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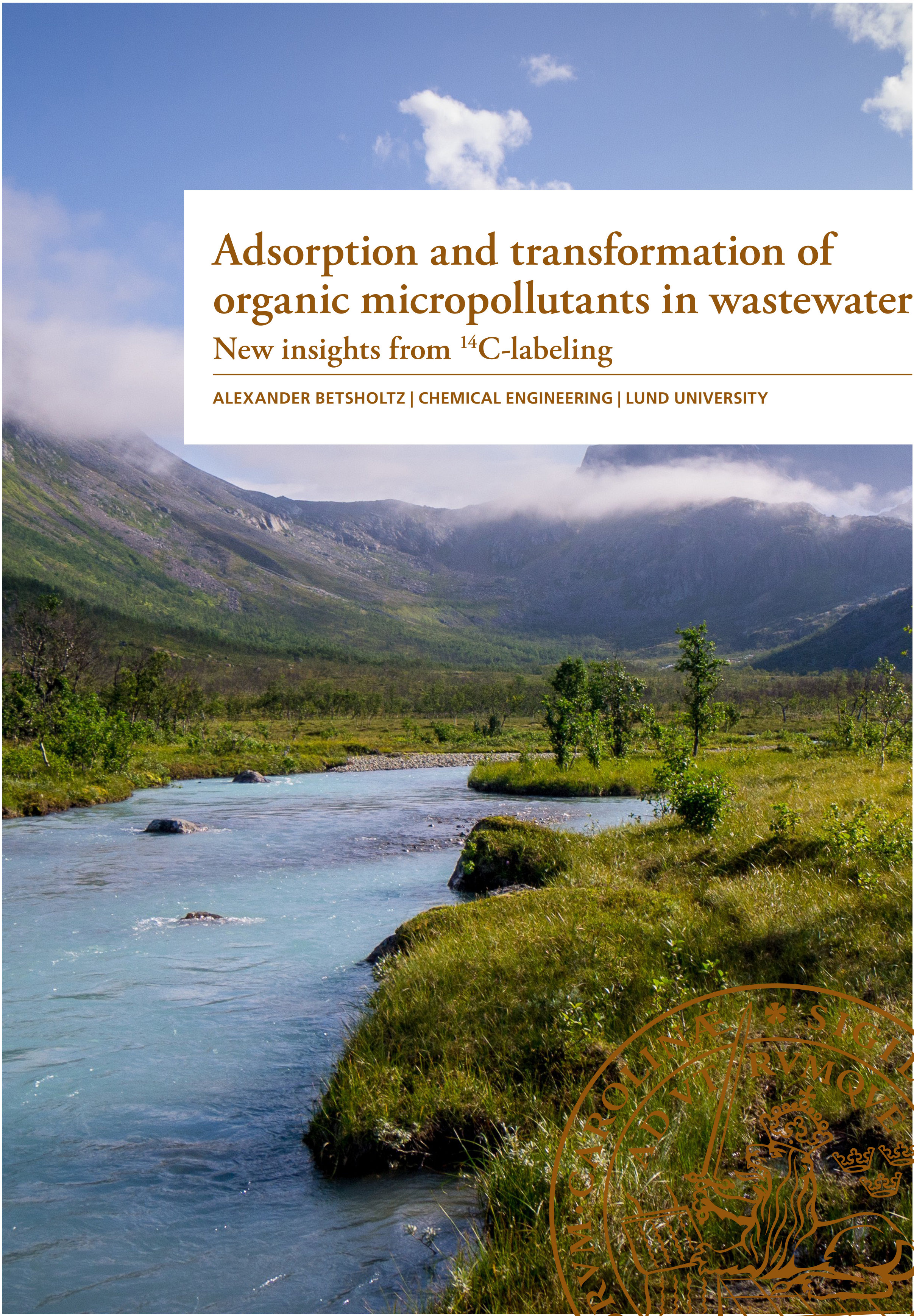

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New insights from ^{14}C-labeling

ALEXANDER BETSHOLTZ | CHEMICAL ENGINEERING | LUND UNIVERSITY

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The author widening his perspective during midnight sun climbing in northern Norway

Pharmaceuticals belong to a large group of pollutants that are discharged daily into our natural waters via municipal wastewater treatment plant effluents. This can be damaging to aquatic ecosystems and pollute our drinking water. To increase the protection of our waters, we must implement additional treatment targeting these compounds. This thesis focuses on the removal of organic micropollutants and transformation products from municipal wastewater using ozone and activated carbon treatment processes. A combination of ^{14}C-labeled and non-radiolabeled organic micropollutants was used to study aspects of micropollutant removal from novel perspectives.

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DOCTORAL DISSERTATION

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When the well is dry, we know the worth of water

Benjamin Franklin

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Abstract

This thesis focuses on the removal of organic micropollutants and transformation products using ozone and activated carbon treatment processes. A combination of ^{14}C-labeled and non-radiolabeled organic micropollutants was used to study aspects of micropollutant removal from novel perspectives.

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Populärvetenskaplig sammanfattning

Läkemedel i avloppsvatten

Årligen stoppar vi i oss omkring 100 gram läkemedel, men bara en liten del av dessa kommer till önskad användning i våra kroppar. Den största delen utsöndras med urinen och hamnar i det avloppsvatten som så småningom släpps ut i våra bäckar, sjöar och hav. Tyvärr renas läkemedel, bekämpningsmedel och andra problematiska ämnen bara delvis i dagens avloppsreningsverk, och trots att de ämnen som släpps ut finns i små mängder har de visat sig kunna orsaka problem för vattenlevande organismer. Till exempel kan hormonstörande läkemedel från p-piller ge fortplantningssvårigheter för fiskar, vilket kan sätta vattendragens ekosystem ur balans. Det finns också en oro för att dessa ämnen ska förorena våra dricksvattenkällor, speciellt då en ökad befolkning, urbanisering och klimatförändringar sätter ökad press på återanvändning av vatten. För att minska mängden läkemedel som släpps ut i våra vattendrag måste vi införa nya reningsprocesser vid våra avloppsreningsverk.

Ozon och aktivt kol de vanligaste reningsteknikerna

De vanligast förekommande teknikerna för rening av läkemedel i avloppsvatten är adsorption till aktivt kol samt ozonering. Med aktivt kol avlägsnas läkemedel genom att dessa adsorberar (fastnar) på det aktiva kolets yta. Vid ozonering tillsätts i stället ozon (O_3) till avloppsvattnet, där det reagerar med läkemedlen.

Synergier mellan adsorption och nedbrytning i kolfilter.

Ett vanligt sätt att använda aktivt kol är i kolfilter, där vattnet filtreras genom en bädd av kolpartiklar. Så småningom börjar mikroorganismer växa i filtret och bildar en så kallad biofilm, som skulle kunna bryta ned vissa ämnen. Med hjälp av kol-14-märkta läkemedel har biofilmens och det aktiva kolets bidrag till läkemedelsreningen kunnat särskiljas inom detta avhandlingsarbete. Det visade sig att det smärtstillande ämnet diklofenak effektivt kunde brytas ned av biofilmen i kolfilter, trots att detta ämne tidigare visat sig vara svårt att bryta ned med andra biologiska processer. Vi tror att just samverkan mellan adsorption och nedbrytning i kolfilter är nyckeln till den ökade nedbrytningen, något som i framtiden skulle kunna användas för att förbättra andra biologiska processer.

Reaktionen med ozon inte komplett

När ozon reagerar med läkemedelsmolekylerna slås de sönder och det bildas i sin tur nya ämnen, så kallade transformationsprodukter. Men hur vet man att dessa ämnen är mindre problematiska än de ursprungliga läkemedlen? Man har tidigare sett att ozon ofta förstör molekylerna på ett sätt som gör att deras huvudsakliga effekt, såsom en hormonstörande påverkan, försvinner. Samtidigt kan nya okända effekter uppstå. Vi vet idag väldigt lite om de ämnen som bildas vid ozonering, och i praktiken blir det därför mycket svårt att förstå hur farliga de är. Vi tar hand om ett problem, men skapar samtidigt nya.

För att få bukt med transformationsprodukter och andra ämnen som bildas vid ozonering så använder man oftast en reningsprocess med mikroorganismer efter ozoneringen, såsom ett sandfilter. På senare tid har man också föreslagit adsorption till aktivt kol som ett möjligt sätt att få bukt med problemet. Troligtvis får man också bort flera ämnen, men i verkligenheten vet vi väldigt lite om hur komplett reningen av transformationsprodukter verkligen är.

Kol-14-märkta läkemedel möjliggör spårning av transformationsprodukter

Men varför är så många transformationsprodukter okända? Dagens analysmetoder är suveräna på att hitta ämnen i vatten, men bara när vi vet exakt vad vi letar efter. Så fort vi behöver hantera okända ämnen blir det en helt annan process som är tidsödande då det finns en närmast oändlig mängd av möjliga transformationsprodukter. Att följa alla blir i praktiken helt omöjligt. I vår forskargrupp har vi därför använt oss av kol-14-märkta läkemedel för att kunna följa transformationsprodukterna på ett nytt sätt. Vi kan inte visa vilka ämnen som bildas, men vi kan spåra hur väl de kan tas bort på ett sätt som inte är möjligt med andra tekniker.

Adsorption av transformationsprodukter – kanske inte en bra lösning

Med hjälp av kol-14-märktningen har vi kunnat visa att en stor del av transformationsprodukterna från ozonering verkar adsorbera dåligt till aktivt kol, något som till viss del motsäger resultat från tidigare forskning. Vi tror att vår metod har lyckats representera en grupp av ämnen som i andra studier varit osynlig, och som generellt adsorberar dåligt till aktivt kol. I den fortsatta forskningen undersöker vi hur transformationsprodukterna kan avlägsnas med hjälp av mikroorganismer samt kombinationen av mikroorganismer och aktivt kol. Även här kan kol-14-tekniken få en avgörande roll för att avgöra transformationsprodukternas öde.

List of Papers

Paper I

Gidstedt, S., **Betsholtz, A**., Falås, P., Cimbritz, M., Davidsson, Å., Micolucci, F., Svahn, O., 2022. A comparison of adsorption of organic micropollutants onto activated carbon following chemically enhanced primary treatment with microsieving, direct membrane filtration, and tertiary treatment of municipal wastewater. *Science of The Total Environment*. 811, 152225.

Paper II

Betsholtz, A., Juárez, R., Svahn, O., Davidsson, Å., Cimbritz, M., Falås, P., 2022. Ozonation of ^{14}C-labeled micropollutants – mineralization of labeled moieties and adsorption of transformation products to activated carbon. *Water Research. 221.*

Paper III

Betsholtz, A., Karlsson, S., Svahn, O., Davidsson, Å., Cimbritz, M., Falås, P., 2021. Tracking ^{14}C-labeled organic micropollutants to differentiate between adsorption and degradation in GAC and biofilm processes. *Environmental Science & Technology*. 55, 11318–11327.

Paper IV

Betsholtz, A., Falås, P., Svahn, O., Cimbritz, M., Davidsson, Å., (YYYY), Can adsorption in GAC filters unlock biodegradation of challenging micropollutants? *Manuscript.*

Author’s contribution to the papers

Paper I

I participated in the design and operation of the pilot plant at Svedala WWTP. I designed and conducted the laboratory experiments with S. Gidstedt and F. Micolucci. I participated in the micropollutant analysis; compilation and evaluation of the initial data; and proofreading of the manuscript.

Paper II

I conceptualized the research idea and designed the experimental setup with the other authors. I conducted most of the experimental work and analysis. I interpreted the results and wrote the manuscript with input from the other authors.

Paper III

I designed the experiments with P. Falås. I performed most of the experimental work and analysis. I interpreted the results and wrote the manuscript with input from the other authors.

Paper IV

I designed the experiment with input from the other authors. I performed most of the experimental work and analysis. I interpreted the results and wrote the manuscript with input from the other authors.

Related publications

Gidstedt, S., **Betsholtz, A.**, Cimbritz, M., Davidsson, Å., Hagman, M., Karlsson, S., Takman, M., Svahn, O., Micolucci, F., 2022a. Chemically enhanced primary treatment, microsieving, direct membrane filtration, and GAC filtration of municipal wastewater: A pilot-scale study. *Environmental Technology.* 1–12.

Nomenclature and abbreviations

AC	Activated carbon
BV	Bed volume
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
COD	Chemical oxygen demand
EBCT	Empty bed contact time
GAC	Granular activated carbon
HRT	Hydraulic retention time
MBBR	Moving bed biofilm reactor
MF	Microfiltration
MP	Micropollutant
OTP	Ozone transformation product
PAC	Powdered activated carbon
PFAS	Per- and polyfluoroalkyl substances
SPE	Solid-phase extraction
VS	Volatile solid
UF	Ultrafiltration
UPLC-MS/MS	Ultra-performance liquid chromatography coupled with tandem mass spectrometry
UVA_{254}	Ultraviolet absorption at 254 nm
WWTP	Wastewater treatment plant

Table of Contents

1 Introduction

Organic micropollutants, such as pharmaceuticals, biocides, and various industrial chemicals, are transported daily to our natural waters through various water flow paths. Municipal wastewater treatment plant (WWTP) effluent is a major source of micropollutants but offers the possibility to reduce their levels before being released into the environment. Unfortunately, conventional wastewater treatment only partially remove these compounds, and as a result, micropollutants from municipal wastewater have been detected worldwide in seas, lakes, rivers, groundwaters, and drinking water (Lin and Tsai, 2009; Luo et al., 2014; Roberts and Thomas, 2006; Schäfer et al., 2011).

Although the concentrations of these micropollutants in wastewater effluent are primarily low (< 10,000 ng/L) and further diluted in recipient waters, they can remain harmful due to their individual, additive, or synergistic toxicity (Backhaus et al., 2011; Cleuvers, 2004; Larsson et al., 1999); persistence (Ng et al., 2022; Rostvall et al., 2018); or ability to bioaccumulate in organisms and food webs (Desiante et al., 2021; Lagesson et al., 2016; Veseli et al., 2022). An notable example is the sexual disruption of roaches (Swe: mört) in English rivers (Jobling et al., 1998) that is linked to the presence of estrogens that originate from the widespread use of contraceptives, which can collapse the fish population at elevated levels (Kidd et al., 2007).

Banning or restricting the use of particularly harmful compounds is an important measure for easing the release of these compound into the environment (e.g., Stokstad, 2018), but this process is slow, considering the global trends in increased chemical use (Z. Wang et al., 2021). Certain compounds are also considered too important for human health (for example, antibiotics and other pharmaceuticals) to limit their use. For such compounds, end-of-pipe treatment at a WWTP or at targeted sites (e.g., hospitals) might be the most feasible option for their removal.

Based on a wide screen of micropollutants, it has been estimated that approximately half of the micropollutant load is removed by conventional wastewater treatment, primarily via biological degradation and sorption to sludge (Luo et al., 2014). Many compounds, however, fail to undergo significant removal by conventional treatment. By upgrading WWTPs with targeted micropollutant removal processes, the elimination of many micropollutants can be improved substantially (e.g., Altmann et al., 2015; Lee et al., 2013). The incentives for such upgrades include greater protection of aquatic environments from the risks that are associated with micropollutants and increased preservation of drinking water supplies (Eggen et al., 2014). Further, this approach can increase the potential of reused wastewater for irrigation, industrial applications, and drinking water production (Takman et al., 2023).

Although few countries regulate micropollutant removal from municipal wastewater by law, a steady increase in full-scale implementations for targeted micropollutant removal are seen worldwide. The need for increased national micropollutant abatement programs has been recognized in the EU, in which an update of the Urban Waste Water Treatment directive (2022/0345/COD) advocates for substantial upgrades to WWTPs throughout Europe.

Ozonation and activated carbon (AC) adsorption are currently the two most viable techniques for removing organic micropollutants from municipal wastewater, albeit through fundamentally different mechanisms. AC adsorbs micropollutants, removing them from the water phase (Worch, 2012). In contrast, in ozonation, micropollutants are oxidized into various transformation products that are generally less persistent and harmful compared with their parent compounds (von Sonntag and von Gunten, 2015). Nevertheless, much fundamental research is needed to determine how to improve treatment efficiencies to remove more of the (potentially toxic) compounds at a lower cost and environmental impact.

An important aspect of micropollutant removal is the amount and type of dissolved organic matter (DOM) in the wastewater. Total amounts of DOM, expressed as dissolved organic carbon (DOC), typically range from 5-15 mg carbon/L in WWTP effluents, over 1000-fold higher than for most individual micropollutants (which generally range from <1-1000 ng/L); the sum concentrations of micropollutants have been estimated to be 10-100 µg/L, based on a screen of over 100 micropollutants (Bourgin et al., 2018; Wang et al., 2018). DOM competes with micropollutants for the adsorption sites on AC (Pelekani and Snoeyink, 1999; Zietzschmann et al., 2014b) and for reactions with ozone (Nöthe et al., 2009; van Gijn et al., 2022), necessitating an understanding of the type of DOM that impedes micropollutant removal and whether these fractions can be removed by suitable pre-treatment methods, such as filtration, biological treatment, and ozonation.

With regard to advanced treatments, ozonation removes certain micropollutants better than AC, and vice versa (Margot et al., 2013). Thus, the combination of ozonation and AC is considered a potential option for increasing overall removal, merging the strengths of both processes (Reungoat et al., 2012; Zietzschmann et al., 2015). However, during ozonation, there is the formation of undesired and potentially toxic by-products (from reactions with DOM and inorganic matter (Gunten et al., 2010; Von Gunten and Hoigné, 1994; Wert et al., 2007) and ozone transformation products (OTPs; from reactions with micropollutants: Prasse et al., 2012; Wei et al., 2021). It remains unknown how well various by-products and

OTPs, most of which are unknown, can be removed via adsorption to AC, biological degradation, or their combination. Much effort has been undertaken to identify the OTPs, but their recovery and identification in a complex matrix of DOM—particularly given the vast range of potential molecular structures and properties—remain challenging.

The use of ^{14}C-labeled micropollutants could circumvent some of the challenges that are associated with conventional measurements of micropollutants and their transformation products. In ^{14}C-labeled micropollutants, one or more carbon atoms are replaced with a radioactive ^{14}C isotope, allowing the compound to be tracked throughout various wastewater treatment processes in a laboratory setting. Applying ^{14}C-labeled micropollutants could guide discussions on OTP removal in post-ozonation treatment, because ^{14}C-labeled carbons will be incorporated into an OTP if they are not mineralized to $^{14}CO_2$ during ozonation. Thus, ^{14}C-labeling enables OTPs to be monitored and separated from DOM, based on radioactivity, but has not previously been applied to study the fate of OTPs in such treatment processes as adsorption to AC.

^{14}C-labeled micropollutants can also be used to study biological degradation (biodegradation) of micropollutants. Examining the formation of $^{14}CO_2$ from ^{14}C-labeled micropollutants can confirm biodegradation and indicate a potential degradation pathway. An additional benefit is that biodegradation can be demonstrated directly via the formation of $^{14}CO_2$ rather than indirectly through measurements of micropollutant removal between the influent and effluent. The formation of $^{14}CO_2$ can also be used to distinguish degradation from other mechanisms of removal that occur simultaneously.

In granular activated carbon (GAC) filters, micropollutants are considered to be removed primarily by adsorption. However, a biofilm develops over time during operation and can increase micropollutant removal, by direct biological degradation (biodegradation) of the micropollutant (Altmann et al., 2016; Fundneider et al., 2021b) or by degradation of DOM, decreasing the competition for adsorption sites (Aktaş and Çeçen, 2007; Simpson, 2008). The degree to which GAC biofilms contribute to micropollutant removal remains unknown, mainly due to difficulties in differentiating removal due to biodegradation versus adsorption (Paredes et al., 2016; Yuan et al., 2022). Notably, the use of ^{14}C-labeled micropollutants can be helpful, because it allows biodegradation to be separated from adsorption during the formation of $^{14}CO_2$.

1.1 Aim

The overall objective of this thesis is to study the removal of organic micropollutants and their transformation products with powdered activated carbon (PAC) and GAC. The results are divided into three sections, each with its associated objectives and research questions.

Part 1. Adsorption of micropollutants and ozone transformation products with activated carbon.

The objectives of this chapter were to *(i)* analyze the competition between DOM and micropollutants for the adsorption to AC after various wastewater treatment processes and *(ii)* examine the adsorption of OTPs to AC. The following research questions were addressed:

- How does pre-ozonation affect the competition between DOM and micropollutants for adsorption to PAC?
- How well can OTPs be removed via adsorption to PAC, after varying degrees of ozonation?

Part 2. Adsorption and biodegradation of micropollutants in GAC filters

The objective of this chapter was to determine the relative contribution of biodegradation and concurrent adsorption to micropollutant removal by GAC filter systems. The following research questions were addressed:

- Can ^{14}C-labeled micropollutants be used to separate biodegradation from adsorption in GAC filter media?
- Can micropollutants that have adsorbed onto GAC be subsequently degraded?
- What is the influence of dissolved oxygen on micropollutant degradation in GAC biofilms?

Part 3. Mineralization of micropollutants during ozonation

The objective of this chapter was to study the mineralization of various micropollutants moieties during ozonation. The following research question was addressed:

- To what extent are various moieties of micropollutants mineralized to CO_2, after varying degrees of ozonation?

1.2 Outline of the thesis

A background section on organic micropollutants and their removal by conventional wastewater treatments and during targeted micropollutant removal with AC and ozonation is presented in Chapter 2, emphasizing adsorption to AC, which is the focus of this thesis.

Chapter 3 introduces the main experimental methods and approaches that were applied in **Papers I-IV**, focusing on the introduction of ^{14}C-labeled micropollutants and how they have been used to study various aspects of adsorption, ozonation, and biological degradation.

The primary results from **Papers I-IV** are presented and discussed in Chapters 4-6. In Chapter 4, the adsorption of micropollutants in various wastewater matrices is discussed with regard to competition for adsorption by DOM. The second half of Chapter 4 focuses on the adsorption of OTPs to AC, in relation to **Paper II.**

Chapter 5 addresses the biodegradation and adsorption of micropollutants in GAC filter systems, as reported in **Papers III and IV**. The individual contribution of biodegradation and adsorption to overall micropollutant removal by GAC filters is discussed, and biodegradation in GAC filters is compared with that of other (non-adsorbing) biological treatments. Finally, the interactions and potential synergies between adsorption and biodegradation are discussed in relation to the properties of micropollutants.

Chapter 6 presents the results on the mineralization of ^{14}C-labeled moieties during ozonation of common ^{14}C-labeled micropollutants, as introduced in **Paper II**. Chapters 7 and 8 summarize the main findings and present a conclusion and proposed direction for future studies.

2 Removal of organic micropollutants in wastewater

The past several decades have witnessed increasing concern over the presence and potential effects of organic micropollutants in our environment (Anderson et al., 2006; Fent et al., 2006). In 2015, the European Commission introduced a watchlist of select compounds of concern to be monitored regularly by member states (European Commission, 2015). Since then, the watchlist has been updated three times and includes such chemicals as hormones, pharmaceuticals, insecticides, herbicides, fungicides, and compounds in personal care products (European commission, 2022, 2020, 2018). Monitoring programs have also been implemented on a national level. In Sweden, the Agency for Marine and Water Management (Havs-och Vattenmyndigheten) has generated a list of river basin-specific pollutants (särskilda förorenande ämnen SFÄ) to be tracked (Swedish Regulation, HVMFS 2019:25).

These extensive monitoring efforts have revealed the presence of organic micropollutants in surface waters, groundwaters, and drinking water worldwide (e.g., Lin and Tsai, 2009; Luo et al., 2014; Ng et al., 2022; Wang et al., 2018), and their possible ecotoxic effects, such as sexual disruption in fish (Jobling et al., 1998) and declines in macroinvertebrate populations (Van Dijk et al., 2013), have been recognized. As a result, the current proposal for and update of the Urban Waste Water Treatment directive (2022/0345/COD) advocate for the implementation of additional micropollutant removal techniques at select WWTPs, which could lead to the extensive upgrade of WWTPs throughout Europe. In Switzerland, micropollutant removal in wastewater is regulated by law and already widely implemented (VSA, 2023). In Sweden, a combination of local decisions and national funding has led to the testing and full-scale implementation of micropollutant removal at a few locations, a figure that will likely increase.

In this chapter, conventional municipal wastewater treatment is briefly introduced, followed by a background section on targeted micropollutant removal with AC and ozonation.

2.1 Conventional wastewater treatment

The overall purpose of municipal wastewater treatment is to (i) reduce effluent levels of biodegradable organic material and nutrients (primarily nitrogen and phosphorous) to prevent oxygen deficiency and eutrophication and (ii) lower pathogen levels in receiving surface waters.

Conventional municipal wastewater treatment comprises a combination of mechanical, biological, and chemical processes (Figure 1). Mechanical treatment entails the removal of particles via screening, grit removal, and primary sedimentation. Biological treatment uses bacteria and other microorganisms to remove easily biodegradable organics and nitrogen by nitrification-denitrification. Phosphorous is commonly removed by chemical precipitation with metal salts but can also be removed to various extents through biological treatment, depending on the treatment configuration. Suspended solids (or sludge) that are generated in the treatment processes due to biomass growth or precipitation are typically removed by sedimentation, although several filtration options can be applied. Sludge management and disposal (not included in Figure 1) generally involves thickening, stabilization, dewatering and subsequent sludge disposal. A large variety of wastewater treatment processes exist. Biological treatment is conducted with suspended growth processes (activated sludge), attached growth processes (such as trickling filters and moving bed biofilm reactors [MBBRs]), or their combination.

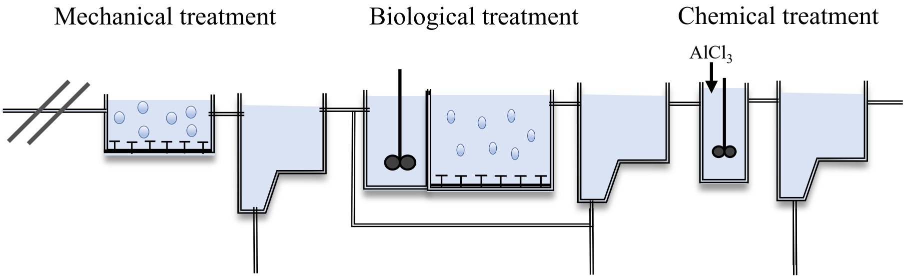


Figure 1
Schematic of typical conventional wastewater treatment, consisting of (i) mechanical treatment, with screens, grit removal, and primary sedimentation; (ii) biological treatment with activated sludge or biofilm processes; and (iii) chemical treatment with precipitation of phosphorous. Sludge management is not included in the overview.

2.1.1 The need for additional treatment

Conventional wastewater treatment decreases the total organic micropollutant load by approximately 50%, occurring primarily by removal via sorption to sludge or biodegradation (Luo et al., 2014). Remaining compounds may show low adsorption affinity sorption to sludge, and may be non-biodegradable, or too slowly biodegradable to be removed at relevant hydraulic retention times. Examples of compounds that are (mostly) well removed in conventional treatment are ibuprofen, estradiol and bisphenol A (Luo et al., 2014). Examples of compounds that are not well removed in conventional wastewater treatment are carbamazepine (Suarez et al., 2010) and oxazepam (Falås et al., 2016). To decrease the emission of these compounds, additional treatments that target micropollutants are required.

2.2 Activated carbon

AC is a highly porous material that consists largely of carbon. Although no widely accepted and detailed definition of its structure exists (Marsh and Rodriguez-Reinoso, 2006), AC is frequently described as consisting of disoriented or twisted polyaromatic sheets (Bansal and Goyal, 2005; Worch, 2012) that are interconnected by aliphatic bridging groups (Baker et al., 2000). Heteroatoms (atoms other than carbon) are mainly present as surface functional groups located at the edges of the aromatic sheets. Surface functional groups typically contain oxygen, vary widely in pK_a values, and can be acidic or basic (Boehm, 2002; Fuente et al., 2003).

The pores in AC can be envisioned as voids between the polyaromatic sheets, allowing compounds to adsorb onto their surface or to functional groups at their edges (Çeçen and Aktaş, 2011) through various electrostatic and non-electrostatic interactions (Moreno-Castilla, 2004) (discussed further in Section 2.2.2). Due to the collective large volume of these pores, the specific surface area of AC ranges from 500-1500 m^2/g.

The pore volumes and pore size distributions vary between types of AC. Pore sizes are typically classified as in Table 1 (Marsh and Rodriguez-Reinoso, 2006), compared with the size of organic micropollutants, which usually have maximum projection diameters of 1-2 nm (for the compounds in Table 1) and can thus be expected to fit into all pore classes. The connection between micropollutant size and adsorption is discussed further in Section 2.3.3.

Table 1. Pore size classification.

	Size (nm)
Micropores	< 2
Mesopores	2 – 50
Macropores	> 50

2.2.1 Production

AC is generally produced from precursor carbonaceous materials that have high carbon content and low levels of inorganics, including coconut shells; wood; and fossil-based sources, such as peat, petroleum coke, lignite, and coal (Çeçen and Aktaş, 2011). Much research has been devoted to examining the use of alternative precursors, such as lignocellulosic materials (González-García, 2018), plastic waste (Kumari et al., 2022), and sewage sludge (Smith et al., 2009).

Regardless of precursor material, the production of AC involves two processes. In the first step, carbonization (or pyrolysis), the material is heated to 400-700°C in an oxygen-deficient atmosphere. During this treatment, volatiles are released, and the carbon atoms reorganize into condensed, polyaromatic sheets that form the core structure of AC.

The second process, activation, is designed to improve the porosity of the char (Bansal and Goyal, 2005) and can be subdivided into physical and chemical activation. During physical activation, the char is heated to 700-1000°C in the presence of CO_2 or water vapor, which opens and widens previously inaccessible pores, increasing porosity (Worch, 2012). In chemical activation, the precursor material is mixed with a dehydrating chemical, such as a strong acid or base, allowing activation to proceed simultaneously with carbonization (Heidarinejad et al., 2020).

The type of precursor, in combination with the carbonization and activation procedures, influences the properties of the resulting carbon with regard to, for example, pore size distribution and the presence of surface functional groups (Heidarinejad et al., 2020). Thus, the production of AC can be tailored to the adsorption of a specific type of compound (Dastgheib et al., 2004; Schaubeder et al., 2023).

2.2.2 Adsorption mechanisms

Adsorption is a process in which a compound (adsorbate) accumulates at the interfacial layer of an adsorbent—for example, the adsorption of micropollutant to the solid structure of AC. Interactions between organic micropollutants and AC are mediated primarily by an interplay between hydrophobic, van der Waals, and coulombic interactions (Moreno-Castilla, 2004).

Hydrophobic interactions are non-specific interactions that originate from a net repulsion between water and the hydrophobic regions and moieties of adsorbates and adsorbents (Belfort et al., 1984), rather than attraction between hydrophobic moieties. Hydrophobicity is often expressed using the octanol-water partition coefficient, K_{OW}. For ionizable compounds, the octanol-water distribution coefficient, D_{OW}, describes their hydrophobicity, based on the distribution between neutral and charged species at the pH of interest. K_{ow} and D_{ow} values for the micropollutants in this thesis are shown in Table 2, Section 3.3.

Coulombic interactions occur between the charged moieties of ionic micropollutants and functional groups on the surface of AC. Attractive interactions arise between oppositely charged groups, whereas like charges leads to repulsion. Coulombic interactions are strongly influenced by pH, which affects the charge of the micropollutant (according to its pK_a value) and the surface of AC (according to its point of zero charge). Phenolic compounds are preferably adsorbed in their neutral forms (Moreno-Castilla et al., 1995), which has been suggested to be due to the lower repulsion between negatively charged phenols and the negatively charged surface of AC at the applied pH. Similarly, opposing charges of a micropollutant and the surface of AC can improve adsorption (Guillossou et al., 2020b). Conversely, ionic forms are more polar (less hydrophobic) compared with their neutral forms, decreasing adsorption due to hydrophobic interactions.

van der Waals interactions are non-specific dispersive interactions between, for example, micropollutants and the condensed polyaromatic sheets of AC (Knappe, 2006). In the adsorption of aromatic micropollutants (encompassing most of the micropollutants in this thesis), the interactions between π-electrons of the aromatic ring and those of the aromatic AC sheets—so called π-π interactions—are particularly important (Moreno-Castilla, 2004) and are discussed further in Section 2.3.3.

Hydrogen bonds are a type of van der Waals interaction that are stronger than π-π interactions (Tong et al., 2019) and develop between an electronegative atom and a hydrogen atom that is covalently bound to an electronegative atom (typically oxygen or nitrogen). Although hydrogen bonds between water and surface functional groups is considered to dominate over those between adsorbates and surface functional groups (Knappe, 2006), special types of hydrogen bonds are considered important for adsorption of certain compounds (Pignatello et al., 2017).

2.2.3 Micropollutant properties that influence adsorption onto activated carbon

Size and shape

The size and shape of an adsorbate in relation to the pores in AC affects its adsorption to AC. In general, a better fit between the size and shape of an adsorbate and the adsorbent pore allows for more interactions and thus greater adsorption (Pelekani and Snoeyink, 1999). Conversely, large adsorbates can be too big to enter pores—a phenomenon that is referred to as size exclusion. Thus, compounds should preferentially adsorb in pores that approximate their size and shape. This relationship is supported by studies that have found that micropollutant adsorption correlates with pores that are in a similar size range (Karanfil and Dastgheib, 2004; Li et al., 2002). For example, Li et al. (2002) reported that trichloroethene and tertiary-butyl ether adsorb primarily in pores that are 1.3-1.8 times their kinetic diameter.

Planarity also influences adsorption: planar aromatic compounds have been shown to adsorb better than globular compounds (Cornelissen et al., 2004). Due to the size of many micropollutants (1-2 nm), they are expected to adsorb primarily in micropores and small mesopores.

Hydrophobicity

In general, hydrophobic compounds adsorb better than hydrophilic compounds (Worch, 2012). For example, the adsorption of PFAS increases with aliphatic chain length (and greater hydrophobicity) (Park et al., 2020). For aromatic compounds, this correlation holds for neutral compounds, whereas coulombic interactions seem to be more important for the adsorption of charged compounds (Guillossou et al., 2020b; Mailler et al., 2015).

Charge

The acid dissociation constant (pK_a) determines the distribution of neutral and charged species at various pHs. Charged compounds are more polar than the corresponding neutral species but have the potential to enter into attractive or repulsive coulombic interactions with the surface of AC. Coulombic attraction/repulsion has been used to explain the high adsorptive capacities of certain hydrophilic and charged compounds (Nam et al., 2014). Yet, adsorptive capacities differ significantly between negatively charged compounds with similar hydrophobicities (Kovalova et al., 2013b), indicating that factors other than hydrophobicity and charge affect micropollutant adsorption.

Aromaticity

Many organic micropollutants are aromatic, which must be considered with regard to reactions with ozone and adsorption to AC via van der Waals interactions. During ozonation, aromatic rings are often the main sites of oxidative attack (von Sonntag and von Gunten, 2015). Aromatic rings allow for adsorption to AC through π-π interactions and contribute to a compound's hydrophobicity (Moreno-Castilla, 2004). Aromatic rings are also more reactive toward ozone than aliphatic rings (von Sonntag and von Gunten, 2015) and adsorb better to AC (Wang et al., 2021).

The presence of electron-donating and electron-withdrawing substituents on aromatic rings also influences both ozonation and adsorption. Electron-donating (activating) substituents, such as OH and NH_2 groups, increase the reactivity of the benzene ring with ozone, whereas electron-withdrawing (deactivating) elements, including NO_2 and COOH groups, decrease the reactivity to ozone. The effect of aromatic activation and deactivation on the adsorption of a compound to AC is more difficult to interpret, because the introduction of a functional group alters several adsorptive mechanisms. Whereas π-π interactions have been reported to be enhanced by both ring-activating (Wang et al., 2021) and ring-deactivating substituents (Liu et al., 2010; Zhu and Pignatello, 2005), concurrent changes to compound hydrophobicity, charge, size and shape due to activation/deactivation may not necessarily be beneficial for adsorption.

2.2.4 Adsorption competition by dissolved organic matter

DOM comprises a complex mixture of predominantly unknown compounds (selected micropollutants being the exceptions) and generally ranges in concentration from 5-20 mgCarbon/L in conventionally treated municipal wastewater. DOM is important to consider during adsorption, because it competes with micropollutants for adsorption sites on AC (De Ridder et al., 2011; Guillossou et al., 2020b; Pelekani and Snoeyink, 1999; Zietzschmann et al., 2014b). Further, the adsorption of DOM can lead to pore blockage, lowering adsorption (Corwin and Summers, 2010; Ebie et al., 2001; Pelekani and Snoeyink, 1999) or slowing the kinetics of adsorption (Guillossou et al., 2020b).

The smallest DOM fractions that also have aromaticity (based on UVA_{254} values) compete the most with micropollutants for adsorption sites (Aschermann et al., 2019; Zietzschmann et al., 2016). This result is perhaps not surprising, because such fractions are the most similar to micropollutants in terms of size and aromatic expression.

To account for the effects of DOM, adsorption can be normalized to the total amount of DOC (Altmann et al., 2014) or to specific components of DOC, such as low-molecular-weight aromatics (Zietzschmann et al., 2016). Ultraviolet absorption at 254 nm (UVA_{254}) is a common indicator of the aromaticity of DOM, which can be measured online and correlated with micropollutant removal during ozonation and adsorption to PAC (Stapf et al., 2016; Zietzschmann et al., 2014a). More sensitive techniques for characterizing DOM, such as fluorescence (Guillossou et al., 2021), liquid chromatography that is coupled to online carbon detection (LC-OCD; Zietzschmann et al., 2016), membrane filtration (Zietzschmann et al., 2014b), and resin fractionation (van Gijn et al., 2022), are also useful for identifying key constituents of the DOM matrix.

Competition by DOM can be mitigated by separating DOM from the liquid phase or changing its properties to render it less adsorbable to AC. By membrane filtration, all DOM fractions that are larger than the applied membrane pore size can be removed. Removal of micropollutants per se, which are primarily 100-1000 Da, would require at least nanofiltration. Membranes with larger pore sizes, such as in ultrafiltration and microfiltration, although they are unable to retain micropollutants directly, can reduce competition for larger AC pores or decrease pore blockage (Ebie et al., 2001).

Biodegradation of DOM is one method of decreasing competition by DOM, by lowering the total amount of DOM or altering its properties in less adsorbable transformation products. Compared with separation using membranes, biodegradation selectively removes small compounds (Zietzschmann et al., 2014b) but is limited by the biodegradability of the DOM.

Ozonation is another option to change the DOM character prior to AC adsorption. Ozonation decreases the hydrophobicity and aromaticity of DOM (De Laat et al., 1991; Treguer et al., 2010) which in turn decreases DOM competition for adsorption sites, resulting in higher adsorption of micropollutants (Guillossou et al., 2020a; Zietzschmann et al., 2015). The adsorption competition by DOM is discussed further in section 4.2.

2.2.5 Other factors that influence micropollutant adsorption

In addition to the characteristics of micropollutants and the presence of DOM, the adsorption of micropollutants is governed by the properties of the AC (such as its pore volume, pore size distribution, and the presence of various surface functional groups) (Mailler et al., 2016), pH (which affects coulombic interactions, as discussed), and temperature (Yuan et al., 2020).

2.2.6 Adsorption isotherms

The adsorption of a particular adsorbate is commonly described by the adsorption isotherm, wherein the adsorption capacity q [$\text{ng}_{\text{adsorbed}}/\text{mg}_{\text{carbon}}$] is a function of the equilibrium concentration c_{eq} [ng/L] in the liquid (Equation 1):

$$q = f(c_{eq}) \qquad \text{(Equation 1)}$$

The isotherm is valid for a specific system (T, pH, water matrix, AC type, etc.) under adsorption equilibrium. Isotherms vary widely between compounds, depending on their adsorptive affinity (Figure 2). To achieve high adsorptive capacities at low equilibrium concentrations, the top isotherm shape is preferred.

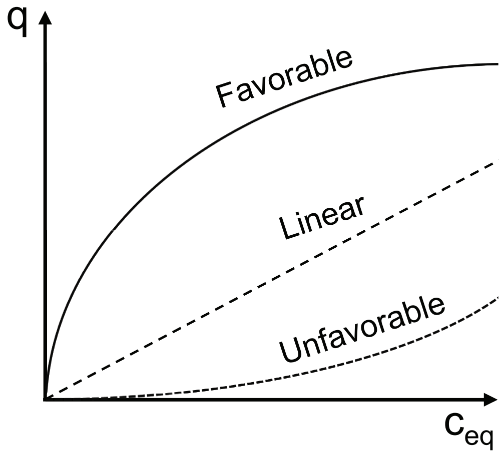


Figure 2
Examples of isotherm shapes.

Isotherm data can be obtained through batch experiments. by varying the dose of AC or the starting adsorbate concentration, per Equation 2:

$$q = \frac{c_{start} - c_{eq}}{c_{AC}} \qquad \text{(Equation 2)}$$

where c_{start} and c_{eq} are the adsorbate concentrations [ng/L] before and after adding AC, respectively, and c_{AC} is the concentration of AC [mg/L].

There are several models—theoretical and empirical—that are used to describe adsorption isotherms. Whereas purely theoretical models are often desirable, it is challenging to describe the adsorption of a contaminant in a complex matrix, such as wastewater, to a highly heterogeneous adsorbent, such as AC. For such systems, the empirical Freundlich isotherm (Equation 3) has become a popular model for simulating the adsorption of many micropollutants in aqueous solutions (Guillossou et al., 2020b). The Freundlich isotherm model has been fitted to micropollutant adsorption data in **Papers I and II**.

$$q = K_F * c_{eq}^{\frac{1}{n}} \qquad \text{(Equation 3)}$$

where K_F is the Freundlich constant [(ng/mg)/(ng/L)$^{1/n}$] and 1/n is the Freundlich intensity parameter [dimensionless].

Although the Freundlich model is empirical, it can be derived from a theoretical footing, grouping adsorption sites into patches with different characteristics and bonding energies of exponential decay and assuming adsorptive mechanisms that are consistent with the Langmuir model (Zeldowitsch, 1934).

2.2.7 Adsorption kinetics

Whereas adsorption per se is a quick process, the time that is needed to reach an adsorption equilibrium depends on the mass transfer rate of the adsorbate from the bulk liquid to the relevant adsorption sites. Figure 3 illustrates the mass transfer processes that are involved in the transport of an adsorbate to adsorption sites on AC.

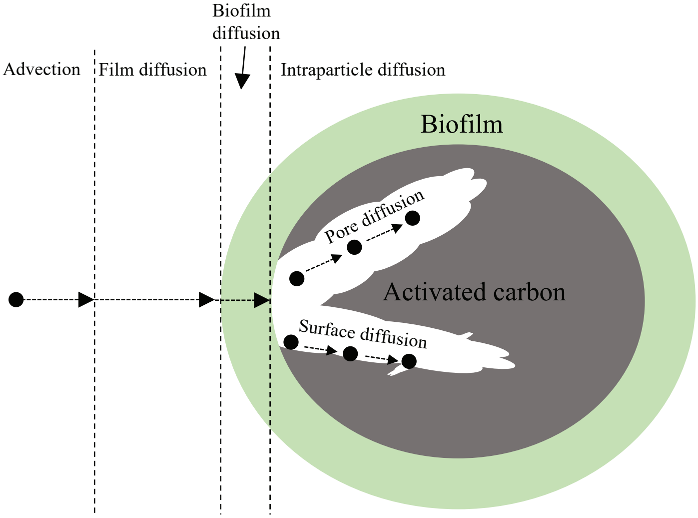


Figure 3
Mass transfer processes underlying the transfer of adsorbate from a bulk liquid to the adsorption sites on activated carbon for an inert compound.

These mass transfer processes comprise (i) *advection* from the bulk liquid to the stagnant film layer, (ii) liquid film *diffusion*, (iii) *biofilm diffusion* (if a biofilm is present), and (iv) *intraparticle diffusion*, which can be subdivided into surface diffusion and pore diffusion. Intraparticle diffusion is often the limiting factor for adsorption onto GAC (Piai et al., 2019; Valderrama et al., 2008; Zietzschmann et al., 2014). With GAC, the time that is required to reach equilibrium (several days to weeks) is also considerately longer than with PAC (24–72 h) (Corwin and Summers, 2010; Nowotny et al., 2007; Randtke and Snoeyink, 1983). Decreasing the particle size of AC, however, might be impractical, due to increased pressure build-up (in GAC reactors) or more difficult separation from AC (PAC processes).

2.2.8 Activated carbon treatment processes

Powdered activated carbon

PAC usually ranges from 10-100 µm in particle size and is typically dosed continuously into existing biological treatments or into a separate contact reactor (Figure 4). Overall micropollutant removal rates of 80% require PAC doses of 10-20 mg/L for DOC concentrations of 5-10 mg/L (Boehler et al., 2012; Margot et al., 2013). The adsorption of individual micropollutants, however, varies widely. Over 25 mg PAC/L (or >2 mg PAC/mg DOC) is needed to remove poorly adsorbing compounds, such as sulfamethoxazole and iomeprol (Altmann et al., 2014).

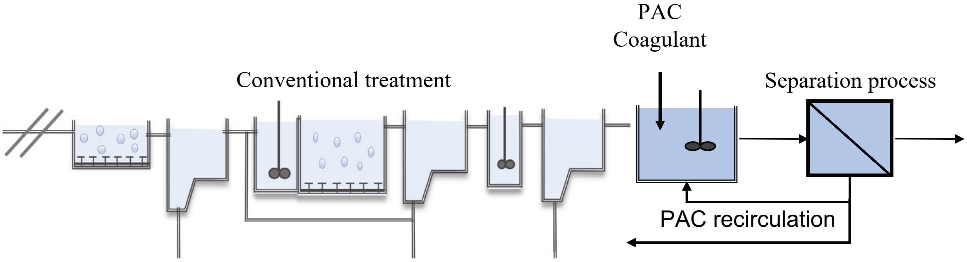


Figure 4
Schematic of PAC process applied after conventional wastewater treatment. Separation can be achieved by various means, such as membrane filtration, deep bed filtration, and sedimentation.

PAC processes require a subsequent separation step, for which there are several options—typically, a combination of coagulation and subsequent sedimentation, membrane filtration, or deep-bed filtration (Krahnstöver and Wintgens, 2018). To better exploit its adsorptive capacity, the PAC can be recirculated back to the biological treatment or to separate contact reactors (Boehler et al., 2012; Meinel et al., 2016). The introduction of PAC into the biological treatment does not negatively impact nutrient removal (Cimbritz et al., 2019; Satyawali and Balakrishnan, 2009). However, if PAC is added to (or recirculated back to) biological treatment with activated sludge, the PAC (with adsorbed micropollutants) mixes with the biological sludge, limiting its use for farmland applications.

Granular activated carbon

GAC is applied primarily in downflow fixed-bed filter applications, obviating the need for a subsequent separation process (Figure 5). However, low concentrations of suspended solids in the inlet are required to avoid excessive clogging of the filter. Thus, mechanical treatment by membranes or sand filtration is typically desired. Pressure can also build up, however, due to microorganismal growth, and GAC filters generally require regular backwash. Although GAC filters are applied mainly for micropollutant removal, effluent qualities can be improved with respect to wastewater parameters, such as phosphorous, BOD, and suspended solids (Altmann et al., 2016).

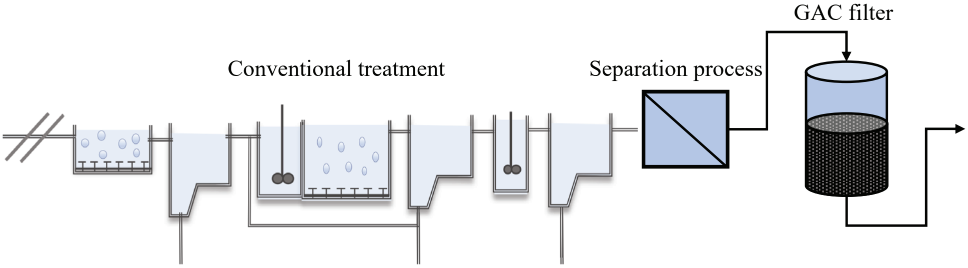


Figure 5
Schematic of downflow GAC process applied after conventional treatment. Separation of suspended solids before GAC filtration can be achieved through several means, such as filtration with membranes and sand filters.

Empty bed contact time (EBCT) is the most common parameter that is used to describe the hydraulic retention time in the filter and considers the volume of an empty filter bed. Because the bed is occupied by granules, the actual retention time will be substantially shorter and can be calculated if the bed porosity is known. EBCTs of 20-30 minutes have been recommended to allow sufficient time for proper adsorption kinetics, whereas longer EBCTs can lead to unnecessary adsorption of DOM (Fundneider et al., 2021a). Nevertheless, longer EBCTs can benefit biological degradation in GAC filters, as discussed in Chapter 5.

During operation, GAC filters initially have an excess of adsorption sites and are typically run for several months before micropollutants appear in the effluent. Comparisons between influent and effluent measurements over time are often presented in so-called breakthrough curves (Figure 6), which chart removal ratios (%) for micropollutants as a function of treated bed volume (BV). The number of BVs that can be treated until a breakthrough of 20% is reached (80% micropollutant removal) varies widely between compounds. Poorly adsorbing compounds, such as sulfamethoxazole, can attain 20% breakthrough at 5000 BVs or lower (Altmann et al., 2015), whereas well-adsorbing substances can be removed adequately at over 30,000 BVs (Boehler et al., 2020). However, micropollutant removal in GAC filters also varies largely due to differences in DOM concentrations and character.

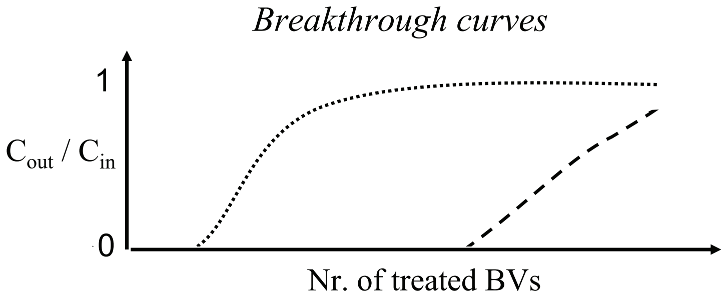


Figure 6
Example of breakthrough curve for two micropollutants with different adsorption affinities.

On saturation, a GAC filter must be replaced with new carbon. To reduce its costs and CO_2 footprint, spent GAC can be reactivated through a similar procedure to that of its production (high temperatures without oxygen and potentially an activation step) (Meier and Remy, 2020; Moore et al., 2001).

Comparisons between GAC and PAC processes

GAC filtration has long been used to treat drinking water but has only more recently been considered for the treatment of effluent wastewater. The performance of GAC filters in treating wastewater has also shown to vary significantly (Benstoem et al., 2017). However, recent studies have shown that GAC can achieve similar or even lower carbon usage rates, compared with PAC (Boehler et al., 2020; Fundneider et al., 2021a). GAC can also be reactivated after use, reducing the CO_2 emissions that are associated with the production of AC to those of ozone (Meier and Remy, 2020).

Another advantage of GAC filters over PAC treatment is the potential to use a higher extent of their adsorptive capacity. In continuously stirred reactors with PAC, the adsorptive capacity of the AC will be limited by the micropollutant concentration in the effluent (assuming an equilibrium). In contrast, operation of a GAC filter allows part of the bed to be more heavily saturated with adsorbate, thus functioning at a higher adsorptive capacity, according to its adsorption isotherm. Operating GAC filters in series is also expected to extend their lifespan substantially (Sperlich et al., 2016), but still has yet to be demonstrated in a large-scale treatment process.

An advantage of PAC is that its smaller particle size, in addition to allowing faster adsorption kinetics, renders it less susceptible to pore blockage, which can impede the access of micropollutants to deeper pores (Corwin and Summers, 2010). Another important benefit of using PAC is that the dose of AC can be controlled according to changes in influent loads and conditions. For example, pre-established correlations between micropollutant removal and reductions in UVA_{254} signals can be determined (Zietzschmann et al., 2014a) and used to control the dose via online UVA_{254} measurements.

2.2.9 Biological degradation in GAC filters

GAC filters primarily remove micropollutants via adsorption. However, a microbial biofilm develops during the several weeks to months of operation, with positive and negative effects on micropollutant removal. The presence of biofilm on the exterior of GAC granules can induce pore blockage or reduce the mass transfer rate of micropollutants to the surface of AC (Paredes et al., 2016). Yet, GAC biofilms can improve micropollutant removal through direct biodegradation of biodegradable micropollutants (Aktaş and Çeçen, 2007) and biodegradation of competing background DOM, liberating additional adsorption sites for biodegradable and non-biodegradable micropollutants (Putz et al., 2005).

The degree to which biofilm improves micropollutant removal in wastewater GAC filters is unknown. Recent studies on long-term operation with GAC (>30,000 BVs) have reported continuous removal of certain compounds, despite the expected saturation of its adsorptive capacity (Boehler et al., 2020; Fundneider et al., 2021b). These observations suggest that GAC biofilms contribute substantially to micropollutant removal via biodegradation, potentially delaying the need to replace the GAC. Nevertheless, the biodegradation of micropollutants in GAC filters remains poorly understood due to the difficulties in separating biodegradation from adsorption, which is addressed further in Section 3.4.3 and Chapter 5.

2.3 Ozonation

During ozonation, micropollutants and other DOM are oxidized via reactions with ozone or via secondarily formed hydroxyl radicals that form from reactions between ozone and DOM. Ozone reacts primarily with electron-rich moieties, such as activated aromatics, olefins, and amines, whereas reactions with hydroxyl radicals are non-selective (von Sonntag and von Gunten, 2015). Reaction rates vary between micropollutants, depending on the presence of reactive moieties, and are listed in Figure 8, section 3.2, for the compounds that were used in **Paper II**. Examples of micropollutants that are removed well during ozonation are carbamazepine, diclofenac, and sulfamethoxazole, whereas compounds such as gabapentin, iodinated x-ray contrast media and PFAS, such as iopromide, undergoes poor to moderate removal (Bein et al., 2022; Edefell et al., 2021; Lee et al., 2013; Takagi et al., 2011).

The reactions between DOM (including micropollutants), ozone, and hydroxyl radicals does not result in complete mineralization of all carbon (to CO_2) that is present as DOM. Instead, considering DOM as a whole, less than 10% of the DOC is mineralized at common doses of ozone (0.3-1 g O_3/g DOC). However, the degree to which different moieties in micropollutants are mineralized during ozonation is unknown and is addressed further in Chapter 6.

DOM and inorganic matter in wastewater compete with micropollutants for reactions with ozone and hydroxyl radicals. To account for the scavenging effect of organics and inorganics, the dose of ozone is usually normalized against the concentration of DOM and, if present, nitrite. Several common wastewater parameters have been used to normalize the ozone dose and predict micropollutant removal rates, including DOC, UVA_{254}, chemical oxygen demand (COD), and specific ultraviolet adsorption (SUVA) (Bahr et al., 2007; Ekblad et al., 2019; Lee et al., 2013; Wert et al., 2009).

Although it degrades many micropollutants efficiently, ozonation results in the formation of undesired and potentially toxic oxidation products—in particular, carcinogenic bromate and nitrosamines from reactions with bromide (Soltermann et al., 2016) and nitrogen-containing DOM, respectively (Hollender et al., 2009; Krauss et al., 2009). Other toxic compounds include quinones and catechols from reactions with DOM (Tentscher et al., 2018) and OTPs from reactions with micropollutants (Kuang et al., 2013).

OTPs often have lower specific toxicities than their parent compounds (Dodd et al., 2009; Huber et al., 2004; Lange et al., 2006). For example, efficient removal of estrogenicity during ozonation of wastewater has been observed (Escher et al., 2009; Stalter et al., 2010), which has been attributed to the destruction of the phenol group that is common in estrogenic compounds and essential for their binding to estrogen receptor (Lee et al., 2008). However, certain OTPs have also shown greater nonspecific toxicity, compared to their parent compound, in experiments with isolated organic micropollutants (Abellán et al., 2008; Sui et al., 2017).

To reduce the toxicity that is associated with ozonation by-products and OTPs, a biological post-treatment step is recommended (Stalter et al., 2010), typically in the form of a rapid sand filter (VSA, 2023). Based on ecotoxicological studies, the combination of ozonation and rapid sand filtration of biologically treated wastewater generally decreases toxicity, based on select endpoints, such as estrogenicity (Stalter et al., 2011) and genotoxicity (Magdeburg et al., 2014). However, mutagenicity due to ozonation was not mitigated by sand filtration in the study by Magdeburg et al. (2014).

Many OTPs have shown not be efficiently removed in biological post-treatment (Bourgin et al., 2018; Edefell et al., 2021; Gulde et al., 2021b; Knopp et al., 2016). Undoubtedly, many potentially toxic OTPs and by-products remain unknown, and the toxicity of polar by-products might be underestimated due to their limited extractability (Stalter et al., 2011).

2.3.1 Combining ozonation and activated carbon adsorption

Ozonation and adsorption are usually operated as separate processes in the removal of micropollutants, but their combination has been considered by many groups (e.g., Bourgin et al., 2018; Gulde et al., 2021b; Zietzschmann et al., 2015) and is being tested on a large scale (VSA, 2023).

Combining ozonation and adsorption to AC has several theoretical benefits. Certain compounds are removed better by ozonation, whereas adsorption is more effective for others (Altmann et al., 2014; Margot et al., 2013). Thus, their combination can more efficiently remove a larger variety of micropollutants. Further, by using ozonation as a pre-treatment before AC, the competition for adsorption by DOM can be lowered, in turn increasing the adsorption of micropollutants (Guillossou et al., 2020a; Zietzschmann et al., 2015).

It is hoped that treatment with AC will eliminate the toxicity of ozonation by-products and OTPs. In particular, a GAC filter could aid in the removal of micropollutants and ozone-recalcitrant micropollutants through adsorption and constitute a biological treatment step to degrade by-products and OTPs (Bourgin et al., 2018). However, the removal of by-products and OTPs using PAC and GAC remains underexamined and is discussed further in Chapter 4.

3 Methods

This chapter introduces the methods that were applied in **Papers I-IV**, focusing on ^{14}C-labeling and its use in studying adsorption, degradation, and mineralization in this thesis. The experiments were performed primarily using laboratory-scale setups (Section 3.4), with biological media and wastewater from pilot plants and full-scale WWTPs (Section 3.5).

3.1 Liquid scintillation counting

Liquid scintillation counting (LSC) is used to detect and quantify radioactivity in liquid samples. The principle of this analysis is illustrated in Figure 7 for ^{14}C, although other radionuclides can be applied. A sample that contains ^{14}C is first mixed with a scintillation cocktail into a homogenous solution. The scintillation cocktail has three main components: an aromatic solvent, an organic scintillator (sometimes referred to as a “flour”), and a surfactant. On decay of ^{14}C (disintegration), the β particles that are emitted are first absorbed by the solvent, which then transfers the energy onto scintillator molecules. These molecules in turn emit photons on de-excitation that are captured and sorted by energy in a photomultiplier tube. Consequently, an emission spectrum is generated, showing the light intensity (number of light pulses, counts) over a span of emission energies (keV).

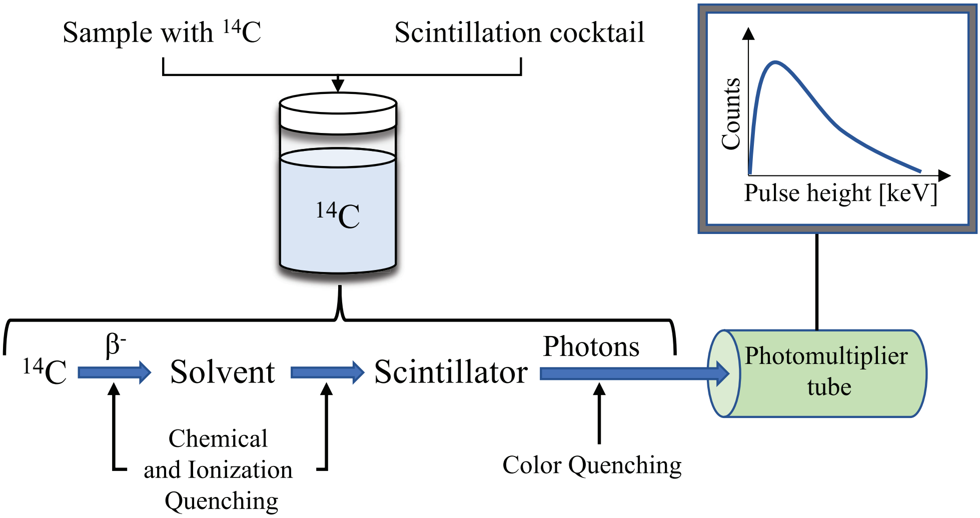


Figure 7
Principle of liquid scintillation.

The maximum energy of the light pulses that are emitted is proportional to the energy of the decay, which varies between radionuclides. For ^{14}C, the photon energies that are released by the scintillator range from 0-156 keV. The total number of counts per minute (CPM) that are registered over the relevant energy range is proportional to the total number of disintegrations by the radionuclide. However, interference due to quenching—chemical, ionization, or color—can mask the signal. Chemical quenching occurs due to the absorption of decay energy by molecules in the sample, preventing the transfer of energy to the scintillator. Ionization quenching can be caused when the density of excited solvent molecules is too high, wherein the combined excitation can result in ionization, preventing further energy transfer. Color quenching is the absorption of photons by sample compounds, precluding them from reaching the photomultiplier tube.

Due to quenching, CPM measurements will be lower than the radioactive decay (disintegrations per minute [DPM]), the difference between which is quantified by the efficiency (%) (Equation 4):

$$DPM = \frac{CPM}{Efficiency} \qquad \text{(Equation 4)}$$

The total level of quenching (and the corresponding efficiencies) is often determined using quench curves, which plot the efficiency at varying degrees of quenching. One common parameter is the transformed Spectral Index of the External Standard (tSIE) value, which is applied in **Papers II-IV**. This method uses a ^{133}Ba source (built into the liquid scintillator) that individually beams each sample with known amounts of energy (gamma rays), generating β decay that can be detected and compared with a theoretical amount. The typical efficiencies in **Papers II-IV** are ~90 %, suggesting minor quenching. However, if the limits of detection are lowered by increasing the sample-to-cocktail ratio, the effects of quenching will rise. More information on liquid scintillation counting and quench curves can be found in L'Annunziata and Kessler (2013).

Several scintillation cocktails are available, depending on the sample type. For aqueous samples with treated and filtered effluent wastewater and for CO_2 traps (1 M NaOH), we used Ultima Gold and Hionic Flour from PerkinElmer. Scintillation counting was performed on a Tri-Carb 4910 TR (PerkinElmer).

3.2 ^{14}C-labeled micropollutants

^{14}C-labeled micropollutants are compounds in which one or more carbon atoms in their molecular structure consist of a radioactive ^{14}C isotope. ^{14}C has a half-life of 5730 years and emits beta particles (electrons) on disintegration, allowing ^{14}C-labeled carbon to be tracked, based on measurements of radioactive decay. An overview of the 11 ^{14}C-labeled micropollutants that were used in this thesis (**Papers II-IV**) and their ^{14}C-labeled positions is shown in Figure 8. Compounds that have been tagged on an aromatic ring are uniformly labeled—i.e., on average, each ring-membered carbon atom in a ^{14}C-labeled compound is labeled to a similar degree.

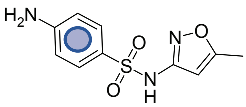
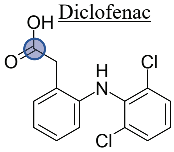
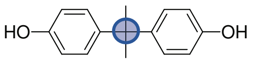
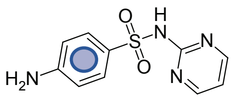
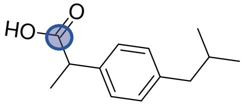
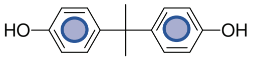
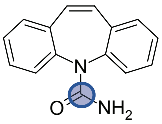
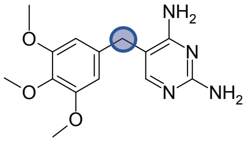
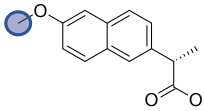
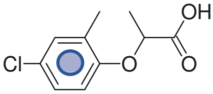
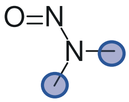
Organic micropollutants		
Sulfamethoxazole  k_{O3}: ~2.5x10^{5} [a] **pKa:** 2.0;6.2 $k_{\cdot OH}$: 5.5x10^{9} [a] **logD:** 0.1	Diclofenac  k_{O3}: ~1x10^{6} [a] **pKa:** 4.0 $k_{\cdot OH}$: 7.5x10^{9} [a] **logD:** 1.4	Bisphenol A [propyl-2]  k_{O3}: 7x10^{5} [c] **pKa:** 9.8 $k_{\cdot OH}$: 10x10^{9} [d] **logD:** 4.0
Sulfadiazine  k_{O3}: - **pKa:** 2.0;7.0 $k_{\cdot OH}$: - **logD:** 0.1	Ibuprofen  k_{O3}: 9.6 [a] **pKa:** 4.9 $k_{\cdot OH}$: 7.4x10^{9} [a] **logD:** 1.7	Bisphenol A [ring-U]  k_{O3}: 7x10^{5} [c] **pKa:** 9.8 $k_{\cdot OH}$: 10x10^{9} [d] **logD:** 4.0
Carbamazepine  k_{O3}: ~3x10^{5} [a] **pKa:** 16 $k_{\cdot OH}$: 8.8x10^{9} [a] **logD:** 2.8	Trimethoprim  k_{O3}: 2.7x10^{5} [b] **pKa:** 7.2 $k_{\cdot OH}$: 6.9x10^{9} [b] **logD:** 0.9	Naproxen  k_{O3}: ~2x10^{5} [e] **pKa:** 4.2 $k_{\cdot OH}$: 9.6x10^{9} [f] **logD:** 0.3
Mecoprop  k_{O3}: 1.1x10^{2} [g] **pKa:** 3.1 $k_{\cdot OH}$: 1.9x10^{9} [g] **logD:** -0.4	NDMA  k_{O3}: 0.052[h] **pKa:** 3.5 $k_{\cdot OH}$: 4.5x10^{8} [h] **logD:** 0.04	

Figure 8
^{14}C-labeled compounds used in Papers II-IV and their parameters: apparent second-order rate constants (k_{O3} and $k_{\cdot OH}$; M^{-1} s^{-1}) with ozone, pH 7, and OH radicals. pK_a and predicted octanol-water partitioning coefficients at pH 7 (log*D*) were obtained using Chemicalize, 2023.05 (https://chemicalize.com/, ChemAxon). The ^{14}C-labeled carbon is indicated by the blue circle. Ring-labeled compounds are uniformly labeled over the entire ring. References: [a](Huber et al., 2003), [b](Dodd et al., 2006) [c](Deborde et al., 2005) [d](Rosenfeldt and Linden, 2004), [e](Huber et al., 2005), [f](Packer et al., 2003), [g](Beltrán et al., 1994), [h](Lee et al., 2007).

3.2.1 Why ^{14}C-labeling?

During ozonation and biological degradation, micropollutants are transformed into new compounds (transformation products), but issues with regard to their potential toxicity have arisen, particularly during ozonation (Kuang et al., 2013; Sui et al., 2017). Further, many OTPs remain unknown. Micropollutants and transformation products are typically identified through a combination of solid-phase extraction (SPE) and subsequent analysis by liquid chromatography-mass spectrometry (LC-MS) (discussed in Section 3.3). However, it has proven difficult to identify many expected transformation products, and mass balances are not possible to obtain due to the lack of reference standards for a wide range of OTPs (Gulde et al., 2021a; Hübner et al., 2015).

The use of ^{14}C-labeled micropollutants could circumvent some of the challenges with conventional measurements of micropollutants and their transformation products. ^{14}C-labeled micropollutants can be monitored throughout wastewater treatment processes, based on radioactivity. Further, applying ^{14}C-labeled micropollutants could guide discussions on OTP removal in post-ozonation treatment, because if they are not mineralized to $^{14}CO_2$ during ozonation, ^{14}C-labeled carbons will be incorporated into an OTP. Thus, ^{14}C-labeling OTPs can be tracked and separated from DOM and allow for ^{14}C mass balance estimations.

^{14}C-labeled micropollutants can also be applied to study the biological degradation (biodegradation) of micropollutants. In analyzing the formation of $^{14}CO_2$ from ^{14}C-labeled micropollutants, biodegradation can be confirmed, and a potential degradation pathway can be implicated. Further, biodegradation can be demonstrated directly via the formation of $^{14}CO_2$, rather than indirectly through measurements of micropollutant removal in the influent/effluent (i.e., before and after). The formation of $^{14}CO_2$ could also be used to distinguish degradation from other co-existing removal mechanisms that do not generate $^{14}CO_2$.

3.2.2 Fate of ^{14}C during treatment of ^{14}C-labeled micropollutants

In this thesis, ^{14}C-labeled micropollutants were used to study various aspects of adsorption and transformation via ozonation and biodegradation. Because ^{14}C activity is measured—not the compound itself—we must consider the potential fates of a ^{14}C-labeled moiety during these treatments, as illustrated in Figure 9.

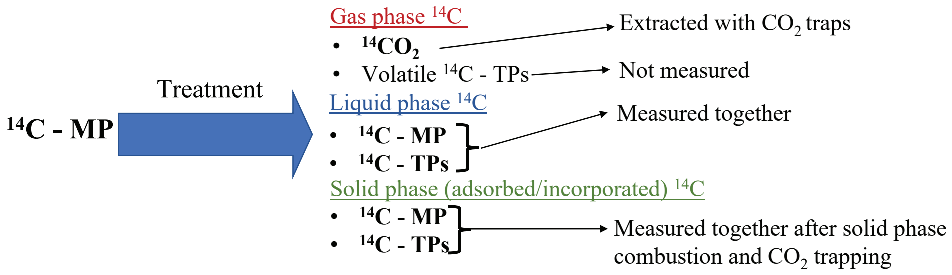


Figure 9
Possible fates of ^{14}C during treatment with biodegradation, ozonation, and adsorption to AC. ^{14}C-MP: ^{14}C-labeled micropollutant, ^{14}C-TPs: ^{14}C-labeled transformation products.

In pure adsorption systems (with little or no biotransformation), ^{14}C activity before and after treatment reflects the concentration of the ^{14}C-labeled parent compound. Conversely, in treatments that transform the compound, ^{14}C activity can be expressed as the remaining parent compound and various ^{14}C-labeled transformation products (^{14}C-TPs).

^{14}C-TPs can be volatile or non-volatile. In **Papers II-IV**, we applied CO_2 traps to extract and trap incipient $^{14}CO_2$ (Figure 10, left). On mineralization of the ^{14}C-labeled moiety, the inorganic ^{14}C that is produced in the liquid phase can consist of H_2CO_3, HCO_3^-, or CO_3^{2-}—the distribution of which is pH-dependent—and the release of CO_2 from H_2CO_3 is governed by the concentration of H_2CO_3 and the partial pressure of CO_2 in the air pocket, per Henry's law. More CO_2 can be released by decreasing the pH (the pK_a of H_2CO_3 is 6.4; Tossell, 2005). However, CO_2 can be transferred to the trap at higher pH values, because the partial pressure of CO_2 in the gas phase always approaches zero due to the capture of CO_2 by the trap.

Based on control experiments with the applied setup, < 24 hours was needed to extract most of the inorganic carbon from the liquid phase (Figure 10, right). In continuous experiments with successive $^{14}CO_2$ formation (**Paper III**), there is thus likely a delay in the capture of $^{14}CO_2$. The levels of volatile ^{14}C-TPs (other than $^{14}CO_2$) are not measured in our setups but are assumed to be minor, based on the complete (100 ± 5%) ^{14}C mass balances for ozonation in **Paper II.**

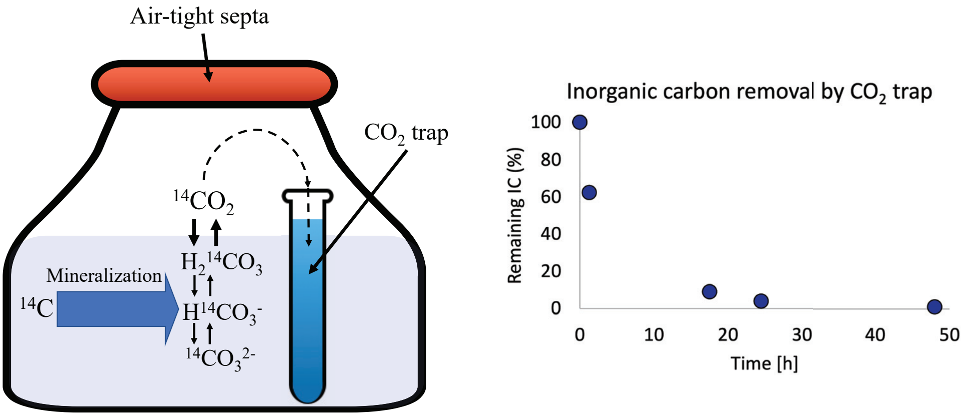


Figure 10
Left: Interaction between inorganic ^{14}C species in the carbonate system and the capture of CO$_2$ with an NaOH trap. Right: Typical removal of inorganic carbon from the liquid phase over time.

In experiments with adsorptive and biologically active media, ^{14}C can be removed from the liquid and gas phases by adsorption or incorporation into biomass. This solid-phase ^{14}C can be expressed as ^{14}C-MPs or ^{14}C-TPs. Solid-phase ^{14}C can be determined through the combustion of solid-phase ^{14}C to ^{14}CO$_2$ and subsequent ^{14}CO$_2$ trapping, as applied in **Paper IV.**

In experiments with ^{14}C-labeled micropollutants, ^{14}CO$_2$ can only originate from the ^{14}C-labeled moiety of the labeled micropollutant and can be used to confirm transformation of the compound and demonstrate a potential degradation pathway. However, any partial transformation of a ^{14}C-labeled moiety (that does not lead to ^{14}CO$_2$ formation) or partial or complete mineralization of any non-radiolabeled moieties will be undetected. Consequently, ^{14}CO$_2$ formation rates will always be lower than the actual degradation rate of the compound.

The extent to which ^{14}C activity in the liquid phase exists as the MP or various TPs in the liquid phase can not be distinguished by measurements of radioactivity but can be determined by measuring the compounds by MS. Due to regulations regarding ^{14}C use and transport, we did not analyze ^{14}C-labeled compounds by LC-MS but conducted parallel experiments with ^{14}C-labeled micropollutants using liquid scintillation and non-radiolabeled micropollutants by MS (**Papers II and IV**). This approach relies on the assumption that radiolabeled and non-radiolabeled compounds behave similarly. However, it is invalid when studying GAC filters that have been pre-loaded with micropollutants (non-radiolabeled) from a full-scale operation (**Paper IV**) but can be used to study micropollutant retention in GAC filters.

3.3 Analysis of micropollutants

The analysis of micropollutants in this thesis was achieved by sample preparation via solid phase extraction (SPE), followed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS), as detailed in Svahn and Björklund (2019, 2016). Briefly, the samples for analysis were collected in 100-ml HPDE bottles and frozen until analysis. After thawing, internal isotope-labeled standards were added to 40 ml of sample. The addition of isotope-labeled standard accounts for losses during sample preparation and for matrix effects during analysis. The samples were prepared by being concentrated on a solid-phase extraction column (Oasis HLB 200 mg). After elution and evaporation, the sample was reconstituted in 1 mL, of which 1 µL was injected into a UPLC-MS/MS instrument (Waters Acquity UPLC H-Class, Xevo TQS Waters Micromass, Manchester, UK) using three different chromatographic methods.

Around 30 compounds were measured at Svedala WWTP within the EU project Less is more, and are given in Table 2 along with predicted hydrophobicity, LOQs and typical concentrations the effluent from the Svedala WWTP. The compounds in Table 2 originated from several lists of suggested priority substances, including compounds from EU watch lists, the Swiss list of priority compounds, and the Swedish Medical Products Agency.

For **Paper I,** 12 compounds were selected for the adsorption studies (see Paper I). In **Papers II-IV**, only compounds with ^{14}C-labeled counterparts were used and were analyzed using the same method as described above.

Table 2
Organic micropollutants used or screened for in this thesis.

Compound	Class	logK_{OW}	logD_{OW} (pH 7)	LOQ (ng/L)	Svedala effluent Concentrations (ng/L) (n=9)
Acetamiprid	Neonicotinoid insecticide	1.1	1.1	0.2	<LOQ
Atenolol	Beta-blocker	0.43	-1.8	2.0	1000 – 2000
Bisphenol A	Plasticizer	4.0	4.0	10.0	100 – 300
Carbamazepine	Antiepileptic	2.8	2.8	0.5	400 – 850
Ciprofloxacin	Antibiotic	-0.77	-0.77	10.0	<LOQ – 80
Citalopram	Antidepressant	3.8	0.63	1.0	120 – 440
Clarithromycin	Macrolide antibiotic	3.24	1.3	2.0	5 – 120
Diclofenac	NSAID	4.3	1.4	2.0	900 – 1600
Erythromycin	Macrolide antibiotic	2.6	0.60	0.5	20 – 300
Estrone	Hormone	4.3	4.3	0.2	5 – 30

Fluconazole	Antifungal	0.56	0.56	0.3	30 – 110
Ibuprofen	NSAID	3.8	1.7	100.0	<LOQ – 1100
Imidacloprid	Neonicotinoid insecticide	0.53	0.53	2.0	5 – 30
Ketoconazole	Antifungal	4.2	4.1	10.0	10 – 60
Losartan	Angiotensin II receptor blocker	5.0	4.1	1.0	1300 – 2700
Methotrexate	Immunosuppressant	-1.6	-5.0	2.0	<LOQ
Metoprolol	Beta-blocker	1.8	-0.47	2.0	1600 – 3500
Naproxen	NSAID	3.0	0.29	10.0	300 – 1200
Oxazepam	Sedative	2.9	2.9	1.0	300 – 650
Paracetamol	NSAID	0.91	0.91	2.0	<LOQ
PFOA	Per- and polyfluoroalkyl substance	5.1	1.6	2.0	1 – 3
PFOS	Per- and polyfluoroalkyl substance	5.4	3.1	1.0	3 – 5
Propranolol	Beta-blocker	2.6	0.36	2.0	60 – 160
Sertraline	Antidepressant	5.1	2.7	0.5	15 – 60
Sulfamethoxazole	Sulfonamide antibiotic	0.79	0.03	2.0	70 – 400
Thiamethoxam	Insecticide	1.1	1.1	1.0	<LOQ
Tramadol	Opioid analgesic	2.5	0.10	1.0	600 – 1400
Trimethoprim	Antibiotic	1.3	0.92	1.0	120 – 370
Venlafaxine	Antidepressant	2.7	0.74	1.0	350 – 900
Zolpidem	Hypnotic	3.0	3.0	0.5	>LOQ – 7

3.4 Experimental overview

3.4.1 Adsorption experiments with PAC in different water matrices

In **Paper I**, we worked with various wastewater matrices that contained background levels (no spiking) of micropollutants, analyzed by SPE-UPLC-MS/MS. Batch adsorption experiments with PAC were performed in **Papers I and II** using similar methods. Falcon tubes (10 or 40 mL) were filled with wastewater, which had either background levels of micropollutants (**Paper I**) or were spiked with ^{14}C-labeled micropollutants or OTPs (**paper II**). A standard solution of PAC in deionized water (1 g/L) was prepared and added to each Falcon tube to concentrations of 0-100 mg/L

(**Paper I**) and 0-20 mg/L (**Paper II**). The tubes were then agitated for 24-40 h until equilibrium or near-equilibrium. The PAC was then separated by centrifugation and, in some cases, filtration before analysis of the supernatants. The amount and aromatic character of the DOM were also determined, based on DOC and UVA_{254} measurements at each PAC dose.

3.4.2 Ozonation and adsorption of ^{14}C-labeled compounds

In **Paper II**, we examined the ozonation of ^{14}C-labeled micropollutants and the subsequent adsorption of ^{14}C-TPs. An overview of the experimental setup is shown in Figure 11. As described in Section 3.2.2, ^{14}C analysis by liquid scintillation counting alone can not distinguish to which degree the liquid-phase ^{14}C that remains after ozonation consists of the parent compound versus ^{14}C-TPs. Thus, parallel experiments were conducted with ^{14}C-labeled and non-radiolabeled micropollutants, added at similar concentrations.

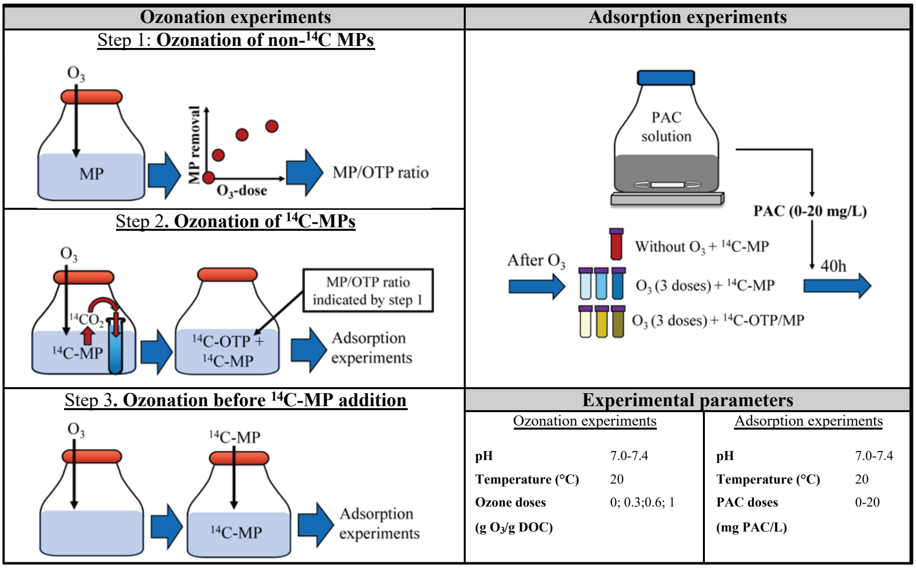


Figure 11
Overview of the experimental setup in Paper II.

The ozonation consisted of three parallel steps; for every step, each micropollutant was studied individually. In the first step, several ozone doses were added to wastewater that was spiked with a non-radiolabeled micropollutant, and the removal of the parent compound was subsequently analyzed by SPE-UPLC-MS/MS. In the second step, ozone was added to wastewater that was spiked with ^{14}C-labeled micropollutants, and $^{14}CO_2$ formation was measured by CO_2 trapping. Any liquid-phase ^{14}C that remains after CO_2 trapping can consist of the parent compound and transformation products, the ratio between which is indicated by Step 1. In the third step, the wastewater was ozonated before ^{14}C-labeled micropollutants were added, to isolate the effect on subsequent adsorption of the parent compound from that of background DOM.

The remaining liquid phases from Steps 2 and 3 were used for subsequent experiments with PAC to study the adsorption of parent compounds and transformation products at various ozone doses, the methods for which are detailed in **Paper II**.

3.4.3 Studying adsorption and degradation with GAC filter media

In **Paper III,** we examined the adsorption and biodegradation of ^{14}C-labeled micropollutants in batch experiments with several biofilm media that were retrieved from full-scale and pilot-scale operations. This approach has been used to study the biodegradation of micropollutants in wastewater (Falås et al., 2018; Popple et al., 2016) but has not been applied to adsorption or combined adsorption-degradation with GAC filter media.

The degree to which biofilms in GAC filters contribute to micropollutant removal via their degradation remains unknown, because it is difficult to discern whether micropollutant removal results from biodegradation or adsorption. Previous studies have attempted to estimate the contribution of GAC biofilms primarily by comparing biologically activate GAC filters and the corresponding sterilized GAC filters. However, this approach has several limitations. For example, estimates of biomass contribution can be masked by high adsorption in the sterilized column (Paredes et al., 2016). Further, achieving complete inhibition of biomass activity without affecting adsorption conditions can be challenging (Yuan et al., 2022). To address these issues, we first developed an approach to directly distinguish biodegradation from adsorption through the formation of $^{14}CO_2$, in batch experiments with GAC filter media (**Paper III**).

Batch experiments with GAC

An overview of the ^{14}C batch degradation experiments is shown in Figure 12. A reactor was partially filled with wastewater that was spiked with ^{14}C-labeled micropollutants. Biomass media (GAC filter media, sand filter media, MBBR carriers, or activated sludge, retrieved from Klippan and Kristianstad WWTP) was added to the reactor, and samples were retrieved over time from the CO_2 trap and liquid phase to study the partitioning of ^{14}C. Although the decrease in liquid-phase ^{14}C can be both due to adsorption and degradation, $^{14}CO_2$ can only form by degradation, allowing adsorption and degradation to be differentiated, which can not be achieved based solely on liquid-phase measurements. The experimental methods are detailed in **Paper III**.

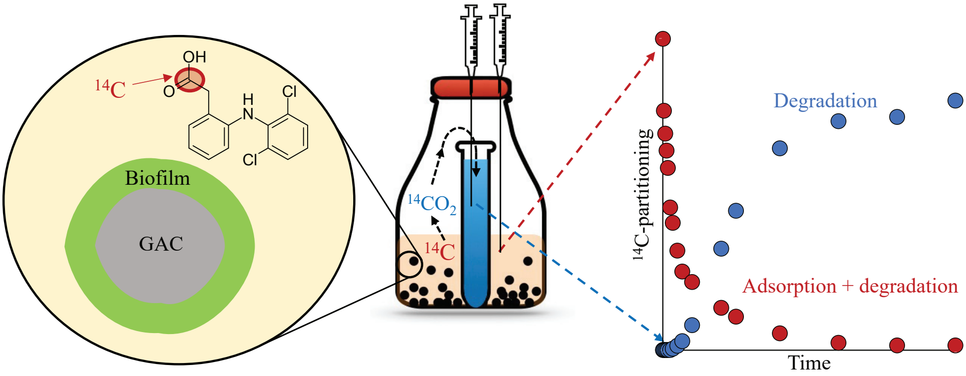
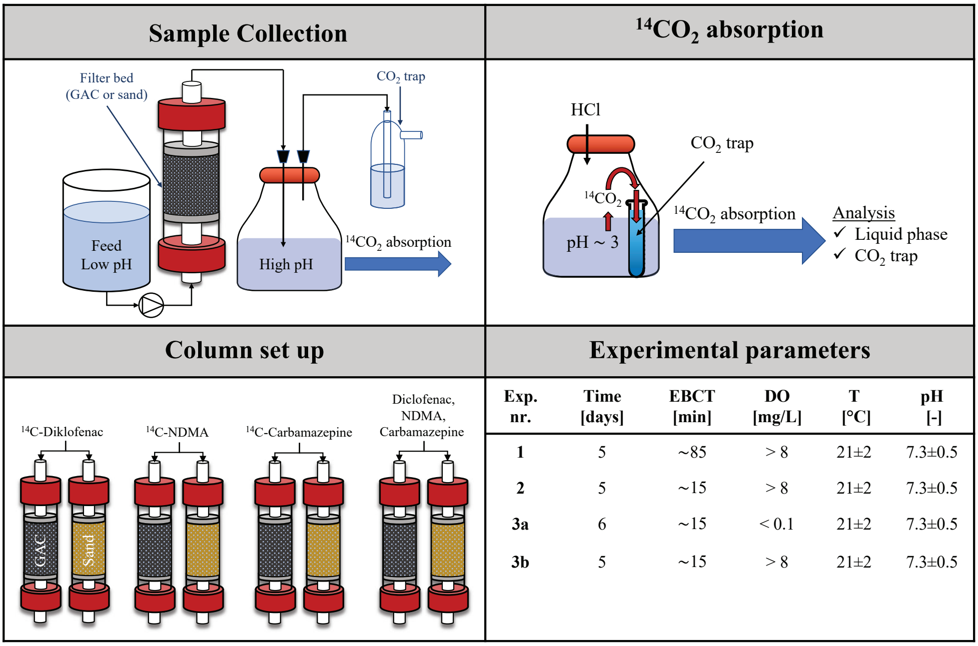


Figure 12
Overview of the experimental setup for the degradation and adsorption batch experiments in Paper III.

GAC column experiments

The results from **Paper III** are promising in terms of the approach for distinguishing biodegradation from adsorption. However, they have limited transferability to what could be expected in continuous GAC filter operation. As a result, I modified the approach to study adsorption and biodegradation in GAC filters and sand filters, under continuous operation (**paper IV**). An overview of the experimental setup is shown in Figure 13.



Exp. nr.	Time [days]	EBCT [min]	DO [mg/L]	T [°C]	pH [-]
1	5	~85	> 8	21±2	7.3±0.5
2	5	~15	> 8	21±2	7.3±0.5
3a	6	~15	< 0.1	21±2	7.3±0.5
3b	5	~15	> 8	21±2	7.3±0.5

Figure 13
Overview of the experimental setup in Paper IV.

A total of eight parallel columns were run in each experiment. The columns were packed with GAC or sand from full-scale filters at Degeberga WWTP and run with effluent wastewater that was spiked with ^{14}C-labeled micropollutants: diclofenac, NDMA, or carbamazepine. Parallel experiments were conducted with non-radiolabeled compounds to monitor the removal of parent compound. Experiments 1 and 2 were run at high (85 min) and low EBCTs (15 min) under aerobic conditions to determine the influence of EBCT on micropollutant degradation and adsorption. In Experiment 3, the effects of limited oxygen (anoxic conditions) were first investigated (Exp 3a), after which aerobic conditions were reintroduced to study the degradation of previously adsorbed micropollutants (Exp 3b).

To monitor $^{14}CO_2$ formation in the columns, effluents were collected over time into different batches. High pH was used to keep $^{14}CO_2$ dissolved (mainly as $^{14}CO_3^{2-}$) during sample collection. The samples were then incubated with a CO_2 trap (similar to **Paper III**) after acid was added to reduce the pH, promoting the release of $^{14}CO_2$ from the liquid. These methods are detailed in **Paper IV**.

3.5 Wastewater treatment plants and pilot plants

In **Papers I-IV**, wastewater and biomass media that were used for the lab experiments were retrieved from full-scale or pilot-scale treatment processes at several WWTPs throughout Scania, Sweden. An overview of the WWTPs and pilot plant process schemes is described in this section.

Figure 14 shows an overview of the Svedala WWTP and pilot plant, the latter being constructed by us within the project Less is More (Interreg south Baltic program). The pilot plant comprised purely chemical and physical treatment steps (no biological treatment), consisting of chemically enhanced primary treatment (CEPT), followed by microsieving and parallel membrane treatment with ultrafiltration (UF) or microfiltration (MF). Also, a pilot-scale sand filter and GAC filter were run with biologically and chemically treated effluent wastewater from conventional treatment. The original rationale was to compare micropollutant removal in this filter with GAC filtration following each of the membranes in the pilot-scale operation. However, due to reoccurring and rapid fouling of the membranes, continuous operation of the GAC filters after MF and UF filtration could not be achieved. Instead, PAC experiments were performed with the effluents from the microsieving, after membrane filtration (UF and MF) and following conventional treatment. More information on the scope of the pilot plant and its results can be found in Gidstedt (2022) and **Paper I**.

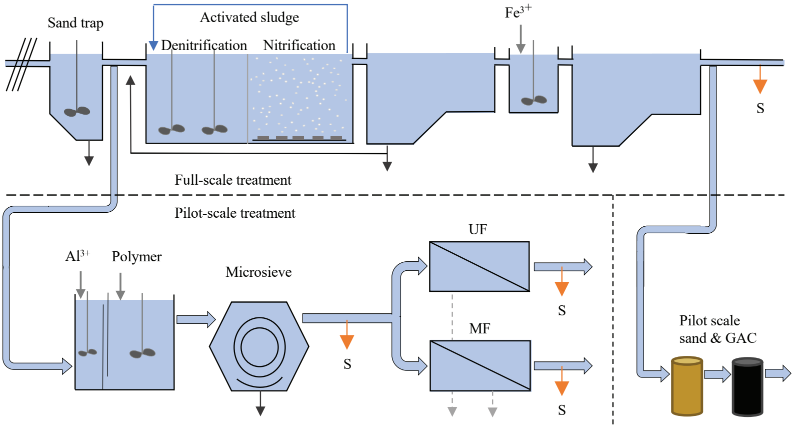
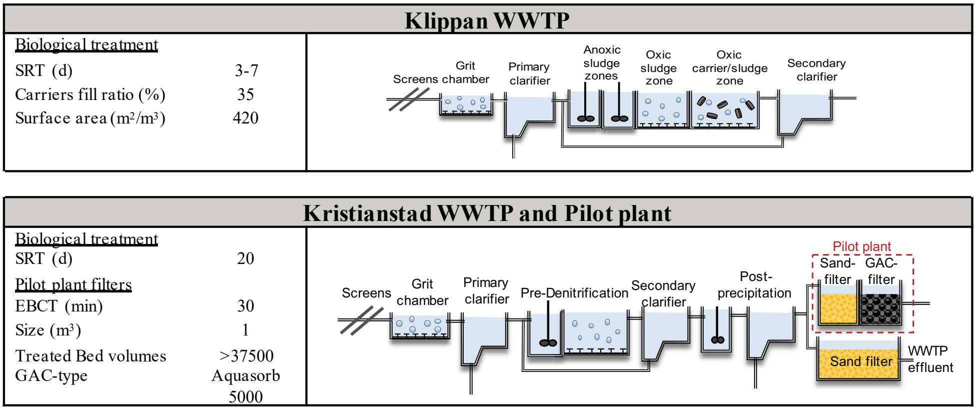


Figure 14
Overview of Svedala WWTP and pilot plant treatment configuration, from Paper I. Orange arrows (S) are sampling points for various wastewater matrices in the PAC experiments.

The biomass media that was used for the lab experiments in **Paper III** was retrieved from Klippan and Kristianstad WWTPs (Figure 15): MBBR carriers from Klippan WWTP; activated sludge from Kristianstad WWTP; and sand and GAC from a pilot plant at Kristianstad WWTP. The GAC pilot filter was operated within the so-called FRAM-project, run by Kristianstad university between 2015-2019 and was quite unique, in that it had been in operation for over 37,500 BVs at the time of our initial batch experiments with GAC in 2019. Thus, we had good reason to believe that a biofilm had developed, which could contribute to micropollutant removal. More information on Klippan and Kristianstad WWTPs can be found in the supplement of **Paper III**.



Klippan WWTP

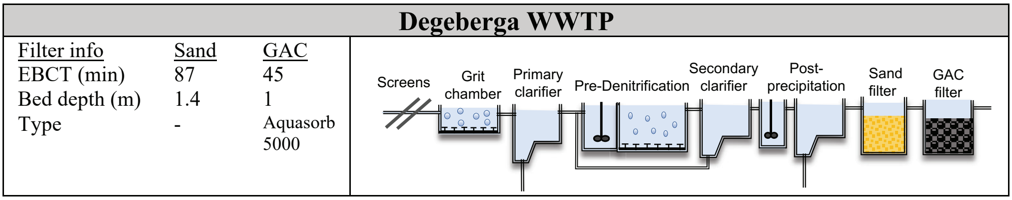
Biological treatment	
SRT (d)	3-7
Carriers fill ratio (%)	35
Surface area (m²/m³)	420

Kristianstad WWTP and Pilot plant

Biological treatment	
SRT (d)	20
Pilot plant filters	
EBCT (min)	30
Size (m³)	1
Treated Bed volumes	>37500
GAC-type	Aquasorb 5000

Figure 15
Overview of the WWTPs and pilot plant configurations in Paper III.

In **paper IV,** sand and GAC filter media were retrieved from each corresponding full-scale filter at Degeberga WWTP (Figure 16). The sand filter in Degeberga has been in operation since 1975 and was the first of its kind in Sweden. The GAC filter was constructed in 2019 and was also the first full-scale GAC filter to be installed in Sweden. At the time of the experiments in paper **IV,** the GAC filter had been in operation for more than 30,000 BVs.



Degeberga WWTP

Filter info	Sand	GAC
EBCT (min)	87	45
Bed depth (m)	1.4	1
Type	-	Aquasorb 5000

Figure 16
Overview of the WWTP configuration in Paper IV.

4 Adsorption of micropollutants and ozone transformation products

The amount and type of dissolved organic matter (DOM) present in the wastewater are key factors affecting the adsorption of organic micropollutants to activated carbon. Therefore, it is of great interest to find suitable pre-treatments to AC treatment which can reduce the competition of DOM for AC adsorption sites. In this chapter, we first look at the competition between DOM and micropollutants for the adsorption onto AC after different extents of filtration and ozonation (section 4.1 and 4.2).

The combination of ozonation and adsorption is an increasingly considered option for the removal of organic micropollutants and ozone transformation products (OTPs). However, the removal of OTPs via adsorption onto AC is still poorly understood since most OTPs are unknown. In section 4.3, trends in the adsorption of OTP following different extents of ozonation are presented.

4.1 Trends in micropollutant adsorption

Micropollutants adsorb through a combination of hydrophobic, van der Waals, and coulombic interactions, as discussed in Section 2.2.2. Based on the results of the PAC adsorption experiments in tertiary treated effluents from Svedala and Stengården WWTPs (Figure 17), hydrophobicity (logD values) did not correlate well with overall micropollutant removal. However, subdividing compounds by charge revealed some trends for these datasets. Positively charged compounds were adsorbed best, followed by neutral compounds and then negatively charged compounds, as observed earlier (e.g., Mailler et al., 2015; Margot et al., 2013).

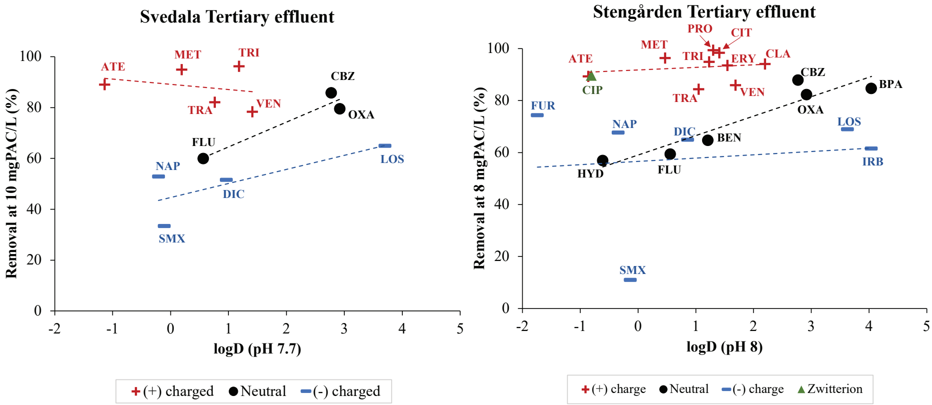


Figure 17
Adsorption of positive, negative, and neutral micropollutants as a function of hydrophobicity (logD) in Svedala tertiary effluent (left, adapted from Paper I) and Stengården tertiary effluent (unpublished data). The DOC was 10.7 mgC/L and 6.7 mgC/L in the Svedala and Stengården effluents, respectively. ATE: Atenolol, CBZ: Carbamazepine, CLA: Clarithromycin, DIC: Diclofenac, ERY: Erythromycin, FLU: Fluconazole, HYD: Hydrochlorothiazide, LOS: Losartan, MET: Metoprolol, NAP: Naproxen, OXA: Oxazepam, TRI: Trimethoprim, CIP: Ciprofloxacin, CIT: Citalopram, IRB: Irbesartan, PRO: Propranolol, SMX: Sulfamethoxazole, TRA: Tramadol, VEN: Venlafaxine, BPA: Bisphenol A, FUR: Furosemide.

The high adsorption of positively charged versus neutral and negatively charged compounds indicated that the surface of the AC was predominantly negatively charged at the applied pH (7.7-8). However, the point of zero charge (pzc) of the alkaline PAC that was used (Norit Sae Super, Cabot) is 9.8 (Kovalova et al., 2013a), suggesting that the net surface was positive and thus should have preferably adsorbed negative compounds. The adsorption of positively charged compounds is enhanced after preloading AC with DOM (Guillossou et al., 2020b). Because DOM is primarily negatively charged, its adsorption has been suggested to convert positively charged adsorption sites into negatively charged areas (Margot et al., 2013; Yu et al., 2012). Another explanation could be an overall preference of AC to adsorb positively charged compounds. For example, interactions have been proposed to form between cations and electron-rich basal planes via cation-π interactions (Pignatello et al., 2017).

Overall, large variations in adsorptive capacity have been observed for charged compounds with similar hydrophobicities (Guillossou et al., 2020b; Kovalova et al., 2013b; Mailler et al., 2015; Margot et al., 2013), suggesting that their adsorption is also affected by other factors. For a specific AC, such factors could include the number of aromatic rings and ring activation, the potential for hydrogen bonding, polarizability, size, planarity, and interactions with DOM (de Ridder et al., 2010; Moreno-Castilla, 2004; Yu et al., 2012).

4.2 Adsorption competition in different wastewater matrices

4.2.1 Size fractionation and biological treatment

In **Paper I**, we examined the adsorption of micropollutants to PAC in several wastewater matrices: three from physicochemical treatment (without a biological treatment step) of wastewater with *(1)* coagulation/flocculation and microsieving (100 µm) and subsequent *(2)* microfiltration (200 nm) or *(3)* ultrafiltration (3 nm) and *(4)* one effluent from tertiary wastewater treatment (see **Paper I** for details). Freundlich isotherms could be fitted ($R^2 \geq 0.90$) to most of the positively charged and uncharged micropollutants but few negatively charged micropollutants.

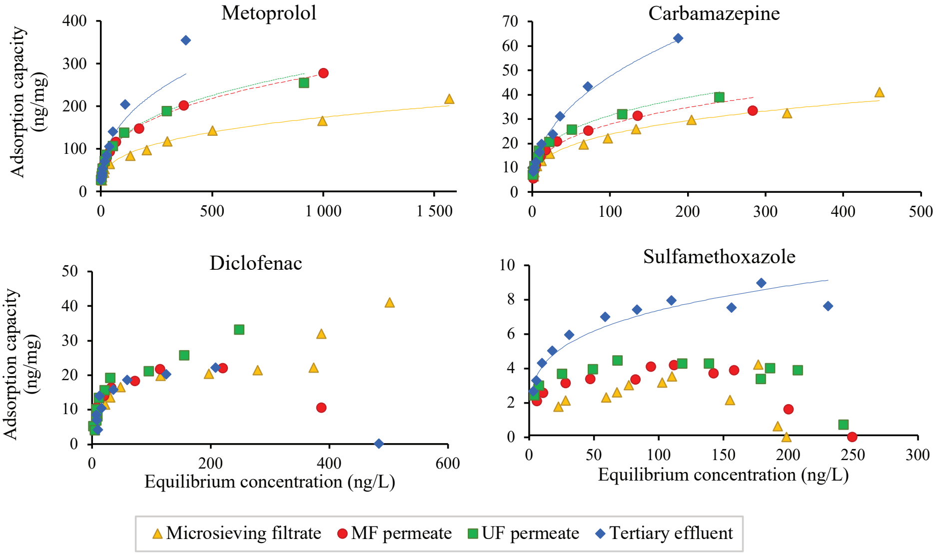


Figure 18
Adsorption isotherms for four micropollutants in four wastewater matrices. From Paper I.

Adsorption isotherms of four selected organic micropollutants are shown in Figure 18. The negatively charged sulfamethoxazole showed negative adsorption trends at increasing equilibrium concentrations—i.e., with decreasing PAC doses—in the membrane-treated wastewaters but followed normal isotherm behavior in biologically treated wastewater. The decrease in the adsorption of weak adsorbates at high equilibrium concentrations occurred at low PAC doses, at which competition with DOM for adsorption sites is the highest, and has been observed for weak adsorbates in biologically treated wastewater (Altmann et al., 2014; Zietzschmann et al., 2014b). Stronger adsorbates, however, seem able to compete better with DOM at the highest equilibrium concentrations (i.e., the lowest PAC doses). A potential consequence of this behavior in GAC columns is a sudden, rapid breakthrough of weak adsorbates as adsorption sites become exhausted at high numbers of treated BVs. Although avoidance of such a breakthrough would be preferable, it would also hinder the long-term operation of GAC.

The adsorptive capacities were highest in the tertiary effluent, despite a similar DOM concentration as in the MF and UF permeates. The lower competition in the tertiary effluent could not be explained by the lower UVA_{254} signal but was supported by lower adsorption of UVA_{254} (see Figure 2 in **Paper I**). These results suggest that biological treatment is more efficient at mitigating the competition by DOM than membrane treatment. In particular, the negative trend of the adsorption isotherm of sulfamethoxazole could be avoided in the biologically treated effluent. A biological pretreatment step upstream of adsorption to AC has also been proposed for removing small DOM fractions (Zietzschmann et al., 2014b).

With regard to extent of filtration, microfiltration (200 nm) improved adsorption slightly compared with microsieving (100 µm), but it was not enhanced notably by ultrafiltration (3 nm). Thus, a DOM fraction of 3-200 nm had little effect on competition for adsorption. DOM concentrations were similar (11-12 mg/L) in the MF and UF permeates, demonstrating that most DOM that was present after microfiltration comprised compounds < 3 nm. Thus, the lack of improvement in adsorptive capacity could be explained by primarily the low concentration of DOM in this size fraction, rather than low competition by this type of DOM. In this wastewater matrix (no biological treatment), UF filtration was unnecessary with respect to enhancing micropollutant removal by PAC, but it might have a different effect in biologically treated (tertiary) wastewater effluent.

To study the effect of membrane filtration on micropollutant adsorption to PAC in a tertiary effluent, a separate lab experiment was performed with permeates from filtration—0.45 µm, UF (25 kDa), and NF (2 kDa)—of tertiary treated wastewater from Stengården WWTP (Figure 19) with initial DOC concentrations as shown in Table 3.

Table 3
DOC concentrations in permeates from varying extents of filtration of tertiary treated wastewater from Stengården WWTP.

Matrix	DOC (mgC/L)
0.45 µm permeate	6.8
UF permeate (25 kDa)	5.3
NF permeate (2 kDa)	3.7

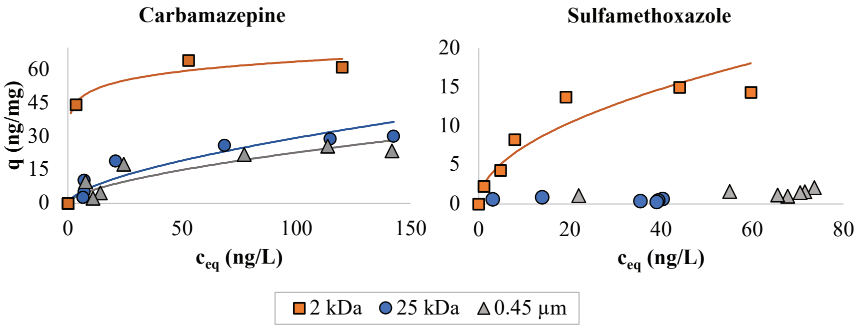


Figure 19
Adsorption isotherms for carbamazepine and sulfamethoxazole in permeates from filtration of tertiary treated effluent wastewater (Stengården WWTP) at 2 kDa, 25 kDa, and 0.45 µm. Unpublished data.

The DOM in the size fraction of 25 kDa to 0.45 µm (1.5 mg/L DOC) was similar to that of the 2–25-kDa fraction (1.6 mg/L DOC). Yet, adsorption improved only after filtration at 2 kDa, indicating that although the latter fraction contributed to competition by DOM, removing the former had little effect. These results thus call into question the viability of UF as an option for improving micropollutant adsorption to PAC. Further, >50% of the DOM was present as compounds below ~2 kDa (Table 3).

4.2.2 Pre-ozonation

To isolate the effects of ozonation on subsequent micropollutant adsorption to AC, we performed experiments in which wastewater was pre-ozonated before being spiked with micropollutants. A successive rise in adsorption of the parent compound with increasing ozone doses was observed (Figure 20), lowering the carbon usage rate. For example, the PAC dose that was required for 80% micropollutant removal could be reduced by 20% to 30% at 0.3 g O_3/g DOC.

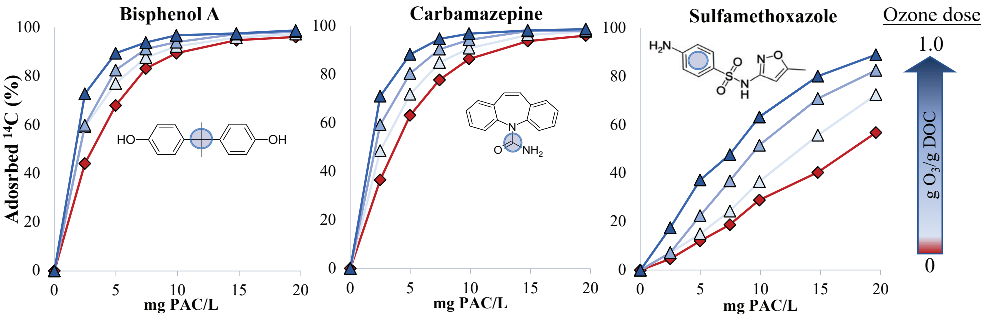


Figure 20
Adsorption of ^{14}C-labeled micropollutants to PAC after pre-ozonation (0-1 g O_3/g DOC). Adapted from Paper II.

Greater removal of micropollutants in wastewater following ozonation has been observed (Guillossou et al., 2020a; Zietzschmann et al., 2015), varying between compounds. Zietzschmann et al. (2015) reported a higher increase in the adsorption of well-adsorbing compounds versus weak adsorbates, although the opposite was noted by Guillossou et al. (2020). The expected differences might be linked to the ability of micropollutants to compete at various DOM concentrations and competition (Guillossou et al., 2020; Zietzschmann et al., 2015; **Paper I**). The adsorption isotherm for sulfamethoxazole had a negative trend at high equilibrium concentrations (Figure 21), as in **Paper I**, which could only be avoided with the highest pre-ozonation dose (~1 g O_3/g DOC). Thus, lower ozone doses do not decrease the competition by DOM sufficiently to allow the adsorption of sulfamethoxazole to follow normal isotherm behavior at high equilibrium concentration (low PAC doses).

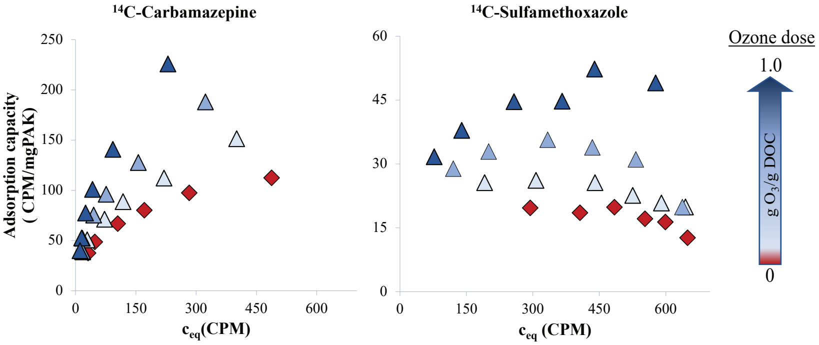


Figure 21
Adsorption isotherms for ^{14}C-labeled carbamazepine and sulfamethoxazole in pre-ozonated (0-1 g O_3/g DOC) wastewater. Modified from Paper II.

The increased adsorptive potential post-ozonation can be explained by a decline in the adsorption (and competition for adsorption) of DOM, as we (Figure 22) and others have observed (De Laat et al., 1991; Treguer et al., 2010; Zietzschmann et al., 2015). Although ozonation of wastewater results in negligible mineralization of DOM (Knopp et al., 2016; Reungoat et al., 2012), the change in its properties is more prominent. Ozonation decreases the aromaticity, hydrophobicity, and size of DOM (De Laat et al., 1991; Świetlik et al., 2004; Treguer et al., 2010). In **Paper II**, we observed low (< 8%) DOC removal, whereas reductions in UVA_{254} (30% to 40%) were obtained already at ~ 0.3 g O_3/g DOC (Table S5, **Paper II**). The expected decrease in compound size has been demonstrated by LC-OCD (Zietzschmann et al., 2015), indicating that neutral and aromatic compounds are transformed into smaller acids. Whereas their smaller size can enable access to previously unavailable pores (and increase competition for adsorption), as stated by Treguer et al. (2010), their reduced aromaticity and hydrophobicity appear to outweigh such effects.

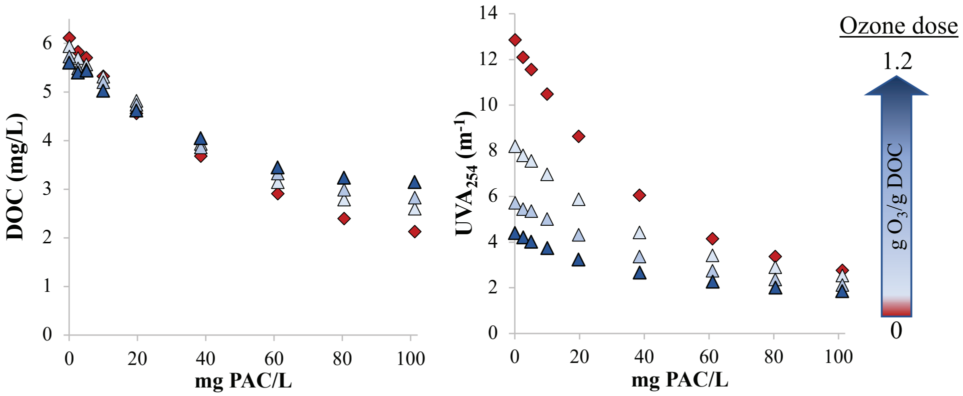


Figure 22
Adsorption of DOC to PAC and UVA_{254} signals after pre-ozonation (0-1.2 g O_3/g DOC), from Paper II.

4.2.3 Summary of micropollutant adsorption

The concentration and properties (e.g., aromatic expression) of DOM affect its adsorption competition with micropollutants. However, weak adsorbates are more susceptible to competition at low doses of AC, and negative adsorption trends may occur, as observed for sulfamethoxazole. This concept is shown in Figure 23. The negative adsorption trend of weak adsorbates can be overcome by decreasing the concentration of DOM or changing its properties, as demonstrated by biological pre-treatment (**Paper I**), pre-ozonation (**Paper II**), and nanofiltration (unpublished results; Figure 19).

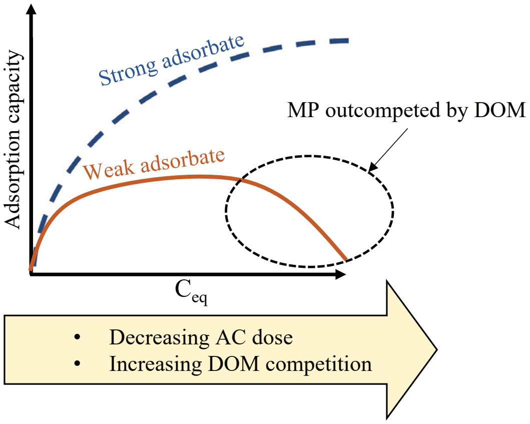


Figure 23
Conceptual view of DOM-induced competition for weak adsorbates at high isotherm equilibrium concentrations. Competition increases at higher equilibrium concentrations, corresponding to lower doses of AC.

4.3 Adsorption of ozone transformation products

As described in Section 3.4.2, ^{14}C-labeled micropollutants were ozonated to generate ^{14}C-labeled OTPs that can be tracked as a group, based on their ^{14}C activity. Figure 24 shows the overall adsorption of OTPs that have been ozonated to various extents, based on the adsorption of ^{14}C. The ^{14}C activity in these samples consisted primarily of various degrees of oxidized ^{14}C-OTPs and small amounts (< 1%) of parent compound micropollutants, as indicated in parallel experiments with their non-radiolabeled counterparts.

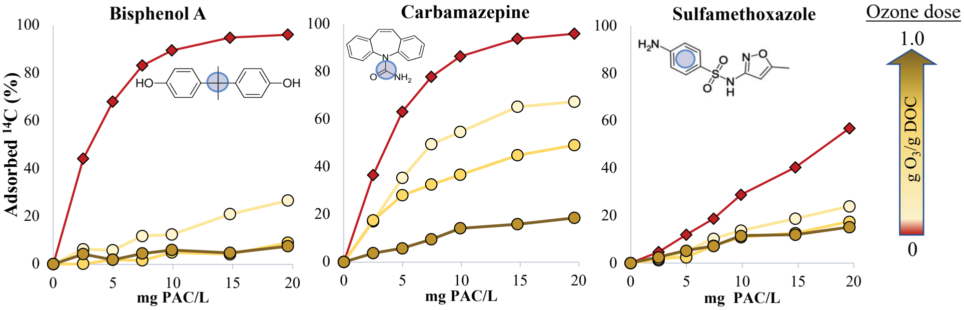


Figure 24
Adsorption of ^{14}C activity by PAC, consisting of parent compound (red line) or the sum of oxidized OTPs (yellow lines) at several ozone doses (0-1 g O_3/g DOC). Adapted from Paper II.

In contrast to the parent compounds, the OTPs underwent a successive and substantial decline in adsorption at increasing ozone doses, as did the six other compounds in **Paper II**. Thus, despite the decreased competition for adsorption sites by DOM after ozonation (Guillossou et al., 2020; Zietzschmann et al., 2015; **Paper II**), OTPs from many compounds are poorly removed via adsorption to PAC at an ozone dose of 0.3 g O_3/g DOC.

Analogous to the behavior of DOM, the ozonation of micropollutants is expected to decrease the hydrophobicity and aromaticity of OTPs, attributed to the removal of double bonds, addition of polar functional groups, and cleavage of activated aromatic rings (von Sonntag and von Gunten, 2015). These modifications, in turn, will generally decrease the potential for adsorption to AC through hydrophobic and π-π interactions (Moreno-Castilla, 2004). Nevertheless, significant differences in the decreased adsorption of OTPs were noted for the compounds in Paper II, which can be related to the expected transformation or destruction of adsorbable moieties within the parent compound, and discussed below.

The largest decrease in the adsorption of OTPs, compared with the parent compound, was observed for bisphenol A (e.g., from 90% to 15% at 0.3 g O_3/g DOC and 10 mg PAC/L). Bisphenol A has two activated aromatic (phenol) rings, and ozonation generates typical phenol-containing OTPs, such as quinone and catechol, and ring-opened muconic acid-type products (Deborde et al., 2008). Considering the predicted hydrophilicities of these products (see SI of **Paper II**), substantial decreases in hydrophobicity were observed primarily after aromatic ring cleavage and the introduction of carboxylic acids. The low adsorption thus suggests that the OTPs from bisphenol A comprise ring-opened products and carboxylic acids. The presence of ring-opened products is also evidenced by the formation of $^{14}CO_2$ from ring-labeled bisphenol A (see **Paper II** and Chapter 6). The low adsorption of ring-opened products is supported by results from Hussain et al. (2013), who noted similar extents of adsorption of phenol, catechol, hydroquinone, and benzoquinone onto a graphite adsorbent, whereas ring-opened maleic and oxalic acids were adsorbed to lesser extents (e.g., ~10-lower at low equilibrium concentrations).

The adsorption of OTPs of carbamazepine did not decrease to the same extent as those of bisphenol A, suggesting that adsorbable moieties are partially conserved during ozonation. The initial attack at the olefin of carbamazepine results in transformation products with two aromatic rings that have low reactivity toward ozone (McDowell et al., 2005). Thus, the high adsorption of the OTPs of carbamazepine versus bisphenol A could be related to partial conservation of the aromatic rings (and, consequently, the potential for π-π interactions). Nevertheless, the primary OTPs of carbamazepine might transform further via reactions with hydroxyl radicals (McDowell et al., 2005), explaining the successive decrease in the adsorption of OTPs that still occurred.

The adsorption trends for sulfamethoxazole and its OTPs are difficult to compare with bisphenol A and carbamazepine, due to the lower adsorption potential of the parent compound. Ozone is expected to attack the aniline group (Dodd et al., 2006), and the presence of ring-cleaved products was indicated by the formation of $^{14}CO_2$ from the aniline ring (see **Paper II** and Chapter 6), consistent with earlier studies on aniline (Tekle-Röttering et al., 2016). Transformation of the aniline nitrogen can also occur and generate nitro-sulfamethoxazole (Abellán et al., 2008; Gulde et al., 2021a; Sierra-Olea et al., 2023; Willach et al., 2017), deactivating the aromatic ring and resulting in low reactivity of the nitro-benzene moiety with ozone (Hoigné and Bader, 1983). The adsorbability of nitro-sulfamethoxazole is likely to be similar to or exceed that of sulfamethoxazole due to the higher hydrophobicity of the former, in combination with conserved aromaticity, and was removed (>50%) at a PAC dose of 13 mg/L (Gulde et al., 2021b). Further, the adsorption of nitro-sulfamethoxazole might be expected to improve due to the decreased competition for adsorption by DOM.

Whereas the adsorption trend for OTPs in **Paper II** might be representative of the OTPs that were generated as a whole, individual transformation products might also adsorb well—or even better than the parent compound—after ozonation, as indicated for nitro-sulfamethoxazole above. In Gulde et al. (2021b), 46 of 53 OTPs were adsorbed by >50% at a PAC dose of 13 mg/L, which is higher than the overall adsorption of OTPs in **Paper II**. However, aromaticity was generally conserved among the 53 OTPs compared with the parent compound.

Detecting OTPs that are generated using regular reversed phase LC-HR-MS/MS-methods might be difficult for small and polar compounds, such as after aromatic ring cleavage, which might not be retained during solid-phase extraction (Gulde et al., 2021a). Thus, primary OTPs are expected to be overrepresented, whereas higher-generation transformation products would be less prevalent. This could explain the lower overall adsorption of OTPs in **Paper II**, compared with that of individual OTPs in Gulde et al. (2021b). Further, one of the few OTPs that underwent proposed ring cleavage (DIC-n_259.9873_15.6; Gulde et al., 2021) was among the OTPs that were removed poorly by PAC.

4.3.1 Consequences for PAC and GAC processes

The results from **Paper II** suggest that many OTPs that form during ozonation of micropollutants are poorly removed via adsorption to AC, likely due to their high polarity and lack of aromatic moieties. The specific toxicity of a compound is expected to decrease at higher degrees of transformation (Hübner et al., 2015; Von Gunten, 2018). Thus, adsorption to AC might perform well for removing the remaining specific toxicity of OTPs but less so for the nonspecific toxicity that is associated with polar and aliphatic compounds. Consequently, adsorption to AC is not recommended without biological treatment post-ozonation.

If biological treatment is applied in combination with AC (e.g., sand filtration or biologically active GAC filter), the importance of removing OTPs likely decreases at greater degrees of transformation, because many OTPs will probably be small, easily biodegradable acids that can be removed efficiently in biological post-treatment steps. However, the formation of ozonation by-products increases at higher ozone doses and might be difficult to remove through adsorption to AC or biological degradation. Compounds that are polar and toxic will be particularly problematic, such as bromate and nitrosamines. Other troublesome, unknown by-products or OTPs, however, are likely to exist. In some studies, the toxicity of polar compounds might have been underestimated, due to their limited extractability (Stalter et al., 2011).

The formation of bromate and NDMA can be decreased by maintaining a low ozone dose. The resulting OTPs might express some specific toxicity, requiring their potential breakthrough to be monitored at high BVs. Also, the effect of decreased competition for adsorption is likely to decline with low ozone concentrations (Guillossou et al., 2020a).

The combined ability of GAC filters to remove various OTPs by adsorption and biodegradation will likely vary over time. Initially, when the adsorptive capacity is high and biological activity is low, parent compounds and low-generation OTPs (with conserved aromaticity and hydrophobicity) will be removed well through adsorption (Gulde et al., 2021b), whereas higher-generation OTPs (polar, non-aromatic compounds) may not be removed (**Paper II**). Conversely, after many treated BVs, high-generation OTPs will be partially removed by biodegradation, whereas parent compounds and low-generation OTPs might break through due to saturation of the adsorptive capacity (Gulde et al., 2021b). The combined removal of various OTPs in GAC filters over time remains to be evaluated further.

5 Adsorption and biological degradation in GAC filters

Biological degradation of dissolved organic matter in GAC filters has long been acknowledged, but it is still uncertain to which extent GAC biofilms contribute to micropollutant removal over time. In this chapter, we explore the relative contribution of biodegradation and concurrent adsorption for the removal of micropollutants in GAC filter systems.

5.1 Biodegradation with GAC-bound biofilm

Batch experiments in **Paper III** showed that the applied approach with ^{14}C-labeled micropollutants could be used to differentiate biodegradation from adsorption in GAC filters through the formation of $^{14}CO_2$. GAC-bound biofilm could partially degrade the same substances (diclofenac, ibuprofen, and naproxen) as other biological media, including MBBR carriers, sand filter media, and activated sludge (**Paper III**). Most notably, however, the degradation rate of diclofenac was substantially higher for GAC-bound biofilm than with other biofilm systems, based on the formation of $^{14}CO_2$ from the ^{14}C-labeled carboxylic carbon in diclofenac (Figure 25). Diclofenac had previously shown to be more readily biodegradable in biofilm compared with activated sludge systems (Falås et al., 2016; Jewell et al., 2016). Yet, its degradation rates are often insufficient to result in substantial removal of diclofenac under hydraulic retention times that are normally applied in biological wastewater treatment of municipal wastewater. The results from **Paper III** indicate that GAC biofilm overcame these limitations through a combination of adsorption and high degradation rates for diclofenac.

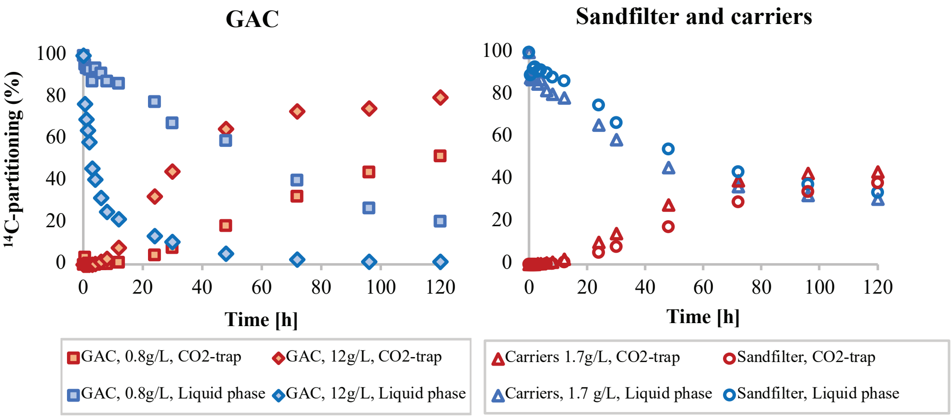


Figure 25
Partitioning of ^{14}C activities in the CO_2 traps (red) and liquid phase (blue) for batch experiments with ^{14}C-labeled diclofenac and (i) GAC (left) and (ii) sand filter and carriers (right).

It was unclear from **Paper III**, however, whether the greater potential for the GAC biofilm to degrade diclofenac would be sufficient to result in its significant removal also in GAC filter systems. To address this question, I modified the approach to examine biodegradation during continuous GAC filter operation in a small-scale setup (Section 3.4.3). Here, we also wished to further evaluate the potential interactions between adsorption and degradation. Since the highest degradation of diclofenac was observed in the GAC filters, we hypothesized that adsorption is the critical mechanism for achieving such high rates.

5.2 Degradation of previously adsorbed micropollutants

To study the retention of micropollutants in GAC filters and determine whether previously adsorbed micropollutants could be degraded at a later stage, ^{14}C-labeled micropollutants were allowed to adsorb under an anoxic phase, with a subsequent oxic phase without ^{14}C (Figure 26). During the initial anoxic phase, most ^{14}C-labeled diclofenac (and its ^{14}C-labeled transformation products) adsorbed to the GAC. On introducing oxygen after 148 hours, we observed a clear peak in $^{14}CO_2$ formation, which must have originated from previously adsorbed diclofenac during the anoxic phase. The maximum rate of this peak in formation exceeded the inflow rate of ^{14}C-labeled diclofenac per unit time during the anoxic phase, suggesting that the biofilm could reach removal rates that were sufficiently high for substantial removal of diclofenac.

These results also show that diclofenac that had previously adsorbed to the GAC could be degraded over time, constituting a significant advantage over other biological systems, in which the time that is available for biodegradation is governed by the hydraulic retention time. In contrast, GAC filters can prolong micropollutant residence times through adsorption-desorption interactions, extending the time for degradation.

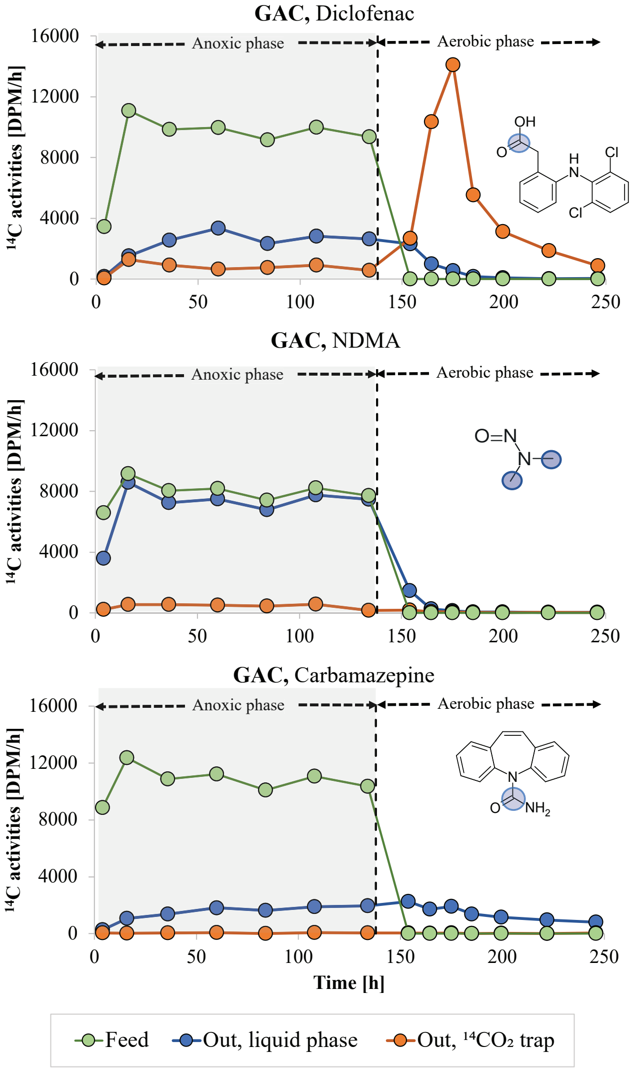


Figure 26
Flows of ^{14}C in the feed (green) and effluent (liquid phase in blue and CO_2 trap in orange) of the columns in the anoxic/oxic experiment at an EBCT of 15 min. After the anoxic (DO <0.1 mg/L) phase (shaded), oxic (DO >8 mg/L) conditions were introduced but without the addition of ^{14}C.

NDMA, which is more polar and hydrophilic than diclofenac, adsorbed to a very low degree during the anoxic phase, rendering it unavailable for degradation in the oxic phase, explaining the absence of the formation of $^{14}CO_2$ after oxygen was introduced. In contrast, ^{14}C-labeled carbamazepine adsorbed well (>80%) during the anoxic phase, but it is considered to be non-biodegradable. Thus, ^{14}C in the effluent from the carbamazepine column can be assumed to consist of ^{14}C-carbamazepine. The continuing leaching and breakthrough of carbamazepine throughout the oxic phase indicate that carbamazepine does not adsorb irreversibly to the column but is instead delayed in its transit through the GAC column through continuous adsorption-desorption interactions.

5.3 Degradation and adsorption during continuous column operation

In comparing the biodegradation and adsorption of ^{14}C-labeled micropollutants that were dosed continuously to GAC and sand columns under oxic conditions at an EBCT of ~15 min, we observed large differences in performance (Figure 27). The GAC column removed > 90% of the diclofenac throughout its 5 days of operation, based on measurements of ^{14}C and the parent compound (diclofenac) in the liquid phase. Based on $^{14}CO_2$ formation, biodegradation contributed to at least 60% of the removal via mineralization of the labeled carboxylic carbon. This rate is a conservative estimate of the fraction that underwent biodegradation, because it can also proceed via pathways that are not targeted by the ^{14}C-labeled carbon (Jewell et al., 2016). Thus, the remainder of the removal (~30%) might have occurred through degradation (which did not lead to $^{14}CO_2$ formation) and adsorption.

Nevertheless, the observed rate of $^{14}CO_2$ formation of ~60% is high compared with degradation rates for other biofilm systems, for which hydraulic retention times of at least 4-16 hours have been required for ~80% removal in high-performance systems (Jewell et al., 2016; Tang et al., 2017). These results show that substantial removal of diclofenac is possible in GAC filters at short hydraulic retention times (or EBCTs), allowing for more compact reactor designs compared with other biofilm systems. Although a sand filter might provide higher biomass concentrations (g/L) than an activated sludge or MBBR system, the removal of diclofenac in the sand column was low versus the GAC filter (Figure 27). These results further support that adsorption is a key component of the high biodegradation in GAC filters, compared with activated sludge or biofilm systems without adsorption.

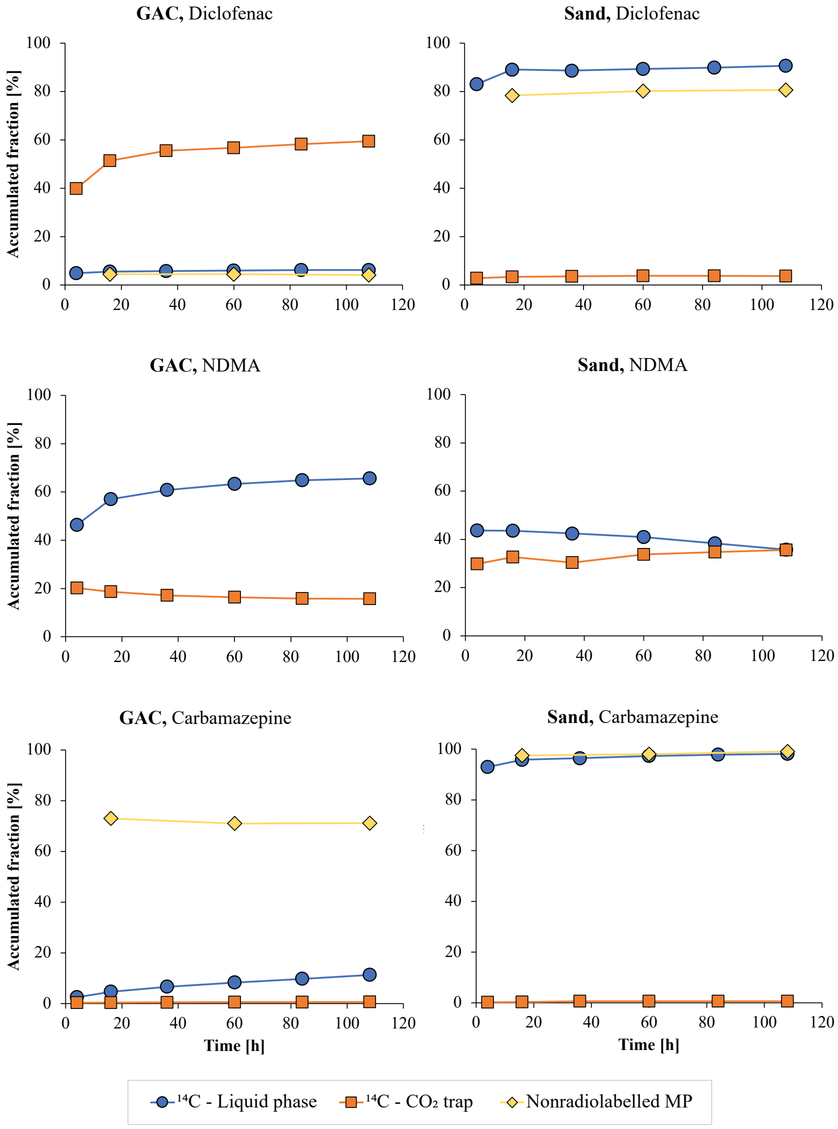


Figure 27
Accumulated fractions of ^{14}C [effluent ^{14}C/influent ^{14}C] in the liquid phase (blue) and CO_2 trap (orange) and of the non-radiolabeled micropollutant fraction [effluent/influent] (yellow) for column experiments with GAC and sand under oxic conditions (DO> 8 mg/L) and an EBCT of ~15 min.

In contrast to diclofenac, the removal of NDMA was higher in the sand filter than in the GAC filter and was accompanied by greater $^{14}CO_2$ formation in the former. Thus, not all biodegradable compounds are removed better in GAC filters versus sand filters, as observed for ibuprofen and naproxen in **Paper III**. Due to the low adsorbability of NDMA, there is also low potential for interactions between adsorption and degradation; thus, the retention time of NDMA in the GAC filter might be similar to that of the sand filter. These results further support the importance of adsorption in the biodegradation of diclofenac in GAC filters.

Large differences in influent/effluent measurements of radiolabeled and non-radiolabeled carbamazepine were observed in the GAC column (blue vs. yellow dots; Figure 27). Whereas non-radiolabeled carbamazepine experienced steady breakthrough (~70%), ^{14}C-labeled carbamazepine underwent low but steadily increasing breakthrough over the 5 days of operation. Thus, although it appears that a significant portion of carbamazepine passes through the bed without being adsorbed (based on measurements of non-radiolabeled carbamazepine), our results indicate that carbamazepine is substantially delayed (by several days to weeks) in its transit through the GAC bed via adsorption-desorption. For biodegradable compounds, such as diclofenac, we hypothesize that this retention is an important factor in improving biodegradation in GAC filters.

Two conceptual models of micropollutant transport in GAC filters are illustrated in Figure 28. At partial breakthrough, influent-effluent measurements of micropollutant suggest that a fraction of micropollutants passes the GAC bed without being adsorbed (Figure 28, top). However, our observations support a second model, in which most micropollutants are adsorbed temporarily in the GAC column, despite it being largely saturated with adsorbates.

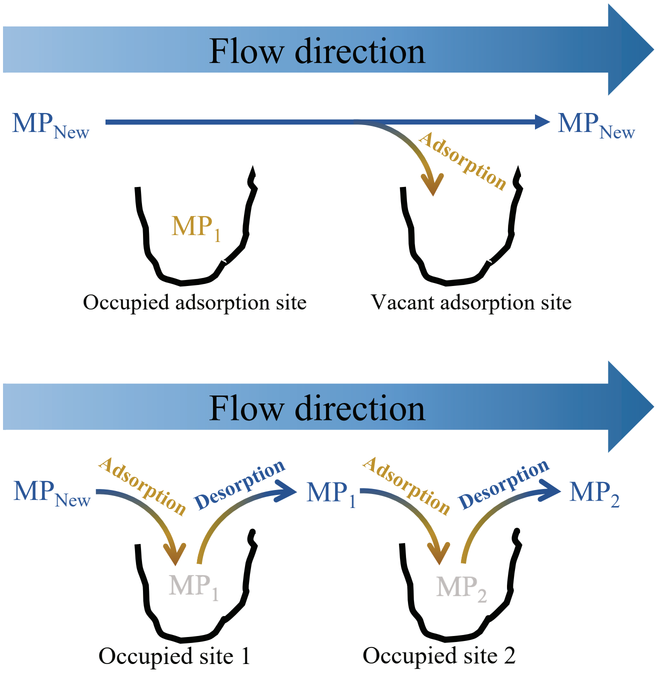


Figure 28
Two models of micropollutant (MP) transport in a GAC column. **Top:** Micropollutants bypass occupied adsorption sites without interaction but can adsorb at vacant adsorption sites. Individual molecules are not substantially retained unless they adsorb to vacant sites. **Bottom:** Micropollutants interact with occupied sites via continuous adsorption/desorption, substantially prolonging the residence time of individual molecules in the GAC bed.

A consequence of this behavior is that sudden changes in influent conditions might fail to be reflected in the effluent conditions until after several days or weeks. Thus, GAC filters potentially track historical events, as discussed with regard to micropollutant extraction from GAC (Edefell et al., 2022). Further, this view calls in to question the commonly applied approach of 24-hour flow-proportional sampling of GAC filter influent/effluents, in which effluent measurements can reflect inflow conditions much earlier than the previous 24 hours.

The retention of micropollutants in GAC filters is likely to be affected by their adsorptive capacity for micropollutants. For example, the retention of NDMA was estimated to be less than 12 hours, whereas carbamazepine, on average, is retained for weeks. The retention of diclofenac, however, was difficult to assess due to its partial degradation but is expected to lie between those of NDMA and carbamazepine. Longer run times would be required to confirm micropollutant retention and the reversibility of adsorption, for which two isotopes of the same compound could be applied, as done in **Paper IV**.

5.4 Synergies between adsorption and biodegradation

There are several potential explanations for the high degradation of diclofenac that we observed in GAC filter media compared with other biofilms. As shown in **Paper IV**, the retention of micropollutants in GAC filters decouples the micropollutant retention time from the hydraulic retention time and substantially prolongs the micropollutant residence time (from minutes-hours to days-weeks) versus other biological systems. This sustained access of micropollutants could aid in the selection of specific microorganisms that target their removal.

Further, AC increases the local micropollutant concentration through adsorption to its surface. Because micropollutant degradation rates are typically higher at elevated micropollutant concentrations (Svendsen et al., 2020), the steady access of micropollutants from the solid phase could increase degradation rates compared with what would have been possible without adsorption. However, adsorbed micropollutants are not considered to be directly accessible for degradation, because they primarily adsorb in micropores and mesopores, which are too small for microorganisms to reach (Aktaş and Çeçen, 2007). Nonetheless, AC can provide a steady transport of micropollutants from the bulk liquid to its surface (during adsorption) or vice versa (during desorption), during which micropollutants pass closely to the biofilm, potentially improving the mass transfer rate of micropollutants to the biofilm.

It is possible that the presence of AC in biological systems per se mediates biological redox reactions by acting as an electron donor or acceptor (Saquing et al., 2016) and promoting electron transfer between enzymes and micropollutants (Nguyen et al., 2016). Such effects have been demonstrated primarily for anaerobic systems (Pereira et al., 2014; Van Der Zee et al., 2003) but have been largely unexplored for the removal of micropollutants in aerobic wastewater treatment processes with PAC or GAC.

GAC filters can also contain a higher overall biomass concentration or a higher amount of specialized biomass, compared with other biofilm systems. However, it is difficult to measure the biomass in GAC filters, because it can not be isolated efficiently or distinguished from the GAC during combustion. The higher degradation of NDMA in the sand versus GAC columns, however, suggests that the overall biomass concentrations were not substantially higher in the GAC filter and that the high diclofenac degradation is attributed to other factors. Due to the sequential operation of the full-scale sand filter and GAC filter used in **Paper IV**, microorganisms in the sand filter effluent can be expected to have colonized the GAC filter. Nevertheless, alternate selective pressure in the filters may have arisen from the slightly lower content of biodegradable DOM in the GAC influent, as well as from interactions between the biofilm and adsorbed DOM (including micropollutants).

Diclofenac is likely not the only micropollutant to undergo greater biodegradation in GAC filters. Sustained long-term removal has been observed for gabapentin, iopromide, amisulpride, metoprolol, and tramadol (Altmann et al., 2016; Fundneider et al., 2021b), but it remains to be confirmed whether these compounds are also degraded efficiently in GAC filters.

Not all compounds, however, are biodegraded more efficiently in GAC filters, as observed for NDMA (**Paper IV**), ibuprofen, and naproxen (**Paper III**). Biodegradability in GAC filters has previously been linked to the reversibility of adsorption (Orshansky and Narkis, 1997), which is a prerequisite for subsequent biodegradation. Thus, the decreased removal of ibuprofen, naproxen, and NDMA might have been attributed to their low availability in GAC filters, which could have been affected by micropollutant retention and the reversibility of adsorption.

6 Mineralization of micropollutants during ozonation

The mineralization (i.e. the CO_2 formation) of dissolved organic carbon (DOC) during ozonation is typically very low (0–10 %) at normal ozone doses. However, specific moieties can be mineralized to much larger degrees, as we show in this chapter. Here, we look at the degree of mineralization of different ^{14}C-labeled moieties of some common micropollutants during ozonation to discuss potential degradation pathways.

6.1 Mineralization of different ^{14}C-labeled moieties

Based on CO_2 trapping during the ozonation of ^{14}C-labled micropollutants, partial mineralization of the ^{14}C-labeled moiety (up to ~40% at 1 g O_3/g DOC) was observed in seven of the nine compounds in **Paper II**; six are presented in Figure 29. A similar degree of mineralization was noted for different compounds that were labeled at the same moiety, including the aniline ring in sulfamethoxazole and sulfadiazine and the carboxylic carbon in diclofenac and ibuprofen. In sulfamethoxazole and sulfadiazine, the mineralization could be explained by the high reactivity of the activated aromatic rings (Dodd et al., 2006) and ring cleavage of aniline (Tekle-Röttering et al., 2016), although ring cleavage of sulfamethoxazole and sulfadiazine had not previously been demonstrated, based on the identification of ring-opened products (e.g., Abellán et al., 2008; Gulde et al., 2021a; Sierra-Olea et al., 2023; Willach et al., 2017).

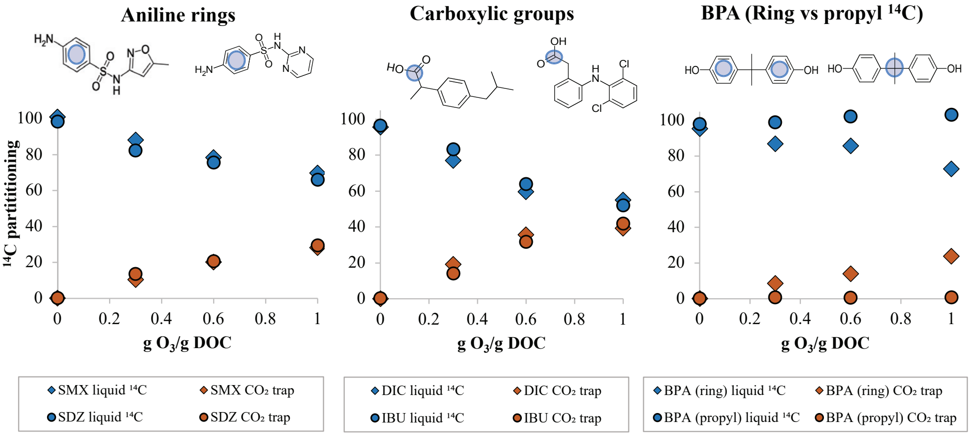


Figure 29
Extent of mineralization for micropollutants labeled at the same moiety and for the same compound, BPA, labeled at different moieties, at ozone doses of 0-1 g O_3/g DOC. SMX: Sulfamethoxazole, SDZ: Sulfadiazine, DIC: Diclofenac, IBU: Ibuprofen, BPA: Bisphenol A.

The ^{14}C-labeled carboxylic carbon in diclofenac and ibuprofen was mineralized substantially and to similar degrees (~40% at 1 g O_3/g DOC) during ozonation, despite the low reactivity of the carboxylic groups with ozone (e.g., $\leq 10\ M^{-1}\ s^{-1}$, based on ibuprofen (Huber et al., 2003)). These results suggest that hydroxyl radicals were involved in the mineralization of the carboxylic groups, as proposed by Alharbi et al. (2021), but this theory was not confirmed by hydroxyl radical scavenging. However, assuming that OH radicals did participate in the mineralization of carboxylic acids in ibuprofen and diclofenac, they might also have participated in the mineralization of other ^{14}C-labeled carboxylic groups that resulted from the transformation of other ^{14}C-labeled compounds. For example, the ozonation of bisphenol A yields ring-opened muconic acid-type products (Deborde et al., 2008), wherein the successive formation of smaller carboxylic acids is expected and decarboxylation is a potential mechanism of CO_2 formation (Yamamoto et al., 1979).

Further experiments with ^{14}C-labeled moieties in the presence and absence of hydroxyl radicals can help confirm or exclude degradation pathways by ozone and hydroxyl radicals and aid in mass balance estimates of OTP yields.

7 Conclusions

This thesis examined the adsorption and degradation of organic micropollutants and OTPs in processes with PAC or GAC. ^{14}C-labeled micropollutants, in combination with non-radiolabeled micropollutants, were used to study the adsorption of OTPs and the mineralization of ^{14}C-labeled moieties and separate biodegradation from adsorption in GAC filter systems.

Part 1 evaluated the adsorption of micropollutants and OTPs onto PAC in several wastewater matrices. The results showed that competition between micropollutants and DOM not only leads to lower micropollutant adsorption capacities but can also result in negative adsorption trends for poor adsorbates, as observed for sulfamethoxazole. Competition for adsorption by DOM could be mitigated in part by membrane filtration and pre-ozonation, but nanofiltration (~3 nm) or high ozone doses (~1 g O_3/g DOC) were required to avoid negative adsorption trends for sulfamethoxazole.

In experiments with ^{14}C-labeled OTPs, the overall adsorption of OTPs declined at higher ozone doses, likely due to their decreased aromaticity and hydrophobicity, which in turn lowered the potential for adsorption via π-π and hydrophobic interactions. Thus, adsorption onto PAC, without biodegradation, is not a viable option for the overall removal of OTPs.

Part 2 was dedicated to studying the relative contributions of biodegradation and adsorption to the removal of organic micropollutants in GAC filters. The use of ^{14}C-labeled micropollutants could separate biodegradation from adsorption via the formation of $^{14}CO_2$. The results further demonstrated the degradation of previously adsorbed micropollutants. Column experiments showed that GAC biofilm could reach biodegradation rates that were sufficiently high for substantial removal of diclofenac, indicating that biodegradation can be responsible for long-term removal of certain micropollutants in GAC filters. The presence of oxygen was important for the degradation of diclofenac and NDMA, which was limited under anoxic conditions.

In comparing the behavior of ^{14}C-labeled and non-radiolabeled micropollutants in GAC filter columns, a substantial delay in micropollutant residence time was observed for carbamazepine, despite an apparent high breakthrough. This decoupling of micropollutant residence time from hydraulic residence time is one explanation for the high biodegradation of diclofenac in GAC-bound biofilms.

In **Part 3**, we examined the mineralization of various ^{14}C-labeled moieties of organic micropollutants during ozonation. Up to 40% mineralization of ^{14}C-labeled moieties was observed at 1 g O_3 /g DOC, which was substantially higher than the overall mineralization of DOM (<10% as DOC). Similar degrees of mineralization were observed for the same moiety in different compounds, including the aniline rings in sulfamethoxazole and sulfadiazine and the carboxylic carbons in diclofenac and ibuprofen. ^{14}C-labeling also confirmed aromatic ring cleavage for sulfamethoxazole and sulfadiazine, which had not been previously verified, based on the identification of ring-opened products.

8 Future work

Through a combination of ^{14}C-labeled and non-radiolabeled micropollutants, this thesis has examined adsorption, ozonation, and biodegradation from novel perspectives. The results have revealed several opportunities for further research using ^{14}C-labeled micropollutants, as discussed below.

The ^{14}C-labeled approach was used in this thesis to study the overall adsorption of OTPs (i.e., the adsorption of all OTPs as a collective). A logical follow-up study would measure the overall removal of OTPs in other post-ozonation processes, including sand filters and GAC filters with and without developed biofilms. An advantage of this approach would be its ability to separate biodegradation from adsorption, as shown in **Papers III and IV**. Future studies would also benefit from investigating additional compounds and to determining the fate of OTPs at lower doses than those that were tested here, especially because low ozone doses are often considered for combined O_3-GAC systems.

For studying the formation (and fate) of transformation products, from ozonation or biodegradation, the applied ^{14}C-based approach would benefit largely from being coupled with HPLC-MS analysis of the same samples. In particular, analysis of samples with ^{14}C-labeled micropollutants and ^{14}C-labeled transformation products through a combination of MS and radioactivity detection could be helpful for identifying and determining potential OTP structures and estimating mass balances of OTP yields. Still, studying the overall behavior of ^{14}C-labeled OTPs, as done here, provides good control of the ^{14}C mass balance and remains a good complement to the identification of individual ^{14}C-labeled compounds.

For examining the presence and toxicity of OTPs, new approaches are needed to selectively target polar compounds that escape solid-phase extraction or fail to be separated well in reversed phase LC columns. The results from **Paper II** implicate the presence of such compounds, and their potential contribution to toxicity may be underestimated due to difficulties with extraction (Stalter et al., 2011).

A clear limitation of the ^{14}C-based approach for studying biodegradation is that biodegradation is only confirmed during $^{14}CO_2$ formation. Thus, it would be beneficial to use a combination of micropollutants that are labeled at all carbon atoms (to demonstrate degradation of the parent compound) and the same micropollutants that are labeled at selected moieties (to confirm transformation pathways). This approach, however, is hampered by the expense of custom-made

^{14}C-labeled micropollutants. Further, the main limitation continues to be that transformation that does not lead to $^{14}CO_2$ formation remains undetected.

With respect to the study of adsorption, the combination of radiolabeled and non-radiolabeled compounds can be used to examine micropollutant retention in activated carbon processes and, for example, the reversibility of adsorption.

Regarding the mineralization of ^{14}C-labeled moieties during ozonation, future studies in which hydroxyl radicals are scavenged or monitored can help confirm its function in various degradation pathways, including the formation of $^{14}CO_2$ from carboxylic carbons.

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