

THESIS FOR THE DEGREE OF DOCTOR OF TECHNOLOGY

Assessing and optimizing biofilter performance in drinking water
treatment

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Division of Water Environment Technology

CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover

Top right Biological filters in one of the studied drinking water treatment plant (Photo Nashita Moona).

Top middle Granular activated carbon (Photo Nashita Moona).

Top left Scanning electron microscope (SEM) images of Filtralite® NC, collected by Amir Saeid Mohammadi.

Bottom Illustration of improved removal of fluorescent DOM by the biofilters created by Nashita Moona.

Chalmers Reproservice

Gothenburg, Sweden 2020

To my mother
Dr Nargis Murshida

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ABSTRACT

Biological filtration is a widely used treatment barrier in drinking water treatment plants to ensure the biological stability of treated water in distribution systems. Biofilters remove particulate and dissolved organic matter (DOM) and biodegradable organic matter from water. However, biofilters are difficult to study at full-scale where they are influenced by many factors that vary over time. Furthermore, there are multiple DOM removal processes occur simultaneously within BAC filter biofilms including adsorption, desorption and biodegradation. This research examined how optical properties of DOM (e.g. fluorescence spectroscopy and absorbance) can be used as an advanced characterization method to provide novel insights into performance and fundamental mechanisms of drinking water treatment via biological filtration processes.

A full-scale study involving experimental manipulation of parallel biofilters with non-adsorptive media allowed the study of DOM removal as a function of empty bed contact time (EBCT). By continuously monitoring effluent turbidity from the filters and measuring DOM removal via fluorescence spectroscopy, it was shown that turbidity and protein-like DOM removal increased linearly with increasing EBCT up until at least 80 min EBCT. Removal of refractory humic-like DOM removal improved, although to a smaller extent. This was contrary to the prevailing view that there is a negligible improvement in DOM removal efficiency at contact times longer than 30 min. Striking a good balance between DOM removal by biofiltration and the cost of longer EBCT can in turn result reduced operational costs while improving finished water quality.

This research was also carried out to distinguish biotic (biological degradation) and abiotic (adsorption and desorption) processes occurring within biofilter media. To distinguish these requires a suitable abiotic control, i.e. filter media with the same chemical properties but no biology. To identify abiotic controls for BAC filter experiments, a batch-scale study was conducted using gamma irradiation as a sterilization method. However, by measuring DOM removal via fluorescence spectroscopy, it was possible to observe that the chemical properties of biofilter materials changed even at low gamma doses (2.5 kGy) and a dose-related release of protein-like fluorophores occurred, possibly from the biofilm. The gamma-irradiation method was therefore deemed to be unsuitable for producing abiotic controls for BAC studies.

In a further attempt to identify abiotic controls for BAC filter experiments, the temperature was utilized as an alternative control strategy. Depending on responses to temperature in batch experiments, it was deduced whether DOM removal predominantly occurred via adsorption (chemisorption/physisorption) or biological degradation. Under the particular experimental conditions, there was little evidence of biological removal; instead, removal of DOM fractions emitting at longer wavelengths (“humic-like”, >430 nm) was consistent with chemisorption,

removal of DOM emitting at intermediate wavelengths (“humic-like”, 390-420 nm) was consistent with physisorption, and multiple mechanisms were indicated for “protein-like” (<380 nm) DOM. Abiotic mechanisms like adsorption are often assumed to be unimportant for aged BAC filters; however, these results suggest that abiotic processes may be important for some DOM fractions.

Ultimately, this research aims to inform the design and operation of full-scale biological filters under Nordic climate conditions. To that end, a simple and cost-effective operational strategy was investigated for improving short-term DOM removal in full-scale biological filters. The strategy involved replacing a small fraction of saturated filter media with new media. Relative to replacing the entire media, this approach required lower capital cost and shorter downtime and maintained conditions for biological filter functioning. The modified biological filters showed improved DOM removal lasting for several weeks.

The results of this thesis demonstrate that fluorescence spectroscopy, due to high analytical precision and sensitivity, is a sensitive method for tracking DOM removal via biological filters. Additionally, it suggests there are opportunities to improve drinking water treatment by promoting one or other of the removal mechanisms depending on the incoming water quality. For example, allowing longer contact time in summer when there is elevated biodegradable DOM removal or performing partial renewal of biofilter media after heavy rains when incoming water has relatively high organic pollutants. Overall, these results are relevant to water producers that aim to optimize biofilters performance under strained operating conditions.

Keywords Biofilter, full-scale biofilters, optical properties, drinking water, dissolved organic matter, treatment optimization, sterilization.

LIST OF PUBLICATIONS

This thesis was developed in the Drinking water research group at Chalmers University, in the Water Environment Technology Division at the Department of Architecture and Civil Engineering. The research work was done under the supervision of associate professor Thomas Pettersson, associate professor Kathleen Murphy, senior Lecturer Mia Bondelind and adjunct professor Olof Bergstedt.

This research was funded by the National drinking water research centre DRICKS at Chalmers University of Technology, Göteborg Stad (Kretslopp och Vatten), Swedish Water and Wastewater Association (SVU), Västvatten AB, VIVAB, Trollhättan Energi, Sydsvatten and Norrvatten.

This thesis includes the following appended papers, referred to by Roman numerals

- I. Moona, N., Holmes, A., Wünsch, U.J., Pettersson, T.J. and Murphy, K.R (2020). Full-scale manipulation of empty bed contact time to optimize dissolved organic matter removal by drinking water biofilters. *Submitted*.
- II. Moona, N., Wünsch, U.J., Bondelind, M., Bergstedt, O., Sapmaz, T., Pettersson, T.J. and Murphy, K.R. (2019). Temperature-dependent mechanisms of DOM removal by biological activated carbon filters. Published in *Environmental Science Water Research & Technology* **5**, 2232-2241. DOI [10.1039/C9EW00620F](https://doi.org/10.1039/C9EW00620F)
- III. Moona, N., Wünsch, U.J., Simonsson, I., Bondelind, M., Bergstedt, O., Pettersson, T.J. and Murphy, K.R. Effects of gamma irradiation as a sterilization method on biological activated carbon. *Manuscript*.
- IV. Moona, N., Murphy, K.R., Bondelind, M., Bergstedt, O. and Pettersson, T.J. (2018). Partial renewal of granular activated carbon biofilters for improved drinking water treatment. Published in *Environmental Science Water Research & Technology* **4(4)**, 529-538. DOI [10.1039/C7EW00413C](https://doi.org/10.1039/C7EW00413C)

The author of this thesis has made the following contributions

Paper I Contributed to the planning and the sample collection from the full-scale drinking water biofilters, performed the DOM measurements (absorbance, fluorescence and DOC), carried out the data analysis, wrote the first draft of the paper, critically revised the manuscript after consultation with co-authors.

Paper II Contributed to the sample collection from the full-scale drinking water biofilters, designed the batch-scale experiments, performed the experiments and DOM measurements, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript after consultation with co-authors and external review until publication.

Paper III Contributed to the sample collection from full-scale drinking water biofilters, designed the experiments, prepared the samples for gamma irradiation, performed the batch-scale experiments, assisted with measurements of irradiated carbons characterizations and DOM

measurements, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript.

Paper IV Contributed to design of the experiment, collected samples from the full-scale drinking water biofilters, ran the experiments, performed the DOM measurements, carried out the data analysis and interpretation, wrote the first draft of the paper and critically revised the manuscript after consultation with co-authors and external review until publication.

Other works that were authored or co-authored during the realization of this dissertation are listed below, which are not appended to the Thesis

Moona, N., Murphy, K.R., Bondelind, M., Bergstedt, O. and Pettersson, T.J. (2018). Partial replenishment of biological activated carbon filters to improve natural organic matter removal. In E-proceedings of the International Water Association (IWA) - World Water Congress & Exhibition.

Rosén, L., Lindhe, A., Bergion, V., Sokolova, E., Bondelind, M., Malm, A., Pettersson, T.J., Moona, N., Murphy, K., Vinas, V., Lång, L., Sörén, K., Sjöling, Å., (2020). Risk-based decision support for safe drinking water supply. Swedish Water and Wastewater Association, Stockholm, In Swedish Riskbaserat beslutsstöd för säker dricksvattenförsörjning.

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Gothenburg, December 2020

Nashita Moona

ACRONYMS AND ABBREVIATIONS

The following notations are used in the main text of the thesis

AC	Activated carbon
AOC	Assimilable organic carbon
BAC	Biological activated carbon
BDOC	Biodegradable dissolved organic carbon
BET	Brunauer-emmet-teller
BOM	Biodegradable organic matter
CDOM	Chromophoric or coloured dissolved organic matter
DBP	Disinfection by-products
DBP-FP	Disinfection by-product formation potential
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWTP	Drinking water treatment plant
EBCT	Empty bed contact time
EEM	Excitation and emission matrices
FDOM	Fluorescent dissolved organic matter
FEEM	Fluorescence excitation and emission matrix
FI	Fluorescence index
FRI	Fluorescence regional integration
GAC	Granular activated carbon
HIX	Humification index
HPSEC	High-performance size-exclusion chromatography
MB	Methylene blue
NOM	Natural organic matter
PAC	Powdered activated carbon
PARAFAC	Parallel factor analysis
PAU	Potential acetate uptake
PLS	Partial least squares
RSF	Rapid sand filtration
RU	Raman unit
Sr	Slope ratio
SUVA	Specific UV absorbance

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1 INTRODUCTION

Drinking water is essential to human health and life. However, one in every three people globally does not have access to safe drinking water (World Health Organization, 2019). Therefore, the United Nations has included ‘Water and Sanitation to all’ (Goal 6) as one of the seventeen sustainable development goals to be achieved by 2030. Several of the other sustainability goals signifies the importance of water-related issues (Goal 5 Gender equality, Goal 10 Reduce inequalities and Goal 14 Life below water) and human health (e.g. Goal 3 Good health and Goal 15 life on land) (United Nations, 2016). Thus, six out of seventeen sustainable development goals can be tied to water.

Achieving the United Nations sustainable development goals are challenging due to many issues, mainly climate change and a large increase in global population. This is evident through the increased flooding or prolonged drought periods and the overall increase in global temperatures that influence the terrestrial and aquatic ecosystems (Preston, 2004; Seekell et al., 2011). As a consequence, an increase in natural organic matter (NOM) in the water sources have been widely observed around Northern Europe (Evans et al., 2005; Ritson et al., 2014; Worrall et al., 2009), Central Europe (Hejzlar et al., 2003) and North America (Monteith et al., 2007), where it decreases the performance of drinking water treatment plants (DWTP), impeding their ability to meet water quality standards year-round (Sjerps et al., 2017). Such influence in raw water quality can occur both abruptly and gradually, for example, through a gradual increase in humic content (main organic constituents of soil (humus), peat and coal) and pathogen levels, or by sudden algal blooms (Moore et al. 2008) and outbreaks of infectious diseases (Murdoch et al. 2000; Burge et al. 2014).

To ensure that safe drinking water is supplied to consumers, more stringent drinking water guidelines have been proposed by the World Health Organization than before (World Health Organization, 2017). DWTPs must adapt to both long- and short-term changes in water quality, to meet these guidelines. One way to do this is to have a clear understanding of the function of each treatment step to upgrade or optimize existing treatment technologies when necessary, or to implement new treatment technologies (Slavik et al., 2009). However, upgrades are usually expensive and require large investments. Therefore, the research presented during this dissertation has focused on understanding the mechanisms within existing biological filters in DWTP and suggest ways to optimize operations of these biofilters using only relatively minor changes in operational practices.

Dissolved organic matter (DOM; organic material that passes through a 0.45 μm filter) poses a constant challenge to proper drinking water treatment. DOM is ubiquitous in all water sources and has characteristics that vary based on the nature and geographical location of its sources, seasonal and chemical factors (e.g. temperature and pH) and human activities connected to the source water catchment (Bridgeman et al., 2011; McDonald et al., 2004). There is on-going research to find efficient ways to remove DOM from the source water. Different treatment steps like coagulation-flocculation-sedimentation-filtration, slow-sand filtration and membrane filtration processes, are applied to reduce both the DOM and pathogen concentrations in the drinking water. However, varying source water quality due to climate change present extra challenges for DOM removal by increasing the cost of water treatment operations (e.g. higher chemical consumption), demanding new infrastructure to remove new target compounds (e.g., pharmaceuticals, algae etc.) and/or associated challenges that they create (e.g., taste and odor compounds, toxic algal by-products) (Emelko et al. 2011). Thus, this increased load on existing treatment processes can exceed the critical design thresholds ranges, and therefore, necessary to optimize the treatment technology currently in use.

Due to the complexity of DOM chemical structure and function, variety requires a various number of different physical and chemical methods are needed to characterize DOM. Dissolved or total organic carbon (DOC/TOC) and absorbance of ultraviolet light at 254 nm (UV_{254}) are commonly used in regular DWTPs operations because these parameters do not require sophisticated instrumentation and can also be implemented for real-time monitoring. Unfortunately, these methods give limited information about DOM character (Weishaar et al., 2003). Therefore, a method is needed that would allow to get more information with respect to DOM concentration, character and treatability regarding DOM removal. Recent advances in fluorescence spectroscopy have succeeded on developing accurate, easy to use and faster instruments with greater optical efficiency and higher sensitivity (Coble, 1996; McKnight et al., 2001; Stedmon et al., 2003). For this reason, the use of fluorescence spectroscopy for the characterization of DOM in the water industry has received increased attention in recent years (Han et al., 2020; Heibati et al., 2017; Vera et al., 2017).

Biological filtration is becoming a widely used treatment step in DWTPs. Biological filters ensure the biological stability of treated water in distribution systems. It is a common practice in North America is to use biofiltration to remove both particles and biodegradable organic matter (BOM) from water. Biological filtration processes can be in the form of soil passage, (e.g. river-bank filtration, dune infiltration), rapid sand filtration (RSF), dual-media filtration

(DMF), slow sand filtration (SSF) and Granular activated carbon (GAC) filtration. During this dissertation, the focus is provided on DOM removal via two biological filtration set-ups DMF filtration using Filtralite® Mono-Multi as media and GAC filtration.

Filtralite® Mono-Multi is a relatively cheap filter media with zero to little adsorption capacity that is quite popular in the Norwegian DWTPs (Eikebrokk, 2001). Thus, the main removal mechanism occurring within this filter is via particle separation and biological degradation (Ødegaard et al., 2010). Filtralite® has shown a better alternative for the biological treatment of drinking water than other alternative carrier material like sand or anthracite (Tyagi et al., 2010). Filtralite® has been extensively studied as an efficient biological as well as physical treatment media (Eikebrokk, 2001; Jonassen, 2016; Pivokonský et al., 2020; Ødegaard et al., 2010). However, optimization of the filtration performances focusing specifically on DOM under actual condition is yet to be evaluated.

GAC filtration is a widely used treatment technology implemented in many DWTPs to remove DOM. GAC filters are good at adsorbing micro-pollutants e.g. Perfluorooctanesulfonic acid (PFOS), algal degradation products, and petroleum residues. However, dissolved organic carbon (DOC) in raw water saturates the GAC filters pores with irreversibly bound DOM and reduces the adsorption capacity (Velten, 2008). A biofilm forms on the filter media converting them to biofilters (Servais et al. 1994; Velten, 2008) in which microorganisms break down and remove biodegradable DOM. BAC filtration reduces biodegradable organic matter (BDOC), chlorine demand, disinfection by-product precursors, taste and odor compounds, turbidity, and indicator organisms such as coliforms (Rittmann et al., 2002). Even though GAC filters are widely used in DWTPs, the actual removal mechanisms and amount of removal via biological degradation and adsorption occurring within these filters are not fully understood (Çeçen et al., 2011).

1.1 Research questions and scope of this thesis

The general aim of this thesis is to determine the extent of DOM removal by existing biofilters in several drinking water facilities around Gothenburg region and investigate ways to improve their performance, using the optical properties of DOM, fluorescence spectroscopy. Two kinds of biofilters were investigated during this dissertation granular activated carbon (GAC) biofilters (also known as biological activated carbon filters (BAC)) and Filtralite® biofilters. GAC biofilters combine both adsorption and biological degradation to remove various DOM fractions, whereas Filtralite® biofilters remove DOM only via biological degradation. The main

aim of this dissertation is to investigate the extent of fluorescent DOM removal by these various mechanisms within the biofilters and link these changes to optimize and improve DOM removal by the biofilters.

Figure 1-1 depicts the connections between the four papers during this dissertation (PI-IV).

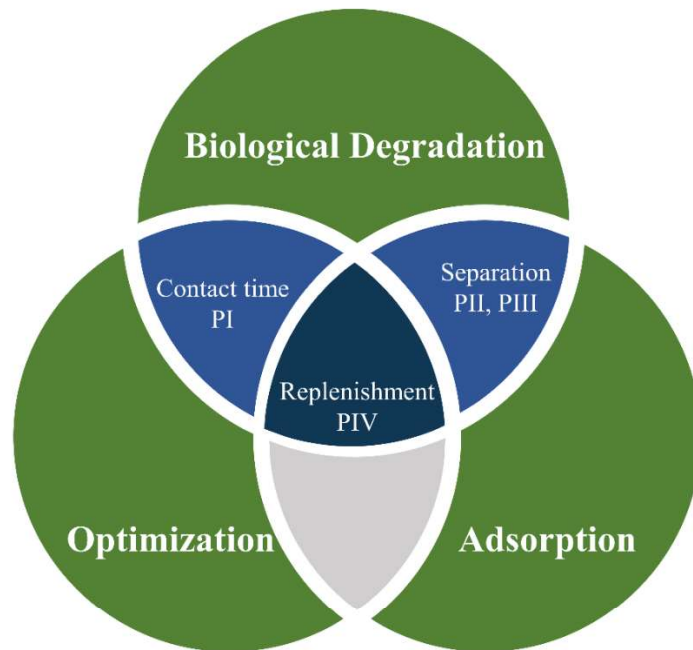


Figure 1-1 Illustration of the research areas studied in the papers (PI-IV) included during this dissertation.

To present the research work in a structured way, a set of research questions were formulated. The following research questions investigated in this PhD study are listed below

RQ1 What are typical fluorescence signals that can be found in DWTPs around Gothenburg, Sweden? [Paper I, II and IV]

RQ2 Can online monitoring of turbidity or UV absorbance track overall DOM removal by the biological filters? [Paper I and IV]

RQ3 How much DOM is removed by biofilters with non-adsorptive media (Filtralite®) in comparison to adsorptive media (GAC)? [Paper I, II and IV]

RQ4 How does the performance of these BAC filters vary seasonally? [Paper II]

RQ5 Is it possible to separate adsorption from biological degradation within a BAC biofilter? [Paper II]

- a) Is gamma irradiation a suitable sterilization method for obtaining an abiotic control for adsorption processes in BAC filters? [Paper III]

RQ6 Can the DOM removal by biofilters at existing DWTPs be improved using simple operational practices?

- a) How do changes in empty bed contact time (EBCT) influence DOM removal in Filtralite® biofilters? [Paper I]
- b) What strategies exist to meet short term concentration peaks of DOM in raw water, and what are their effects on outgoing water quality? [Paper IV]

1.2 Overview of the thesis and included papers

This thesis is based on the work reported in Paper I-IV. The purpose of this section is to provide a high-level overview of the work and the papers.

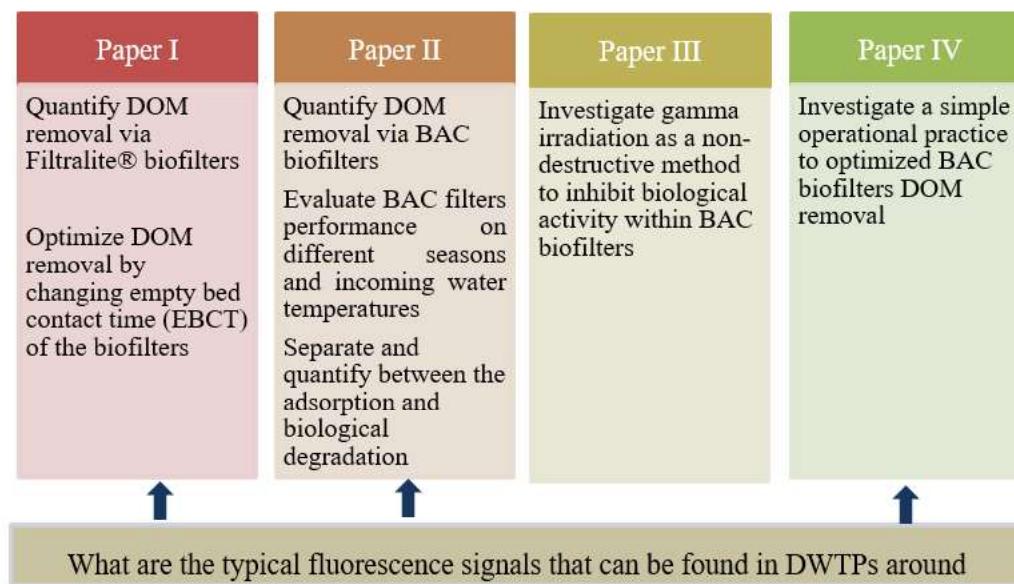


Figure 1-2 Overview of research questions studied in included papers of this dissertation.

In *Paper I*, the optimization of DOM fractions removal by Filtralite® biofilters were studied in full-scale filters at Kungälv (a city in Sweden) DWTP. Optimizing DOM fraction removal by the biofilters is an important factor to consider when these filters are used to treat drinking water. The four biofilters in the DWTP were operated at four empty bed contact time (EBCT) typically found in the DWTPs (ranging from 15 – 80 min) for a period of 8 weeks and removal efficiency of DOM were monitored using several DOM measurement parameters. It was concluded that a contact time beyond 30 min is necessary to remove the DOM fractions that are likely to be removed via biofilters. This conclusion is expected to have an impact to design future DWTPs that want to have biofilters as a treatment step.

Seasonal variability in DOM removal by drinking water BAC filters is often attributable to temperature changes. DOM removal within the BAC filters occurs by a combination of

adsorption, desorption and biodegradation while each of these mechanisms responds differently to temperature. To properly understand the dynamics occurring among these mechanisms at different seasons, it is important to properly understand the response of these mechanisms at different temperatures. In *Paper II*, the aim was to decouple these mechanisms occurring within the BAC filters by measuring DOM removal fractions at different temperatures typically observed from summer to fall season in Sweden. Under the experimental condition, there was little evidence of biological removal. Non-biological mechanisms of DOM removal by aged BAC filters are often assumed to be unimportant; however, these results suggested they are important for some DOM fractions, especially during the periods of reduced microbial activity.

Biodegradation, adsorption and desorption mechanisms occur simultaneously within the activated carbon-based BAC filtration system used for DOM and micropollutants removal. To fully understand the contribution of each of these three processes occurring within BAC biofilters, it was necessary to discriminate the respective contributions of biotic and abiotic mechanisms. This is specifically important for DOM fractions that are both adsorbable and amendable by biological oxidation. To the end, gamma irradiation was studied in *Paper III* as a method to suppress biological activity. It was demonstrated that gamma irradiation did not change the surface pore structures of BAC filters, but it did change the adsorption capacity of DOM onto BAC filters allowing the BAC filter material to perform differently after gamma irradiation. As an outcome of the study, it is concluded that even though gamma irradiation is a method used in the food industry to sterilize spices, it is not suitable as a sterilization method for BAC filter studies.

In *Paper IV*, a strategy was utilized within existing full-scale BAC filtration process in DWTPs, to prevent system overload during short-term deterioration in raw water quality. In this full-scale study, 10% bed volume of saturated GAC was replenished with new GAC. Afterwards, the performance of the modified and reference filters was monitored and compared using real-time monitoring as well as grab sampling. Using fluorescence spectroscopy, different DOM fractions were identified. It was observed that specific DOM fractions were more preferentially adsorbed whereas some of the DOM fractions were biological degradation. As an outcome of this full-scale study, recommendations for the water producers regarding short term DOM peak management were formulated.

2 BACKGROUND

This chapter begins by describing the problem related to DOM in drinking water sources and gives a general overview of drinking water treatment processes. Afterwards, details of the biological filtration processes for drinking water treatment are described since DOM removal through this treatment process is the main focus of the thesis. Various DOM characterization techniques are included that as well were utilized to investigate the DOM removal performance by the filtration processes.

2.1 What is Dissolved organic matter (DOM)

Drinking water is derived from raw surface and groundwater sources around the world. To convert raw water to drinking water and reduce the risk of water-borne diseases, raw water often needs to be converted by various kinds of treatment steps to remove DOM and pathogens from treated water. Natural organic matter (NOM) is part of the substances that need to be removed from drinking water. NOM is produced from different hydrological, biological and geological processes within surface and ground waters. NOM quality and quantity vary from one location to another as well as within same water body as a result of natural phenomena such as droughts, floods, and rainfalls (Kundzewicz et al., 2014; Matilainen et al., 2002; Sharp et al., 2006). It can be produced/degraded through biological activities of algae and microbes (autochthonous NOM) or introduced from outside of the water body via drainage within watersheds containing a breakdown of terrestrial organisms (Allochthonous NOM) (Eikebrokk et al., 2004).

NOM can be present in various forms like dissolved, colloidal and particulate organic matter. Dissolved organic matter (DOM) is an operational definition which indicates the fraction of NOM that passes through the 0.45 – 1 μm filter. DOM can have both hydrophobic and hydrophilic fractions with dominant components as humic and non-humic substances (Fabris et al., 2008). The former includes residual degradation products, largely from decomposition and solubilization of soil organic matter having high molecular weight aromatic and aliphatic organic compounds and the latter includes biomolecular classes like fulvic acids, proteins, amino acids and carbohydrates of various molecular size and properties (Hudson et al., 2007; Huguet et al., 2009; Thurman, 2012). Differentiating DOM based on their origin can also be of interest, whether DOM is produced within the water body (i.e. microbially derived or autochthonous) or from outside sources (i.e. terrestrial derived or allochthonous) (Lee et al., 2006).

2.1.1 Problems related to DOM in drinking water treatment and distribution

DOM is a carrier of toxic organic and inorganic pollutants like pesticides and radionuclides and increases the solubility of these hydrophobic anthropogenic compounds while making them more bioavailable (Reid et al., 2000). The humic acids and fulvic acids fraction of DOM forms strong metal complexes with heavy metals that have high transportation ability, bioavailability and toxicity (Matilainen et al., 2011). Presence of DOM affects many aspects of water treatment by a deteriorating performance of individual unit processes (i.e. coagulation, adsorption and oxidation). In the drinking water treatment plant (DWTP), DOM increases coagulant demand and production of sludge (Jarvis et al., 2006). The humic fraction of DOM competes with undesirable micro pollutants adsorption through by decreasing available adsorption sites, reducing the surface area of GAC by blocking pores and increases negative surface charge by adsorbing humic substances (Newcombe, 1994). DOM can as well foul/clog the membranes used in drinking-water treatment (Carroll et al., 2000). Therefore, it is important to remove DOM within the DWTPs by optimization of treatment processes. DOM is a precursor of disinfection by-products (DBPs) and unremoved fractions of DOM produce DBPs like halogenated Trihalomethanes (THMs), Haloacetic acids (HAAs), Haloacetonitriles (HANs), Haloketones and trichloronitromethane (Bond et al., 2012; Jiang et al., 2017; Serrano et al., 2015) along with numerous aromatic halo-DBPs. The biodegradable dissolved organic carbon (BDOC) promotes bacterial growth in the water distribution network (Van der Kooij et al., 1984) and reduces the quality of finished water by altering their organoleptic properties (color, taste and odor). (Matilainen et al., 2011; Owen et al., 1995; Singer, 1999).

2.1.2 Quantification and characterization of DOM

The characterization and quantification of DOM are difficult due to their chemical complexity and underlying variability. To understand the underlying mechanisms of DOM impacts on water treatment, significant research has been conducted to use bulk physiochemical properties to characterize DOM. However, this identification represents averaged parameters for the mixture of components within DOM (Hur et al., 2009). Commonly used surrogates for DOM quantification are total organic carbon (TOC) or dissolved organic carbon (DOC) or absorbance at 254 nm (Gone et al., 2009). TOC/DOC provides an overall quantity of organic matter in the particulate and dissolved pools (Hur et al., 2009). UV-Vis spectroscopy is a simple and fast optical measure that has gained popularity to estimate concentrations of organic matter

(Matilainen et al., 2011). However, absorbance over 250 nm is thought to be caused by aromatic moieties within DOM (Korshin et al., 2009) and indicator of specifically aromatic organic matter and do not capture all organics (Matilainen et al., 2011). Additionally, chemical compositions that cannot be captured by TOC/DOC and UV absorbance have been shown to influence different treatment processes e.g. causing fouling in membranes (Henderson et al., 2011) and may cause regrowth in the distribution network (Van der Kooij et al., 1984). To study the composition and source of additional DOM fractions in water, various laboratory-based analytical technologies and methods have been employed such as infrared spectroscopy, nuclear magnetic resonance (NMR), mass spectrometry, and chromatographic methods (Matilainen et al., 2011). Furthermore, advanced techniques like Fourier transform ion cyclotron resonance mass spectrometry and NMR spectroscopy can provide diverse information on molecular structures within the DOM pool (Lavonen et al., 2015). These methods are tedious, requires expensive instrumentation and expertise involving complex data interpretation.

Spectroscopic properties of the optically-active fractions of DOM such as UV-visible spectra and fluorescence spectra can identify the concentration, composition and source of DOM (Coble et al., 2014). As a result, these methods of DOM characterization have gained significant attention due to the low cost and minimal sample analysis time as well as have high sensitivity while having the potential to be used as an on-line monitoring tool (Bridgeman et al., 2011; Shutova et al., 2014).

2.2 Optical properties of DOM

In this section, the theories behind the measuring and analyzing the optical properties of DOM, utilized during this dissertation are briefly described.

2.2.1 Absorbance

Dissolved organic fractions of NOM that can absorb ultraviolet and visible light, is referred to as chromophoric or colored DOM (CDOM) (Coble et al., 1998). CDOM comprises 10-90 % of the total DOM pool and therefore constitutes a significant DOM fraction in aquatic ecosystems controlling the photochemical reactions of the surface water and nutrient and light availability for aquatic organisms (Thurman, 1985). CDOM absorbs light in visible wavelengths (380-700 nm) as well as from ultraviolet UVA (315-400 nm), UVB (280-315), UVC (200-280nm) range. CDOM light absorption decreases in an approximately exponential manner with increasing irradiation wavelength across the visible-UV spectrum. Most CDOM that absorb light have

aromatic groups and are associated with a humic fraction of DOM (Korshin et al., 1997a). Thus, absorbance is a semi-quantitative indicator of DOM concentration in natural waters.

Some of the common absorbance spectral parameters used to characterize CDOM in drinking water treatment are listed below

Absorption at 254 nm (UV₂₅₄)

Aromaticity of organic matter influences the reactivity of DOC and humic substances to oxidants like chlorine (Reckhow et al., 1990). The absorbance of light above 250 nm is believed to be due to aromatic moieties within the molecules (Korshin et al., 1999) and therefore is selective towards aromatic organic matter and not all organics are captured in the measure (Matilainen et al., 2011). Therefore, in the absorption spectra analysis, UV₂₅₄ is widely used as an aromaticity monitoring tool for DOC concentration within DWTPs (Helms et al., 2008; Weishaar et al., 2003). Ozonation and adsorption onto activated carbon (AC) are known to reduce UV₂₅₄ from the treated water (Altmann et al., 2014; Bahr et al., 2007).

Specific UV absorbance (SUVA)

Another indicator used for UV absorbance analysis is the absorption at 254 nm normalized to DOC and referred to as a specific UV absorbance (SUVA) and calculated as shown in Equation 1.

$$\text{SUVA} = \frac{\text{UV}_{254}}{\text{DOC}} \quad (1)$$

SUVA was shown to correlate strongly with the percentage of DOM aromaticity determined by ¹³C-NMR of humic isolates ($R^2 = 0.97$) by Weishaar et al. (2003). Additionally, SUVA is a good indicator of the humic fraction of DOM and effectiveness of coagulation to remove these humic fractions (Edzwald et al., 1999). High SUVA value indicates that the organic matter is largely composed of hydrophobic, high molecular weight organic material, whereas low SUVA value indicates that mostly hydrophilic and low molecular weight fraction with low charge density (Figure 2-1) (Edzwald et al., 1999).

SUVA >4 L/m-mgC	SUVA ≈2-4 L/m-mgC	SUVA <2 L/m-mgC
<ul style="list-style-type: none"> • Aquatic humic • High hydrophobicity • High molecular weight • High UV₂₅₄ • High chlorine demand • High DBP-FP 	<ul style="list-style-type: none"> • Mixture of aquatic humics and other NOM • Mixture of hydrophobic and hydrophilic NOM • Mixture of different molecular weight • Medium UV₂₅₄ • Medium chlorine demand • Medium DBP-FP 	<ul style="list-style-type: none"> • Mostly non-humics • Low hydrophobicity • Low molecular weight • High UV₂₅₄ • High chlorine demand • High DBP DBP-FP

Figure 2-1 Interpretation of SUVA values for freshwaters adopted from Edzwald et al. (1999).

Spectral slope and Slope ratio (S_r)

A spectral slope parameter can be obtained by fitting the absorption values to the exponential function. The spectral slope of the short-wavelength intervals, S_{275_295} and S_{350_400} , can be determined using linear regression of the log-transformed a spectra (Helms et al., 2008). This slope describes the relative steepness of the spectra (Twardowski et al., 2004). CDOM composition and molecular weight can be characterized using the spectral slope. Helms et al. (2008) used the absorption spectral slope ratio to identify the sources of DOM along the estuarine transect. The slope ratio (S_R), calculated from S_{275_295} divided by S_{350_400} was also determined for water samples and found to correlate with molecular weight obtained from size-fractionation analyses (Helms et al., 2008).

2.2.2 Fluorescence excitation and emission matrix (FEEM)

Due to its structural properties, some organic matter can absorb light and fluoresce. Fluorescence as a type of luminescence can be explained using a Jablonski Energy Diagram (Figure 2-2) (Lakowicz, 1983). An electron in an atom or a molecule is excited to a higher energy level after the absorption of photon energy from the ground state. Fluorescence occurs when energy is lost as light (photon) when the excited electron rapidly returns to the ground stage (Lakowicz, 1983). The DOM exhibit fluorescence in both ultraviolet and visible range is referred to as fluorescent dissolved organic matter (FDOM).

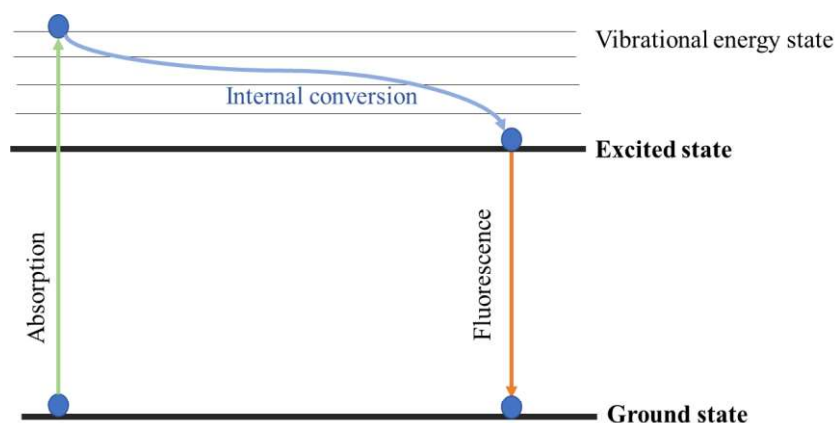


Figure 2-2 Simplified Jablonski diagram.

The wavelengths at which absorption of energy (excitation) and emission occur are specifically controlled by molecular structure. Therefore, a fluorophore or group of fluorophores that are present in FDOM can be identified using their specific optical properties (Hudson et al., 2007).

By fluorescence spectroscopic analysis, based on the presence of FDOMs associated with humic-fulvic and protein-like compounds, rapid characterization of DOM with high sensitivity and minimal sample preparation can be achieved (Sanchez et al., 2013).

During fluorescence analysis is done by exciting a sample by a light source (a xenon arc lamp) and measuring the emitted light. FDOMs are identified by collecting fluorescence excitation-emission matrices (FEEM) emitted by FDOMs present in water at multiple excitation wavelengths (Baker, 2001; Coble et al., 2014). By observing the location of a prominent peak of an excitation-emission pair (Figure 2-3), specific organic compound groupings of FDOM within DOM can be identified and the maximum intensity of the peak correlates with concentration (Bieroza et al., 2011). Thus humic-like DOM having longer emission wavelength (>350 nm) and protein-like NOM having shorter emission wavelength (<350 nm) can be distinguished by peak location.

Different regions within the fluorescence spectra can be linked with a different fraction of DOM (Chen et al., 2003). In Table 2-1, the classification of various DOM fraction according to previous literature is presented. These previously reported fluorescence fractions that have been observed in drinking water samples have additionally been observed in diverse aquatic samples. The fractions typically contain humic-like components from the terrestrial or autochthonous origin, and protein-like components containing tyrosine-like or tryptophan-like fluorophores.

Fluorescence intensity usually correlates with DOC. However, since different DOC fraction has different absorbance characteristics, this increasing trend with DOC might not be linear especially at higher concentration. Measured intensity can be reduced by other light-absorbing molecules or ions (McKnight et al., 2001). Thus absorbance correction is necessary for samples having greater than 0.05 cm^{-1} absorbance or DOC concentration higher than 1 mg C/L before the experiment (Kothawala et al., 2013). Fluorescence analysis is sensitive to pH (Patel-Sorrentino et al., 2002), temperature (Baker, 2005), the polarity of solvent (Lakowicz, 1983), metal ion plus organic substances interactions (Reynolds et al., 1995).

Table 2-1 Different fluorescent peaks and excitation/emission wavelengths and source of origin according to literature (Coble, 1996; Coble et al., 1998; Murphy et al., 2008; Stedmon et al., 2003).

Peak name	Description	Possible sources	Excitation/Emission
A	UVC humic-like	Terrestrially delivered allochthonous	< 250-260 / < 380-480
B	Tyrosine-like Protein-like	Microbially delivered autochthonous	< 270 – 280 / 300 - 320
C	UVA humic-like	Terrestrially delivered allochthonous	< 320 – 360 / 420 - 460
M	Marine humic-like	Microbially delivered autochthonous	290-310 / 370 - 410
T	Tryptophan-like	Microbially delivered autochthonous	270 – 280/ 320 – 350

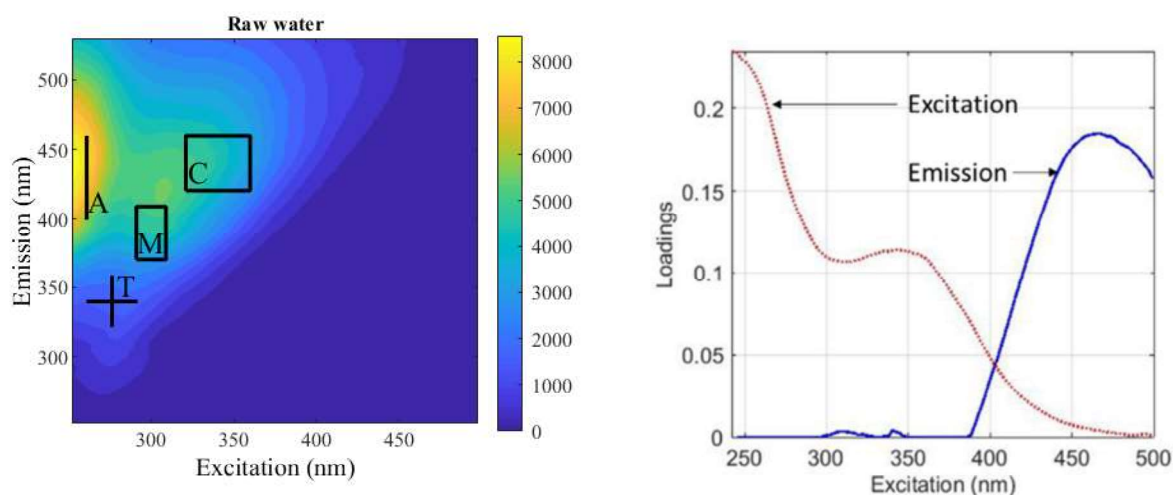


Figure 2-3 A raw water FEEM. Collected at Lackarebäck DWTP during sample collection for Paper IV (left), Fluorescence regions are denoted as Peak C fulvic-like fluorescence, Peak A humic-like fluorescence, Peak T tryptophan-like fluorescence and Peak M Marine humic-like. Excitation and emission spectra of a component identified using parallel factor analysis in Paper IV (right).

Some other well-known methods for DOM characterization using FEEMs are

Fluorescence regional integration

The fluorescence regional integration (FRI) model proposes to integrate the fluorescence spectra instead of specific peak information (Figure 2-4). FEEMs were divided into five regions Protein regions (I) and (II), fulvic acid-like (III), microbial by products-like (IV) and humic acid-like (V), by determining the volume of fluorescence beneath a given region, the particular importance of the fluorescence region was quantified (Chen et al., 2003). Regional integration techniques have been previously applied to characterize drinking and wastewater samples (Chen et al., 2003), landfill leachates (He et al., 2011) and membrane bioreactor permeate and foulant (Wang et al., 2009). However, in FRI method it is assumed that different groups of fluorophore to have different peaks, but in reality, fluorescent components generally possess multiple overlapping peaks (Ishii et al., 2012).

Fluorescence index (FI)

The ratio of fluorescence intensity measured at 470 to 520 nm at an excitation wavelength of 370 nm (Cory et al., 2005). FI has been used to estimate the contributions of microbial vs terrestrially derived DOM within DOM pool (Cory et al., 2005; Fellman et al., 2010; Huguet et al., 2009). FI is found to have an inverse relationship with DOM aromaticity (McKnight et al., 2001). Additionally, as FI value increases, the C/N ratio decreases (Wolfe et al., 2002).

Freshness index ($\beta\alpha$)

The ratio of emission intensity at 380 nm divided by the maximum intensity between 420 and 435 nm at 310 nm excitation) (Parlanti et al., 2000). Freshness index is an indicator of the contribution of recently produced DOM, where β represents more recently derived DOM and α represents more decomposed DOM (Fellman et al., 2010).

Humification index (HIX)

HIX was first proposed by Zsolnay et al. (1999) as the peak area under the emission spectra between 435–480 nm divided by 300–445 nm, at 254 nm excitation. (Ohno, 2002) afterwards updates area from emission 435–480 nm divided by the peak area 300–345 nm and 435–480 nm at 254 nm excitation. HIX indicates the extent of humification of DOM (Fellman et al., 2010).

2.3 Multivariate data analysis

FEEMs contain large volumes of intricate data, whose explanation can be difficult (Park et al., 2018). To reduce the high dimensionality of 3-D fluorescence excitation-emission matrices (EEMs) multivariate analysis tools have been extensively used (Bridgeman et al., 2011). Parallel factor analysis (PARAFAC) is the dominant tool used in the water treatment field (Murphy et al., 2011; Stedmon et al., 2000). Some other analysis techniques have also been applied to fluorescence spectra, for instance, artificial neural networks (ANN), self-organized maps (SOM; a type of ANN), partial least squares (PLS), multiple linear regression (MLR), and multivariate curve resolution (MCR) (Bieroza et al., 2011).

Parallel factor analysis (PARAFAC)

Multivariate analysis techniques like parallel factor analysis (PARAFAC) can separate collected excitation-emission matrices into chemically and mathematically independent fluorescence components. PARAFAC maybe the most useful of the available multivariate analysis techniques in investigating DOM in a diverse environment (Stedmon et al., 2005).

PARAFAC modelling can decompose multi-way data of FEEMs (sample \times excitation \times emission) into a set of model parameters (Figure 2-4) that are independently-varying using the alternating least-squares algorithm (Bro, 1997). Thus the result of PARAFAC modelling finds independent fluorescent ‘components’ with unique excitation-emission spectra and the intensity of each component in each sample is termed as ‘score’ (Bro, 1997). PARAFAC utilizes Equation 2 to reduce a dataset of FEEMs into a set of trilinear terms and a residual array (Bro, 1997)

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + \varepsilon_{ijk} \quad i = 1, \dots, I; j = 1, \dots, J; k = 1, \dots, K \quad (2)$$

Here, x_{ijk} is the fluorescence intensity of the i th sample at the k th excitation and j th emission wavelength, a_{if} is directly proportional to the concentration of the f -th fluorophore in the i th sample (defined as scores), and b_{jf} and c_{kf} are the estimates of the emission and excitation spectrum of the f -th fluorophore (defined as loadings), respectively (Stedmon et al., 2003) (Stedmon et al., 2003). The residuals (ε_{ijk}) represent unexplained signal containing noise and other un-modelled variations. According to *Beer-Lamberts law*, in an ideal case, there are no interactions between the underlying fluorophores in the FEEM (Stedmon et al., 2008). This implies that the fluorescence peaks wavelengths position for each fluorophore does not “shift”

but the fluorescence maxima of the mixture (e.g. in the FEEM of raw water and treated water samples) may shift depending on the relative contribution of each of the fluorophores (wavelength position of the fluorescence peaks representing each fluorophore (Stedmon et al., 2008)).

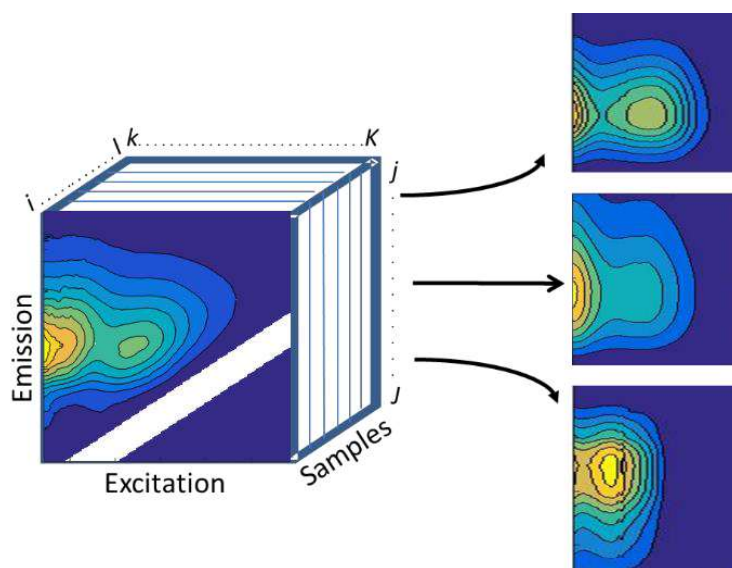


Figure 2-4 A drinking water FEEM dataset was decomposed into three underlying fluorescence components using PARAFAC (Paper IV, Figure 4)

PARAFAC model is sensitive to the number of components for fitting. Therefore, selection of the correct number of component is essential for samples containing unknown fluorophore composition (Stedmon et al., 2005).

2.3.1 Application of optical properties of DOM in drinking water

Fluorescence analysis is becoming a popular analysis method to monitor organic matter composition within natural and engineered water systems. Individual components of FDOM fractions of DOM have been revealed to correlate well with biochemical oxygen demand (BOD) (Hudson et al., 2008), chemical oxygen demand (COD) (Baker et al., 2004; Bridgeman et al., 2013), an indicator of total coliforms and *E. coli* (Cumberland et al., 2012).

Spectral slopes derived from the absorbance spectra of DOM absorbing between 280-350 nm has been shown to correlate with the yields of commonly regulated DBPs like Trihalomethanes (THMs) and Haloacetic acids (HAAs) (Korshin et al., 1997b). UV absorbance at 272 nm has been reported as the best indicator of total organic halogen (TOX) (Korshin et al., 1997a). TOX

is the sum of all halogenated organic products present in water TOX, regardless of their identity. Differential absorption is another approach to detect subtle changes in NOM structure (Ates et al., 2007).

2.4 Biological filters used in drinking water treatment

The following sections provide a brief description of DOM removal via biological filtration treatment step used in drinking water treatment specifically in GAC/BAC and Rapid sand filters biofiltration processes.

2.4.1 Biologically activated carbon (BAC) filtration

Activated carbon (AC) is used for the removal of pesticides and other organic chemicals, taste and odor compounds, cyanobacterial toxins and total organic carbon. AC has been produced from porous media from natural sources like wood, coal, coconut shells or peat. These carbonaceous materials are thermalized under a controlled condition and a porous structure with a large surface area (500-1500 m²/g) is formed that has a high affinity for organic compounds. Activated carbon is used either as powdered (PAC) or in granular (GAC) form. PAC has typically diameter less than 0.15 mm and GAC has diameters ranging from 0.5 to 2.5 mm. Both form activated carbon fundamentally has similar adsorption properties despite differences in particle size (Karanfil, 2006).

GAC filters are employed as fixed bed adsorbers such as granular media filters or post-filters. It is an effective barrier against many dissolved contaminants present in water. GAC can preferentially absorb contaminants from water due to its large surface area, surface chemistry and fast adsorption kinetics (Wei et al., 2008). It can remove a hydrophobic fraction of humic acids (HAs), lower molecular weight humic- and fulvic acids (Matilainen et al., 2006; McCreary et al., 1980). On the contrary, some researcher has found that lower molecular weight matter is more amendable than higher molecular weight matter due to size exclusion effect (Ignatev et al., 2019; Karanfil et al., 1999; McCreary et al., 1980). Therefore the adsorption NOM is mainly controlled by the molecular size distribution of NOM and pore size distribution of carbon (Newcombe et al., 2002). Background NOM reduces the adsorption of trace level contaminants. Therefore if the purpose of installing GAC filtration is to remove trace organics, then the filter must be placed as a post-filter filtration unit (Binnie et al., 2002).

The main mechanism of adsorption onto GAC are adsorption of soluble NOM, physical filtration of particulate NOM (Emelko et al., 2006). NOM adsorption occurs in the mesopores

(100-1000 °Å) and large micropores (<100 °Å) of GAC. Large size NOM (>10,000 °Å) is not well removed due to size exclusion effect and lower molecular size is also not absorbable as a majority of them are hydrophilic (Ignatev et al., 2019; Matilainen et al., 2006).

DOM imparts negative influence on GAC filters adsorption capacity and thus the adsorption capacity reduces rapidly and a biofilm forms on the filters material converting them to biologically active GAC filter (BAC). There are many modification and methods that are proposed to improve water treatment processes, the most promising, environmentally friendly and economical solution is BAC treatment (Liao et al., 2013). It can mitigate the limitations of GAC filtration treatment (reduction of adsorption capacity over time and requires frequent regeneration). The active biofilm that covers GAC filters increased the life span of exhausted GAC filters since NOM and artificial organic pollutants are continuously removed by biodegradation and partial adsorption (Liao et al., 2013).

Four processes describe the removal mechanisms for NOM in BAC filters under different temperature regimes. First, physisorption is a physical process that is relatively weak in nature, exothermic and potentially reversible. Thermodynamic considerations predict that physisorption is favored by decreasing temperature (Rashed, 2013). Second, chemisorption involves chemical reactions between the adsorbate and the surface functional groups on BAC. Chemisorption is rather strong in nature and typically irreversible (Rashed, 2013), and chemisorbed species tend to accumulate on the BAC surface reducing its adsorption capacity. Higher temperatures favor chemisorption (until saturation point) as this provides the activation energy required to form adsorbate–adsorbent bond (Alkathiri et al., 2020; Schnelle Jr et al., 2015; Summers et al., 1988). Third, biodegradation occurs when microbes use the surfaces provided by GAC to metabolize biodegradable substances in their surroundings. Biological degradation is governed by enzyme activity, which increases with temperature up to a species-dependent tolerance limit (Aktaş et al., 2006). Finally, desorption from BAC can be a source of reversibly attached DOM if there is a lower concentration of DOM in the water than on the BAC surface (Aktaş et al., 2006). Desorption from activated carbon is an important mechanism affecting BAC and GAC performance when operating conditions change suddenly (Aktaş et al., 2007; Churchill et al., 2020). Desorption can occur by two mechanisms displacement and/or back-diffusion. Displacement occurs when adsorbed compounds are displaced by compounds with a higher adsorption affinity, releasing the less adsorptive compounds back into solution. Back-diffusion occurs when the concentration of DOM in the water surrounding the BAC material decreases rapidly.

The concentration gradient is addressed by the diffusion of compounds back into solution (Corwin et al., 2011). While displacement may occur constantly during the operation of a BAC filter system. Back-diffusion is most likely only noticeable during times of sudden changes in operating conditions, e.g. following rainfall events or clean water backwashing during which DOM concentrations decrease rapidly.

BAC filtration process is usually placed after advanced oxidation processes (AOP) or ozonation processes to remove small molecular, hydrophilic, and biodegradable organic carbon (BDOC) fraction of NOM produced through the partial oxidation of NOM. DOC removal through BAC filters is relatively small in the context of an entire DWTP (Hozalski et al., 1995).

The benefit of BAC filters

BAC filters have the following added benefit over GAC filters

- BAC filters extend the service life of GAC filters and it does not require frequent regenerations of the filter media (Aktaş et al., 2007).
- BAC filters ensure the biostability of effluent by removing biodegradable organic compounds (BDOC) and assimilable organic carbon (AOC). These parts of NOM are not affected by coagulation and remains in high concentration after conventional treatment (Volk et al., 2000).
- The removal of non-biodegradable compounds benefits as well by BAC filters biofilm as bio-regeneration increases the adsorptive capacity of GAC (El Gamal et al., 2018; Seredyńska-Sobecka et al., 2006).
- BAC filtration reduces the significant fraction of disinfection by-product formation potential (DBP-FP) especially for THMs and chlorine demand of treated water (Graham, 1999; Volk et al., 2000).

2.4.2 Non-adsorptive media (Filtralite®) biofiltration

During this dissertation, one study focused on biofiltration using non-adsorptive media, Filtralite® (Paper I). Filtralite® is a filter material designed with a special porosity to allow higher flow rates and longer running times that can be used in both drinking water preparation, wastewater treatment and other more specialized applications. Filtralite® consists of expanded clay and is made up mainly of SiO₂ (63%), Al₂O₃ (17%) and Fe₂O₃ (7%). Filtralite® has gained considerable attention as an alternative to sand/anthracite filter media due to its rough and angular surface, sharp edges and high porosity which allows large surface area for microbial

growth (Melin et al., 1999). Consequently, Filtralite® can be used as a suitable media for biological filter design and can reduce primarily ammonium, iron and manganese. In DWTPs in Canada observed effective removal of both microbial energy and nutrient compounds even at low temperatures (6°C) where Filtralite® biofilters were used as a biological pre-treatment step before membrane filtration (Peterson et al., 2007).

Studies focusing on DOM removal via Filtralite® filter as biofiltration media reported TOC reductions of 13–28% ($C_0 = 2\text{--}5\text{ mg/L}$) across biofilters receiving pre-ozonated water spiked with a humic concentrate (Melin et al., 1999). In Sweden, Filtralite® has been used in Boden DWTP (Norrbotten) as a prefiltration process to remove iron and manganese from raw water and found Filtralite® to reduce both metals by 95% (Winkler, 2017). Persson et al. (2007) compared Filtralite® with GAC to remove Geosmin and MIB from a Swedish drinking water source and found Filtralite® constitutes a viable option as a carrier medium for direct biological filtration of surface water. However, as pointed out by Davies et al. (2012), a single medium tends to show worse removal performance but slower head loss development due to the high porosity of the material. Thus, two different grades of Filtralite® (NC Normal density and HC high density) called Filtralite® MonoMulti is recommended to improve turbidity removal while keeping the benefit of slower head loss (Saltnes et al., 2002; Ødegaard et al., 2010). The physical characteristics of the filter media, as specified by the manufacturers, are given in Table 2-2. Scanning electron microscopy pictures of the filter materials from the full-scale filter at Kungälv DWTP (Fig. 2-5) clearly show the differences in pore size between two different Filtralite® HC and NC.

Table 2-2 Filtralite® Filter material physical data, as reported in the manufacturers' datasheets.

Parameter	Filtralite® HC	Filtralite® NC
Grain size, nominal range (mm)	0.8–1.6	1.5 - 2.5
Effective grain size, d_{10} (mm)	0.9	1.7
Uniformity coefficient, d_{60}/d_{10} (-)	<1.5	<1.5
Primary porosity (-)	0.4	0.73
Grain density (kg/m^3)	1600	1260
Bulk density (kg/m^3)	820	530

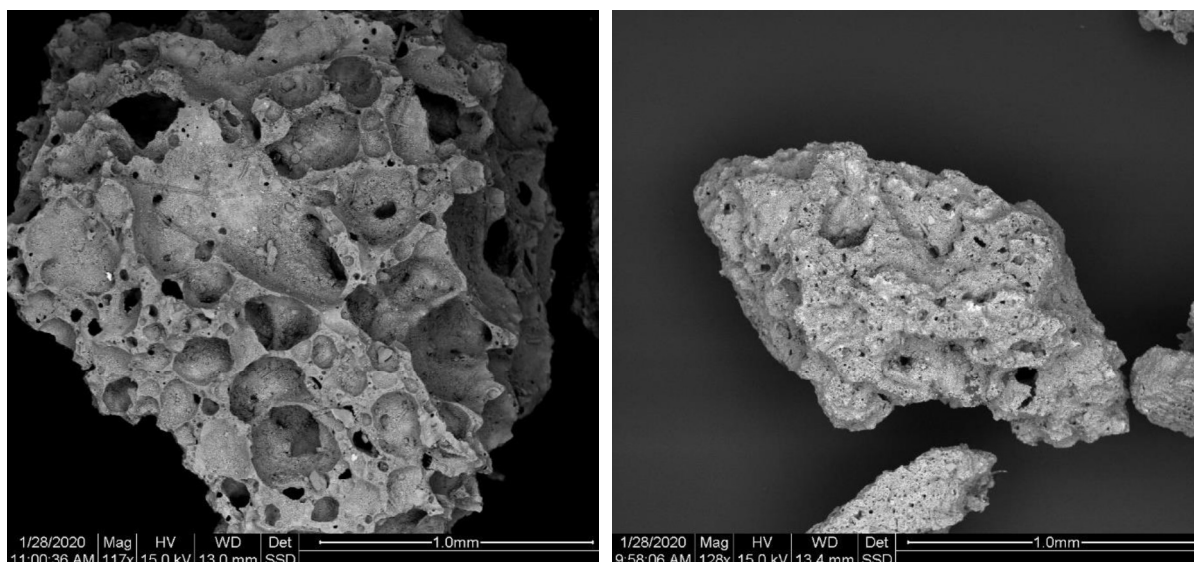


Figure 2-5 Scanning electron microscope (SEM) images of Filtralite® NC 1.5–2.5mm (left) and Filtralite® HC 0.8–1.6 (right) with SEM. Samples were collected from Kungälv DWTP (Paper I).

2.5 Research gaps

In the early 1970s, the capability of bacteria which proliferate in biofilter materials to remove organics in the water was first reported. It is now known that GAC surface acts as a support material favorable for some environmental bacteria (such as nitrifying bacteria or heterotrophic bacteria) to metabolize biodegradable organic matter from water (Huck, 2000). In the 1980s, many European DWTP incorporated a combination of pre-ozonation and BAC filters in their treatment processes. Presently, BAC filters are mostly operated in a passive process, and the design and operational parameters are generally focused on media configuration, backwash strategy and loading rate (Lauderdale et al., 2012). Recently the study of removal mechanisms of DOM within drinking water biofilters have resurfaced since monitoring and assessment of biofilters performance has historically proved to be problematic (Moona et al., 2019; Peleato, 2017).

DOM removal by biofilters is influenced by many factors. From operation perspective the performance of biofilters for NOM removal is known to be affected by the empty bed contact time (EBCT), temperature, backwashing strategy and pretreatment steps (e.g. ozonation) (Emelko et al., 2006). While many biofilters are operated passively, improved performance in terms of both higher levels of removal and additional organics removal may be achievable, when the design and operation of biofilters are optimized (Basu et al., 2016). Optimization of

BAC filter performance by influencing design and operational parameters such as media configuration, backwash strategy and loading rate to improve the pre-flocculation (without any chemical coagulation and settling step) and post-flocculation filters performance have been investigated extensively for sand/anthracite and GAC filters (Fu et al., 2017; Lauderdale et al., 2012; Wilson, 2015). Most studies on Filtralite® biofilters focused on comparing NOM removal performance in pilot-scale GAC, sand/anthracite and/or Filtralite® filters (Azzeh et al., 2015; Persson et al., 2005). Eikebrokk (2001) studied removal NOM from drinking water by pilot-scale coagulation-filtration experiments within Chitosan and Filtralite® filters and concluded Filtralite® was a good alternative to anthracite, with lower rates of head loss build-up, and increased filter run length and filter storage capacity. Helmer et al. (2019) studied particle removal at different EBCT by pilot-scale parallel filters of Filtralite® MonoMulti, sand and sand/anthracite and confirmed Filtralite® had better efficiency of the Filtralite® media than the best conventional media. However, DOM removal studies using full-scale Filtralite® biofiltration without pretreatment for membrane filtration is scarce.

In GAC biofilters/BAC filters, adsorption (physisorption and chemisorption), biological degradation and desorption of previously adsorbed organics occur simultaneously (Korotta-Gamage et al., 2017). Temperature has a distinct and explicit influence on all these processes. For example, Schreiber et al. (2005) and Moll et al. (1999) observed that biological degradation is governed by enzyme activity, which increases with temperature up to a species-dependent tolerance limit. In case of adsorption, increasing temperatures increase adsorption rate due to a faster adsorbate diffusion (Taghdiri et al., 2013) but the overall adsorption capacity can be either increased or reduced (Moreno-Castilla, 2004), depending on whether the adsorption process is endothermic or exothermic. Since these processes are temperature-dependent, for treatment plants located in regions where there is a large seasonal temperature variation, the processes controlling BAC-mediated DOM removal would be expected to vary seasonally. Thus, it may be possible to decouple these simultaneous processes by observing temperature-dependent responses on the removal of various DOM fractions measured by e.g. fluorescence spectroscopy, LC-OCD or HP-SEC to identify the removal mechanism responsible for removing a specific DOM fraction.

DOM is a complex mixture that in treatment plants, is usually assessed by monitoring its overall abundance using bulk parameters like color, total/dissolved organic carbon (TOC/DOC) or UV absorbance at 254 nm (UV₂₅₄) (Fu et al., 2017; Weishaar et al., 2003). However, such bulk indicators do not distinguish between different DOM fractions, although for example, lower-

molecular-weight DOM fractions are known to be more efficiently removed by adsorption, and protein-like components, known to be removed more effectively by biodegradation (Ciputra et al., 2010; Peleato, 2017). Specific DOM fractions based on source and compositional changes in DOM can be distinguished from bulk DOM sensitively and accurately using fluorescence spectroscopy. Thus, monitoring DOM fractions using fluorescence spectroscopy may give more specific information on DOM removal performance.

Another possible technique to separate biological from adsorption processes is to suppress biological degradation. Comparing the performance of abiotic controls to regular BAC filter material will help to understand the scope of biodegradation to remove organic pollutants. Many different mechanisms are present in literature to look for ways to create abiotic controls to suppress biodegradation. Autoclaving, treatment with sodium azide or air drying are some of the methods used in literature to produce abiotic controls. The difficulty is that all these techniques (including autoclaving, treatment with sodium azide (NaN_3), gamma irradiation, air drying) alter the chemical and physical properties of the BAC samples as well as the biology. Sodium azide (NaN_3) is among the most common strategies evaluated, however, bacteria are not equally impacted by this compound (Klimenko et al., 2010) while adding NaN_3 increases the ionic strength of the sample thereby modifying the adsorption of dissolved compounds (Lotrario et al., 1995). Autoclaving is rather simple to perform but was found to cause loss of integrity of the biofilm and subsequent release from the surface where it is attached (Berns et al., 2008).

A sterilization method that has been shown to work in soil samples is gamma irradiation (Berns et al., 2008). However, gamma irradiation as a possible mechanism to suppress biodegradation from BAC filter material is yet to be investigated. Therefore, one of the objectives was to evaluate gamma irradiation as a potential technique to generate an abiotic control for BAC filter material.

While understanding the scope of these removal mechanisms occurring within BAC filters. It is necessary to utilize this knowledge to optimize and enhance the DOM removal via BAC filters during stressful conditions. Seasonal periods of elevated NOM and organic pollutant concentrations in raw water due to e.g. heavy rainfall, snowmelt runoff, or lake turnover and algae bloom, leads to rapid changes in raw water quality (Hood et al., 2003), affecting treatment efficiency and making it difficult to meet water-quality standards year-round (Parsons et al., 2005; Vogt, 2003). Hence, it is crucial that DWTPs can adapt to both long- and short-term changes in water

quality, to ensure that safe and reliable drinking water can always be provided. One way to ensure this is to upgrade or optimize existing treatment technologies, or to implement new treatment technologies (Slavik et al., 2009). However, upgrades are usually expensive to implement and require large investments. For economic and practical reasons, efforts to improve the removal of NOM in continuously-operating treatment plants are usually directed towards optimizing and improving existing treatment steps instead of implementing costly upgrades (Collins et al., 1985). An objective of this thesis was to investigate how to optimize existing DTWP operations using only minor changes.

3 MATERIALS AND METHODS

This chapter presents a summary of the developed methods, described in full and employed in the appended papers.

3.1 Study areas and experimental set-up

3.1.1 Full-scale studies

Kungälv DWTP (Paper I)

In Paper I, four full-scale biofilters at Kungälv DWTP were utilized. Kungälv DWTP is in Kungälv Municipality, Sweden (Figure 3-1) and receives raw water from river Göta Älv which is the second-largest water source of Sweden. The DWTP produces 8000 m³/day (design capacity is 170,000 m³/day). The treatment train in the DWTP consists of aeration, biofiltration through Filtralite® rapid sand filters, direct coagulation over membrane filtration (ultrafilter), GAC filtration and UV disinfection (Figure 3-2). The biofilters act as a pretreatment step before membranes.

The focus of the full-scale study on Kungälv DWTP was to study the effect of EBCT on DOM removal. This study took place on fall period (August-October 2019). The EBCT during the regular operation was 80 min. On 15th September 2019, the EBCT was changed from 80 min to 15-, 30- and 50 min in three of the parallel filters. One filter was kept at 80 min EBCT as a reference filter (Paper I, Figure 1). Samples were collected once-twice weekly before the EBCT change, to establish a baseline condition and six weeks following the EBCT change.



Figure 3-1 Map (Google Maps) of southern Sweden showing the location of the three drinking water treatment plants (DWTPs) that were sampled within this PhD project.

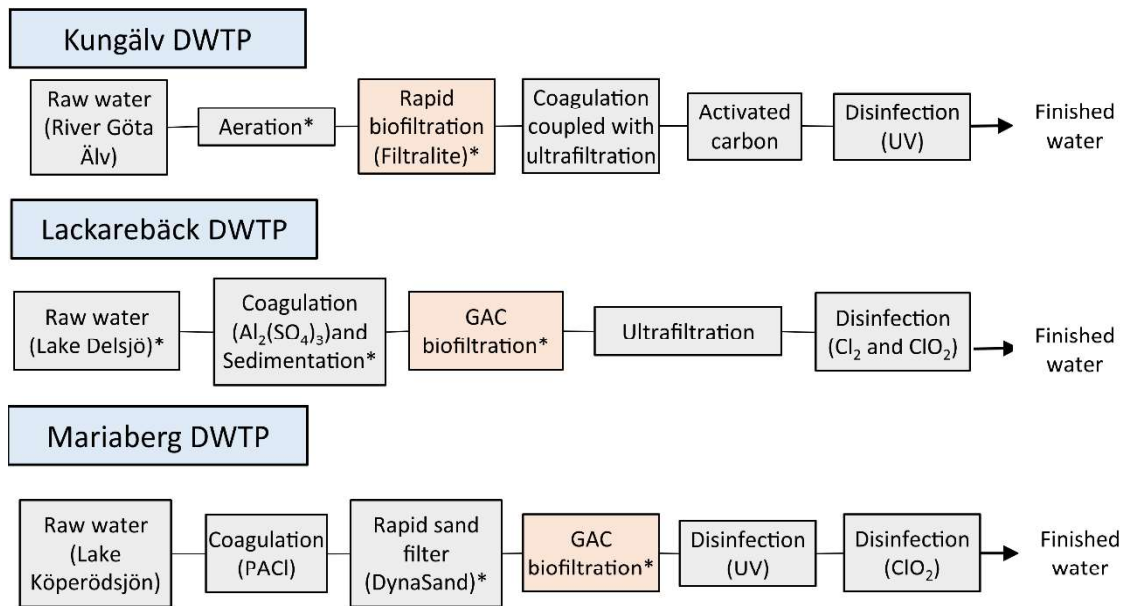


Figure 3-2 Overview of treatment processes used at the three drinking water treatment plants studied in paper I-IV. Sampling points are marked with asterisks.

Marienberg DWTP (Paper IV)

In Paper IV, full-scale BAC filter study took place in a DWTP called Marienberg in Uddevalla Municipality, Sweden (Figure 3-1). Marienberg DWTP is and receives raw water from Lake Köperödssjön which is in a forested area. The treatment train consists of flocculation using poly-aluminum chloride, rapid sand filtration using DynaSand™ filters (divided in two halls, A and B, consisting of 24 and 22 filters respectively), followed by GAC filters and disinfection using UV and chlorine (Figure 3-2 and Figure 1, Paper IV). The experiment was carried out during the summer (July – August 2015). This study focused on the optimization of DOM removal by BAC filters using simple operational practices.

In Marienberg DWTP (Paper IV) three full-scale BAC filters (F6, F7 and F4) were replenished with fresh GAC, and two filters were used as references (Rf2 and Rf5). Hydraulic modelling was performed to quantify the proportions of inflow to the BAC filters from the two DynaSand™ filter halls. Details of the replenishment steps are provided in Paper IV (section 2.3 ‘Experimental design’).

3.1.2 Lab-scale studies

Lackarebäck DWTP (Paper II and III)

Lackarebäck DWTP is the second largest in Sweden and located in Gothenburg municipality (Figure 3-1), Sweden. The water is collected from Lake Stora Delsjön and the lake is a reservoir where water is pumped from river Göta älv. The water treatment steps in Lackarebäck includes conventional treatment, with coagulation using aluminum sulphate, sedimentation, rapid filtration through activated carbon, membrane filtration using ultrafilter, and final disinfection with chlorine and sodium hypochlorite (Figure 3-2).

Two studies were performed on the full-scale biofilter material collected from Lackarebäck DWTP. Both studies took place during summer to fall period (July–October 2018) from a single randomly-selected filter that had been in operation for over three years. Details of the filters and experimental set-up are presented in Paper II (Figure 1) and III. The main aims were i) to study the removal of different DOM fractions via GAC biofilters in this DWTP (Paper II) ii) to study the seasonal influence on the DOM removal performance and can adsorption and biodegradation process be separated using temperature influence (Paper II), iii) can gamma irradiation be used as a method to separate biodegradation (Paper III).

3.2 Analytical methods and data processing

In this section, short summaries of the analytical methods used during this dissertation are given. Detailed information can be found in the respective papers.

3.2.1 Dissolved organic carbon (DOC)

DOC was measured using a Shimadzu TOC-V_{CPH} carbon analyzer with auto-sampler TOC-ASI-V. Samples were acidified to pH = 2 using HCl (37% v/v) prior to analysis. Non-purgeable organic carbon (NPOC) method was used to analyze DOC were all the inorganic carbon were removed through purging the sample with CO₂ free purified air for 5 minutes. DOC concentration was calibrated using a 5-point calibration curve for potassium Phthalate standards solutions (between 1.0-10.0 mg C/L).

3.2.2 Fluorescence and absorbance spectroscopy

CDOM fluorescence and absorbance analysis were measured using Aqualog spectrofluorometer (Horiba Inc.) with a 10-mm path length. The excitation and emission matrices (EEMs) were measured at 20°C with 2-3 sec integration time. The emission

wavelengths ranged from 245 nm to 800 nm at 2.33 nm increments and the excitation wavelengths ranged from 220 nm to 700 nm.

Raman scans of MilliQ water in a sealed cell was obtained every day as blank FEEMs. The measured FEEMs were imported into MATLAB for post-processing. Fluorescence intensities were converted to Raman unit (RU) by dividing to the Raman area of the blank within the emission wavelength of 378 - 424 nm at an excitation wavelength of 350 nm (Lawaetz et al., 2009; Murphy et al., 2010). Before modelling, the scatter bands (Raman and Rayleigh) were removed and data were corrected for concentration biases (inner filter effects) (Andersen et al., 2003; Lakowicz, 1983).

The absorbance spectra were measured simultaneously to fluorescence measurement in Aqualog fluorescence spectrophotometer for wavelength from 200-700 nm. Absorbance data were used to calculate the specific UV absorbance SUVA, by dividing the absorbance (in m^{-1}), at 254, with the DOC concentration.

3.2.3 Online monitoring

At Kungälv DWTP (Paper I), Filtralite® filter effluents were monitored online for turbidity using an A spectrophotometer multi-parameter probe (Spectrolyser™ iscan, Messtechnik GmbH) iscan. The probe was calibrated and was installed at the outlet of the Filtralite® filters.

At the Mariaberg DWTP (Paper IV), to monitor the continuous relative changes in treated water from the filters, a multi-parameter spectrophotometer probe Spectrolyser was placed at the outlet from the BAC filters. Parameters that were measured by this probe were TOC, UV absorbance 254, turbidity (in FNU and NTU units), color and transmittance. More details on sampling in Paper IV.

3.3 Biofilm characterization analysis

3.3.1 Potential acetate uptake rate

Acetate consumption of bacteria on the biofilters was measured according to Stoquart et al. (2014), which estimates heterotrophic biomass from the rate of acetate consumed. Potential acetate uptake rate (PAU) was measured in 1 L beakers containing 500 ml of test medium, which contained a saturating initial concentration of sodium acetate (15 mg Na-acetate/L, equivalent to 4.4 mg C/L) and was supplemented with NH_4Cl (0.65 mg N/L) and phosphate buffer (K_2HPO_4) (0.06 mg P/L). Filtralite® (40g ww) was added to the beakers containing test

medium, then the slurries were maintained at $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ under agitation (ca. 80 rpm) for 24 h. Aliquots (5 ml) were withdrawn every 120 min and filtered through a pre-rinsed $0.45\text{-}\mu\text{m}$ polyethersulfone membrane. Acetate concentration was measured in each aliquot using a high-performance liquid chromatography (HPLC) system equipped with a UV detector (Shimadzu) and an Aminex HPX-87H column (Bio-Rad), with 5 mM H_2SO_4 eluent pumped at 0.5 ml/min.

3.4 Surface characterization techniques

3.4.1 Brunauer-Emmet-Teller (BET)

The specific surface area, pore-volume, and pore size of the irradiated and non-irradiated BAC material after gamma irradiation (Paper III) were determined by Brunauer-Emmet-Teller (BET) (ASAP 2020, Micromeritics).

3.4.2 Methylene blue

To measure the change in adsorption capacity due to gamma irradiation, MB adsorption kinetics were studied (Paper III). A stock solution of 1.0 g/L was prepared by dissolving the appropriate amount of MB in 100mL and completing to 1000mL with ultrapure water. From this stock solution, 0.2 mg/L MB solutions were prepared. In 10 mL plastic flasks, 0.1 g of BAC material were added and kept in contact for 20-hours. The solution was shaken at 125 rpm under 20°C in an orbital shaker. The sample solution was then removed using a syringe and analyzed with a spectrophotometer at a wavelength of 660 nm a Shimadzu UV-VIS 2600 spectrophotometer. The amount of MB absorbed onto BAC filter material was calculated based on Equation (3)

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

Here, C_0 and C_e (mg/L) are the initial and equilibrium liquid phase concentration of MB, respectively, V (L) is the volume of solution and W (g) is the mass of adsorbents used.

4 RESULTS AND DISCUSSION

4.1 DOM removal by biological filters

During this dissertation, two different kinds of biological filters with two different type of media were studied. One of the media was of a non-adsorptive kind, called Filtralite® (Paper I) and other media was of an adsorptive kind, granular activated carbon (GAC), (Paper II, III and IV). These biofilters had different pre-treatment steps as described in section 3.1. In all the drinking water treatment plants (Kungälv, Lackarebäck and Mariaberg) optical properties as well bulk measurement parameter of DOM (DOC) were utilized to monitor and optimize biological filters performances.

4.1.1 Bulk DOM removal by biofilters

From Table 4-1, the observed removal of DOC within these three DWTP is presented. Removal of DOC by the biofilters was within 10-20% by the biofilters. Additionally, relatively similar removal of DOC by biofilters with different media and different pre-treatment processes were observed in the biofilters. As opposed to new GAC filter, where around 50% removal of DOC can be expected via adsorption (Servais et al., 1994), removal within biological filters is less pronounced. This removal range is within the typical removal range of DOC (5–20%) by biological filters and the removal kinetics is highly impacted by various operational factors (Moll et al., 1999; Terry et al., 2018).

4.1.2 Optical properties of DOM

Absorbance

UV absorbance at 254 nm (UV_{254}) indicates the presence of unsaturated carbon bonds including aromatic compounds, which are generally recalcitrant to biodegradation; therefore, a decrease in UV absorbance results in an increase in biodegradability (Lawrence, 1980; Novak et al., 1992). It is used widely in drinking water production for DOM characterization and process optimization (Korshin et al., 2009; Matilainen et al., 2011).

Coagulation-flocculation treatment considerably reduced UV absorbing CDOM from raw water in Lackarebäck ($68 \pm 7\%$, Paper II and Table 4-1) and Marieberg DWTP ($85 \pm 4\%$, Paper III and Table 4-1). Removal of UV absorbing CDOM were 10 and 14% in Lackarebäck and Mariaberg DWTP respectively. On the contrary in Kungälv DWTP (Paper I), the biofilters were placed at the beginning of the treatment chain and influent UV_{254} to the biofilters were

considerably higher than Lackarebäck and Mariaberg DWTP (Table 4-1). At Kungälv DWTP, the biofilters were not reducing UV₂₅₄ at a contact time of 15-50 min whereas a contact time of 80 min reduced UV₂₅₄.

Table 4-1 DOC removal by biofilters for the four studies in this dissertation.

DWTP	Kungälv (Paper I)	Lackarebäck (Paper II and III)	Mariaberg (Paper IV)
Biofilter material	Filtralite®	Granular activated carbon	Granular activated carbon
Pre-treatment	Aeration	Coagulation-flocculation-sedimentation	Coagulation-rapid sand filtration via DynaSand™ filters
Surface load (m/h)	1.9-2.0	3.9-4.4	3.1-3.5
Media depth (m)	2.5	0.9-1.0	0.9-1.0
Contact time (min)	15-80	15-20	20-22
Incoming DOC range (mg/L)	7.0-7.4	3.8-4.8	3.1-3.7
DOC Removal by biofilters (%)	14 ± 2 ¹	10 ± 1 ²	13 ± 1 ³
Incoming UV₂₅₄ to biofilters (/cm)	0.13 ± 0.02	0.05 ± 0.02	0.05 ± 0.07
UV₂₅₄ Removal by biofilters (%)	10 ± 2 ¹	10 ± 4 ²	14 ± 3 ³

¹ Removal by biofilter at 80 min EBCT, ² removals measured during the autumn season, ³ removal by biofilter without new GAC replenishment

Fluorescence

From fluorescence spectroscopic analyses, the fluorescent fingerprint of dissolved organic matter (DOM) was collected by scanning the excitation-emission matrixes (EEMs). Various methods were utilized to track the changes of fluorescent DOM within biofilters.

In Kungälv DWTP, peak picking method and fluorescence indexes were used to monitor changes in fluorescent DOM at different EBCT. By observing the intensity of specific peaks (peak T, A, M and C in this case, Figure 4-1), change in DOM character can be quantified. There were measurable variations observed for humic-like peak A, M, C and protein-like peak T among the influent and effluent from the filters in Kungälv DWTP (Paper I).

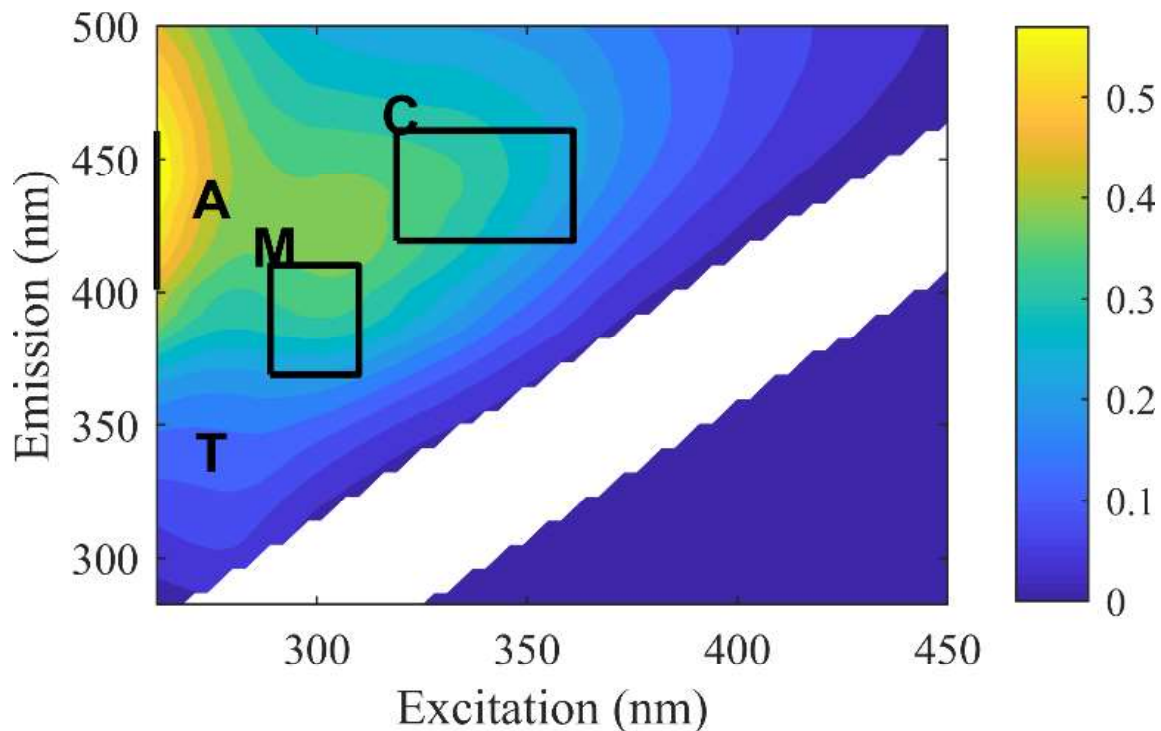


Figure 4-1 Fluorescence FEEM from the effluent of the biofilter from Kungälv DWTP.

In Lackarebäck DWTP (Paper II and III), batch-scale studies were performed on biological filter media. The PARAFAC decomposition of the fluorescence datasets featured seven underlying FDOM components. In Mariaberg DWTP (Paper IV), PARAFAC decomposition of collected FEEM found three independently varying FDOM components (Paper IV, Figure 4). The excitation and emission maxima of all identified components and their characteristics obtained from samples collected during this dissertation are listed in Table 4-2. Five of the identified components (three humic-like and two protein-like) were similar among the studies.

4.2 Opportunities for optimizing biofilters

One of the main aims of this dissertation is to suggest optimization strategy to improve DOM removal by DWTP without major investments and allow the DWTPs to meet both long- and short-term changes in water quality, furthermore to ensure that safe and reliable drinking water can be provided at all times. Consequently, this dissertation has focused on how to optimize existing DTWP operations using only minor changes. Two optimizations suggestions were made, and the resulting change in DOM removal efficiency was investigated within full-scale parallel biological filters.

Table 4-2 Identified PARAFAC components derived in each of the four studies. The datasets underlying each model were obtained from the biofilters of three DWTP (Paper I - IV) and their relation to conventional peaks as described by Coble (1996), Yamashita et al. (2003), Ishii et al. (2012), Murphy et al. (2018).

Components	Ex/Em	Paper I	Paper II and III	Paper IV	Characteristics	Cobles Peak	Removal by biofilters (%)
C1	380/ 380, 435	✓	✓		Terrestrial humic material, Relatively larger molecular weight	Peak M and A	18 - 22 ¹ (2% ²)
C2	310/315, 390	✓	✓	✓	Terrestrial humic-like DOM modified by microbial reprocessing, the relatively smaller molecular weight fraction	Peak M and C	24-32 ¹
C3	260, 340/ 460		✓	✓	Humic-like compound		10-20
C4	410/ 410, 520		✓		Ubiquitous fluorescent component with more conjugated double bonds and aromatic nature	Not in Coble's system	10-20
C5	350/420	✓	✓		Terrestrial humic-like	Peak M or Peak C	
C6	280, 320/320	✓	✓		Tyrosine protein-like character and associated with microbial degradation of DOM	Peak T	
C7	290/340	✓	✓	✓	Tryptophan protein-like character and associated with algal and microbial-derived organic	Peak T	23-26 ¹

¹ Removal by biofilter at 80 min EBCT, ² removals measured during the autumn season, ³removal by biofilter without new GAC replenishment

4.2.1 Partial renewal

In Paper IV, a simple and cost-effective operational strategy was investigated to improve short-term NOM removal in a full-scale treatment plant. Three GAC media biofilters were modified by replacing a small fraction of saturated filter media with new media. Relative to replacing the entire biofilter media, this approach required lower capital cost and shorter downtime and maintained conditions for biological filter functioning. This modification strategy was investigated in Marieberg DWTP, where three full-scale filters (modified filters) were replenished partially with fresh GAC, and two reference filters were monitored simultaneously to compare the DOM removal efficiency. The efficiency was compared based on the removal of the optical properties of DOM (Fluorescence and UV spectroscopy) as well as DOC.

Fluorescence intensity of effluents from modified filters was lower than reference filters indicating modified filters were better at removing FDOM than reference filters. DOM fractions were removed over the complete range of excitation and emission wavelengths by the modified filters (Figure 4-2). It is noticeable from the intensity scale that the DOM fractions were removed more efficiently during the first few days following GAC replenishment and continued to exhibit better removal for filter F4 compared to reference filter after 30 days. Comparing Figure 4-2 with Figure 4-1, it is detectable that this modified filter (F4) is efficient at removing terrestrial humic-like peaks A and C (in Figure 4-1), as well as protein-like peak T than the reference filters.

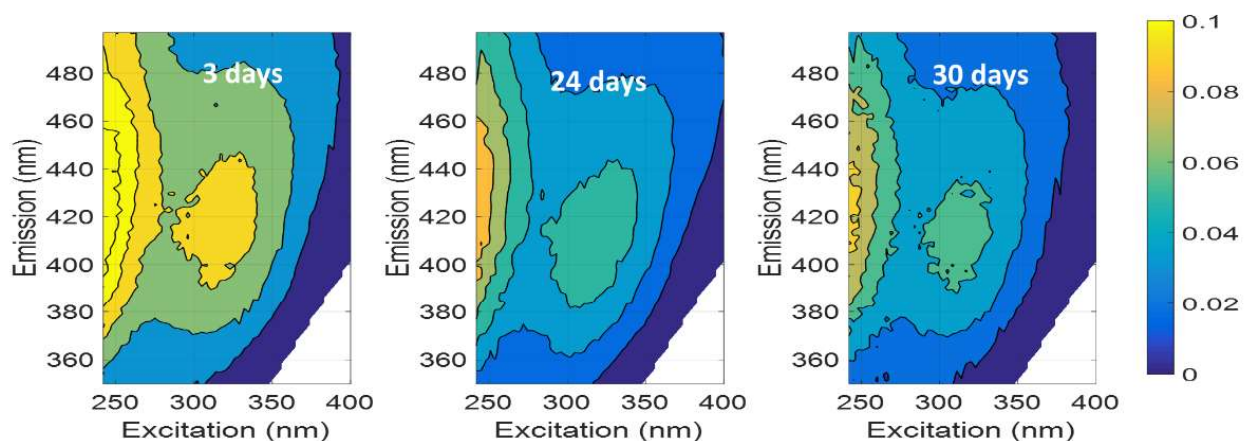


Figure 4-2 The removed fraction of FDOM by the modified filter in comparison to the reference filter. Differential FEEM calculated between Reference filter Rf5 and modified filter F4 at Marieberg DWTP. Signal intensities are presented at the right of the Figure in the color bar where colors represent absolute intensity in Raman unit.

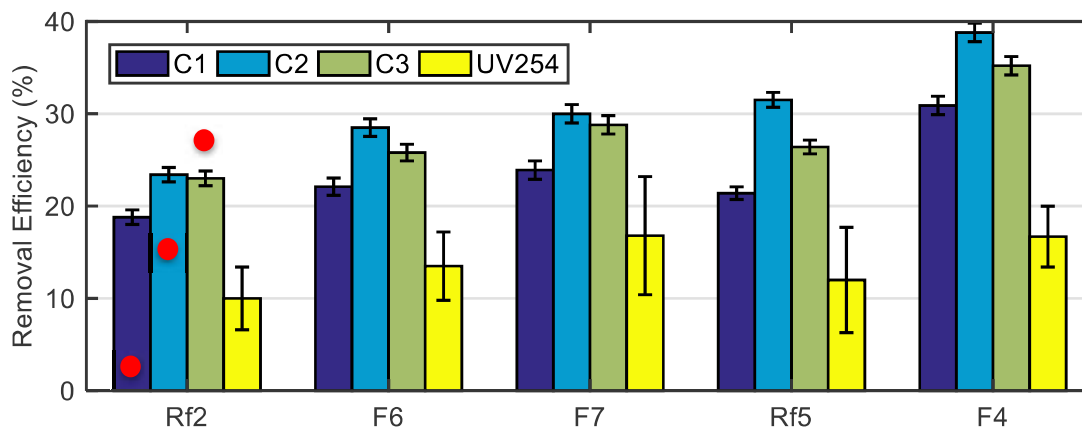


Figure 4-3 Removal efficiencies of three fluorescence components (C1-C3) and UV₂₅₄ during the four weeks following GAC replenishment. Modified filters F6 and F7 should be compared with reference filter Rf2 and modified filter F4 with reference filter Rf5 (Paper I, Figure 5). The removal efficiency in Peleato et al. 2016 is 3.7%, 14.6% and 27.8% respectively for C1, C2 and C3 (depicted in Rf2 using solid red circle).

In Mariaberg DWTP (paper IV), the modified filters reduced all PARAFAC components with higher efficiency than reference filters (Figure 4-3). Similar removal efficiencies of PARAFAC components were previously observed by other researchers such as (Baghoth et al. 2011); Peldszus et al. (2011). The highest removal was observed for microbially reprocessed humic-like DOM fraction (C2) followed by protein-like DOM (C3). PARAFAC component C2 was the most abundant FDOM in incoming water to the BAC filters and was removed to the greatest extent. Terrestrial humic-like component (C1) is the humic fraction of DOM that is removed by adsorption onto fresh GAC (Velten et al., 2011) and is known not to be removed by biofiltration (Baghoth et al., 2011). Therefore, improved removal of C1 after replenishment indicates higher adsorption ability of the BAC filters. Previously component C1 and C2 have been found to correlate strongly with chloroform which is the most abundant DBP formed by chlorination (Pifer et al., 2012). Thus, improved reduction of C1 and C2 decreases the formation potential of chloroform. In Paper IV following replenishment, protein-like fluorescence DOM fraction C3 removal was moderately high by both reference and modified BAC filters differing to the study done by Fu et al. (2017) on GAC biofilters. In their pilot-scale study, they found that proteins are refractory to the BAC filtration processes. However, in our study in Paper IV, there was a noticeable increase in the removal of protein-like fluorescence.

Online monitoring of UV absorbance provided real-time information about the performance of the filter and allowed to observe subtle changes in water quality. Before the replenishment, biofilters had similar UV absorbance (Paper IV, Figure 2). After replenishment, a sharp drop is

visible which recovers back to original performance after 10-20 days indicating improved removal of aromatic groups and the humic fraction of DOM as represented by UV absorbance. Ideally, UV absorbing DOM fractions or CDOM are recalcitrant to biodegradation (Lawrence, 1980; Novak et al., 1992), therefore, their improved reduction they are removed by the improved adsorption capacity of the modified BAC filters. This is consistent with previous findings where UV absorbing DOM are removed by non-biological means, namely by adsorption (Chowdhury, 2013).

Reduction in FDOM components was always greater than UV absorbance for both modified and reference BAC filters. Indicating that the modified filters were better than reference filters to remove FDOM fractions of DOM (Paper IV, Figure 5). DOC removal in modified and reference filters were moderate (Figure 4-3, Paper IV, Table 2). This is expected since not all fractions of DOC are biodegradable (Hozalski et al., 1995). The removal by reference filters (Rf2 and Rf5) were 0.2 - 0.5 mg C L⁻¹ and the removal by modified filters (F4, F6 and F7) were 0.7 - 0.8 mg C L⁻¹. The removal by reference filters is comparable to removal rates obtained in several studies done on full-scale BAC filters (Baghoth et al., 2011; Fu et al., 2017; Hozalski et al., 1995). The BAC filters at Marieberg DWTP are over 3 years old and have thus reached a steady-state during which the DOC removal becomes low (Hozalski et al., 1995). Modified filter performance was similar to the engineered biofilters (0.4 – 0.75 mg C L⁻¹) that have had phosphorous and nitrogen added to their incoming water to enhance biofilm growth (Lauderdale et al., 2012). Thus, rather than adding phosphorous and nitrogen into the incoming water, GAC replenishment onto existing BAC filters can ensure higher DOC removal.

To conclude, the results presented here demonstrate that the partial replenishment with new GAC improved the performance of the BAC filters at Marieberg DWTP. The improved performance of the filters lasted between 10 to 20 days and is dependent on the surface load to the filters.

4.2.2 Optimizing empty bed contact time (EBCT)

After the partial renewal of BAC filters in Mariaberg DWTP (Paper IV), the removal by biofilters was dependent on the incoming flow or surface load to the filter. A similar effect of EBCT /surface load or flow rate on BAC filters performance were reported in works of literature where reduced EBCT have decreased the removal efficiency of DOM in BAC filters (Chaudhary et al., 2003; Fu et al., 2017; Rui et al., 2020). In Kungälv DWTP (Paper I), EBCT of four full-scale biofilters was manipulated and DOM removal was monitored following

shifting their EBCT from the same EBCT of 80 min to 15, 30 and 50 min in three filters while keeping a filter at 80 min as reference filter.

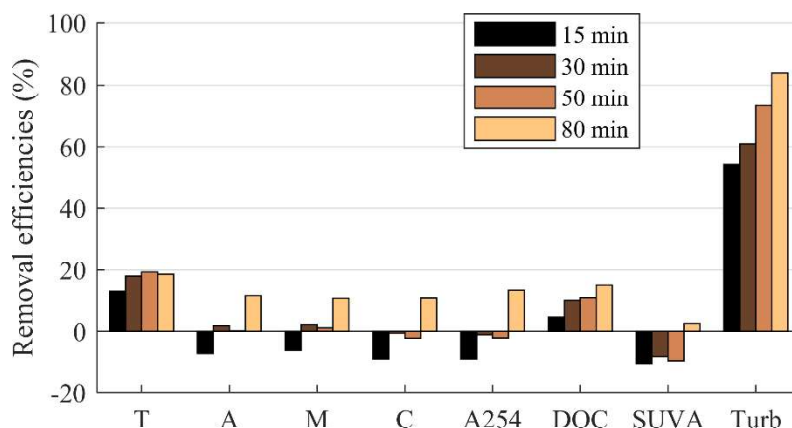


Figure 4-4 Removal of water quality parameters by biofilters having different EBCT

To determine which regions of the fluorescence FEEMs were more influenced at various EBCT, peak picking method was used to look at changes in specific peak intensities (peak A, M, C and T in this case) at different EBCT between influent raw water and effluent from the filters. Measurable changes were detected in the shorter emission wavelengths (<350 nm emission) region of FEEM at different EBCT which is typically associated with protein-like DOM and named as Peak T. Peak T fluorescence has previously been directly associated with the growth stage of bacterial communities and is a more labile fraction of DOM which is preferentially degraded through biofiltration processes (Cammack et al., 2004; Elliott et al., 2006). Removal of Peak T (tryptophan) was highest compared to Peak A, M and C (Figure 4-4). This result implies biodegradation within the Filtralite® biofilters caused rapid decay of peak T. In the Kungälv DWTP, biofiltration is utilized as a pre-treatment step for the ultrafiltration (UF) membranes and peak T has previously been established to be the main foulant of UF membranes by Aryal et al. (2009); Henderson et al. (2011); Yu et al. (2014). Therefore, efficient removal of peak T by biofiltration would reduce fouling of the UF membranes.

On the contrary, removal of humic-like FDOMs represented by peak A, M and C were not visible within these filters for 15 to 50-minute EBCT. Similar lower removal of humic-like FDOMs by biofilters have previously been observed by Chen et al. (2016) and Peleato et al. (2016) and it is established that these fractions are not removed by biodegradation. At 80-minute contact time, the removal of these humic peaks was at around 18%. Thus, a longer EBCT allowed biodegradation of these refractory fractions that were not removed at low EBCT.

4.3 Online monitoring

Continuous monitoring of water quality offers a large amount of data that can help to make the right decisions and also to implement in proper time accordingly (Bhardwaj, 2011). Online monitoring of incoming and outgoing water from the biofilters was utilized for Kungälv (Paper I) and Mariaberg DWTP (Paper IV) to track the changes implemented at each DWTP and allowed to quickly identify the influence of the changes on the outgoing water quality.

4.3.1 Absorbance

Online monitoring of UV absorbance in Mariaberg DWTP (Paper IV) showed DOM removal is dependent on the incoming flow or surface load to the filters. The last modified filter (Filter F4) were more efficient and for a longer duration than the other filters, since it did not receive increased surface load while other filters were out of operation (Figure 4-5, Paper IV, Figure 2 and 3). Fu et al. (2017) reported a similar effect of flow or surface load on BAC filters performance where the increased flow rate reduced the empty bed contact time (EBCT) and decreased the removal efficiency of DOM in BAC filters. For this reason, surface load or flow rate is a key design and operating parameter of a biofilter/contacter (Chaudhary et al., 2003). During high production period when the DWTPs need to increase flow to the filters, it can be recommended to the DWTP operators to replenish the exiting BAC filters with fresh GAC to handle the extra flow to ensure good filtered water quality.

4.3.2 Turbidity

In the full-scale study that manipulated EBCT in Kungälv DWTP (Paper I), online turbidity measurement showed turbidity removal was proportional to the duration of EBCT (Figure 4-6). Continuous monitoring of turbidity of the incoming and outgoing water from the filters allowed to get high-frequency data and track changes in water quality immediately after EBCT change. All the four filters had the same EBCT of 80 min and were changed to 15, 30 and 50 min in three filters and one filter was kept at 80 min as a reference filter. The removal efficiency of turbidity within the Filtralite® filters before EBCT change were similar and at around 80% (Figure 4-4 and Figure 2 in Paper I). Following EBCT change, the removal of turbidity was proportional to EBCT (Figure 4-6). Removal efficiency decreased from 80% for an 80 min contact time to an average of 60% (± 10) for a 15 min EBCT. Thus, longer EBCT did improve turbidity removal. A reduction of turbidity indicates less efficient removal of particles by the filters with short EBCT. Interestingly, turbidity removal by filters having 30 min to 50 min contact time was relatively similar. Consequently, a contact time of 30 min could be utilized

instead of 50 min at times of high-water demand to produce water with relatively similar quality as regards to turbidity.

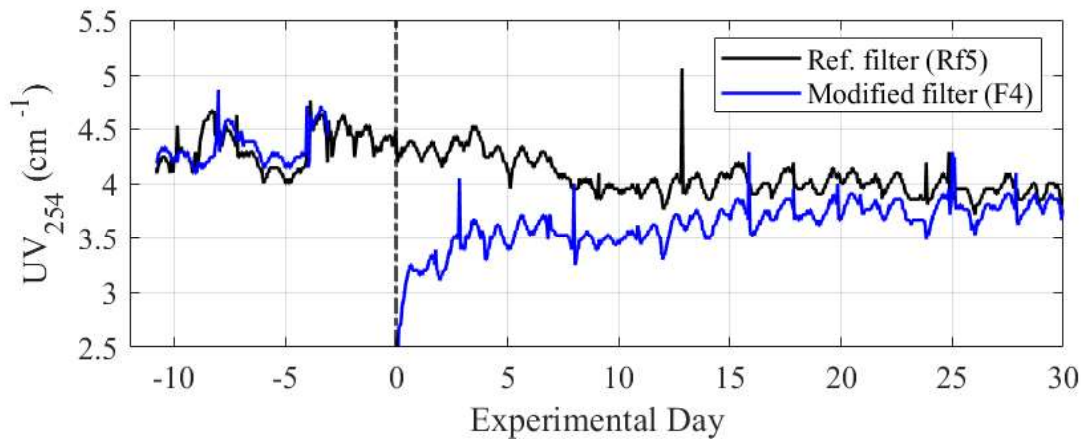


Figure 4-5 Water quality in effluents from modified (F4 blue line) and reference (Rf5 black line) filters. Vertical dotted lines denote filter start-up after GAC replenishment. Data for 40 days are presented here.

Turbidity measurement is a common operational parameter utilized by water treatment operators to monitor filtered water quality. The main removal of a particle within biological filters occurs by physical interception, adsorption onto biofilm and biological degradation within the biofilm (Urfer et al., 1997). Turbidity is removed efficiently by biological filters thus biofiltration step is usually one of the main turbidity removing a step in the DWTPs (Hong et al., 2018). There is an association between turbidity values and gastrointestinal diseases (Mann et al., 2007). Thus, higher removal of turbidity by the biofilters indicated better removal of microbiological contaminants as well as particles and organics by the biological filters. In Kungälv DWTP (Paper I), the turbidity removal by the biofilters achieved around 80% turbidity removal (Figure 4-4, Paper I Figure 2). This confirms the objective of placing biofilters as a particle removing step in the Kungälv DWTP.

4.4 Removal mechanisms

This section of the dissertation focuses on understanding and assessing both biodegradation and adsorption mechanisms occurring within biological filters under realistic operational conditions.

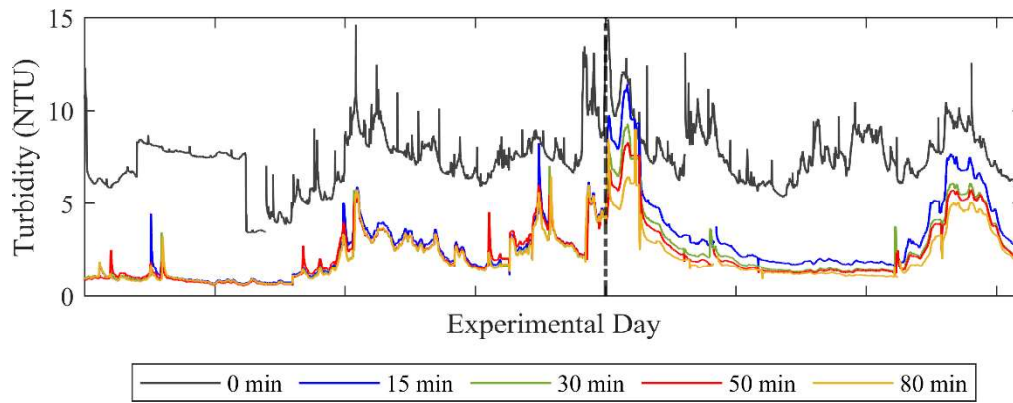


Figure 4-6 Online measurements of turbidity for influent and effluent water from the four full-scale parallel biofilters. Vertical dotted lines denote filter start-up after changing the empty bed contact time (EBCT). (0 min indicate incoming raw water from river Göta Älv.)

4.4.1 Effect of temperature

The batch-scale study on biofilter material collected from Lackarebäck DWTP (Paper II) was designed to decouple the underlying processes involved by examining the impact of temperature on biological filters performance to remove DOM from water.

The dominant mechanisms of DOC removal by the BAC filters are through a combination of physio-chemical adsorption onto GAC surface and biofilm, together with biodegradation of the biodegradable organic fraction within the biofilm (Laurent et al., 1999). The removal is benefited at elevated temperature due to faster metabolism of organics within the biofilm (Huck et al., 2009; Laurent et al., 1999). In the study performed on Paper II, a decrease in DOC removal was observed with increasing temperature indicating removal mechanism was via exothermic physisorption processes (Figure 4-7, Paper II, Figure 4a). The DOC data also suggested that different types of continuously ongoing regeneration mechanisms within the filter had freed up previously occupied adsorption sites for physisorption. It is noteworthy that there was an insignificant effect of temperature on the removal of aromatic DOM as measured by UV_{254} via BAC filter in this study. Fluorescence result indicated that some FDOM fractions were significantly influenced by temperature, but this effect could not be tracked using UV absorbance because it is a less sensitive and less specific method, i.e. it only shows their combined abundance (Pan et al., 2016).

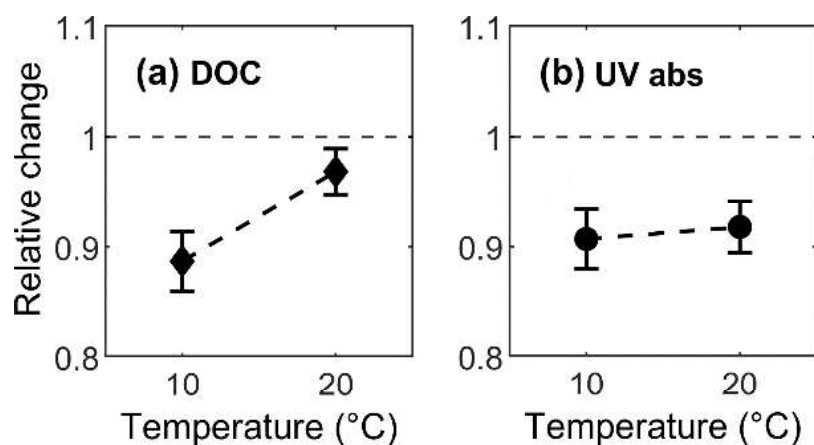


Figure 4-7 Temperature dependence of a) bulk DOC and b) UV-absorbing material removed by BAC. Shown here is the fall experiment where the ambient temperature was 10 °C. All response values were normalized to the signal observed in the control sample. The dashed reference line represents the control sample. Values higher than one represent apparent production of material, while values lower than one represent apparent removal. Error bars represent the standard error across the five treatment replicates.

From fluorescence analysis, the underlying mechanisms of DOM removal by the BAC filters could be separated (Paper II, Figure 3). Previously, humic-like components were identified to resist biodegradation and be adsorbed onto BAC material (Baghoth et al., 2011; Peleato, 2016). But specifics of the type of adsorption (chemisorption or physisorption) were not elucidated. From the temperature study in Paper II, four specific response to temperature change observed for all identified the fluorescent components except tryptophan-like component

- The removal followed a v-shaped curve to temperature for long emission wavelength humics (C430 and C460)
- Decreased with increasing temperature, exothermic in nature. The probable mechanism is probably physisorption for short-emission wavelength humics (C390 and C420)
- A weak response to temperature changes in both summer and fall experiments (weakly exothermic physisorption) large-molecular-sized humic-like DOM, C520

There was a variable response to temperature changes visible in summer and fall experiments for protein-like FDOMs, tyrosine-like C320 and tryptophan-like C340. This is an indication of simultaneous microbial uptake and release of the protein-like components. It was therefore not possible to unambiguously attribute a primary mechanism to the dynamics of protein-like fluorescence components.

To conclude, the results presented here demonstrate the temperature-dependent behavior of BAC filters can indicate the underlying removal mechanisms occurring within the biological filters.

4.4.2 Gamma irradiation a sterilization method to produce abiotic control

A significant amount of DOM removal can be attributed to biological degradation occurring within the biofilm attached to the saturated and aged GAC, it is necessary to have a proper method to produce abiotic control of the biologically active carbon to properly discriminate the adsorption from the biological oxidation of the compounds. In this section of the thesis, gamma-irradiation is investigated, whether it can be used as a suitable technique that inhibits the biological activity on biologically active carbon without affecting its adsorptive properties (i.e. adsorption capacity and kinetics).

Firstly, to establish the proper dose required to sterilize the BAC filter materials, potential acetate uptake (PAU) rate was used as a proxy to quantify the remaining active biomass at different gamma dosages (from 0 – 10 kGy). Acetate was added in excess for a contact time of 20 hours and afterwards, remaining acetate concentration was measured to quantify the presence of active biomass at the end of the contact period. BAC filter material dosed at 10 kGy had zero consumption of acetate indicating an absence of microbial activity at dosages over 10 kGy (Figure 4-8a).

Secondly, Brunauer–Emmett–Teller (BET) surface area measurement was performed to monitor any change in pore size distribution from gamma irradiation (Table 1, Paper III). BET surface area analysis did not reveal any change in surface area between irradiated and non-irradiated BAC filter materials.

Thirdly, adsorption capacity between irradiated and non-irradiated BAC filter materials was compared using adsorption of a non-biodegradable surrogate for organic matter-methylene blue (MB) and removal of different DOM fractions from coagulated, settled water.

From methylene blue (MB) test it was found that there was not a statistically significant difference ($p>0.33$) in MB number among BAC samples irradiated at different dosages (Figure 4-8b). Lack of influence on MB number indicated gamma irradiation did not affect the adsorptive behaviors of the irradiated BAC filter material. This result is similar to the one suggested by Stoquart et al. (2013), where a dosage of less than 15 kGy was suggested as a safe

dosage to not influence the removal of MB. Thus, Gamma irradiation at a dosage rate between 0-10 kGy did not change the MB adsorption rate from BAC filter material.

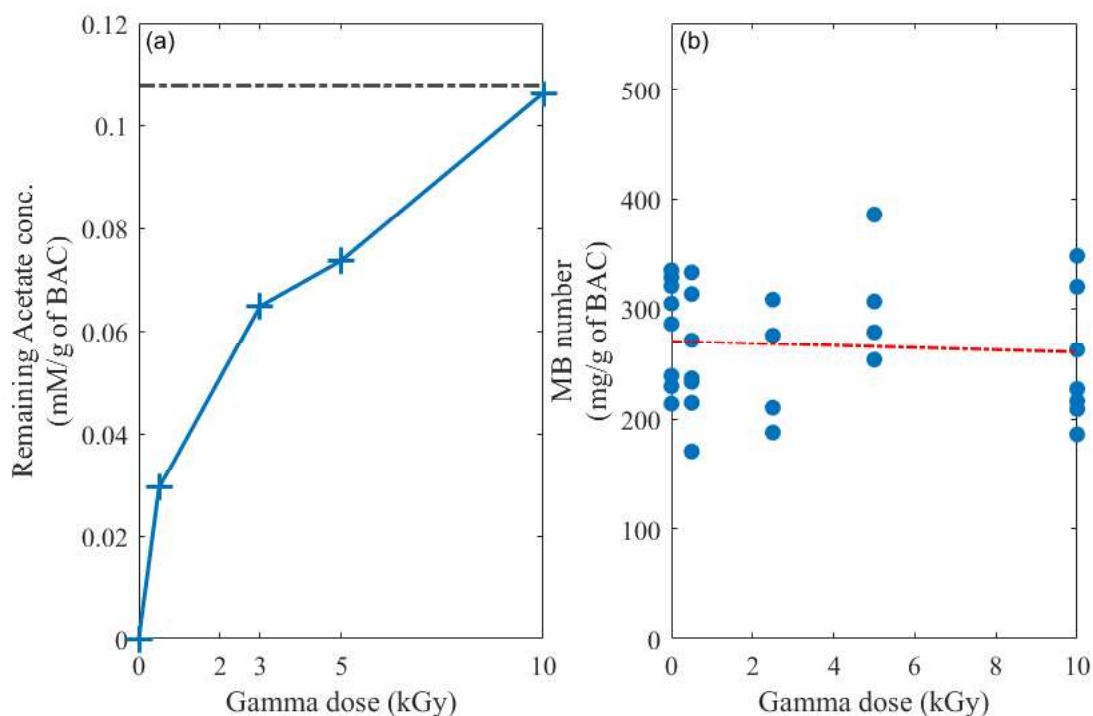


Figure 4-8 a) Remaining Acetate concentration after 20 h contact time by irradiated and non-irradiated samples of biologically activated carbon (BAC). The black dashed reference line represents acetate concentration in the control sample. b) Methylene blue adsorption after a contact time of 20 hours. The red line shows a linear fit between the gamma dose and MB number.

The impact of the irradiation on the BAC filter materials adsorptive characteristics were further studied by monitoring DOM adsorption kinetics. Relative removal of DOC changed with increasing gamma dosages (Figure 4-9, left), these can be representative of inactivation of biofilm with gamma dosages and thereby decreasing biological degradation. At 0 kGy DOM removal is around 20% (± 10) which is acceptable removal range of DOC by biofilters found in the literature (Moll et al., 1999). DOC can be removed at 10 kGy only by adsorption (since the biofilm is inactivated at 10 kGy, Figure 4-8a). However, removal via adsorption is not occurring at 10 kGy rather there is a release. The release of DOC around 10% (± 10), possibly due to breakdown of biofilm or release of already adsorbed DOC from the pores of BAC filter material. This release of DOC with gamma irradiation was previously observed in soil samples by Berns et al. (2008). In their study, there was an observed disaggregation of soil structure and they concluded that lysis of microorganisms led to this release of DOC from the soil sample.

The influence of gamma on UV absorbing DOM is negligible. This indicates that probable removal mechanism of these chromophoric DOM (CDOM) fractions occurs via non-biological mode. However, non-significant influence on UV_{254} is surprising, since the release of DOC from pores should allow more adsorption of UV absorbing DOM, on the contrary, this fraction was unaffected. For SUVA there is a decrease in aromaticity due to gamma irradiation (Figure 4-9, left). This probably could be due to less UV_{254} relative abundance within DOC concentration.

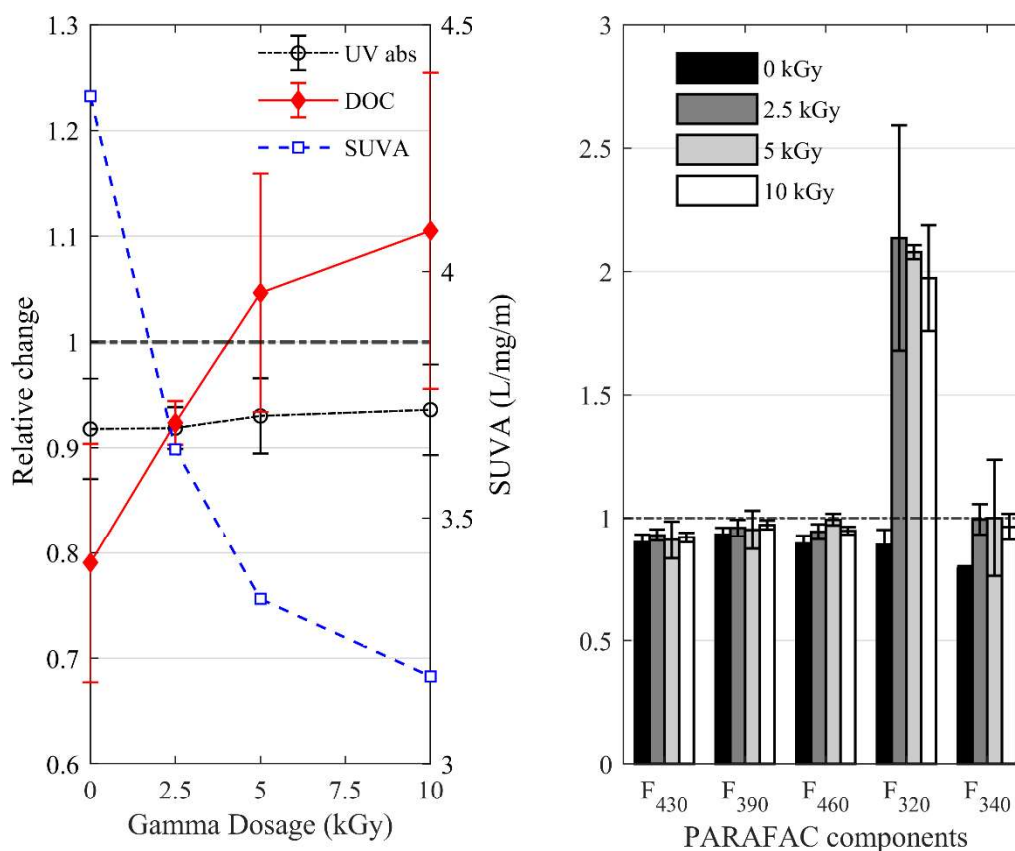


Figure 4-9 Relative change of DOC, UV_{254} , SUVA and PARAFAC components at different gamma dosages. All response values were normalized to the signal observed in the control sample. The dashed reference line represents the control sample. Values higher than one represent apparent production of material, while values lower than one represent apparent removal. Error bars represent the standard error across the five treatment replicates.

There was a slight increase in the relative concentration of humic-like components (F₄₃₀, F₃₉₀, F₄₆₀, F₅₂₀, F₄₂₀) due to gamma irradiation (Figure 4-9, right). This further indicated that gamma irradiation did in fact influence that characteristics of the biofilm and this influence can be monitored using FDOM component F₃₂₀. The release of F₃₂₀ represents lysis of microorganisms

within the biofilm that led to this release of F_{320} from the sterilized sample. However, this observation is opposed to Berns et al. (2008), where they observed a significant decrease in humification index following gamma irradiation in soil samples.

To conclude, the result presented here demonstrates that gamma irradiation at 10 kGy is enough to sterilize the active biomass. From the MB number, the influence of gamma dosages could not be identified. Using adsorption of DOM on sterilized vs unsterilized on BAC filter material, a significant release of protein-like FDOM was monitored which was released from the sterilized biofilm.

5 CONCLUSIONS

The general aim of this thesis was to determine the extent of fluorescent DOM removal by the biofilters and link these changes to optimize and improve DOM removal by the biofilters. The most important conclusions from this dissertation are as follows (answering the research questions in section 1.1)

Identification of typical fluorescence signals in DWTPs around Gothenburg, Sweden (RQ1)

- Water samples were collected from biofilters influents and effluents. Similar underlying fluorescent DOM components were identified in raw source water and biofiltered water in three different Swedish DWTPs.

Online monitoring of turbidity and UV absorbance to monitor DOM removal (RQ2)

- Online turbidity measurement showed that the Filtralite® biofilters effectively removed turbidity from incoming raw water. However, turbidity data overestimated the removal of DOC and chromophoric DOM. Online monitoring of UV₂₅₄ absorbance revealed improved adsorption capacity following a partial renewal of biofilters with new GAC. However, online monitoring of UV₂₅₄ absorbance also overestimated the removal of DOC and fluorescent DOM.

Quantification of DOM removal by biofilters with non-adsorptive vs. adsorptive media (RQ3)

- In three DWTPs, relatively similar DOC removal by biofilters was observed despite different media and pre-treatment processes.
- Fluorescent DOM removal was much higher at full scale than in batch-scale experiments. Caution must be applied to extrapolating results from batch-scale experiments to full-scale.

Investigation of the seasonal performance variation of BAC filter (RQ4)

- Removal of fluorescent DOM fractions was sensitive to temperature changes and indicated the underlying removal mechanisms.
- BAC is a potential source of DOM under negative concentration gradients and in times of sudden temperature shifts. Such conditions can be met when water sources or intake depths are changed during the operation of drinking water treatment plants.

Concentration gradient induced release of microbial humic-like fluorophores had not previously been reported in the literature.

- Fluorescence spectroscopy indicated that certain long-emission wavelength fluorescent DOM fractions (humic-like C₄₃₀ and C₄₆₀) were influenced by temperature whereas other identified fluorescent fractions were not.

Separating adsorption mechanisms from biological degradation in a BAC biofilter (RQ5)

- Fluorescence spectroscopy provided more in-depth compositional information of removal mechanisms of different DOM fractions compared to UV₂₅₄ and bulk DOC. However, for some fluorescent DOM fractions, an unambiguous assignment of mechanisms was difficult due to removal and release occurring simultaneously.
- Gamma irradiation at 10 kGy sterilized the active biomass without changing the surface pore structures. However, a significant release of protein-like fluorescent DOM fractions from sterilized biofilms was observed. Thus, gamma irradiation did not impact BAC's surface pore structures but rather influenced the biofilm composition to release previously adsorbed organics.

Optimizing DOM removal by biofilters using simple operational practices (RQ6)

- Increasing the EBCT well beyond 30 min improved DOM removal in Filtralite® biofilters
- Partial renewals of BAC biofilters could meet short term concentration peaks of DOM in raw water.

6 RECOMMENDATIONS FOR THE WATER INDUSTRY

Based on the work presented during this dissertation, the following recommendations for the water industry are made

- If an increase or decrease in water demand requires rapid change in EBCT, then the change should be performed gradually to maintain the microbial community within the biofilters (Paper I). A rapid change in operational parameter e.g. EBCT or incoming water quality e.g. DOM concentration or temperature can hamper the performance of DOM removal by the biofilters (Paper I).
- A longer EBCT improved removal of peak T fluorescence (microbially derived DOM) and turbidity in Filtralite® filters (Paper I). However, the peak T removal was relatively similar for filters with EBCT of 30-, 50- and 80 min. Thus, the application of longer EBCT might not be beneficial for all DWTPs and needs to be tailored to investigated for specific incoming water quality.
- Significant release of DOC and specific fluorescent DOM fractions from biofilters were observed from the desorption study (Paper II). Thus, depending on which DOM fraction gets released into the water, the subsequent microbial regrowth potential may change in the outgoing water from the DWTP. Therefore, the extent of the DOM release from the biofilter must be accounted for in the subsequent treatment steps.
- Partial renewal of BAC filters can improve NOM removal for a short period. The suggested modification strategy can be used during periods of expected high NOM or pollution loads. Such events could be after snowmelt runoff period (resulting in high fluorescent NOM and aromatic NOM), during heavy rain (high flow to the filters), algal blooms in source waters, or during lake turn-over period (indicated by high fluorescent NOM in incoming raw water) (Paper IV).
- Reactivation or replacement of multiple GAC filters when the adsorption capacity has reduced will result in taking those filters out of operation for a certain period and the process can be expensive. Utilizing the biological activity wisely is therefore important during such periods. A better understanding of NOM adsorption can also be utilized for saving adsorption capacity to when it is most needed.

7 FUTURE PERSPECTIVES

Results from studies undertaken during this dissertation give rise to several new questions

- Long term studies of biologically activated carbon filters are needed, focusing specifically on the transition period from adsorptive to biodegrading function. The focus should be monitoring change in optical properties of DOM during the transition period while simultaneously monitoring the bacterial community dynamics within the filters.
- Increased removal of DOC and protein-like fluorescent DOM with increasing empty bed contact time was observed for Filtralite® biofilters. There is a need to further study this covariance by monitoring different waters with varying DOC, fluorescence and microbial quality backgrounds. The study should be expanded to verify whether online monitoring of protein-like fluorescent DOM can track real-time water quality changes due to biofilters at different treatment plants.
- During this dissertation, continuous online monitoring of influent and effluent water quality from biofilter was conducted at full-scale for several months. Application of continuous organic characterization using online fluorescence system over a longer period would be useful to understand the influence of seasonal water quality on biofilters performance.
- A batch scale study of biofilter materials failed to capture biological DOM removal. The biology may have been suppressed due to a stress-response or the experimental conditions were otherwise unfavorable for microbial degradation, e.g. due to insufficient microbe to DOM ratios. Future research with an improved experimental design may better capture the influence of temperature variation on biofilter performance.
- At batch-scale, it was possible to tentatively identify the removal mechanisms of humic-like fluorescent DOM in terms of chemisorption vs physisorption. This work should be continued at both a fundamental and applied level to provide an in-depth understanding of the possible interactions between removal mechanisms. It is suggested for fundamental work to use model water with organic surrogates since it will improve the control over water quality parameters. On a practical side, the results observed at batch-scale should be repeated at pilot-scale using biofilter columns to confirm the observed trend in fluorescent DOM.

- Performance of the biofilters is highly dependent on raw water characteristics. Climate change will influence the raw water quality and therefore the performance of the biological filtration process. Future studies should provide concrete guidelines for design and operation of biofilters with realistic predictions of raw water quality due to future changes in climate and hydrology.
- Partial renewal of biofilters had a positive influence on effluents from the biofilters. It would be useful to investigate whether the disinfection by-products formation reduced simultaneously. The study should be expanded to assess the influence of partial renewal on the microbial activity within the filters.

For future DWTP design, it is suggested to consider the degree of DOM desorption from the biofilter for treatment steps following biofiltration. Further research should concentrate on quantifying the microbial quantity and bacterial community dynamics during the periods of elevated release of DOM from biofilters.

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