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Abstract

Safe and clean drinking water is recognised as a human right by the United Nations, but water sources world-wide are affected by the widespread use of synthetic chemicals, creating a challenge that drinking water producers must address. Many of these synthetic chemicals, here referred to as organic micropollutants (OMPs), are not well removed by conventional drinking water treatment, and thus additional treatment steps are needed.

Granular activated carbon (GAC) is a commonly used sorption material in water treatment processes. This thesis explores different roles of GAC filters in drinking water production: as a chemical barrier, as a biofilter, as a post-treatment step after ozonation and as a waste management step after nanofiltration. In two pilot-scale experimental set-ups, different kinds of raw and process water were treated in processes involving GAC filtration. Removal rates of a broad range of OMPs (including per- and polyfluoroalkyl substances; PFAS) were studied, along with microbial abundance and several parameters characterising natural organic matter (NOM) content.

The results showed that GAC filters were more efficient with pre-ozonation, but the efficiency of OMP removal decreased over time. Inclusion of ozone treatment also introduced new challenges, as it was shown to increase bioavailability of NOM, which GAC filters were not fully able to remove. However, the GAC filters inevitably transitioned into biofilters over time, and these biofilters were able to remove more NOM when pre-ozonated. The in-depth information provided by this thesis on GAC filter performance over time under different conditions provides new insights into water treatment options to protect human health.

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Utforskande av granulerat aktivt kols roll i dricksvattenberedning

Sammanfattning

Säkert och rent dricksvatten erkänns som en mänsklig rättighet av FN, men vattenkällor över hela världen påverkas av den utbredda användningen av syntetiska kemikalier, vilket skapar en utmaning för dricksvattenproducenter. Många av dessa syntetiska kemikalier, s.k. organiska mikroföroreningar (eng: OMP), avlägsnas inte effektivt genom konventionell dricksvattenbehandling, och därför behövs ytterligare reningssteg.

Granulärt aktivt kol (eng: GAC) är ett vanligt förekommande sorptionsmaterial i vattenreningsprocesser. Denna avhandling utforskar de olika roller som GAC-filter kan spela i dricksvattenproduktion: som en kemisk barriär, som ett biofilter, som ett efterbehandlingssteg efter ozonering och som ett avfallshanteringssteg efter nanofiltrering.

I två försöksuppställningar i pilotskala behandlades olika typer av råvatten och processvatten i reningsprocesser som involverade GAC-filtrering. Borttagning av ett brett spektrum av OMP:er (inklusive per- och polyfluoroalkylsubstanser; PFAS) studerades, tillsammans med mikrobiell förekomst och flera parametrar som ger information kring innehållet av naturligt organiskt material (NOM).

Resultaten visade att GAC-filter var effektivare med förozonering, men effektiviteten av OMP-borttagning minskade med tiden. Införandet av ozonbehandling introducerade också nya utmaningar, eftersom det visade sig öka biotillgängligheten av NOM, som GAC-filtren inte helt kunde ta bort. Men GAC-filtren skiftade oundvikligen till biofilter med tiden, och dessa biofilter kunde ta bort mer NOM när de förozonerades. Den djupgående informationen som tillhandahålls av denna avhandling om GAC-filterprestanda över tid under olika förhållanden, ger nya insikter om vattenbehandlingsalternativ för att skydda människors hälsa.

Nyckelord: Ozonering, nanofiltrering, biofiltrering, assimilerbart organiskt kol, flödescytometri, naturligt organiskt material, organiska mikroföroreningar, PFAS

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Till farfar,
  du hade älskat att få gå på disputation på Ultuna

"The situation is a lot more nuanced than that!"
Rebecca Bunch

Contents

List of publications

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

I. **Ullberg, M.**, Lavonen, E., Wiberg, K. & Köhler, S.J. Assessing the transition between adsorption and biological natural organic matter removal by granular activated carbon – a spatially and temporally resolved pilot study. (Manuscript, under review in *Water Research*.)

II. **Ullberg, M.**, Lavonen, E., Köhler, S.J., Golovko, O. & Wiberg, K. (2021). Pilot-scale removal of organic micropollutants and natural organic matter from drinking water using ozonation followed by granular activated carbon. *Environmental Science: Water Research & Technology* 7, 535-548.

III. Franke, V., **Ullberg, M.**, McCleaf, P., Wålinder, M., Köhler, S.J. & Ahrens, L. (2021). The price of really clean water - Combining nanofiltration with granular activated carbon and anion exchange resins for the removal of per- and polyfluoroalkyl substances (PFASs) in drinking water production. *Environmental Science & Technology Water* 1, 782-795.

IV. **Ullberg, M.**, Lavonen, E., Danielsson, M.., Wiberg, K., Köhler, S.J. & Paul C. J. Mapping the dynamics of bacterial release from pilot-scale granular activated carbon filters using flow cytometry. (Manuscript)

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The contribution of Malin Ullberg (MU) to the papers included in this thesis was as follows:

I. MU designed and planned parts of the study together with the co-authors. She had the main responsibility for evaluating the data and writing the manuscript, with support from the co-authors.

II. MU designed and planned parts of the study together with the co-authors. She conducted sampling and extraction of OMP samples and had the main responsibility for evaluating the data and writing the manuscript, with support from the co-authors.

III. MU designed and planned the study together with the co-authors. She conducted sampling and analysis of organic carbon samples and had shared responsibility (with V. Franke) for evaluating the data and writing the manuscript, with support from the co-authors.

IV. MU designed and planned parts of the study together with the co-authors. She had the main responsibility for evaluating the data and writing the manuscript, with support from the co-authors.

Abbreviations

AFFFs   Aqueous film-forming foams

AIX   Anion exchange resin

AOC   Assimilable organic carbon

BB   Building blocks

BDOC   Biodegradable dissolved organic carbon

BP   Biopolymers

BV   Bed volume

DOC   Dissolved organic carbon

DWTP   Drinking water treatment plant

EBCT   Empty bed contact time

FCM   Flow cytometry

GAC   Granular activated carbon

HNA   High nucleic acid

HS   Humic substances

IS   Internal standard

LC   Liquid chromatography

LC-MS/MS   Liquid chromatography + tandem mass spectrometry

LMW   Low molecular weight

LNA   Low nucleic acid

MS	Mass spectrometry
NF	Nanofiltration
NOM	Natural organic matter
OCD	Organic carbon detection (as in LC-OCD)
OMPs	Organic micropollutants
PAC	Powdered activated carbon
PFASs	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutane sulfonic acid
PFCAs	Per- and polyfluoroalkyl carboxylic acids
PFHpS	Perfluoroheptane sulfonic acid
PFHxA	Perfluorohexaanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPeS	Perfluoropentane sulfonic acid
PFSAs	Per- and polyfluoroalkyl sulfonic acids
POP	Persistent organic pollutant
RO	Reverse osmosis
SPE	Solid phase extraction
TCC	Total cell concentration
TOC	Total organic carbon
UV_{254}	Ultraviolet light of wavelength 254 nm
UVD	Ultraviolet light detection (as in LC-UVD)

1. Introduction

The United Nations states that "The human right to water is indispensable for leading a life in human dignity. It is a prerequisite for the realization of other human rights", while defining the right to water as "the right of everyone to sufficient, safe, acceptable, accessible and affordable water for personal and domestic uses" (United Nations, 2015).

Before serving as drinking water, most water sources require some level of treatment. In the past, such treatment generally focused on clarification by filtration and later on disinfection to remove pathogens (Çeçen, 2011). Today, however, drinking water producers are facing new challenges, as increasing use of synthetic chemicals, hereafter referred to as organic micropollutants (OMPs), poses a growing threat to raw water sources and the environment (Reemtsma et al., 2016).

This thesis explored granular activated carbon (GAC) filtration, in conjunction with ozonation or membrane filtration, as a solution to this threat. It also examined another function of GAC filters, namely their ability to act as biological filters that can reduce the dissolved organic matter content in water.

2. Objectives and research questions

The overall aim of the work presented in this thesis was to better understand the function and capacity of GAC filters under different operating conditions, in terms of biological degradation and adsorption of natural organic matter (NOM), biological activity and adsorption of a range of OMPs. The work addressed the following four research questions, as described in Papers I-IV:

1. How do removal patterns (adsorptive and biodegradation) of NOM change over time as a GAC filter transitions to becoming a biofilter? (**Paper I**).

2. How does pre-treatment (ozonation) change the removal characteristics (adsorption vs. biodegradation) of NOM within a GAC filter? (**Paper I**).

3. How does pre-treatment (ozonation) alter the pattern of adsorption of OMPs and NOM to GAC materials? (**Paper II**).

4. How is the removal efficiency of target substances affected by the presence of NOM? (**Papers II and III**).

5. What happens in a GAC filter with respect to bacterial counts and distribution, with and without ozonated feedwater? (**Paper IV**).

3. Background

3.1 Water quality and drinking water production

Water quality is a concept that relates chemical, biological and physical characteristics to those characteristics required for safe human consumption. Natural threats to the supply of safe water include drought, salt-water intrusion, input of nutrients from agriculture and weathering of harmful substances from soil or rock (e.g. naturally occurring uranium). Other threats are inputs of anthropogenic chemicals such as pesticides, industrial chemicals and pharmaceuticals, and of harmful organisms such as viruses, parasites and harmful bacteria (i.e. pathogens), which are often connected with wastewater and poor sanitation (Benner et al., 2013).

Conventional drinking water treatment generally involves a number of physio-chemical process steps which aim to eliminate pathogens, reduce turbidity and address potential taste and odour problems. The process for a particular location is chosen to fit the water source, also called raw water, which is typically either surface water (lake or river) or groundwater. For surface water, which is generally more challenging to treat, the typical treatment process in Sweden includes a coagulation step followed by sedimentation (or flotation), passage through a rapid sand filter and finally disinfection (e.g. chlorination or ultraviolet light-treatment), before release to the distribution network and customers (Svenskt Vatten AB, 2010). A biologically active filter is sometimes added to address taste and odour problems.

Groundwater is typically cleaner to begin with and the treatment process is generally shorter. However, groundwater has challenges of its own, such as excessive hardness, contamination with pesticides from agriculture and

salt intrusion (American Water Works Association, 2014; Sonne et al., 2018). Conventional treatment process steps are not optimised to remove organic micropollutants (OMPs) and other pollutants in the water, but may still have an effect depending on the properties of the contaminant. To address specific OMP threats, additional treatment steps are necessary (Alexander et al., 2012; Marais et al., 2018; Stackelberg et al., 2007; Tröger et al., 2020; Yang et al., 2017).

3.2 Granular activated carbon (GAC)

3.2.1 A brief history of carbon as a water purifier

The use of activated carbon in its current form does not have a very long history, but the use of carbon in the form of charcoal for different purposes dates back to ancient times. There are documents showing that back in 3750 BC, the Egyptians and Sumerians used charcoal for medical purposes, for fuel and in metal production, while later (450 BD) Hindu documents state that sand and coal can be used for water purification (Crittenden et al., 2012).

During the 1700s and 1800s, industrial applications for carbon were developed, e.g. as a means of decolourising sugar syrups, and in the early 1800s activation of carbon by chemical and thermal processes was first described. In the first years of the twentieth century, the Swedish chemist von Ostreijko was granted two patents relating to the basic concepts of carbon activation. With the emerging use of chemical weapons during WWI, granulated activated carbon (GAC) products were developed on an industrial scale for use in gas masks, for adsorption of harmful gases (Bubanale and Shivashankar, 2017; Çeçen, 2011).

Since the beginning of the twentieth century, activated carbon materials have been produced on an industrial scale. However, it was not until 1960s and 1970s that filtration through GAC became a common drinking water treatment method, mainly for taste and odour control and for removal of excess chlorine (Çeçen, 2011).

3.2.2 Manufacturing and removal mechanism

Activated carbon is produced by carbonising a source material through burning without oxygen, and thereafter activating it by heating to a certain

temperature in the presence of selected gases. The source material can be one of a variety of carbon-based materials and, depending on the material and the manufacturing process, the finished activated carbon will have different characteristics and properties (Aschermann et al., 2018; Yapsakli and Çeçen, 2010).

Common activated carbon materials used for drinking water treatment are wood, coal, coconut shells, almond shells, bituminous material and waste products (Delgado et al., 2012). The activation process creates a large specific surface area (commonly around 1000-3000 m^2/g for GAC) and a porous structure with interconnected macropores (entrance dimension commonly given as >50 nm), mesopores (between 2 nm and 50 nm) and micropores (<2 nm), and with a large number of adsorptive sites to which charged substances can adsorb (Marsh, 2006; Piai et al., 2019) (Figure 1).

The surface of activated carbon is principally hydrophobic, but may also comprise polar functional groups containing oxygen, hydrogen, chorine, nitrogen and sulphur that are formed during the activation process. The nature of these functional groups will condition the specific interactions with adsorbed compounds (Çeçen, 2011). When the GAC material is saturated, it can be reactivated several times and can regain much of its original adsorption capacity (Chowdhury et al., 2011a; Marques et al., 2017).

For many compounds of interest in drinking water applications, adsorption on activated carbon occurs most commonly by non-specific physical adsorption, rather than by site-specific chemical adsorption. Physical adsorption is due to secondary binding mechanisms, meaning that electrons are shared between the adsorbate and the adsorbent, whereas in chemical adsorption electrons are transferred. Physically adsorbed molecules can be re-suspended in response to changes in concentration gradient between the main liquid phase and adsorbed solid phase (Chowdhury, 2013). Uptake is considered a two-step process. The first step involves external mass transfer from the bulk liquid phase through the hydrodynamic layer surrounding the particle, a process also known as film diffusion, after which internal mass transfer delivers the adsorbate to adsorption sites within the pores. The second step is adsorption, which is a rapid process (Chowdhury, 2013).
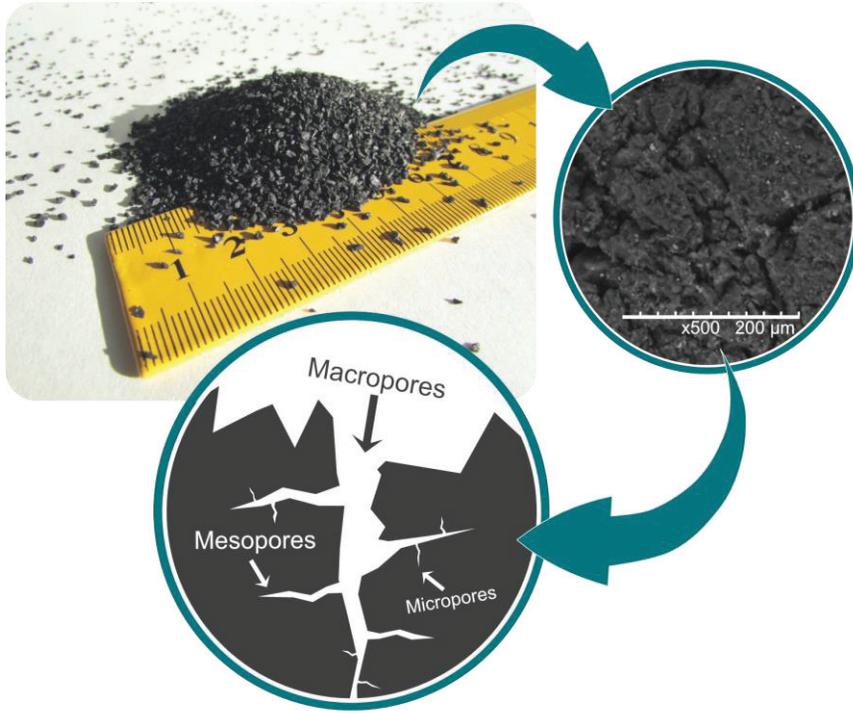
Figure 1. Illustration of granular activated carbon (GAC) showing grain size, a scanning electronic microscope image of GAC surface and a schematic illustration of the pore distribution in GAC.

3.2.3   Applications

In drinking water treatment, two main types of activated carbon are used. One is powdered activated carbon (PAC), which is distributed into the water in a reactor or in a mixing stage. Adsorption is rapid, and the PAC is then collected and discarded. This practice is expensive for continuous use and creates a large volume of sludge that needs to be taken care of. However, PAC can be useful for isolated events of e.g. petroleum spills or algal blooms (Chowdhury et al., 2011b).

The other main type is granulated activated carbon (GAC), which is the focus of this thesis. The grains or aggregates in GAC are larger (around 1 mm diameter) and it is therefore possible to utilise GAC as a filter medium, whereas PAC would not be permeable enough and would be flushed away during backwashing. When used as a filter, GAC is placed in large basins and the water to be treated is passed through it (by either upward or

downward flow). The basins are commonly connected in parallel, but two or more are sometimes also connected in series (Chowdhury et al., 2011b; Vahala, 2002).

Granular activated carbon has been proven to be efficient in removing a wide range of pollutants from water and wastewater (e.g. Benstoem et al., 2017; Corwin and Summers, 2012; Kennedy et al., 2015; Zietzschmann et al., 2016). However, the pores and adsorption sites become saturated over time and the removal efficiency diminishes, so eventually the GAC needs to be re-activated or replaced and incinerated. The appropriate (or optimal) timing of replacement or reactivation of GAC with respect to adsorptive or biofilter function is a question that is still poorly understood. There are currently no clearly defined and validated methods for estimating the condition of GAC filters, so decisions to replace are generally based on existing data from tables or on advice given by the GAC supplier.

3.3 Ozonation

Oxidation by ozone is a common and effective treatment technique in drinking water production. Typical treatment aims include colour removal, disinfection, improvement of taste and odour and conversion of potentially hazardous OMPs into harmless degradation products (Crittenden et al., 2012).

Ozone reacts with natural organic matter (NOM) in the water, creating hydroxyl radicals (HO•), simplified as follows:

$$O_3 + NOM \rightarrow HO \bullet + \text{By-products}$$

The HO• production that occurs in this reaction is suggested to be the most important mechanism for destruction of target OMP compounds in water (Elovitz and Von Gunten, 1999; Westerhoff et al., 1999).

A side-effect of ozonation when NOM is present is the formation of low molecular weight compounds such as ketones, aldehydes and organic acids. These compounds are commonly more bioavailable and may therefore promote unwanted bacterial growth in the distribution system, unless handled during post-treatment (Srinivasan and Harrington, 2007). A common way of addressing this issue is installation of a biological treatment step (usually with a biofilter) farther down in the treatment chain (Seredyńska-Sobecka et al., 2006). However, if bromide is present in the

water, harmful concentrations of bromate can be formed during ozonation and thus inclusion of an ozonation step might not be a suitable option for such waters (Crittenden et al., 2012; Neale and Leusch, 2019).

3.4 Biofiltration

Biofiltration is one of the oldest ways of purifying drinking water. The most direct examples include rapid and slow sand filtration, but as drinking water is never sterile, a GAC filter kept in operation over time will eventually develop a biofilm and become a biofilter. These biofiltration methods aids biofiltration by providing a matrix which can host a biofilm.

Biofilm is a substance that forms on available surfaces. It consists of cells, amoebae, bacteria, DNA and decomposed material, held together by a sticky material called extracellular polymeric substance, which consists of natural polymers of high molecular weight secreted by microorganisms (Staudt et al., 2004). In filtration using GAC, the bacterial flora remaining in the water after the initial treatment steps consumes biodegradable dissolved organic carbon (DOC) as substrate, and establishes a biofilm on the surface of the GAC particles (Gibert et al., 2013; Velten et al., 2011a). The large specific surface area and well-developed porous structure of GAC make it a suitable base for biofilm (Gibert et al., 2013; Oh et al., 2018; Yapsakli and Çeçen, 2010). Eventually, after the adsorptive capacity of the GAC has declined and adsorptive sites of the micropores and mesopores in the filter medium have been saturated (unless exchanged or reactivated), the main function of a GAC filter is biological degradation. One pilot-scale study found that this occurs after only 90 days (Velten et al., 2011a). Therefore GAC filters are sometimes referred to as biologically activated carbon filters (BACs) in the literature (Cuthbertson et al., 2020).

The amount of biomass attached to filter particles accumulates rapidly during the initial months of operation. The actual amount of biomass decreases from the top (or just below the top) of the filter towards the bottom during start-up (Velten et al., 2011b). This difference is less pronounced later on, and some studies have found no statistically significant difference between the top and bottom of the filter once it has reached steady-state (Gibert et al., 2013; Velten et al., 2011a).

This bioactive phase can be beneficial or detrimental for water quality, depending on the purpose of filtration (e.g. Cuthbertson et al., 2020; Wan et

al., 2021). Accumulation of biofilm can lead to pressure build-up caused by clogging and can result in a higher frequency of backwashing being required (Gibert et al., 2013). Bioactive filters tend to remove less DOC than fresh adsorptive GAC, but instead target the biodegradable fraction specifically, which can result in a more biostable water leaving the drinking water treatment plant (DWTP). This in turn results in less bacterial re-growth in the distribution network, so less disinfection (e.g. chlorination) is needed and fewer disinfection by-products (DBPs) are formed (Oh et al., 2018; Velten et al., 2011a). If combined with pre-ozonation (as is commonly done), the biofilm can utilise the increased bioavailable fraction as large NOM molecules are oxidised into smaller organic molecules during the ozonation treatment (Velten et al., 2011b).

3.4.1 Flow cytometry

Flow cytometry (FCM) has been used in a number of contexts to count different types of cells. The first studies applying this method to drinking water were performed in the early 2000s (Grégori et al., 2001). Flow cytometry measures the total numbers of bacterial cells and small particles in a water sample, by counting them one by one with a laser. Information about whether the cells are intact (alive) or not (compromised membrane, and considered dead) and a general indication of the low and high nucleic acid (LNA and HNA) content can be obtained by staining the cells with different fluorescent dyes (commonly SYBR Green and Propidium Iodide) and using different detectors (Nescerecka et al., 2016; Prest et al., 2013) (Figure 2. Flow cytometry can be used both for measuring cell count in the water phase and for quantifying cells leaving the biofilm and suspended in water or buffer (Chan et al., 2019; Velten et al., 2011a).

3.5 Other treatment processes

Besides use of GAC, which is the main focus of this thesis, more advanced treatment techniques that are commonly used in drinking water production are membrane filtration, strong oxidation and anion exchange resin (Crittenden et al., 2012). In membrane filtration processes, contaminants and unwanted constituents in water are removed mainly by size exclusion.
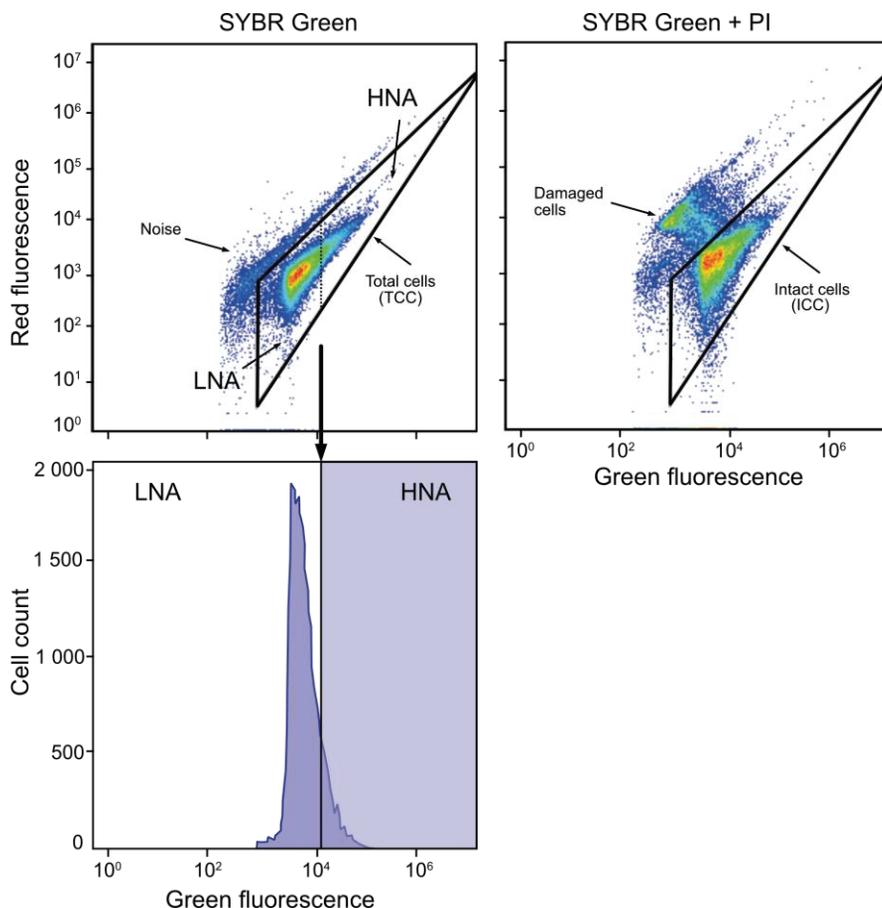
Figure 2. Use of fluorescent channels and gating to determine total cell concentration, intact cell concentration and low/high nucleic acid (LNA/HNA) content with flow cytometry. Each dot represents a cell/particle in the sample. PI = Propidium Iodide. Diagram based on data from **Paper IV**.

The membranes used are generally classified as low-pressure systems (microfiltration and ultrafiltration) (Guo et al., 2010) or high-pressure systems (nanofiltration and reverse osmosis (RO)) (Tang et al., 2007; Van Der Bruggen et al., 2003). Low-pressure systems are only suitable for removing large particles (algae, sediment, bacteria), while high-pressure systems can efficiently remove OMPs and RO membranes can remove even small inorganic molecules, an effect most commonly applied as a de-salinisation process (Crittenden et al., 2012).

Besides GAC, another adsorption type process common in drinking water production is anion exchange resins (AIX), where the removal mechanism is obviously anion exchange. Synthetic AIX can be tailored to fit specific adsorbates, such as per- and polyfluoroalkyl substances (PFASs). However, the most common application in water production is demineralisation (water softening). When saturated, the AIX material is either regenerated using brine/solvent or incinerated, where the latter option is often best for highly persistent and toxic pollutants such as PFASs (Boyer et al., 2021).

3.6 Natural organic matter

Natural organic matter (NOM) consists of a heterogeneous mixture of thousands of different organic compounds occurring naturally in water. It is normally dominated by hydrophobic organic acids, such as fulvic and humic acids of terrestrial origin (allochthonous NOM), but also contains smaller, more hydrophilic compounds that are produced within water bodies (autochthonous NOM) (Sillanpää et al., 2015). Natural organic matter is typically harmless if consumed in drinking water and NOM levels are not directly regulated in European Union drinking water quality standards. However, proxies for NOM (e.g. chemical oxygen demand (COD)) are regulated in Swedish legislation (European Union, 2020; Swedish Food Agency, 2017). Natural organic matter can react with disinfectants used in water treatment to produce disinfection by-products, some of which may have adverse effects on human health (Hammes et al., 2006; Neale and Leusch, 2019). Thus, low amounts of NOM in water entering the disinfectant step are highly desirable (Gilca et al., 2020; Mazhar et al., 2020). Natural organic matter will also compete with target OMPs for binding sites in adsorptive treatment steps (e.g. using GAC) (e.g. Aschermann et al., 2019; Zietzschmann et al., 2015).

Furthermore, chemical usage (coagulants, disinfectants) for treatment increases with NOM content, while the presence of NOM can also require more frequent cleaning and costly replacement of membrane filters due to organic fouling (Sillanpää and Matilainen, 2015a, 2015b). To limit the NOM content, drinking water producers must tailor their treatment processes to the quantity and quality of NOM present in their source water (Zhang et al., 2015).

The ultraviolet (UV)-absorbing fraction of NOM is effectively removed by coagulation and sedimentation (Sillanpää et al., 2018), and NOM removal with membrane filtration can be high depending on the molecular weight cut-off of the membrane (Peters et al., 2021). To understand how NOM is changed by e.g. different treatment processes, characterisation and quantification of sub-groups of NOM can be valuable. In the case of activated carbon, the most easily and strongly adsorbed NOM constituents are low and medium molecular weight hydrophobic compounds. Hydrophilic NOM constituents of any size have low affinity to the adsorbent surface, and high molecular weight compounds are excluded from internal adsorption sites and can block inner pores, and therefore impair adsorption of other compounds (Chowdhury, 2013).

3.6.1 Analytical approaches for NOM

Total organic carbon (TOC) is a measure of the total amount of organic carbon per volume (or per mass) in a sample, e.g. a water sample. Dissolved organic carbon (DOC) is a technical distinction and refers to what is left when the water has passed through a 0.45 μm filter. In drinking water production, and especially in the finished product, the difference between TOC and DOC is often negligible (Sillanpää et al., 2015).

The composition of NOM can be characterised based on differences in properties such as size, charge, hydrophobicity, optical properties and biodegradability.

Ultraviolet light absorption (usually at 254 nm wavelength, i.e. UV_{254}) is commonly used in drinking water applications to measure the chromophoric fraction of NOM (Zhang et al., 2021). Measuring UV_{254} is a fast and cheap way to assess the presence of aromatic structures or approximate the amount of DOC as the relationship between UV_{254} and DOC is linear.

Biodegradable dissolved organic carbon (BDOC) is a comparatively small fraction of TOC defined as the fraction that is degradable by microbial activity. It is measured as the difference in DOC concentration before and after inoculation with bacteria and incubation (Escobar and Randall, 2001).

Assimilable organic carbon (AOC) is the carbon that can be converted into microbial biomass. It is measured by inoculating and incubating the water sample, and then converting the amount of bacteria (often by flow

cytometry) to µg L^{-1} organic carbon (Zhao et al., 2013). In order to obtain information about the size of different NOM fractions, a separation technique can be useful. One suitable approach is size-exclusion chromatography, which can be coupled with e.g. organic carbon or UV detection. An example of this application is liquid chromatography-organic carbon/ultraviolet detection (LC-OCD/UVD) (Huber et al., 2011).

3.7   Organic micropollutants

Organic micropollutants (OMPs) are commonly defined as organic compounds of man-made origin and occurring at low ng L^{-1} to µg L^{-1} levels in water. Organic micropollutants as a group consist of many thousands of known and unknown compounds with diverse properties (Schwarzenbach et al., 2006; Zearley and Summers, 2012). Increasing numbers of OMPs are now being detected in natural waters and drinking water. This is partly due to the fact that more sophisticated analysis methods have become available, but also due to accumulation of anthropogenic compounds in the environment (Luo et al., 2014; Rehrl et al., 2020). Some of these compounds have been shown to have adverse health effects or to pose a significant risk even at low concentrations (Pomati et al., 2008, 2006; Schwarzenbach et al., 2006).

Typically, semi-polar to polar substances are found in the aqueous phase because of their relatively high water solubility and high mobility in the environment, whereas less polar (more hydrophobic) compounds are generally adsorbed to soil particles and therefore sequestered (Reemtsma et al., 2016).

Organic micropollutant groups of interest in this thesis were pharmaceuticals, PFASs and a few industrial chemicals and personal care products. The levels of pharmaceuticals detected in monitoring studies of surface waters are often below the predicted no effect concentrations (PNECs). However, in aquatic systems with sensitive flora and fauna, even low concentrations of OMPS can have a detrimental effect on aquatic organisms (Miller et al., 2018).

3.7.1   Per- and polyfluoroalkyl substances

Per- and polyfluoroalkyl substances (PFASs) are a group of compounds classified as persistent organic pollutants (POPs) under the Stockholm

Convention that have attracted great attention recently due to their environmental persistence, potential toxicity and global distribution (Ahrens et al., 2011; Du et al., 2014). The PFASs make up a large family, of more than 4700 Chemical Abstracts Service (CAS)-registered substances to date (OECD, 2018). They are characterised by a partly or fully fluorinated carbon chain (linear or branched) with a functional group at the end. The vast majority of PFASs are of anthropogenic origin. They have been widely used in a variety of materials and applications since the 1950s. due to their unique property of being amphiphilic, i.e. both hydrophilic and hydrophobic, which makes them water-, dirt-, and grease-repellent and therefore useful for many industrial purposes (Borg and Håkansson, 2012). The stable and extremely strong saturated carbon-fluorine bond creates a main structure of PFASs that is both thermally and chemically stable, and also resistant to chemical, physical and biological degradation (Buck et al., 2011; Giesy and Kannan, 2002; Rahman et al., 2014).

As a result of their persistence and widespread use, PFASs have been found globally in all environmental compartments, including in humans and wildlife (Borg and Håkansson, 2012). One major pathway of PFASs to drinking water sources is from aqueous film-forming foams (AFFFs) used in firefighting, of which a major constituent is PFASs. At firefighting training sites, where AFFFs are used repeatedly, PFASs risk infiltrating the soil and eventually reaching the groundwater or other water bodies (OECD, 2013). In Uppsala, Sweden, increasing levels of PFASs are being detected in the blood of human residents (Glynn et al., 2012), with worrying exponential increases for some substances since the 1990s. The increasing trends in some cases have been traced to ingestion of drinking water, with the likely source being PFASs in AFFFs leached to groundwater (Glynn et al., 2012, 2007). PFAS exposure have been linked to adverse health effects in humans, such as testicular and kidney cancer (Steenland and Winquist, 2021) and problems with reproductive health and fertility (Rickard et al., 2022).

3.7.2 Analytical approach for OMPs

The method of OMP analysis deemed most relevant for this thesis was liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). It is a target approach with high sensitivity that is well suited for water contaminants. The water samples are filtered, extracted and volume

reduced before being separated and analysed. Quantification is possible by the use of commercially available reference compounds and internal standards (Fifield and Haines, 2000), which in this thesis always consisted of mass-labelled compounds.

3.7.3   OMPs in legislation

Regulation of OMPs in drinking water has only been introduced in recent years. The list of regulated OMPs varies globally and includes various compound groups. The only OMPs studied in this thesis that are regulated in European and Swedish legislation for drinking water are PFASs. The European Union has set a limit of 100 ng L^{-1} for the sum of 20 PFASs and 500 ng L^{-1} for total PFASs (European Union, 2020). European Union member countries can choose to adopt those limits or to set stricter guideline values. The Swedish Food Agency has set a limit of 90 ngL^{-1} for sum of 11 PFASs, with levels above this limit requiring countermeasures, but producers are not legally bound to lower the PFASs levels (Swedish Food Agency, 2021, 2017).

4. Materials and methods

4.1 General study design

In **Papers I, II** and **IV**, a pilot-scale GAC filtration process was studied over 18 months. The GAC filter was used to treat sand filtrate water from a full-scale drinking water treatment plant (DWTP), with and without pre-ozonation. The impact of the ozonation and GAC filtration treatment on a number of target analytes and NOM parameters was investigated over time. In **Paper II**, the quality of the conventionally treated water from the full-scale DWTP was analysed for comparison.

In **Paper III,** a pilot-scale set-up consisting of GAC and AIX columns treating PFAS-contaminated groundwater, with and without nanomembrane filtration pre-treatment was studied over six months at another full-scale DWTP.

The locations of the two DWTPs are shown in Figure 3.

4.2 Important terms and calculations

Three key terms to define when studying GAC filter performance are: bed volume (BV), empty bed contact time (EBCT) and removal efficiency. The BV of a filter (sometimes referred to as throughput) is given as:

$$BV = \frac{t \cdot r}{V_{Adsorbent}}$$

t is the time from start to sampling (h), r is the flow rate (mL h^{-1}) and $V_{adsorbent}$ is the wet volume of the absorption material (mL). Thus BV is a unitless parameter.

The empty bed contact time (*EBCT*) is given in minutes and is calculated as:

$$EBCT = \frac{V_{Adsorbent}}{Q}$$

where *Q* is the volumetric flow rate (m^3 min^{-1}), calculated as:

$$Q = \frac{v}{A}$$

v is the flow velocity (m min^{-1}) and *A* is the cross-sectional area (m^2) of the filter (Chowdhury, 2013).

A typical EBCT value in full-scale operation of a GAC filter is 4-25 min (Corwin and Summers, 2012; Crittenden et al., 1987; Zietzschmann et al., 2016).

The removal efficiency of different analytes by a specific treatment is calculated as:

$$Removal\ efficiency(\%) = 100 \cdot \left(\frac{C_0 - C}{C_0}\right)$$

where *C_o* is the concentration before treatment and *C* the concentration after treatment.

4.3   Experimental set-up

4.3.1   Adsorption materials in column experiments

Three commercially available GAC materials (Norit 830 W[©], Norit 1240 W[©], Filtrasorb 400[©]), were used in the experiments (Table 1). The Norit materials were manufactured by Cabot Norit Nederland (Amersfoort, Netherlands) and the Filtrasorb material by Calgon Carbon Corporation (Feluy, Belgium). According to available fact sheets provided by the manufacturers, there is a substantial difference in pore size distribution between the materials, with Filtrasorb 400 having a broader distribution of pores (micro-, meso- and macropores) than Norit 1240 W, which is mainly microporous. The Norit 830 W material was retrieved from

Figure 3. Map showing the location of the two study sites, Bäcklösa drinking water treatment plant (DWTP) in Uppsala (**Papers I, II, IV**) and Görväln DWTP in Stockholm (**Paper III**). Map adapted from Esri (2021).

a full-scale filter in operation without drying or storage and thus contained an active and stable biofilm.

In addition, two anion exchange materials, Purolite A600 and Purofine PFA694 (Purolite Corporation, King of Prussia, PA, USA), were explored in **Paper III**, with the latter being specifically designed for efficient removal of PFASs.

4.3.2   Full-scale treatment at Görväln DWTP

The site for the experiments described in **Papers I, II** and **IV** was Görväln DWTP. It is one of the primary drinking water producers in Sweden, with annual production of ~50 million m^3 and serving more than 600 000 people in the northern Stockholm area. The raw water is taken from Lake Mälaren, the third largest lake in Sweden, in an area with high population density. In short, the treatment steps at Görväln DWTP are (in order): micro-sieving

Table 1. Characteristics and properties of granular activated carbon (GAC) materials used in the experiments described in **Papers I-IV**.

	Norit 1240 W	Norit 830 W	Filtrasorb 400
Mesh size (mm)	0.43-1.7	0.60-2.36	0.43-1.7
Effective size (mm, D_{10})	0.6-0.7	0.9	0.55-0.75
Base material		Bituminous	
Re-agglomerated		No	Yes
Density, backwashed and drained (kg m^{-3})	425	445	420
Age of material	New	>14 years	New
Included in Paper:	**I-IV**	**I** and **IV**	**II** and **III**

(250 μm), coagulation (Al$_2$(SO$_4$)$_3$), flocculation, sedimentation, rapid sand filtration, GAC filtration (material in use >14 years), UV disinfection, monochloramine disinfection and pH adjustment.

The four sampling points for the full-scale treatment in **Paper II** were *i*) at the raw water intake, *ii*) after the rapid sand filter, *iii*) after one of the GAC filters and *iv*) in the finished drinking water.

4.3.3   Pilot-scale experiment at Görväln DWTP

The pilot-scale experiment presented in **Papers I, II** and **IV** (set up at Görväln DWTP) received water from the full-scale treatment, after rapid sand filtration. The duration of the experiment was 18 months (between May 2018 and November 2019). The pilot plant consisted of pre-ozonation followed by six experimental columns, each filled with 6.4 L GAC material (Figure 4). The ozone concentration directly after the first reaction tank (4.2 minutes) was 0.75 ± 0.2 mg L^{-1}. The 45 min residence time in contact tanks between ozone dosing and GAC filtration was sufficient to ensure that the ozone had decomposed completely. Five of the six columns received pH-adjusted ozonated water, while the sixth received rapid sand filtrate directly. The columns were fed with continuous flow from the top and the water passed through the filter by gravity. Backwashing took place roughly bi-weekly to avoid pressure build-up.

Taps mounted along the columns enabled sampling at different heights (corresponding to different EBCTs) (taps shown in Figure A1 in an Appendix to this thesis). One column was run on 12 min EBCT, which corresponded to the tap located 60 cm from the top of the GAC for the

columns that were run at 20 min EBCT. This provided a way to verify that mixing of the layers did not occur by backwashing and that sampling at different heights was representative for distinct EBCTs.
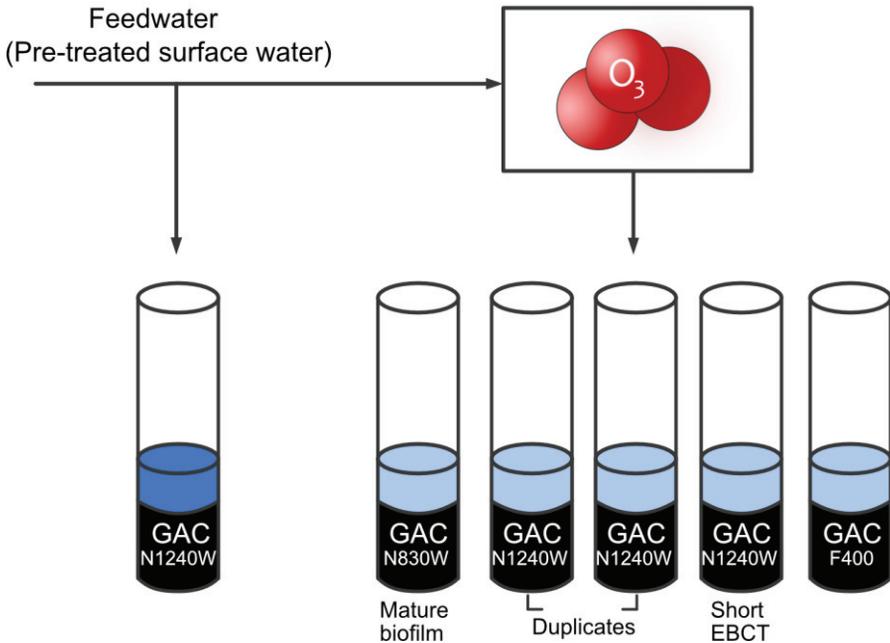
Figure 4. Conceptual diagram of the ozone+granular activated carbon (GAC) experimental set-up at Görväln drinking water treatment plant (DWTP) that was studied in **Papers I, II** and **IV**. N: Norit; F: Filtrasorb.

4.3.4 Pilot-scale experiment at Bäcklösa DWTP

The pilot-scale experiment presented in **Paper III** was set up at Bäcklösa DWTP, where it received untreated groundwater contaminated with PFASs ($\sum$PFAS 100-200 ng L^{-1}). The duration of the experiment was March to September 2019 (six months). The pilot process consisted of nanofiltration and six experimental columns, each filled with 0.5 L absorption material (Figure 5). A two-stage nanofiltration process was employed. It consisted of six spiral-wound membranes followed by three spiral wound membranes (NF90−400 and NF270−400 respectively; Dow Filmtech Membranes). Two of the six columns received untreated groundwater, while the other four received membrane concentrate. The columns were fed by continuous

flow, from the top, and the water passed through the filter by gravity. Backwashing took place, as needed, after sampling to avoid pressure build-up. All columns were operated with an EBCT of 5 min.
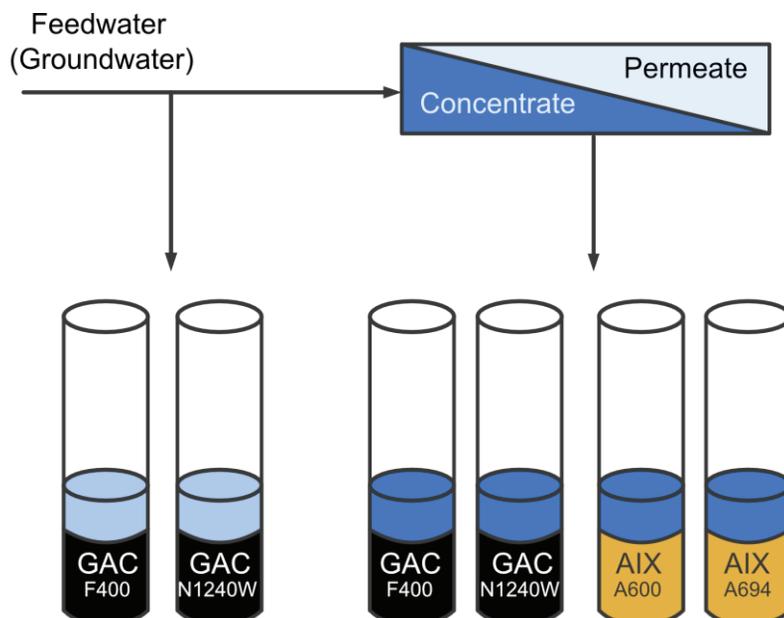
Figure 5. Conceptual diagram of the nanofiltration+granular activated carbon/anion exchange resin (GAC/AIX) experimental set-up at Bäcklösa DWTP that was studied in **Paper III** (diagram adapted from **Paper III**). N: Norit; F: Filtrasorb.

4.4   Chemical analysis

4.4.1   Selection of target compounds

In **Paper II**, a total of 99 OMPs were selected for target analysis (see Table A1 in Appendix). They consisted of pharmaceuticals ($n=66$), PFASs ($n=13$) and other compounds ($n=20$). The selection was made based on information about the ubiquitous occurrence of compounds in waste water and in the aquatic environment (e.g., Patel et al., 2019; Petrie et al., 2015; Yang et al., 2017).

In **Paper III**, 37 PFASs were selected for target analysis (Table A2 in Appendix). Selection of PFASs was made based on national analysis requirements (Σ_{11}PFASs) and PFASs with the same functional group, but

different perfluorocarbon chain length. In addition, several PFASs previously reported in water matrices influenced by AFFFs were included in the analysis.

4.4.2 Water sampling and analysis of OMPs

In **Paper II**, sampling for OMP analysis was performed monthly, using 1-L polypropylene (PP) bottles. The bottles were stored at 4 °C (dark) if extraction could commence within two days, or otherwise frozen. The method used is described in detail in Sörengård et al. (2019). In short, 500 mL per sample were filtered (pre-baked glass-fibre filters) and then spiked with an internal standard (IS) mixture containing mass-labelled compounds (Table A1 in Appendix). Samples were extracted by solid phase extraction (SPE) using HLB cartridges (200 mg, Waters Oasis, MA, USA) and in total concentrated 500 times prior to instrumental analysis.

The final extracts were analysed using a DIONEX UltiMate 3000 ultra-performance liquid chromatography (UPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (TSQ Quantiva, Thermo Fisher Scientific, Waltham, MA, USA). The data were evaluated using TraceFinder™ (Thermo Fisher Scientific, MA, USA).

In **Paper III**, samples were collected in 1-L PP bottles and stored at 4 °C (dark) until analysis. Sampling was conducted frequently in the beginning of the experiment, in order to capture breakthrough, and less often later in the experiment. Samples were spiked with IS mixture and and SPE were carried out using WAX cartridges (Oasis®, 6 cc, 500mg, 60 µm; Waters, Ireland) according to a method described in Ahrens et al. (2010). Sample extracts were analysed on the same instrument as above. All Teflon parts of the instrumental set-up were replaced prior to analysis.

4.4.3 Quality assurance and quality control (QA/QC) for OMP analysis

In short, for OMP analysis in **Paper II**, calibration curve solutions were prepared for individual OMPs (0.01 ng mL^{-1} to 250 ng mL^{-1}) and used for linear curve fitting and quantification. Limit of quantification (LOQ) was calculated as 25% of the lowest calibration point in the calibration curve, where the relative standard deviation of the mean response factor was less than 30% (LOQs are presented in Table A1). Duplicates every 10th sample were used to assess the precision of the method. The matrix effect and ion

suppression/enhancement were corrected for using matrix-matched standards. Laboratory blanks (MilliQ water) were prepared and extracted identically to the samples. Further, method blanks consisting of equal amounts of MilliQ and methanol (no target analytes detected) were prepared.

For PFAS analysis in **Paper III**, linear seven-point calibration curve solutions (1.0 ng mL^{-1} to 200 ng mL^{-1}) were prepared and used for all compounds. The LOQ was calculated as average concentration found in the blank samples multiplied by eight times the standard deviation (LOQs are presented in Table A2). Laboratory blanks (MilliQ water) were prepared and extracted identically to the samples. Duplicate samples collected on three occasions showed relative standard deviation of <10% for all compounds detected.

4.4.4 Organic carbon

Organic carbon in water samples was characterised using several different methods, as described below.

Total and dissolved organic carbon

In **Papers I** and **II**, samples for organic carbon measurements were collected weekly in 500-mL plastic bottles. Levels of TOC and DOC, respectively, were analysed in the laboratory on-site at Görväln DWTP, using a catalytic combustion analyser (Multi N/C 3100; Analytik Jena AG. Jena, Germany), with the only difference being that DOC samples were filtered through 0.45 µm filters (polypropylene, pre-rinsed with MilliQ). The difference between TOC and DOC was 0.04 mg L^{-1} for feedwaters and GAC effluents, which is smaller than the instrument precision.

In **Paper III**, samples for analysis of organic carbon were collected in triplicate, daily during the first few days and later weekly, in pre-cleaned 15-mL glass bottles. Sampling for organic carbon was discontinued after ~19 000 bed volumes (~10 weeks). The TOC content was measured as the non-purgeable organic carbon content by acidifying unfiltered samples with hydrochloric acid and analysing with a catalytic combustion analyser (TOC-VCPH with an ASI-V autosampler; Shimadzu, Kyoto, Japan).

Ultraviolet (UV) light absorbance

In **Papers I**, **II** and **IV**, ultraviolet light absorbance (UV_{254}) was measured at 254 nm wavelength with a spectrophotometer (Hitachi U.1100; Hitachi Ltd. Tokyo, Japan) on-site at the DWTP, in 5-cm quartz cuvettes.

In **Paper III**, UV_{254} was measured in triplicate in 5-cm quartz cuvettes (AvaSpec-ULS3648 high-resolution Spectrometer; Apeldoorn Netherlands).

Liquid chromatography with organic carbon and UV detection (LC-OCD/UVD)

In **Papers I** and **II**, samples were collected monthly and shipped to Het Waterlaboratorium, (Harleem, Netherlands) for analysis. Results were presented as five quantified size fractions and as chromatograms (raw data). The fractions presented were (in order of decreasing size): biopolymers, humic substances, building blocks, neutrals and low molecular weight (LMW) acids.

Assimilable organic carbon (AOC)

The easily biodegradable fraction was approximated by use of assimilable organic carbon (AOC) (**Paper I**). Sampling was conducted monthly, on the same occasion as LC-OCD/UVD and OMP samplings. Two standard bacterial strains (*Aquaspirillum* NOX and *Pseudomonas fluorescens* P17) were used. Sterilised samples were sent to Water Microbiology Laboratory, National Institute for Health and Welfare, Kuopio, Finland, for analysis.

4.4.5 Residual ozone

Ozonation was utilised as a pre-treatment in **Papers I, II** and **IV**. The residual ozone concentration was measured at four points within the reaction tank system and in the water fed to the experimental columns. Duplicate samples of 40 mL were taken weekly and each was analysed twice, using Ozone Accuvac 0.01-1.5 mg L^{-1} O_3 ampoules (HachLange, Colorado USA) and a spectrophotometer (Hitachi U.1100; Hitachi Ltd. Tokyo, Japan).

4.5 Microbial analysis

In **Paper IV**, flow cytometry with fluorescent staining was used to quantify and to some extent describe the suspended bacteria in the water. Sampling was conducted weekly and samples were analysed on the same day, in a laboratory on-site at the DWTP. Each sample of 500 mL (sterile bottles) was split into two and thereafter stained and analysed. In short, SYBR Green 1 was added to samples for total cell concentration (TCC) analysis and a mixture of SYBR Green 1 and Propidium Iodide (PI) was added separately for intact cell concentration (ICC) analysis.

Autoclaved MilliQ water was used as the negative control and *Escherichia coli* (in MilliQ water/KH_2PO_4/$MgSO_4$ buffer) as the positive control. Green and red fluorescence detectors were used for data gathering. Gating was done identically for all samples, to enable direct comparison (see Figure 2).

4.6 Temperature

Water temperature for Görväln DWTP (**Papers I, II** and **IV**) was recorded at raw water intake once every hour.

5. Results and discussion

The main results obtained in **Papers I-IV** are presented and discussed in the following sections. A summary of the most important findings is presented in Figure 6.

5.1 Changes in natural organic matter composition

In **Papers I** and **II**, the NOM content was described both with bulk parameters (DOC and UV_{254}) and more specific analysis of its constituents (AOC and LC-OCD/UVD). **Paper III** included only DOC and UV_{254}.

5.1.1 Pre-treatment

Ozonation

The pre-ozonation in the Görväln pilot-scale experiment (**Papers I** and **II**) altered the NOM amount and character of the water fed to the GAC columns. The DOC level was significantly reduced, by $1.8 \pm 1.8\%$, and the chromophoric fraction within DOC (UV_{254}) was reduced by $47 \pm 6\%$ (two tailed paired t-test; $p = 2.7 \ 10^{-11}$ and $p = 4.4 \ 10^{-57}$, respectively, $n = 68$).

The LC-OCD measurements were used to look further into the character of the NOM. The largest reduction was seen in the humic substances fraction (significant, molecular weight ~ 1000 g mol^{-1}), followed by LMW neutrals (significant, ~ 350 g mol^{-1}) and biopolymers (significant, $\gg 20\ 000$ g mol^{-1}) (Figure 7).
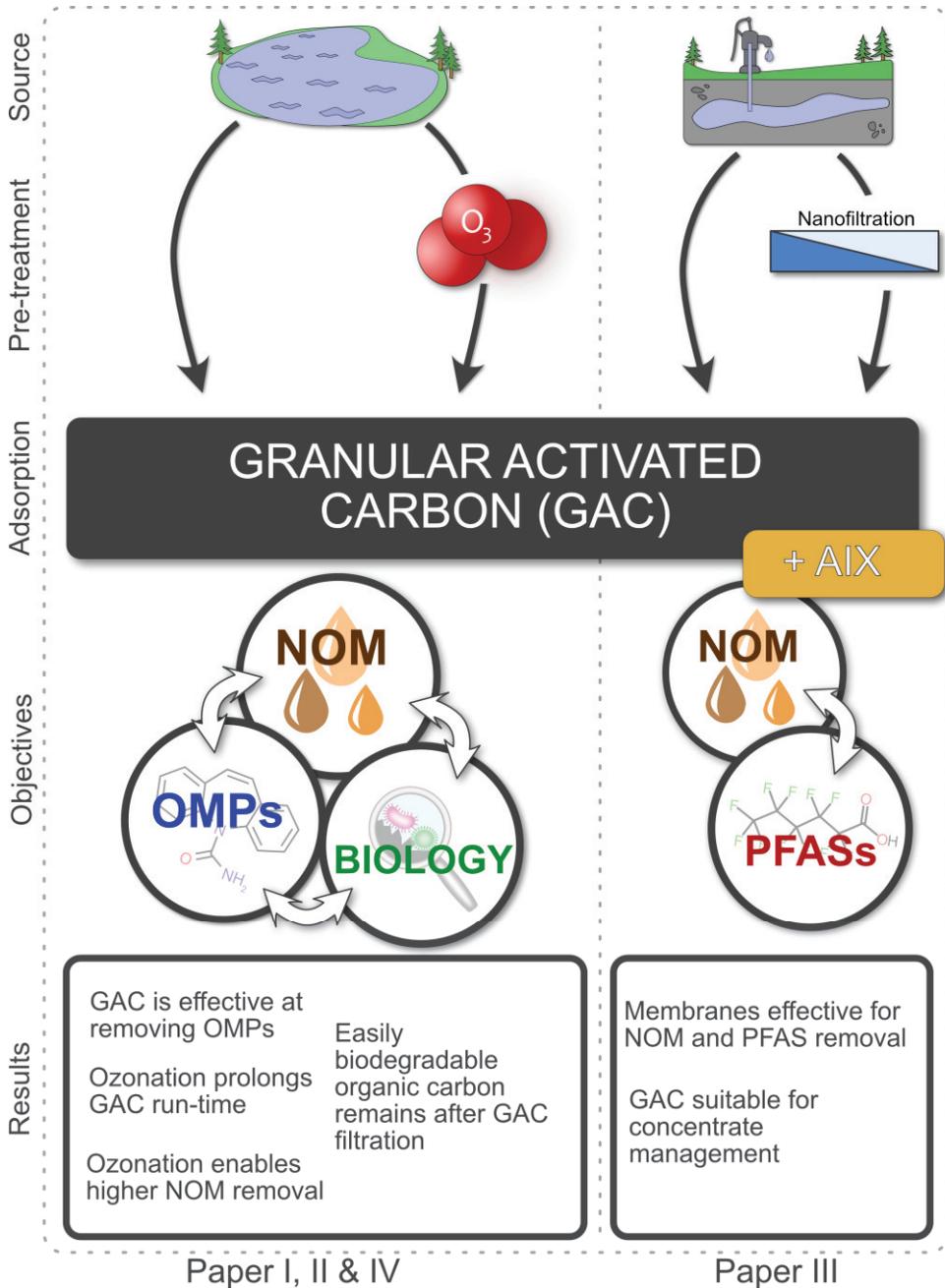
Figure 6. Schematic diagram of results from **Papers I-IV**. O$_3$: ozone; AIX: anion exchange resin; NOM: natural organic matter; OMPs: organic micropollutants; PFASs: per- and polyfluoroalkyl substances.
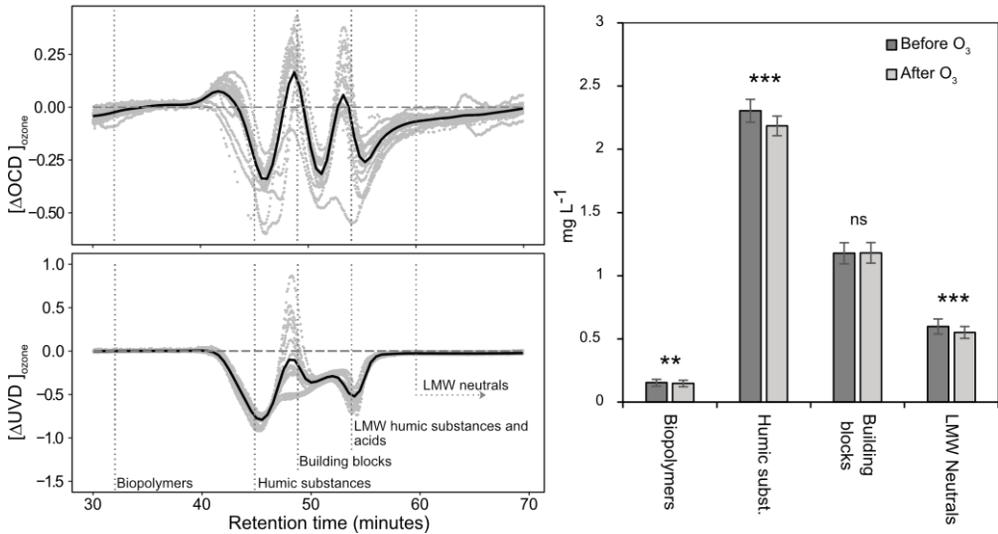
Figure 7. Ozone-induced changes in natural organic matter (NOM) fractions measured by LC-OCD (upper left) and LC-UVD (bottom left) and expressed as ΔUVD_{ozone} and ΔOCD_{ozone}. Positive values are indicative of formation within that specific fraction and vice versa. Black lines represent the average chromatogram. The bar graph shows average quantified fractions before and after ozonation. Two-tailed paired t-test. LMW = low molecular weight. Left panel adapted from **Paper I**.

Another fraction of NOM that overlaps with the LC-OCD fractions is AOC, which is a measure of the biodegradability. The AOC with the *Aquaspirillum* NOX bacterial strain (AOC_{NOX}) increased by 1660% (from 15 ± 6.3 µg L^{-1} to 271 ± 83 µg L^{-1}; $n = 16$) due to ozonation (Figure 8, upper panel). The AOC with the *Pseudomonas fluorescens* P17 bacterial strain (AOC_{P17}) increased by 85% (from 45 ± 24 µg L^{-1} to 76 ± 34 µg L^{-1}; $n = 16$) (Figure 8, lower panel). These observations show that ozonation rendered the NOM more available to microorganisms.

Nanofiltration

The nanofiltration (NF) unit in **Paper III** concentrated the DOC content from 3.0 ± 0.27 mg L^{-1} in the raw water (untreated groundwater) to 14 ± 0.5 mg L^{-1} in the NF concentrate, leaving drinking water (NF permeate) with levels of ~0.5 mg L^{-1}. The UV_{254} of the raw water was 0.27 ± 0.02 5 cm^{-1}, compared with 1.34 ± 0.17 5 cm^{-1} in the NF concentrate. The permeate values were below the limit of detection for the instrument.
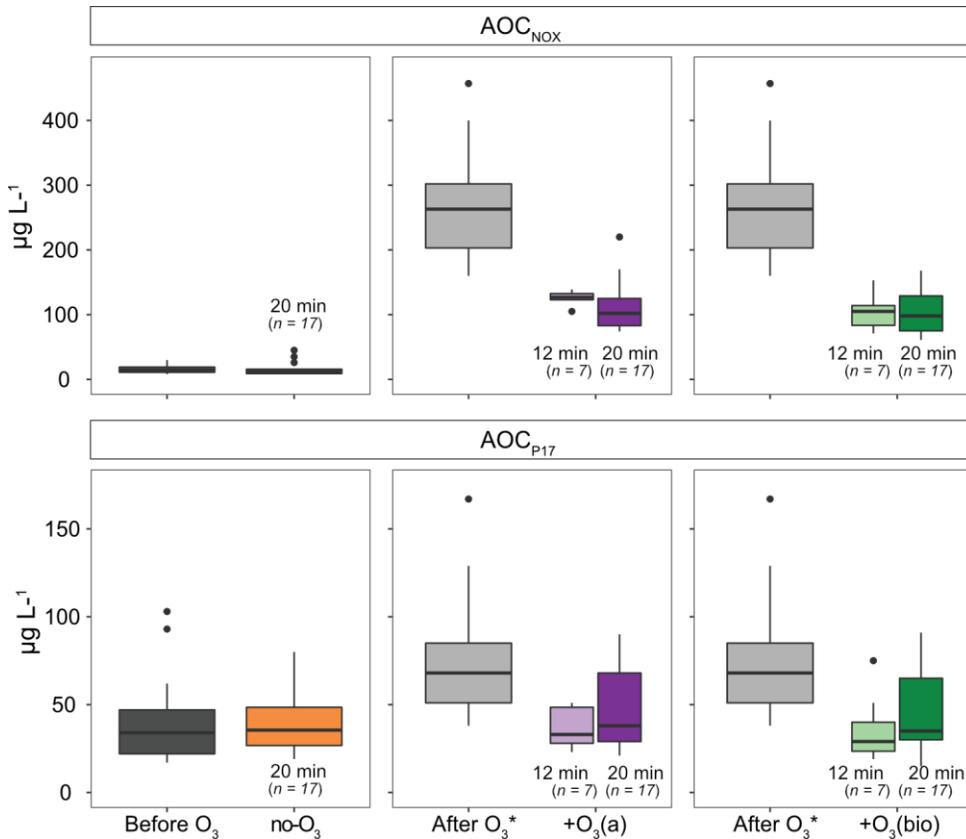
Figure 8. Assimilable organic carbon (AOC) concentrations for *Aquaspirillum* NOX oxalate (upper) and *Pseudomonas fluorescens* P17 acetate (lower) strains in granular activated carbon (GAC) columns with the respective feedwater. Diagram from **Paper I**.

5.1.2 GAC filtration

Removal efficiency of the bulk parameters DOC and UV_{254} decreased rapidly following the start of the experiments in both **Papers II** and **III** (Figure 9). The removal efficiency of NF concentrate decreased the fastest and was down to zero before 10 000 BVs. After reaching steady state or near-steady state, the column receiving ozonated water maintained a removal of 9.9 ± 2.3%, compared with 5.1 ± 2.9% for the column receiving non-ozonated water. This maintained removal capacity was attributed to biological degradation and was higher in the column receiving ozonated water, likely because of the increased bioavailability discussed in section 5.1.1. The Filtrasorb 400 material was able to remove more DOC than

Norit 1240 W, particularly in the pre-equilibrium phase, a pattern that was found for both pilot-scale experiments. Removal of DOC and UV_{254} was found to increase linearly with increasing EBCT (4-20 minutes).

Further focusing on removal of NOM constituents for the Görväln pilot-scale experiment (**Paper I**), humic substances and neutrals were removed primarily by adsorptive processes, while LMW humic substances/neutrals and building blocks were removed by biodegradation. At ~20 000 BVs after the start of the experiment (~300 days), all fractions had reached steady state.

The AOC_{P17} value was reduced back to pre-ozonation levels by GAC filtration, but only 60% of AOC_{NOX} was removed by GAC, implying that elevated levels remain compared with the case of no pre-ozonation. An increase from 12 min EBCT to 20 minutes did not further increase removal.
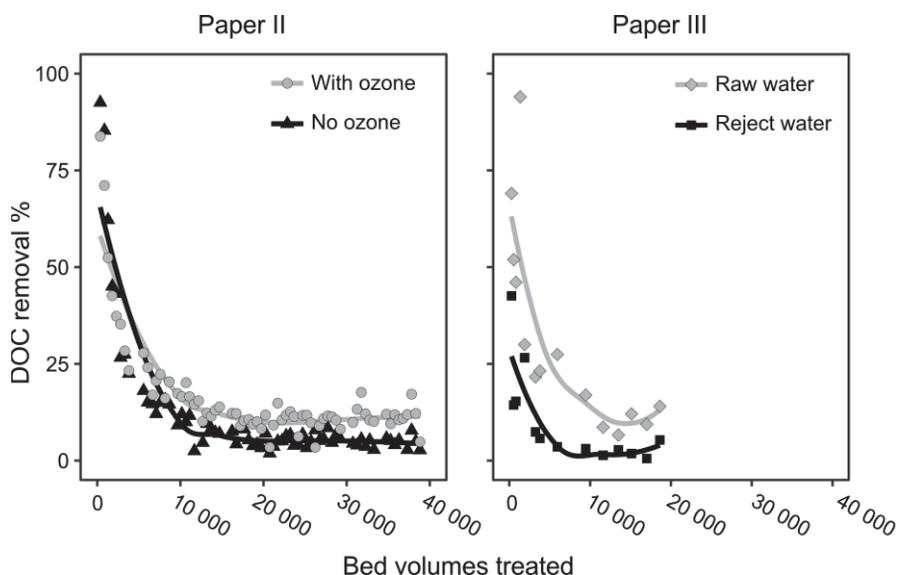
Figure 9. Removal efficiency of dissolved organic carbon (DOC) as a function of bed volumes treated for: two columns from **Paper II** (left) and two columns from **Paper III** (right). All columns were filled with Norit 1240 W granular activated carbon (GAC) medium.

5.2 Removal of organic micropollutants

Out of the 99 compounds analysed in **Paper II**, 29 were consistently detected and quantified (Table 2). A seasonal trend was observed in the raw water, with higher concentrations in summer months and lower in winter months.

5.2.1 Full-scale treatment

In the full-scale treatment at Görväln DWTP, most compounds slipped through the different treatment steps and were detected at similar levels in raw water as in finished water. The exceptions were: metoprolol (removed by 51%), lamotrigine (27%), tolyltriazole (27%) and clindamycin (>96%), with the last compound presumably mostly affected by UV-irradiation or by monochloramine oxidation.

5.2.2 Pre-treatment

Ozonation

Ozonation is a destructive treatment technique where target compounds are removed by being converted into transformation products or by being completely mineralised. The target approach by LC-MS/MS utilised in the **Paper II** cannot identify or quantify such transformation products. The term 'removal' can thus be misleading, and it should be noted that in the following text only target compounds are considered.
Sixteen compounds were removed, on average, to more than 90%, of which 13 were reduced to below the limit of quantification (Table 2). The PFASs were unaffected.

Nanofiltration

The nanomembrane system utilised in **Paper III** efficiently removed PFASs, by on average >98%, producing drinking water (i.e. permeate) with low concentrations of PFASs (1.6 ng L^{-1} Σ_{11}PFAS). However, 20% of the feedwater was rejected as concentrate with high levels of PFASs (580 ng L^{-1} Σ_{11}PFAS, of which PFHxS comprised 300 ng L^{-1}), in need of further treatment.

Table 2. Average concentration before ozonation, removal efficiency by ozonation and removal efficiency for individual compounds ($n = 12$; ± *standard deviation*)

Group	Compound	Average ingoing concentration (ng L^{-1})	Average removal by ozone (%)
Pharmaceuticals	Carbamazepine	7.3 ± 1.1	100 ± 0.4
	Lidocaine	1.4 ± 0.4	99 ± 0.4*
	Fexofenadine	1.8 ± 0.4	99 ± 2.4
	Tramadol	1.4 ± 1.1	99 ± 1.1*
	Metoprolol	2.1 ± 1.2	98 ± 1.0*
	O-desmethyl-venlafaxine	2.6 ± 3.0	98 ± 2.0*
	Clindamycin	0.3 ± 0.1	98 ± 1.2*
	Cetirizine	2.9 ± 0.6	98 ± 2.5
	Losartan	1.2 ± 0.4	98 ± 1.4*
	Citalopram	0.2 ± 0.1	97 ± 1.6*
	Propranolol	0.1 ± 0.02	96 ± 0.4*
	Mirtazapine	0.1 ± 0.01	96 ± 1.3*
	Venlafaxine	1.4 ± 0.3	95 ± 2.0*
	Irbesartan	0.1 ± 0.1	93 ± 5.6*
	Trimethoprim	0.8 ± 0.4	86 ± 12
	Diazepam	0.03 ± 0.01	75 ± 13*
	Oxazepam	1.9 ± 0.4	73 ± 8.0
	Phenazone	0.4 ± 0.2	72 ± 26
	Ifosfamide	0.3 ± 0.04	71 ± 6.6*
	Lamotrigine	9.1 ± 1.5	58 ± 10
	Bicalutamide	1.7 ± 0.6	53 ± 11
	Fluconazole	1.5 ± 0.5	43 ± 14
PFASs	PFOS	2.5 ± 0.7	17 ± 29
	PFNA	0.9 ± 0.2	8.1 ± 36
Other OMPs	Tolyltriazole	13 ± 6.9	97 ± 1.7
	Caffeine	22 ± 3.8	95 ± 5.1
	Sulisobenzone	1.2 ± 0.5	87 ± 5.8*
	DEET	1.9 ± 0.5	61 ± 12
	Tris(2-butoxylethyl) phosphate	1.5 ± 0.6	60 ± 33

*Effluent water concentration was below LOQ, and 0.5 LOQ was used in the calculation.

5.2.3 GAC filtration

For the OMPs in **Paper II**, all GAC columns were initially able to remove all OMPs to below LOQ. For the column receiving non-ozonated water (EBCT 20 min), the first OMPs emerged in effluent after 7500 bed volumes (~16 weeks) (top row in Figure 10). For columns receiving ozonated water, breakthrough was delayed and OMPs emerged in effluent after 16 000 bed volumes (~31 weeks) (lower two rows in Figure 10). Compounds with low partitioning coefficient for organic carbon and water (K_{oc}) tended to break through earlier than those with higher K_{oc}. In all columns, breakthrough occurred much earlier for DOC than for the OMPs Even after 12 months, the capacity of the GAC material for removing OMPs remained quite high. For Norit 1240 W, pharmaceuticals were removed to 73% without pre-ozonation and to 91% with ozonation (average for last three months). PFASs were removed to 15% without and 45% with ozonation. The other OMPs were removed to 94% without and 87% with ozonation. The performance of the Norit 1240 W and Filtrasorb 400 materials was comparable.

In **Paper III**, PFASs were detected in GAC effluents in the following chronological order: PFHxA > PFOA > PFBS > PFPeS > PFHxS > PFHpS and lastly PFOS. The removal efficiency of PFCAs (carboxylic acid functional group) declined faster than that of PFSAs (sulfonic acid functional group), for the same perfluorocarbon chain length. The compound PFHxA, the PFCA with the shortest perfluorocarbon chain length among the target compounds, declined first (considerably lower removal efficiency already before 5000 BVs) and PFOS, with the longest chain length, declined last.

The GAC materials removed more PFAS mass from the nanofilter (NF) concentrate than from the groundwater, with all other parameters unchanged (NF: 15 and 18 µg g^{-1}, respectively for Filtrasorb 400 and Norit 1240 W; groundwater: 8.9 and 8.4 µg g^{-1}).

As also found in **Paper III**, the removal efficiency of organic carbon (DOC and UV$_{254}$) declined faster than the removal efficiency of PFAS for all absorption materials tested.
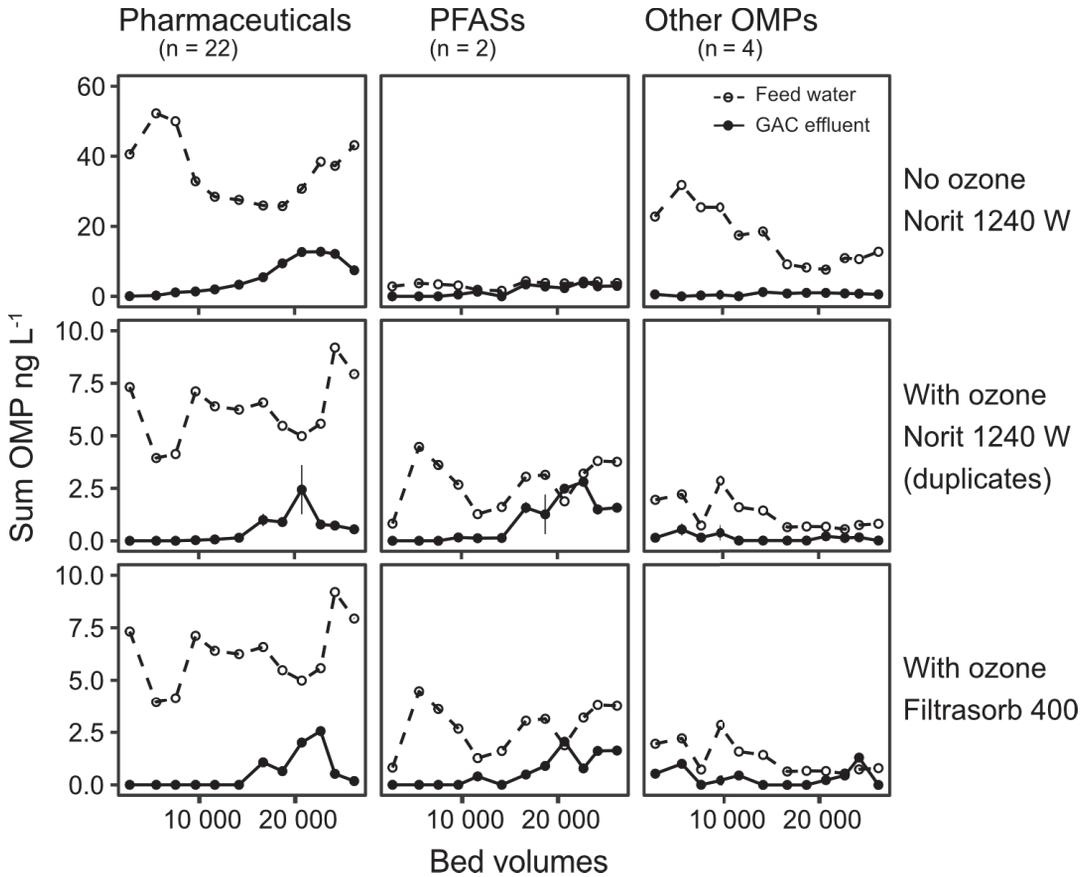
Figure 10. Sum of concentrations of pharmaceuticals, per- and polyfluoroalkyl substances (PFASs) and other organic micropollutants (OMPs) in influent and effluent from granular activated carbon (GAC) columns as a function of bed volumes treated. Caffeine was excluded from the calculations. Error bars represent standard deviation between duplicate columns. Concentrations below LOQ are given as 0 ng L^{-1}. Diagram adapted from **Paper II**.

5.2.4   Biological removal of OMPs (unpublished data)

To assess possible biological removal of OMPs, influent and effluent concentrations from the full-scale GAC filter at Görväln DWTP were evaluated and compared with values for the pilot-scale column. The full-scale filter had been in use for more than 14 years at the time of sampling and can be considered to be acting solely as a biofilter by that stage, with no capacity left to consistently remove NOM or OMPs by adsorption. It was operated with an EBCT of 5-6 minutes. Out of the 29 commonly

detected OMPs, no consistent removal of individual compounds was found (see Figure A2 in the Appendix), meaning that there was no evidence of biological degradation of individual OMPs.

For comparison, influent and effluent concentrations from the pilot-scale filter, filled with old GAC media from the full-scale filter referred to above, were evaluated. This filter received ozonated water with considerably lower concentrations of target analytes. For three of the 29 commonly detected OMPs (caffeine, carbamazepine and tolyltriazole, see Figure A3 in the Appendix), the concentration in effluent was consistently considerably higher than that in influent, indicating desorption of previously (reversibly) bound molecules. Conversely, bicalutamide and lamotrigine were consistently removed. Since these two compounds did not show the same pattern in the full-scale GAC filter, the explanation is either recovery of adsorption capacity created by the ozonated feedwater, dependent on a longer EBCT (5 vs. 20 min) or biological degradation by specialist bacteria not present in the non-ozonated water.

5.3 Adsorption competition between NOM and OMPs

Simultaneous sorption (and/or desorption) of NOM and OMPs in drinking water treatment systems using natural water is complex and may lead to changes in performance and dynamics over time. It is often assumed that NOM influences OMP adsorption to GAC negatively in the long term, as NOM competes for and blocks/fouls adsorption sites.

For PFASs in **Paper III**, presence of DOC was found to even enhance adsorption in the pre-steady-state phase, emphasising the complex influence of background DOC presence on PFAS adsorption. In **Paper II**, recovery of OMP removal capacity was observed towards the end of the experiment, which might be attributed to OMPs binding to adsorbed NOM molecules on the GAC surface.

The later breakthrough of OMPs in GAC columns receiving ozonated water (**Paper II**) could possibly be explained by changes in adsorption competition. The ozonated water contained lower levels of large humic molecules, more polar compounds and less aromatic NOM (indicated by a 50% decline in UV_{254} absorption). The neutrals fraction of NOM, with molecular weights in the same range as the OMPs studied in this
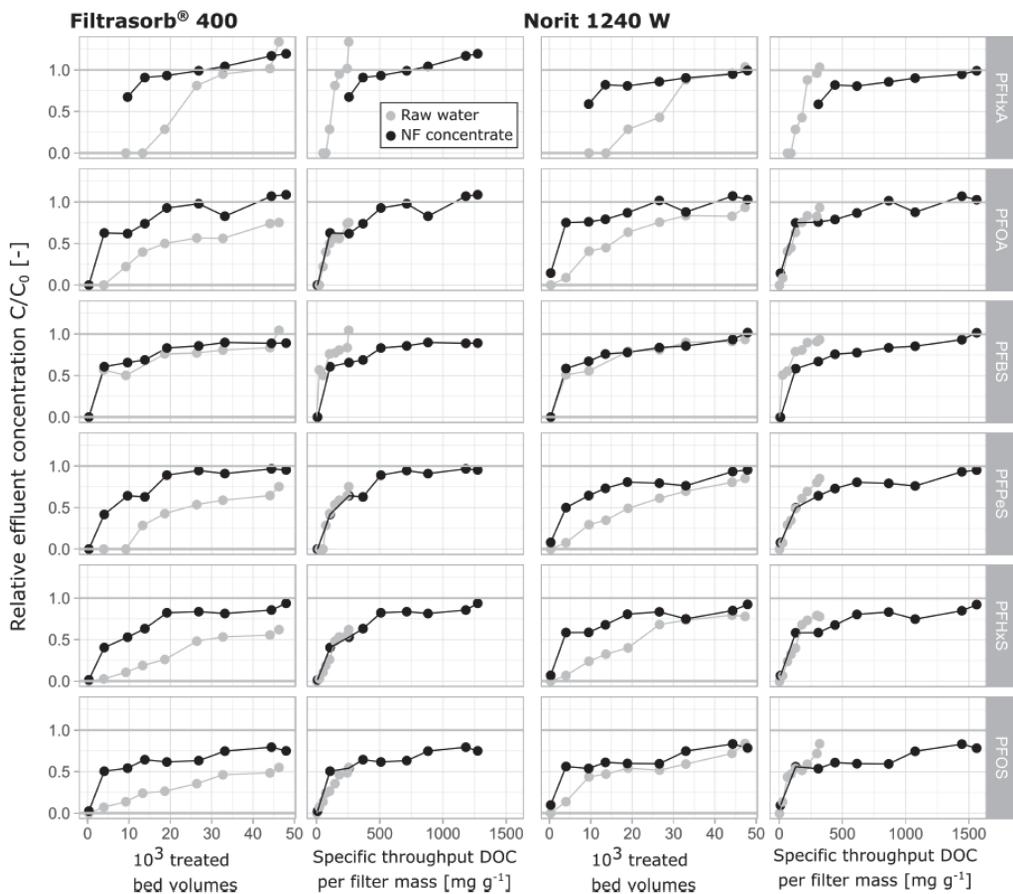
Figure 11. Relative effluent concentration (C/C_0) as a function of bed volumes and specific throughput of dissolved organic carbon (DOC) for six per- and polyfluoroalkyl substances (PFASs) in the granular activated carbon (GAC) materials (a) Filtrasorb 400 and (b) Norit 1240 W. Diagram from **Paper III**, reproduced with permission from the publisher.

experiment, showed the strongest retention within the GAC filters. Because of this, the adsorption competition between NOM and OMPs can be expected to be smaller for ozonated water than for non-ozonated water, presumably leading to the later breakthrough. The large difference in total OMP loading between the two waters (on average 82% less in ozonated water) likely also affected the competition.

Filtrasorb 400 removed considerably more DOC from the water, while the removal of OMPs was comparable to that by Norit 1240 W. This

pattern was observed in both **Papers II** and **III**. In contrast, removal of PFASs by AIX materials was relatively unaffected by the background concentration of DOC.

When normalising the specific throughput (defined as the absolute mass of the DOC that was fed to the GACs, in g DOC per g filter material), the curves for raw water and NF concentrate came close to superimposing for most of the PFASs that were consistently detected in effluents (**Paper III**) (Figure 11). This means that DOC loading can explain the difference between the two waters relatively well regarding PFAS breakthrough.

The profile of high nucleic acid (HNA) content in the GAC effluents receiving ozonated water indicated that the microbiome coming off GAC media after ozonation was likely markedly different from that in a non-ozonated system.

5.4   Microbial changes

Bacterial content in the Görväln DWTP pilot-scale experiment were assessed by flow cytometry (**Paper IV**). Ozonation acted as a disinfecting oxidant. This resulted in a 99.6% (on average) reduction (2.4 log) in total cell concentration (TCC), producing feedwater for the columns that contained virtually no bacteria.

The influent and effluent TCC from the GAC filter receiving non-ozonated water were practically the same, but for the columns receiving ozonated water a stark difference in TCC was observed (Figure 12), with much higher concentrations leaving the columns than entering them. This indicates that biofilm will still grow on GAC even if the incoming water has been disinfected and that ozone in combination with GAC filtration is therefore not a solution to limit bacterial count and prevent regrowth on GAC.

5.5   The role of GAC in drinking water production

The results in **Papers I-IV** in this thesis showed that GAC filters can have several important functions in drinking water production. However, the results also highlighted some inherent challenges.

An advantage of GAC is that it can remove a wide range of OMPs, including PFASs, and thus likely protects drinking water consumers from
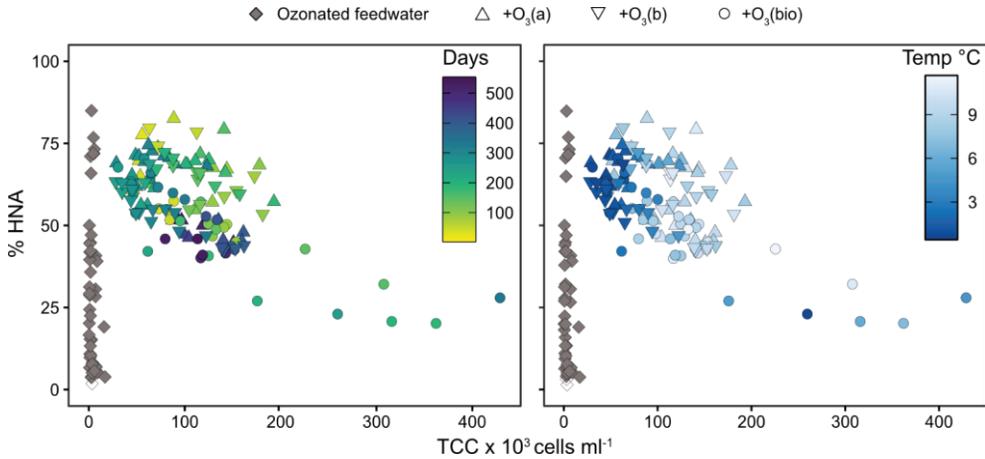
Figure 12. Fraction of high nucleic acid content (%HNA) as a function of total cell concentration (TCC) for duplicate columns ($+O_3(a/b)$) and column filled with old granular activated carbon (GAC) media ($+O_3(bio)$) along with ozonated feedwater (grey ◊). Left panel: days from start as colour scale. Right panel: temperature at intake as colour scale. Diagram from **Paper IV**.

threats of hazardous OMPs, both known and not yet discovered (Tröger et al., 2021). However, this thesis and other studies (e.g. Kennedy et al., 2015; Tröger et al., 2020; Zietzschmann et al., 2016) clearly show that to achieve optimal protection from OMPs, GAC filters must be replaced or re-activated on a regular basis. **Paper II** showed that when preceded by ozonation, GAC will reduce already low OMP levels to even lower levels, and the filter will last longer than without ozonation.

Paper I and other studies (e.g. Gibert et al., 2013; Korotta-Gamage and Sathasivan, 2017; Velten et al., 2011b) demonstrate that if GAC filters are utilised as biofilters, reduction of NOM will go on indefinitely without the need for re-activation, but the filter will have little or no use as a chemical barrier against OMPs. If the filter is fed with ozonated water the NOM reduction will be even greater (**Paper I**) but, as shown here, even a 20-minute EBCT will remove all easily biodegradable NOM formed by ozonation, potentially creating problems with bacterial regrowth farther down in the distribution system. Further, the findings in this thesis (**Paper IV**) and other studies (e.g. Gerrity et al., 2018; Proctor and Hammes, 2015) indicate that ozonation radically changes the microbiome, with unknown consequences.

It is clear from this thesis (**Papers I** and **II**) and other studies (e.g. Fundneider et al., 2021; Lechevallier et al., 1992; Seredyńska-Sobecka et al., 2006) that a longer EBCT will allow more adsorption of OMPs and higher removal of biodegradable NOM, but at the expense of either more material (volume) or lower flow (more basins needed).

6. Conclusions and future perspectives

The main conclusions from the work presented in this thesis are that:

- Filtration through fresh GAC material is a powerful water treatment method capable of removing a broad range of OMPs (including PFASs). When coupled with pre-ozonation, low amounts of OMPs in finished water and longer run times for the GAC filters can be achieved.

- The easily biodegradable organic carbon fraction increased after ozonation and, although effective, GAC treatment was unable to reduce the levels down to pre-ozonation levels.

- Membrane is an effective method for controlling NOM and OMPs in drinking water. The resulting concentrate can be efficiently treated with adsorption (GAC or AIX). GAC filtration of the raw water directly (without membranes) can also be an economically viable option.

- Ozonation effectively reduces the number of cells (bacteria) in the water. Regrowth occurs in the following GAC filters, with the nucleic acid profile indicating a markedly different microbiome from that in a non-ozonated system.

Whether it makes sense to treat water directly with GAC, or to create very clean drinking water with the aid of nanofiltration and use GAC to clean the waste, is a matter of cost, but additional benefits of nanofiltration (removal of e.g. mineral hardness, uranium, bromide and manganese) must be taken into account in the comparison. Even if membrane technology,

which is a very effective treatment, continues to dominate drinking water treatment in the future, GAC filtration will still play an important role as a waste management option.

Further, improved knowledge of transformation pathways and analysis methods (e.g. suspect and non-target screening approaches) for OMPs are needed to evaluate whether transformation products created during ozonation slip through the GAC filter. More research is also needed to determine whether such transformation products are hazardous for human health.

In conclusion, GAC filtration is a powerful tool for drinking water production, especially when used in conjunction with other methods, and will continue to be so in the future.

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Popular science summary

According to the United Nations, safe and clean drinking water is a basic human right and should be accessible to everyone. However, lakes, rivers and groundwaters around the world are increasingly being negatively affected by the widespread use of man-made chemicals, such as pharmaceuticals, per- and polyfluoroalkyl substances (PFAS) which is a group that is regarded as 'forever chemicals' and other long-lasting chemicals used in industrial manufacturing. These compounds, in this thesis referred to as organic micropollutants (OMPs), are released into the environment by different pathways. At high enough concentrations, these micropollutants might pose a threat to wildlife and the environment as well as to human health. In particular, PFASs has gotten a lot of attention lately, as exposure (e.g. through drinking water) has been linked to certain cancers and to reproductive problems.

As such compounds inevitably find their way into water intended for use as drinking water, they have to be removed in drinking water treatment plants to make the water safe for human consumption. However, many of these chemicals are not easily removed by conventional drinking water treatment techniques, which are mainly designed to perform clarification and removal of bacteria or viruses (pathogens), and not removal of OMPs. Thus, additional treatment steps tailored for removal of OMP substances are needed.

Carbon as a water purifier has a long history. Carbon in the form of charcoal was used for treatment of water as early as 450 BD, and since the mid-twentieth century sophisticated products made from granular activated carbon (GAC) have been available commercially for various filtration purposes. Granular in this case means that the carbon is in the form of granules roughly one millimetre in diameter, while activated means that the carbon has been heated to high temperatures with steam or other gases to create a porous

structure with a surprisingly large surface area (5 grams of GAC as the same area as a football pitch). This large surface area enables large amounts of OMPs and other chemicals to adhere, in a process called adsorption, thereby removing them from water. Over time, good bacteria in the water will also adhere to the GAC granules and grow and multiply there, creating what is called a biofilm. At this stage, the GAC filter will have lost most of its ability to adsorb OMPs and will instead be a biological filter (biofilter) that removes pollutants or organic matter mainly by biological degradation.

This thesis examined the effects of combining GAC filters with ozonation, a process which breaks apart molecules, and nanomembrane filtration, which essentially involves passage through a very fine sieve that is able to trap individual molecules. Nanofiltration produces very clean water but leaves behind a watery sludge (*concentrate*) containing all the pollutants too large to pass through the membrane.

This thesis explored different roles that GAC filters could play in drinking water production, e.g. as a barrier against OMPs, as a biological filter, as a post-treatment step after ozonation and as a waste (concentrate) management step after nanofiltration. Two experimental treatment processes, each featuring a miniature version of full-scale treatment (i.e. pilot-scale processes) were set up at two existing drinking water treatment plants in Sweden, one in Stockholm treating water from Lake Mälaren and one in Uppsala treating groundwater. The treatment plant in Uppsala has a known problem with high concentrations of several PFASs. A broad range of OMPs were analysed (including PFASs), as were the amounts of bacteria present in the water. Indicators reflecting the carbon content, or natural organic matter (NOM) content, found in incoming water were also analysed.

The GAC filters were found to be efficient in removing OMPs, particularly when the water was ozonated first. However, the removal rate decreased over time until little of the original capacity remained. In addition, ozone treatment introduced new challenges, as it was found to make NOM in the water more available as feed to microbes, which the GAC filters were not fully able to remove. As biological filters, the GAC filters were able to remove more organic matter when the water was ozonated first. These new findings on GAC filter performance under different conditions can be used to design better water treatment options to protect human health in the future.

Populärvetenskaplig sammanfattning

Enligt FN är säkert och rent dricksvatten en grundläggande mänsklig rättighet och bör vara tillgänglig för alla. Sjöar, älvar och grundvatten runt om i världen påverkas dock i allt högre grad negativt av den utbredda användningen av konstgjorda kemikalier, såsom läkemedel, per- och polyfluoroalkylsubstanser (PFAS) en grupp som i naturen är i stort sett oförstörbara och andra kemikalier som används i industriell tillverkning. Dessa föroreningar, i denna avhandling kallade organiska mikroföroreningar (OMP), släpps ut i miljön via olika vägar. Vid tillräckligt höga koncentrationer kan dessa mikroföroreningar utgöra ett hot mot djurlivet och miljön såväl som för människors hälsa. Speciellt PFAS har fått mycket uppmärksamhet på sistone, eftersom exponering (t.ex. genom dricksvatten) har kopplats till vissa cancerformer och till reproduktionsproblem.

Eftersom sådana föreningar oundvikligen hamnar i vatten avsett att användas som dricksvatten, måste de avlägsnas i dricksvattenreningsverk för att göra vattnet säkert för mänsklig konsumtion. Men många av dessa kemikalier är inte lätta att avlägsna med konventionella behandlingstekniker, som huvudsakligen är utformade för att klarna vattnet och avlägsna bakterier eller virus (patogener), och inte avlägsnande av OMP. Därför behövs ytterligare behandlingssteg som är skräddarsydda för avlägsnande av OMP-ämnen.

Kol som vattenrenare har en lång historia. Träkol har använts för rening av vatten så tidigt som 450 f.Kr., och sedan mitten av nittonhundratalet har sofistikerade produkter gjorda av granulerat aktivt kol (eng. GAC) funnits kommersiellt tillgängliga för olika filtreringsändamål. Granulerat innebär i detta fall att kolet är i form av granulat (korn) ungefär en millimeter i diameter, medan aktiverat betyder att kolet har hettats upp till höga temperaturer med ånga eller andra gaser för att skapa en porös struktur med en förvånansvärt stor

yta (5 gram GAC har samma yta som en fotbollsplan). Denna stora yta gör att stora mängder OMP och andra kemikalier kan fästa, i en process som kallas adsorption, och därigenom avlägsnas från vattnet. Med tiden kommer också goda bakterier i vattnet att fästa sig vid GAC-granulatet och växa och föröka sig där, vilket skapar vad som kallas en biofilm. I detta skede kommer GAC-filtret att ha förlorat det mesta av sin förmåga att adsorbera OMP och kommer istället att vara ett biologiskt filter (biofilter) som tar bort föroreningar eller organiskt material främst genom biologisk nedbrytning.

Denna avhandling undersökte effekterna av att kombinera GAC-filter med ozonering, en process som bryter isär molekyler, och nanomembranfiltrering, som i stora drag innebär passage genom en mycket fin sil som kan fånga individuella molekyler. Nanofiltrering ger mycket rent vatten men lämnar efter sig ett vattenhaltigt slam (koncentrat) som innehåller alla föroreningar som är för stora för att passera genom membranet.

I denna avhandling undersöktes de olika roller som GAC-filter kan spela vid produktion av dricksvatten: som en barriär mot OMP, som ett biologiskt filter, som ett efterbehandlingssteg efter ozonering och som ett avfallshanteringssteg efter nanofiltrering. Två experimentella försöksuppställningar användes, var och en med en miniatyrversion av fullskalig rening (dvs. i pilotskala). De sattes upp vid två befintliga dricksvattenreningsverk i Sverige, en i Stockholm som behandlar vatten från Mälaren och en i Uppsala som renar grundvatten. Reningsverket i Uppsala har ett känt problem med höga halter av flera PFAS. Ett brett spektrum av OMP analyserades (inklusive PFAS), liksom mängden bakterier som fanns i vattnet. Indikatorer som återspeglar kolhalten, eller innehållet av naturligt organiskt material (NOM), som finns i inkommande vatten analyserades också.

GAC-filtren visade sig vara effektiva för att ta bort OMP, särskilt när vattnet först ozonerades. Borttagningen minskade dock med tiden tills endast lite av den ursprungliga kapaciteten återstod. Dessutom introducerade ozonbehandling nya utmaningar, eftersom det visade sig göra NOM i vattnet mer tillgängligt som föda till mikrober, som GAC-filtren inte helt kunde ta bort. Som biologiska filter kunde GAC-filtren ta bort mer organiskt material när vattnet först ozonerades. Dessa nya rön om GAC-filterprestanda under olika förhållanden kan användas för att designa bättre vattenbehandlingsalternativ för att skydda människors hälsa i framtiden.

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Further, I wish the '*new*' PhD crew all the best, although I regret that these times of home-office kept us from getting to know each other better.

I would like to give a huge hug and a kiss on the nose to my beloved dog **Morgan**, who came to me during my lowest times and has since been my 'mental-health-support'-dog – for sure saving me both my physical and psychological health!

Sist men absolut inte minst vill jag tacka min närmsta familj: mamma **Birgitta**, pappa **Gunnar**, faster **Anna**, farbror **Johan**, mormor **Ingegerd** och mina bröder **Emil** och **Lasse**. Ni har alltid trott på mig och min förmåga att ro i land detta – även när jag själv tvivlat!

Wonderful things lie ahead, and I cannot wait to start my post-PhD life!

Appendix
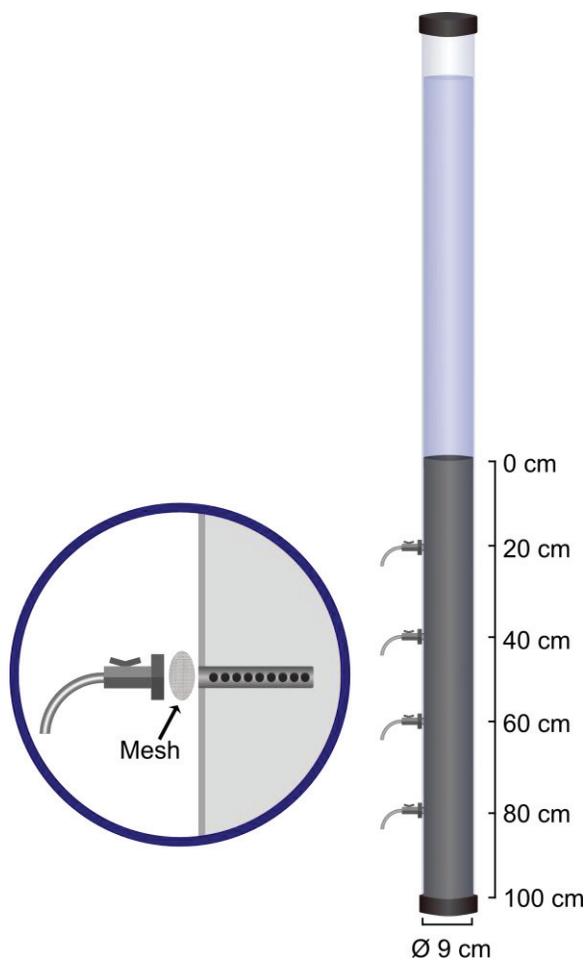
Figure A1. Conceptual sketch of a granular activated carbon (GAC) column, showing depth of GAC medium, position of sampling taps and tap structure.

Table A1. Compounds (n = 99) analysed in **Paper II**, with their respective average limit of quantification (LOQ) and internal standard

Compound	Average LOQ, ng L^{-1}	Internal standard
3-(4-Methylbenzylidene)camphor	3	Oxybenzone, D_5
4-Chloro-2-isopropyl-5-methylphenol	0.72	Isoproturon, D_3
4-Chloro-3-methylphenol	2.7	Isoproturon, D_3
Acesulfame (E950)	1.2	Diazepam, D_5
Acetaminophen	33	Acetaminophen, D_4
Albuterol (Salbutamol)	0.047	Atenolol, D_7
Amitriptyline	0.043	Diazepam, D_5
Atenolol	0.049	Atenolol, D_7
Atovastatin (Lipitor)	0.17	Atorvastatin, D_5
BAM (Dichlorobenzamide)	0.43	DEET, D_{10}
Bezafibrate	0.47	Bezafibrate, D_4
Bicalutamide	0.012	Diazepam, D_5
Bisoprolol	0.018	Diazepam, D_5
Caffeine	0.54	Caffeine, $^{13}C_3$
Carazolol	0.042	Venlafaxine, D_6
Carbamazepine	0.032	Oxazepam, D_5
Cetirizine	0.011	Oxazepam, D_5
Chloramphenicol	0.34	Tramadol, ^{13}C, D_3
Chlorzoxazone	6.8	Bezafibrate, D_4
Citalopram	0.01	Oxazepam, D_5
Clarithromycin	1.6	Diazepam, D_5
Climbazole	0.031	Diazepam, D_5
Clindamycin	0.01	Diazepam, D_5
Clozapine	0.12	Diazepam, D_5
Codeine	0.056	Codeine, D_3
Daidzein	0.34	Venlafaxine, D_6
Di-(2-ethylhexyl)phosphoric acid	0.71	Isoproturon, D_3
Diazepam	0.01	Diazepam, D_5
Dibutyl phosphate	0.62	Bezafibrate, D_4
Diclofenac	1.4	Diclofenac, $^{13}C_6$
Diltiazem	0.055	Diltiazem, D_4
Erythromycin	0.45	Lidocaine-(diethyl), D_{10}

Ethylparaben	0.34	Tramadol, ^{13}C, D_3
Fexofenadine	0.011	Diazepam, D_5
Fluconazole	0.045	Codeine, D_3
Fluoxetine	0.67	Fluoxetine, D_5
Furosemide	3.8	Furosemide, D_5
Gemfibrozil	2.4	Diltiazem, D_4
Genistein	2.6	Venlafaxine, D_6
Hydrochlorothiazide (HCTZ)	0.61	Hydrochlorothiazide, ^{13}C, D_2
Ifosfamide	0.12	Bezafibrate, D_4
Iopromide	1.6	Diazepam, D_5
Irbesartan	0.01	Irbesartan, D_7
Lamotrigine	0.01	Oxazepam, D_5
Lidocaine	0.025	Lidocaine-(diethyl), D_{10}
Loperamide	0.018	Diazepam, D_5
Losartan	0.047	Losartan, D_4
Mefenamic acid	2	Mefenamic acid, $^{13}C_6$
Memantine	1.3	Diazepam, D_5
Methotrexate	2	Codeine, D_3
Methylparaben	1.3	Propylparaben, D_7
Metoprolol	0.062	Atenolol, D_7
Metronidazole	3	Metronidazole, D_4
Metronidazole-OH	0.53	Metronidazole, D_4
Mirtazapine	0.01	Oxazepam, D_5
N,N-diethyl-3-methylbenzamide (DEET)	0.3	DEET, D_{10}
Nicotinamide	0.63	Atenolol, D_7
Nicotine	0.04	Caffeine, $^{13}C_3$
Norsertraline	20	Cis-Sertraline, D_3
O-desmethyl-venlafaxine	0.035	Venlafaxine, D_6
Omeprazole	0.028	Losartan, D_4
Oxazepam	0.01	Oxazepam, D_5
Paroxetine	0.14	Oxazepam, D_5
Phenazone	0.033	Codeine, D_3
Propranolol	0.01	Atenolol, D_7
Propylparaben	0.12	Propylparaben, D_7
Pyrimethamine	0.011	Diazepam, D_5
Ramipril	0.024	Lidocaine-(diethyl), D_{10}
Ranitidine	14	Caffeine, $^{13}C_3$

Roxithromycin	0.058	Diazepam, D_5
Salicylic acid	0.83	Metronidazole, D_4
Sertraline	0.42	Cis-Sertraline, D_3
Sotalol	0.097	Atenolol, D_7
Sulfamethoxazole	0.97	Trimethoprim, D_9
Sulindac	0.23	Bezafibrate, D_4
Sulisobenzone	0.21	Bezafibrate, D_4
Tamoxifen	2	Diltiazem, D_4
Terbutaline	0.17	Atenolol, D_7
Thiabendazole	0.078	Bezafibrate, D_4
Tolyltriazole	0.35	Bezafibrate, D_4
Tramadol	0.024	Tramadol, ^{13}C, D_3
Triisopropanolamine	0.053	Atenolol, D_7
Trimethoprim	0.01	Trimethoprim, D_9
Tris(2-butoxylethyl) phosphate (TBEP)	0.1	Isoproturon, D_3
Valsartan	0.27	Propylparaben, D_7
Venlafaxine	0.12	Venlafaxine, D_6
Perfluorobutanesulfonic acid (PFBS)	2	$^{13}C_3$-PFBS
Perfluoroctanoic acid (PFOA)	1.5	$^{13}C_8$-PFOA
Perfluorodecanoic acid (PFDA)	0.27	$^{13}C_6$-PFDA
Perfluorododecanoic acid (PFDoDA)	0.4	$^{13}C_2$-PFDoDA
Perfluoroheptanoic acid (PFHpA)	2.5	$^{13}C_4$-PFHpA
Perfluorohexanesulfonic acid (PFHxS)	2.1	$^{13}C_3$-PFHxS
Perfluorohexanoic acid (PFHxA)	10	$^{13}C_5$-PFHxA
Perfluorononanoic acid (PFNA)	0.15	$^{13}C_9$-PFNA
Perfluorooctane sulfonate (PFOS)	0.8	$^{13}C_8$-PFOS
Perfluorooctanesulfonamide (FOSA)	0.14	$^{13}C_8$-FOSA
Perfluoropentanoic acid (PFPeA)	2.6	$^{13}C_5$-PFPeA
Perfluorotetradecanoic acid (PFTeDA)	0.21	$^{13}C_2$-PFTeDA
Perfluoroundecanoic acid (PFUnDA)	0.32	$^{13}C_7$-PFUnDA

Table A2. Compounds (n = 37) analysed in **Paper III**, with their respective limit of quantification (LOQ) and internal standard

Compound	Compound name	LOQ ng L^{-1}	Internal standard
PFBA	Perfluoro-n-butanoic acid	2	$^{13}C_4$-PFBA
PFPeA	Perfluoro-n-pentanoic acid	0.3	$^{13}C_5$-PFPeA
PFHxA	Perfluoro-n-hexanoic acid	0.3	$^{13}C_5$-PFHxA
PFHpA	Perfluoro-n-heptanoic acid	0.3	$^{13}C_4$-PFHpA
PFOA	Perfluoro-n-octanoic acid	0.3	$^{13}C_8$-PFOA
PFNA	Perfluoro-n-nonanoic acid	0.3	$^{13}C_9$-PFNA
PFDA	Perfluoro-n-decanoic acid	0.3	$^{13}C_6$-PFDA
PFUnDA	Perfluoro-n-undecanoic acid	0.3	$^{13}C_7$-PFUnDA
PFDoDA	Perfluoro-n-dodecanoic acid	0.3	$^{13}C_2$-PFDoDA
PFTrDA	Perfluoro-n-tridecanoic acid	0.3	$^{13}C_2$-PFUnDA
PFTeDA	Perfluoro-n-tetradecanoic acid	0.3	$^{13}C_2$-PFTeDA
PFHxDA	Perfluoro-n-hexadecanoic acid	0.3	$^{13}C_2$-PFHxDA
PFOcDA	Perfluoro-n-octadecanoic acid	0.3	$^{13}C_2$-PFHxDA
PFBS	Perfluorobutanesulfonic acid	0.3	$^{13}C_3$-PFBS
PFPeS	Perfluoropentane sulfonic acid	0.3	$^{13}C_3$-PFHxS
PFHxS	Perfluorohexanesulfonic acid	0.3	$^{13}C_3$-PFHxS
PFHpS	Perfluoroheptanesulfonic acid	0.3	$^{13}C_3$-PFHxS
PFOS	Perfluorooctanesulfonic acid	0.3	$^{13}C_8$-PFOS
PFNS	perfluorononane sulfonic acid	0.3	$^{13}C_8$-PFOS
PFDS	Perfluorodecanesulfonic acid	0.3	$^{13}C_8$-PFOS
PFDoDS	Perfluorodecane sulfonic acid	0.3	$^{13}C_8$-PFOS
DONA	Dodecafluoro-3H-4,8-dioxanonanoic acid	10	$^{13}C_8$-PFOA
HFPO-DA	2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoate	50	$^{13}C_3$-HFPO-DA
P37DMOA	Perfluoro-3,7-dimethyloctanoic acid	10	$^{13}C_8$-PFOS
9Cl-PF2ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	10	$^{13}C_8$-PFOS
4:2 FTSA	4:2 Fluorotelomer sulfonic acid	0.3	$^{13}C_2$-4:2 FTSA
6:2 FTSA	6:2 Fluorotelomer sulfonic acid	0.3	$^{13}C_2$-6:2 FTSA

8:2 FTSA	8:2 Fluorotelomer sulfonic acid	0.3	$^{13}C_2$-8:2 FTSA
10:2 FTSA	10:2 Fluorotelomer sulfonic acid	0.3	$^{13}C_6$-PFDA
FOSA	Perfluorooctanesulfonamide	0.3	$^{13}C_8$-FOSA
MeFOSA	N-methyl perfluorooctane sulfonamide	2	$^{13}C_3$-MeFOSA
EtFOSA	N-ethyl perfluorooctane sulfonamide	2	$^{13}C_5$-EtFOSA
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol	2	$^{13}C_8$-MeFOSE
EtFOSE	N-ethyl perfluorooctane sulfonamide	2	$^{13}C_9$-EtFOSE
FOSAA	Perfluorooctane sulfonamidoacetic acid	1	$^{13}C_3$-MeFOSA
MeFOSAA	N-methylperfluorooctanesulfonamido acid	1	$^{13}C_3$-MeFOSAA
EtFOSAA	N-ethylperfluorooctanesulfonamido acid	1	$^{13}C_5$-EtFOSAA
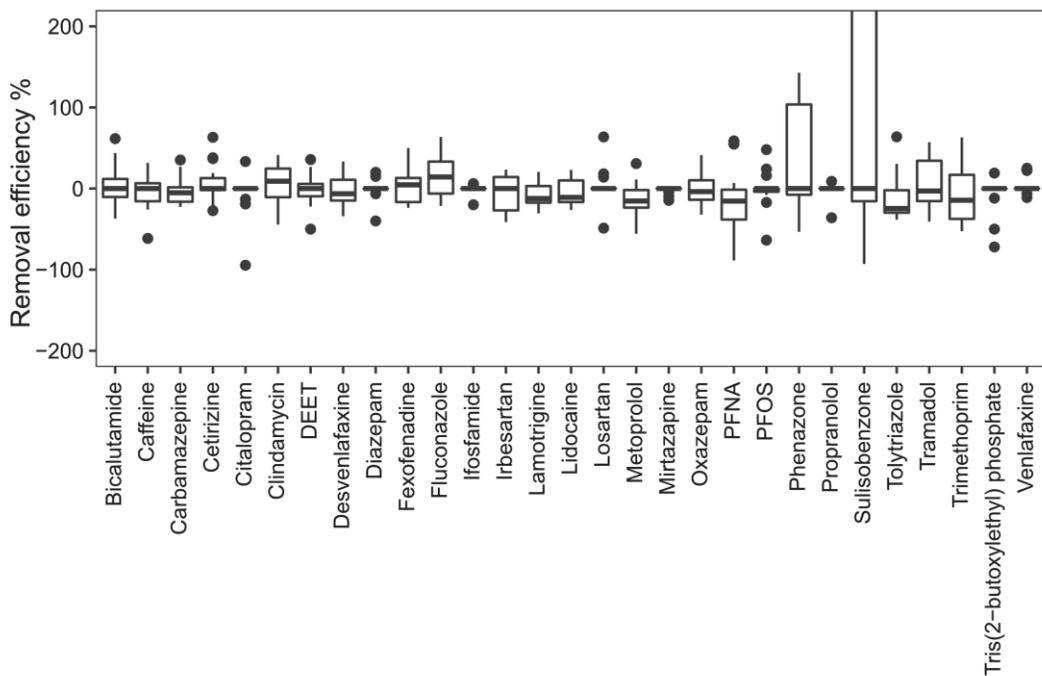
Figure A2. Boxplot of removal efficiency by an old granular activated carbon (GAC) filter (>14 years in use) in full-scale treatment (*n*=15). (Unpublished data.)
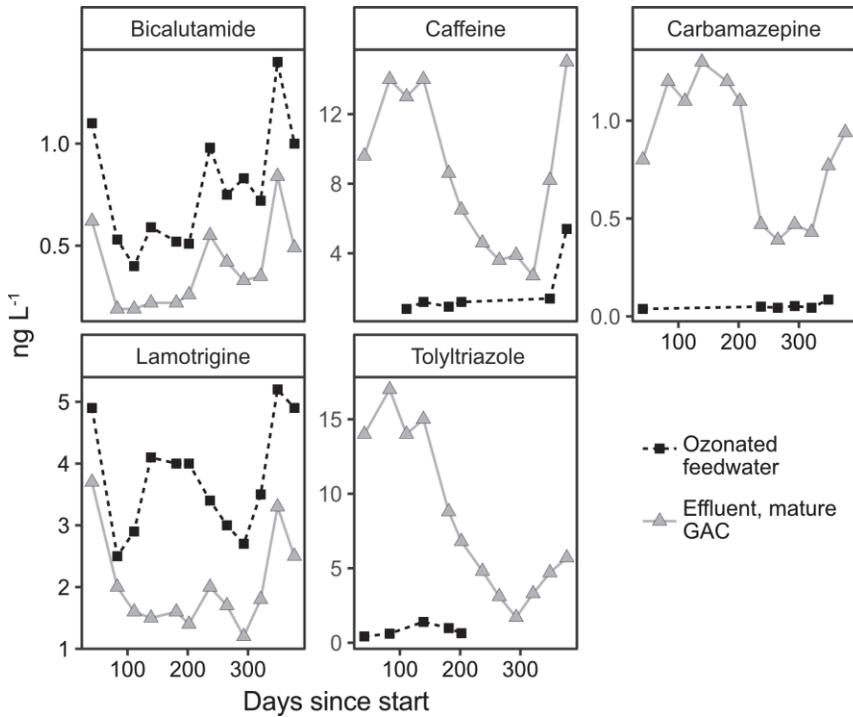
Figure A3. Concentrations of individual organic micropollutants (OMPs) in effluent from a mature granular activated carbon (GAC) filter (Görväln DWTP pilot experiment) compared with concentrations in the feedwater. Measurements <LOQ are omitted from the graph. (Unpublished data.)

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Water sources world-wide are affected by the widespread use of synthetic chemicals, creating a challenge that drinking water producers must address. Granular activated carbon (GAC) is a commonly used sorption material in water treatment processes. This thesis explores different roles of GAC filters in drinking water production: as a chemical barrier, as a biofilter, as a post-treatment step after ozonation and as a waste management step after nanofiltration.

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