

Table 4. Common aquatic fluorophores nomenclatures coined by Coble (1996) and based on the fluorophore type (adapted from Hudson et al., 2007).

Coble	Type	Ex wl (nm)	Em wl (nm)
A	Humic-like	237-260	400-500
C	Humic-like	300-370	400-500
M	Marine Humic-like	312	380-420
B	Protein-like (Tyrosine-like)	225-237 275	309-321 310
T	Protein-like (Tryptophan-like)	225-237 275	340-381 340

Since the mid-1990s, the state-of-the-art technique for fluorescence measurements is the excitation emission matrix fluorescence spectroscopy (EEMs). Raw EEMs data needs to be pre-processed before interpretation (Lavonen 2015). Among the methods used for their interpretation, peak picking, differential EEMs and fluorescence indices were used in the thesis and are described in the following:

- Peak picking

Peak picking extracts the maximum intensity (z) in a region (x, y) and classifies the fluorescence peaks into A, C, M, B and T. It allows to calculate the relative concentrations after calibrating the fluorescence intensity (I) against TOC, as well to get an indication of the protein/humic-like or hydrophobic/hydrophilic features by comparing the peak intensities (Coble 1996).

- Differential fluorescence

Differential fluorescence is useful to detect small changes which occur during the treatment processes in drinking water production. Differential EEMs (ΔEEMs) can be calculated using the relation:

$$\Delta EEM = EEM_{before} - EEM_{after}$$

- Fluorescence indices

Fluorescence indices are calculated by using the intensities of the EEM spectra in certain excitation and emission wavelength ranges. Table 5 reports these ranges for commonly used fluorescence indices. Humification index (HIX) refers to the degree of humification, i.e. the humic substance content, and a higher value stands for a lower H/C ratio (Ohno 2002). The freshness index (β: α) indicates the DOM age, with β for more recently derived DOM and α for more decomposed DOM (Parlanti *et al.* 2000). The fluorescence index (FI) refers to the DOM source, which is microbial for FI≈1.8 (extracellular release and leachate from bacteria and algae) or terrestrial derived for FI≈1.2 (terrestrial plant and soil organic matter) (Cory & McKnight 2005).

The fluorescence technique can be used to investigate the efficiency of the drinking water treatment processes. For example, differential fluorescence was used to detect changes between coagulation and slow sand filtration (Lavonen 2015). Another application of fluorescence is the investigation of membrane fouling. As a result, fractions of organic matter attributed to humic substances and biopolymers were identified as contributors to irreversible fouling of ultrafilter UF membranes, i.e. foulants that can't be removed by physical cleaning and backwashing but only by expensive chemical cleaning including clean-in-place (Peiris *et al.* 2012).

Table 5. Description and calculation of different fluorescence indices. The indices are obtained by computing the ratio of emission (Em) intensities at certain range of wavelengths of the excitation emission matrix fluorescence spectroscopy spectra obtained at a certain excitation (Ex) wavelength (adapted from Fellman *et al.* (2010)). HIX, β:α and FI are the abbreviations for humification, freshness and fluorescence indices, respectively.

Fluorescence index	Ex (nm)	Em (nm)	Description
HIX	254	$\dfrac{435-480}{(300-345)+(435-480)}$	degree of humification
β:α	310	$\dfrac{380}{\max I\,(420-435)}$	DOM age
FI	370	$\dfrac{470}{520}$	DOM source

LC-OCD

Liquid chromatography coupled with organic carbon detection (LC-OCD) is a highly sensitive and reproducible method which gives quantitative or close to quantitative results for all dissolved organic compounds, except triazines and some N-heterocyclic compounds (Huber *et al.* 2011). It is a chromatographic technique that separates NOM into six fractions on the basis of size exclusion, ion interaction, and hydrophobic interaction.

The chromatographic DOC (CDOC) consists, in order of elution, of biopolymers (BPs), humic substances (HSs), building blocks (BBs), low molecular-weight acids (LMW-A) and low molecular-weight neutrals (LMW-N). The first two peaks represent the refractory organic matter, while the others correspond to the biogenic organic matter. Table 6 reports the typical size and composition for each fraction. In addition to the CDOC, whose compounds are quantified down to the low ppb-range, also the hydrophobic organic carbon (HOC) and the inorganic colloids can be detected. This fraction might include natural hydrocarbons or soluble humins and typical values for surface waters range between 1-5 %. The inorganic colloids are negatively charged inorganic polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si (polyhydroxide and clay particles). They elute slightly before the biopolymers.

Table 6. Typical size and composition of chromophoric dissolved organic matter (CDOM) fractions separated by LC-OCD (adapted from (Villacorte 2016).

CDOM fraction	Typical size ($g \cdot mol^{-1}$)	Typical composition
Biopolymers	>20000	Polysaccharides, proteins, amino sugars, polypeptides, transparent exopolymer particles (TEPs), extracellular polymeric substances (EPS)
Humic substances	≈1000	Humic and fulvic acids
Building blocks	300-500	Weathering and oxidation products of humics
LMW neutrals	<350	Mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids
LMW acids	<350	All monoprotic organic acids

Based on the information obtained from the LC-OCD analysis, some conclusions concerning the water treatment can be drawn. In particular, the flocculation efficiency in DOC reduction decreases when the HS average molecular weight is too low; the fouling potential of UF membranes increases with the amount of biopolymers present, including proteins; the biodegradability of NOM increases with the amount in LMW acids and LMW-neutrals.

PTR-MS

Proton-transfer-reaction mass spectrometry (PTR-MS) is a recent method for molecular analysis of aquatic DOM (Peacock *et al.* 2018), although it was originally designed for quantitative trace gas analysis of volatile organic compounds in the atmosphere. PTR-MS including the time-of-flight (TOF) mass spectrometer (PTR-TOF-MS) generates high mass resolution spectra on short response times (< 100 ms), with upper mass limit over 100 000 atomic mass unit (amu), high sensitivity (even for large masses yielding several tens of $cps \cdot ppbv^{-1}$) and an extremely low detection limit (a few pptv) (Jordan *et al.* 2009). Materić *et al.* (2017) used a Thermal Desorption (TD)– PTR-MS to detect LMW OM ranging from 28 to 500 amu, while HMW DOM is more difficult to detect. Mean ion concentrations range over

multiple orders of magnitude and decline when m/z values increase. The method is fast and requires only evaporation/sublimation as pre-treatment prior to analysis to remove water and retain residues of semivolatile and nonvolatile organic matter.

Since this method is quantitative, it can be used to compute the total number of the C, H, O, N atoms in each sample and therefore the mean oxidative state of carbon (OSc), the average number of carbon atoms per molecule (nC), as well as the mean total concentration of organics (Holzinger *et al.* 2013). Peacock *et al.* (2018) showed how to relate LMW DOM of 11 streams and lakes in the Gårdsjön forest catchment in southwest Sweden to DOM optical properties and reactivity. The use of this advanced technique can help increase the current knowledge on labile LMW DOM.

1.3   Sensors for NOM quantification and characterisation

Automation plays an essential role in DWTPs and sensors are becoming ubiquitous in modern DWTPs. In-situ ("Off-the-shelf") online spectrometers and spectrofluorometers monitor water quality in real-time, using the principle of absorbance and fluorescence of dissolved constituents in water, respectively. They give information on type and concentration of constituents in water, based on the wavelength and the amount of light absorbed or emitted.

Sensors are used for optimized dosing (Xia *et al.* 2007; Köhler *et al.* 2016; Keucken *et al.* 2017), water quality control (Kumar *et al.* 2019; Wu *et al.* 2019) and early-warning systems (Bartrand 2017). The advantages of using in-situ optical sensors coupled with grab sampling compared to grab sampling alone are many, including high frequency sampling rate, no chemical use, long-term deployment capability, as well as reduced measurement errors since sampling, transport, storage and dilution of the sample are not necessary.

However, they have a big initial investment cost (approximately $15000-25000 for online spectrometers and $2000-5000 for online spectrofluorometers), as well as for instrument service and maintenance (Pellerin & Bergamaschi 2014). It is also important to control for drift in the data and to consider that sensitivity and reliability are usually lower than many benchtop alternatives.

Some examples of available in-situ UV-Vis spectrometers for DOC quantification under field conditions are ProPS-UV (Trios GmbH, Germany), CarboVis (WTW GmbH, Germany), spectro::lyser, carbo::lyser and multi::lyser (Scan Messtechnik GmbH). Examples of fluorescence probes used for online monitoring in drinking water treatment were installed on two data loggers, EXO2 (YSI, USA) and Cyclops 7 (Turner Designs, USA) (Shutova *et al.* 2016).

Among the available sensors on the market, this thesis focuses on the use of two optical sensors, the spectro::lyser and EXO2.

Spectro::lyser

The Spectro::lyser is a portable and submersible UV (200-400 nm) or UV-Vis (200-735 nm) spectrophotometer (ca. 0.6 m long and with a 44 mm diameter) for high-resolution spectroscopic measurements. The sensor measures total light attenuation in water along a straight light path of defined length, due to it being absorbed by dissolved organic molecules or else scattered by particles. Figure 2 is a schematic representation of the sensor which consists of dual-beam from a Xenon lamp (one travelling through the sample and one used as reference), a 256-pixel detector, an internal data logger and a water level meter.
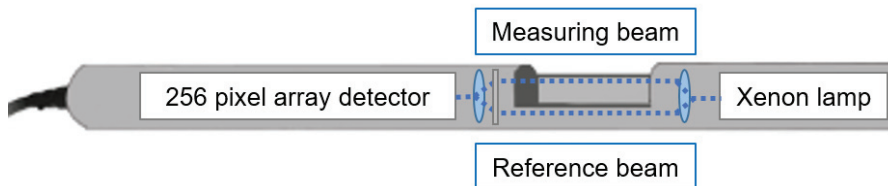

Figure 2. Schematic representation of the spectro::lyser (Scan Messtechnik GmbH). Adapted from https://www.s-can.at/products/spectrometer-probes.

UV-Vis probe is suitable for measuring changes in overall water quality. The choice of the path length is related to the matrix to analyse and to the SUVA of the DOC to study. The sensitivity increases with the path length. In particular, a path length of 100 mm is suitable for drinking water, 35 mm and 10 mm for surface water and 5 mm for wastewater applications. The results are indicated in [Abs·m^{-1}] to allow a direct comparison of the data obtained at different path lengths. The instrument allows the measurement of single compounds (e.g. nitrate, nitrite, benzene, toluene, xylene, ozone, phenol) once their fingerprint is known, as well as surrogate parameters (e.g.

UV$_{254}$, turbidity, TOC$_{equivalent}$ and DOC$_{equivalent}$). In order to measure these parameters, the internal algorithm of the sensor performs a multivariate calibration with partial-least square (PLS) regression to the pre-preprocessed attenuation data (Langergraber *et al.* 2003).

The pre-processing consists of a manual removal of wrong spectra, followed by a turbidity compensation of the raw spectra and a stepwise exclusion of outliers, based on F- and T-Tests and Cook's distance. Turbidity influences absorption over the whole spectrum and the intensity of the scattered light is a function of five variables: concentration, particle diameter, measuring angle, wavelength of the light and the refractive index of the particles relative to the surrounding medium (the shape has to be considered for non-spherical particles) (Huber & Frost 1998). The algorithm used for the turbidity compensation estimates two parameters: the spectral shape related to the suspended solids depends on the wavelength (λ) as a function of the particle diameter (x), with a factor λ^x. The aim is to measure the turbidity to achieve a baseline compensation of the measurement of dissolved substances (Langergraber *et al.* 2003).

As default configuration, the manufacturer provides a so-called global calibration based on the application of PLS to the raw data spanning a wide range of wavelengths to predict the concentration of the parameters of interest from the recorded spectra and no samples need to be analysed. However, the user can improve the accuracy and the precision of the measurements for the quantification of the parameters of concern by performing a so-called local calibration, preferentially prior to initiating the main sampling campaign. This procedure consists in modifying the slope-intercept of the regression function by using laboratory data from reference grab samples. To achieve good calibration results, it is crucial to get grab samples representative of what was measured by the spectro::lyser and cover the whole measurement range with equally distributed reference samples.

The maximum sensitivity achieved for drinking water contaminants is $\mu g \cdot L^{-1}$ (phenylurea herbicides) and $mg \cdot L^{-1}$ for compounds characterised by a lower extinction coefficient or in presence of high sediment load or high DOC concentration. Therefore, the spectro::lyser probe can be used to monitor natural fluctuations of surface and drinking water and sudden changes in the overall quality, but not to look at very low concentrations of pollutants. It can be suitable for monitoring filtration and coagulation steps coupled with conventional turbidity sensors, giving further insight in the

process. If the natural variation occurrence is known, which requires measurements of the fingerprint spectrum across several months, it is possible to train the alarm function to recognize anomalous changes in the water quality.

For a survey of applications of the sensor, as well as assessment of detection limit and reproducibility, see Van den Broeke (2005).

EXO2

The EXO2 probe is a battery-supplied multi-parameter 6-port device with an automated anti-fouling wiper in the middle. Different typologies of sensors can be plugged in to measure parameters including pH, conductivity/temperature, dissolved oxygen, turbidity, fDOM (λex/λem = 365 ± 5 nm/480 ± 40 nm) and total algae (chlorophyll and blue-green algae). EXO2 has been used for several field measurements to monitor water quality of marine water, freshwater and groundwater as well as to determine effectiveness of drinking water treatment processes for DOM removal (Shutova *et al.* 2016; Carstea *et al.* 2020).

Prior to the main sampling campaign, also the EXO2 needs to be calibrated and a measurement frequency decided on. Sensors can be calibrated according to manufacturer guidelines and the measurement frequency adjusted according to the application. It was shown that for drinking water treatment where DOM concentration and characteristics can quickly vary (within less than 2 hours), a measurement frequency below 5 minutes is advised (Carstea *et al.* 2020).

A pre-processing of the acquired fDOM data is necessary since measurements can be significantly affected by temperature and light attenuation in field. Therefore, corrections for temperature quenching, inner-filter effect (IFE) and turbidity need to be applied (Baker 2005; Downing *et al.* 2012; Kothawala *et al.* 2013). These corrections are site-specific due to variations of DOM characteristics and particle size distribution of suspended sediments in space and time (Saraceno *et al.* 2017; Franklin de Oliveira *et al.* 2018). Therefore, applying the same correction equation calculated for one study-site to a different one can lead to overcompensation of fDOM.

2. Background, materials and methods

2.1 The Genomljusning project

On the basis of previous knowledge from the FORMAS (a Swedish research council for sustainable development) funded project "Colour of Water" (CoW) and the SVU (Swedish Water and Wastewater Association) funded project "GenoMembran" ("through membranes"), the work presented in this thesis was conducted within the SVU (16-103) funded "Genomljusning" ("light screening") project. Genomljusning is a collaboration between researchers from the Swedish University of Agricultural Sciences (SLU, Uppsala, Sweden) and Chalmers University of Technology (Gothenburg, Sweden) and five drinking water producers in Sweden: Gästrike Vatten AB (Sätra WTP, Gävle), Göteborgs stad, Kretslopp och vatten (Lackarebäck WTP, Mölndal), Norrvatten (Görväln WTP, Stockholm), Uppsala Vatten och Avfall AB (Bäcklösa WTP, Uppsala) and VIVAB (Vatten & Miljö i Väst AB, Kvarnagården WTP, Varberg).

The project mainly aims at evaluating and implementing two different optical online sensors to improve the drinking water treatment processes in relation to NOM.

2.2 Study sites and sampling

2.2.1 Full-scale drinking water treatment plants

Uppsala Vatten och Avfall AB (Paper I and unpublished data)

The city of Uppsala is supplied with drinking water from two DWTPs, Gränby and Bäcklösa. The two DWTPs use groundwater withdrawn from

different wells along the Uppsala esker as water source. In order to compensate for the withdrawal, the water from River Fyrisån, after passing through a series of filters (e.g. the sand filter at the Storvad facility, ca. 12 km upstream of the city), is pumped to the infiltration basins at Stora Vallskog and Tunåsen. The water in the esker takes approximately six months to naturally flow from the River Fyrisån to the groundwater well of Galgbacken, at a distance of 2025 m from the MAR site. In the DWTPs, the withdrawn water goes through an aeration basin, softening, pH adjustment, sand filtration (at the Bäcklösa plant also through an activated carbon filter) and disinfection with chlorine.

Over the course of a year, the DOC content of the water to be infiltrated varies between 8 and 25 mg·L^{-1}. During its travel through the esker, the water is diluted due to natural mixing with groundwater (1-2 mg·L^{-1}). The dilution varies along the esker (see numbers in Section 4 and for details of the discussion, see Stenberg (2018)). All samples along the esker were taken within a few days during January 2018.

More than 8 million m^3 of water were infiltrated in 2017 and in the last 25 years, 3700 metric tons of DOC were introduced into the esker. The water volume to be infiltrated is expected to rise to 28 million m^3 per year by 2100 (GrundvattengruppenforUppsalaVatten 2017). The resulting increase in the organic carbon levels in the River Fyrisån, especially in periods with high particle content (> 20 FNU), might compromise the functionality of the Uppsala esker in the long term.

For monitoring DOC content and turbidity values, two optical sensors (spectro::lyser and EXO2) were deployed between March and November 2017 at Storvard and compared with regard to handling and accuracy in DOC estimation. The EXO2 recorded pH, conductivity/temperature, turbidity and fDOM data. Measurements with both optical sensors were taken every 15 minutes. Prior to the DOC estimation with the sensor data, the following sensor- and site-specific corrections were performed. The attenuation data were corrected to account for the baseline shift and the DOC concentration was estimated from the attenuation data at specific wavelengths using a PLS regression model (in Paper I, DOC$_{AbsMod}$). The fDOM signal was corrected for inner-filter effects (IFE), temperature quenching and turbidity, based on the equations provided by Downing *et al.* (2012) and Kothawala *et al.* (2013). The DOC concentration (in Paper I, DOC$_{fDOM}$) was subsequently estimated by linear regression between the corrected signal and the data from

the grab samples, which were collected during the whole period in which the sensors were measuring (in Paper I, $DOC_{Observed}$).

The implementation of a pre- or post-coagulation-flocculation treatment was also considered and both scenarios were tested at laboratory-scale (for details see paragraph 2.2.2).

Göteborgs stad, Kretslopp och vatten (unpublished data)
The city of Gothenburg is supplied with drinking water from two DWTPs, including Lackarebäck. This DWTP uses the water from Delsjö lakes as water source, used as a natural reservoirs of water coming from the River Göta Älv (1000 $L\cdot s^{-1}$). River flux into the lakes is closed for up to 100 days per year due to insufficient quality of the water from the river (Lavonen 2015). In the DWTP, the main treatment steps are coagulation-flocculation with aluminium sulphate at pH in the range 6.3-6.5, sedimentation (decanted water in the following), GAC filtration (TL 830), UF membranes and disinfection with chlorine dioxide and chlorine.

For two years, the River Göta Älv has been monitored with EXO2 sondes to quickly identify deviations in water quality, including one sonde at the intake of the DWTP. Currently, the coagulant dose is adjusted on the basis of laboratory data of colour. The DWTP aims to extend the life time of GAC filters and UF membranes. If measurements of colour, as well as TOC and DOC are low, they are not well suited to optimize the coagulation-flocculation treatment. With these measurements, fast changes in water quality cannot be directly counteracted.

Using the EXO2 sonde, the quantitative effects of adjusting certain process variables of coagulation (dose and pH) and introducing pre-chlorination on NOM removal were evaluated at full-scale. The effect of these changes on GAC filters at different saturation levels was tested. Measurements from three online EXO2 sondes were collected every 15 minutes. The measurements were taken in incoming water, decanted water (DEC, i.e. water taken after the coagulation treatment, alternatively DEC 1 and 7) and after GAC filters (alternatively GAC filters 1, 19). GAC filters 1 and 19, corresponding to DEC 1 and 7, respectively, were selected to have results for reactivated (GAC 1) and old GAC filters (GAC 19). Two out of the three sondes were moved between the two sets of DEC and GAC. All the EXO2 sondes measured fDOM, pH, conductivity/temperature, turbidity and were equipped with an automated central wiper. In addition, the sondes measuring in the incoming water and decanted water were equipped with

total algae (chlorophyll and blue-green algae (phycocyanin)) and dissolved oxygen sensors. In the period October 28th – November 6th 2019, the following full-scale experiments were performed:

a) increase of aluminium sulphate coagulant (ALG) dose from the operational $12+0.7 \cdot$ colour$_{laboratory}$ to $15+0.7*$ colour$_{laboratory}$ [mg·L^{-1}];
b) decrease of coagulation-pH from the operational pH 6.5 down to 6.2;
c) return to normal operational coagulant dose and pH to test pre-chlorination with sodium hypochlorite (chlorine 0.25 g·m^{-3}), not used in normal operation nowadays.

Grab samples were collected before the starting and after the ending of each experiment alternatively for the two different sets of DEC and GAC.

Norrvatten (Paper II and unpublished data)

The northern part of Stockholm is supplied with drinking water from Görväln DWTP. The water source is the eastern part of Lake Mälaren with a fluctuating water quality according to the contribution from different basins, which in certain years can change by a few mg·L^{-1} within days (Köhler *et al.* 2013). In the DWTP, the water, taken at a depth of 22 or 4 m according to seasonal water quality, is treated with the following main steps: a microsieve (200 μm nominal pore size), a coagulation-flocculation treatment with aluminium sulphate, sedimentation, rapid sand filtration, GAC filtration (Norit® 830W, currently working only as biological filters) and disinfection with UV-light and monochloramine.

Since 2016, the coagulation dosing is adjusted based on surrogate values for colour, TOC and UV using the data taken every 2 minutes from the two spectro::lyser units located at the surface water intake and after rapid sand filtration, respectively. In 2013 and 2018, the DWTP encountered problems with the sand filtration. A 8-year time series of spectro::lyser data starting from 2010 is available and can be used to analyse whether the spectral metrics can be related to the observed problem. However, the raw spectral data from the sensor is currently not used, which potentially leads to the loss of valuable information.

In order to be able to analyse and interpret the raw data, an efficient pre-processing method needs to be developed to deal with the large amount of data. The method developed for Paper III can be used for this purpose.

Additionally, the enhancement of NOM removal in GAC filters was tested in two pilot-scale experiments (see paragraph 2.2.3).

VIVAB (Paper III)

The town of Varberg on the west coast of Sweden is supplied with drinking water from Kvarnagården DWTP. The water source is a mixture of water from Lake Neden and groundwater (80 %/20 %). In the DWTP, the main treatment steps are rapid sand filtration, a two-stage UF membrane process with in-line coagulation using prepolymerized polyaluminium chloride and disinfection with UV irradiation and monochloramine. Although the DOC level in Lake Neden is low (data reported in Paper III), Kvarnagården WTP was upgraded to in-line coagulation over UF due to increasing levels of organic carbon registered in the nearby lakes. Today it is among the most advanced DWTPs in Sweden in terms of using sensors for water quality monitoring. The coagulant dosing is controlled online with the attenuation, colour and turbidity measurements from two spectro::lyser units in the sand filtrate and in the permeate in order to obtain permeate water of good and stable quality and decrease membrane fouling.

As for Norrvatten, the aim is to develop a method to extract valuable information from the large amount of available attenuation data. This method is explained in detail in Paper III. Measurements were taken every 2 minutes in the surface water and every 3 minutes after rapid sand filtration and in permeate water between September 2017 and December 2018. Grab samples were taken between March and December 2018.

Gästrike Vatten AB (Paper IV)

The town of Gävle, one-hour north of Uppsala, is supplied with drinking water from two DWTPs, including Sätra. The water source is the River Gavleån which is pumped up and infiltrated at Johanneslöt into the Gävle-Valbo esker ($100 \ \text{L} \cdot \text{s}^{-1}$). The water takes up to four months to reach the consumers, after being treated at Sätra DWTP for pH adjustment, UV treatment and chlorination. A pre-treatment step of microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) precedes the water infiltration. This combination of managed aquifer recharge (MAR) and membrane filtration is unique in Sweden and a response to the high organic carbon load and temporarily high content of particulate matter of the Gavleån water, which easily leads to membrane fouling (Hägg 2018). A significant contribution to these turbidity spikes (> 20 FNU) is related to the presence of dams for hydroelectric power (Gävle Energi AB) that lead to rapid

changes in flow rates as the dams are opened/closed. The closest dam is Prästforsen at a distance of 480 m upstream of the intake site.

The main goal of the project is to monitor the surface water quality in order to protect the membranes prior to the MAR. We deployed two optical sensors in a facility next to the water intake: a spectro:lyser and a EXO2 sonde measured the surface water every 2 and 15 minutes, respectively. The EXO2 was equipped with probes measuring fDOM, turbidity, temperature, pH and conductivity from February until October 2018 with four breaks due to technical problems. The attenuation data were recorded from December 2017 until February 2019 and the grab samples were collected between November 2017 and November 2018. The EXO2 data were corrected as explained in Paper I and a new algorithm to correct the attenuation data from the spectro::lyser for turbidity is introduced in Paper IV.

2.2.2 Laboratory-scale experiments for coagulation-flocculation (unpublished data)

In order to compare the NOM removal in the Uppsala esker (see paragraph 2.2.1) to a classical coagulation-flocculation method, coagulation experiments were performed on six 1 L cylindrical jar tester (Kemira Kemwater Flocculator) at room temperature. A ferric salt, ferric chloride ($FeCl_3$), was selected as coagulant due to its common use in coagulation processes and its advantages in comparison to aluminium-based coagulants (Matilainen et al. 2010). Two speeds were used with a 3-minute rapid mix at 200 revolutions per minute (rpm), followed by a 10-minute slow stir phase at 20 rpm and a 45-minute settling time. After sedimentation, the supernatant was transferred with a syringe to the sample bottles for organic matter analyses.

First, preliminary coagulation optimization tests (50-100 $mg \cdot L^{-1}$ $FeCl_3$) were carried out at natural pH (7.5-7.7) on samples taken in November 2017 to find the optimum coagulant dose for organic removal and turbidity residual. Then, using the same coagulant dose of 100 $mg \cdot L^{-1}$ $FeCl_3$, pH adjustments in the range 5.6-6.8 with 0.3 pH unit steps were tested and the optimum pH was found to be around 6. For the final experiment on samples taken in January 2018, a coagulant dose of 100 $mg \cdot L^{-1}$ $FeCl_3$ at natural pH, pH 5.9 and 6.3, and a coagulant dose of 133 $mg \cdot L^{-1}$ $FeCl_3$ were used to perform the coagulation experiments on the samples taken in January 2018.

2.2.3 Pilot-scale experiments for GAC filtration (Paper II and unpublished data)

Within the project for Norrvatten, two pilot-scale experiments were performed to enhance NOM removal in GAC filtration.

The first experiment was designed on the basis of results obtained within our research group from a laboratory-scale experiment performed with rapid small-scale column tests (RSSCTs) at the DWTP (for details see Morell Bonin (2017)). The effect of using two different types of GAC material (FiltraSorb® 400 and Norit® 830W, the latter currently used at full-scale) and residence times (EBCT, 6 and 18 minutes) on the removal of organic matter and organic micropollutants (OMPs) was investigated between April 2017 and March 2018. In order to evaluate these effects, a pilot-scale setup with four parallel GAC filters was used.

A second GAC pilot-scale experiment was performed in the same DWTP to investigate the effect of organic matter and the introduction of a combined ozonation/GAC treatment for OMP removal. In this project the focus was on the LMW compounds (for details of the discussion on OMPs, see Ullberg *et al.* (2021)) using an advanced organic matter characterization method (PTR-MS). One sampling was performed in July 2018. Figure 3 displays the pilot-scale setup with six parallel GAC filters (arbitrary numbering of the filters). The filters differ in terms of GAC material (new Norit® 1240W and/or full-scale saturated Norit® 830W in use for 14 years), EBCT (12 or 20 minutes) and incoming water. The feed water for the ozonation of the pilot-scale GAC filters is the full-scale water after sand filtration (O3in) and, except for GAC1 which is a control experiment with no ozone, first undergoes a pH adjustment to pH 6.5 and ozone treatment (pH 6.8). One filter (GAC6) is a control for effects caused by an aged filter. For this filter, used GAC from the full-scale was employed. In all cases, except for GAC1 and GAC2, pH in the water is subsequently adjusted to pH 7.8 (O3out). Higher pH is thought to reduce TOC binding as the negative charge of TOC rises with pH.

Samples were collected in 100 mL glass bottles at the location indicated in Figure 3 and 150 µL of thiosulphate was added to stop the ozone reaction. The same operation was performed for Milli-Q blanks from the DWTP.
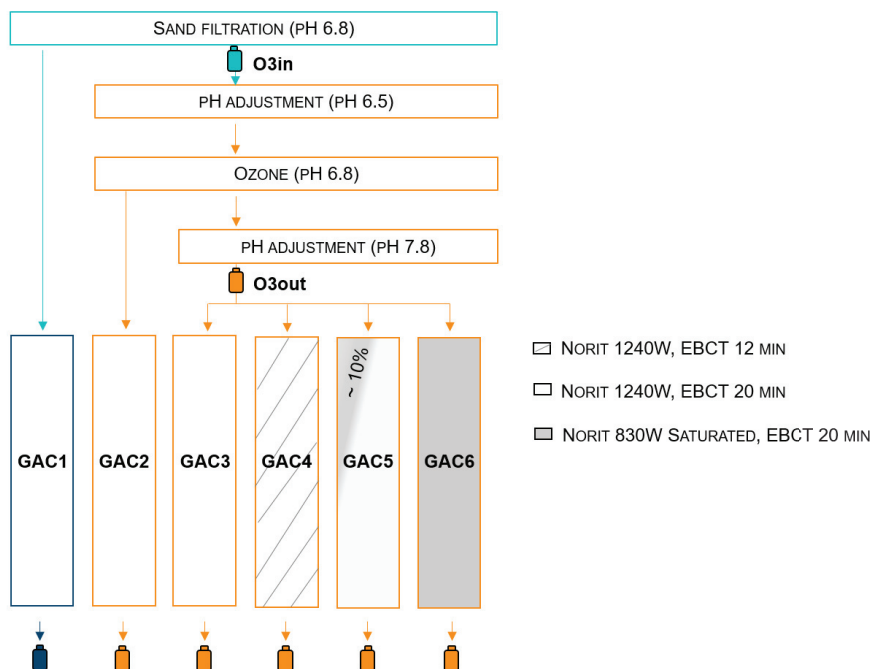
Figure 3. Pilot-scale setup with six parallel granular activated carbon (GAC) filters, which differ for GAC material (new Norit® 1240W or full-scale saturated Norit® 830W), EBCT (12 min or 20 min) and incoming water (indicated by the arrows). The bottles represent the sampling points. The turquoise colour is used for the full-scale, the dark blue for the part of the pilot-scale without ozonation and the orange for the part of the pilot-scale with ozonation.

2.3 Chemical analyses

The analyses were performed according to standard methods as reported in paragraph 1.2. Details regarding the collection of grab samples and analyses performed at each DWTP are summarized in Table 9 in Section 3.

Briefly, samples were filtered using pre-combusted glass microfiber filters (GF/F) with a 0.7 µm nominal pore size prior to DOC, absorbance and fluorescence analyses. TOC and DOC were measured with a TOC-VCPH carbon analyser (Shimadzu) with a measurement error of $\pm$ 0.2 mg·L^{-1} and coefficient of variation (CV) below 2 %. Measurements of UV absorbance were performed at 254 nm using an AvaSpec-ULS3648 high resolution

spectrometer (Avantes) in a 1- or 5-cm quartz cuvette with CV below 1 % according to the water quality. The analyses of DOC and UV were performed in duplicates. Fluorescence was measured using an Aqualog spectrofluorometer (Horiba Jobin Yvon) with a 1-cm flow-through quartz cuvette. The resulting fluorescence excitation emission matrices (EEMs) were pre-processed as discussed in Paper I. External standards were analysed for quality assurance. In particular, EDTA (10 ± 0.15 mg·L^{-1}) was used for TOC and DOC analyses and k-phthalate (10 mg·L^{-1}) for UV absorbance and fluorescence analyses.

LC-OCD analyses were carried out by external laboratories, indicated in parenthesis in Section 4.

PTR-MS analyses were carried out at Utrecht University in the Netherlands. The sample preparation consisted in filtering the samples and Milli-Q water with syringe filters (0.2 µm PTFE Membrane) into 10 mL chromatography vials capped with Teflon caps, which were baked overnight at 250 °C. Then, 1 mL was transferred to a 10 mL chromatographic vial with Teflon caps with 2 mm holes. Three replicates for each sample were prepared for analysis as well as Milli-Q blanks and system blanks (clean vials) and they were randomised for analysis. The vials were then placed in the desiccator followed by low-pressure evaporation/sublimation for 2 hours and then loaded in a thermal desorption (TD) unit to transfer the sample into a PTR-TOF 8000 (IONICON Analytik, Austria) in a clean carrier gas stream. TD and PTR-TOF-MS settings as well as data analysis were performed as described in Materić *et al.* (2017). Briefly, peaks were identified and integrated with PTRwid and the signal from blanks analysed the same day subtracted from each mass. The limit of detection was determined for each ion using the 3σ method and samples below it were excluded.

3. Objective and research questions

Following the discussion in Section 2, the following chapter summarises the goals for each DWTP in terms of improving their treatment processes and gives an overview of the different experiments performed within the thesis to achieve these goals (Table 8). Table 7 introduces the symbol of the different companies used in Table 8 and Table 9.

Table 7. List of drinking water treatment (DWT) companies involved in this thesis.

DWT company	Symbol	DWT company	Symbol
Uppsala Vatten och Avfall AB	UPPSALA VATTEN	VIVAB	VIVAB
Göteborgs stad, Kretslopp och vatten	Göteborgs stad Kretslopp och vatten	Gästrike Vatten AB	gästrike VATTEN
Norrvatten	NORRVATTEN		

Table 9 schematically shows the experimental setup used at the different DWTPs including the sensor location, the grab sample analyses as well as the corresponding paper for reference. The abbreviations used for the water treatment processes indicate surface water (SW), managed aquifer recharge (MAR), coagulation-flocculation (COAG), rapid sand filtration (RSF), sedimentation (DEC), granular activated carbon (GAC) filtration, ultrafilter (UF) membrane filtration and UF with in-line coagulation (COAG-UF).

Table 8. Summary of the research goals for each DWTP and the conducted experiments.
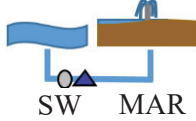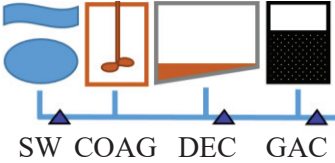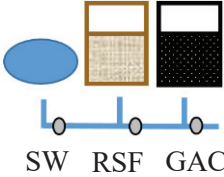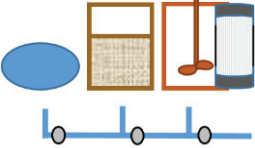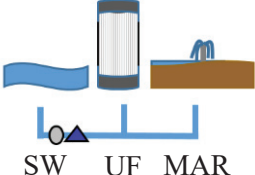
DWTP	DWTP goals	Experiments
	Protect MAR in periods with high DOC and particle content.	Compare the accuracy of two optical sensors in estimating DOC content.
	Couple a pre- or post-coagulation-flocculation treatment with MAR.	Laboratory-scale tests at different coagulant doses and pH.
	Extend the life time of GAC filters and UF membranes: evaluate the effects of adjusting dose and pH during coagulation and of introducing pre-chlorination on NOM removal. Compare GAC filters at different saturation level.	Monitor fDOM data.
	Optimise coagulation and protect SF and GAC: extract valuable information from absorbance-based sensor data.	Test the Python AbspectroscoPY toolbox on a 8-year dataset.
	Enhance NOM and OMPs removal through GAC filtration.	Two pilot-scale experiments to test the effect of using different GAC materials, EBCT and of introducing ozonation. Investigate LMW compounds.
	Protect the UF: extract valuable information from absorbance-based sensor data.	Develop the Python AbspectroscoPY toolbox.
	Protect membrane pre-treatment prior to MAR: deal with turbidity spikes.	Test the Python AbspectroscoPY toolbox and develop an algorithm for turbidity compensation.

Table 9. Schematic representation of the experimental setups, the performed analyses and the corresponding papers. The circles and the triangles indicate the location of the spectro::lyser and the EXO2 sensors, respectively, where grab samples were collected.

DWTP	Experimental setup	Grab samples	Papers
	SW MAR	TOC, DOC, UV, fluorescence	Paper I
	COAG: jar tester	TOC, DOC, UV, fluorescence, LC-OCD	Unpublished data
	SW COAG DEC GAC	TOC, DOC, UV, fluorescence	Unpublished data
	SW RSF GAC		Unpublished data
	GAC: pilot-scale	TOC, DOC, UV, fluorescence, LC-OCD, PTR-MS	Paper II, unpublished data
	SW RSF COAG-UF	TOC, DOC, UV, fluorescence	Paper III
	SW UF MAR	TOC, DOC, UV, fluorescence	Paper IV

4. Results and discussion

4.1 NOM removal: early warning for managed aquifer recharge (MAR) systems and improved coagulation

4.1.1 Evaluating the effects of adjusting coagulant dose and pH on NOM removal at laboratory-scale (unpublished data)

A full-scale MAR facility (Uppsala esker, Sweden) was evaluated for DOM removal. Considering that the introduction of a high DOC load for an extended period of time might compromise the esker functionality, the implementation of a pre- or post-coagulation-flocculation treatment was considered and both scenarios were tested at laboratory-scale.

The main questions addressed are:

a) How does DOM removal spatially distribute along the Uppsala esker in terms of DOC removal and DOM character?
b) How does classical coagulation-flocculation compare to the natural DOM removal observed along the esker?
c) Shall a pre- or post-coagulation-flocculation treatment be implemented?

In order to address the first question, throughout the discussion we refer to DOC analyses to estimate its removal along the esker and to SUVA, fluorescence and LC-OCD analyses to estimate the changes in character. In order to address the second question, the natural removal of organic matter along the esker with increasing distance from the MAR site was compared to the reduction achieved with a coagulation-flocculation process at different

coagulant doses and pH values. Unless indicated otherwise, the pH value is the natural in-situ pH 7.5-7.7. The results allow tentative conclusions regarding the choice of pre- or post-coagulation-flocculation.

DOC and SUVA results

Figure 4, presenting DOC data analysed by the Geochemical laboratory at SLU (Uppsala) along the esker, documents how an increased retention time (i.e. larger distance from the MAR site) positively affects the DOC removal efficiency (Helmisaari 2006). The data presented account for the different dilution of DOC due to mixing with groundwater along the esker (Table 10). Figure 5 displays the percentage removal of the DOC introduced with managed aquifer recharge and indicates that after 80 days (corresponding to a distance of 875 m from the MAR) about 60.5 % of the DOC is naturally removed. This result is comparable to what is obtained by adding a coagulant dose of 100 mg·L^{-1} FeCl$_3$ to the water at the MAR site (58.9 %). If the pH is lowered to 6.3 before dosing the coagulant at the MAR site, a larger DOC removal (77.1 %) is achieved compared to the natural process (72.3 %) along the whole transect.
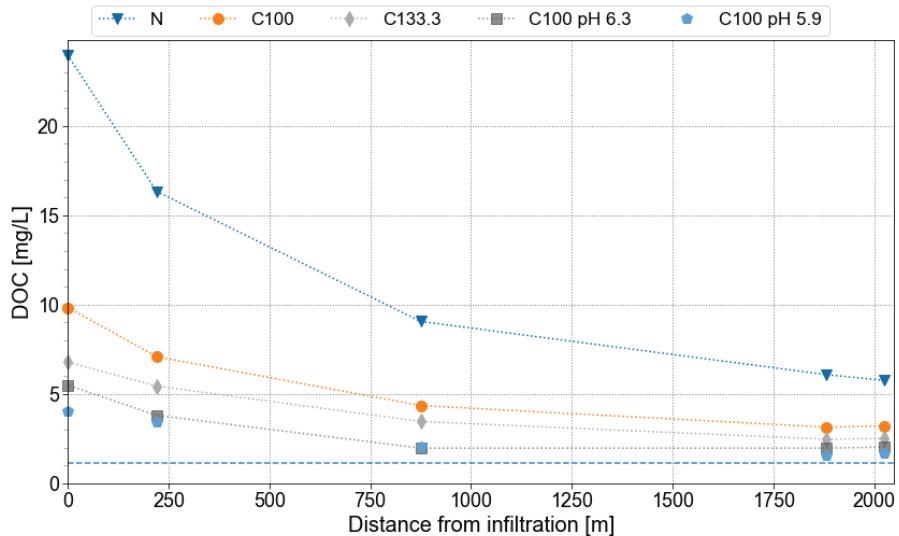
Figure 4. Quantification of DOC [mg·L^{-1}] (Geochemical laboratory, SLU, Uppsala) along the Uppsala esker (N) and after chemical coagulation-flocculation (C), using different coagulant doses (100 – 133.3 mg·L^{-1} FeCl$_3$) and at different pH (6.3 and 5.9). The samples were taken in January 2018 at locations with increasing distance from the MAR site. The DOC level of the groundwater is indicated with a dashed light blue horizontal line.

Table 10. Average residence time and groundwater fraction at increasing distance from the MAR site, based on oxygen isotopes analysis.

Distance from MAR [m]	Average residence time [days]	Groundwater fraction [%]
0	0	0
220	35	5-10
875	80	0-5
1880	230	10-15
2025	240	15-20

The best result is obtained when the pH is lowered to 5.9. However, the pH decreases to values lower than 4 after coagulation-flocculation. These observations confirm the results from earlier studies on ferric-based coagulation which indicated an optimum pH value in the range of 4.5-6 and a corresponding DOC removal rate of 29-70 % for coagulant doses of up to 100 mg·L^{-1} (Matilainen *et al.* 2010). The high DOC removal is explained by the high coagulant dose chosen and the high SUVA value (3.87 L·(mg·m)$^{-1}$), which indicates that organic matter mainly consists of hydrophobic and HMW compounds that are removed more easily by coagulation than the hydrophilic fraction. SUVA values decreased to 2.33 L·(mg·m)$^{-1}$ at the outlet of the esker and further to 1.72 L·(mg·m)$^{-1}$ after coagulating the water at the
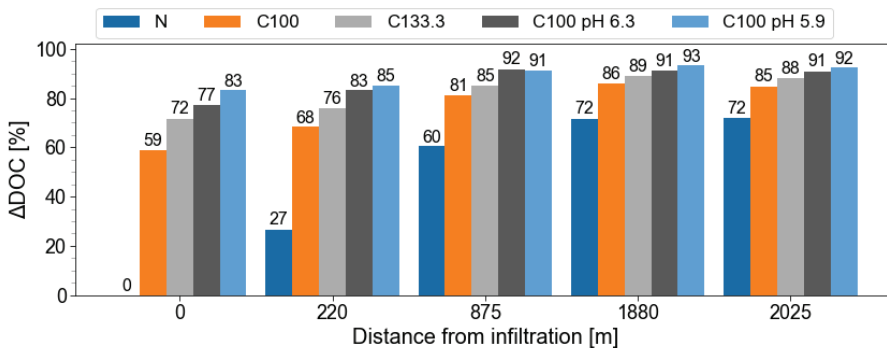
Figure 5. Comparison between natural removal (N) of the DOC introduced with managed aquifer recharge along the esker [%] and removal after chemical coagulation-flocculation (C), using different coagulant doses (100 – 133.3 mg·L^{-1}FeCl$_3$) and at different pH (6.3 and 5.9). The calculations take into account the mixing with groundwater. The samples were taken in January 2018 at locations with increasing distance from the MAR site.

infiltration site with 100 mg·L^{-1} FeCl$_3$ at pH 6.3. Increasing the coagulant dose from 100 mg·L^{-1} to 133.3 mg·L^{-1} implies a greater DOC removal, but not a clear improvement in terms of DOC removed per mass of coagulant used (data shown in Stenberg 2018).

Fluorescence results

Fluorescence spectra were used to identify potential changes in composition of organic matter. Figure 6 displays the ΔEEMs obtained by subtracting the EEMs resulting from the coagulation-flocculation experiments at different coagulant doses and pH values (C) to the EEMs from the natural sample (N), defined as:

$$\Delta EEM_C^N := EEM_N - EEM_C \qquad (1)$$

The ΔEEM plots confirm that the highest removal affects the hydrophobic fraction, the humic-like fraction at 237-260/400-500 and 300-370/400-500 Ex/Em wavelength (corresponding to peaks A and C respectively in Hudson *et al.* (2007)). They also confirm that increasing the coagulant dose and especially lowering the pH improves organic matter removal. The same pattern was found at all the sampling sites along the esker. These results indicate that the coagulation-flocculation process is highly selective towards removal of terrestrial DOM (Lavonen 2015). These results are supported by the fluorescence indices, which indicate which type of DOM are most easily removed. The fluorescence indices show a higher removal of humic acids (humification index) when lowering the pH and an enrichment of decomposed DOM (freshness index) from a microbial origin (fluorescence index) when increasing the coagulant dose and pH. Figure 7 reports the ΔEEMs obtained by subtracting the EEMs at two different distances from the MAR site for the natural sample and the coagulation-flocculation experiments. For clarity, the ΔEEM from sampling location b to a (different distances from the MAR site), is defined as:

$$\Delta EEM_b^a := EEM_b - EEM_a \qquad (2)$$

Comparing the ΔEEM_{875}^{220} (Figure 7a) with ΔEEM_{1880}^{875} (Figure 7b), it is clear that the largest removal occurs between 220 and 875 m from the MAR
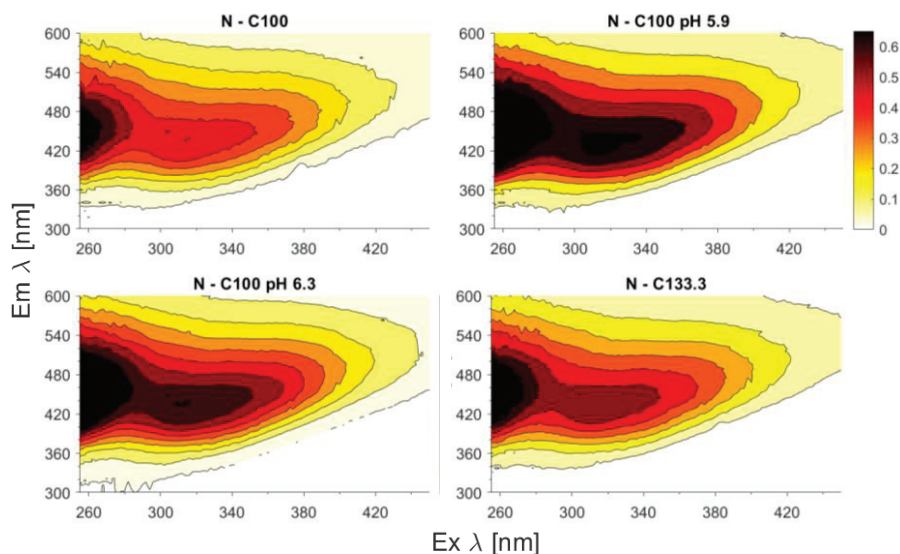
Figure 6. Differential excitation emission matrices (ΔEEMs) obtained subtracting the EEMs of the water sample after chemical coagulation-flocculation, using different coagulant doses (C100 and C133.3 mg·L⁻¹ FeCl₃) and at different pH (6.3 and 5.9), to the natural sample (N) taken in January 2018 at a distance of 2025 m from the MAR site. The x- and y-axis indicate the excitation and emission wavelength, respectively, and the colour bar represents the fluorescence intensity in Raman units. The ΔEEMs do not take into account the mixing with groundwater.

site. We refer to this region as a "hotspot" of the DOC removal along the Uppsala esker. The results indicate that lowering the pH mainly affects the removal at the MAR site while the removal further along the esker is largely unchanged and that the coagulant dosing has a greater effect on the locations closer to the MAR site, probably due to a decrease of HSs with increasing distance from the MAR site.

LC-OCD results

Changes in organic matter were also characterised using LC-OCD data. Figure 8 reports the hydrophobic and hydrophilic fractions of DOC obtained from LC-OCD analysis (D.O.C. LABOR, Institute in Karlsruhe, Germany) for natural water and samples taken after coagulation-flocculation (100 mg·L⁻¹ FeCl₃ at pH 6.3) with increasing distance from the MAR site, as well as a groundwater sample. The results from the coagulation- flocculation experiment seem to indicate a decrease in HSs fraction and an increase in
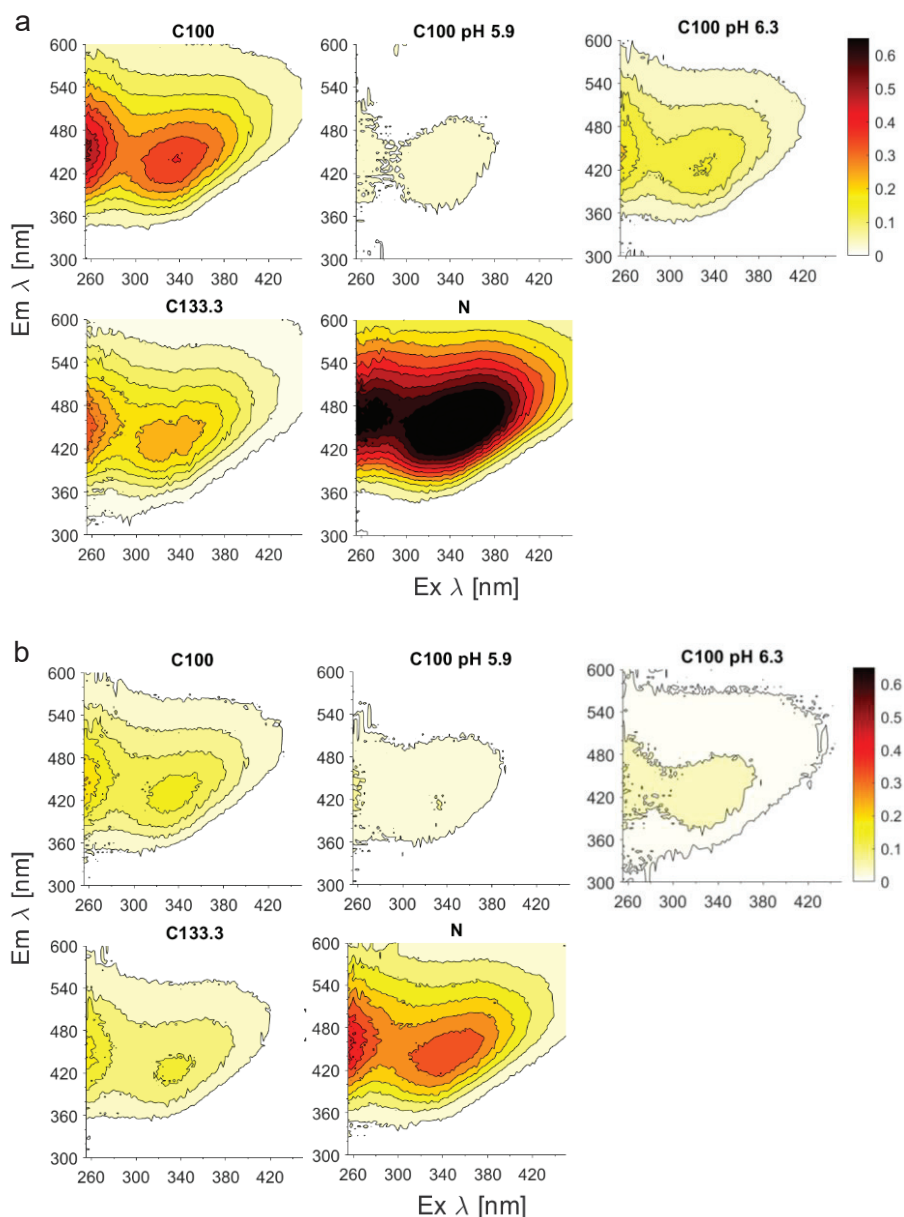
Figure 7. Differential excitation emission matrices (ΔEEMs) obtained subtracting the EEMs of the water samples taken in January 2018 at 875 m from the MAR site, both natural (N) and after chemical coagulation-flocculation (C) using different coagulant doses ($100 - 133.3$ mg·L^{-1} $FeCl_3$) and at different pH (6.3 and 5.9), to the sample taken at 220 m (figure a). The same procedure was applied to the sample taken at 1880 m from the MAR site in comparison to the one taken at 875 m (figure b). The x- and y-axis indicate the excitation and emission wavelength, respectively, and the colour represents the fluorescence intensity in Raman units. The ΔEEMs do not take into account the mixing with groundwater.

LMW fractions. However, the data shown in Figure 8 do not account for the groundwater dilution effect. Groundwater consists of a larger fraction of LMW compounds compared to the infiltrated water and a lower fraction of HSs. Figure 9 documents the percentage removal of DOC fractions along the esker introduced with managed aquifer recharge, considering the groundwater dilution effect, for natural water (N) and samples taken after coagulation-flocculation (C100 pH 6.3). The measured LMW-A were below the limit of quantification for the groundwater and the water at the MAR site. A greater removal of the hydrophobic fraction (HOC) and HSs in comparison to other DOC fractions is observed for both N and C100 pH 6.3 samples. Compared to what naturally occurs along the esker, the HSs are removed faster (within less distance from the MAR) and to a higher degree in the
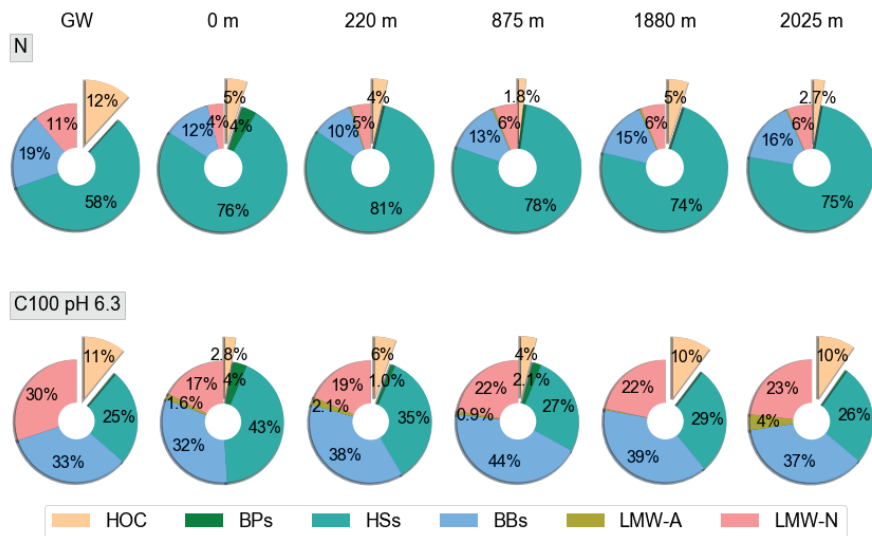
Figure 8. Quantification of DOC fractions [%] obtained by LC-OCD analysis (D.O.C. LABOR, Institute in Karlsruhe, Germany) of the groundwater (GW), natural samples collected along the Uppsala esker (N) and the same samples after chemical coagulation-flocculation (100 mg·L^{-1} FeCl$_3$ at pH 6.3) with increasing distance from the MAR site [m]. The samples were taken in January 2018. The dissolved organic carbon fractions consist of a hydrophobic (HOC) and hydrophilic part, whose abbreviations stand for biopolymers (BPs), humic substances (HSs), building blocks (BBs), low molecular-weight acids (LMW-A) and low molecular-weight neutrals (LMW-N). The hydrophobic fraction is visually separated from the hydrophilic fractions. The indicated percentages are approximate values by excess or defect, with one digit for values < 3.5 % (arbitrary value for visualisation purposes).
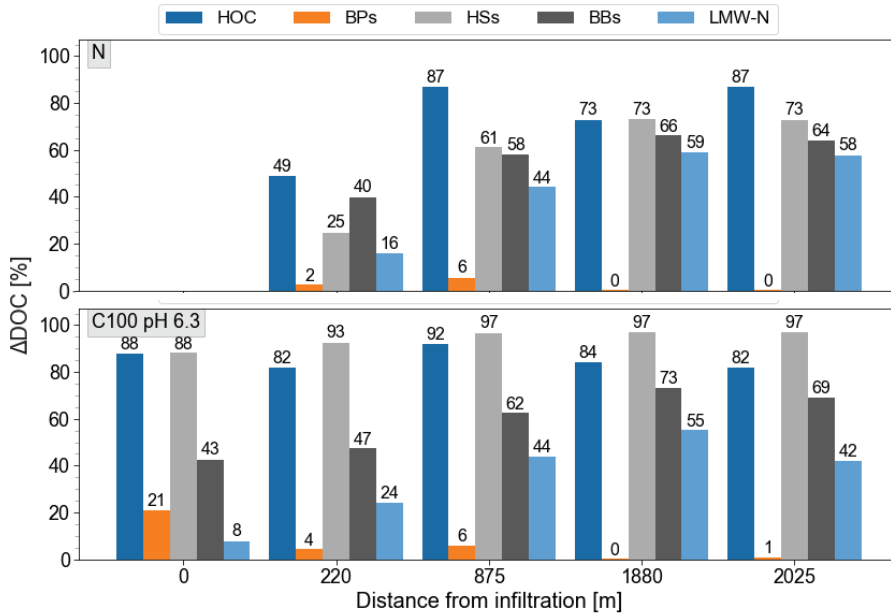
Figure 9. Comparison between natural removal of the DOC fractions introduced with managed aquifer recharge along the esker [%] and removal after chemical coagulation-flocculation (100 mg·L^{-1} FeCl$_3$ at pH 6.3). See Figure 8 for explanation of the dissolved organic carbon fractions obtained by LC-OCD analysis. The calculations take into account the mixing with groundwater. The samples were taken in January 2018 at locations with increasing distance from the MAR site.

coagulation-flocculation experiment. BBs and LMW compounds are not considerably affected by coagulation-flocculation (Huber *et al.* 2011).

Pre- and post-coagulation-flocculation scenarios

A series of considerations arise from the obtained results concerning the implementation of a pre- or post-coagulation-flocculation treatment. Using a pre-coagulation-flocculation process results in a more efficient DOC removal in terms of required coagulant dose due to the higher HSs fraction at the infiltration site compared to the outlet as well as a reduced impact on the future esker functionality. However, this also results in a higher use of coagulants with a consequently greater sludge production incurring higher economic and environmental costs. The post-coagulation-flocculation might require the use of less coagulants overall since the esker naturally removes part of the DOC and therefore less needs to be taken care of using the

coagulation. However, this consideration needs to be validated with further testing. In order to mitigate long term negative effects on the esker functionality in this case, we recommend to adjust the volumes and timing of DOC infiltration using real-time analysis based on turbidity peaks and current DOC concentrations measured at the MAR site. This possibility is followed up in Paper I that is described below.

4.1.2 Moving from grab sampling to real-time analysis to adjust infiltration volumes (Paper I)

In order to estimate the real-time DOC concentrations at the MAR site, two in-situ optical sensors were deployed at Storvad, where the river water is representative of the water that is infiltrated in the Uppsala esker.

The main questions addressed are:

a) Are real-time measurements with optical sensors suitable to protect the esker from water with high DOC and particle content (turbidity)?

b) How accurately an absorbance- and a fluorescence-based sensor predict DOC?

For the fDOM sensor, a temperature correction factor of ca. 1.2 % °C^{-1}, an attenuation of 15 % at a turbidity of 50 FNU and of 14 % due to IFE at an absorbance of 0.5 at 254 nm were found in agreement with the literature (Henderson *et al.* 2009; Downing *et al.* 2012). The resulting coefficient of determination (R^2) and root-mean-square error (RMSE) were 0.92 and 1.3 mg·L^{-1} for the spectro::lyser and 0.71 and 2.5 mg·L^{-1} for the fDOM sensor, respectively. The absorbance-based sensor led to a better estimation of the DOC concentration in comparison to the fluorescence-based sensor, especially in the period between May and September (in Paper I, Figure 2).

The decrease in HSs concentration from ca. 80 % during the spring flood to ca. 50 % in September, calculated as in Grundvattengruppen for Uppsala Vatten (2017), is the main explanation for the underestimation of the DOC concentration by the fDOM sensor. In addition, this underestimation might also be explained by the potential quenching of the protein-like fDOM by the humic-like components, considering that the protein-like fluorophores are mainly located in HMW fraction and the humic-like ones in LMW fraction (Wang *et al.* 2015; Xu *et al.* 2020). These hypotheses are supported by the optical indices calculated from the spectroscopic laboratory analyses. During low-flow summer conditions, the trend of the fluorescence indices

(lower HIX and higher β:α) together with the shift from humic-like (peak C) to protein-like peak (peak T) and the decrease of the aromaticity (SUVA) show a greater contribution of autochthonous DOC (less-humified material) compared to allochthonous DOC.

Despite the higher accuracy of the spectro::lyser, the fDOM sensor might be sufficient to quickly decide on adjustment of infiltration volumes or of the coagulant dose in the coagulation-flocculation treatment process. Indeed, the HS fraction, which is the most easily removed DOC fraction by coagulation-flocculation (Figure 8), correlated well with the corrected fDOM ($R^2 = 0.96$). On the other hand, data from the EXO2 obtained from Gavleån (Paper IV) lead to a better prediction of DOC content (RMSE = 0.44 mg·L^{-1}) which could be due to a lower range of SUVA variability in Gavleån.

4.1.3 Moving from grab sampling to real-time analysis to adjust coagulant dose, pH and chlorination for NOM removal at full-scale (unpublished data)

The possibility of using the fDOM sensor installed on the EXO2 sonde to adjust the coagulant dose, pH and pre-chlorination was tested at full-scale at Lackarebäck DWTP (Mölndal, Sweden). The final goal is to extend the life time of GAC filters and UF membranes.

The main questions addressed are:

a) Can the fDOM sensor detect changes in DOM after adjusting certain process variables of coagulation (coagulant dose and pH) and introducing pre-chlorination?
b) Does the GAC regeneration positively affect the fDOM removal?

During the period of investigation, the water quality at the intake had low fluctuations in TOC (Median = 5.55 (IQR = 0.48) mg·L^{-1}), DOC (Median = 5.47 (IQR = 0.39) mg·L^{-1}) and UV254 (Median = 15.9 (IQR = 1.1) m^{-1}) (Geochemical Laboratory, SLU, Uppsala). When comparing TOC and DOC measurements before and after each adjustment of process variables, the results were within the instrumental error. Time series of data from selected EXO2 parameters are displayed in Figure 10 for DEC 1, 7 and effluent of GAC 1, 19 filters in the period when the full-scale experiments were performed. Preliminary results indicate that the sondes measure accurately
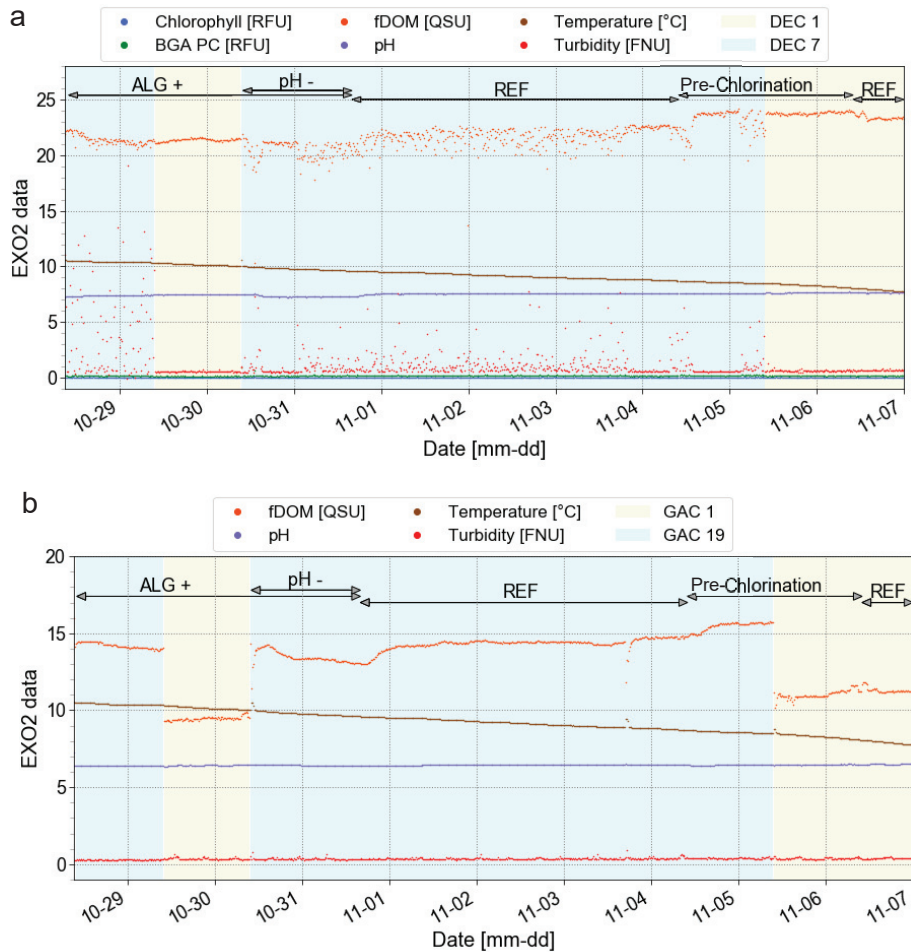
Figure 10. Data from two EXO2 sondes (YSI) collected during a full-scale experimental period in autumn 2019 in Lackarebäck DWTP for decanted water (DEC 1 and 7, in figure a) and for effluent of the corresponding granular activated carbon (GAC) filters (the regenerated GAC 1 and an older GAC, GAC 19, in figure b). The parameters fDOM and BGA PC stand for fluorescent dissolved organic matter and blue-green algae (phycocyanin), respectively. The background colors indicate the placement of the EXO2 sonde. The arrows indicate the full-scale experiments and their duration: increase of aluminium sulphate coagulant dose from $12 + 0.7 \cdot colour_{laboratory}$ to $15+0.7* colour_{laboratory}$ [mg·L^{-1}]; decrease of precipitation-pH from 6.5 to 6.2; reset of the normal operational coagulant dose and pH (reference values, REF) with no chlorination; pre-chlorination with sodium hypochlorite (chlorine 0.25 g m^{-3}).

enough to detect small changes in dose, pH and effects of even small changes in pre-chlorination can be detected. Increasing the coagulant dose as well as lowering the pH slightly improves the fDOM removal, while pre-chlorination does not seem to have a positive effect with respect to fDOM removal. When considering the fDOM increase during pre-chlorination, it is important to consider that the TOC and DOC measurements as well as the fDOM measured in the intake water were higher compared to the previous days. In addition to this, chlorination of DOM was shown to substantially increase the intensity of fluorescence (Korshin *et al.* 1996). Proper estimates of DOC removal require correction of the fDOM results as described in paragraph 4.1.2. In contrast to the data from the River Fyrisån, the DOC data estimated by the fDOM sensor did not indicate a period of underestimation of DOC concentration (data not shown). Results in Figure 10 indicate that the effluent of GAC 1 has lower fDOM values than GAC 19, which indicates that regeneration positively affects the organic matter removal efficiency.

4.2 NOM removal: optimisation of the granular activated carbon (GAC) process at pilot-scale

A deeper investigation on which parameters can influence organic matter removal in GAC filtration was conducted at Görväln DWTP (Järfälla, Sweden) at pilot-scale.

The main questions addressed are:

a) To what extent do different materials and EBCT affect DOM breakthrough in GAC filters?
b) Is an absorbance-based sensor a reliable tool?
c) Can DOM breakthrough data be used to explain OMPs breakthrough in GAC filters?

4.2.1 Effect of GAC material and EBCT on breakthrough (Paper II)

Figure 11 documents the DOC breakthrough in the four GAC filters of the first pilot-scale setup in paragraph 2.2.3 as an example of organic matter removal efficiency. The first letter in the label after the column number indicates the initial of the GAC material and the number the EBCT. FiltraSorb® 400 was the best performing material overall, with an optimum

Figure 11. Breakthrough profile of dissolved organic carbon (DOC) as function of number of bed volumes in four granular activated carbon (GAC) pilot-scale filters at Görväln DWTP: two GAC filters filled with Norit® 830W and with an empty bed contact time (EBCT) of 18 and 6 min (C1-N18 and C2-N6, respectively) and two filters with FiltraSorb® 400 and with 18 and 6 min EBCT (C3-F18 and C3-F6, respectively).

at 18 min EBCT (hydraulic load = 2.7 m h⁻¹) in comparison to 6 min (hydraulic load = 8.0 m h⁻¹). However, comparing the results for the two GAC filters filled with FiltraSorb® 400, it is clear that the improved performance at longer EBCT is limited to a certain number of bed volumes (BVs). The DOC breakthrough curve for C2-N6 showed a transient 7 % decrease at ca. 9500 BVs which is due to a regeneration experiment with an alkaline solution performed in June.

In this study a number of different measures for characterisation of DOM breakthrough were compared. Figure 12 reports the breakthrough profiles obtained for TOC, UV, DOC as well as protein- and humic-like fractions for the three GAC filters in operation for the entire duration of the experiment. The obtained rate of breakthrough was in order DOC>UV254>fDOM, in line with previous results reported in literature (Anumol *et al.* 2015). The fluorescence results in terms of protein- and humic-like fDOM breakthrough confirm that C3-F18 is the best performing GAC filter. Prior to steady-state, all GAC filters show a faster breakthrough of the protein-like fDOM in comparison to the humic-like fDOM. After that, the breakthrough pattern is reversed. In order to explain this behaviour, different hypotheses need to be considered. As stated earlier in the discussion of the underestimation of the
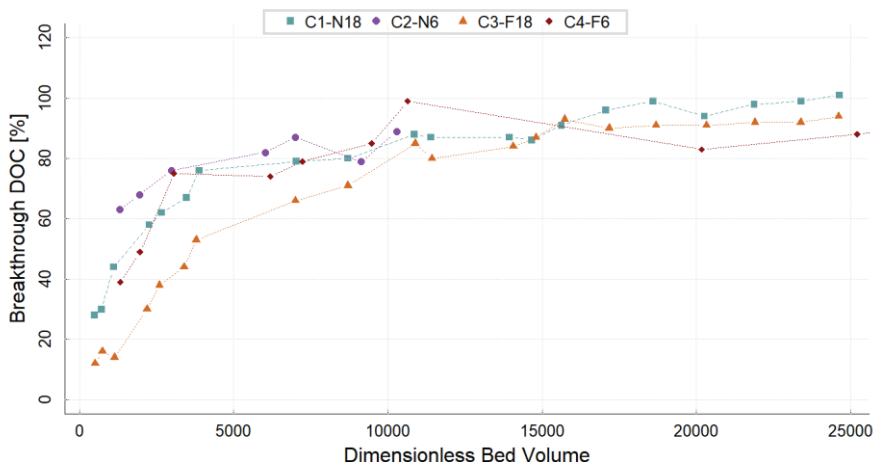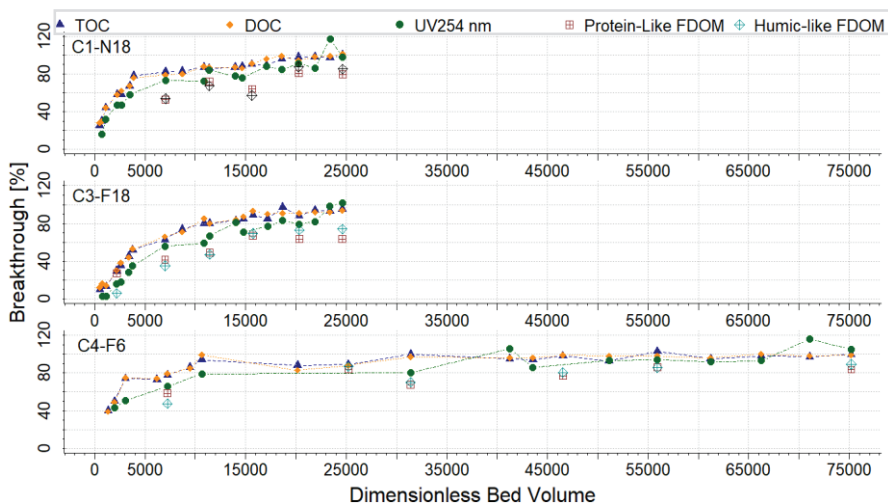
Figure 12. Breakthrough profile of natural organic matter as function of number of bed volumes in three granular activated carbon (GAC) pilot-scale filters in Görväln DWTP: a GAC filter filled with Norit® 830W and with an empty bed contact time (EBCT) of 18 min (C1-N18), a GAC filter with FiltraSorb® 400 and 18 min EBCT (C3-F18) and a GAC filter with FiltraSorb® 400 and 6 min EBCT (C3-F6). The monitored parameters are total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV254 nm) and protein- and humic-like fluorescent dissolved organic matter (fDOM).

DOC concentration by the fDOM sensor, when quantifying differences between the two fDOM fractions, the potential quenching of the protein-like fDOM by the humic-like components should be accounted for, considering that the protein-like components are mainly found in HMW fraction and the humic-like ones in LMW fraction (Wang *et al.* 2015; Xu *et al.* 2020). Furthermore, adsorbability increases with decreasing molecular size (humics < building blocks < LMW organics). Therefore, assuming a removal mainly due to adsorption and not to biological degradation with no removal of biopolymers (Velten *et al.* 2011), it can be concluded that GAC treatment is more efficient on water with more LMW compounds.

4.2.2 Moving from grab sampling to real-time analysis as a potential tool for early warning system of organic matter breakthrough (unpublished data)

Besides grab sampling, it was originally planned to use the absorbance-based sensor (spectro::lyser) introduced in paragraph 4.1.2. as a reliable tool that

could be used for early warning of DOC breakthrough. Unfortunately, due to maintenance problems including formation of bubbles in the system, the full spectra results were not useable. However, the linear regression model between specific UV data obtained from the spectro::lyser and from laboratory analyses in Figure 13 confirmed the accuracy of the sensor. This indicates that the sensor could be used as early warning system for breakthrough of compounds for which UV could be used as surrogate parameter, including DOC.

As discussed in more detail in Paper II, the online solid-phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) could be used as a fast tool for early warning of imminent OMPs breakthrough. The breakthrough of two antihistamines (cetirizine and fexofenadine), an antidepressant (oxazepam), an antifungal drug (fluconazole), a pesticide (N,N-diethyl-meta-toluamide, DEET) and two antiepileptic drugs (carbamazepine and lamotrigine) was investigated. Carbamazepine, lamotrigine and fexofenadine are seen to be late indicators of breakthrough of OMPs in GAC. The main process is the physical adsorption process, since the compounds at the prevailing pH (ca. 6.9) are not charged. In addition to this, carbamazepine, lamotrigine and cetirizine are relatively resistant to biodegradation. Although the differences in the OMPs breakthrough profiles could not be explained satisfactorily using the organic matter data in this
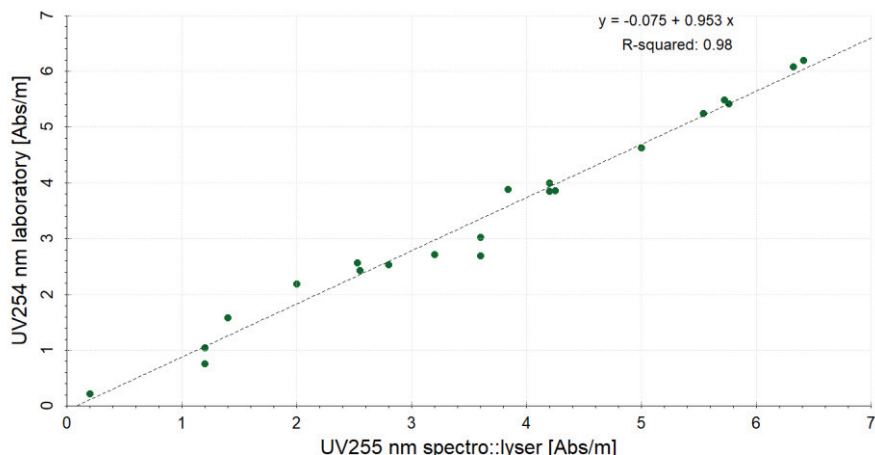
Figure 13. Measured UV at 254 nm in the laboratory versus measured UV at 255 nm from the spectro::lyser at Görväln DWTP. The dashed line represents the linear regression line.

study, it is reported that their breakthrough is mainly governed by the concentration of LMW-A and LMW-N organics (Zietzschmann *et al.* 2016).

4.2.3 PTR-MS analysis to target LMW compounds (unpublished data)

Labile LMW DOM is known to be readily assimilated by bacteria (Bertilsson & Stefan 1998; Berggren *et al.* 2010). Its investigation is of interest to improve the knowledge on biostability of water, i.e. ensuring a tap water with the same microbial quality as the produced water at the DWTP (Prest *et al.* 2016). For this reason, as well for the major role of LMW organics in the breakthrough of OMPs, we moved to a detailed analysis of LMW compounds observed during GAC breakthrough.

The main questions addressed are:

a) How can LWM compounds be quantified and characterised?

b) To what extent and how does a combined ozonation/GAC treatment affect DOM removal? How is it influenced by different EBCT and GAC saturation levels?

On the basis of these considerations, the second pilot-scale experiment at Görväln WTP (paragraph 2.2.3) was designed. At the moment of the sampling (July 2018), the TOC concentration in the effluent from all the GAC filters except GAC6 had just passed the initial phase of strong increase in the breakthrough profile (cf. Figure 11). GAC6 was already saturated at the beginning of the experiment and therefore showed a high and nearly constant TOC breakthrough value. TOC breakthrough percentage from the GAC filters align in the following way 74 %, 65 %, 70 %, 78 %, 71 % and 93 % (GAC1-GAC6). TOC analyses were performed at Görvälnverkets Laboratorium Norrvatten (Stockholm county, Sweden). The second fastest breakthrough rate obtained for GAC4 is explained by its short EBCT. In a next step GAC1, GAC2 and GAC3 that have the same material and EBCT can be compared. The slower breakthrough rate for GAC2 compared to GAC3 can be explained by its lower pH value, since it has been shown that higher pH negatively affects the organic matter adsorption (Hong 1998). The fact that GAC1 does not receive ozonated water explains its faster breakthrough rate compared to GAC2.

Ozonation results in chemical fragmentation due to the addition of oxygen functional groups to the carbon skeleton that weaken the C-C bonds

(Atkinson 2007). This process involves a decrease of HMW compounds in favour of LMW compounds, with subsequent increase in biodegradability (Amy *et al.* 1988). Ozonation increases DOM polarity and hydrophilicity, forming hydroxyl, carbonyl, and carboxyl groups and decreasing double bonds and aromaticity (Urfer *et al.* 1997). This is confirmed by differences in DOM absorbance properties. The SUVA values indeed decreased from 1.70 L·(mg·m)$^{-1}$ for O3in to 1.37 L·(mg·m)$^{-1}$ for GAC1 and 0.51 L·(mg·m)$^{-1}$ for GAC2. Based on these arguments and the increase of adsorbability with decreasing molecular size, we confirm that breakthrough is probably governed by the concentration of LMW organics.

To quantify the LMW compounds, both the LC-OCD (Het Waterlaboratorium, Harleem, Netherlands) and PTR-MS were used. Some of the PTR-MS results are reported in Figure 14 for atomic ratios, mean oxidative state (OSc), average number of carbon atoms per molecule in the sample (nC) and mean total concentration of organics. In all three plots, considering the standard deviation, full- and pilot-scale samples can be distinguished. The first two plots reveal the major underlying chemical processes. The upper plot shows that ozonation increases the atomic H/C ratio, since it breaks the double bonds, with a smaller effect on saturated GAC filters, as well as the atomic O/C ratio, possibly due to the formation of oxidation intermediates (Wang *et al.* 2012). The middle plot indicates how ozonation, as well as ongoing sorption, reduces nC. GAC1 and GAC2 present the more oxidized DOC and are well separated along the OSc-axis processes. The DOC mean mass weighted carbon oxidation state is generally negative (Safieddine & Heald 2017). The results of the mean total concentration of organics in the lower plot confirms the order of the GAC filters in terms of TOC breakthrough percentages, with GAC2 and GAC6 having the lowest and highest concentration, respectively. These results are also confirmed by the LC-OCD results, which indicate the highest and lowest removal of both HSs and LMW-N for GAC2 and GAC6 in comparison to O3in, 31 % and 4 % for HSs and 56 % and 14 % for LMW-N, respectively. Results for the analyses of assimilable organic carbon (the most bioavailable fraction of the bioavailable organic material; THL, Kuopio, Finland) also confirm a higher concentration of carbon available to the microbes in GAC2. GAC1 shows a lower removal for both the organic matter fractions, 18 % for HSs and 42 % for LMW-N.
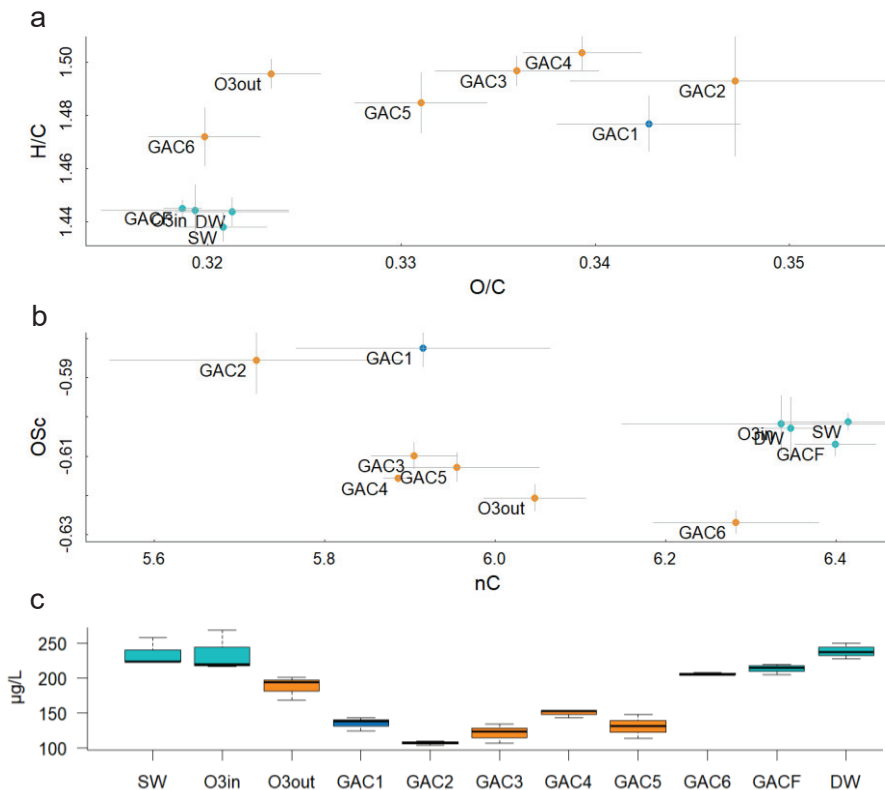
Figure 14. Atomic O/C ratio versus H/C ratio (van Krevelen diagram) (a), scatter plot of the average number of carbon atoms per molecule in a sample (nC) and the mean oxidative state of carbon (OSC) (b) and total concentration of organics [µg L^{-1}] (c). The standard deviation is calculated from three field triplicates per sample. The turquoise colour is used for samples taken at full-scale (SW = surface water intake, O3in = water after sand filtration, GACF = water after biological active granular activated carbon (GAC) filter in use for 14 years filled with Norit® 830W and with an empty bed contact time (EBCT) of 5-6 min, DW = finished drinking water after UV disinfection and dosing of monochloramine and lime), the dark blue for samples at pilot-scale with no ozonation (GAC1) and the orange for samples at pilot-scale after ozonation (GAC2, GAC3, GAC4, GAC5, GA6). More details on the pilot-scale setup are given in Figure 3.

Some preliminary results obtained from correlating the BBs and LMW compounds from the LC-OCD analysis with the ions from the PTR-MS indicate the possibility to deduce a fingerprint of these two organic matter fractions using PTR-MS (Paper in preparation).

4.3 Towards automated process control using optical sensor data (Paper III, Paper IV)

The studies above have revealed that high frequency data on the different treatment processes is an essential element in the increasing automation of process control in drinking water treatment and is especially important for the implementation of real-time early warning systems. One option is to use sensor packages available on the market that include the software to condense the raw data for analysis. With this approach, the DWTP has little control over the details of the calibration and relies on the proprietary algorithms provided with the sensor. In order to use the sensors to their full potential, the raw data can be analysed directly but this requires specialised software for efficient pre-processing and analysis of the large datasets. In order to bridge this gap, we have developed an open-source toolbox AbspectroscoPY ("Absorbance spectroscopic analysis in Python") for the analysis of absorbance-based sensor data.

The main objectives for the toolbox are:

a) What are the main challenges in dealing with large sensor datasets and how to address them?
b) How to select the appropriate variables for the interpretation of absorbance data and how to compute them efficiently?
c) How can we differentiate between outliers and artefacts on the one side and important events relating to operational changes in the DWTP on the other side?
d) What is the connection between changes in the absorbance spectra and the DWTP operation such as dosing changes or variations in membrane performance?

The toolbox provides a set of functions for data pre-processing including handling of duplicates and missing data, the correction of systematic time shifts, baseline correction, data filtering as well as outlier detection and removal. Once the data are cleaned, the toolbox computes a number of common spectral metrics such as absorbance ratios, exponential fits, slope ratios and spectral curves. These data are computed for the full time-series obtained from the sensor which allows for the identification of rapid changes in the DWTP with a temporal accuracy that cannot be achieved with

traditional laboratory analyses. The toolbox offers an automated process for the removal of known outliers/artefacts and a simple algorithm for the identification of outliers based on the interquartile range (IQR). The toolbox is an open-source project written in Python, a popular language for data processing, that allows new features to be implemented and added easily.

The toolbox has been applied to a dataset spanning a 15-month period for three sensors including surface water from Lake Neden and processed water from the Kvarnagården DWTP (Paper III). Despite the low variability of the water quality in the lake, changes in coagulant dosing and drops in membrane permeability were related to the spectral metrics obtained from the data. In order to assess the applicability of the toolbox to other water sources and large datasets, it was used for the analysis of absorbance data from the Gavleån river (Paper IV) and tested on a dataset spanning several years (2010-2018) in the Lake Mälaren. Figure 15 shows the application of the median filter with a window size of 60 minutes to the raw data from Lake Mälaren that removes many isolated outliers (e.g. attenuation data close to 0). The data also clearly show that the years 2013 and 2018 were anomalous with considerably increased attenuation compared to the surrounding periods.
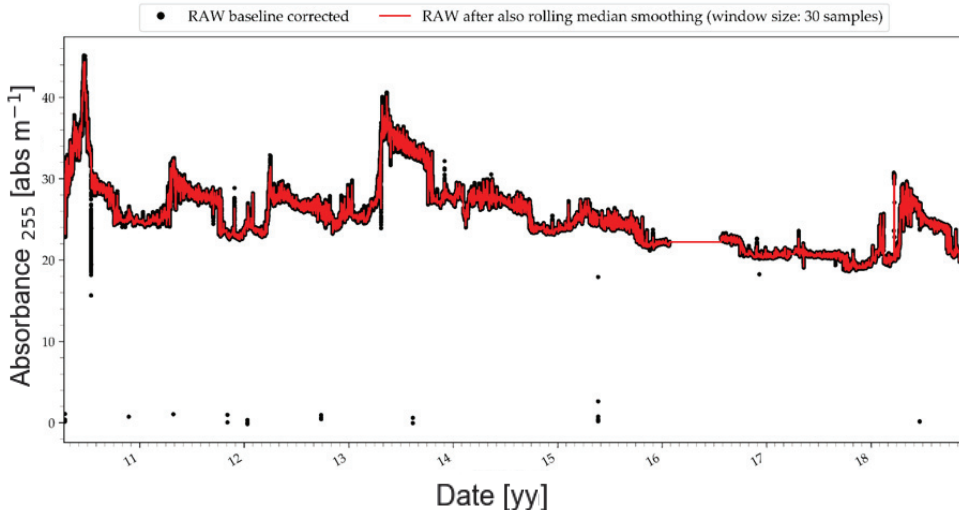
Figure 15. Full span of attenuation data at wavelength 255 nm (spectro::lyser) from lake Mälaren. The raw data is shown in black and the pre-processed dataset using the median-filter with a width of 60 minutes (covering 30 samples) is shown in red.

Figure 16 presents an example of the application of the spectral slope analysis (spectral curve) to the spectro::lyser dataset from the sandfiltrate water during a particularly challenging period in 2018. The figure shows the large variation of the spectral slope over a 2-month period, especially for wavelengths close to 290 nm.

An ongoing project is the optimisation of the turbidity compensation algorithm presented in Paper IV that will be added to the toolbox. Briefly, the algorithm led to an underestimation of the absorbance data during very large turbidity spikes, but in the overall provided corrected absorbance data very close to laboratory data, outperforming the built-in compensation algorithms on the sensor.
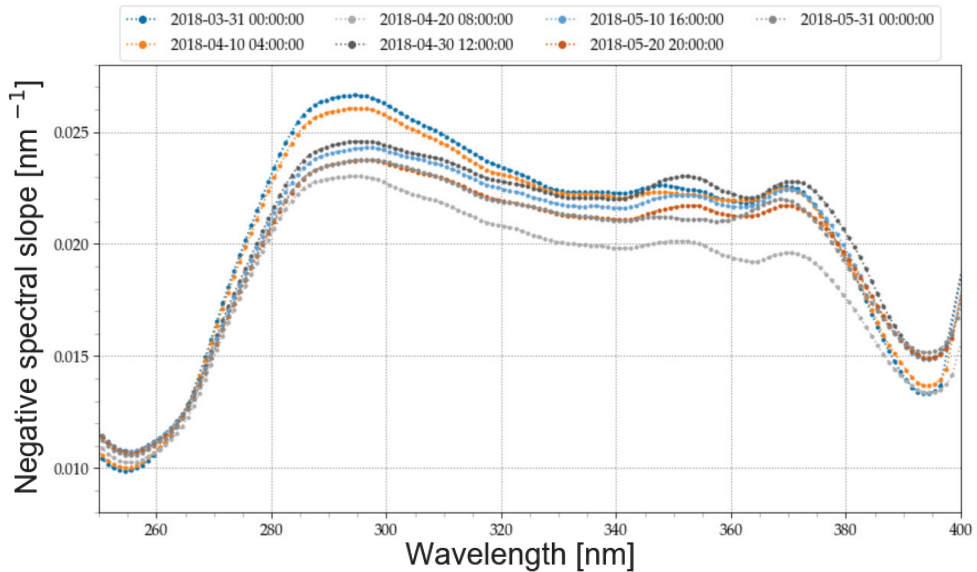
Figure 16. Variation of the spectral slope of spectro::lyser data for sandfiltrate water in Görväln DWTP over the period of 2 months in 2018.

5. Conclusions and outlook

In this thesis, the applicability, accuracy and reliability of optical sensors for the estimation of DOC concentrations and composition was investigated at different steps in the water treatment process in five DWPTs in Sweden.

The main results of the studies are the following:

1. Both absorbance-based (spectro::lyser) and fluorescence-based (EXO2) sensors used in this thesis are suitable for the estimation of DOC concentration prior to MAR and could be used for an early warning system to identify periods during which infiltration is not advisable. Although the quality of the prediction is site-specific, the absorbance-based sensor performed better overall in DOC estimation (Paper I).

2. The addition of a coagulation-flocculation treatment step at the MAR site and along the Uppsala esker significantly increased the DOC removal, especially when coupled with optimal pH conditions. In terms of DOM composition, the largest effect of the treatment step was observed on HSs while LMW compounds are less affected (unpublished data).

3. Fluorescence-based sensor measurements give rapid results and can therefore be used for real-time monitoring of water quality with respect to fDOM. These data can be used to adjust operational parameters in the coagulation-flocculation process at the DWTP (unpublished data).

4. The GAC filtration step can be optimised by extending the EBCT and the choice of material. The positive effect of longer EBCT was observed before GAC breakthrough (Paper II).

5. The PTR-MS analysis method, recently extended to aquatic DOM, has been shown to yield promising initial results in terms of investigating LMW compounds in drinking water (unpublished data).
6. A new open-source toolbox for pre-processing and analysis of large absorbance datasets was developed to be able to use the raw data from high-frequency measurements directly. This allows for the analysis and interpretation of the full spectral data in addition to the estimated water quality parameters provided by the sensor algorithms (Paper III).
7. The applicability of the toolbox was shown for different water sources including surface water (Lake Neden, Lake Mälaren) and river water (Gavelån) (Paper III, unpublished data and Paper IV).
8. A turbidity compensation algorithm to pre-process absorbance-based sensor data was developed. The algorithm was successfully applied to Gavleån, a river system experiencing rapid variations of turbidity due to its proximity to hydroelectric dams (Paper IV).

Based on the results from these studies, optical sensors have proven an accurate and reliable tool for real-time monitoring of different steps in drinking water treatment that can complement grab sampling. The advantage of using sensors is the fast response time and the fact that continuous time-series of events in the DWTPs are available. These data are crucial for real-time process control and the increasing automation of DTWP operations to further improve drinking water quality. The use of high-frequency measurements from online sensors must go hand in hand with the use of dedicated pre- and post-processing tools that can deal with the large datasets efficiently.

This thesis contributes to the evaluation of the use of optical sensors in drinking water treatment. In order to include them in a robust and efficient automation framework at the DWTP, more analysis is required. In particular, data quality from the sensors needs to be assured and included in the control system. This requires more research on automated outlier detection and removal as well as the calibration of an early warning system with datasets that span sufficiently long periods of time to cover the seasonal variability of the site-specific water source. This should be coupled with regular validation studies to eliminate temporal drifts and maintain accuracy. The toolbox

developed in this work is open-source so that it can be easily updated and expanded to address some of these issues.

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Popular science summary

Have you ever thought how precious it is to have direct access to tap water and in some cases even use it directly for drinking?

In the Nordic countries, drinking water is mostly provided by drinking water treatment plants (DWTPs), which use surface water (lake, river) and/or groundwater as water sources. In some cases, before arriving to the DWTP, the river water is infiltrated in the esker to have a first treatment and/or to recharge the groundwater with it, since the groundwater level is dropping due to global warming. This technique is known as managed aquifer recharge (MAR). Before arriving in your glass, the water goes through several treatment steps in the DWTP and their combination differs from one DWTP to another.

When it enters the plant, the water contains small particles (turbidity) and dissolved compounds, including natural organic matter (NOM). NOM consists of carbon-based compounds originated from the remains of plants and animals. Over the past decades, the concentrations and fluctuations of NOM in boreal and northern European surface waters have significantly increased. NOM creates several problems for the water treatment since high concentrations can affect the taste and smell of the produced water, promote growth of bacteria after the treatment, viruses and parasites and the formation of carcinogenic compounds during disinfection. Furthermore, it also negatively affects the overall performance of the treatment processes.

For example, in my studies I performed some experiments to improve two treatment steps that are affected by NOM: coagulation-flocculation and activated carbon filtration (GAC). The coagulation process consists in the addition of coagulants (e.g. aluminium and iron salts) to the incoming water which make the turbidity particles and NOM stick together and drop to the

floor so they can be removed easily. Another important step is GAC filtration. The material in the GAC has many small holes in which the NOM gets stuck or adsorbed and is removed from the water. Higher concentrations of NOM are bad for the coagulation process because it means that you need more coagulants and you create more waste that needs to be disposed of. This leads to higher economic and environmental costs. In the GAC treatment, NOM competes with micropollutants (e.g. pharmaceuticals) and other compounds for adsorption on the activated carbon, which results in having potentially harmful components in the produced water.

The results obtained at laboratory or at pilot-scale (i.e. reproduction of full-scale treatment processes at a smaller scale for testing) are useful to upgrade DWTPs with new technologies or better operational conditions. Nowadays, DWTPs are moving towards the use of sensors to further improve the treatment processes and thus water quality. With sensors, measurements can be taken at a much higher rate than in the laboratory. There are different types of sensors that are used in drinking water treatment, including sensors that measure absorbance (how much light is absorbed by the water) and fluorescence of the organic matter (how much light it emits).

In my studies, I used sensors to monitor the concentration of organic matter to evaluate variations in coagulation associated with operational changes at the DWTP, and to protect the components in the treatment process from degradation. Besides using the information from the sensors to estimate the concentration of organic matter in water, it is very interesting to use the raw data from the absorbance-based sensors, for example to determine its different characteristics.

However, since the sensors are taking very frequent measurements (often once every few minutes) for extended periods of time, this produces a lot of data that cannot be treated manually. Instead, it is necessary to use algorithms to clean the data for analysis by checking for missing data points and duplicates, correcting time shifts and identify and remove outliers. Outliers are particularly difficult to deal with because they can be due to measurement errors, maintenance work at the DWTP or other interferences. They are sometimes hard to tell apart from sudden events in the treatment process that need to be picked up because they might indicate a problem in the plant that needs to be addressed. Therefore, the outlier detection, while being partially automated, needs to be cross-checked with information about operational

changes at the DWTP. After the cleaning, the data can be analysed using specific software.

In my work, I developed an open-source software package called AbspectroscoPY with which the sensor data can be both prepared and subsequently analysed and plotted for interpretation.

Populärvetenskaplig sammanfattning

Har du någonsin tänkt på hur värdefullt det är att ha direkt tillgång till kranvatten och att i vissa fall till och med dricka det direkt ifrån kranen?

I de nordiska länderna tillhandahålls dricksvatten främst av dricksvattenreningsverk som använder ytvatten (sjöar, älvar) och/eller grundvatten som vattenkällor. I vissa fall infiltreras älvvattnet genom en rullstensås innan det anländer till vattenverket, som förbehandling och/eller för att höja grundvattennivån, eftersom nivån sjunker på grund av global uppvärmning. Denna teknik kallas konstgjord grundvattenbildning (MAR, engelska: *managed aquifer recharge*). Innan det hamnar i ditt glas har vattnet gått igenom genom flera reningssteg i vattenverket, och kombinationen av dessa steg skiljer sig från verk till verk.

När det kommer in i vattenverket innehåller vattnet små partiklar (grumlighet) och lösta föreningar, inklusive naturligt organiskt material (NOM). NOM består av kolbaserade föreningar som härstammar från nebrytningsrester av växter och djur. Under de senaste decennierna har koncentrationerna och fluktuationerna av NOM i borealt och nordeuropeiskt ytvatten ökat avsevärt. NOM skapar flera problem för reningsprocessen eftersom höga koncentrationer kan påverka smaken och lukten på det färdiga vattnet, främja tillväxt av bakterier, virus och parasiter i ledningsnätet och bilda cancerframkallande ämnen. Dessutom påverkar det också reningsprocessernas övergripande prestanda.

I mina studier utförde jag till exempel några experiment för att förbättra två behandlingssteg som påverkas av NOM: flockulering och filtrering med aktivt kol (GAC, engelska: *granular activated carbon)*. Flockulationsprocessen består i tillsats av koaguleringsmedel (t.ex. aluminium- och järnsalter) till det inkommande vattnet vilket gör att små

partiklar och NOM klibbar ihop och sjunker till botten där de lätt kan avlägsnas. Ett annat viktigt steg är GAC-filtrering. Materialet i GAC har många små håligheter där NOM fastnar eller adsorberas och därigenom tas bort från vattnet. Högre koncentrationer av NOM är ogynnsamt för flockulationsprocessen eftersom det innebär att mer koaguleringsmedel behövs vilket skapar mer avfall som behöver tas om hand. Detta leder i sin tur till högre ekonomiska och miljömässiga kostnader. I GAC-reningen konkurrerar NOM med mikroföroreningar (t.ex. läkemedel) och andra föreningar för adsorption på det aktiva kolet, vilket resulterar i att potentiellt skadliga ämnen kan finnas kvar i det färdiga dricksvattnet.

De resultat som erhålls vid laboratorietester eller tester på pilotskala (dvs. återskapande av fullskaliga reningsprocesser i mindre skala för enklare testning) är användbara för att uppgradera vattenverk med ny teknik eller för att förbättra driftsförhållanden. Numera går många vattenverk mot att använda sensorer för att ytterligare förbättra reningsprocesserna och därmed vattenkvaliteten. Med sensorer kan mätningar göras i mycket högre takt än med laboratorieinstrument. Det finns olika typer av sensorer som kan användas vid dricksvattenrening, inklusive sensorer som mäter absorbans (hur mycket ljus som absorberas av vattnet) och fluorescens av det organiska materialet (hur mycket ljus det avger).

I mina studier använde jag sensorer för att övervaka koncentrationen av organiskt material för att utvärdera variationer i flockuleringen i samband med driftsförändringar på vattenverket och för att skydda känsliga komponenter i reningsprocessen från nedbrytning. Förutom att använda informationen från sensorerna till att uppskatta koncentrationen av organiskt material i vattnet så är det mycket intressant att använda rådata från de absorbansbaserade sensorerna för att till exempel bestämma dess olika byggstenar.

Men eftersom sensorerna gör mycket frekventa mätningar (så ofta som minutvis) under längre tidsperioder, ger detta mycket data som inte kan behandlas manuellt. Istället är det nödvändigt att använda algoritmer för att städa upp och strukturera datan för vidare analys genom att söka efter saknade datapunkter och dubbletter, korrigera tidsförskjutningar samt identifiera och ta bort extremvärden (s.k. outliers). Extremvärden är särskilt svåra att hantera eftersom de kan bero på till exempel mätfel, underhållsarbete vid vattenverket eller andra störningar. De är ibland svåra att skilja från plötsliga händelser i reningsprocessen som bör

uppmärksammas eftersom de kan indikera ett problem i verket som måste åtgärdas. Därför måste avvikelsedetekteringen, även om den är delvis automatiserad, dubbelkontrolleras mot information om operativa förändringar vid verket. Efter uppstädningen kan datan analyseras med specifik programvara.

I mitt arbete utvecklade jag ett programvara med öppen källkod som heter AbspectroscoPY med vilken sensordata både kan förberedas och därefter analyseras och visualiseras för tolkning.

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Acta Universitatis Agriculturae Sueciae

Doctoral Thesis No. 2021:17

Over the past decades, the concentration and fluctuation of natural organic matter (NOM) in boreal and northern European surface waters have significantly increased. Within this thesis, absorbance- and fluorescence- based sensors were deployed in five drinking water treatment plants in Sweden. The goal was estimating NOM concentration and composition in different water sources and during treatment processes. In order to pre-process the large amount of absorbance data and compute spectral metrics for analysis, an open-source Python toolbox was developed.

Claudia Cascone received her doctoral education at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences. She received her master's degree in Environmental Sciences at the University of Salerno (UNISA), Italy.

Acta Universitatis Agriculturae Sueciae presents doctoral theses from the Swedish University of Agricultural Sciences (SLU).

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