THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Partial renewal of granular activated carbon filters for improved drinking water treatment

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Cover:
Changes in fluorescence excitation-emission matrix after partial renewal of granular activated filters
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ABSTRACT

Drinking water is widely collected from surface water sources. In these water sources, both the quantity and quality of natural organic matter (NOM) have been affected around the world during the last decades, especially in Northern Europe and North America. This increasing NOM and its composition change challenge the drinking water treatment plants (DWTPs) due to e.g. increased coagulant demand, and because NOMs constituents act as precursors for potentially harmful disinfection by-products. Many DWTPs employing conventional treatment are currently struggling to maintain sufficient NOM removal, and are facing significant investments to upgrade existing treatment processes.

In this thesis, a modification strategy to improve NOM removal by existing biological activated carbon (BAC) filters was tested. Analytical techniques like dissolved organic carbon, spectroscopic methods (absorbance and fluorescence) were used to monitor the performance of the modified filters in comparison to reference filters. In the second phase of the study, the modification strategy was employed in a different DWTP with different source water and coagulation treatment in order to validate the effectiveness of the proposed strategy under diverse conditions.

Results show that replenishment of about 10% activated carbon media with new carbon media in BAC filters resulted in improved performance. The modified biofilters showed improved organic matter removal lasting for 10-20 days, depending on surface loading. In addition to improving the adsorption of humic-like NOM fractions, biological removal by the saturated filter media was enhanced. A subsequent validation study showed that improvement of biodegradation and adsorption mechanisms occurred in different DWTPs regardless of differences in NOM composition and coagulation processes prior to the BAC filters.

Keywords: Biofiltration, Drinking water treatment, Fluorescence, Granular activated carbon filter, Natural organic matter, Online monitoring, Spectroscopic properties.

LIST OF PAPERS

This thesis includes the following papers:

Paper I
N. Moona, K. Murphy, M. Bondelind, O. Bergstedt, T. J. R. Pettersson (2017).
Partial renewal of drinking water biofilters for short-term enhancement of organic matter removal. Submitted to *Environmental Science: Water Research & Technology*.

Paper II
N. Moona, M. Bondelind, K. Murphy, O. Bergstedt, T. J. R. Pettersson (2017).
Effect of water source and coagulation on NOM removal by partially-replenished biologically activated carbon filters. To be submitted to *IWA World Water Conference 2018, Tokyo Japan.*

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Gothenburg, November 2017

Nashita Moona

LIST OF NOTATIONS

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

AC	Activated carbon
AOC	Assimilable organic carbon
ATP	Adenosine triphosphate
BOD	Biochemical Oxygen Demand
BDOC	Biodegradable organic compounds
BAC	Biologically activated carbon
COD	Chemical oxygen demand
CDOM	Chromophoric dissolved organic matter
DBP	Disinfection by product
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-emission matrix
F-EEM	Fluorescence excitation-emission matrices
FRI	Fluorescence regional integration
FDOM	Fluorescent dissolved organic matter
GAC	Granular activated carbon
HAA	Haloacetic acids
HANs	Haloacetonitriles
HPSEC	High-performance size exclusion chromatography
HAs	Humic acids
LC-OCD	Liquid chromatography-organic carbon detection
MW	Molecular weight
NOM	Natural organic matter
PARAFAC	Parallel factor analysis
PFOS	Perfluorooctanesulfonic acid
PLFA	Phospholipid fatty acid
PAC	Powdered activated carbon
PCA	Principal component analysis
SEM	Scanning electron microscopy
SUVA	Specific UV absorbance
TOC	Total organic carbon

TOX	Total organic halides
THM	Trihalomethanes
UV_{254}	UV absorbance measured at 254 nm

TABLE OF CONTENTS

1 Introduction

This chapter of the thesis states the aim and objectives of the thesis and provides an overview of the papers attached.

Drinking water is an essential part of human health and life. However, around 663 million people around the world are without access to potable drinking water (United Nations 2017). Therefore, United Nations has included ‘Water and Sanitation to all’ as one of the 17 sustainable development goals (Goal 6) to be achieved by 2030. Several of the other sustainability goals includes potable drinking water and human health as well (United Nations 2016).

Achieving these sustainable development goals is challenging due to many aspects, including climate change and global increases in population. Lack of proper sanitation, and access to potable drinking water, is the major source of gastrointestinal diseases in the developing countries (Ashbolt 2004). Potable water quality in developed countries suffers as well, due to changes in water resources affected by anthropogenic activities, including large scale industrialization and discharge of municipal wastewater into the raw water sources. Climate change also affects global drinking water quality and availability; this is evident in increased precipitation or prolonged draught periods and the overall increase in global temperatures that influence the terrestrial and aquatic ecosystems (Preston 2004; Seekell & Pace 2011). Thus, climate change can negatively influence the raw water quality both suddenly and gradually by increasing humic content (main organic constituents of soil (humus), peat and coal) and pathogen levels, and by increasing the frequency of short-term algal blooms (Moore *et al.* 2008) and outbreaks of infectious diseases (Murdoch *et al.* 2000; Burge *et al.* 2014).

This increase in humic substances in water sources has been widely observed around Northern Europe and North America (Evans *et al.* 2005; Worrall & Burt 2009; Ritson *et al.* 2014), where it decreases performance in drinking water treatment plants (DWTP), impeding their ability to meet water quality standards year round (Collins *et al.* 1985). In order to meet water quality requirements, more stringent guidelines have been proposed. 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 be provided at all times. One way to ensure this is to upgrade or optimize existing treatment technologies, or to implement new treatment technologies (Slavik & Uhl 2009). However, these upgrades are usually expensive to implement and require large investments. Alternatively, the research presented in this thesis has focused on how to optimize existing DTWP operations using only minor changes.

Natural organic matter (NOM) poses a constant challenge to drinking water treatment. NOM is present in all source water and has characteristics that vary based on the nature of and geographical location of the sources, seasonal variation (e.g. temperature and pH) and human activities located around the source catchment. There has been on-going research to find efficient ways to remove NOM from the raw water. Different treatment steps like conventional treatment, coagulation, flocculation, sedimentation and filtration processes, are applied in order to reduce both NOM and pathogen concentrations in the drinking water. However, changing raw quality due climate change present extra challenges on NOM removal by increasing cost of water treatment operations (due to e.g. increased chemical consumption), demanding new infrastructure to remove new target compounds (e.g., chemical compounds, algae etc.) and/or associated challenges that they create (e.g., taste and odour compounds, toxic algal by-products) (Emelko et al. 2011). Thus, this increased load on existing treatment processes can be beyond critical design threshold ranges, and it is therefore necessary to optimize the treatment technology currently in use.

Granular activated carbon (GAC) filtration is a widely-used treatment technology implemented in many surface water treatment plants. GAC filters are good at adsorbing micro-pollutants e.g. Perfluorooctanesulfonic acid (PFOS), algal degradation products, and petroleum residues. However, dissolved organic matter (DOC) in raw water saturates the GAC filters pores with irreversibly bound NOM and reduces the adsorption capacity (Velten 2008). A biofilm forms on the filter media converting them to biofilters (BAC) (Servais *et al.* 1994; Velten 2008) in which microorganisms break down and remove biodegradable NOM. 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 & Stilwell 2002).

This research evaluates a low-cost technique to improve NOM removal by existing BAC filtration process in DWTPs in order to prevent system overload during short-term deterioration in raw water quality.

1.1 Aim and objectives

The aim of this research is to study the improved NOM removal by existing BAC filters using a simple modified operational strategy.

To fulfil this aim several specific objectives are included in this thesis.

The specific objectives are:

- To study the improved removal of NOM by modifying the operation of existing BAC filters in full-scale DWTPs (Paper I, Paper II)
- To monitor the qualitative and quantitative changes in NOM concentration after GAC replenishment and identify if different NOM fractions react differently to the BAC filter modification (Paper I, Paper II)
- To compare the effect of BAC filter modification for two DWTPs with different raw water, and identify factors influencing removal of various fractions of NOM (Paper II)

1.2 Summary of the attached papers

Two papers are attached to this thesis. A short summary of these papers is given below.

In Paper I, improvement of NOM removal by replenishing BAC filters with fresh GAC was investigated in a full-scale drinking water treatment plant in Uddevalla municipality, Sweden. This treatment plant has seven parallel GAC filters which contains saturated GAC (more than three years old) that are currently functioning as BAC filters. Intermittent complaints from consumers regarding drinking water taste and odor indicated that the treatment plant need extra support during periods of reduced raw water quality. The effects of improvement measures on NOM removal was monitored by dissolved organic carbon (DOC), optical measurements techniques like fluorescence spectroscopy and ultra violet absorbance at 254 nm.

Paper I indicated that replacing a thin layer of activated carbon from the existing BAC filters with fresh GAC can improve its treatment performance. Both adsorption and biological degradation improved within the filter bed for a period of 10-20 days after this modification. Paper I presents the strategy where combination of fresh GAC and saturated GAC are utilized within existing BAC filters to improve absorbable and biodegradable NOM removal.

In Paper II, a similar experiment as in Paper I was implemented at Lackarebäck DWTP, which receives raw water from a different source, and was compared with experiment at Uddevalla. In this paper, the results from Lackarebäck were compared to the full-scale experiment in Paper I. Paper II paper focuses on the robustness of the proposed strategy to remove different NOM fractions.

The same measurements tools were used to characterize the NOM removal in both papers.

1.3 Scope

This thesis focuses on NOM removal using optical properties NOM as well as bulk NOM concentration properties like DOC.

Since the studies were performed in operating full-scale DWTPs, the experimental design had to follow the layout and operation steps of the full-scale plant. Thus backwashing of the filters could not be controlled during the experiment.

2 Background

In this chapter the problem related to NOM in drinking water sources and a general overview of drinking water treatment processes are included in the beginning. Afterwards, detailed description of the GAC and BAC filtration processes for drinking water treatment are described since NOM removal through these two treatment processes are the main focus of the thesis. Various NOM characterization techniques are included as well that were utilised to investigate the NOM removal performance by the filtration processes.

2.1 Natural organic matter (NOM)

Drinking water is derived from the available 3% fresh and saline water around the world. In order 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 NOM and pathogens from treated water. NOM is part of the substances that needs 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 varies from one location to another as well as within same water body as a result of natural phenomena such as droughts, floods, and rainfalls (Matilainen *et al.* 2002; Sharp *et al.* 2006b; Kundzewicz *et al.* 2014). It can be produced through biological activities of algae and microbes (autochthonous NOM), or introduced from outside of the water body via drainage within watersheds containing breakdown of terrestrial organisms (Allochthonous NOM) (Eikebrokk *et al.* 2004).

NOM can be present in various forms like dissolved and particulate organic matter (Figure 2-1). Fraction of NOM that passes through the 0.45 – 1 µm filter is defined as dissolved organic matter (DOM) (Hansell & Carlson 2014). NOM can have both hydrophobic and hydrophilic fractions with dominant components as humic and fulvic acids, proteins, amino acids and carbohydrates of various molecular size and properties (Huguet *et al.* 2009; Thurman 2012).

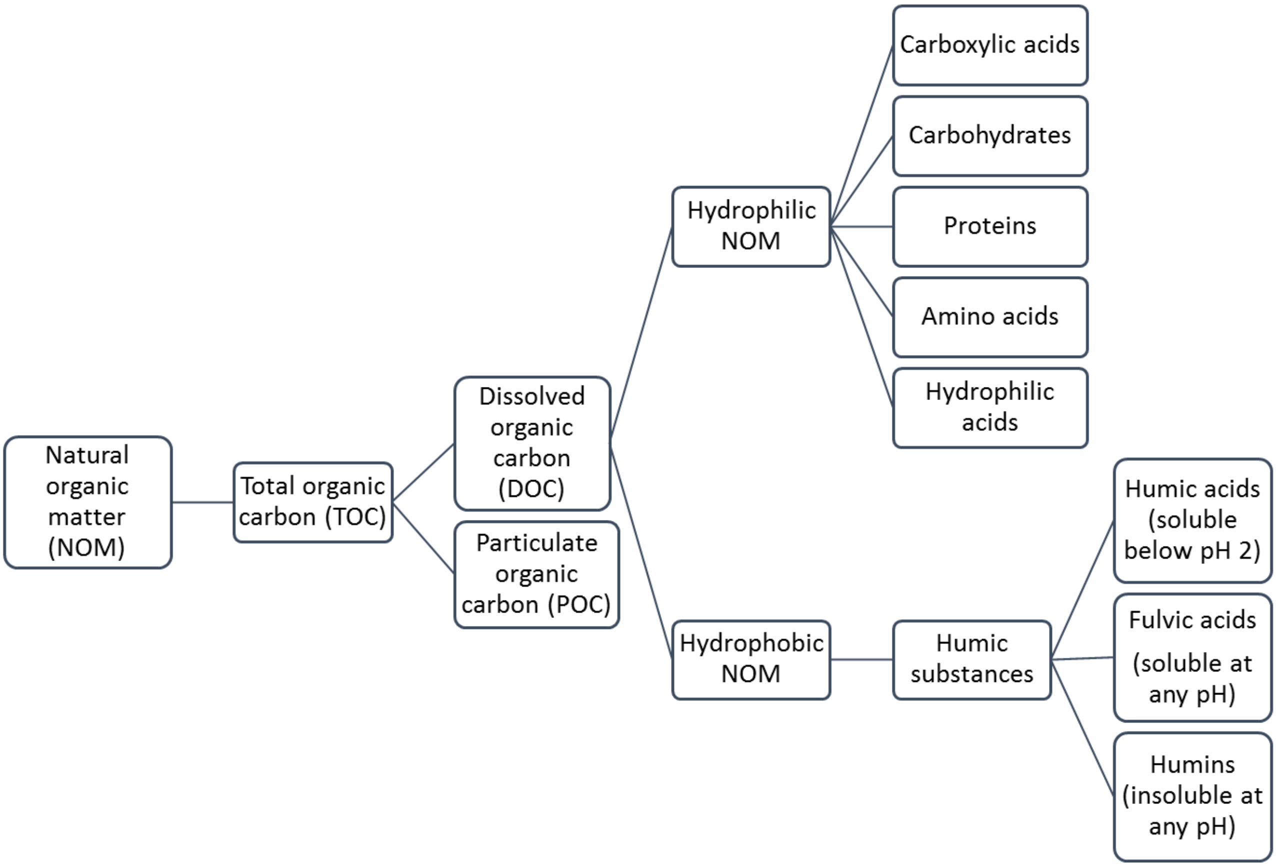

Figure 2-1: Different fractions of Natural organic matter.

2.2 Treatment processes of drinking water

Around 1750 municipal DWTP has been established until now in Sweden (Svenskt Vatten 2016). 50% of these DWTP use surface water for their production and the other 50% uses ground water infiltration and ground water (Svenskt Vatten 2016). In order to convert the raw water collected from natural water sources like streams, river or underground aquifers to drinking water, DWTPs have treatment steps like:

- *Pre chlorination:*

To meet different treatment objectives of removing microorganisms and to remove iron and manganese.

- *Conventional treatment or Coagulation, flocculation and sedimentation:*

Main purpose is to eliminate pathogens, reduce turbidity and taste and odor related problems. The colloidal particles in raw water are destabilization by the addition of a chemical reagent called as coagulant. Then the microflocs formed by agglomeration of destabilized particles and after into bulky floccules/flocs which can be settled. The addition of another reagent called flocculants or a flocculants aid may promote formation of the flocs. Conventional treatment can reduce micro pollutants but their removal might not be complete during this process. Conventional treatment is the most important treatment step in determining the subsequent GAC filtration and disinfection processes (World Health Organization 2008) performance.

- *Filtration:*

Rapid gravity and pressure filters are commonly used to filter water that are pre-treated by coagulation and sedimentation. Direct filtration in another alternative where coagulant is added to the water and then precipitated flocs are removed directly from the filter. To remove the flocs and particles, there are different filtration processes involved in drinking water treatment. For example, granular, slow sand, precoat and membrane (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) filtration (World Health Organization 2008).

- *Post-chlorination*:

Removes or inactivates microorganisms, stops regrowth of microorganisms in the distribution network.

There are periods of extra challenging water quality when there is a short term peaks in NOM concentrations in raw water (especially during Lake Turnover period, snow melt run-off or periods of algal bloom). Some of the short term treatment improvement approaches are improving existing coagulation step, addition of powdered activated carbon (PAC) to the raw water or to reduce surface load of the filters.

2.2.1 Problems related to NOM in drinking water treatment

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

2.3 Activated carbon in water treatment

In the following sections a brief description of activated carbon in drinking water treatment and detailed description NOM removal via GAC and BAC filtration processes in drinking water treatment are provided.

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 controlled condition and a porous structure with large surface area (500-1500 m^2/g) is formed that has 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).

2.3.1 Powdered activated carbon (PAC)

PAC has high carbon usage or dosage rate since PAC cannot be recovered or regenerated. PAC has lower capital cost than GAC and are used to control seasonal occurrences of taste- and odor-compounds and pesticides. For emergency control of spikes and spills from municipal and industrial wastewater discharges and agricultural runoff, many utilities keep PAC on-site (Chowdhury 2013). PAC is beneficial to use due to low capital cost (Najm *et al.* 1991; Najm *et al.* 1994). But PAC application is only limited to low concentration of organic pollutants due to short contact time (Kim & Kang 2008)

2.3.2 Granular activated carbon (GAC) filtration

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 hydrophobic fraction of humic acids (HAs), lower molecular weight humic- and fulvic acids (McCreary & Snoeyink 1980; Matilainen *et al.* 2006). On the contrary, some researcher have found that lower molecular weight matter is more amendable than higher molecular weight matter due to size exclusion effect (McCreary & Snoeyink 1980; Karanfil & Kilduff 1999). 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 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 mesophores (100-1000 °A) and large micropores *(*<100 °A) of GAC (Figure 2-2). Large size NOM (>10,000 °A) is not well removed due to size exclusion effect and lower molecular size is also not absorbable as majority of them are hydrophilic (Matilainen *et al.* 2006).

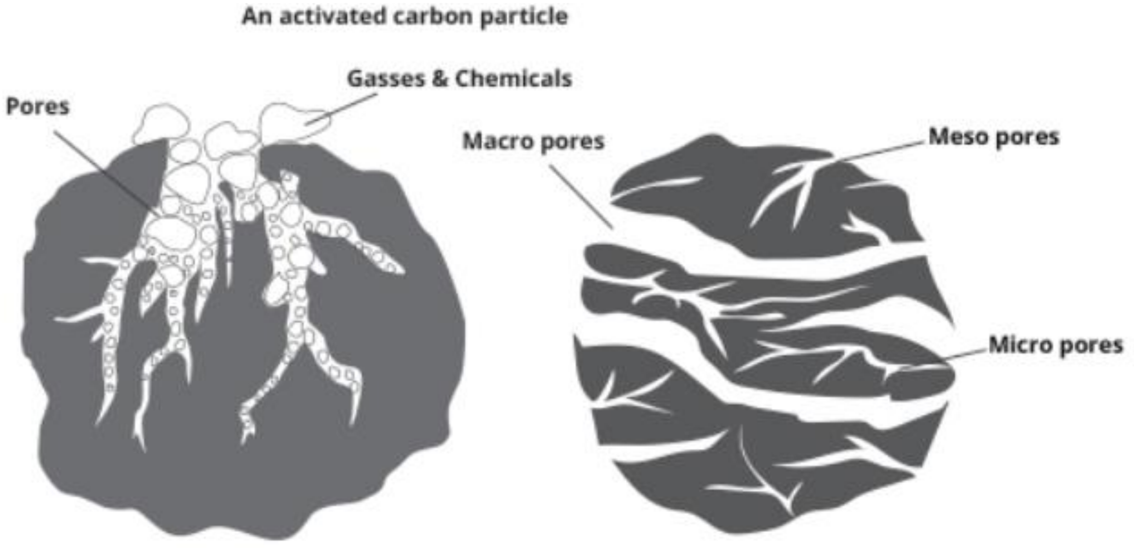

Figure 2-2: Pore size distribution of GAC and NOM removal mechanism (from webpage 'Aqua-cache').

2.3.3 Biologically Activated carbon filter

NOM 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).

Around early seventies, the capability of bacteria which proliferate in GAC filters to remove organics in the filter was first reported. Since then it is now known that GAC surface acts as a support material favourable for some bacteria that are widely found in the environment (such as nitrifying bacteria or heterotrophic bacteria) to develop and metabolize biodegradable organic matter (Huck 2000). Around '80s many European DWTP incorporated the combination of pre-ozonation and BAC filter in their treatment processes. Presently, BAC filters are mostly operated as 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 concept of *Engineered Biofiltration* is becoming popular where biofilters are operated as a purposefully operated biological system rather than a passive process. The aim is to target specific water quality objectives while maintaining or improving hydraulic performance. Nutrient supplement has been proposed in the feed water to promote bacterial growth and biofilm formation and subsequent enhancing removal of NOM. A handful of studies have investigated the *Engineered Biofiltration* (Lauderdale *et al.* 2012; Azzeh *et al.* 2015; McKie *et al.* 2015) and the information on such processes remains rather limited.

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). DOC removal takes place through four stages on BAC filters. On the first stage removal is mainly through adsorption of molecules in fresh GAC media. 40-90% of DOC and 70-90% removal of DBP and THM precursors' removal was observed during this period (Dussert & Van Stone 1994; Servais *et al.* 1994; Lohwacharin *et al.* 2011). The second phase lasts at about 2-3 months and is required to biologically colonize the GAC media. Biological degradation of DOC rate increases at this this stage while the physical adsorption continues to drop. Third stage is the steady state period as the physical adsorption capacity of AC is exhausted the biological degradation is the predominant process for DOC removal (Dussert & Van Stone 1994). There is 15-45% removal of DOC from ozonated water as the BDOC concentration increases (Simpson 2008; Lohwacharin *et al.* 2011). On the fourth phase of BAC filters operation is beyond 13 months when DOC removal gradually decreases (Hozalski *et al.* 1995).

Benefit of BAC filters:

Thus BAC filters has the following added benefit over GAC filters:

- BAC filters extends the service life of GAC filters and it does not require frequent regenerations of the filter media (Aktaş & Çeçen 2007).
- BAC filters ensures bio stability of effluent by removing biodegradable organic compounds (BDOC) and assimilable organic carbon (AOC). These part 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 benefit as well by BAC filters biofilm as bio-regeneration increases the adsorptive capacity of GAC (Seredyńska-Sobecka *et al.* 2006).
- BAC filtration reduces 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 NOM characterization

In the following section a summary of the analytical methods and data processing methods used in this thesis is given. Detailed description can be found in the respective papers.

Characterization of NOM is a difficult task due to wide range chemical composition included within NOM. Therefore, rather than using one analysis technique to measure total quantity of NOM, a combination of different analytical techniques are used to gather information on sub-fractions of NOM (Peleato *et al.* 2017) based on similar physiochemical properties. Some of these methods include adsorption/desorption on resins (Yan *et al.* 2010), membrane filtration (Summers & Roberts 1988; Yan *et al.* 2010), fluorescence spectrophotometry (Baghoth *et al.* 2011b) and high-performance size exclusion chromatography (HPSEC) (Matilainen *et al.*

2002). Some of the conventional NOM characterisation techniques are total organic carbon (TOC), colour and UV absorbance (Volk *et al.* 2002). The spectroscopic properties of optically active NOM fractions provides information regarding concentration, composition and source of NOM (Coble *et al.* 2014). These spectroscopic technique of NOM characterisation (i.e. Fluorescence and UV absorption at 254nm are rapid and highly sensitive techniques that does not require extensive sample preparation and require very little sample volume (Bieroza *et al.* 2009; Beggs & Summers 2011).

2.4.1 Optical properties of NOM/DOM

UV_{254} and SUVA

Dissolved organic fractions of NOM that can absorb ultraviolet and visible light, is referred to as chromophoric or coloured DOM (CDOM) (Coble *et al.* 1998). Absorbance is a semi-quantitative indicator of NOM concentration in natural waters. Most CDOM that absorb light have aromatic groups and are associated with humic fraction of NOM (Korshin *et al.* 1997a). Aromaticity of organic matter influences the reactivity of DOC and humic substances to oxidants like chlorine (Reckhow *et al.* 1990). Therefore, UV absorption at 254 nm (UV_{254}) is widely used monitoring tool for DOC concentration within DWTPs. Ozonation and adsorption onto AC is known to reduce UV_{254} from the treated water (Bahr *et al.* 2007; Altmann *et al.* 2014).

Specific UV absorbance (SUVA or $SUVA_{254}$) is another method based on UV_{254} and DOC to estimate the aromaticity of DOC in a sample. It is the ratio of the samples' UV absorbance at 254 nm to the DOC concertation of the solution.

$$SUVA = \frac{UV_{254}}{DOC}$$

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 (Edzwald & Tobiason 1999; Sharp *et al.* 2006a). SUVA is a good indicator of the humic fraction of NOM and effectiveness of coagulation to remove these humic fractions.

SUVA >4 L/m-mgC	SUVA ≈2-4 L/m-mgC	SUVA <2 L/m-mgC
• Aquatic humic • High hydrophobicity • High molecular weight • High UV_{254} • High chlorine demand • High DBP-FP	• Mixture of aquatic humics and other NOM • Mixture of hydrophobic and hydrophilic NOM • Mixture of different molecular weight • Medium UV_{254} • Medium chlorine demand • Medium DBP-FP	• Mostly non-humics • Low hydrophobicity • Low molecular weight • High UV_{254} • High chlorine demand • High DBP DBP-FP

Figure 2-3: Interpretation of SUVA values for freshwaters adopted from Edzwald and Tobiason (1999).

Fluorescence excitation and emission matrix

NOM fractions that exhibit fluorescence in both ultraviolet and visible range is referred to as fluorescent dissolved organic matter (FDOM) (Helms *et al.* 2008). By fluorescence spectroscopic analysis, based on presence of FDOMs associated with humic-fulvic and protein-like compounds, rapid characterization of NOM with high sensitivity and minimal sample preparation can be achieved (Sanchez *et al.* 2013). 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 (F-EEM) 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 a excitation-emission pair (Figure 2-4), specific organic compound groupings of FDOM within NOM can be identified and the maximum intensity of the peak correlates with concentration (Bieroza *et al.* 2011). Thus humic-like NOM 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 different fraction of NOM (Chen *et al.* 2003).

In Table 2-1, the classification of various NOM fraction according to previous literature is presented:

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

Peak name	**Description**	**Excitation/Emission**
A	Humic-like Terrestrially-delivered Allochthonous	< 250-260 / < 380-480
B	Tyrosine-like Microbially delivered Autochthonous	< 270 – 280 / 300 - 320
C	Humic-like Terrestrially-delivered Allochthonous	< 330 – 350 / 420 - 480
M	Marine humic-like Microbially delivered Autochthonous	310 – 320 / 380 - 420
T	Tryptophan-like Microbially delivered Autochthonous	270 – 280/ 320 - 350

Some other well-known methods for NOM characterisation using F-EEMs are:

- Fluorescence regional integration (Chen *et al.* 2003): The fluorescence regional integration (FRI) model proposes to integrate the fluorescence spectra instead of specific peak information (Figure 2-4). EEMs were divided in to 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).

- Multivariate data analysis (e.g. principal component analysis, PCA and partial least square regression (Persson & Wedborg 2001).
- Multiway data analysis using parallel factor analysis (PARAFAC) (Stedmon *et al.* 2003).

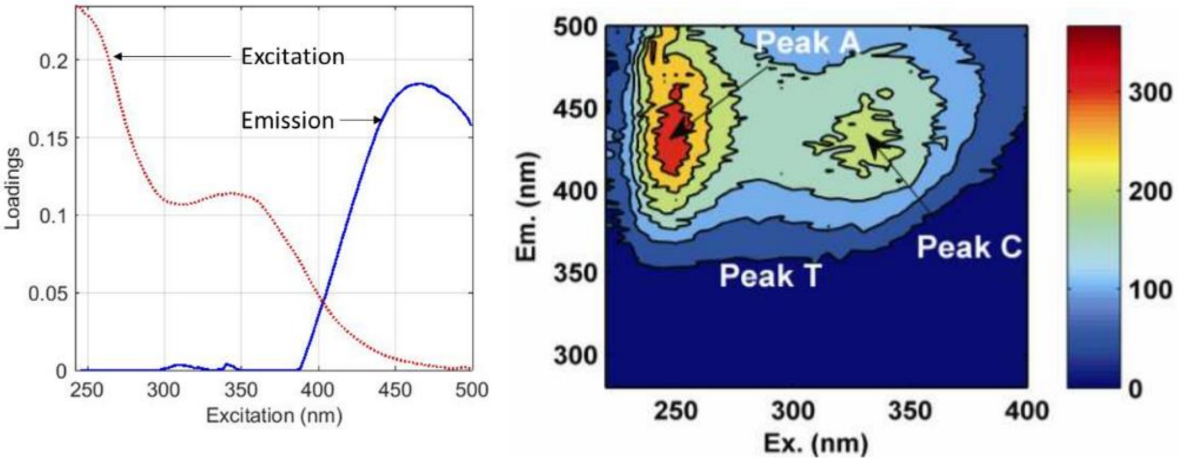

Figure 2-4: Excitation and emission spectra of a FDOM component identified using parallel factor analysis in Paper I (left) and fluorescence EEM of raw water. Fluorescence regions are denoted as Peak C: fulvic-like fluorescence, Peak A: humic-like fluorescence and Peak T: tryptophan-like fluorescence adopted from Bieroza et al. (2009).

Fluorescence intensity usually increases 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 concertation higher than 1 mg C/L prior to experiment (Kothawala *et al.* 2013). Fluorescence analysis is sensitive to pH (Patel-Sorrentino *et al.* 2002), temperature (Baker 2005), polarity of solvent (Lakowicz & Masters 2008), metal ion plus organic substances interactions (Reynolds & Ahmad 1995).

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 NOM in diverse environment (Stedmon & Markager 2005).

PARAFAC modelling can decompose multi-way data of EEMs (sample x excitation x emission) into a set of modelled parameters (Figure 2-5) that are independently-varying using 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 1 to reduce a dataset of EEMs into a set of trilinear terms and a residual array (Bro 1997):

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

Here, x_{ijk} is the fluorescence intensity of the ith sample at the kth excitation and jth emission wavelength, $a_{if}$is directly proportional to the concentration of the fth fluorophore in the ith sample (defined as scores), and b_{jf} and c_{kf} are the estimates of the emission and excitation spectrum of the fth fluorophore (defined as loadings), respectively (Stedmon *et al.* 2003). The residuals (εijk) 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 EEM (Stedmon & Bro 2008). This implies that the fluorescence peaks wavelengths position for each fluorophore do not “shift” but the fluorescence maxima of the mixture (e.g. in the EEM 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 & Bro 2008).

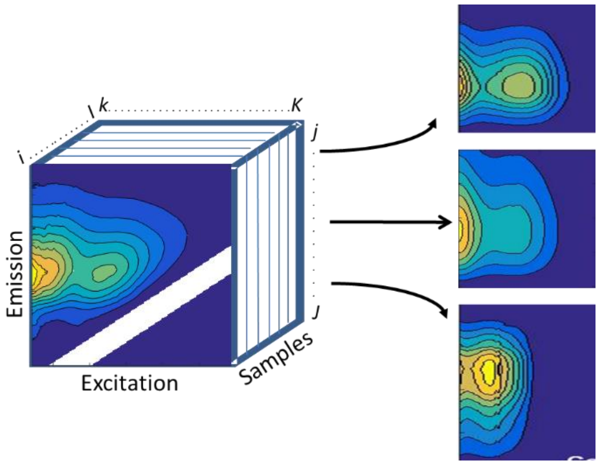

Figure 2-5: A drinking water EEM dataset can be decomposed into underlying fluorescence components using PARAFAC (Paper I).

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 & Markager 2005).

Differential excitation emission matrix

Differential EEMs allow to observe the treatability of NOM fractions by each treatment processes. Contour plot of EEMs collected from each treatment step is deducted from the contour plot of samples of reference treatment using the following equation:

$$\textit{Differential EEM} = \textit{EEM}_{\textit{Reference filter}} - \textit{EEM}_{\textit{Fresh GAC added filter}} \qquad (2)$$

Differential fluorescence spectra allows to detect small changes in NOM compositions and visualize over a range of excitation and emission wavelengths that represent different characteristics of the NOM.

EEM spectra were divided into three regions representing specific components of organic matters:

- Region I: Ex: 220–300/Em: 220–350, microbial by-products, proteins, polypeptides and amino acid-like
- Region II: Ex: 220–300 / Em: 350–550, fulvic acid-like
- Region III: Ex: 300–480/Em: 300–550, humic acid-like

2.4.2 Optical properties of NOM/DOM in natural and engineered water systems

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

2.4.3 High performance Size exclusion chromatography (HPSEC)

HPSEC is used to fractionate NOM in a sample based on higher to lower molecular size (Croue *et al.* 2000; Her *et al.* 2003). Thus molecular size distribution of NOM within a sample can be achieved. The larger the molecular weight the faster they are eluted from the chromatographic packing column. Molecular size is an important characteristic in water treatment as diffusion coefficients and removal efficiencies are directly dependent on the size of the solute (Haarhoff *et al.* 2010). HPSEC allows effectively to follow changes in NOM distribution along the DWTP trains (Vuorio *et al.* 1998). Matilainen *et al.* (2002) used HPSEC to monitor NOM content in DWTP in a one year study and found that high molecular weight NOM fractions are better removed by coagulation and filtration process and GAC filtration was ineffective in removing lower molecular weight fraction. Contrary to the study done by Haarhoff *et al.* (2010), where they found that GAC filtrations targets low to intermediate molecular weight fraction of NOM. They also found that rapid sand filters removes low and high molecular weight fractions and ultrafilters targets high molecular weight fraction.

2.4.4 How to optimize NOM removal in GAC and BAC filters?

In the following section some relevant research work in published literatures are summarised.

Optimization of BAC filters by influencing design and operational parameters such as media configuration, backwash strategy and loading rate to improve the filters performance have been investigated extensively (Lauderdale *et al.* 2012). BAC filters allows greater microbial biomass concentration than sand and anthracite biofilters and have higher removal rate of organic matters present in water (Miltner *et al.* 1995; Wang *et al.* 1995; Klymenko *et al.* 2010). From operation perspective it is now known that performance of biofiltration for NOM removal is affected by the empty bed contact time (EBCT), temperature, backwashing strategy and presence of other treatment step (e.g. ozonation) (Emelko *et al.* 2006). Up-flow biofilters have higher removal of NOM and allows more diverse and equitability in bacterial community compared to down-flow filters (Han *et al.* 2013). Recent studies have suggested to operate biofilters as a purposefully operated biological system, i.e., engineered Biofiltration. In these engineered biofilters, feed water is supplemented with nutrients to promote the microbial growth and biofilm formation and subsequently enhance the removal of NOM (Lauderdale *et al.* 2012; Azzeh *et al.* 2015).Cheng *et al.* (2005) used modification techniques to improve virgin GAC using heat activation, ammonia treatment and iron-impregnation to increase the dissolved organic matter removal from water. Their result showed that even though mass-basis performance of modified GAC was better compared to virgin GAC for dissolved organic matter uptake. But no specific selectivity was visible for specific size fractions and for UV absorbing fractions of NOM. Comparison between old GAC filter and regenerated GAC filters showed that removal efficiency improved after regeneration for intermediate molecular weight fractions (Matilainen *et al.* 2006). However, this improvement changes within few months after regeneration.

A limited number of studies combines optical properties of NOM measured through UV absorbance and fluorescence spectroscopy to monitor the reduction of NOM in full-scale DWTP (Ishii & Boyer 2012). Some of these studies have investigated the application of PARAFAC analysis to track changes in NOM in DWTPs.

Baghoth *et al.* (2011a) studied two full-scale treatment facilities to track the changes to PARAFAC component due to several treatment processes like rapid sand filtration, ozonation, biological activated carbon filtration, and coagulation, together with another NOM characterization technique called liquid chromatography-organic carbon detection (LC-OCD) for a combined set of samples. Their study revealed unique process impacts on individual FDOM fractions of NOM, suggesting the possible use of fluorescence spectroscopy for online monitoring. Sanchez *et al.* (2013) performed a long term study demonstrating the suitability of fluorescence and PARAFAC analysis for selection of coagulant to optimize organic concentration reduction. Bieroza et al. (2011) has compared different analysis techniques of fluorescence measurements collected from 16 full-scale treatment plant’s treatment processes and compared different decomposition and calibration models used for fluorescence data. Peleato and Andrews (2015) compared the performance of four drinking water treatment plant using fluorescence spectroscopy and LC-OCD. They concluded that coagulation/settling removed both humic and protein-like material with higher removal of larger molecular weight, hydrophobic humic-like NOM. This result is also in consistent with previous researchers like (Beggs et al. 2009b; Baghoth et al. 2011; Sanchez et al. 2013; Peleato & Andrews 2015). Peleato *et al.* (2016) later performed a pilot scale study on BAC filters and found that the biofilter using GAC as media, with exhausted absorptive capacity, provided the highest removal of all identified PARAFAC components. They also showed that deep GAC layer filters gave greater protein- and humic-like removal. A microbial or processed humic-like component was found to be most amenable to biodegradation by biofilters and removed mainly by conventional treatment (Peleato *et al.* 2017). Protein-like DOM (especially tryptophan) are removed mainly removed by degradation by microorganisms attached to the GAC in the filters (Wang *et al.* 2017). Previous studies observed fresh GAC filters have high removal of humics through adsorption.

3 Materials and methods

This chapter includes a description of the study area, description of the two full-scale drinking water treatment plants and the experimental set-up and as well as a description of the analytical methods (DOC, optical measurements: fluorescence spectroscopy and UV absorbance at 254nm) that are used to compare the water quality are included.

3.1 Operational strategy

In order to combine the benefits of both fresh GAC and BAC filters in a simple manner, a strategy is here proposed whereby a portion (10%) of saturated activated carbon from the BAC filter top is replaced by fresh activated carbon filter media.

3.2 Study areas

Marieberg DWTP

One full-scale drinking water treatment plant (Marieberg DWTP) was used during the investigation of applicability of the proposed strategy in Paper I. Marieberg DWTP is located in Uddevalla municipality, Sweden (Figure 3-1) and receives raw water from Lake Köperödssjön which is located in a forested area. Water is pumped to the lake from a creek that runs through an agricultural area. The treatment train consists of flocculation using poly-aluminium 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 I).

Figure 3-1: Study areas for the experiments.

Lackarebäck DWTP

To study the robustness of the proposed strategy, the full-scale experiment was repeated in another DWTP called Lackarebäck and NOM removal performance was compared with Marieberg DWTP. Lackarebäck DWTP is the second largest in Sweden and located in Gothenburg municipality, Sweden. The water is collected from a 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 Aluminium sulphate, sedimentation, rapid filtration through activated carbon, membrane filtration using ultrafilter, and final disinfection with Chorine and sodium hypochlorite (Figure 3-2, Figure 1 and Table 1, in Paper II).

There are seven activated carbon filters in Marieberg WTP and 24 filters in Lackarebäck DWTP. GAC filters in Marieberg were over three years old at the time of the study whereas GAC filters in Lackarebäck were two years old. Details of the filters are presented in *Paper II.*

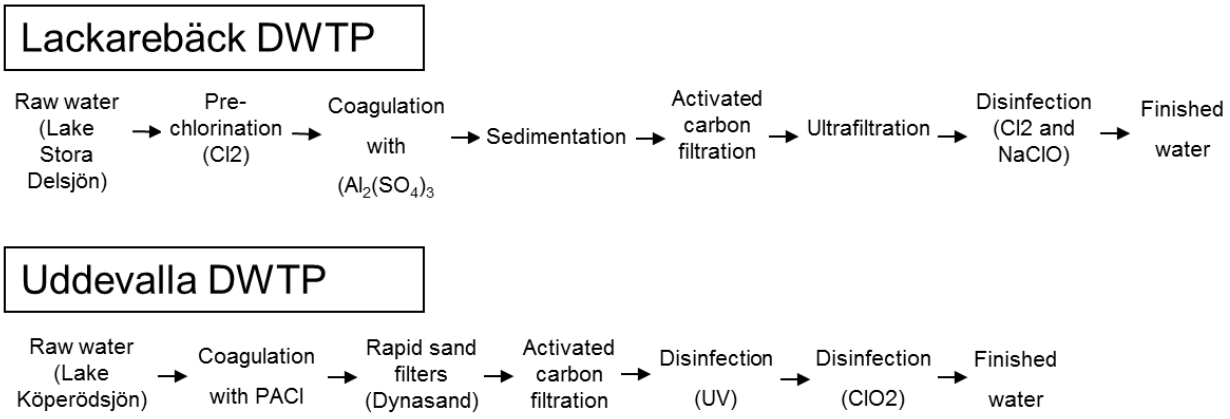

Figure 3-2: Lake water sources and treatment processes for Lackarebäck and Uddevalla DWTP.

3.3 Experimental design

In Marieberg DWTP (*Paper I)* 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 I (section 2.3 ‘Experimental design’). It is important to mention that the replenishment operation, in Marieberg DWTP, of the three filters was performed in sequence F6, F7 and F4. During the replenishment operation the filter was taken out of operation and the flow in the remaining filters increased accordingly. This implies, Filter F6 received higher flow two times during the period when filter F7 and F4 were taken out of operation during replenishment.

In Lackarebäck DWTP (Paper II), one full-scale filter was selected for replenishment and a reference filter was selected for monitoring.

3.4 Sampling

In Marieberg DWTP, the experiment was carried out during the summer of 2015 (July – August). Regular weekly sample collection from four sampling sites were performed. Inflow and outflow water of the BAC filters were sampled at seven sampling points. Inflow (after two Dynasand filter halls) and outflow for the five filters (F4, F6, F7, Rf2 and Rf5) were sampled. In total 138 samples were collected from the treatment plant. In order to monitor the continuous relative changes in treated water from the filters, a multi-parameter spectrophotometer probe Spectro::lyser was placed at the outlet from the carbon filters. Parameters that were measured by this probe were TOC, UV absorbance 254, turbidity (in FNU and NTU units), colour and transmittance. More details on sampling in Paper I.

Figure 3-2: Sampling points after BAC filters.

In Lackarebäck DWTP, the experiment was carried out in the fall 2016 (September – October). In total 70 samples were collected in the treatment plant. Sampling took place 1-2 times per week for 4 weeks. Samples were collected for UV absorbance, fluorescence and dissolved organic carbon (DOC) in both DWTP. More details on sampling in Paper II.

3.5 Analytical method

3.5.1 Fluorescence spectroscopy

Aqualog fluorescence spectrophotometer (Horiba Inc.) with a 10 mm path length was used for CDOM fluorescence and absorbance analysis. The F-EEMs were measured (at 20°C) by scanning the excitation wavelengths ranged from 220 nm to 500nm in 3nm steps and 2sec integration time and emission ranged from 245nm to 825nm with 2.33nm increment.

Raman scans of Milliq water in a sealed cell was obtained every day as blank. Aqualog fluorescence spectrophotometer can measure the absorbance spectra (200-500 nm) at the same time as the fluorescence spectral analysis.

3.5.2 Dissolved organic carbon (DOC)

DOC was measured using a Shimadzu TOC-V_{CPH} carbon analyser with auto-sampler TOC-ASI-V. Non-purgeable organic carbon (NPOC) method was used to analyse DOC were all the inorganic carbon were removed through purging the sample with CO_2 free purified air for 5 minutes. DOC concentration was calibrated using 5 point calibration curve for potassium Phthalate standards solutions (between 1.0-10.0 mg C/L).

3.5.3 High performance size exclusion chromatography (HPSEC)

HPSEC analysis was carried out to check the influence of GAC replenishment on molecular size of NOM, on one of the DWTP samples. Details of this analysis is presented in Paper II.

4 Results and discussion

4.1 Did the proposed modification strategy improve BAC filters performance at Marieberg?

In Paper I, the modification strategy was investigated in Marieberg DWTP, where three full-scale filters were replenished and two reference filters monitored to compare the NOM removal efficiency. The efficiency was compared based on optical properties of NOM (Fluorescence and UV spectroscopy) as well as DOC removal capacity.

Online monitoring of UV absorbance provided real-time information about the filter performance and allowed to observe subtle changes in water quality. In Figure 4-1 (Paper I, Figure 2), it can be seen that before replenishment, modified filter F4 and reference filters Rf5 had similar UV absorbance. After replenishment, a sharp drop is visible which recovers back to original performance after 10-20 days. UV absorbance is an indicator of aromatic groups and humic fraction of NOM, thus their reduction indicate preferential removal of these fractions of NOM by the modified filters. UV absorbing NOM fractions or CDOM are recalcitrant to biodegradation (Lawrence 1980; Novak *et al.* 1992). Thus their improved reduction indicates that they are not removed by biodegradation within the BAC filters, rather they are removed by the improved adsorption capacity of the modified BAC filters. This is consistent with previous findings where it was seen that UV absorbing NOM are removed by adsorption (Chowdhury 2013). However, UV absorbance does not detect hydrophilic fraction of NOM which are known to be DBP precursors (Shon *et al.* 2006). Neither can it detect easily biodegradable NOM which are small in molecular size and non-UV-absorbing (Yavich & Masten 2003; Bond *et al.* 2011). Therefore, UV absorbance measurements needs to be complemented with other NOM characterisation techniques to get the full-picture of NOM fraction removal via filtration process.

From the online monitoring of UV absorbance data, it was seen that the removal is dependent on the incoming flow or surface load to the filter. The last modified filter (Filter F4) were more efficient and for longer duration than the other filters, since it did not receive increased surface load while other filters where out of operation (Paper I, Figure 2 and 3). Fu *et al.* (2017) reported 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 NOM in BAC filters. For this reason, surface load or flow rate is a key design and operating parameter of a biofilter/contactor (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 in order to ensure good filtered water quality.

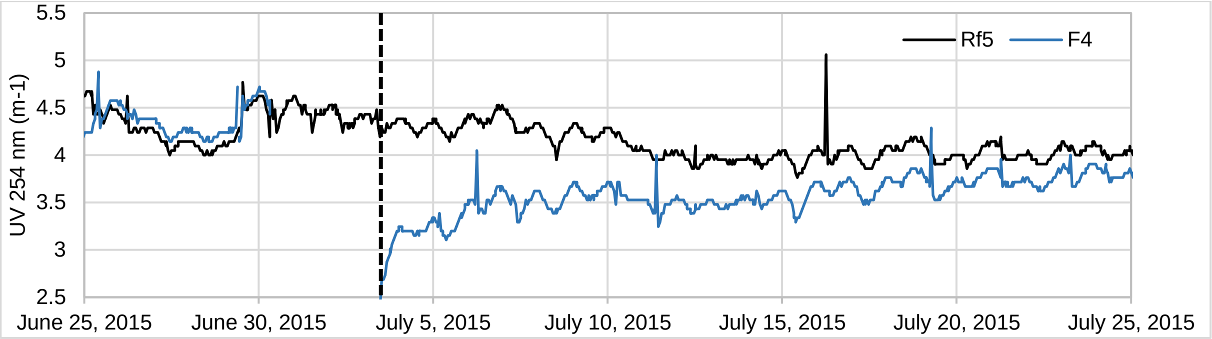

Figure 4-1: Water quality in filtrates from modified (F4: blue line) and reference (Rf5: black line) filters. Vertical dotted lines denote filter start-up after GAC replenishment. Data for 30 days are presented here.

DOC removal in modified and reference filters were moderate (Paper I, 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 are comparable to removal rates obtained in several studies done on full-scale BAC filters (Hozalski *et al.* 1995; Baghoth *et al.* 2011b; Fu *et al.* 2017). 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 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.

Fluorescence intensity of effluents from modified filters was lower than reference filters. The reduction of fluorescent dissolved organic matter (FDOM) (calculated by differential EEMs using Equation 1) reduces with bed volume treated by the filters. From Figure 4-2, it can be seen that fluorescent NOM fractions were removed over the complete range of excitation and emission wavelengths. From the intensity scale, it can be seen that the NOM 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. Thus, visualising EEM data in this manner allows to observe which type of FDOM is the easiest to remove by the modified filters compared to the reference filters. Thus, fluorescence analysis can separate bulk NOM concentrations (measured using UV and DOC) into fractions, each reacting differently to different treatment processes. Comparing Figure 4-2 with Figure 2-4, it can be seen that modified filter is efficient at removing terrestrial humic like peaks A and C (in Figure 2-4), as well as protein-like peak T than the reference filters.

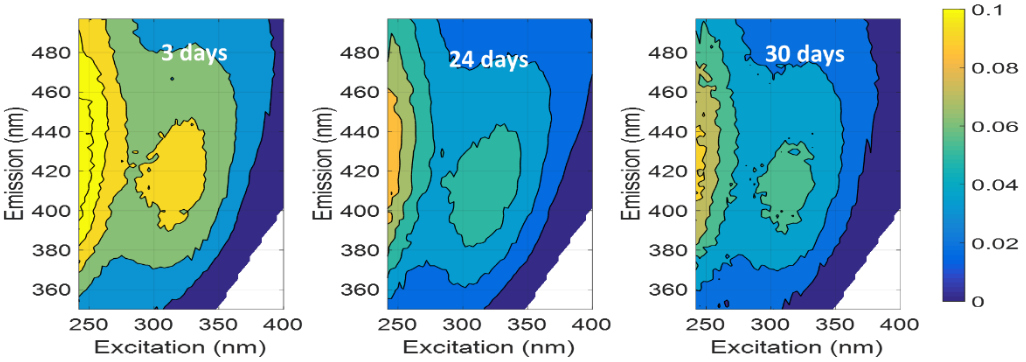

Figure 4-2: Removed fraction of FDOM by the modified filter in comparison to the reference filter. Differential EEM calculated between Reference filter Rf5 and modified filter F4 at Marieberg DWTP. Signal intensities are presented at the right of the Figure in color bar where colors represent absolute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

PARFAC decomposition of collected EEM found three independently varying FDOM fractions (Paper I, Figure 4). The excitation ad emission maxima of identified components are listed in Table 4-1.

Table 4-1: Identified PARAFAC components and their characteristics as well as removal by the modified filters (Paper I)

Component	Excitation (nm)	Emission (nm)	Characteristics	Removal by reference filters (%)	Removal by modified filters (%)
C1	<250, 330	480	Terrestrial humic material Relatively larger molecular weight	12-14	16-24
C2	<250, 330	410	Terrestrial humic-like NOM modified by microbial reprocessing Relatively smaller molecular weight fraction	17-22	24-33
C3	<250, 290	360	Tryptophan protein-like character and associated with algal and microbial-derived organic	15-19	20-28

The modified filters reduced all PARAFAC components with higher efficiency than reference filters. Similar removal efficiency of PARAFAC components was previously observed by other researchers such as Baghoth *et al.* (2011a); Peldszus *et al.* (2011). The highest removal was observed for microbially reprocessed humic-like NOM fraction (C2) followed by protein-like NOM (C3). PARAFAC component C2 was the most abundant FDOM in incoming water to the BAC filters and was removed to the greatest extent. In our study, protein-like fluorescence NOM fraction removal were moderately high by both reference and modified BAC filters contrary to the recent study done by Fu *et al.* (2017) on GAC biofilter. They found in their study that proteins are refractory to the BAC filtration process. However, in this study there was noticeable increase in removal of protein-like fluorescence. Terrestrial humic-like component (C1) is the humic fraction of NOM that is removed by adsorption onto fresh GAC (Velten *et al.* 2011) and is not removed by biofiltration (Baghoth *et al.* 2011a). Therefore, removal of C1 improved after replenishment indicating higher adsorption ability of the BAC filters. Previously component C1 and C2 has been found to correlate strongly with chloroform which is the most abundant DBP formed by chlorination (Pifer & Fairey 2012). Thus improved reduction of C1 and C2 decreases formation potential of chloroform.

PARAFAC decomposition of collected excitation emission revealed three components (Paper 1, Table 2). Reduction in FDOM components were always greater than UV for both modified and reference BAC filters (Paper1, Figure 5). Indicating that the modified filters were better than reference filters to remove FDOM fractions of NOM (Figure 4-3).

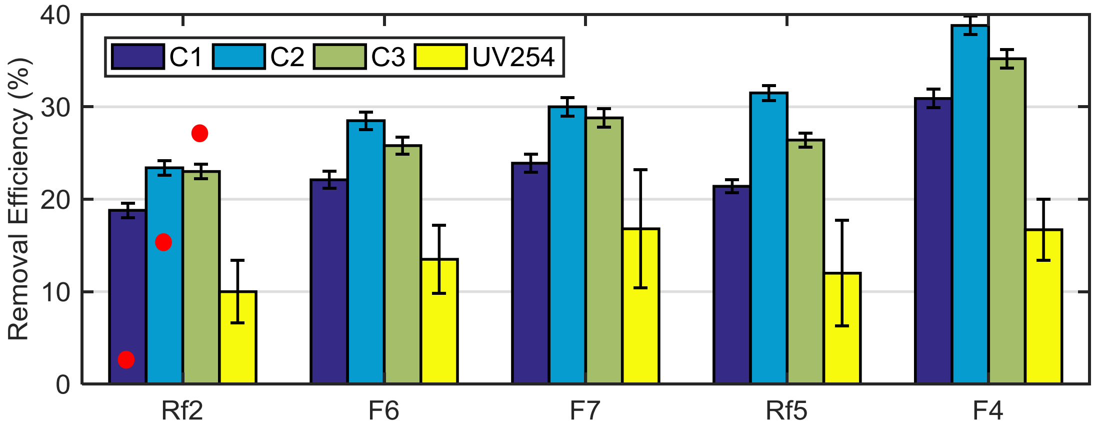

Figure 4-3: Removal efficiencies of three fluorescence components (C1-C3) and UV_{254} during the four weeks following GAC replenishment. Modified filters F6 and F7 should be compared with reference filter Rf2 and modified filter F4 with reference filter Rf5. (Paper I, Figure 5). The removal efficiency 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).

To conclude, the results presented here demonstrates that the proposed modification strategy 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. However, this only proves the robustness of the modification strategy at one plant. Therefore, in order to check the robustness of the strategy there is a need to implement this at a second plant.

4.2 Does the proposed modification strategy work for different NOM source and treatment trains?

In order to check the robustness of the proposed strategy, replenishment of the one BAC filters was performed in Lackarebäck DWTP and compared with Marieberg DWTP. The two plants have different raw water quality and different treatment processes before their BAC filtration step. The general raw water quality and quantity of the pre-treated water (water after conventional treatment) is presented in Table 4-2 and 4-3.

Table 4-2: Raw water quality and average treatment capacity for Lackarebäck and Marieberg DWTP

	Lackarebäck	**Marieberg**	**Observation**
Capacity (m^3/day)	180,000	11,300	Lackarebäck higher capacity
Consumers served	500,000	35,000	
Temp (°C)	2.1-19.2 (8.2)	2.2–19.8 (10.2)	Marieberg has higher temperature
pH	7.0–7.4 (7.2)	6.4–7.1 (6.9)	Typical for surface water
TOC (mg/L)	4.5–5.1 (4.7)	9.0*	Marieberg has higher DOC
Turbidity (NTU)	0.7–1.8 (1.0)	0.8-2.9 (1.5)	Lackarebäck has higher turbidity
UV$_{254}$ (1/cm)	0.11–0.17 (0.12)	0.26-0.48 (0.37)	Marieberg has higher UV absorbance
SUVA (mg/L-m)	3.2- 5.2 (2.6)	3.2*	Both have water with mixture of aquatic humics and mixture of hydrophobic and hydrophilic NOM of different molecular weight

* Data not available for the whole year. Median value is in parenthesis. For Lackarebäck data is collected from Göteborgs Stad Kretslopp och Vatten (2017)

During coagulation treatment, close to 50 – 60% DOC was removed in both DWTPs. This is expected from the SUVA values of the raw waters (Table 4-2), since 25-50% removal efficiency from waters having SUVA from 2 – 4 is found through previous research (Matilainen *et al.* 2010).

Table 4-3: Average (4 weeks) results of DOC, UV254 and SUVA values measured at Lackarebäck and Marieberg DWTP

	Lackarebäck DWTP			**Marieberg DWTP**		
Sample	DOC[a] (mg C/L)	UV$_{254}$[a] (cm^{-}1)	SUVA[a] (L/mg/m)	DOC[a]	UV$_{254}$[a] (cm^{-1})	SUVA[a] (L/mg/m)
Incoming water to BAC filters	3.85 ± 0.3	0.038 ± 0.003	0.98 ± 0.1	3.3 ± 0.2	0.056 ± 0.003	1.7 ± 0.13
BAC filter effluent (ref. filter)	3.54 ± 0.6	0.031 ± 0.003	0.84 ± 0.2	2.9 ± 0.4	0.05 ± 0.003	1.7 ± 0.15
BAC filter effluent (modified filter)	3.28 ± 0.4	0.027 ± 0.003	0.82 ± 0.17	2.7 ± 0.1	0.04 ± 0.002	1.5 ± 0.1
Water quality	Less SUVA, Less aromatic fraction			Higher SUVA, more aromatic fractions		

[a] Mean value ± standard deviation, for n = 23 and 12 (raw water and coagulated settled water samples) for Lackarebäck and Marieberg DWTP, respectively

From a combined PARAFAC model, the same FDOM components were found in both DWTP, indicating similarity in FDOM character despite different source waters. Modified BAC filters in both DWTPs had improved removal of DOC, SUVA, UV$_{254}$ and FDOM components. Higher removal for UV$_{254}$, SUVA and FDOM components was observed in Lackarebäck compared to Marieberg DWTP (Table 4-3, Figure 4-4).

Lackarebäck had lower SUVA in the BAC filter influent, indicating higher biodegradability (Yapsakli & Çeçen 2010). Since UV-absorbing fractions are non-biodegradable and are removed by adsorption, their additional reduction indicate improved adsorption in modified filters compared to reference filters. Higher removal of the non-biodegradable fraction on fresh

GAC filter allows the biodegradable fraction to be better removed within the modified BAC filters. This is evident from improved reduction of microbially reprocessed humics (C2) and proteins (C3) which are removed via biodegradation. Higher removal for FDOM components in Lackarebäck DWTP (Table 4-3, Figure 4-4) can be caused by longer retention time within BAC filters in Lackarebäck than Marieberg DWTP (Table 4-2) which further assists in removing more NOM in Lackarebäck (Pramanik et al. 2015). Furthermore, Lackarebäck has pre-chlorination, which is known to produce smaller and more bioavailable NOM fraction from humic substances (Ji *et al.* 2008). These smaller size humics are both easily adsorbed and degraded within the modified filters resulting improved reduction of both C1 and C2 FDOM fractions (Matilainen et al. 2006).

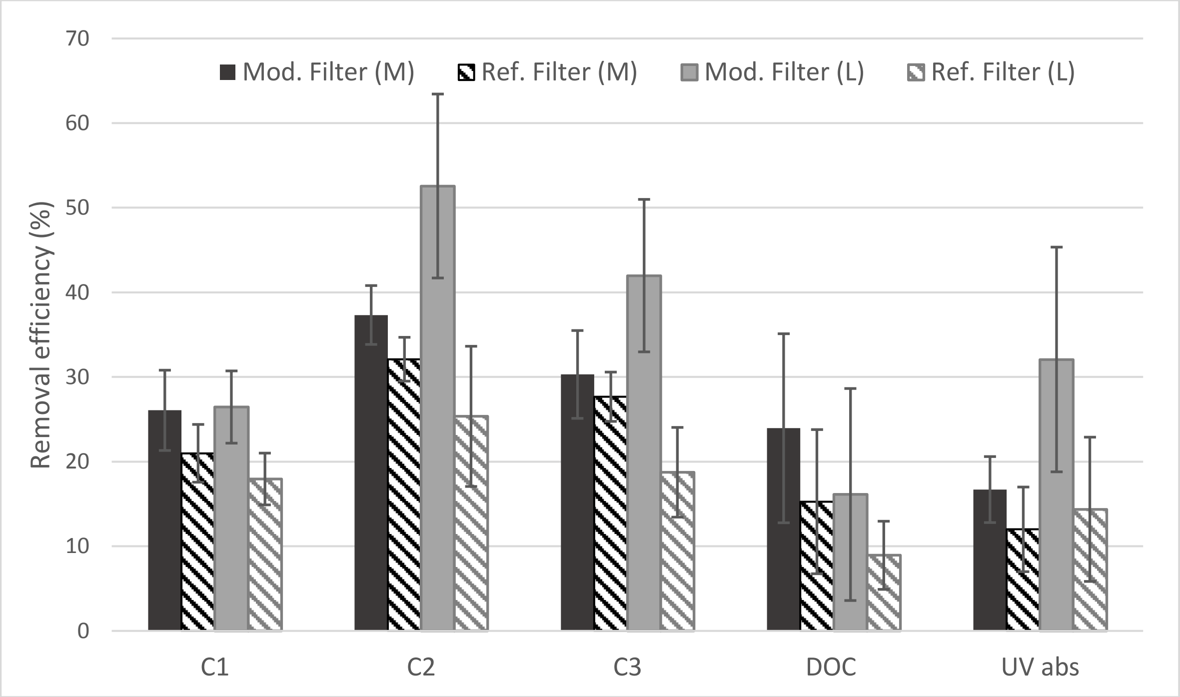

Figure 4-4: Removal efficiency of Identified PARAFAC component, DOC and UV_{254} by modified and reference filters in Lackarebäck (L) and Marieberg (M) (F4 and Rf5) drinking water treatment plant. (Average value over 4 weeks following GAC replenishment).

DOC removal, on the other hand, was higher in Marieberg DWTP. Higher removal of DOC in this DWTP probably results from chlorinated backwashing of the BAC filters. Chlorinated backwashing diminishes microbial biomass within the biofilm, which then needs to build up again during the filter cycle period (Miltner et al. 1995). Degradation of DOC is higher during the build-up stage of biomass after chlorinated backwashing compared the mature biomass, at the steady state of the biofilm (that has not been through chlorinated backwashing) (Hozalski et al. 1995; Velten et al. 2011a).

Overall, the proposed modification strategy improved the performance of NOM removal in BAC filters, regardless of source water characteristics and upstream treatment processes. Lower SUVA in the incoming water allowed for better removal of biodegradable NOM fractions by the modified BAC filters.

5 Conclusions and recommendations

5.1 Summary and conclusions

In this chapter the summary and conclusions regarding the modification of BAC filters using fresh GAC replenishment are presented. Some recommendations for the water industry based on the research questions are included, as well as suggestions for future research questions.

A modification strategy to improve NOM removal by biologically activated carbon (BAC) filter is presented in this thesis. The strategy involves replenishing a small portion of saturated filter media with fresh filter media in order to improve NOM removal. Full-scale experiments, using three modified and two reference BAC filters, have been carried out (Paper I). Additionally, validation of the robustness of the modification strategy has been carried out by comparing two DWTPs with varying source water and coagulation treatment (Paper II). The modified filter was monitored to evaluate the effect of partial replenishment of BAC filters on NOM removal. Various NOM characterisation techniques like dissolved organic carbon (DOC) and optical measurement techniques (fluorescence and absorbance) were used to investigate the performance of modified and reference filters.

A summary of the findings obtained is presented below:

- Partial renewal of filter media with fresh GAC in BAC filters improved the removal of various NOM fractions.
- The efficiency of GAC replenishment was monitored online using UV_{254}. The online measurements showed that the adsorption capacity was enhanced for a period of 10-20 days. Improved reduction of UV_{254} indicates that the filter effluent had lower aromatic groups and humic fractions. These fractions are preferentially removed by adsorption onto fresh GAC, accordingly, reduction of the UV absorbing NOM indicates improved adsorption onto the modified BAC filters.
- Enhanced removal of the UV absorbing NOM indicated improved adsorption onto the modified BAC filters. UV absorbing NOM are known to indicate regulated disinfection by-products.
- SUVA values decreased following GAC replenishment. A lower SUVA value is an indicator of higher biodegradability and lower aromaticity in the modified filter effluent.
- From the fluorescence measurement, three NOM fractions were identified. Two fractions were humic-like (terrestrial humic-like and microbially reprocessed humic-like) and one component was protein-like. Modified filters showed an improved removal of these identified fluorescent components.
- Improved removal of absorbable (terrestrial humic-like) fluorescent NOM fraction further supported the reduction of UV absorbing NOM fractions and confirmed that adsorption capacity improved within the modified filters.

- Biodegradable (microbially reprocessed humics and protein-like) NOM fractions improved after GAC replenishment. Higher removal of biodegradable NOM fraction compared to absorbable fraction indicate that the biodegradation capacity improved significantly within the modified filters.
- Reference filters were not good at removing DOC. Possibly due to desorption of already adsorbed DOC in the filters. Removal of DOC was higher after replenishment of BAC filters compared to reference filter.
- HPSEC analysis showed that the removal efficiency of smaller molecular weight fractions (<500 kDa) was slightly better in the modified filters, and that the removal improvement was still evident 21 days after GAC replenishment.
- Improved removal lasted for different periods in different DWTPs. Improved removal of humic substances were observed for 10-20 days in Marieberg DWTP and more than 6 weeks in Lackarebäck DWTP.

5.2 Recommendations for the water industry

Based on work presented in this thesis, the following recommendations for the water industry are made:

- Partial renewal of BAC filters can improve NOM removal for a certain period. However, DWTPs that utilise pre-chlorination will have longer enhanced NOM reduction by the modified filters.
- 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 in order to ensure good filtered water quality.
- DWTPs that have less aromatic fractions (lower SUVA) in the incoming water to the filters will benefit more from replenishing their BAC filters.
- The suggested modification strategy can be used during periods of expected high NOM loads. Such events could be after snow melt run off 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).

5.3 Areas of future investigation

In this study, the focus was to improve NOM removal in BAC filters by partially replenishing saturated filter media with fresh media. The evaluation of filter performance was based on NOM removal assessed by various NOM characterization techniques. GAC replenishment will, however, also influence the biofilm and microbial community that colonize the pores of GAC particles, but these effects were beyond the scope of this study. Future research should assess the effect of GAC replenishment on biological activity in the filter media using various techniques such as:

- Scanning electron microscopy (SEM): SEM images can demonstrate the morphology of suspended filter material surfaces (Weber *et al.* 1978).
- Adenosine triphosphate (ATP) measurement: ATP analysis can measure the detachment of the biomass as well as biological activity on the filter media (US EPA 1991; Servais *et al.* 1994).
- Phospholipid fatty acid (PLFA) analysis: The changes of biomass and bacterial community in the BAC filters after GAC replenishment can be measured using this method (Findlay *et al.* 1989).

In the current study, potential changes in sorption capacity of the filter media were not monitored. To improve our understanding of the changes in sorption capacity of the filters, iodine number (IN) and apparent surface area (S_{BET}) should be monitored on a regular basis.

NOM removal by GAC and BAC filters is controlled by the relationship between the molecular size distributions of NOM and pore size distribution of carbon (Newcombe 1994). To improve our understanding of the effects of partial GAC replenishment on BAC filters, the pore size distribution in the filter media, in addition to a comparison between different DWTPs, should be assessed. Finally, there is a need to investigate whether the positive effect of GAC replenishment on NOM removal by modified BAC, improved the reduction of DBP formation as well.

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