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micropollutant adsorption onto activated carbon

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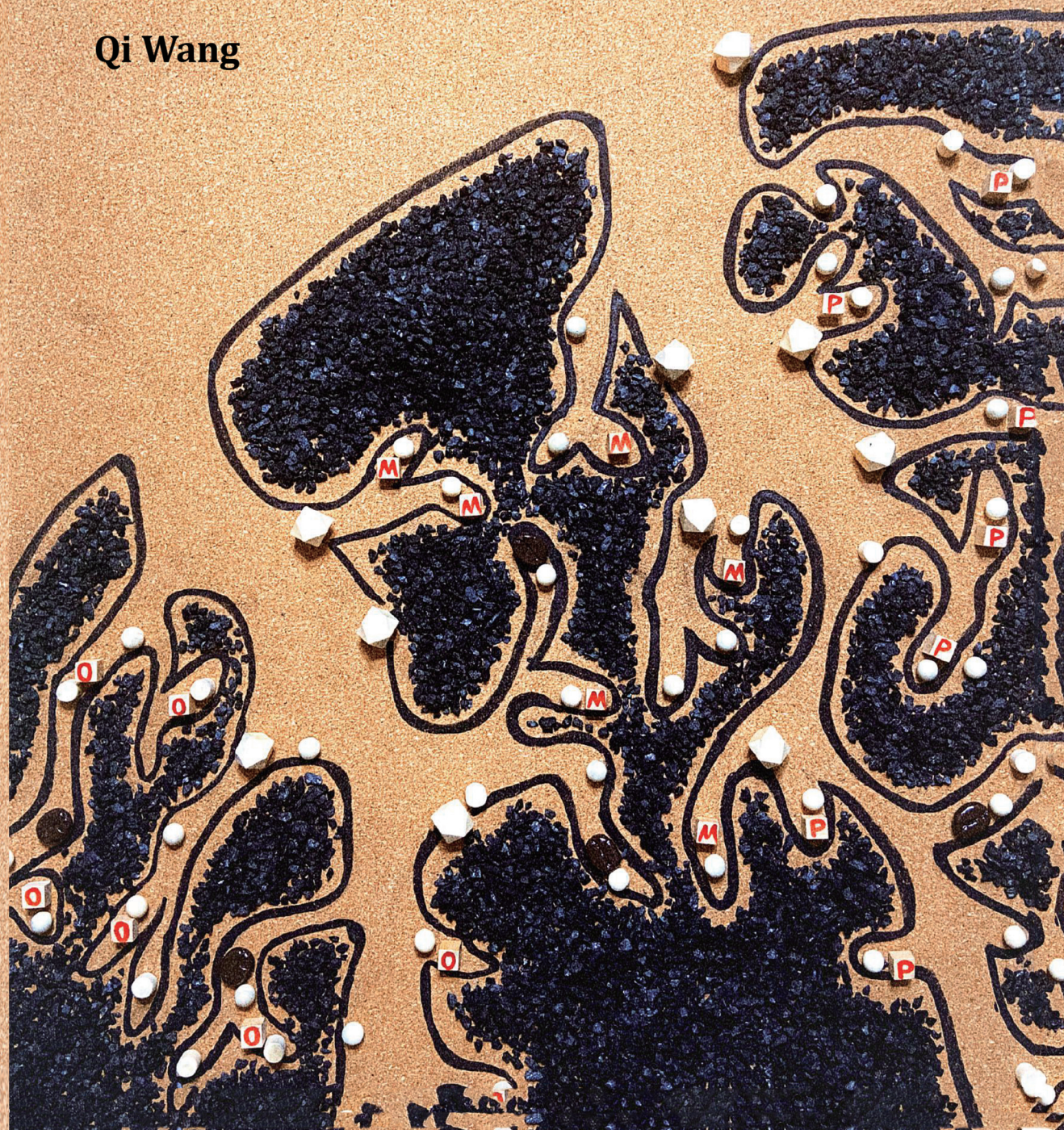# Associating Properties of Dissolved Organic Matter to Competitiveness against Organic Micropollutant Adsorption onto Activated Carbon

Qi Wang

# Associating Properties of Dissolved Organic Matter to Competitiveness against Organic Micropollutant Adsorption onto Activated Carbon

# Associating Properties of Dissolved Organic Matter to Competitiveness against Organic Micropollutant Adsorption onto Activated Carbon

**Dissertation**

For the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus Prof.dr.ir. T.H.J.J. van der Hagen
chair of the Board for Doctorates
to be defended publicly on

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by

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This dissertation has been approved by the promotors.

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# Chapter 1
# Introduction

# 1. Occurrence of organic micropollutants in the environment

The control of organic micropollutants (OMPs) has been a major concern for many water utilities for the last decades (Schulze et al., 2019; Yang et al., 2021). OMPs, occurring in source waters, mainly originate from urban stormwater runoff (e.g. polycyclic aromatic hydrocarbon pollutants), effluents from wastewater treatment plants (pharmaceuticals, personal care products), agricultural runoff (pesticides, herbicides), and industrial discharges (perfluorinated compounds, flame retardants), or are even from the endogenous origin, produced by microbes (odorants, algal toxins) (DiBlasi et al., 2009; Hou et al., 2021; Jekel et al., 2015; Pivokonsky et al., 2016). Comprehensive analyses on the occurrence of emerging OMPs have been advanced due to the reduction in detection limits and the development of non-targeted analysis methods (Been et al., 2021; Du et al., 2022; Guardian et al., 2021). At low aquatic concentrations (ng/L-µg/L), a cocktail of a wide variety of OMPs, at individually non-observed effect concentrations, can result in toxicological and/or odorous effects (Backhaus et al., 2011; Guo et al., 2020; Jacob et al., 2020). Moreover, OMPs can be transformed into highly toxic byproducts, mostly remaining unknown, during natural transformations due to e.g., UV radiation or biodegradation, or during water treatment, because of oxidation or chlorine disinfection processes (Dong et al., 2018; Hubner et al., 2015; Li et al., 2020; Postigo et al., 2021).

A complete absence of any OMPs in treated drinking water would certainly be desired by customers, but it is hard to achieve in practice. As detection limits continue to decrease, "non-detectability" (typically < 0.1 µg/L for pesticides in the 1980s) is no longer a feasible guideline for OMP control in high-quality drinking water production. Alternatively, the Threshold of Toxicological Concern (TTC) approach has been introduced as a method for OMP management, where OMPs have been classified based on their modes of action (e.g., developmental toxicity, haematological effects), and the target values have been proposed to be 0.1 µg/L for each mode of action. In addition, a total value of 1.0 µg/L has been suggested for all the other OMPs with unknown health effects (Mons et al., 2013).

Oxidation, dense membrane filtration and activated carbon are usually employed in OMP control. However, an excessive dose of oxidants may result in a concentration of byproducts to an unacceptable level (e.g., bromate as the hazardous byproduct in ozonation) (Chon et al., 2015). During dense membrane filtration (e.g., reverse osmosis), the operation cost is

usually high, problems with the disposal of concentrated waste streams occur, and the inorganic composition of the permeate is influenced (Crittenden et al., 2012), while it is not the perfect option to remove some neutral and positively charged OMPs (Ebrahimzadeh et al., 2021). By contrast, the application of activated carbon adsorption has been proven to be effective (also in terms of cost) for the removal of a broad spectrum of OMPs (Crittenden et al., 2012; Yang et al., 2017), and does not have concerns in relation to the formation of toxic/mutagenic by-products.

## 2. Activated carbon adsorption

Activated carbon adsorption is a typical mass transfer process, with the adsorbates being transported from the liquid phase to the external surface, diffused into the pore structures and accumulated on the surface of the activated carbon. As adsorption is a surface process, a large internal surface area is crucial for sufficient adsorption sites of the effective adsorbents(Sontheimer et al., 1988; Worch, 2012). OMPs have been reported to be primarily adsorbed on the adsorption sites where the pore size ranges approximately 2-3 times the dynamic diameter of the OMPs (Table 1). As the molecular weight (MW) of the OMPs is usually low, microporous activated carbon (rich in micropores that pore size < 2 nm) is thus highly favored in water treatment for OMP abatement.

A broad range of organic substances can be adsorbed on activated carbon due to reversible van-der-Waals forces (dipole interactions, induction, dispersive forces), while the hydrophobic interaction, π-π interactions, H-bonding, and electrostatic interactions could superimpose and contribute to the adsorption of some subgroups of organics (Li et al., 2015; Worch, 2012).

*Table 1 OMP geometry and the correlated pore size reported for OMP preferential adsorption.*

| OMPs | Molecular weight | Minimum projection radius* | Maximum projection radius* | Optimum pore size region | Reference |
|---|---|---|---|---|---|
| 2-methylisoborneol (2-MIB) | 168.28 | 3.89 Å | 4.41 Å | 10-12 Å | (Newcombe et al., 2002b) |
| Methyl tertiary-butyl ether (MTBE) | 88.15 | 3.36 Å | 3.87 Å | 8-11 Å | (Quinlivan et al., 2005) |
| Trichloroethene (TCE) | 131.38 | 3.23 Å | 3.85 Å | 7-9 Å | (Quinlivan et al., 2005) |
| | | | | <10 Å | (Guo et al., 2007) |
| Atrazine | 215.69 | 4.79 Å | 6.36 Å | 7.5-10 Å | (Pelekani and Snoeyink, 2000) |
| | | | | 10-20 Å | (Guo et al., 2007) |
| Phenol | 94.11 | 3.4 Å | 3.96 Å | 8-14 Å | (Lorenc-Grabowska et al., 2016) |

* Data from Chemicalize, data accessed on Dec 20th, 2021 (ChemAxon, 2021).

Adsorption isotherm tests, conducted at constant temperature in the lab, are often employed to characterize the OMP adsorbability on activated carbon at an equilibrium state. A magnitude of isotherm models has been proposed to describe the OMP adsorption isotherm, where the most known are the Langmuir and Freundlich isotherms. As compared to the Langmuir model, which assumes homogeneous adsorption sites and mono-layer adsorption, the Freundlich model is usually preferred to describe adsorption on activated carbon, since its adsorption sites are energetically heterogeneous and multi-layer adsorption is possible for the aqueous adsorption onto the activated carbon surface (Worch, 2012; Yang et al., 2010).

In waterworks, activated carbon adsorption is often applied either in the form of powder (1-100 μm diameter) or granules (0.1-4 mm diameter). Powdered activated carbon (PAC) works as a periodical pretreatment technology for seasonal-occurring OMPs like odorants and pesticides (Crittenden et al., 2012). The PAC dose is applied at the beginning of the

treatment train, e.g., in the coagulation tank, or the inlet of the transmission pipeline of source water. The contact time for PAC adsorption is usually from 0.5 h to 4 h, which is frequently insufficient to approach the PAC adsorption capacity at equilibrium (Ho et al., 2011; Shimabuku et al., 2016). As the internal surface diffusion is the rate-limiting step for OMP adsorption, the application of superfine PAC (< 1 µm diameter) could increase the OMP adsorption kinetics considerably, nearing the equilibrium adsorption within 10-30 min (Matsui et al., 2013). By coupling with optimized coagulation, the penetration of superfine PAC particles through the treatment train could be minimized (Nakazawa et al., 2021; Nakazawa et al., 2018).

Granular activated carbon (GAC) is employed in fixed-bed filters to adsorb the target OMPs, existing at low concentrations for a long time (Crittenden et al., 2012). Additional biological degradation by the attached biofilm could also be beneficial for the degradation of the adsorbed OMPs during long-term operation and lead to longer filter operation times and/or reduced replacement intervals (Kim et al., 2014; Lu et al., 2020). By tracking ^{14}C-labeled OMPs, OMP removal has successfully been differentiated between adsorption and biodegradation. Adsorbed ibuprofen and diclofenac could be biodegraded up to 46% and 68%, respectively, providing evidence for the bio-regeneration in OMP removal (Betsholtz et al., 2021). When saturated, the adsorption capacity of the used GAC could be restored by thermal reactivation several times (Worch, 2012). The operation costs usually drop accordingly, due to repeated GAC reuse, but attention should be given to the decomposition efficiency of recalcitrant OMPs during the reactivation process. Inadequate degradation of perfluoroalkyl substances may for example occur when the temperature is not high enough (700 °C) (Xiao et al., 2020), potentially resulting in poor effluent quality of regenerated GAC filters.

## 3. DOM competition

### 3.1 DOM adsorption

Dissolved organic matter (DOM), also named natural organic matter or background organic matter, is a complex mixture of organics with diverse characteristics. Various origins (allochthonous, autochthonous and anthropogenic sources) and the transformations in the aquatic system (chemical reactions like hydrolysis, solar radiation, biodegradation, and

mineral fractionation) are the main factors responsible for the heterogeneity of the DOM composition (Jiao et al., 2010; Lee et al., 2018; Riedel et al., 2012; Sillanpaa et al., 2018). DOM concentrations in natural water are usually in mg C/L, whereas OMPs are in the ng/L-µg/L range. The main driving forces for DOM adsorption on activated carbon are hydrophobic interactions and π-π attractions, while H-bonds and electrostatic forces also have a contribution to the adsorption of some of the compounds (Bhatnagar and Sillanpaa, 2017; Kah et al., 2017; Wang et al., 2009). The molecular size of DOM is usually larger than that of OMPs, and adsorptive interactions of DOM may occur on multiple adsorption sites (Pan et al., 2008). Therefore, DOM adsorption is usually highly irreversible, as observed by low recovery (approximately 10%-20%) in DOM desorption tests, implying that DOM fouling of activated carbon cannot be simply mitigated by desorption using water or even a strong alkali solution (Aschermann et al., 2019; Pelekani and Snoeyink, 1999; Summers, 1986).

It has been hypothesized that low molecular weight (LMW) DOM mainly adsorbs in the secondary micropores (1-2 nm) of activated carbon, while high molecular weight (HMW) DOM cannot penetrate micropores and adsorbs in the mesopores (2-5 nm) (Li et al., 2002a; Li et al., 2003b). DOM uptake is therefore lower when the primary micropores (< 1 nm) are predominant (Karanfil et al., 2006). In addition, it has been found that the diffusion of HMW DOM is only limited to the shell region near the external surface of activated carbon (penetration depth ~1 µm), since they are tightly adsorbed in the pores near the outer surface (Ando et al., 2010; Matsui et al., 2015). Therefore, activated carbon (Ando et al., 2011)with a small particle size (i.e., enlarging shell region) is more effective in increasing DOM uptake (Ando et al., 2010; Bonvin et al., 2016; Randtke and Snoeyink, 1983; Weber et al., 1983).

To interpret the adsorbability of the DOM with complex compositions, DOM adsorption isotherm tests are often performed and evaluated by measuring the dissolved organic carbon (DOC) concentrations. However, it has been found that a simple two-parameter isotherm model (like the Freundlich model) is not appropriate to fit the DOC isotherm. Therefore, the so-called DOM adsorption analysis has been introduced to increase the comparability of DOM adsorbabilities, by dividing the bulk DOM into several fictive fractions with given adsorbabilities (Sontheimer et al., 1988; Worch, 2012). It is then possible to compare the adsorptive performance of the various activated carbon samples and DOM matrices, and evaluate pretreatment effects (e.g., ozonation, coagulation, or biodegradation)

on DOM adsorbability (Matsui et al., 1999; Sontheimer et al., 1988; Worch, 2012; Zietzschmann et al., 2015b).

## 3.2 Competitive adsorption between DOM and OMPs

The adsorption on activated carbon of OMPs in DOM-containing waters can be profoundly affected due to DOM competition, by a multitude of factors. The most straightforward explanation for the competition is the large concentration asymmetry (mg C/L for DOM, ng/L - µg/L for OMPs) (Shimabuku et al., 2017b). When the initial OMP concentration is at trace levels (µg/L-ng/L), a large concentration asymmetry occurs and OMP adsorption capacities have been found to drop substantially, e.g., 60-90% adsorption capacity of 2-MIB at 100 ng/L (1 µg/L initially) was deprived by co-adsorbing DOM (1.5 mg C/L initially) in various natural waters (Matsui et al., 2012). It has also been found that OMPs could indeed outcompete DOM, when initial OMP concentrations are in mg/L too (i.e., no concentration asymmetry).

Direct site competition by LMW DOM and pore blockage by HMW DOM are further the major mechanisms for DOM competition (Figure 1) (Li et al., 2003b). Adsorbent properties like average pore size and particle size influence pore blockage, while LMW competitive DOM adsorbates influence the level of direct competition. Micropores are the optimal region, where LMW DOM can directly compete with OMPs, while HMW DOM compounds block the external micropores near the activated carbon surface and reduce the internal diffusion. Larger activated carbon particles suffer more from pore blockage than smaller particles, which has been observed by the decreased reversibility of OMP adsorption (i.e., lower desorption). Similarly, a stronger pore blockage has been observed for activated carbon with a higher percentage of micropores (Ebie et al., 2001). In water treatment, pretreatment such as coagulation can remove the HMW DOM compounds (biopolymers, humics) selectively, considerably improving OMP adsorption kinetics, due to alleviation of pore blockage, while leaving equilibrium adsorption capacity mostly unchanged, because of remaining competition by LMW DOM.
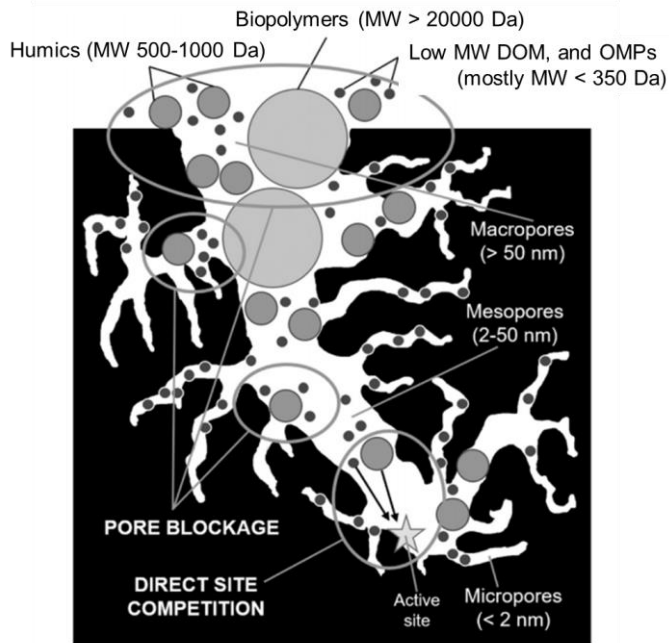
***Figure 1*** *Competitive adsorption mechanisms between DOM (in different MW) and OMPs (modified from (Pivokonsky et al., 2021)).*

To study the interplay of OMPs and DOM fractions in activated carbon adsorption, the most common way is to execute equilibrium isotherm tests with variable carbon doses, where virgin adsorption sites are exposed to the mixture of OMPs and DOM at the same time, and three influencing factors vary simultaneously: (i) number of adsorption sites (caused by variable activated carbon doses), (ii) adsorption sites with heterogeneous adsorptive energy, (iii) differently adsorbable DOM fractions (Carter et al., 1995; Worch, 2012). However, at a low activated carbon dose, only strongly adsorbable DOM occupies the limited number of adsorption sites (both high-energy sites and low-energy sites) and then competes against OMPs. The high-energy sites become more abundant at higher PAC doses and are then also available for the more weakly adsorbable DOM. In addition, as mentioned above, initial OMP concentrations also influence competition (Najm et al., 1991; Shimabuku et al., 2017b). For example, a 70% reduction in the PAC loading of 2,4,6-trichlorophenol (TCP) has been observed at the equilibrium liquid concentration of 1 µg/L as the initial concentration decreased from 492 to 22.5 µg/L, in presence of a surface water DOM (Najm et al., 1991).

Although the PAC loading is changed at various initial OMP concentrations, it is proportional to the initial OMP concentration. Briefly, the remaining percentages of OMPs are independent of the initial OMP concentration, which would be quite beneficial for practical application (American Water Works and James, 2011; Knappe et al., 1998). There are upper thresholds for the initial OMP concentration as a precondition of the invariant remaining OMP percentages, where weakly adsorbable OMPs (e.g., <1300 μg/L for asulam) had higher thresholds than strongly adsorbable OMPs (e.g., <30 μg/L for simetryn) (Matsui et al., 2003). Otherwise, the practical carbon usage would be seriously underestimated if OMP isotherm tests are performed at unreasonably high initial OMP concentrations, where OMPs may outcompete DOM competitors (Shimabuku et al., 2017b). Consequently, it is important to select an environmentally relevant OMP concentration in isotherm tests to simulate the authentic competitive relationship between DOM adsorbable fractions and OMPs.

During adsorption in GAC filters, the front of the DOM breakthrough curve usually moves faster than that of the OMPs, due to the presence of DOM that is less adsorbable than OMPs, and then preloads the activated carbon before OMPs' adsorption. The sequence of adsorption onto GAC is then: weakly adsorbable DOM, strongly adsorbable DOM, and, finally, OMPs (assuming that OMPs are strongly adsorbable). Although the preloading effect has been reported to reduce the OMP adsorption considerably, OMP displacement with already adsorbed DOM could still alleviate the adverse impacts from preloading (Li et al., 2002b). Therefore, OMP adsorption capacity during GAC adsorption cannot be well estimated with batch-wise OMP adsorption isotherm tests in DOM-containing waters (Crittenden et al., 2012), where simultaneous adsorption is studied.

Although DOM competition is considered ubiquitous, complementary adsorption has also been reported between some model organic substances with a high accumulative adsorption capacity but low/no competition. The various co-adsorbates may then target different adsorption sites (Pan and Xing, 2010; Sander and Pignatello, 2005; Zhang et al., 2012), or interact with each other through π-π interactions or complexation (Guillossou et al., 2020; Shimabuku et al., 2017b; Zhang et al., 2020a).

## 3.3 Key characteristics of competitive DOM

DOM competition does not originate from all DOM components and the competitiveness would be overrated if all DOM is considered as effective competitors (Najm et al., 1991;

Worch, 2010). Distinguishing effectively adsorbable DOM components from the bulk is therefore important for the prediction of competitive OMP adsorption and the development of mitigation strategies for DOM competition.

The top-down approach (using real DOM samples) and bottom-up approach (using model DOM compounds) are typically employed for studies identifying key DOM characteristics (e.g., the formation or toxicity of disinfection by-products). Examination of competitive adsorption, using a limited number of model organics, provides direct evidence for elucidating the role of key DOM molecular characteristics, but is far from the water treatment practice. However, systematically analyzing multiple DOM properties is a challenge in the characterization of real DOM matrices.

More than molecular size, hydrophobicity/polarity, aromaticity, and charge are crucial for determining DOM adsorbability and competitiveness. Although the terms hydrophobicity and polarity are used separately, they are similar in terms of DOM characteristics: a low polarity usually indicates a high hydrophobicity (Rummel et al., 2021; Wang et al., 2019b). Table 2 shows the use of both terms to describe DOM properties at different levels. DOM hydrophobicity is commonly used with regard to DOM fractions or specific DOM molecules, because of the widely used DOM fractionation by hydrophobic resins (Croué, 2003), and the quantitative logD at specific pH values (ChemAxon, 2021). However, in high-resolution mass studies, there is no available method to define hydrophobicity for molecular formulas, whereas their polarity, derived from the molecular elemental composition, is usually adopted (Riedel et al., 2012). Charged DOM in solution has usually a lower hydrophobicity than the undissociated species. Therefore, the logD gap of LMW DOM between undissociated species and dissociated species is large (~3 for the two examples in Figure 2), implying that the hydrophobicity of DOM molecules can be decreased due to dissociation of the molecules, although the dissociation potential cannot be derived from the elemental compositions of molecular formulas.

*Table 2* *The usage of hydrophobicity and polarity to describe DOM characteristics at different levels.*

|  | Hydrophobicity | Polarity |
|---|---|---|
| Fraction level | (Preferred) resin fractionation (Croué, 2003) | elemental analysis; (O+N)/C (Kang and Xing, 2008) |
| Molecular formula level | not available | (Preferred) nominal oxidation state of carbon (NOSC); NOSC = 4-((4C+H-3N-2O-2S)/C) (Riedel et al., 2012) |
| Molecule level | (Preferred) logD at specific pH (ChemAxon, 2021) | polarizability (Jensen et al., 2002) |
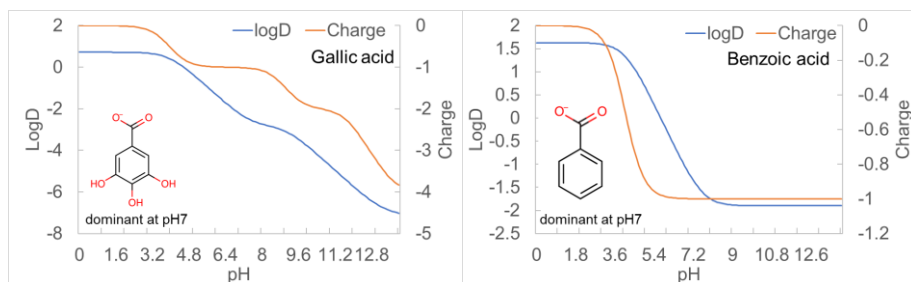


*Figure 2* *Log D and charge gallic acid and benzoic acid (two typical LMW DOM) at different pH. Data from Chemicalize (ChemAxon, 2021).*

With similar pore accessibility as OMPs (similar MW), DOM hydrophobicity and aromaticity are considered to be the most determining factors for DOM adsorbability, through influencing hydrophobic interaction and π-π interaction on the activated carbon surface. The role of hydrophobicity on DOM adsorption and competition against OMPs have experimentally been verified by DOM fractionation on hydrophobicity (with frequently-used XAD resins) (Karanfil et al., 2006; Lerman et al., 2013). However, the studies on the contribution of aromaticity to DOM competitiveness are still lacking. In real DOM matrices, aromatic structures are ubiquitous and the collective assessment of aromaticity is usually estimated using specific ultraviolet absorbance (SUVA) at 254 nm or 260 nm. Higher values of SUVA have been found in the hydrophobic and HMW DOM fractions, so it is usually recognized that hydrophobic and/or HMW DOM have higher aromaticity (Kennedy et al.,

2005; Song et al., 2016; Stenson, 2008). Nevertheless, in a previous study, a large decrease in SUVA has been observed after DOM pretreatment using anion exchange resin (AER), without much alleviation of DOM competition (Hu et al., 2014), which calls for more studies on how aromaticity impacts DOM competitiveness.

Moreover, the impact of DOM dissociation on DOM hydrophobicity, adsorbability and competitiveness could be considerable but is often undervalued. The presence of carboxyl or phenol groups induces DOM dissociation negatively, affecting the adsorbability and thus decreasing the competitiveness against OMPs. This is possibly due to the reduced hydrophobicity after the dissociation, or to electrical repulsion by co-adsorbing/adsorbed DOM. For example, Yang et al. (2010) found that the adsorption of (apolar) naphthalene was suppressed by neutral species 2,4-dichlorophenol (DCP) and 4-chloroaniline (PCAN), but not by their dissociated species. Regardless of the concentration of the dissociated competitors, little impact was observed on the loading of the neutral adsorbate; but reducing ionic (disassociated) DCP/PCAN loading with an increasing number of nonpolar competitors. Similar results have been obtained by the competition between dissociated sulfamethoxazole/17α-ethinyl estradiol and neutral bisphenol A (Pan et al., 2008; Zhang et al., 2012), and between dissociated sulfamethoxazole and neutral carbamazepine (Wang et al., 2013a). This may explain the unaltered isotherms of nonpolar OMPs (atrazine and caffeine) after DOM removal by AER (especially targeting the dissociated species), as found by Hu et al. (2014). Neutral DOM could thus have played a major role in the competition against OMPs on account of its superiority over ionic DOM regarding adsorbability and competitiveness.

While the above-discussed DOM properties are used to categorize different DOM substances, there is profound collinearity among them. DOM properties are not independent variables, and consequently, it is often difficult to distinguish the impact of a single DOM characteristic on competitiveness. On the other hand, experimental DOM fractionation on multiple properties (e.g., MW and hydrophobicity) at the same time is usually impossible, as it suffers from the low accuracy of DOC measurements (e.g., < 0.5 mg C/L) for an increased number of DOM fractions at lower concentrations. However, novel LC-based DOM characterization methods, using size exclusion chromatography coupled with synchronous measurements using UV absorbance, DOC, and even fluorescence detection and mass spectrometry (Cai et al., 2019; Han et al., 2021; Park et al., 2020a; Spranger et al., 2019), are promising to

decouple the collinearity of DOM properties and explain how properties influence DOM competitiveness.

## 3.4 Mitigating DOM competition

The alleviation of DOM competition is beneficial to increase the OMP removal and maximize the carbon usage efficiency in practice. Restricting the DOM adsorbability, especially for LMW fractions, is the core of existing ideas on reducing DOM competitiveness. Oxidation, coagulation, and biodegradation can assist in the alleviation of the negative DOM impact on OMP adsorption in different ways. Pre-oxidation is used to reduce DOM hydrophobicity and aromaticity, for both the HMW and the LMW fractions (Stylianou et al., 2018). However, it should be considered that the increased LMW DOM from degraded HMW components may counterbalance the reduced DOM competitiveness from oxidation-induced reductions in DOM hydrophobicity/aromaticity (Deng et al., 2015; Newcombe et al., 2002b). Alleviated DOM competition by ozonation pretreatment was e.g., observed in wastewater treatment plant effluent, where the break-up of a low percentage of HMW compounds did not result in strongly adsorbing LMW competitors, and the overall reduced aromaticity and hydrophobicity resulted in a lower DOM adsorbability and competitiveness. (Zietzschmann et al., 2015b). Non-oxidative pre-treatment, such as coagulation and anion exchange, reduce DOM competition only marginally during PAC adsorption, but it has been found that these pretreatment methods can postpone OMP breakthrough in GAC filtration (especially for poor adsorbates like bentazon), and prolong the GAC lifetime, by mitigating the continuous DOM preloading and pore blocking during GAC operation (Hu et al., 2014; Kennedy and Summers, 2015). Microbial degradation of adsorbed DOM in biological activated carbon (BAC) also contributes to postpone the GAC saturation, preceded by desorption from micropores/mesopores to micro-level macropores where biomass is attached (de Jonge et al., 1996; Lu et al., 2021; Lu et al., 2020). Long-term removal of DOM and OMPs, and a longer GAC service time, are thus expected in water treatment with BAC (Altmann et al., 2016b; Ross et al., 2019).

Adjustment of the adsorbents' characteristics, like pore structure and surface chemistry, has also been considered as an alternative for mitigating DOM competition. A larger volume of primary micropores (< 0.8 nm) benefits the adsorption of small aliphatic OMPs (TCE or 2-MIB) in DOM-containing waters by minimizing DOM penetration (Karanfil et al., 2006),

while rich secondary micropores (0.8-2 nm) and small mesopores are more important for alleviating direct site competition against atrazine (Karanfil et al., 2006; Li et al., 2003d; Pelekani and Snoeyink, 2000). For activated carbon with rich oxygen-containing functional groups, the adsorption of a hydrophobic OMP (e.g., TCE) is more suspectable to the interference from the co-adsorbing DOM, but no increased competition against the hydrophilic MTBE has been observed as compared to activated carbon with a low oxygen content (Quinlivan et al., 2005).

## 4. OMP adsorption prediction

From a practical perspective, accurate estimation of OMP removal at different locations/conditions is crucial for designing and operating the activated carbon adsorption process. The common approaches mainly consist of DOM surrogate deduction and model prediction.

### 4.1 Deduction using DOM surrogates

Deriving the OMP removal could be empirically realized by measuring the removal of online measurable DOM surrogates like UV absorbance or fluorescence peaks (Zietzschmann et al., 2016a), of which the feasibility has been demonstrated during ozonation and other advanced oxidation processes (Chen et al., 2017; Sgroi et al., 2017). The adsorptive performance of OMPs has been correlated with the change in $UV_{254}$ or total fluorescence intensity during PAC adsorption in a slurry reactor (Zietzschmann et al., 2014a; Ziska et al., 2016). The different slopes, of the linear sections of the established correlations, have been attributed to the different preferences of OMP removal as compared to DOM removal. Increased preferences of activated carbon for OMPs adsorption have been found in ozonated water, compared to the reduction of $UV_{254}$, an indication of decreased DOM competitiveness, whereas they remained unchanged in coagulated water (DOM competitiveness unaffected) (cf. Figure 3), implying that the derived slopes may help to indicate the level of DOM competitiveness (Altmann et al., 2015; Zietzschmann et al., 2015b). The method has been transferrable to different DOM compositions (Zietzschmann et al., 2016b), and usable for the adsorption of PACs of varying characteristics (BET surface, iodine number, etc.). However, for some OMPs, such as sulfamethoxazole and benzotriazole (weakly adsorbable OMPs), the correlation had to be established for every applied PAC individually (Zietzschmann et al., 2014a).
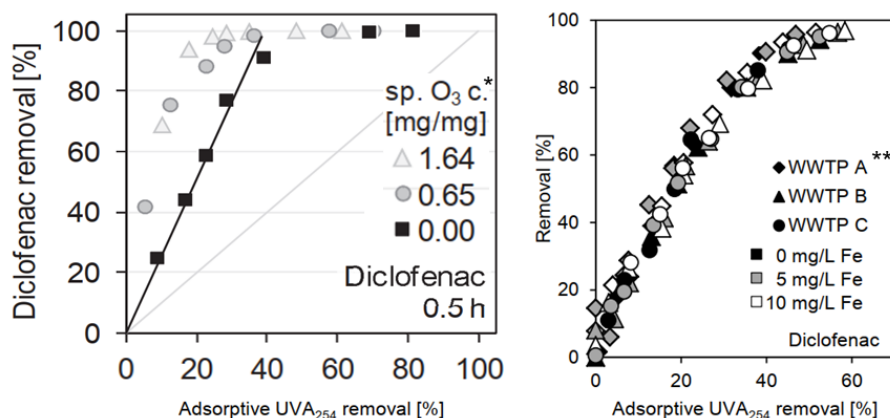
**Figure 3** *PAC adsorptive removals of diclofenac removals versus adsorptive UV$_{254}$ removals in ozonated /non-ozonated waters after 0.5 h of adsorption (left panel) (Zietzschmann et al., 2015b); coagulated /noncoagulated waters from different wastewater treatment plants (WWTPs) (right panel) (Altmann et al., 2015).*

The GAC breakthrough of UV$_{254}$ and/or total fluorescence intensity has also been correlated to OMP breakthrough in water with similar DOM composition (e.g., among wastewaters) (Anumol et al., 2015; Sgroi et al., 2017). Proteins and tyrosine-like fluorescence-active organics ($\lambda_{ex}/\lambda_{em}$ = 225/290 nm) are preferentially adsorbed over humic-like fluorescence-active ($\lambda_{ex}/\lambda_{em}$ = 245,350/450 nm) and UV-active compounds. Therefore, proteins and tyrosine-like fluorescence peaks are suitable for monitoring the strongly adsorbable OMPs, while the humic-like fluorescence peak has been associated with moderately adsorbable OMPs (Sgroi et al., 2017). In addition, a high fluorescence index (the ratio of $\lambda_{em}$ at 470 and 520 nm, at $\lambda_{ex}$ 370 nm) has been recognized as a good indicator for lower average DOM sizes and higher competitiveness against OMPs (Ren et al., 2021; Shimabuku et al., 2017a). In addition, the breakthrough of LMW organics (as measured via LC-OCD) can directly be related to OMP adsorption in different waters, compensating for the large difference in DOM MW distribution, from drinking water to wastewater effluents (Zietzschmann et al., 2016b). However, the most biodegradable OMPs and the poorly adsorbable OMPs are the least predictable with the above DOM indices (Guillossou et al., 2021).

## 4.2 Model prediction

Precise model predictions toward OMP adsorptive removal can be an efficient tool to reduce laboratory testing and to proactively estimate the treatability of emerging contaminants. As shown in Figure 4, accurate OMP removal prediction with *an ideal knowledge-based process model* requires the input of (i) OMP descriptors for elemental composition and chemical structure; (ii) carbon properties; (iii) parameters related to water matrix, for example, pH and DOM descriptors for competitiveness (on OMP equilibrium adsorption capacity and kinetics), and (iv) key process conditions to describe the hydrodynamic conditions and mass transfer dynamics (for instance, the mixing and contact time for PAC slurry reactors; or empty bed contact time in a GAC filter) (Crittenden et al., 2012; Wols and Vries, 2012; Worch, 2012). To predict the single-solute OMP equilibrium adsorption onto activated carbon, only OMP descriptors and carbon properties are required, while DOM characteristics and process conditions should be considered to achieve a more advanced prediction of non-equilibrium OMP adsorption in the presence of background DOM.
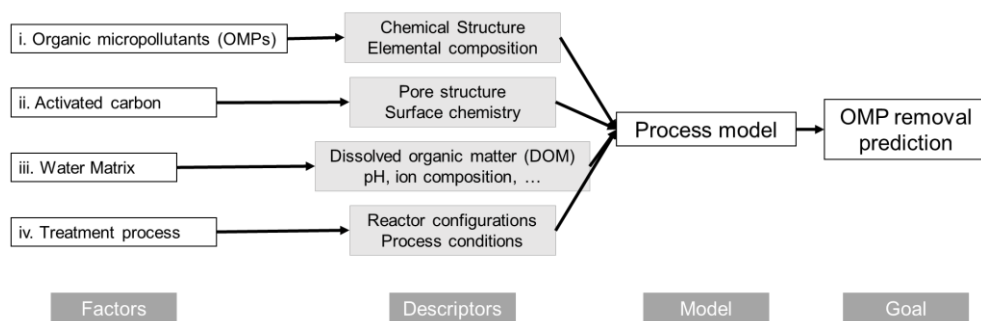


*Figure 4* *The framework for an ideal knowledge-based model to predict the OMP removal by activated carbon adsorption.*

To predict OMP affinity on activated carbon in deionized water, recent progress in machine learning techniques (such as neural networks) has expanded the effective prediction to the adsorption of 165 organic pollutants on 35 GACs and some other carbonaceous materials (Zhang et al., 2020b). Polyparameter linear free energy relationships (pp-LFERs), including E (excess molar refraction), S (dipolarity/polarizability), A (H-bond acidity), B (H-bond basicity), and V (molar volume), have been selected to describe organic pollutants, while pH

was considered and BET surface area and pore volume have been identified as the key parameters for the adsorbents (Zhang et al., 2020b). The abundance of negatively/positively charged species has further been included for better prediction of ionizable and polar OMPs (Sigmund et al., 2020). Regarding activated carbon properties, Bunmahotama et al. (2015) have proposed to only use the pore volume with a diameter less than 3.2 nm, including micropores and small mesopores, instead of the total pore volume, to describe the properties of activated carbon. The surface chemistry was not considered due to the relatively high hydrophobicity of examined OMPs (Bunmahotama et al., 2015). For a practical-oriented OMP adsorption prediction, the trace level concentrations have not been well discussed in established models, due to high pollutant concentration (usually in mg/L, not environmentally relevant) in the collected adsorption dataset, which calls for more studies in this field.

To quantify the impact of DOM on the OMP removal, the ideal adsorbed solution theory (IAST) has been used as the basis for multi-solute competitive adsorption (Worch, 2012). However, the complicated composition and the heterogeneity of DOM compounds have restricted the applicability of IAST (Najm et al., 1991). Therefore, the equivalent background compound model (EBCM) has been developed to describe DOM competitors as a fictive background compound and assigns all DOM competition to this fictive competitor (Najm et al., 1991). The initial objective of IAST-EBCM was to describe the interplay of competitors and the OMP at different initial concentrations, and predict the corresponding OMP isotherms (see section 1.2 for variable DOM competition at various initial OMP concentrations). The feasibility of the IAST-EBCM used in non-equilibrium prediction has also been explored (Zoschke et al., 2011). However, the difficulty in generalizing the IAST-EBCM prediction in different waters has mainly been attributed to the lack of knowledge of DOM characteristics (Zietzschmann et al., 2016a). Therefore, to compare the DOM competitiveness in differently pretreated waters, EBCM has been simplified using a simplified Freundlich Isotherm model with fixed 1/n, and global K values for the respective constants, while only varying initial EBC concentrations ($C_{0,EBC}$). Zietzschmann et al. (2016a) have correlated the DOC concentrations and UV absorbance of LMW organics to quantify DOM competitiveness using $C_{0,EBC}$. A similar relationship has been found between $C_{0,EBC}$ and the fluorescence index (Ren et al., 2021; Shimabuku et al., 2014; Shimabuku et al., 2017a).

However, until now little is known about how $C_{0,EBC}$ behaves across different activated carbon samples.

The homogeneous surface diffusion model (HSDM) is the most commonly used to predict the kinetics of OMP adsorption onto activated carbon (Worch, 2012). With OMP isotherm experiments (at various PAC doses) and kinetic experiments at one PAC dose, the OMP diffusion coefficient can be determined in the presence of DOM and, subsequently, OMP removal at various PAC doses could be estimated (Zhang et al., 2009). Further attempts in simplifying the HSDM showed that, by assigning the Freundlich 1/n constant in the range of 0.1-1.0, the value for the Freundlich equilibrium parameter K and the diffusion coefficient $D_s$ value could be obtained through an adsorption kinetics test of only 6 h (Yu et al., 2016). An HSDM-based three-component competitive adsorption model (OMP, directly competing DOM and pore blocking DOM) has successfully been verified in PAC/membrane systems and in fixed-bed/moving-bed GAC adsorbers (Ding et al., 2006; Li et al., 2003a; Schideman et al., 2006a; Schideman et al., 2006b; Schideman et al., 2007). Note that no linkage between parameters in the adsorption kinetics models and carbon properties or DOM characteristics have been established so far.

## 5. Objectives and research questions

LMW DOM has been recognized as the primary competitor against OMPs for the adsorption sites in activated carbon adsorption. However, different DOM molecular properties have a strong influence on the adsorption capacity. It is still not clear how these (LMW) DOM molecular properties and the (LMW) DOM adsorbability relate to the competitiveness against OMPs, which is a key limiting factor for the precise prediction of adsorptive OMP removal in DOM-containing waters. Although numerous studies have attempted to reveal DOM competition mechanisms, the strategy to separate DOM competitors has not been well developed; and thus the molecular composition and adsorption behavior of DOM competitors, as compared to the co-adsorbing non-competitors, is also not elucidated.

Therefore, the objective of this study is to relate DOM characteristics to the DOM competitiveness against OMPs in activated carbon adsorption and to clarify the mechanism of direct site competition, in order to obtain a widely applicable method in the prediction of DOM competition against OMPs.

To realize the objective above, several research questions were proposed and addressed in the different chapters of the thesis. The structure of thesis is shown in Figure 5.
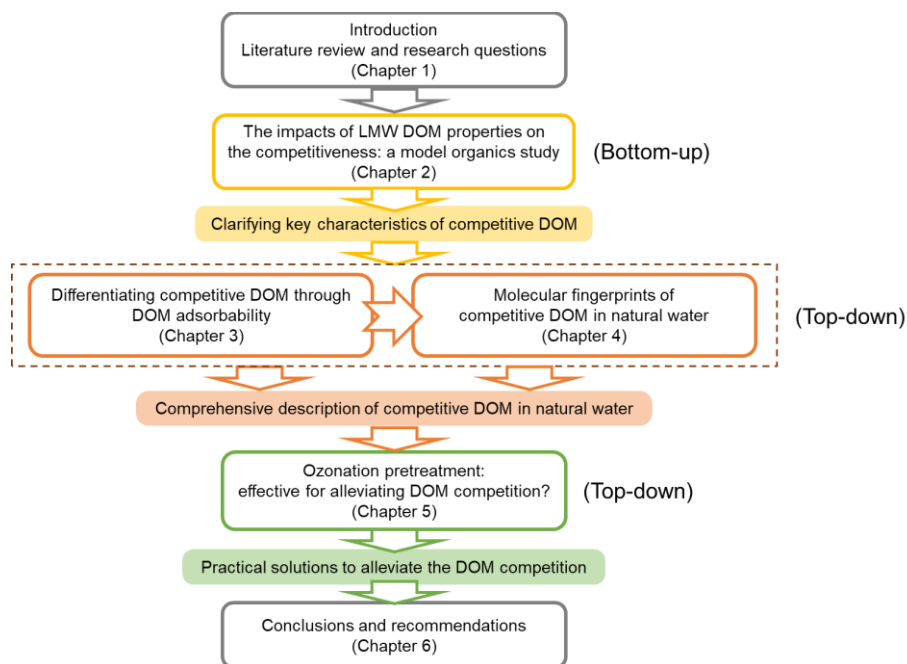


*Figure 5* *A framework of the thesis and the relationship between chapters.*

**How do properties of model LMW DOM impact OMP adsorption onto activated carbon at environmentally relevant (asymmetric) concentrations?**

**Chapter 2** aims at elucidating the role of key DOM molecular characteristics on the competitiveness against OMPs. Fifteen LMW model DOM compounds (mDOM) compounds, different in several functional groups, (hydroxyl groups, phenol groups, carboxyl groups, etc.), were used to assess the impact of LMW DOM characteristics on DOM competitiveness against six OMPs that differed in physicochemical properties. Three DOM characteristics (hydrophobicity, aromaticity and adsorbability) were discussed and related to competitiveness. It is further illustrated how the adsorbability of mDOMs and OMPs influenced the level of competitive adsorption.

**What is the impact of OMP adsorbability and concentration on competitive adsorption with DOM in natural water?**

Based on the DOM competitiveness indicator (i.e., adsorbability) found in Chapter 2, **Chapter 3** was designed to use DOM adsorbability to differentiate DOM competitors in natural water. The focus was to separate adsorbable DOM fractions that do not compete with OMPs. The adsorption characteristics of DOM fractions and OMPs were therefore determined by removing various DOM adsorbable fractions with PAC pretreatment and then revealing the competitiveness against OMPs of the remaining DOM. The impact of OMP adsorbability and initial OMP concentration on the variability of DOM competitiveness was also discussed.

**What is the interplay between molecular weight, aromaticity, and polarity of natural water DOM in competitive adsorption against OMPs?**

In **Chapter 4**, the competitive DOM was separated using PAC and AER, respectively, according to the DOM adsorbability and DOM dissociation capacity at neutral pH. A molecular-level analysis was conducted to analyze the DOM fractions with different competitiveness using ultrahigh-resolution Fourier transform mass spectrometry, and the composition of molecular formulas in competitive DOM was revealed. Subsequently, semi-quantitative removal of molecular formulas was related to MW, polarity and aromaticity, to discuss their roles in determining DOM adsorbability and competitiveness. DOM isomers with different polarities were investigated to elucidate the influence of molecular configuration on the preference of PAC adsorption.

**How decreased DOM aromaticity and accumulated LMW DOM influence the competition of various ozonated waters, with a large difference in DOM molecular size distribution (Chapter 5)?**

During ozonation, usually, LMW DOM is produced, and the DOM aromaticity/hydrophobicity is reduced, which has contradicting impacts on the DOM competitiveness against OMP in activated carbon adsorption. In **Chapter 5**, the effects of

ozonation on the DOM characteristics, and the related impacts on the competitiveness against 2-MIB, were studied in four waters with largely heterogenous DOM characteristics, varying in DOC, specific ultraviolet absorbance (SUVA) and molecular weight distribution. By measuring the amount of adsorbed LMW DOM, it is discussed how reduced aromaticity/hydrophobicity counterbalanced the increased amount of LMW DOM in determining DOM competitiveness. Two surrogates for DOM competitiveness were compared by relating to the initial concentrations of competing DOM estimated by EBCM.

# Chapter 2

# How properties of low molecular weight model competitors impact organic micropollutant adsorption onto activated carbon at realistically asymmetric concentrations
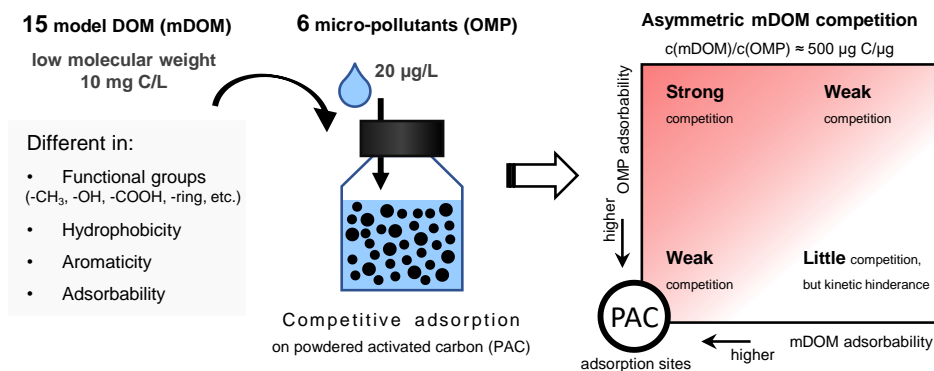
# Abstract

Low molecular weight (LMW) dissolved organic matter (DOM) is the predominant competitor for adsorption sites against organic micropollutants (OMPs) in activated carbon adsorption. However, top-down approaches using highly complex mixtures of real water DOM do not allow for a concise examination of the impacts of specific LMW DOM molecular properties on competitive adsorption. Therefore, we followed a bottom-up approach using fifteen model compounds (mDOM) to elucidate how important DOM characteristics, including hydrophobicity and unsaturated structures (ring, double/triple bond), impact competitiveness. Large concentration asymmetry (~500 µg DOC/µg OMP) made mDOM compounds, which were overall less preferentially adsorbed than OMPs, become competitive against OMPs and inhibit OMP adsorption kinetics by pre-occupation of adsorption sites. Our results revealed that both hydrophobicity interactions and π-interactions increased mDOM competitiveness, while π-interactions outweighed hydrophobic interactions. However, π-interactions could not be satisfactorily evaluated with a parameter such as specific ultraviolet absorbance (SUVA) due to interferences of carboxyl groups in aromatic mDOMs. Instead, mDOM adsorbability, described by mDOM adsorption capacity, proved to be a comprehensive indicator of mDOM competitiveness. To our knowledge, this is the first study that systematically clarifies the impacts of intricately interacting molecular properties on DOM adsorption and the related competition against OMP adsorption. DOM adsorbability may inspire a new fractionation, and assist the further isolation, identification and detailed characterization of LMW DOM competitors in real DOM-containing waters.

# 1. Introduction

Organic micropollutant (OMP) removal is important in advanced drinking water and wastewater treatment and for that purpose activated carbon adsorption is commonly used (Fundneider et al., 2021; Guillossou et al., 2020; Reemtsma et al., 2016). However, adsorptive OMP removal efficiency is substantially restricted by simultaneous competitive adsorption of coexisting dissolved organic matter (DOM) (Kilduff et al., 1998; Nakayama et al., 2020).DOM is a complex mixture of mostly unknown constituents, reflected by a wide molecular weight (MW) distribution and broad molecular composition (Zhang et al., 2020c), varying in time and per location. In addition, DOM concentrations (in mg/L) are usually several orders of magnitude higher than those of OMPs (in ng/L-µg/L) (Jeirani et al., 2017), known as concentration asymmetry.

Pore blockage and direct site competition are the primary DOM interference mechanisms, but contribute differently according to the pore size distribution of the applied activated carbons (Ebie et al., 2001; Guillossou et al., 2020).*E.g., a smaller portion of mesopores in the pore structure might lead to pore blockage becoming a more important mechanism, even for powdered activated carbon (PAC)* (Ebie et al., 2001). High molecular weight (HMW) DOM usually adsorbs on the shell region of activated carbon and inhibits OMP diffusion into micropores, and is barely relevant in relation to direct site competition (Ando et al., 2010; Li et al., 2003d). Low molecular weight (LMW) DOM is the dominant site competitor against OMPs at equilibrium adsorption (Zietzschmann et al., 2014b). However, characterizing distinctively and systematically the key molecular properties of bulk LMW DOM and their relation to DOM competitiveness is difficult using top-down approaches with real DOM matrices.

Using model DOM compounds (mDOM) is a typical bottom-up method, providing direct evidence for elucidating the role of key DOM molecular characteristics (Dittmann et al., 2018). A variety of molecular characteristics can be responsible for adsorbability and competitiveness, including hydrophobicity, aromaticity (π-interaction capacity), polarity, charge and geometrical configurations, while hydrophobicity and aromaticity were proved to be two predominant properties affecting LMW DOM/OMP adsorption in previous model compounds studies (Ersan et al., 2017; Kah et al., 2017; Ling et al., 2019). The impacts of LMW DOM have been well confirmed with mDOM (Li et al., 2003b; Matsui et al., 2012; Wang

et al., 2020), but few studies have been performed to systematically examine the simultaneous impacts of LMW DOM properties like hydrophobicity and aromaticity on competitiveness against OMPs. Increasing hydrophobicity or aromaticity ameliorated mDOM adsorption (Lin and Xing, 2008) and aggravated competitiveness against perfluorinated compounds (Deng et al., 2015). However, complementary adsorption was previously reported in bisphenol A and sulfamethoxazole adsorption, where competition at a low level was found (Zhang et al., 2012). The partially contradicting findings from these important studies underline that there is still a knowledge gap on DOM properties and the related influence on DOM adsorption and competitiveness against OMP adsorption. A reason for this gap might be the difficulty to differentiate between several molecular properties as well as between their impacts: changing a single molecular property whilst keeping all others constant is typically not possible.

Therefore, the objective of the present study was to identify the impacts of LMW mDOM characteristics on their competitiveness against OMP adsorption onto PAC, focusing on direct competition at realistically asymmetric concentrations (DOC/OMP $\approx$ 500 μg C/μg). For this purpose, fifteen LMW mDOM compounds, different in functional groups in six subgroups (hydroxyl groups, phenol groups, carboxyl groups, etc.), were used to represent several primary DOM structures. Apart from equilibrium adsorption, the competition at non-equilibrium adsorption was also included to represent the competitive adsorption at practical contact times. The results of this study facilitate the understanding of DOM adsorption and asymmetric competition with OMPs, and could be used for targeted separation and control of LMW competing DOM in water/wastewater treatment processes.

## 2. Materials and Methods

### 2.1 Model DOM compounds and OMPs

Fifteen LMW organic substances with different functional groups (hydroxyl, phenol, carboxyl groups, rings of carbon atoms), and with varying hydrophobicity and aromaticity, were used as mDOM competitors adsorbates in PAC batch experiments (Table 1). The descriptors of the mDOM molecular structures/properties are given in Table 2; Log D and charge at pH 7 were derived from Chemicalize (ChemAxon, 2021). In order to exclude the impacts of multi-site adsorption and over-complicating geometrical configurations (e.g the "butterfly" configuration of bisphenol A was favorable for adsorption) (Pan et al., 2008) on
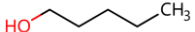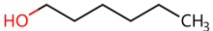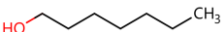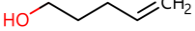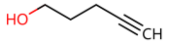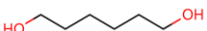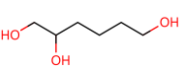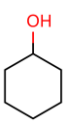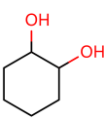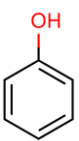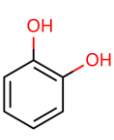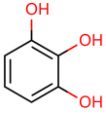
mDOM adsorbability and competitiveness, lower molecular weight mDOMs (84-210 g/mol) were used, comparing to real-water DOM whose majority of molecules ranges around 1000 g/mol. Using relatively small mDOMs here allowed to differentiate more easily between the effects of different molecular properties (e.g. hydrophobicity, aromaticity).
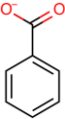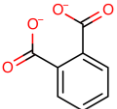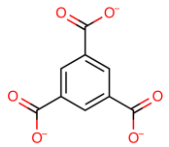
Ultra-pure water (ELGA Labwater, Germany; resistivity >17 MΩ·cm, DOC <0.2 mg/L) was used for preparing the synthetic waters, containing a mixture of six frequently observed OMPs in wastewater treatment plants (WWTPs) effluents (benzotriazole, sulfamethoxazole, iopromide, carbamazepine, diclofenac, and bezafibrate, characteristic parameters in Table S1) and each one of the mDOM substances, respectively. Prior to the preparation of the synthetic waters, the ultra-pure water was treated with an excess amount of PAC (> 1 g/L) for ≥ 24h, to completely remove any adsorbable molecules; the PAC was subsequently removed by membrane filtration (0.2 μm cellulose nitrate membrane filter rinsed with ultra-pure water, Whatman, Germany). The target concentrations of the employed mDOMs were ~10 mg C/L to simulate the DOC level of organic-rich source waters or WWTP secondary effluents (Hu et al., 2016) and attain the envisaged realistic concentration asymmetry (Table S2). pH was adjusted to 7-8 for all mDOM samples.

***Table 1*** *Overview of model substances used to examine hydrophobicity and aromaticity.*

| Substance group | Varied functional groups | Substances | Varying property |
|---|---|---|---|
| alcohols | carbon atoms in aliphatic chain of alcohol | pentanol, hexanol, heptanol | Hydrophobicity (by log D at pH7, from Chemicalize) |
| | hydroxyl groups | hexanol, hexanediol, hexanetriol | |
| | double/triple bonds | pentanol, 4-penten-1-ol, 1-pentyn-5-ol | |
| | hydroxyl groups, on a cycloalkane | cyclohexanol, cyclohexanediol | |
| phenols | hydroxyl groups, on an aromatic ring | phenol, benzenediol, benzenetriol | aromaticity aromatic ring activation/deactivation (by SUVA, experimentally determined) |
| aromatic carboxylic acids | carboxyl groups, on an aromatic ring | benzoic acid, phthalic acid, trimesic acid | |

***Table 2*** *Molecular properties of competitive mDOM compounds. SUVA values were experimentally calculated while other parameters were from Chemicalize (ChemAxon, 2021).*

| Name | Predominant species at pH 7[a] | CAS # | MW (g/mol) | logD at pH7 | Charge at pH7 | SUVA (L/mg/m) |
|---|---|---|---|---|---|---|
| pentanol | | 71-41-0 | 88 | 1.25 | 0 | - |
| hexanol | | 111-27-3 | 102 | 1.69 | 0 | - |
| heptanol | | 111-70-6 | 116 | 2.14 | 0 | - |
| pentenol | | 821-09-0 | 86 | 0.94 | 0 | - |
| pentynol | | 5390-04-5 | 84 | 0.44 | 0 | - |
| hexanediol | | 629-11-8 | 118 | 0.26 | 0 | - |
| hexanetriol | | 106-69-4 | 134 | -0.82 | 0 | - |
| cyclohexanol | | 108-93-0 | 100 | 1.28 | 0 | - |
| cyclohexanediol | | 1792-81-0 | 116 | 0.63 | 0 | - |
| phenol | | 108-95-2 | 94 | 1.67 | 0 | 0.66 |
| benzenediol | | 120-80-9 | 110 | 1.36 | -0.04 | 0.90 |
| benzenetriol | | 87-66-1 | 126 | 1.06 | -0.1 | 4.64 |

| Name | Predominant species at pH 7[a] | CAS # | MW (g/mol) | logD at pH7 | Charge at pH7 | SUVA (L/mg/m) |
|---|---|---|---|---|---|---|
| benzoic acid | | 65-85-0 | 122 | -1.20 | -1 | 0.86 |
| phthalic acid | | 88-99-3 | 166 | -3.65 | -2 | 1.28 |
| trimesic acid | | 554-95-0 | 210 | -7.90 | -3 | 1.56 |

## 2.2 PAC batch tests

PAC SAE Super (Norit, the Netherlands) was used in all experiments. The mesopore percentage of the selected PAC was ~50% (Table S3), underlining the relevance of direct site competition in the present study, and rendering pore blockage less relevant (high amount of mesopores unlikely to be completely blocked) (Ebie et al., 2001), also relating to somewhat faster diffusion and shorter time required for adsorption equilibrium (Piai et al., 2019).

The applied PAC was dried in a drying cabinet at 105 °C for ≥ 24 h and cooled in a desiccator before use. The six OMPs were spiked into the various mDOM solutions with 20 µg/L of each OMP before PAC dosage. A 100 mL bottle-point method was used during PAC batch tests, with several PAC dosages (2.5-150 mg/L). The bottles were placed on a linear shaker to ensure a completely turbulent mixing of PAC and sample solution. Samples for every PAC concentration were prepared in parallel, once for 30 minutes and once for 48 hours of adsorption time, to examine the adsorption competition at both non-equilibrium and equilibrium conditions. Samples were filtrated using a 0.45 µm membrane (Chromafil Xtra, RC-45/25, regenerated cellulose, rinsed with ultra-pure water) before analysis.

## 2.3 Analytical methods

OMP concentrations were determined using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS), equipped with a HSS T3 HPLC column (compound size 2.5 μm, 50 * 2.1 mm, Waters, USA). The mobile phases were 0.1 % formic acid (Sigma Aldrich) and methanol (HPLC gradient grade, J.T. Baker, USA). The mass spectrometer was a triple stage quadrupole mass spectrometer (TSQ Vantage, Thermo Scientific, USA) using positive electrospray ionization. OMPs were identified with two mass fragments and quantified with deuterated internal standards.

DOC analysis was performed on a Vario TOC CUBE (Elementar Analysensysteme, Germany). $UV_{254}$ was measured by a UV-Vis spectrophotometer (Lambda 12, Perkin-Elmer, USA) and specific ultraviolet absorbance (SUVA) in Table 2 was subsequently calculated by dividing $UV_{254}$ by DOC concentration (Weishaar et al., 2003).

## 2.4 Evaluation of mDOM adsorption and competitiveness

To be able to compare the overall mDOM adsorbability of mDOM, the PAC demand for removing 20% of the respective mDOM from the aqueous solution (in short, DOC-PAC20%) was calculated (Zietzschmann et al., 2015b). The value was determined by linear interpolation. 20% DOC removal was chosen to avoid too much extrapolation for weakly adsorbable mDOM (for trimesic acid, 20 % mDOM removal was not reached with the maximum carbon dose of 150 mg/L; here the DOC-PAC20% was extrapolated using the two highest carbon doses). The same procedure was used to calculate the PAC demand for 80% OMP removal (OMP-PAC80%), as 80% OMP removal of micropollutants is an often-applied elimination target (Swiss Confederation, 2016). To be able to disregard any initial concentration differences of the competitor adsorbates, these two parameters were normalized for the initial concentrations of the respective competitor adsorbates. Plotting OMP-PAC80% values against DOC-PAC20% values enabled the comparison of mDOM competitiveness against OMPs in relation to the respective mDOM adsorbability.

## 3. Results and discussion

### 3.1 Competitive adsorption for different OMPs

The removals of the six OMPs are depicted in Figure 1 (original data in Figure S1), in absence and presence of mDOM adsorbates, and with adsorption times of 0.5 h and 48 h, in order to illustrate the differences among OMPs in adsorption and competition by co-existing mDOM competitors. 2.5 mg/L PAC dose was chosen here for better visualization of the OMPs adsorption differences, mDOM impacts and adsorption time effects. Bezafibrate had the highest removal after 48 h equilibrium adsorption without mDOM interference, followed by diclofenac, carbamazepine, iopromide, sulfamethoxazole and benzotriazole. Furthermore, the strongly adsorbing OMPs were less affected by coexisting mDOM competitors, which was consistent with previous studies (Guillossou et al., 2020; Zietzschmann et al., 2016a). The overall reduction in OMP removal by mDOM competition (OMP removal in mDOM-free water minus OMP removal in mDOM-containing waters) was the opposite of the order of OMP adsorbability (benzotriazole > sulfamethoxazole > iopromide > carbamazepine > diclofenac > bezafibrate). Regarding the strongly adsorbing OMPs (bezafibrate, diclofenac, carbamazepine), only a few mDOM competitors could considerably reduce their removal efficacy at equilibrium adsorption. In contrast, nearly all mDOM competitors substantially decreased the adsorption of the weak OMP adsorbates (benzotriazole, sulfamethoxazole). Apparently, a larger number of mDOM compounds were able to compete for the adsorption sites on the activated carbon surface with the weakly adsorbing OMPs. Iopromide was the only examined OMP adsorbate with a relatively high MW (791 g/mol) and its adsorption was also impacted by LMW mDOM competitors (84 - 210 g/mol), implying that the adsorption sites for this larger OMP could also have been occupied by LMW mDOM. Micropores are considered as the dominating position for LMW adsorbates' adsorption and competition (Ding et al., 2008; Park et al., 2020b), however, the adsorption capacity reduction of iopromide at 48 h indicated the existence of adsorption of LMW mDOM competitors in the larger pores, too.

The adsorption competition was found to be more pronounced for all six OMPs at non-equilibrium adsorption (0.5 h) than at equilibrium adsorption (48 h). Due to the mDOM coexistence, the removals of both strongly adsorbing OMPs and weakly adsorbing OMPs were obviously decreased, compared to OMP removal in mDOM-free water at 0.5 h. The

majority of the mDOM competitors had little competition against strongly adsorbing OMPs at 48h (e.g. little removal reduction from 99.7% for bezafibrate). However, the difference between strongly adsorbing OMPs removal and weakly adsorbing OMP removal was much smaller at 0.5 h adsorption, and similar reduction levels, 5-20% compared to mDOM-free water removal, were found for all six OMPs. For instance, the removal of bezafibrate reduced from 60.4% in mDOM-free water to 40%-55% in presence of most mDOM. Also, the removal of benzatriozole decreased from 36.9% to 15%-30%, where the reduction level is comparable with bezafibrate. A similar phenomenon has been observed in another OMP adsorption kinetics study (Matsui et al., 2013), but mass transfer restriction by macromolecules in DOM has been proposed as the major reason, which is different from our findings, since here only LMW mDOM molecules were involved as competitors.
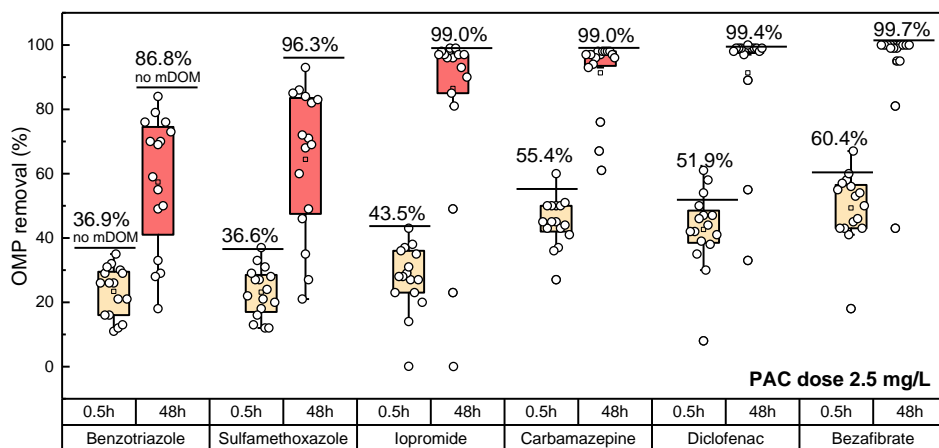


**Figure 1** *OMP removals with 2.5 mg PAC/L in presence of all fifteen different mDOMs. The long solid reference lines above the boxes indicate the corresponding OMP removal without mDOM. Two adsorption times (0.5 h and 48 h) were adopted. OMP removal data were presented as box plot (box, 25–75%; central point, average) overlaid with dot plot (individual data points showing original data in Figure S1).*

## 3.2 mDOM properties and competitiveness

To study the role of DOM functional groups in competitiveness with OMPs, Figure 2 displays the impact of molecular characteristics on mDOM adsorption (indicated by DOC-PAC20%) and competitiveness (indicated by OMP-PAC80%) on OMP adsorption at 48h. A higher OMP-

PAC80% means an additional PAC dose requirement because of stronger mDOM competitive adsorption, while a *higher* DOC-PAC20% of mDOM implies a *weaker* affinity on PAC and consequently a need for a larger dose for 20% mDOM removal.

### 3.2.1 Hydrophobic effect in aliphatic mDOM

The effect of varying hydrophobicity due to different aliphatic chain lengths of alcohols (pentanol, hexanol and heptanol) on the related mDOM adsorption and competitiveness is shown in Figure 2a. A clear positive relation between increasing alcohol chain length (C5 to C7) and alcohol adsorbability (represented by decreasing DOC-PAC20% values) was observed. The longer the alkyl chain is, the more the hydrophobic alkyl chain outweighs the hydrophilicity of the hydroxyl group, increasing overall molecule hydrophobicity (increasing logD values, Table 2). The increase in competitor adsorbate adsorbability with longer alkyl chains negatively affected OMP removal. The higher the alcohol adsorbability is, the stronger the competition against OMPs and, thus, the higher the PAC dose requirement for OMP removal (OMP-PAC80%). As the most hydrophobic one (logD = 2.14) in the examined mDOM collection, heptanol induced remarkably strong competition against iopromide (Figure S2a), potentially related to a combination of outer-shell adsorption of iopromide (Ando et al., 2010) and heptanol may act as an organic solvent at much higher concentrations (Dean, 1998).

The hydrophobic effect was then further tested by increasing the number of hydroxyl groups on the fixed alkyl chain or alkyl ring of the mDOMs. Two monohydric alcohols (hexanol and cyclohexanol) and three polyhydric alcohols (hexanediol, hexanetriol and cyclohexanediol) were selected to keep the molecular structure (alkyl chain / ring) uniform, while adding hydroxyl groups. The decreasing logD shows their increasing hydrophilicity with each additional hydroxyl group, while the alcohol adsorbability deteriorated (Figure 2b/c). Compared with hexanol (logD = 1.69), cyclohexanol has a lower hydrophobicity (logD = 1.28), but it is higher than that of hexanediol (logD = 0.63). However, the adsorbability of cyclohexanol was lower than that of hexanediol. A possible explanation is that due to the cyclic molecular structure, the cycloalkanols have rigid geometries and do not have any rotatable bonds. In contrast, the straight chained alkanols have four rotatable bonds. This has been found to enable them to fit into pores that are unavailable for the cyclic alkanols and may also enable them to adapt to small adsorption sites (e.g. slit-type) as well as allow for adsorption onto multiple adsorption sites (Endo et al., 2009). Lower alcohol

adsorbability should be translated to lower OMP competitiveness in each group. However, despite having the lowest degree of adsorbability, the competitiveness of hexanetriol and cyclohexandiol were still comparable with the mDOM having fewer hydroxyl groups. This means that although the hydroxyl group on the aliphatic mDOMs considerably impacted mDOM adsorbability, competitiveness was only slightly affected.
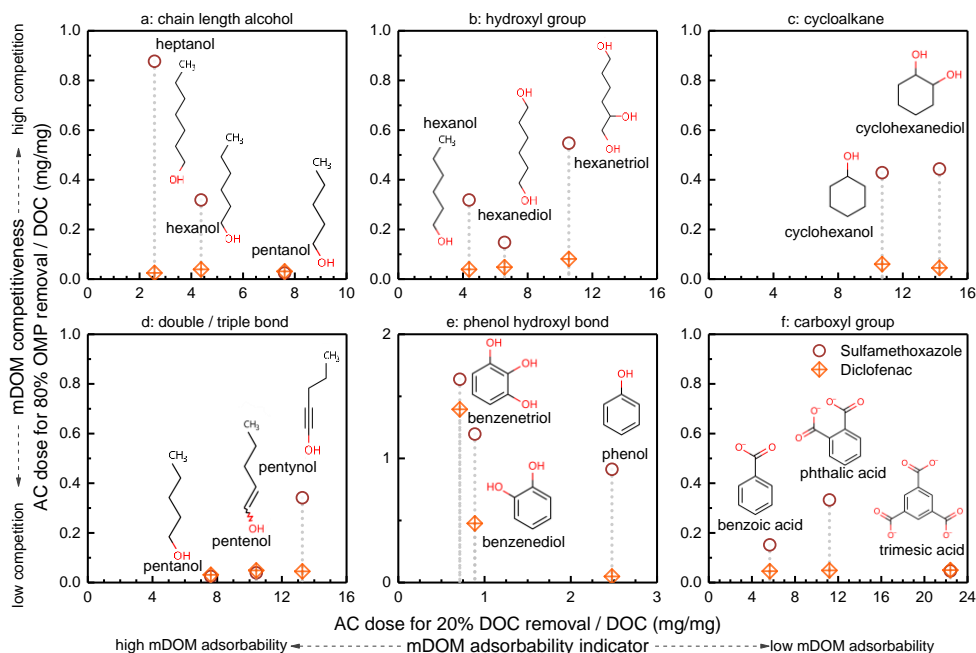


**Figure 2** *AC doses for 80% OMP removal versus AC doses for 20% mDOM removal, grouped by different tested mDOM properties (panels a-f), for sulfamethoxazole (as an example of weakly adsorbing OMP) and diclofenac (as an example of strongly adsorbing OMP). Data for other four OMPs (benzotriazole, iopromide, carbamazepine, bezafibrate) in Figure S2. Note the different scales in subfigure e. Adsorption time was 48h.*

### 3.2.2 π-bonding effect in aliphatic mDOM

In aliphatic mDOM, double and triple bonds can facilitate interactions with the aromatic π-system of the activated carbon. Pentenol and pentynol with double or triple bonds were used as competitor mDOM adsorbates to examine this effect. The $sp^2$ or sp hybridization induces a slight electron-withdrawing effect of the carbon atom. The electron richer area causes pentenol/pentynol to have a higher polarized area other than the hydroxyl group,

leading to less hydrophobic molecular character (McMurry, 2011). In Figure 2d it can be observed that, with increasing DOC-PAC20% values from pentanol to pentynol, the addition of a double and a triple bond to a saturated alcohol reduced mDOM adsorbability, despite the increased potential of unsaturated structures to interact with the surface of activated carbon.

OMP-PAC80% values show that the OMPs adsorbed best in the presence of pentanol and least in the presence of pentynol. This means that mDOM competitiveness, only with weakly adsorbing OMPs, increased even though mDOM adsorbability *deteriorated* by a limited amount. Even though higher hydrophilicity makes pentenol and pentynol harder to remove from the water, π-interaction in adsorption processes may inhibit OMP adsorption (Belfort, 1979). All examined OMPs had aromatic structures, the observed stronger competition may thus be attributed to similar π-adsorption sites for OMPs and unsaturated mDOM (Ersan et al., 2017). This phenomenon might be related to saturated mDOM and OMPs targeting partially different adsorption sites, whereas unsaturated mDOM and the OMPs mostly target similar sites. The results presented above highlighted that hydrophobicity affected more the aliphatic mDOM adsorbability, while aliphatic mDOM competitiveness was impacted more by π-interaction.

### 3.2.3 hydrophobic and π-bonding effect in aromatic mDOM

To examine the effect of π-bonding and aromatic activation/deactivation on the adsorbability and their impact on OMP adsorption, phenol, benzenediol and benzenetriol as well as benzoic acid, phthalic acid and trimesic acid were used as aromatic mDOM competitors. Phenols had a much higher adsorbability than cyclohexanols, aliphatic mDOMs with a similar structure but without aromaticity (Figure S3; cf. Figure 2c & e). Both the higher hydrophobicity of the phenols (cf. Table 2) and their aromatic structure might have facilitated their adsorbability and competitiveness (Lin and Xing, 2008) as compared to similar structure but non-aromatic cycloaliphates. In this circumstance, the competitiveness difference of cycloaliphates and phenols cannot help distinguish the roles of hydrophobicity and aromaticity on mDOM competitiveness as they both increased with the existence of aromatic structure. Instead, hydrophobicity decreased as aromaticity increased within the phenol mDOM group (Figure 2e), which could help to clarify the effect of hydrophobicity and aromaticity. The order of adsorbability was phenol < benzenediol < benzenetriol. As the hydroxyl group is hydrophilic and electron-donating for the aromatic ring, additional

hydroxyl groups on the benzene ring not only activate its aromaticity, but also increase the molecule hydrophilicity (Table 2) (Tang et al., 2018). Regarding the carboxylic acids, hydrophilicity grows with the carboxyl groups, due to their dissociation at neutral pH (Table 2). Additionally, carboxyl groups are electron-withdrawing and deactivating, thereby reducing the aromaticity and π-interactions on the PAC surface. Both effects reduced the adsorbability of benzoic acids (Figure 2f), which was lower than that of the phenols.

Corresponding competitiveness of aromatic mDOMs is also shown in Figure 2e/f. The mDOM adsorbability could be translated into mDOM competition with OMPs. From the lower OMP-PAC80% values of selected benzoic acids, OMP removal was much better in the presence of the benzoic acids than in the presence of the phenols, which is in accordance with mDOM adsorbability. As the isoelectric point of the applied PAC is around pH 9, the internal surface charge is overall positive at pH 7-8 (Aschermann et al., 2019). Therefore, hydrophobic effects, electrostatic attraction and π-interactions are, in principle, all possible for benzoic acid adsorption. However, the large differences between phenols and benzoic acids in competitiveness against (partially) negatively charged OMPs (sulfamethoxazole, diclofenac and bezafibrate, in Figure 2e/f and Figure S2e/f) indicate that π-interactions and hydrophobicity effects were more important for mDOM competition against those OMPs than electrostatic interaction between mDOM/OMPs/PAC surfaces. Furthermore, for the strongly adsorbing OMPs (such as carbamazepine, diclofenac and bezafibrate), only the phenols could induce competition. The previously reported strong DOM competition against strongly adsorbing OMPs thus implies that the LMW DOM competitors may have been aromatic DOM with rich phenol or polycyclic structures (Deng et al., 2015; Zietzschmann et al., 2015b).

## 3.3 Indicators for projecting mDOM competitiveness

### 3.3.1 Hydrophobicity and aromaticity

To project mDOM competitiveness among all examined species, mDOM adsorbability and competitiveness are plotted against hydrophobicity and aromaticity, quantified with logD and specific ultraviolet absorbance (SUVA) in Figure 3. Aliphatic mDOM with a higher hydrophobicity had a higher adsorption affinity ($R^2$ = 0.49) (Figure 3a), but no increasing trend for competitiveness was found (Figure 3b/c and Figure S4a-d). Aromatic mDOM compounds with log D > 0 at pH 7 had better adsorbability and higher competitiveness. e.g.

although benzenetriol was not very hydrophobic (logD = 1.06), it was highly adsorbable and competitive because of aromaticity. This confirmed the high relevance of aromaticity compared to other molecular characteristics like hydrogen bonding, van-der-Waals interactions, and hydrophobic interactions (Tang et al., 2018). Accordingly, DOM fractionization on hydrophobicity/hydrophilicity appears inappropriate for competing DOM isolation and identification in practice.
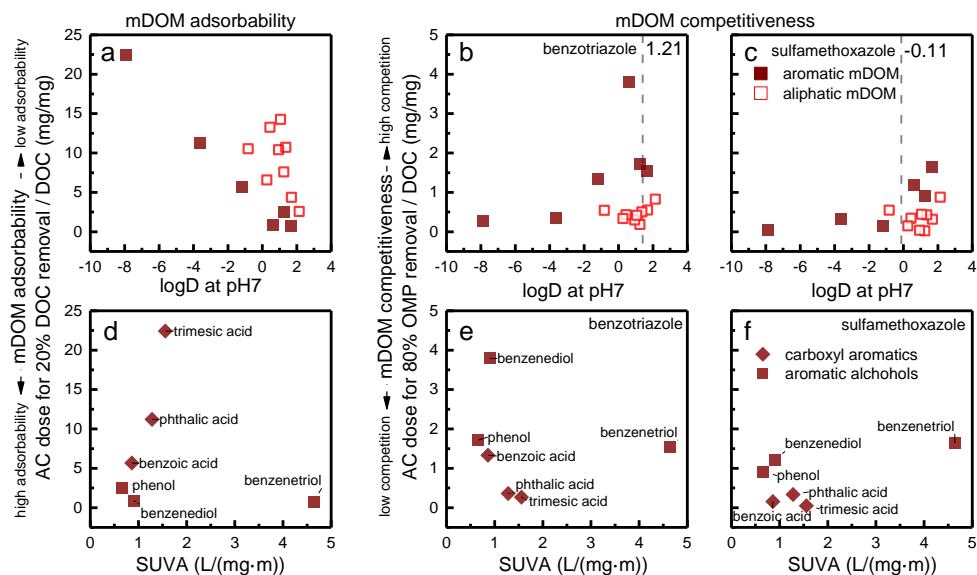


***Figure 3*** *mDOM adsorbability versus logD (a) and SUVA (d), and mDOM competitiveness versus logD and SUVA for benzotriazole (b, e) and sulfamethoxazole (c, f), respectively. Data for other four OMPs (iopromide, carbamazepine, diclofenac, bezafibrate) in Figure S4. mDOM competitor names omitted in a, b, c due to reasons of clearness to the caption. Reference lines in subfigure b/c showing the logD of the specific OMP at pH 7. The adsorption time was 48h.*

Aromaticity is defined to relate with the specific π-electronic structures, and SUVA is a common optical indicator representing the aquatic DOM aromatic character and reactivity in practice (Edzwald et al., 1985; Matilainen et al., 2011). Table 2 indicates that SUVA raised with an increasing number of phenol groups or carboxyl groups on the benzene ring. The hydroxyl group is auxochrome for aromatic compounds, inducing a bathochromic shift and enhancing UV absorbance at 254 nm as well. In contrast, additional π-electrons in carboxyl

groups of phthalic/trimesic acid also contribute to SUVA increase in benzoic acid groups (despite their electron-withdrawing effect). Figures 3d-f show the relationship between SUVA and mDOM adsorbability/competitiveness, indicating that SUVA was not always adequate to explain mDOM adsorbability and competitiveness, especially for carboxyl-rich aromatic mDOM. For aromatic carboxylic acids, mDOM adsorbability decreased with increasing SUVA, whereas, for aromatic alcohols, mDOM adsorbability increased with increasing SUVA, which agreed with the limitation for SUVA in directly projecting DOM reactivity (Weishaar et al., 2003). Although aromaticity has been estimated by the percentage of aromatic carbon in DOM with nuclear magnetic resonance spectroscopy (NMR) (Weishaar et al., 2003), we found SUVA was not a good parameter to estimate aromaticity for carboxyl-rich mDOM. The good applicability of SUVA in estimating reactivity may be a result of the complex DOM composition of the diverse DOM chemical properties, but apparently does not directly quantify the ability of π-interaction, especially for individual mDOM.

### 3.3.2 mDOM adsorbability and competitiveness

mDOM competitiveness (indicated by OMP-PAC80%) is depicted over mDOM adsorbability (indicated by DOC-PAC20%) under adsorption equilibrium (48h) in Figure 4 (benzotriazole, sulfamethoxazole and diclofenac) and Figure S5 (iopromide, carbamazepine and bezafibrate). Overall, mDOM adsorbability relates to mDOM competitiveness in most cases (cf. Figure 2). Adsorption of strongly adsorbing OMPs (carbamazepine, diclofenac and bezafibrate) were only prone to compete with highly adsorbable mDOM (DOC-PAC20% < 2.5 mg PAC/mg C). Regarding the weakly adsorbable OMPs, such as benzotriazole and sulfamethoxazole, weaker adsorbable mDOM (DOC-PAC20% > 2.5 mg PAC/mg C) was also capable to exert mild competition.

The adsorption sites on activated carbon are not identical in energy and stronger adsorbates prefer higher-energy adsorption sites. In this study, OMPs were in a low initial concentration (μg/L), while mDOM concentrations (~10 mg/L) were much higher. Even though mDOM is usually a weaker adsorbate than OMP (Figure S6), the higher concentration of mDOM restricted OMP from adsorbing on the preferred adsorption sites. However, weaker mDOM competitors could not affect OMP adsorption on the targeted sites and a state of complementary adsorption was probably reached. As reported previously with two model substances both at high initial concentrations (0.1 mg/L – 40 mg/L), they targeted different

adsorptions sites and little competition was observed (Pan et al., 2008; Zhang et al., 2012). In our study, both concentration asymmetry and adsorbability difference are possible reasons for complementary adsorption.

Figure S7 displays mDOM adsorption and competition at non-equilibrium (0.5 h). In contrast to mDOM competition at 48 h, medium adsorbable mDOMs also exerted competition against OMP adsorption at 0.5 h. For aromatic mDOM, the mDOM adsorbability could also project their competitiveness. Different adsorption kinetics between mDOM and OMPs might be a reason for this circumstance. Figure S8 compares mDOM adsorbability at 0.5 h and 48h. The concentration difference between OMPs and mDOM resulted in a higher driving force of mDOMs towards the adsorption sites, making some mDOM reach the adsorption sites in the micropores faster than the OMPs. The adsorption equilibrium of a majority of mDOMs at 0.5h was observed as nearly identical DOC-PAC20% values for weakly adsorbing mDOMs between 0.5h and 48h. Several OMPs had a higher adsorbability but lower kinetics than mDOM, so high-energy adsorption sites, occupied by mDOM at 0.5 h, could be displaced by OMPs afterwards. Displacement usually prolongs OMP equilibrium time (To et al., 2008), being another competition mechanism for non-equilibrium adsorption in water treatment. Moreover, the adsorption of some strongly adsorbing mDOMs like phenols did not finish at 0.5 h, shown as larger DOC-PAC20 values at 0.5h than 48h (Figure S8), and, thus, their competitiveness against OMPs was not maximized at non-equilibrium. In short, because of slow adsorption kinetics of strongly competing aromatic mDOMs and sites pre-occupation by weakly competing aliphatic mDOMs, the gap for competitiveness between aromatic mDOMs and aliphatic mDOMs has been narrowed at non-equilibrium state.
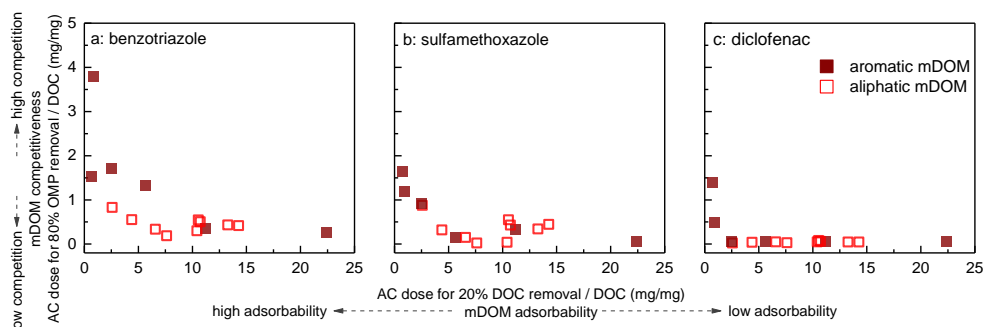
*Figure 4 mDOM adsorbability versus mDOM competitiveness for benzotriazole (a), sulfamethoxazole (b) and diclofenac (c) respectively. Data for other three OMPs (iopromide, carbamazepine and bezafibrate) in Figure S5. The adsorption time was 48h.*

To summarize the adsorbability impacts on competitive adsorption in this study, mDOM competitive adsorption against OMPs under large concentration asymmetry (concentration ratio was ~500 µg DOC/µg OMP) is illustrated in Figure 5. Strong competition between mDOM and OMP is only found in the combination of highly adsorbable mDOM and weakly adsorbable OMPs. It should be noted that the adsorbability of the strongest adsorbable mDOM (benzenetriol here) is still weaker than the weakest adsorbable OMP (benzotriazole here), suggested by preferential OMP removal in Figure S6. This phenomenon might also be caused by the intended concentration dissimilarity between OMPs and mDOM. In addition, the more OMP and mDOM differ in their adsorbability (e.g. bezafibrate and trimesic acid), the weaker the corresponding competition. When the concentration asymmetry is larger than the ratio (c(mDOM)/c(OMP) ≈ 500 µg C/µg) in this case (e.g. OMPs in ng/L), stronger competition from mDOM might be expected (Newcombe et al., 2002b). Hence concentration asymmetry between DOM and OMPs is suggested to be well quantified and discussed in the upcoming DOM competition studies. Moreover, the co-adsorption of some mDOM and OMPs with little/no competitiveness was highlighted in this study (bottom-right section of Figure 5). Weaker adsorbable mDOM has no competitiveness at equilibrium adsorption of stronger adsorbable OMPs, as the mDOM loading on PAC (mg/mg) was considerably higher than OMPs (µg/mg), but the OMP adsorption kinetics could be obviously hindered by mDOM through pre-occupying PAC adsorption sites. Therefore, research on the relationship between DOM adsorbability and competitiveness in natural waters is highly recommended.
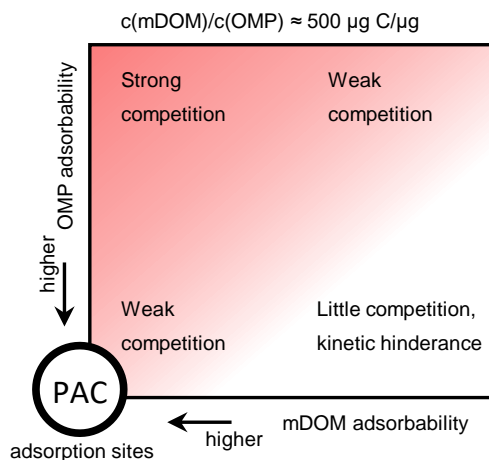
*Figure 5* *Scheme diagram showing mDOM competitive adsorption against OMPs under concentration asymmetry (concentration ratio of mDOM and OMP ≈ 500 µg C/µg). mDOM adsorbability depicted against OMP adsorbability. Color regions meant mDOM competition against OMP with a different extent.*

## 4. Conclusions

- Fifteen LMW mDOM compounds were studied to determine the effect of hydrophobicity and aromaticity on competitive adsorption against six differently adsorbable OMPs.

- The adsorption of strongly adsorbing OMPs was only slightly reduced by a small number of mDOM compounds. A wide range of mDOM adsorbates exerted more intense competition against weakly adsorbing OMPs. The adsorption of the largest OMP (iopromide, 791 g/mol) was also negatively impacted by LMW mDOM.

- The existence of unsaturated structures (benzene ring, double/triple bond) enhanced mDOM competitiveness, even with lower hydrophobicity (polyphenols) or adsorbability (unsaturated aliphatic mDOMs), implying the importance of π-interaction in adsorption competition.

- Rather than hydrophobicity (logD) and aromaticity (SUVA), mDOM adsorbability could indicate overall mDOM competitiveness. Weakly adsorbable LMW mDOM could co-adsorb with OMPs without too much interference, and high mDOM adsorbability (DOC-PAC20% < 2.5 mg PAC/mg C) was a prerequisite for considerable competition against OMPs.

- At non-equilibrium adsorption (0.5 h), insufficient adsorption of strongly adsorbing mDOMs and site pre-occupation by weak adsorbing mDOMs made DOM characteristics less important for competitiveness against OMPs than equilibrium state (48 h), especially for aliphatic mDOM as compared to aromatic mDOM.

- A scheme was proposed to explain adsorption competition under large concentration asymmetry ($c_{mDOM}/c_{OMP} \approx 500$ µg C/µg). Strong competition between mDOM and OMPs was only found in the combination of strongly adsorbable mDOM and weakly adsorbable OMPs. Competition became less important if less adsorbable mDOM competitors or stronger adsorbable OMPs were present.

## Supporting information

***Table S1*** *Selected OMPs for examination of adsorption-competitive mDOM. Properties were from Chemicalize (ChemAxon, 2020).*
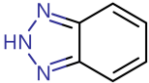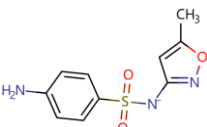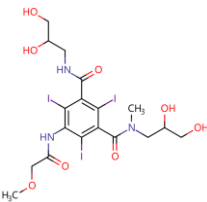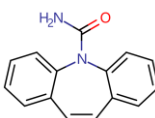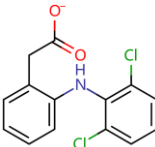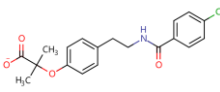
| Name | Predominant species at pH7 | CAS # | Molecular weight | logD at pH7 | Charge at pH7 | pKa |
|---|---|---|---|---|---|---|
| benzotriazole | | 95-14-7 | 119 | 1.26 | 0 (0/-) | 0.22/9.04 |
| sulfamethoxazole | | 723-46-6 | 253 | 0.14 | -0.87 (-/0) | 1.97/6.16 |
| iopromide | | 73334-07-3 | 791 | -0.45 | 0 | 3.37 |
| carbamazepine | | 298-46-4 | 236 | 2.77 | 0 | 15.96 |
| diclofenac | | 15307-79-6 | 295 | 1.37 | -1 (-) | 4 |
| bezafibrate | | 41859-67-0 | 362 | 0.97 | -1 (-) | 3.83 |

***Table S2*** *Final mDOM concentrations for competitive adsorption tests.*

| Model Substance | Molecular Formula | DOC (mg C/L) |
|---|---|---|
| benzoic acid | C7H6O2 | 10.85 |
| phthalic acid | C8H6O4 | 10.18 |
| trimesic acid | C9H6O6 | 9.99 |
| pentanol | C5H12O | 16.15 |
| 4-pentenol | C5H10O | 10.21 |
| 4-pentyn-1-ol | C5H8O | 10.95 |
| hexanol | C6H14O | 12.65 |
| 1,6-hexanediol | C6H14O2 | 10.4 |
| 1,2,6-hexanetriol | C6H14O3 | 6.1 |
| heptanol | C7H16O | 17.87 |
| cyclohexanol | C6H12O | 8.23 |
| cyclohexanediol | C6H12O2 | 10.84 |
| phenol | C6H6O | 10.13 |
| 1,2-benzenediol | C6H6O2 | 10.39 |
| 1,2,3-benzenetriol | C6H6O3 | 10.02 |

***Table S3*** *Pore characteristics of PAC (Norit SAE Super)* [*].

| B.E.T. surface [m2/g] | Total pore volume [cm3/g] | Primary micropores <0.8 nm [cm3/g] | Secondary micropores 0.8-2 nm [cm3/g] | Mesopores 2-50 nm [cm3/g] | Average pore diameter [nm] |
|---|---|---|---|---|---|
| 1122 | 0.74 | 0.15 | 0.22 | 0.37 | 2.807 |

[*]Pore characteristics were determined from Ar gas-physisorption isotherms measured with an Autosorb iQ Station 2 (Quantachrome, USA).
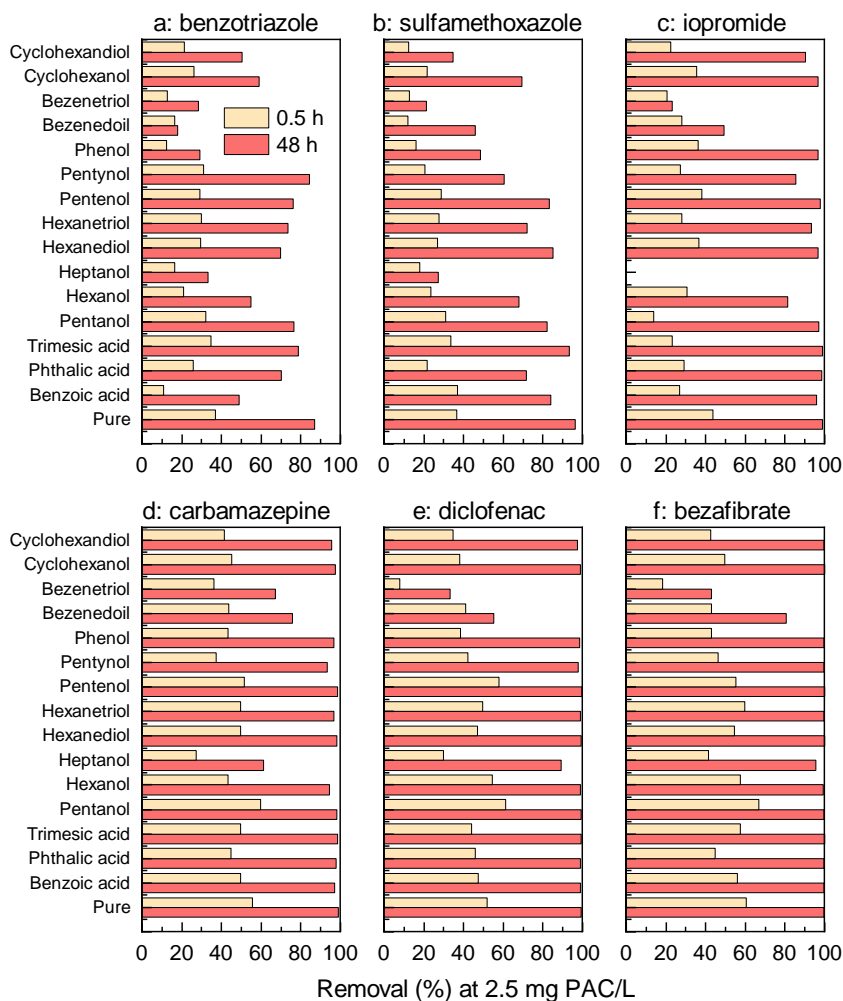
**Figure S1** *OMP removals with 2.5 mg PAC/L in presence of examined mDOMs. Adsorption time was 0.5 h and 48h.*
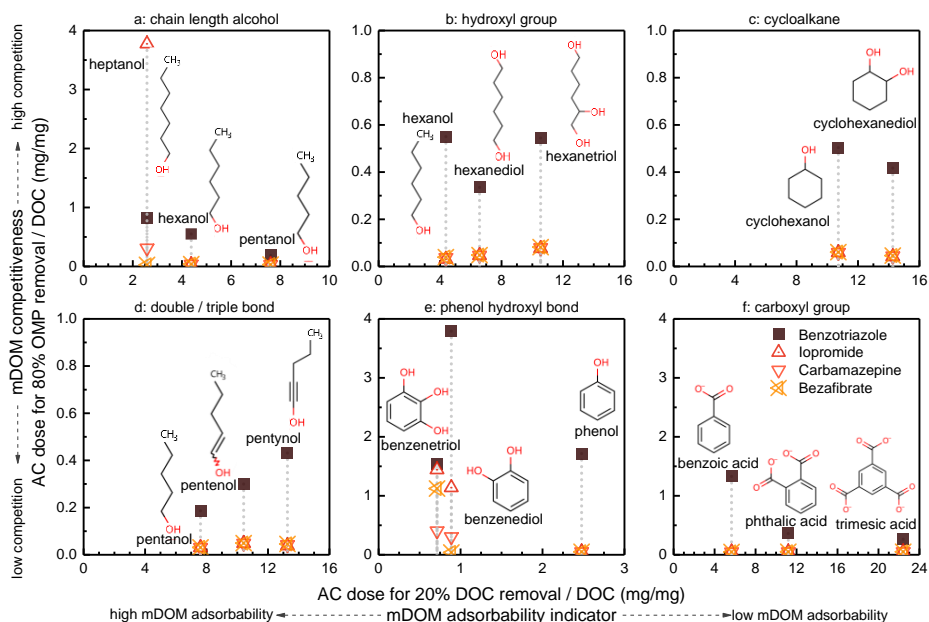
***Figure S2*** *AC doses for 80% OMP removal versus AC doses for 20% mDOM removal, grouped by different tested mDOM properties (panels a-f), for the tested four OMPs (benzotriazole, iopromide, carbamazepine, bezafibrate, in varied symbols). Note the different scales. Adsorption time was 48h.*
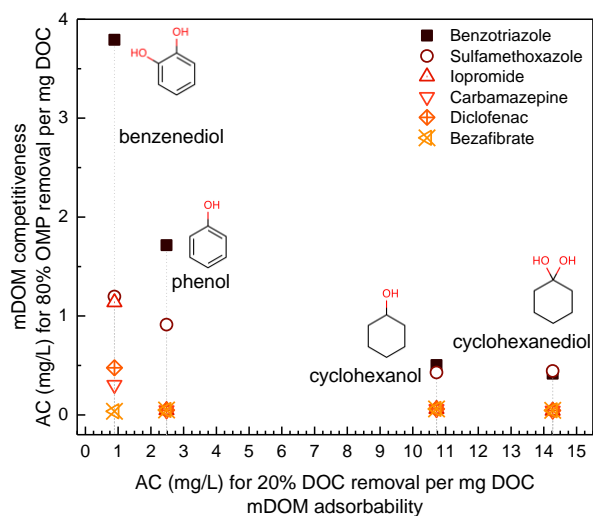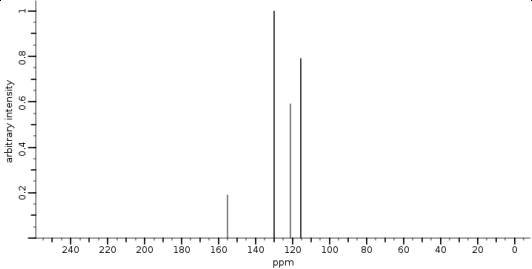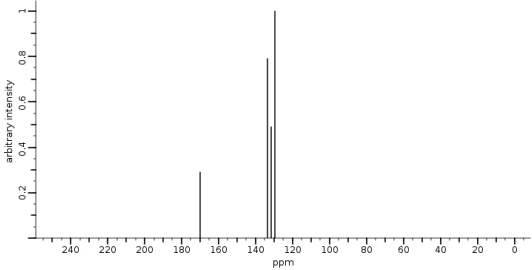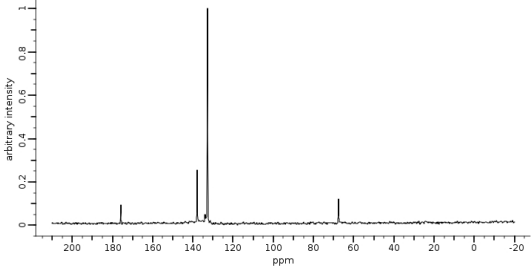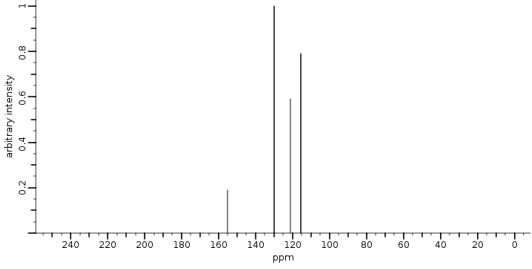
**Figure S3** *AC doses for 80% OMP removal versus AC doses for 20% mDOM removal for selected mDOMs varying in hydroxyl groups and aromatic structure. Six tested OMPs in varied symbols. Adsorption time was 48h.*

***Table S4*** *¹³C NMR spectra for examined aromatic mDOMs.*

| mDOM name | ¹³C NMR spectra |
|---|---|
| benzoic acid |  |
| phthalic acid |  |
| trimesic acid |  |
| phenol |  |

| mDOM name | $^{13}C$ NMR spectra |
|---|---|
| benzenediol |  |
| benzenetriol |  |
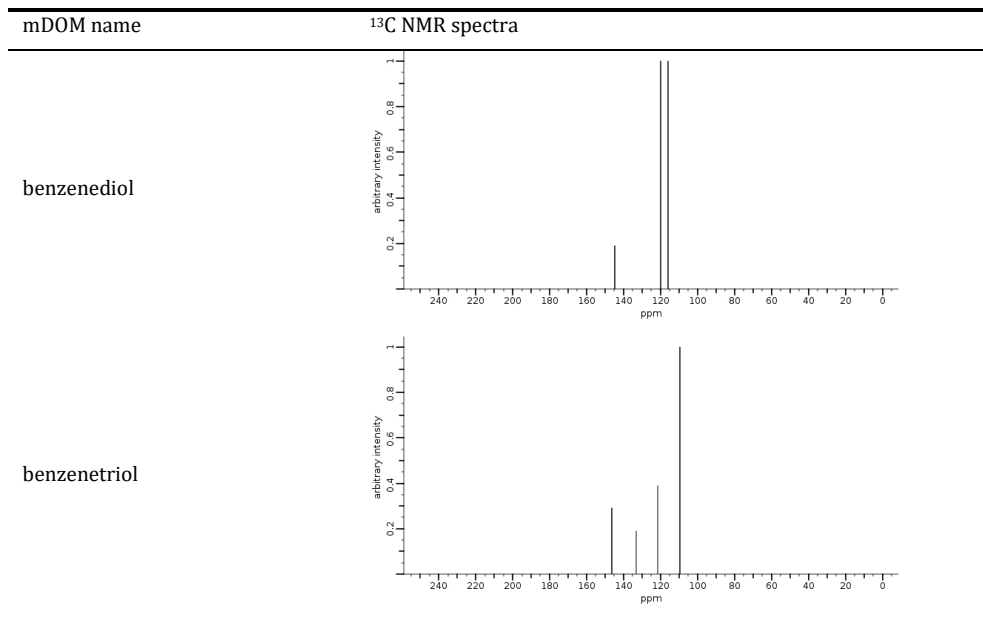
*Data from Scifinder, CAS.
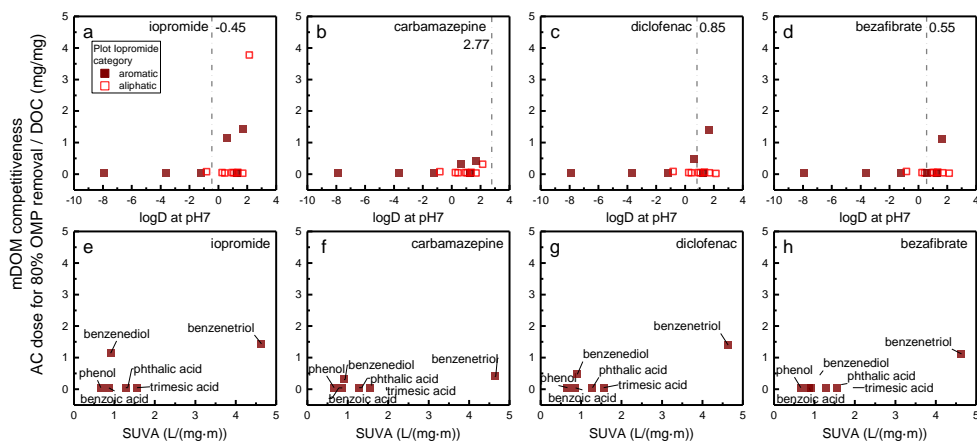


***Figure S4*** *mDOM competitiveness versus logD (a-d) and SUVA (e-h), mDOM competitor names omitted in a-d due to reasons of clearness to the caption. Reference lines in subfigure a-d showing the logD of the specific OMP. The adsorption time was 48h.*
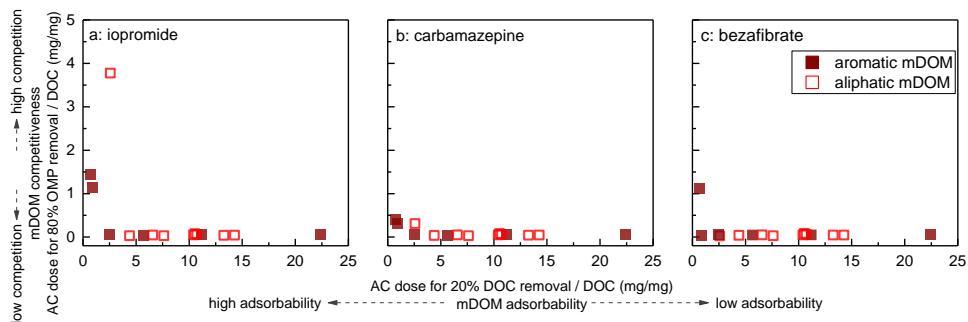
**Figure S5** *mDOM adsorbability versus mDOM competitiveness for iopromide (a), carbamazepine (b) and bezafibrate (c) respectively. Adsorption time was 48 h.*
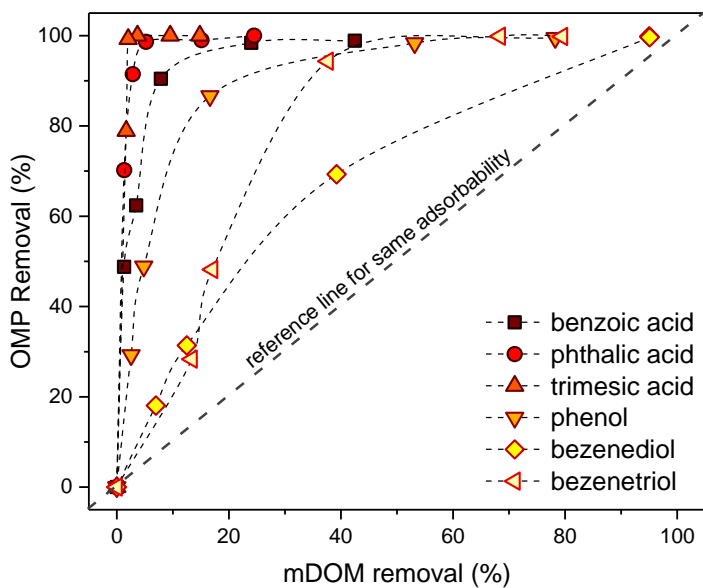


**Figure S6** *Benzotriazole removal versus mDOM removals. The reference line for same mDOM/OMP absorbability included. Adsorption time was 48 h.*
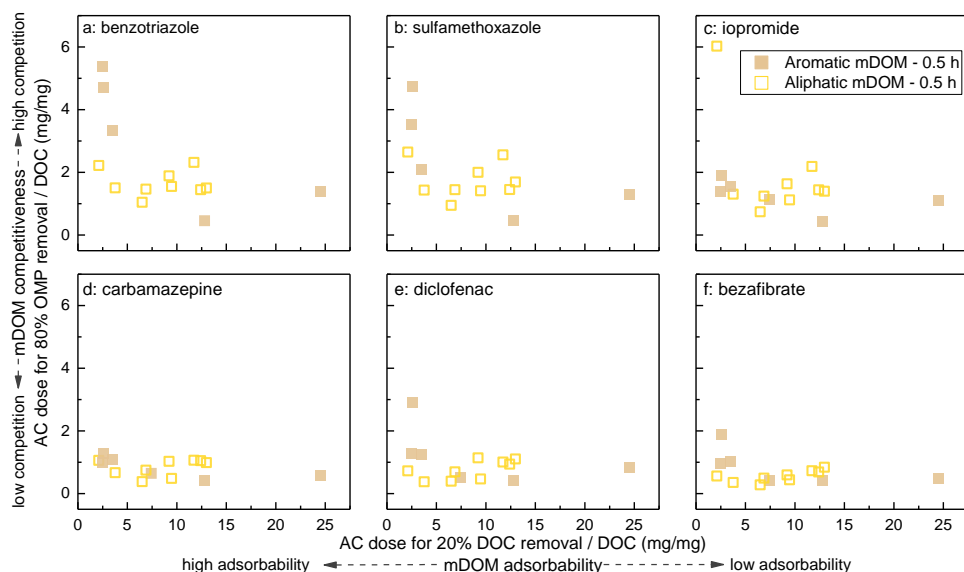
*Figure S7 Relationship of mDOM absorbability and competitiveness against examined OMPs. Note that OMP adsorbability in mDOM-free water increasing from subfigure a-f. Adsorption time was 0.5 h.*
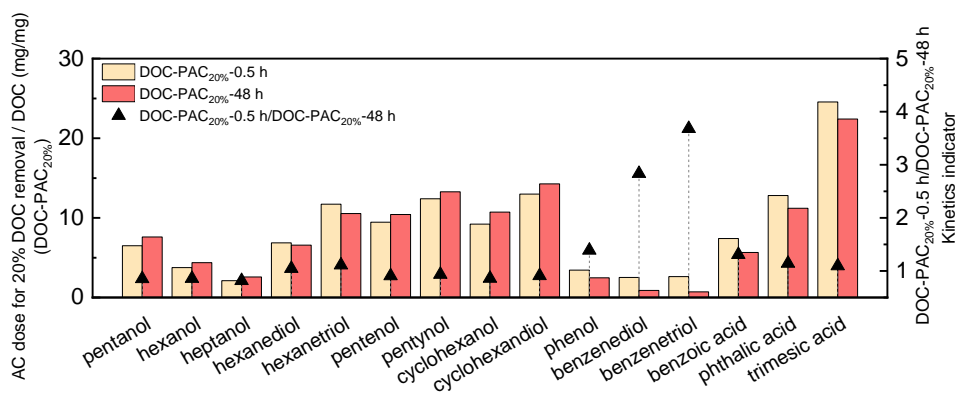


*Figure S8 mDOM adsorbability at non-equilibrium adsorption (DOC-PAC20%-0.5 h) and equilibrium adsorption (DOC-PAC20%-48 h). The ratio of DOC-PAC20%-0.5 h and DOC-PAC20%-48 h calculated as a kinetic indicator to evaluate how far mDOM reaches adsorption equilibrium.*

# Chapter 3

# Unravelling competition versus adsorbability of dissolved organic matter against organic micropollutants onto activated carbon
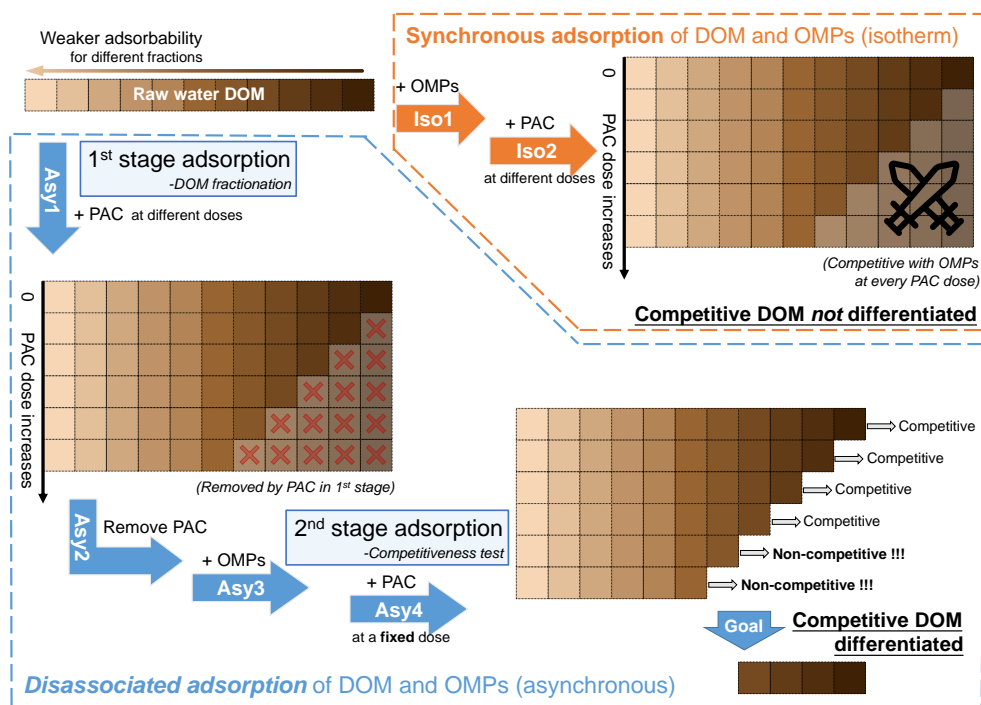


This chapter is based on: Wang, Q., Zietzschmann, F., Hofman, R. Jiang N.., Schuster J., Wang Z., Yu, J., Yang, M., Rietveld, L.C. Unraveling competition versus adsorbability of dissolved organic matter against organic micropollutants onto activated carbon. Submitted to Separation and Purification Technology.

## Abstract

It was widely acknowledged that dissolved organic matter (DOM) in natural water has ubiquitous competitiveness against organic micropollutants (OMPs) during adsorption onto activated carbon. However, some (model) low molecular weight organics have been reported to adsorb onto activated carbon, but were not competitive against co-adsorbates. The objective of this study is to identify which adsorbable DOM fractions in natural water contribute to the DOM competitiveness, and what the impact of the OMP adsorbability and initial OMP concentration is on this competitiveness. We, therefore, disassociated the adsorption of DOM fractions and OMPs (carbamazepine, caffeine and sulfamethoxazole) using a two-stage adsorption procedure, removing various adsorbable DOM fractions with powdered activated carbon pretreatment and then unraveling the competitiveness against OMPs of the remaining DOM. Our results demonstrated that DOM competition was not ubiquitous for all adsorbable fractions in natural water, and ~25% of the adsorbable DOM was not competitive. The poorly adsorbable DOM was shown to be a non-competitive co-adsorbate, and its complexation even elevated the adsorption capacity of one of the OMPs (carbamazepine). The amount of DOM competitors increased for weaker adsorbable OMPs, and at higher initial OMP concentrations. The variability in DOM competition, differentiated by DOM adsorbability, has advanced the understanding of DOM competition, from ubiquitous competition to variable roles (varying competitiveness/complementary adsorption) of differently adsorbable DOM fractions during OMP adsorption.

## 1. Introduction

The existence of organic micropollutants (OMPs) is a major concern for human health and the aquatic environment (Barbosa et al., 2016; Volker et al., 2019). Adsorption onto activated carbon is widely used for OMP abatement in water purification (Huang et al., 2022; Morsch et al., 2021; Park et al., 2020b). The adsorption affinity of OMPs towards activated carbon depends on a variety of factors, including activated carbon properties (pore structure, surface chemistry), OMP molecular characteristics, and adsorption competition due to dissolved organic matter (DOM) (Ross et al., 2019; Webb et al., 2020; Zietzschmann, 2021). DOM competition dramatically decreases OMP adsorption capacity through direct site competition or pore blocking (Li et al., 2003b). As DOM is a multi-component mixture with unknown composition (Kellerman et al., 2015; Sgroi et al., 2017), the determination of DOM competitors from the bulk is important for the exploration of DOM competition mechanisms, but the complex DOM composition makes the separation by DOM competitiveness difficult to achieve.

Although low molecular weight (LMW), high hydrophobicity, certain aromaticity and neutral charge have been mentioned as important characteristics of DOM competitors in previous studies (Hu et al., 2014; Kennedy and Summers, 2015; Lerman et al., 2013; Newcombe et al., 1997), a clear and comprehensive understanding is still lacking. Previous attempts on competitive DOM separation using hydrophobicity (via hydrophobic resin) or molecular weight (via ultrafiltration) neither fully eliminated nor completely preserved the competitive DOM, and therefore all adsorbable DOM had been considered to be ubiquitously competitive against OMPs, either strongly or weakly (Jiang et al., 2017b; Kah et al., 2017). However, in a previous study, we found that some model LMW organics were medium/poorly adsorbable but exerted no competition against OMPs (Wang et al., 2021). Thus, to which extent such "adsorbable, non-competitive" DOM exists in real water matrices remains to be answered.

To evaluate the DOM competition against OMPs, the isotherm test is the most commonly used method (Worch, 2012). The assessment of DOM competition (by using OMP isotherms in DOM-containing/DOM-free waters) and DOM adsorbability (by using DOM adsorption analysis with DOC isotherm) could be executed together (Zietzschmann et al., 2015b), but the complicated interplay between OMPs and DOM fractions makes it difficult to describe

the competitiveness of DOM fractions with varying adsorbability (Matsui et al., 2003; Zietzschmann et al., 2015b). Specifically, a low activated carbon dose provides a limited number of available adsorption sites, and highly adsorbable DOM can occupy both high-energy and low-energy adsorption sites, which leads to strong competition against OMPs, as indicated by partially downward-bent isotherms of weakly adsorbable DOM (e.g., sulfamethoxazole) at low activated carbon doses (Knappe et al., 1998; Zietzschmann et al., 2015b). When sufficient high-energy adsorption sites are available, at a high activated carbon dose, also more weakly adsorbable DOM fractions are able to adsorb and might also compete against OMPs. However, the competitiveness of these more weakly adsorbable DOM fractions can usually not be determined independently, due to the ever-present impact of co-existing, highly adsorbable and strongly competing DOM. If the adsorption of differently adsorbable DOM fractions could be disassociated by fractionation, it would thus be possible to assess the competitiveness of a complex DOM sample on this dimension of DOM adsorbability.

Therefore, the objective of the present study was to differentiate DOM competitors against OMPs with regard to DOM adsorbability, and with regard to related impact factors including OMP adsorbability and initial OMP concentration. Assessing DOM competitors from varyingly adsorbable DOM was realized through a novel two-stage DOM-OMP, asynchronous adsorption procedure: Weakly and more strongly adsorbable DOM fractions were fractionated by pretreating surface water using different activated carbon doses (1st stage batches), and subsequently, the respective DOM competitiveness against OMPs of the fractionated DOM samples was assessed individually in an additional adsorption batch (2nd stage). Three OMPs with largely different activated carbon affinities were employed and various initial OMP concentrations were used to examine how the DOM competitors varied under various competition conditions. DOM adsorption analysis and the equivalent background compound model (EBCM) were used to assist the quantitative description of the DOM adsorbability and competitiveness, respectively. The successful differentiation between competitive DOM and adsorbable DOM in this study elucidated the hypotheses of various DOM competition studies during the last decades, on the variability of DOM competitors, against different OMPs or at different initial OMP concentrations.

## 2. Materials and methods

### 2.1 Water samples

A representative surface water sample was obtained from the Schie (Delft, The Netherlands), a canal affected by humic substances of natural origin and wastewater treatment plant effluents, on September 2nd, 2020 and December 28th, 2020 (20 L in rinsed plastic jerricans). The experimental conditions of the water samples for adsorption batch tests are summarized in Table S1 (isotherm tests) and Table S2 (DOM-OMP asynchronous adsorption tests). 0.45 μm polyethersulfone membrane filters (Millipore), rinsed with ultrapure water (ELGA Labwater, Germany; resistivity >18 MΩ·cm), were used to remove suspended solids. The filtered water was stored at dark and cold (4 °C) to minimize potential changes in DOM properties. The DOM characteristics of the sampled waters are listed in Table S3.

### 2.2 Batch adsorption tests

**Selected adsorbent.** SAE Super powdered activated carbon (PAC) (Norit, Netherlands) was selected because of its wide commercial application in water treatment, and its high percentage of mesopores (~50%) (Wang et al., 2020), implicating a higher relevance of direct site competition rather than pore blockage (Ebie et al., 2001). The PAC was dried (at 105 °C), cooled, and suspended in ultrapure water at concentrations of 4 g/L and 20 g/L, respectively. The PAC suspensions were then degassed using a vacuum pump and an ultrasonic bath for 10 minutes. Before dosing into the batches using pipettes (Eppendorf, Germany), 30 min stirring was applied to homogenize the PAC suspensions.

**Examined OMPs.** Carbamazepine, caffeine and sulfamethoxazole (Sigma-Aldrich) were chosen for the experiments, due to their frequent occurrence in aquatic environments and their large difference in PAC absorbability, as reported in earlier studies (Hu et al., 2014; Zietzschmann et al., 2015b).

**Adsorption isotherm test.** OMP isotherm tests served for examining the overall competitiveness of DOM samples. Figure 1 (top) displays the experimental procedures and aims of the conventional isotherm test. Table S1 provides details on examined waters, PAC doses, and initial OMP concentration for different batches. The bottle point method (100 mL) was used for the adsorption isotherm tests. The concentrations of the three selected OMPs

were adjusted to ~6 μg/L (or ~50/500 μg/L for different initial concentration batches, cf. Table S1), respectively, before the PAC dose (marked as Iso1 in Figure 1). PAC doses (1-300 mg/L) were applied at 20 ℃ and adsorption was conducted on a shaker (120 rpm) for 7 days (Iso2) (Matsui et al., 2012). OMP samples were obtained by filtering PAC through regenerated cellulose membrane filters (0.2 μm, SPARTAN, Whatman, rinsed with tap water). For DOM analysis, 0.45 μm syringe filters (polyethersulfone, Chromafil Xtra PES-45/25, Macherey-Nagel, Germany) were employed for obtaining DOM samples. In addition, the DOM-free water isotherm test was conducted with mixed OMPs in ultrapure water, amended with inorganic ions (all inorganics from Sigma-Aldrich, in analytical grade), according to the ion composition of the untreated water sampled in September (Table S4). The final pH, measured by Multi 9420 (WTW), of all adsorption batches, was close to the initial pH (± 0.1).
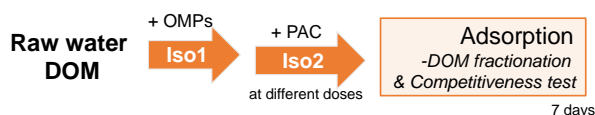


*Figure 1 Scheme of the experimental approach to perform DOM-OMP asynchronous adsorption test and comparison with conventional isotherm test.*

**DOM-OMP asynchronous adsorption test.** In this adsorption test, varyingly adsorbable DOM fractions and OMPs were adsorbed in different adsorption stages (also at different times, so-called DOM-OMP asynchronous adsorption). The two adsorption stages in the asynchronous adsorption test served for fractionating DOM (1st stage) and analyzing the DOM competitiveness (2nd stage), respectively (Figure 1 bottom left). In the 1st stage adsorption, varying adsorbable DOM fractions were removed by diverse PAC doses (marked as Asy1 in Figure 1). The range of PAC doses in the 1st stage adsorption (5-300 mg/L here) could cover the adsorption of nearly all adsorbable DOM fractions (Worch, 2012). PAC was

then filtered after 7 days of adsorption at 20°C and 120 rpm (Asy2). Subsequently, a 2nd stage competition analysis was performed with the DOM fractions remaining after the 1st stage PAC pretreatment. The three examined OMPs were spiked at ~6 μg/L (or ~50/500 μg/L for different initial concentration batches, cf. Table S2), respectively, into the PAC-pretreated waters (Asy3), followed by sampling for analysis prior to the 2nd stage PAC dosage. Note that 5 mg/L fresh PAC ($PAC_{5mg/L}$ as abbreviation) was chosen as the the 2nd stage adsorption dose here (Asy4), since (i) low PAC doses typically relate to the more pronounced competition against OMP adsorption (Zietzschmann et al., 2015b), (ii) the gap of the OMP removals (removals between carbamazepine and sulfamethoxazole in untreated water) was maximized at $PAC_{5mg/L}$ (OMP adsorption in untreated water was evaluated in Figure S1), and (iii) the error for analyzing OMP removal was too high for lower PAC doses (< 5 mg/L, cf. Figure S1). After a contact time of 7 days, water samples were taken and OMP concentrations were analyzed. Zero PAC dose (0 mg /L) in 1st stage adsorption was employed as a reference for the original DOM competition. OMP removal with $PAC_{5mg/L}$ adsorption in DOM-free waters (inorganics added, cf. Table S4) for 7 days was taken as a non-competitive scenario for OMP adsorption. All the DOM-OMP asynchronous adsorption tests were performed with duplicate samples to minimize the potential experimental error.

Table S2 provides more details about the experimental conditions of the DOM-OMP asynchronous adsorption tests. It should be noted that there were also two variants in DOM-OMP asynchronous adsorption tests for different purposes. Firstly, to preliminarily examine if the DOM competition could be fully alleviated by DOM fractionation via adsorbability, $PAC_{200mg/L}$ pretreatment was conducted in the 1st stage adsorption, to remove as much adsorbable DOM as possible for minimizing competition, followed by a 2nd stage isotherm test (varied PAC doses – as opposed to one single PAC dose of 5 mg/L described above), was subsequently performed (cf. Table S1). Secondly, to compare the adsorption kinetics of competitive DOM (assessed by EBCM) with bulk DOM (evaluated by DOC and $UV_{254}$) and OMPs, the PAC dose in 1st stage adsorption was fixed (at 40 mg/L, competitiveness alleviated for caffeine, see the section "Variability of DOM competitors for different OMPs"), while the adsorption time in 1st stage adsorption varied (0.5 hours to 7 days) (cf. Table S2). Note that adsorption time in the 2nd stage adsorption (7 days) was not changed for adsorption equilibrium of remaining DOM and OMPs.

## 2.3 Analytical methods

The OMP concentrations were determined with high-performance liquid chromatography combined with tandem mass spectrometry (LC-MS/MS), using an ACQUITY UPLC BEH C18 column (1.7μm particle size, 2.1×50 mm, Waters, USA). More details are available in the Supporting Information (Text S1). To examine the DOM characteristics, aromatic DOM, determined by specific ultraviolet absorbance (SUVA), was measured on a UV-Vis spectrophotometer (GENESYS 10S, Thermo, USA) at 254 nm. DOC was determined by catalytic combustion using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). The DOM molecular distributions were obtained using liquid size exclusion chromatography on a HW50S column (Toyopearl, Japan) coupled with organic carbon detection (LC-OCD) (DOC-Labor Huber, Germany). The ion composition of the river water was determined by ion chromatography (818-anion coupled with 838-cation system, Metrohm, Switzerland) and potentiometric titrator (Titrino 702, Metrohm, Switzerland).

## 2.4 Data analysis

**Freundlich isotherm fits and interpretation**. To quantify the OMP adsorption using adsorption isotherms, the Freundlich model was used to fit the isotherms, using OriginPro. Single-solute or pseudo-single-solute (in DOM-containing waters) Freundlich parameters ($K_F$ and $1/n_F$) and respective standard errors were calculated for describing the OMP adsorption in DOM-free and DOM-containing waters.

**Operating lines.** To visualize how OMP adsorption varied in the presence of differently PAC-pretreated DOM, operating lines were used to describe the OMP equilibrium adsorption in the 2nd stage adsorption (PAC$_{5mg/L}$ only) of the DOM-OMP asynchronous adsorption test. The adsorption started at the initial concentration of OMPs ($c=c_0$) and fresh PAC ($q=0$) and ended at equilibrium with $c=c_e$ and $q=q_e$ (index "e" refers to equilibrium). The slope of the operating line is $-\frac{1}{D_{PAC}}$, the negative reciprocal value of the adsorbent dose (Worch, 2012). Specifically, the operating lines for 2nd stage OMP adsorption shared the same initial points ($c=c_0$, $q=0$) and the same slope of PAC$_{5mg/L}$, but ended at different equilibrium capacities (i.e., different $c_e$ and $q_e$). The equation for deriving operating lines is provided in Eq. 1 (Worch, 2012).

$$q_e = \frac{1}{D_{PAC}}c_0 - \frac{1}{D_{PAC}}c_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 1)}$$

**DOM adsorption analysis.** To explain the removal of differently adsorbable DOM fractions during various PAC doses in isotherm tests and the 1st stage adsorption of the DOM-OMP asynchronous tests, DOM adsorption characteristics were described by the ideal adsorbed solution theory (IAST)-based adsorption analysis, using the DOC isotherms of the untreated water, by allocating the examined DOM into several fictive components with varying adsorbability, defined by different Freundlich isotherm coefficients $K_F$ (0, 20, 70, 140 $(mg/g) \cdot (L/mg)^{1/n}$) and $1/n_F$ (0.25 for all fictive components). Removals of each fictive adsorbable DOM component were then simulated by fitting concentrations of each component in the IAST model. More details are given in literature (Johannsen and Worch, 1994; Zietzschmann et al., 2014b).

**IAST-equivalent background compound model (IAST-EBCM).** The IAST-EBCM was used to calculate the removal of competing DOM during the DOM-OMP asynchronous adsorption tests, as well as to evaluate the accuracy of the predicted OMP adsorption at different initial OMP concentrations. In the IAST-EBCM, one fictive single competing component (EBC) is defined and characterized by its initial concentration $c_{0,EBC}$ and isotherm parameters ($K_{F,EBC}$, $1/n_{EBC}$) (Najm et al., 1991). Regarding the DOM-OMP asynchronous adsorption tests, $c_{0,EBC}$ of different 1st stage PAC-pretreated waters, was fitted to the 2nd stage adsorption data (which only consisted of the one isotherm data point, $PAC_{5mg/L}$), with a global value for $K_{F,EBC}$ (same as $K_{F,EBC}$ in untreated water) and $1/n_{EBC}$ (same as $1/n_F$ of OMP isotherm in DOM-free water) for each of the three OMPs, respectively (Worch, 2010). The PAC-pretreated water $c_{0,EBC}$ and untreated water $c_{0,EBC}$ were used to determine the EBC removal at different 1st stage PAC doses. To verify the usefulness and applicability of the simplified approach (one isotherm point for $c_{0,EBC}$ fitting), the modeled $c_{0,EBC}$ fitted from all data points from untreated water in the isotherm test, should be similar to the values of $c_{0,EBC}$ when only using a single isotherm data point ($PAC_{5mg/L}$) from the same isotherm test, and the error is smaller than 10% (Table S5). In terms of the IAST-EBCM application on OMP adsorption prediction at different initial OMP concentrations, the EBCM parameters, including $c_{0,EBC}$, $K_{F,EBC}$ and $1/n_{EBC}$, were initialized from the adsorption isotherm at medium $c_{0,OMP}$ (~50 µg/L), and the prediction was conducted, based on the same parameters (Najm et al., 1991), for the OMP isotherm at lower or higher initial concentrations (~6 µg/L or ~500 µg/L in this study). The rest of the basics and calculation of IAST-EBCM can be found in the supporting information (Text S2).

## 3. Results and discussion

### 3.1 Adsorbable, non-competitive DOM in natural water

The characteristics of untreated DOM and $PAC_{200mg/L}$-treated DOM (both Sept. samples) are shown in Table S3. A substantial decrease was observed by $PAC_{200mg/L}$ treatment in DOC concentration (75%), $UV_{254}$ (84%), as well as in the concentration of LMW organics (LC-OCD chromatogram in Figure S2). Accordingly, the DOM adsorbability on PAC was diminished, as indicated by the decreased $UV_{254}$ removal by $PAC_{5mg/L}$ from 12% for untreated DOM to 4% for $PAC_{200mg/L}$-treated DOM (Table S6).

Figure 2 shows the isotherms of the three selected OMPs in DOM-free water, untreated canal water (Sept. sample) and $PAC_{200mg/L}$-treated water. Carbamazepine was the strongest adsorbable OMP in DOM-free water (e.g., indicated by loadings at given liquid-phase concentrations: ~10 nmol/mg at 1 nmol/L), followed by the medium adsorbable caffeine (~5 nmol/mg) and the weakly adsorbable sulfamethoxazole (~2.5 nmol/mg). DOM competition in the untreated Schie water did not change the ranking of OMP adsorbabilities, but considerably decreased PAC loading (Figure 2) and $K_F$ values (Table 1) for the OMPs, especially for the weaker adsorbable OMP sulfamethoxazole, implying that the weaker adsorbable OMPs were more vulnerable to DOM competition. Stronger inhibition from DOM competitors for weaker adsorbable OMPs has also been reported in earlier studies (Altmann et al., 2015; Wang et al., 2021; Zietzschmann et al., 2015b). However, from these results, it cannot be concluded if this stronger competition was (partially) attributed to the same amount of DOM competitors.
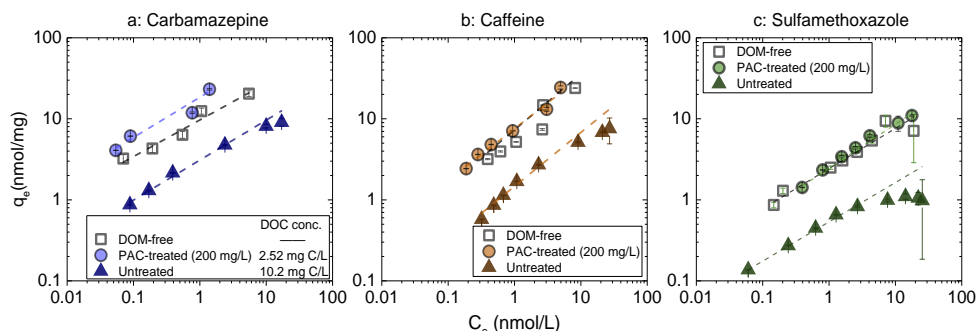
***Figure 2*** *Adsorption isotherms of three examined OMPs (carbamazepine, caffeine and sulfamethoxazole) in DOM-free water, untreated water of river Schie and PAC$_{200mg/L}$-treated water (Sept. sample). Freundlich model was applied to fit isotherms (Fitted results in Table 1). Error bars derived from experimental duplicates.*

***Table 1*** *Freundlich isotherm parameters (pseudo-single-solute for DOM-containing waters) obtained from OMP adsorption isotherm data collected in examined waters.*

|  |  | Carbamazepine | Caffeine | Sulfamethoxazole |
|---|---|---|---|---|
| DOM-free water | $K_F$ (nmol/mg)/(nmol/L)$^{1/n}$ | 9.67±0.75 | 7.29±0.93 | 2.43±0.06 |
|  | $1/n_F$ (-) | 0.45±0.05 | 0.69±0.12 | 0.50±0.03 |
| Untreated water (Sept. sample) | $K_F$ (nmol/mg)/(nmol/L)$^{1/n}$ | 3.09±0.11 | 1.48±0.04 | 0.53±0.02 |
|  | $1/n_F$ (-) | 0.49±0.02 | 0.69±0.07 | 0.49±0.01 |
| PAC$_{200mg/L}$-treated water | $K_F$ (nmol/mg)/(nmol/L)$^{1/n}$ | 18.41±4.84 | 7.54±0.31 | 2.44±0.07 |
|  | $1/n_F$ (-) | 0.50±0.10 | 0.64±0.04 | 0.54±0.02 |

From Figure 2 it can also be observed that PAC$_{200mg/L}$-treated DOM was competition-free, as the OMP isotherms in PAC$_{200mg/L}$-treated water overlapped with (caffeine and sulfamethoxazole), or partially exceeded (carbamazepine), the OMP isotherms in DOM-free water. Although, the DOC concentration of the remaining DOM in PAC$_{200mg/L}$-treated water was still much higher than the concentration of the OMPs (2.52 mg C/L as compared to 6 µg/L for OMPs), and the SUVA (1.94 L/(mg·m)), indicated that there were still some aromatic fractions present, important for DOM competitiveness (Wang et al., 2021), but this weakly adsorbable, PAC$_{200mg/L}$-treated, DOM was not competitive against OMPs anymore.

This result aligned with our previous study on model DOM compounds, where weakly adsorbable DOM (e.g., pentanol and trimesic acid) did not interfere with OMP adsorption (e.g., carbamazepine and sulfamethoxazole) (Wang et al., 2021). These preliminary results thus demonstrate that, also in natural water, an LMW adsorbable DOM fraction (i.e., in $PAC_{200mg/L}$ pre-treated DOM) exists, occurring in large concentration asymmetry, occupying adsorption sites, but do not compete against OMPs. To the authors' knowledge, a similar observation has not been obtained before during conventional isotherm tests.

Competition-free adsorption (also known as complementary adsorption) for OMPs and simultaneously present DOM, was previously found, but restricted in studies with model LMW organics and heavy metals, and the examined concentrations were relatively high (usually in mg/L) than OMPs (Lerman et al., 2013; Zhang et al., 2012; Zhang et al., 2020a). Regarding the mechanism of competition-free adsorption, several adsorbates could complementarily occupy different sorption sites on the adsorbents (Pan and Xing, 2010; Zhang et al., 2012). The remaining DOM fraction in the $PAC_{200mg/L}$ pre-treated water may have had different preferred sorption sites compared to OMPs, with large differences in adsorption energy, on the energetically heterogeneous surfaces of activated carbon (Worch, 2012). Moreover, some co-adsorbates could provide extra π-π interaction sites for OMPs (Shimabuku et al., 2017b; Zhang et al., 2020a), or even complex with OMPs (Guillossou et al., 2020), potentially leading to an enhanced OMP removal. For example, carbamazepine and other OMPs (bisphenol A and ibuprofen) have been found to form complexes with hydrophilic humic substances from the aquatic environment (Bai et al., 2008; Ruiz et al., 2013; Wang et al., 2018; Wang et al., 2016). This was also observed in our study, which showed a higher carbamazepine adsorption capacity in presence of PAC-treated DOM than in DOM-free water.

Overall, the PAC pretreatment at a high dose can separate adsorbable, non-competitive surface water DOM from adsorbable competitive fractions, by removing the highly adsorbable DOM in advance. For a more advanced DOM fractionation across DOM adsorbability and better differentiation of competitive DOM for specific OMPs we, therefore, extended the range of PAC doses during pretreatment, which will be discussed in the following sections.

## 3.2 Variability of DOM competitors for different OMPs

For a more advanced DOM fractionation based on DOM adsorbability, and better differentiation of competitive DOM for specific OMPs, multiple PAC doses during pretreatment (i.e., 1st stage PAC doses in DOM-OMP asynchronous adsorption test) were used and related with the 2nd stage OMP percentage removals as shown in Figure 3 (OMP remaining percentages used in Figure S3). In DOM-free water, the percentage removals of the three selected OMPs were all above 85% (most right data point in Figure 3). However, in the untreated DOM-containing water, shown as $PAC_{0\ mg/L}$ pretreatment points in Figure 3 (most left data points), there was a large gap for OMP removal between carbamazepine (91 %) and sulfamethoxazole (19 %). After increasing the 1st stage PAC dose in the pretreatment, the 2nd stage OMP removal increased correspondingly, approaching the removals as observed in DOM-free water and closing the gap between removals of the various OMPs. The strongly adsorbable carbamazepine reached 2nd stage removals similar to DOM-free water at a relatively low 1st stage PAC dose (20 mg/L), whereas the weaker adsorbates reached such 2nd stage removals at considerably higher 1st stage PAC doses (caffeine, 40 mg/L; sulfamethoxazole, 200 mg/L). This result reveals that the various DOM fractions did not compete for the same (sub-)population of adsorption sites for different OMPs. The highly adsorbable DOM, removed in PAC pretreatment at a low dose (e.g., 20 mg/L), was competitive against all examined OMPs. For less adsorbable DOM, competitive adsorption and complementary adsorption took place at the same time during the co-adsorption with different OMPs. For instance, the $PAC_{40\ mg/L}$-treated DOM was a complementary co-adsorbate with carbamazepine and caffeine but competitive against sulfamethoxazole, which, to the authors' knowledge, was first observed.
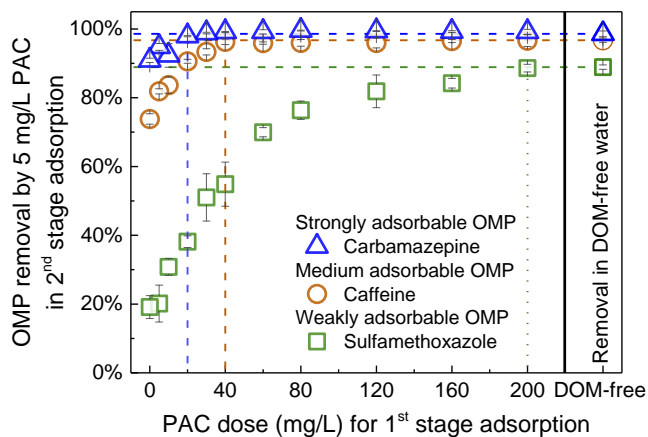
***Figure 3*** *Second stage OMP removals with 5 mg PAC/L after pre-DOM removal at variable first stage PAC doses for different OMPs, with horizontal dashed lines indicating OMP removals in DOM-free water, and vertical dashed lines indicating the first stage PAC doses required for full removal of competitive DOM, respectively. Error bars derived from experimental duplicates.*

DOM molecular weight analysis (see Figure S2) shows that there were remaining LMW organics (LMW acids and LMW neutrals) in the various PAC-treated waters (40 mg/L and 200 mg/L), which were competition-free against some/all examined OMPs. This result confirms that LMW organics also vary in competitiveness and should not be indiscriminately considered as effective DOM competitors. In a combined process of ozonation and adsorption, it was preliminarily found that ozone-modified DOM samples, richer in LMW organics but less adsorbable (due to lower hydrophobicity and aromaticity), appeared to be even less competitive against OMPs than the untreated sample (Wang et al., 2020; Zietzschmann et al., 2015b).

The varying OMP adsorption in the 2nd stage adsorption is illustrated in Figure 4 using operating lines (scheme in Figure 4a (Meinel et al., 2016; Zietzschmann et al., 2015a), and data applied in Figure 4b), to further interpret the results of DOM-OMP asynchronous adsorption in the context of isotherms. OMP adsorption capacities (shown as black dots) in 2nd stage adsorption moved upward, on the operating line of 5 mg PAC/L (2nd stage PAC dose), from untreated water isotherm towards DOM-free water isotherm ($q_e$ from 4.25 to 8.63 nmol/mg), with gradually removed DOM competitors with an increasing 1st stage PAC

dose. With certain 1st stage PAC doses (PAC$_{40mg/L}$ for caffeine), the operating line intersected with DOM-free isotherm, as competitive DOM was almost depleted in 1st stage adsorption.
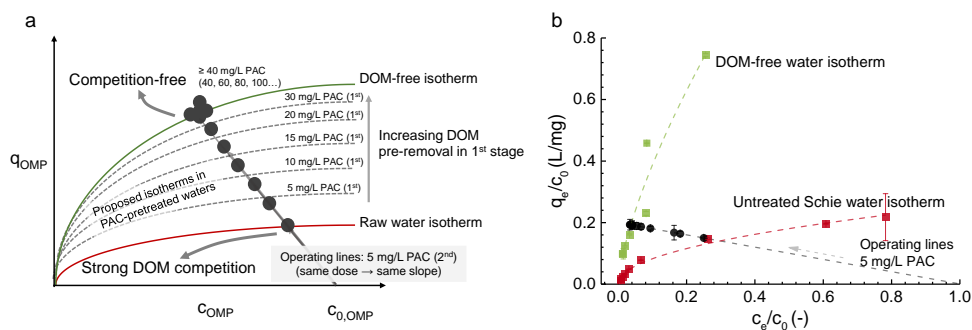


***Figure 4*** *OMP isotherms of untreated water and DOM-free water, and corresponding operating lines of the second stage OMP adsorption (PAC$_{5mg/L}$, a fixed PAC dose) in DOM-OMP asynchronous adsorption tests; theoretical scheme shown in subfigure a and experimental data (caffeine) in b. Note that OMP equilibrium liquid concentrations and PAC loadings were normalized to correct small deviations of initial OMP concentrations.*

To relate DOM adsorbability to competitiveness against different OMPs, Figure 5 displays the removals of (fictive) differently adsorbable DOM components at varying first stage PAC doses, generated using the IAST-based DOM adsorption analysis, and PAC doses required for alleviating competition against OMPs were also included for comparison. The results indicate that strongly adsorbable DOM fractions ($K_F$ = 140 (mg/g)/(L/mg)$^{1/n}$, $1/n_F$ = 0.25) adsorbed well, even at low PAC doses. The strongly adsorbable OMP, carbamazepine, only competed with this strongly adsorbable DOM fraction, since, even at relatively low 1st stage PAC doses, un-hampered 2nd stage removal of carbamazepine occurred (20 mg/L, also cf. Figure 3). This resulted in a high percentage of non-competitive adsorbable DOM (~70%, cf. Figure S4) and the percentage should be higher if the effect of MW was considered (Zietzschmann et al., 2014b). In contrast, the weakly adsorbable sulfamethoxazole suffered from the competition even by moderately adsorbable DOM adsorbates ($K_F$ = 70 (mg/g)/(L/mg)$^{1/n}$, $1/n_F$ = 0.25), since relatively high 1st stage PAC doses (removing moderate and weak DOM competitors) were needed to achieve 2nd stage removals of sulfamethoxazole similar to those in DOM-free water (200 mg/L). Hence, only a small percentage of adsorbable DOM (~25%) are irrelevant for DOM competition against the

sulfamethoxazole, and the weakly adsorbable DOM fraction ($K_F$ = 20 $(mg/g)/(L/mg)^{1/n}$, $1/n_F$ = 0.25) was the primary component (Figure S4). In order to alleviate competition against OMP removal by adsorption onto activated carbon, pretreatment should thus be focused on DOM adsorbability as the leading parameter, by removing the strongly (K=140) and moderately (K=70) adsorbable DOM from natural waters. Our results thus confirmed the hypothesis from an earlier study that a larger DOM fraction should be considered to affect the weakly adsorbable OMP (asulam, an herbicide) as compared to strongly adsorbable OMP (simazine, an herbicide) (Matsui et al., 2003). The stronger DOM competitiveness for weakly adsorbable OMPs was attributed not only to stronger inhibition by the same DOM sub-population (Wang et al., 2021), but also to a wider range of competitors.
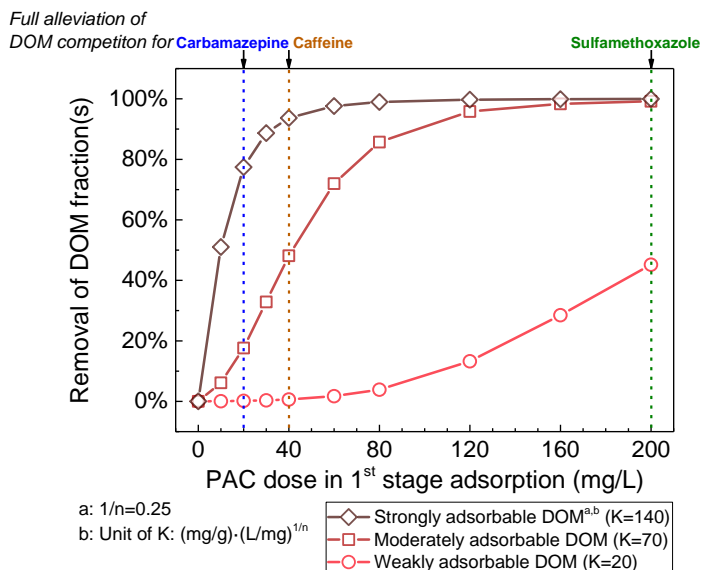
*Figure 5* *The removals of the fictive DOM components at different first stage PAC doses, and the thresholds (required first stage PAC doses in pretreatment) for alleviating DOM competition against different OMPs (marked as vertical drop lines, also cf. Figure 3). The removals of differently adsorbable DOM fractions were calculated using DOM adsorption analysis (K = 0, 20, 70, 140 $(mg/g) \cdot (L/mg)^{1/n}$, $1/n = 0.25$).*

Assisted by EBCM, the results of the DOM-OMP asynchronous test (2nd stage OMP removals in different 1st stage PAC-treated waters) were further translated into the removal of DOM competitors against caffeine (described by the removals of fictive EBC) during the 1st stage adsorption (see Figure 6), comparing to the caffeine removal (data extracted from isotherm test or kinetic test), as well as to the DOM removal, evaluated by bulk DOM parameters (DOC and $UV_{254}$). In order to obtain the $c_{0,EBC}$ removal, $K_{F,EBC}$ of the varying PAC-treated waters was assumed to be constant, making $c_{0,EBC}$ the only varying parameter, where $c_{0,EBC}$ removal was found to be almost identical regardless of $K_{F,EBC}$ (21.84 $(nmol/mg)/(nmol/L)^{1/n}$ in the EBCM fit of untreated water, or 7.29 $(nmol/mg)/(nmol/L)^{1/n}$ as the same with $K_{F,caffeine}$; cf. Figure S5) (Wang et al., 2020; Zietzschmann et al., 2015b). From Figure 6a it can be observed that the EBC removal (i.e., the decrease of DOM competitiveness, derived from asynchronous adsorption results) was slightly lower than the caffeine removal (derived from isotherm results), while there was a large gap between EBC removal and DOC removal (and change in

UV absorbance). In addition, the fictive DOM competitors (shown as EBC) approached the adsorption equilibrium faster than that of the bulk DOM (represented as DOC and $UV_{254}$), but slower than the OMP (Figure 6b). Here $PAC_{40mg/L}$ was used for the adsorption kinetics of DOM competitors due to the little competitiveness of $PAC_{40mg/L}$-treated DOM in the equilibrium test (cf. Figure 3). Note that $c_{0,EBC}$ removal was overestimated due to the constant $K_{F,EBC}$ in the presumption. This overestimated $c_{0,EBC}$ removal was still lower than OMP removal, indicating it is harder to remove DOM competitors (especially the medium/weak adsorbable competitors) than OMPs. Therefore, a rank of preferential adsorption on PAC surface could be derived for both equilibrium adsorption and non-equilibrium adsorption: OMP > DOM competitors > DOM non-competitors.

**a: Adsorption equilibrium**

**b: Adsorption kinetics**
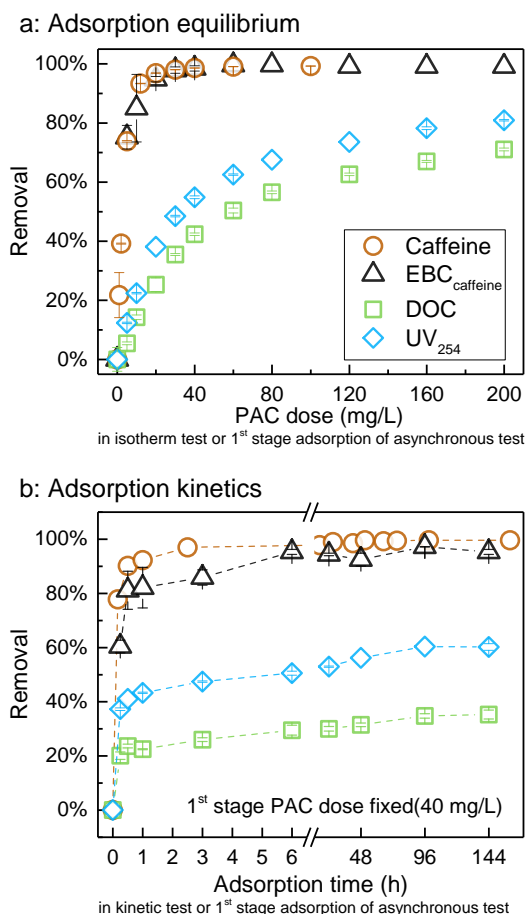
***Figure 6*** *The removal of DOM competitor (fictive–EBC, and sum parameters including DOC and UV$_{254}$) in the first stage of DOM-OMP asynchronous adsorption as compared to removal of caffeine (data extracted from OMP-spiked isotherm/kinetic test) at (a) adsorption equilibrium with various first stage PAC doses; (b) adsorption kinetics with PAC$_{40mg/L}$ pretreatment in the first stage adsorption. Note that second stage adsorption were all in 7 d; EBC removal calculation was based on fixed K$_{F,EBC}$ (21.84 (nmol/mg)/(nmol/L)$^{1/n}$) and 1/n$_{EBC}$ (0.69).*

## 3.3 Impact of initial OMP concentration on DOM competitors

To illustrate the varying DOM competitors at different initial OMP concentrations, Figure 7 relates the 2$^{nd}$ stage OMP percentage removals at different initial OMP concentrations to varying PAC pre-treatment doses in the 1$^{st}$ stage, and to the corresponding OMP removals in DOM-free water. Carbamazepine was used individually in the DOM-OMP asynchronous

test, without other co-existing OMPs (prevent competition at high initial OMP concentrations), at initial concentrations from 5.80 μg/L to 541 μg/L (Table S3). With a limited number of high-energy adsorption sites, the OMP at higher initial concentrations had lower removal percentages, whether or not DOM was present. But more importantly, the "adsorbable, non-competitive" was reproducible in the various DOM matrices (at a much higher DOC level in Dec. sample than Sept. sample, cf. Table S3). The increasing doses of PAC, needed to alleviate competition (i.e., bringing it to a similar level as in DOM-free water), suggest that some DOM fractions (with medium/weak adsorbability) that do not compete at low OMP concentrations, become extra competitors for OMP at high initial concentrations (cf. Figure 7). The reason might be that OMP at higher concentrations also adsorbs onto (energetically) less favorable adsorption sites that are still relatively favorable for some DOM molecules (Carter et al., 1995).
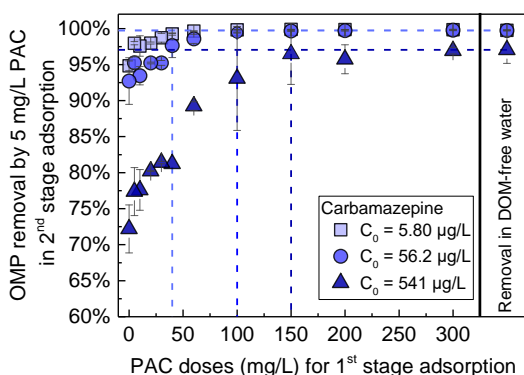


*Figure 7 Second stage removals of carbamazepine with 5 mg PAC/L after pre-DOM removal at variable first stage PAC doses for carbamazepine in different initial concentrations. Horizontal droplines showing averaged carbamazepine removals in DOM-free water, with vertical dashed droplines indicating competition alleviation achieved for carbamazepine in DOM-OMP asynchronous adsorption tests. Error bars derived from experimental duplicates.*

Again, EBCM was used to illustrate the impact of varying DOM competitors on OMP adsorption prediction, due to different initial OMP concentrations. In Figure S6 the EBCM prediction, initialized with $c_{0,EBC}$, $K_{F,EBC}$ and $1/n_{EBC}$ from adsorption isotherm test at medium $c_{0,OMP}$ of carbamazepine (57.1 μg/L), is compared with experimental isotherm data for OMP adsorption at the various initial OMP concentrations. Obvious overestimations for 524 μg/L OMP isotherm, particularly for low PAC doses were found, aligned with an earlier study (Qi

et al., 2007). The extra DOM competitors found at higher initial OMP concentrations, experimentally validated in this study, challenged the presumption towards constant concentration of DOM competitors ($c_{0,EBC}$), which could well explain the observed deviation in EBCM prediction. This is also why it is important to study the upper thresholds of initial OMP concentrations, which varied for differently adsorbable OMPs (e.g., ~3 µg/L for 2-methylisoborneol (Graham et al., 2000), ~30 µg/L for simetryn and ~1300 µg/L for asulam (Matsui et al., 2003)), for accurately predicting the OMP removal in DOM-containing waters.

## 4. Conclusions

- A DOM-OMP asynchronous two-stage adsorption procedure, adsorbing different DOM fractions *before* OMPs, was demonstrated in natural water for separating fractions of differently adsorbable DOM (1st stage) as well as evaluating their competitiveness (2nd stage). Therefore, the DOM competitors could be distinguished by DOM adsorbability.

- (LMW) adsorbable DOM did not ubiquitously exert competition against OMP adsorption onto activated carbon. The competitive role of DOM fractions was highly dependent on OMP adsorbability. Strongly adsorbable DOM fractions were strong competitors but moderately adsorbable DOM fractions only served as competitors against weakly adsorbable OMPs, or were complementary adsorbates to strongly adsorbable OMPs, and, in some cases, even enhanced OMP adsorption (potentially via complexation).

- The adsorption capacity and kinetics of DOM competitors were slightly lower than the respective OMP, but considerably higher DOM non-competitors.

- The amount of DOM competitors strongly varied for OMP at various initial concentrations. Increasing amounts of DOM became competitors for weaker adsorbable OMPs at higher initial OMP concentrations.

## Supporting information

***Text S1*** *OMP quantification with LC-MS/MS.*
High performance liquid chromatography combined with tandem mass spectrometry (LC-MS/MS) was employed to quantify OMPs in this study. Ultrapure water and acetonitrile (LC-

MS grade, Biosolve, France) phases, both acidified with 0.1 % LC-MS grade formic acid (Biosolve, France), were applied as mobile phases on an ACQUITY UPLC® BEH C18 (1.7μm particle size, 2.1x50 mm, Waters, Ireland) column, at a flow rate of 0.35 ml/min. Tandem mass spectrometry was conducted on a Xevo TQ-S micro (Waters, USA), equipped with electrospray ionization in positive modes. Two daughter ions from the mother ion were combined for detecting each OMP and quantification was performed with deuterated internal standards. Data evaluations were conducted with TargetLynx.

***Text S2*** *Modeling with equivalent background compound model (EBCM) for competing DOM analysis.*

EBCM was a fictive two-component competitive adsorption model based on the ideal adsorbed solution theory (IAST). EBCM was fitted to the experimental data (Najm et al. 1991). For each PAC dose, the best fitted $q_{OMP}$ and $q_{EBC}$ were searched by using the two EBC equations (Eqs. 1 & 2), then the corresponding $c_{OMP}$ and $c_{EBC}$ was calculated. The minimizer calculation was improved by integrating the relative error (e.g. $|(c_{OMP,meas} - c_{OMP,mod})/c_{OMP,meas}|$) and absolute error ($c_{OMP,meas} - c_{OMP,mod}$) at the same time (Eq. 3), rather than considering the relative error only. This helped avoid giving too much weight for the data points at high PAC doses (low absolute error but high relative error) during EBCM fitting process. The algorithm tried various parameter combinations for finding lowest *Min*, then the corresponding parameter sets were the best fitted one in EBCM.

$$c_{0,OMP} - d \times q_{OMP} - \frac{q_{OMP}}{q_{OMP}+q_{EBC}} \left( \frac{n_{OMP}q_{OMP}+n_{EBC}q_{EBC}}{n_{OMP}K_{F,OMP}} \right)^{n_{OMP}} = 0 \dots\dots\dots\dots(Eq.\ 1)$$

$$c_{0,EBC} - d \times q_{EBC} - \frac{q_{EBC}}{q_{OMP}+q_{EBC}} \left( \frac{n_{OMP}q_{OMP}+n_{EBC}q_{EBC}}{n_{EBC}K_{F,EBC}} \right)^{n_{EBC}} = 0 \dots\dots\dots\dots(Eq.\ 2)$$

where

| | |
|---|---|
| $d$ | PAC dose |
| $c_{i,0}$ | initial concentrations |
| $q_i$ | PAC loadings |
| $q$ | PAC loading |
| $1/n_i$ | Freundlich exponents |
| $K_{F,i}$ | Freundlich coefficients |

$$Min = \frac{1}{N} \times \sum_{j=1}^{N} \left( \frac{(c_{OMP,meas} - c_{OMP,mod})^2_j}{c_{OMP,meas}} + \frac{(q_{OMP,meas} - q_{OMP,mod})^2_j}{q_{OMP,meas}} \right) \dots\dots\dots\dots(\text{Eq. 3}) \text{where}$$

*Min*  minimization term

*N*  number of data points for different PAC doses

*c*  liquid phase concentrations

*q*  PAC loading

*meas*  Measured data experimentally

*mod*  Modeled data

***Table S1** Experimental conditions of adsorption isotherm tests in this study.*

| Section | Water sample | Mixed/single OMP | Initial OMP concentration (μg/L) | PAC doses (mg/L) |
|---|---|---|---|---|
| 3.1 | Untreated water (Sept. sample) | Mixed OMPs | ~6 for each | 1, 2, 5, 12, 20, 30, 40, 60, 100, 200 |
| | DOM-free water (Inorganics amended for Spet. sample) | Mixed OMPs | ~6 for each | 1, 2, 4, 6, 8, 10, 20, 30, 40 |
| | PAC pretreated water (200 mg/L PAC for Sept. sample) | Mixed OMPs | ~6 for each OMP | 1, 2, 4, 6, 8, 12, 20, 40, 60 |
| 3.3 | Untreated water (Dec. sample) | Carbamazepine | ~6 | 1, 2, 3, 5, 8, 10, 12, 16, 20 |
| | | | ~50 | 2, 5, 8, 12, 16, 20, 25, 30, 40 |
| | | | ~500 | 2, 5, 8, 10, 15, 20, 30, 40, 60 |
| | DOM-free water (Inorganics amended for Dec. sample) | Carbamazepine | ~50 | 1, 2, 3, 4, 5, 6, 7, 8, 10 |

*Table S2* *Experimental conditions of DOM-OMP asynchronous tests in this study.*

| Section | Water sample | Mixed/single OMP | Initial OMP concentration ($\mu g/L$) | PAC doses (mg/L) 1st stage | 2nd stage |
|---|---|---|---|---|---|
| 3.2 | Untreated water (Sept. sample) | Mixed OMPs | ~6 for each | 0, 5, 10, 20, 30, 40, 60, 80, 120, 160, 200 | 5 |
| | DOM-free water (Inorganics amended for Spet. sample) | Mixed OMPs | ~6 for each | 0 (OMP removal in DOM-free water for reference) | 5 |
| | Untreated water (Sept. sample) | Mixed OMPs | ~6 for each | 40 (Adsorption time: 0, 0.25, 0.5, 1, 3, 6, 12, 24, 48, 96, 144 h) | 5 (7 d) |
| 3.3 | Untreated water (Dec. sample) | Carbamazepine | ~6 ~50 ~500 | 0, 5, 10, 20, 30, 40, 60, 100, 150, 200, 300 | 5 |
| | DOM-free water (Inorganics amended for Dec. sample) | Carbamazepine | ~6 ~50 ~500 | 0 (OMP removal in DOM-free water for reference) | 5 |

*Table S3* *DOM characteristics of examined waters.*

| | PAC dose | pH | DOC | UV$_{254}$ | SUVA |
|---|---|---|---|---|---|
| **Units** | mg/L | - | mg C/L | 1/cm | L/(mg·m) |
| Untreated water (Sept.) | - | 8.08 | 10.2 | 0.299 | 2.93 |
| PAC pretreated water (Sept.) | 200 | 8.17 | 2.52 | 0.049 | 1.94 |
| Untreated water (Dec.) | - | 8.17 | 18.6 | 0.535 | 2.88 |

**Table S4** *Ionic concentrations in Schie water.*

|  | Sample in September [mmol/L] | Sample in December [mmol/L] |
|---|---|---|
| $Ca^{2+}$ | 1.79 | 3.44 |
| $Mg^{2+}$ | 0.68 | 0.80 |
| $Na^+$ | 3.08 | 1.93 |
| $K^+$ | 0.32 | 0.31 |
| $Cl^-$ | 3.21 | 1.82 |
| $SO_4^{2-}$ | 0.48 | 1.80 |
| $NO_3^-$ | 0.03 | 0.15 |
| $HCO_3^-$ | 4.01 | 5.12 |

**Table S5** *EBCM-fitted $c_{0,EBC}$ values fitted from isotherm test and one data point ($PAC_{5mg/L}$) using in 2nd stage adsorption of DOM-OMP asynchronous adsorption test.*

|  |  | Carbamaz epine | Caffeine | Sulfametho xazole | Additional details |
|---|---|---|---|---|---|
| Untreated water (Sept. sample) | $K_{F,EBC}$ $(nmol/mg)/(nmol/L)^{1/n}$ | 15.30 | 21.84 | 10.62 | Fitted by $K_{F,EBC}$ optimizing algorithm |
|  | $1/n_{F,EBC}$ (-) | 0.45 | 0.69 | 0.50 | same with $1/n_F$ in single-solute OMP isotherm |
|  | $c_{0,EBC,iso}$ (nmol/L) | 161 | 11469 | 717 | fitted from isotherm test |
|  | $c_{0,EBC,one}$ (nmol/L) | 161 | 11645 | 776 | fitted from one data point (5 mg PAC/L) |
|  | Relative error of $c_{0,EBC}$ | 0% | 1.5% | 8.2% |  |

***Table S6*** *DOM adsorption in 1st and 2nd stage adsorption, shown as UV absorbance at 254nm.*

| 1st stage PAC dose (mg/L) | UV$_{254}$ after 1st stage (1/cm) | UV$_{254}$ removal in 1st stage | 2nd stage PAC dose (mg/L) | UV$_{254}$ after 2nd stage (1/cm) | UV$_{254}$ removal in 2nd stage | Additional UV$_{254}$ removal during 2nd stage* |
|---|---|---|---|---|---|---|
| 200 | 0.057 | 81% | 5 | 0.055 | 4% | 1% |
| 160 | 0.065 | 78% | 5 | 0.062 | 5% | 1% |
| 120 | 0.079 | 74% | 5 | 0.075 | 5% | 1% |
| 80 | 0.097 | 68% | 5 | 0.09 | 7% | 2% |
| 60 | 0.112 | 63% | 5 | 0.102 | 9% | 3% |
| 40 | 0.135 | 55% | 5 | 0.122 | 10% | 4% |
| 30 | 0.154 | 48% | 5 | 0.138 | 10% | 5% |
| 20 | 0.185 | 38% | 5 | 0.165 | 11% | 7% |
| 10 | 0.232 | 22% | 5 | 0.203 | 13% | 10% |
| 5 | 0.262 | 12% | 5 | 0.229 | 13% | 11% |
| 0 | 0.299 | 0% | 5 | 0.261 | 13% | 13% |

\* Calculation based on UV$_{254}$ of untreated DOM.
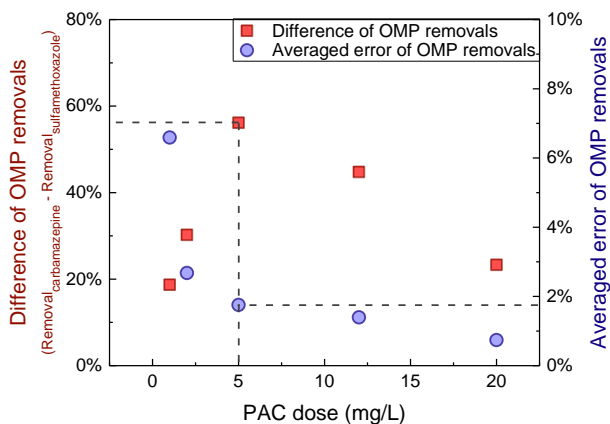


***Figure S1*** *Difference of OMP removals (largest difference between carbamazepine and sulfamethoxazole shown here) and averaged error of OMP removals (all selected OMPs) at different PAC doses. Data from OMP isotherm test in untreated water.*
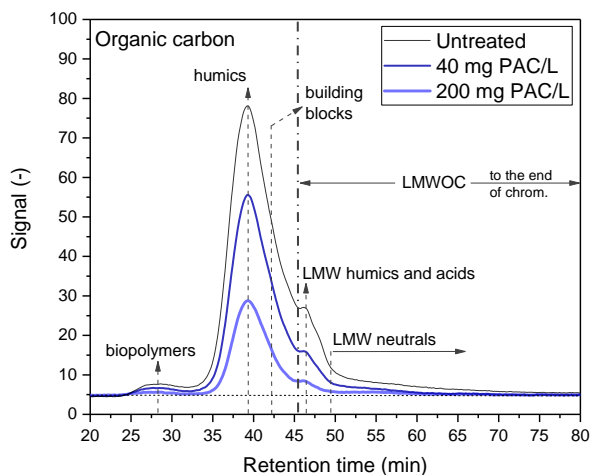
**Figure S2** *LC-OCD chromatograms of the untreated water and differently PAC-treated water (40 and 200 mg/L).*
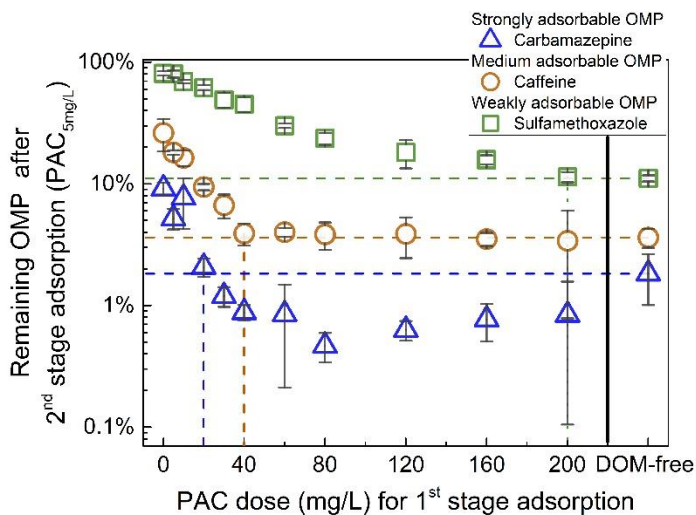


**Figure S3**. *Remaining percentages of OMPs after second stage adsorption (PAC_{5mg/L}) in PAC-treated waters at variable first stage PAC doses, with horizontal dashed lines indicating OMP removals in DOM-free water, and vertical dashed lines indicating the first stage PAC doses required for sufficient removal of competitive DOM, respectively. Error bars derived from experimental duplicates.*
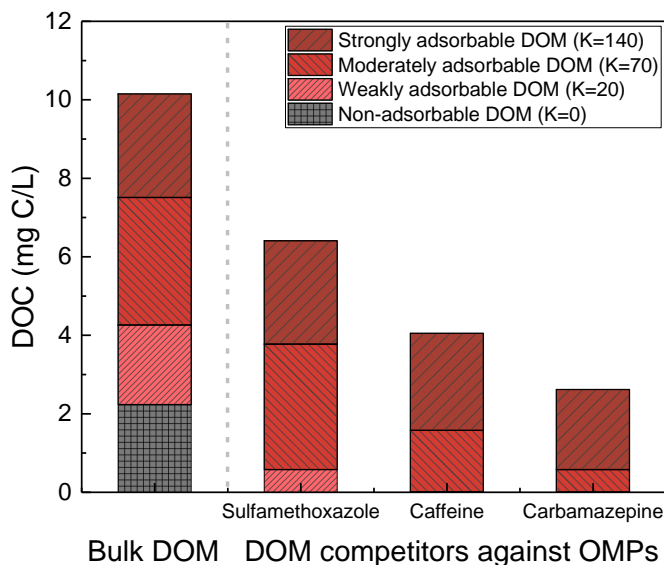
**Figure S4** *Comparison of bulk DOM and DOM competitors determined during asynchronous adsorption tests, in which only DOM adsorbability considered regardless of DOM molecular weight. The DOC concentrations of differently adsorbable DOM fractions were calculated using DOM adsorption analysis (K = 0, 20, 70, 140 (mg/g)·(L/mg)$^{1/n}$, 1/n = 0.25, also cf. Figure 5).*
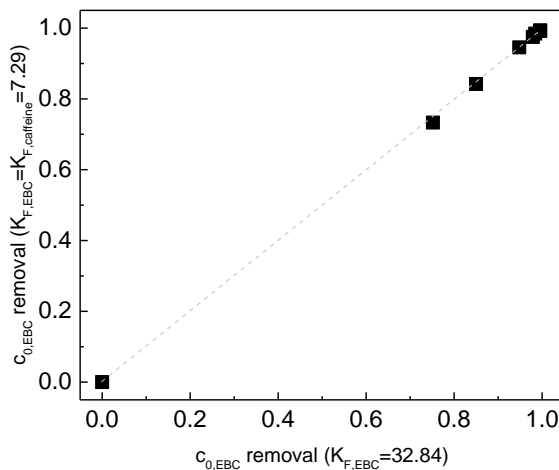


**Figure S5** *Comparison of $c_{0,EBC}$ removal with different $K_{F,EBC}$ values (unit: (nmol/mg)/(nmol/L)$^{1/n}$) applied. Reference line (grey) for the identical $c_{0,EBC}$ removal.*
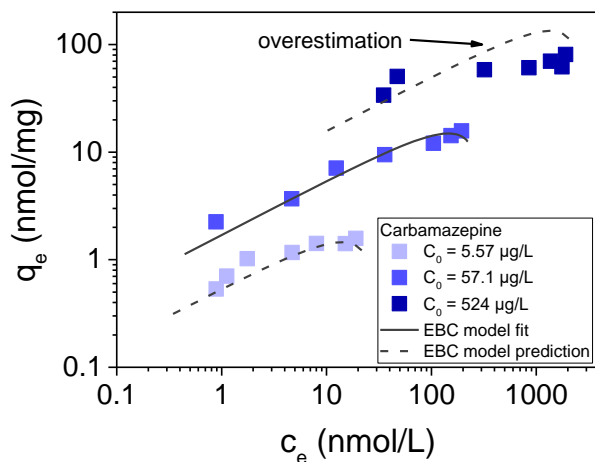
***Figure S6*** *Comparison of EBCM prediction with experiment data for OMP adsorption (carbamazepine) in different initial concentration. Medium OMP concentration were used for fitting EBCM parameters ($c_{0,EBC}$ = 24506 nmol/L and $K_{F,EBC}$ = 37.92 (nmol/mg)(L/nmol)$^{1/n}$, $1/n_{EBC}$ = 0.51) to predict OMP isotherms at higher/lower initial OMP concentration.*

# Chapter 4

# The interplay between molecular weight, aromaticity, and polarity of dissolved organic matter in competitive adsorption against organic micropollutants
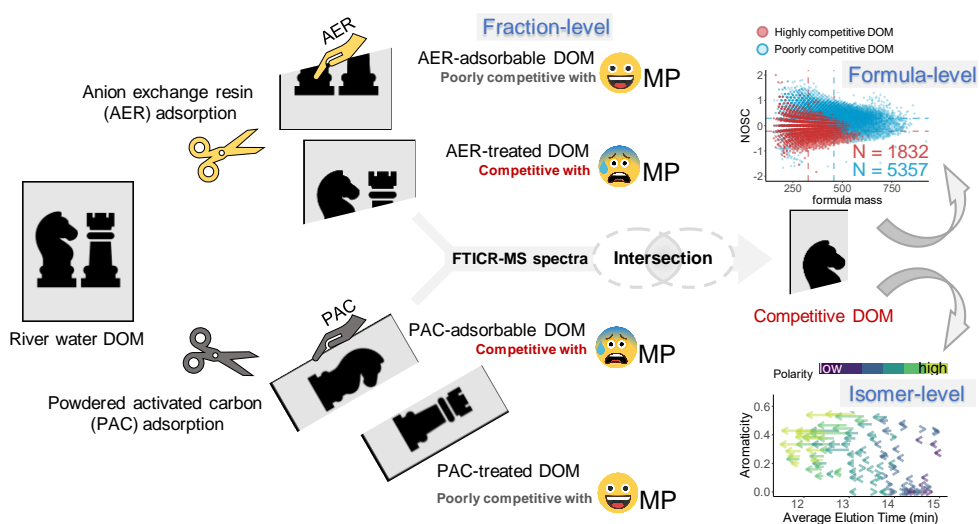


This chapter is based on: Wang, Q., Lechtenfeld O. J., Rietveld, L.C, Yu, J., Yang M., Schuster J., Ernst M., Hofmann R., Kaesler J., Zietzschmann F. The interplay between molecular weight, aromaticity, and polarity of DOM in competitive adsorption against OMPs. In preparation.

## Abstract

In water treatment, competitive adsorption from background dissolved organic matter (DOM) is the main reason for the reduced efficacy of organic micropollutants (OMPs) removal via adsorption onto activated carbon. However, the molecular composition of competitive DOM fractions and dominant molecular properties that affect DOM adsorbability and competitiveness are still largely unexplored. To differentiate competitive DOM, powdered activated carbon (PAC) and anion exchange resin (AER) served as pretreatments and the competitiveness was assessed in a subsequent PAC sorption step. We used direct sample injection liquid chromatography (LC) coupled with ultrahigh-resolution mass spectrometry to reveal how molecular weight (MW), polarity and aromaticity influence DOM competitiveness against OMPs. While a large percentage of DOM components could adsorb on PAC, many of them were categorized as poorly competitive, since they were removed during AER pretreatment without much alleviation of DOM competition against OMPs. The dominant factor of DOM adsorbability was aromaticity for low MW DOM, and transited to polarity with increasing MW. DOM compounds with relatively high adsorptive removal were not necessarily competitive against OMPs, due to DOM dissociation induced by high polarity, by which DOM compounds with high MW and high aromaticity were affected. In addition, N-containing compounds (CHNO) had higher PAC adsorbability and competitiveness over compounds only with CHO. For molecular formulas with an overall high aromaticity and high polarity, selective adsorption of less polar DOM isomers (as revealed by LC) was firstly observed and higher adsorbability (or competitiveness) of these compounds could be expected than the removal calculated based on formula-level.

# 1. Introduction

Activated carbon adsorption is widely applied in water treatment to abate the potential health concerns from organic micropollutants (OMPs) (Betsholtz et al., 2021; Jiang et al., 2017a). However, adsorptive OMP removal can vary due to multiple factors, including activated carbon properties (pore size distribution, surface chemistry)(Huang et al., 2020a; Huang et al., 2020c; Yu et al., 2007), molecular characteristics of OMPs (e.g. molecular weight, aromaticity, polarity), and competitive adsorption from background dissolved organic matter (DOM). DOM concentrations (in mg C/L) are usually much higher than those of OMPs (in ng/L-μg/L), and OMP adsorption is thus reduced through direct site competition or pore blockage by coexisting DOM (Shimabuku et al., 2014; Worch, 2012). Direct site competition originate from a subpopulation of LMW DOM compounds, and the competitors varied for different OMPs and different initial OMP concentrations (cf. Chapter 3). However, little is known about the molecular composition of the DOM fractions responsible for competition, and the related DOM properties.

An integrated analysis of the interactions of different DOM properties is therefore essential. Although previous studies on individual DOM characteristics (e.g., molecular weight (MW) (Li et al., 2003b; Matsui et al., 2012; Zietzschmann et al., 2014b), polarity/ hydrophobicity (Lerman et al., 2013), aromaticity (Wang et al., 2021), isoelectric point (Hu et al., 2014; Newcombe et al., 2002b)) have substantiated their impact on DOM competition. However, because DOM characteristics are interrelated, some contradicting interpretations impede a comprehensive understanding of the characteristics of competitive DOM. For example, pretreatment using anion exchange resin (AER) or coagulation removes negatively charged

(with low isoelectric point, mostly high MW) DOM from the solution but the remaining DOM has been found to be still strongly competing against (uncharged) OMPs (caffeine, atrazine, or 2-methylisoborneol) during subsequent AC adsorption (Hu et al., 2014; Newcombe et al., 2002b; Zoschke et al., 2011). At the same time, aromaticity, determined by UV absorbance or specific ultraviolet absorbance (SUVA) (Weishaar et al., 2003), dropped considerably, thus contrasting with studies that highlight aromaticity as crucial in determining DOM adsorbability (Ersan et al., 2017) and/or competitiveness (Wang et al., 2021). Therefore, simultaneous multi-dimensional DOM characterization at a molecular level is necessary for in-depth DOM competitiveness analysis.

Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) has been extensively used to characterize DOM fractions during sorption (soil (Chen et al., 2022), clay (Avneri-Katz et al., 2017), hydrophobic resin (Perminova et al., 2014; Subdiaga et al., 2020), and metal salts/oxides (Lavonen et al., 2015; Lv et al., 2016; Riedel et al., 2012; Subdiaga et al., 2020)) at a molecular level. However, few studies have specifically focused on competitive DOM (or basically, adsorbable DOM) in activated carbon adsorption. By coupling reversed-phase liquid chromatography (RPLC), RPLC-FTICR-MS allows for the direct injection of water samples, avoiding potential chemical fractionation during solid phase extraction (Kong et al., 2021). Charge competition and matrix effects are then reduced as compared to the direct infusion electrospray ionization (Han et al., 2021). Varying RPLC retention of different DOM isomers is an additional polarity indicator, superimposed on the calculated formula polarity, advancing the understanding of DOM diversity from the level of molecular formulas to isomers (Jennings et al., 2022).

Therefore, the objective of the present study was to simultaneously evaluate the influence of real-water DOM characteristics on competitiveness using RPLC-FTICR-MS. Surface water DOM was fractionated by pre-treatment with powdered activated carbon (PAC) and AER, respectively, to isolate highly competitive DOM through charge and adsorbability. The features of competitive DOM were then identified by intersecting FTICR-MS spectra of two DOM fractions with high competitiveness (less charged DOM, and strongly PAC adsorbable DOM). In addition, DOM properties and their relation with respect to competitiveness against OMPs, were then assessed at the formula/isomer level.

## 2. Materials and methods

**Water samples.** A water sample from river Schie (Delft, the Netherlands; sampled on September 2nd, 2020, dry weather) was filtered by 0.45 μm polyethersulfone membrane filters (Millipore, rinsed with ultrapure water). Additionally, inorganic-amended ultrapure water was prepared for the reference "competition-free" scenario for OMP adsorption, of which the ion composition was similar to the untreated river water (Table S1).

**OMPs.** Carbamazepine, caffeine and sulfamethoxazole (from Sigma-Aldrich) were selected as exemplary OMPs because of their high environmental relevance and the large difference in PAC absorbability (Hu et al., 2014; Zietzschmann et al., 2015b).

**Sorbents.** A strongly basic, granular AER (Lewatit 8071, Bayer, UK) was used for AER pretreatment due to its high performance in the removal of negatively charged DOM, especially from surface water (Hu et al., 2014). Resin samples were rinsed with sodium chloride solution (~1 mol/L) and ultrapure water before use. A mesoporous PAC (SAE Super,

Norit, Netherlands; ~50% pore volume for mesopores) was selected for batch adsorption tests, to reduce DOM pore blocking (Ebie et al., 2001). PAC samples were rinsed with ultrapure water, dried at 105°C overnight, and degassed in a vacuum for preparing PAC stock suspensions at 4 g/L and 20 g/L. Homogenization by 0.5 h stirring was applied before dosing PAC (using pipettes) into the adsorption batches.

**DOM pretreatments and competitiveness tests.** AER pretreatment was conducted at an overdose (15 mL/L) and 60 min contact time (Hu et al., 2014). PAC pretreatment was conducted at various PAC doses (exact doses see the next paragraph) for 7 days, removing various adsorbable DOM fractions and functioning as a DOM fractionation by adsorbability. To test the DOM competitiveness of the remaining DOM after AER/PAC pretreatment, additional OMP adsorption tests (isotherm test or asynchronous adsorption tests) were conducted, after removing the adsorbents, used for pretreatment.

Isotherm tests were performed in DOM-free water, untreated water, AER-treated water and $PAC_{200mg/L}$-treated water (i.e., treated with 200 mg PAC/L). OMPs were spiked to the different examined water samples at ~6 μg/L, before PAC dosages (1-200 mg/L) were applied. To further differentiate the competitive DOM against different OMPs, the PAC doses for pretreatment were reduced from 200 mg PAC/L to 5 mg PAC/L (10 doses in total, 5, 10, 20, 30, 40, 60, 80, 120, 160, 200 mg PAC/L), and an additional second stage adsorption test was performed. OMPs were subsequently spiked (~6 μg/L) in the untreated water and the various PAC-pretreated waters. Then $PAC_{5mg/L}$ (i.e., 5 mg PAC/L) was used in the second-stage adsorption, revealing the competitiveness of the remaining DOM (after first-stage adsorption) against OMPs.

PAC adsorption tests were all conducted on a shaker (120 rpm) for 7 days at 20 ℃. Upon finishing, regenerated cellulose syringe filters (0.2 μm, SPARTAN, Whatman, rinsed with tap water) and polyethersulfone filters (0.45 μm Chromafil Xtra PES-45/25, Macherey-Nagel, Germany) were employed for OMP and DOM sampling, respectively.

**OMP partition coefficients on activated carbon.** High performance liquid chromatography tandem mass spectrometry (LC-MS/MS, Xevo TQ-S, Waters), using an ACQUITY UPLC BEH C18 column (1.7μm particle size, 2.1×50 mm, Waters, USA), served for analyzing the OMP concentrations. A qualitative analysis was performed with two daughter ions of OMPs and deuterated internal standards were used for OMP quantification (details in Text S1). The partition coefficients of OMPs on activated carbon ($K_{d,OMP}$) at $PAC_{5mg/L}$ (i.e, fixed number of total adsorption sites) were determined by dividing the solid-phase OMP loading on the activated carbon with the liquid-phase OMP concentrations at equilibrium adsorption.

**Conventional DOM characterization.** A UV-Vis spectrophotometer (GENESYS 10S, Thermo, USA) was employed to measure the UV absorbance at 254 nm ($UV_{254}$). DOC was determined on a TOC analyzer (TOC-VCPH, Shimadzu, Japan). $SUVA_{254}$ was subsequently calculated by dividing $UV_{254}$ by the DOC concentration. Liquid chromatography coupled with organic carbon and UV absorbance detection (LC-OCD-UVD, DOC-Labor Huber, Germany), using a HW50S column (Toyopearl, Japan), was applied for obtaining the MW distributions (biopolymers, >20000 g/mol; humics, ~1000 g/mol; building blocks, 300-500 g/mol; LMW humics and acids, <350 g/mol; LMW neutrals, <350 g/mol) of examined DOM samples.

**RPLC-FT-ICR MS measurement.** DOM samples for FT-ICR MS measurements were prepared as process triplicates but without an OMP spike. PAC doses were 40 and 200 mg/L for untreated water and 10 mg/L for AER-treated water, resulting in a similar specific PAC dose (~2.5 mg PAC/mg DOC) as compared to 40 mg PAC/L in untreated water, respectively. Samples were kept in the dark at 4 °C before measurement. Samples were directly injected without further sample preparation in a C18 reversed-phase column (ACQUITY HSS T3, 1.8 µm, 100 Å, 150 × 3 mm, Waters, Milford, MA with 5 mm guard column), installed in an ultra-high performance liquid chromatography system (UltiMate 3000RS, Thermo Fischer Scientific, Waltham, MA, USA), for DOM separation. The LC setup includes a dual pump setup supplying a post-column counter gradient (CG) as described in Han et al. (2021) and Jennings et al. (2022). Ultrapure water (0.05% formic acid added, Milli-Q Water (MQW); Merck, Germany) and methanol (0.05% formic acid added, MS grade; Biosolve, Netherlands) were used as mobile phases. The specific gradient program (100% MQW for 0.5 min, then a linear increase to 100% MeOH within 14 min) allowed for efficient separation of the matrix from the DOM and hence direct injection of water samples at their native concentrations.[22] The LC system was hyphenated with a FT-ICR MS (12T solariX XR, Bruker Daltonics, Billerica, USA), equipped with an electrospray ionization (ESI) source (Apollo II, Bruker Daltonics), and operated in negative mode (4.3 kV capillary voltage). The use of a post-column CG stabilizes solvent composition of the ESI source to 50% MQW/50% MeOH and facilitates the ionization of the most polar DOM fractions.[21] Mass spectra for LC-MS measurements were acquired in full profile broadband mode (147 to 1000 m/z) with 0.8 s ion accumulation time and 2 megaword data size (resolution approximately. 231000 @ m/z 400) resulting in a scan rate of approximately 1 Hz.

Due to the broad distribution of individual m/z values across the chromatographic retention time and to facilitate data processing, a formula-average spectrum between 10 and 15.8 min (338 individual mass spectra) was generated. Later eluting DOM was excluded in this step due to a few large mass peaks in the spectra > 15.8 min (cf. Figure S1), but were considered in the extracted ion chromatogram (EIC) analysis. Mass peaks in averaged spectra were considered with a signal to noise (S/N) ratio > 4 and the average mass spectra were internally recalibrated with a mass list of known DOM masses using DataAnalysis (version 5.0).

**FT-ICR MS data processing.** Molecular formulas were assigned to m/z values in averaged LC-MS spectra using an in-house software with the following parameters: mass range (150-1000 m/z), maximum mass error of ±0.9 ppm, $C_{1-80}$, $H_{1-198}$, $O_{0-40}$, $N_{0-4}$, $S_{0-1}$. Isotopologues ($^{13}C_1$ and $^{34}S$) were used for quality control and removed from the final data set. Additional filters were applied to the calculated molecular formulas as follows: $0.3 < H/C < 2.5$, $0 < O/C < 1$, $0 < N/C < 1.5$, $0 < DBE$ (double bond equivalent) $< 25$, $-10 < DBE-O < 10$ as proposed by Herzsprung et al. (2014) and element probability rules proposed by Kind and Fiehn (2007).

Molecular formulas present in the blank samples, including solvent blanks and triplicate treatment blanks (using ultrapure water instead of river water in PAC/AER treatment) were removed from the final data set. Results from the samples were averaged into a single molecular formula list comprising of only molecular formulas present in at least two replicates ($n$ = 3). Due to issues with intensity and/or calibration, up to one of the three triplicate measurements were excluded in the final averaged spectra (Table S2). In the average spectra, only one CHS formula was assigned in all samples and it was therefore not further considered.

Three molecular descriptors were used as summary parameters linking DOM properties to DOM adsorbability/competitiveness, including aromaticity (using modified aromaticity index (AI_mod) in Eq. 1) to describe π-π interaction[Koch and Dittmar, 2016], polarity (using nominal carbon oxidation state (NOSC) in Eq. 2) to describe hydrophobic interactions, and formula mass, to assess the pore accessibility (Jennings et al., 2022). A comparison of independent samples (before/after pretreatment) was performed with Mann-Whitney U-test.

$$AI_{mod} = 4 - \frac{1+C-0.5O-S-0.5(N+H)}{C-0.5O-N-S} \quad \dots\dots\dots\dots\dots\dots\dots\text{(Eq. 1)}$$

$$NOSC = 4 - \frac{4C+H-3N-2O-2S}{C}\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 2)}$$

Raw mass peak intensities were used as a semi-quantitative measure to calculate the loss (i.e., percent intensity removed per molecular formula) of DOM compounds due to PAC/AER pretreatment from untreated water (i.e., DOM sorbed on PAC/AER). The remaining intensity in the solution was defined as DOM remaining after PAC/AER pretreatment (for specific adsorbent doses). Raw mass peak intensities in combination with the original DOC concentration of the injected samples into LC-FT-ICR MS were found to be superior to other normalization methods, i.e., lower relative standard deviation (Figure S2), while maintaining good relation between DOC concentrations and the sum peak intensity (Figure S3) (Jennings et al., 2022). Only molecular formulas with an intensity difference of > 5% were considered as DOM compounds that could sorb on adsorbents.

To assess the isomer polarity of molecular formulas, extracted ion chromatograms (EIC) were generated from the raw LC-MS data using a mass window of 5 ppm. Based on the EIC data, an

intensity weighted average retention time (AET) for individual molecular formulas was calculated to describe the overall polarity of the examined isomers. EIC data were smoothed using a Savitzky-Golay filter (n = 31, 3 cycles) for visualization. AET was calculated based on the intensity distribution of each DOM formula, within the elution time ranging from 10.0 minutes to 15.8 minutes to match the retention time used for averaging the spectra.

Both DOM *remaining* after AER pretreatment and DOM *adsorbed* onto $PAC_{40mg/L}$ (i.e, 40 mg PAC/L) were identified as highly competitive DOM, but had a large difference in the molecular composition (cf. section "Molecular composition of DOM after pretreatment"). In literature, it has been found that AER pretreatment did not alleviate DOM competition against OMPs.(Hu et al., 2014) Therefore, through an intersection of their molecular formulas, DOM sorbed onto $PAC_{40mg/L}$ was further classified into two types, DOM sorbed on $PAC_{40mg/L}$ and remaining after AER pretreatment (strongly competitive) and DOM sorbed on $PAC_{40mg/L}$ yet undetected after AER pretreatment (poorly competitive), to visualize the compositions of the DOM fractions with different competitiveness. A semi-quantitative comparison of the adsorption behavior of sorbed DOM on $PAC_{40mg/L}$ was based on the removal percentages (Chen et al., 2022). It should be noted that the molecular formulas with a low peak intensity ($<10^5$ in untreated DOM) were not included in the quantitative comparison, as the intensity in the treated sample may be below the detection limits (S/N = 4), thus leading to overestimated removals. The relationship between peak intensity and removal is described in Figure S4. To assess if there was PAC preferential adsorption of particular isomers in highly competitive DOM (sorbed on $PAC_{40mg/L}$ and remaining after AER pretreatment), some molecular formulas were selected

(peak intensity rank < 1000, removal < 100% for $PAC_{40mg/L}$, $PAC_{200mg/L}$ and AER pretreatment) to calculate the AET variation, with their EICs.

# 3. Results and discussion

## 3.1 Varying DOM-OMP competition after AER/PAC pretreatment

To analyze the overall competition of DOM on the adsorption of OMPs onto PAC during the stage with $PAC_{5mg/L}$ (i.e, 5 mg PAC/L), the PAC-water partition coefficients of the OMPs, in the differently pretreated samples (untreated water, AER-treated water, $PAC_{40mg/L}$-treated water, $PAC_{200mg/L}$-treated water), are shown in Figure 1, along with background DOM characteristics. Compared to DOM-free water, the $K_d$ in untreated water was reduced to 14%, 9%, and 3% for the well, moderately, and poorly adsorbable carbamazepine, caffeine, and sulfamethoxazole, respectively. Despite the high DOM removal in AER pretreatment (75% DOC, 93% $UV_{254}$-active DOM), slightly higher $K_d$ was observed for the two uncharged OMPs (carbamazepine and caffeine) (Figure 1), and their adsorption isotherms in AER-treated water were close to the isotherms in untreated water (Figure S5). For the negatively-charged sulfamethoxazole, three times higher adsorption was found in AER-treated water, but the remaining competition was still strong as compared to DOM-free water. The results indicate that the DOM competitors may differ for OMPs with different charges. DOM remaining after AER pretreatment, with on average fewer anionic functional groups, has been found to be the major competitor against both negatively charged and uncharged OMPs (Hu et al., 2014; Humbert et al., 2008), while the removed, negatively charged DOM, competed for the PAC adsorption sites and potentially exerted electrostatic repulsion against negatively charged

OMPs (sulfamethoxazole here). In other competition studies between model DOM compounds, it has been found that the dissociation of 2,4-dichlorophenol and 4-chloroaniline at neutral pH increased their polarity/hydrophilicity and thus reduced their adsorbability. The dissociated species have higher hydrophilicity and are less adsorbable and non-competitive against nonionic naphthalene (Levchuk et al., 2018; Newcombe and Drikas, 1997), while naphthalene is always competitive against 2,4-dichlorophenol and 4-chloroaniline regardless of their dissociation.
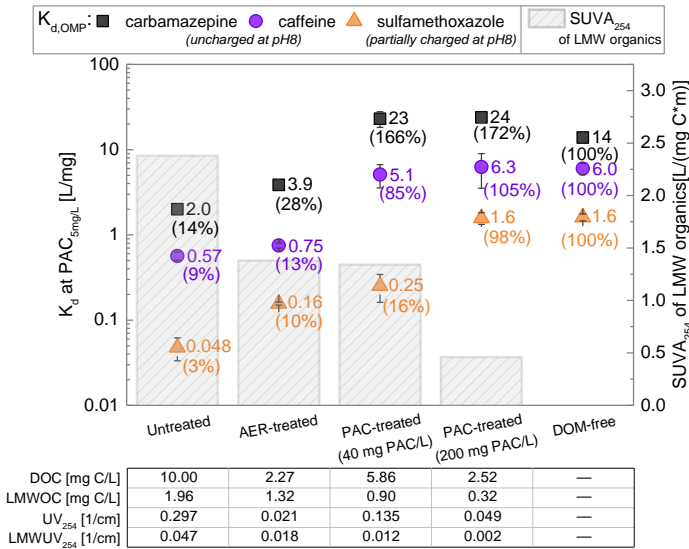


**Figure 1** *OMP partition coefficients ($K_d$) between solid phase (PAC) and liquid phase in the pretreated waters at $PAC_{5mg/L}$ (i.e.,5 mg PAC/L), with percentages (in brackets) of the respective $K_d$ in DOM-free water, along with $SUVA_{254}$ of LMW organics (grey columns), and DOC and LMWOC concentrations, as well as $UV_{254}$ and LMW $UV_{254}$ (table). Note that $PAC_{5\ mg/L}$ is the second stage adsorption, to assess the competitiveness of $PAC_{40mg/L}$-pretreated DOM and $PAC_{200mg/L}$-pretreated DOM.*

The OMP adsorption on $PAC_{5mg/L}$ increased substantially in the PAC-pretreated water. Only weakly competitive adsorption for carbamazepine and caffeine occurred in $PAC_{40mg/L}$-pretreated water. In $PAC_{200mg/L}$-pretreated water also the competitive adsorption was mostly alleviated for the weakly adsorbable sulfamethoxazole (cf. Figure S6). This phenomenon, where a fraction of (PAC-) adsorbable DOM has no competitiveness against OMPs (e.g., $PAC_{200mg/L}$-sorbed DOM vs. all examined OMPs or $PAC_{40mg/L}$-sorbed DOM vs. carbamazepine/caffeine), has been termed as complementary adsorption in previous studies (*cf. Chapter 3*), suggesting that DOM competitiveness could be neglected when the strongly adsorbable DOM is removed. Thus, overall, the $PAC_{40mg/L}$-adsorbable DOM fraction represented virtually all DOM compounds with high competitiveness against uncharged OMPs.

DOM remaining after AER pretreatment was much more competitive than DOM remaining after $PAC_{40mg/L}$ pretreatment, although both DOM had a similar $SUVA_{254}$ of LMW fractions (cf. Figure 1 and LC-OCD chromatogram in Figure S7). In literature, it has been suggested that LMW DOM may serve as a powerful DOM competitiveness indicator (Zietzschmann et al., 2016a; Zietzschmann et al., 2016c), but our results imply that LMW DOM compounds vary with respect to their competitiveness against OMPs, and molecular characterization is required to associate DOM competitiveness with chemical properties like aromaticity and polarity.

## 3.2 Molecular composition of DOM after pretreatment

In the untreated sample, 7352 molecular formulas of DOM were assigned and nitrogen-containing formulas (CHNO) accounted for 45.7%, followed by CHO (33.3%), CHNOS (10.8%),

and CHOS (10.1%) (Table S3). After pretreatment with PAC or AER, the number of assigned formulas and total spectrum intensity decreased linearly with the decreasing DOC concentrations (Figure S3). The DOC concentrations were similar for DOM remaining after PAC$_{200mg/L}$ pretreatment and after AER treatment (around 2.4 mg C/L, Table S3), and the SUVA of LMW organics was similar for DOM remaining after PAC$_{40mg/L}$ pretreatment and after AER treatment (around 2.4 mg C/L, Table S3). The percentage of CHNO formulas dropped in DOM remaining after PAC pretreatments (to 45.2 % for PAC$_{40mg/L}$ and to 39.8% for PAC$_{200mg/L}$), while an increased percentage was observed in DOM remaining after AER pretreatment (54.0%). This suggests that CHNO formulas preferentially adsorb on PAC and not on AER, underlining the different selectivity of the two adsorbents.

Regarding molecular descriptors, a pronounced decrease in molecular mass (expressed as intensity-averaged mass to charge ratio, m/z$_{wa}$) from 400.61 to 326.88 Da (p <0.001, Mann-Whitney U-test, cf. Table S3) was observed after AER pretreatment, indicating preferential adsorption of HWM DOM by AER which is in alignment with the removed humics (~1000 g/mol) and building blocks (~300-500 g/mol) in AER treated water (cf. LC-OCD results in Figure S7) (Hu et al., 2014). In contrast, a similar preference for molecular weight was not found in water after PAC$_{40mg/L}$ pretreatment (m/z$_{wa}$ shift from 400.61 to 386.68 Da, p <0.001; to 366.84 Da for PAC$_{200mg/L}$). Both AER and PAC pretreatment removed aromatic/unsaturated DOM at different levels, as the AI$_{mod,wa}$ decreased significantly from 0.32 to 0.23 (p < 0.001) after AER pretreatment, and only to 0.31 (p < 0.001) for PAC$_{40mg/L}$-sorbed DOM. The decrease in SUVA$_{254}$ was also more pronounced during AER than PAC pretreatment (Table S3). The DOM polarity index NOSC$_{wa}$ decreased after AER pretreatment from 0.10 to -0.23 (p < 0.001),

while it slightly increased from 0.11 to 0.12 (p < 0.001) during the $PAC_{40mg/L}$ treatment, indicating that the (partially) negatively charged DOM (preferred by AER) are rich in polar compounds, while neutral DOM (preferred by PAC) are apolar compounds, which is in line with earlier studies working on the extraction of negatively charged DOM (Han et al., 2022; Waska et al., 2015).

The DOM adsorption by $PAC_{40mg/L}$ is further visualized with molecular fingerprints (NOSC vs molecular mass, Figure 2d). From the difference spectra of untreated DOM, and DOM remaining after $PAC_{40mg/L}$ pretreatment, 97.8% of all molecular formulas ($n$ = 7190) appeared to be (completely or partially) sorbed on $PAC_{40mg/L}$ (Figure 2d; for DOM sorbed on $PAC_{200mg/L}$: $n$ = 7348 or 99.9%, cf. Figure S8), spreading across the entire examined MW range. The large percentages of molecular formulas in PAC-sorbed DOM, compared to the limited DOC removal (41.5% for $PAC_{40mg/L}$ treatment, and 71.8% for $PAC_{200mg/L}$ treatment) indicate nonspecific adsorption of DOM compounds onto PAC which has been preliminary found in literature (Andersson et al., 2020; Wang et al., 2020). From Figure S9 it can be observed that DOM compounds undetected after $PAC_{40mg/L}$ pretreatment were located at low NOSC values across the $AI_{mod}$ range. This preferential adsorption of nonpolar DOM by PAC can also be revealed from the total ion chromatograms derived from RPLC-FTICR-MS (Figure S10). DOM components with lower NOSC values were eluted later (Figure S11), while at the same time DOM compounds with on average higher retention time were preferentially removed by $PAC_{40mg/L}$.

AER had a higher affinity for DOM compounds with higher MW. 97.1% of the molecular formulas with m/z > 500 Da were undetected after AER pretreatment (Figure 2b). Molecular

formulas in DOM remaining after AER pretreatment were mostly located at m/z < 500 Da and
NOSC values < 0.5, whereas these low NOSC values were rarely found in DOM remaining after
$PAC_{40mg/L}$ treatment. Polar DOM components (with high NOSC) were thus preferentially
removed in AER pretreatment, as only low NOSC compounds (mostly ranging from -0.5 to 1)
remained in the DOM (Figure 2b). NOSC only accounts for the average oxidation state of
carbon, which is linked to the polarity of molecular formulas, and does not account for the
dissociation of carboxylic acids, which leads to an increase in actual polarity (i.e.,
hydrophilicity)(Jennings et al., 2022). As ion exchange is the main mechanism of DOM
removal in AER pretreatment (Boyer et al., 2008; Finkbeiner et al., 2018), high removal of
HMW DOM by AER is attributed to the higher likelihood to have ionizable functional groups
(Finkbeiner et al., 2020). Our results here could also help explain why well-studied standard
natural organic matter (i.e., Suwannee river humic/fulvic acids, SRHA/SRFA) is only poorly
competitive (Matsui et al., 2012; Wang et al., 2020), even with high $SUVA_{254}$ (> 6 L/(m·mg C))
and LMW organics present: the applied extraction protocol favors negatively charged DOM
(by eluting with alkaline solution) and potentially excludes neutral/more competitive DOM
(high retention in the columns for SRHA/SRFA preparation) (Wang et al., 2020). Therefore,
neither high $SUVA_{254}$ nor high $AI_{mod}$ suffices to explain the high DOM competitiveness of DOM
remaining after AER pretreatment, and the low polarity of the DOM remaining after AER
pretreatment must be considered, too.
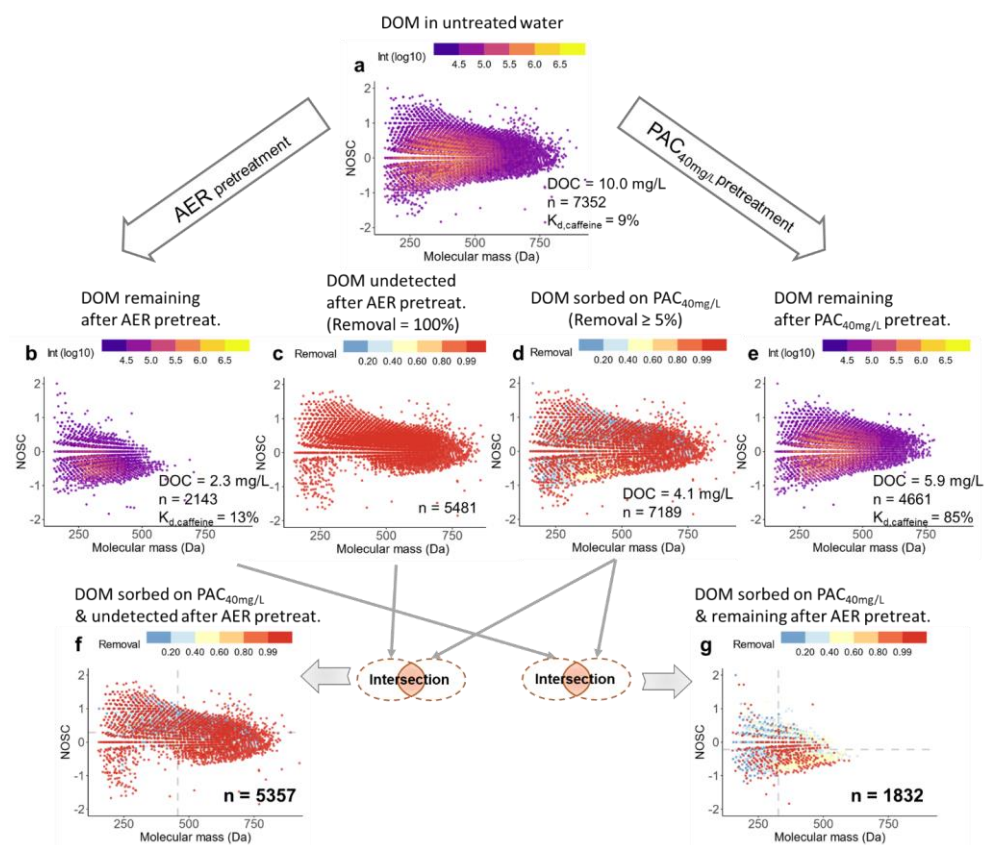
*Figure 2* FT-ICR MS derived polarity (expressed as nominal oxidation state of carbon, NOSC) versus molecular mass for molecular formulas in untreated DOM (a), DOM remaining after AER/PAC$_{40mg/L}$ pretreatment (b, e), DOM undetected after AER treatment (c), DOM sorbed on PAC$_{40mg/L}$ (d), DOM sorbed on PAC$_{40mg/L}$ and undetected after AER pretreatment (f), DOM sorbed on PAC$_{40mg/L}$ and remaining after AER pretreatment (g); Mean NOSC and molecular mass (dashed lines, in f/g), the number of molecular formulas (N) detected in each sample, the respective DOC concentrations (a, b, d, e), and relative partitioning of caffeine (K$_{d,caffeine}$) as compared to DOM-free water (a, b, e) are indicated.

## 3.3 Types of PAC-sorbed DOM varying in competitiveness

As PAC$_{40mg/L}$ sorbed the highly competitive DOM and substantially alleviated the competition between the remaining DOM and uncharged OMPs, the DOM sorbed on PAC$_{40mg/L}$ included the most competitive DOM fraction (Figure 2d). However, the non-selectivity of PAC adsorption towards DOM compounds, is indicated by the unmatched percentages between the moderate losses of DOC (41.4%), total mass peak intensities (39.5%) and the large number of molecular formulas observed with an intensity loss (97.8%), makes identification of specific molecular formulas responsible for remaining OMP competitiveness difficult. In contrast to the PAC pretreatment, the AER pretreatment was more selective (and more efficient) in DOM removal, and DOM remaining after AER pretreatment comprised of fewer molecular formulas in a more confined range of NOSC values and molecular mass. Yet, DOM remaining after AER pretreatment demonstrated competitiveness comparable to untreated DOM (cf. Figure 1). Therefore, the molecular formula-level based intersection of PAC$_{40mg/L}$-sorbed DOM (relevant competitors against OMPs) and DOM remaining after AER pretreatment (highly competitive) revealed the strongly competitive DOM components within the PAC$_{40mg/L}$-absorbable DOM. The number of molecular formulas in the DOM fraction sorbed on PAC$_{40mg/L}$ and remaining after AER pretreatment, was only 25.5% of molecular formulas in PAC$_{40mg/L}$-sorbed DOM, suggesting that a minor fraction of DOM compounds adsorbing on PAC$_{40mg/L}$ has profound competitiveness against OMPs. As CHNO compounds were preferentially sorbed to PAC and less so to AER, the fraction of CHNO class was larger (55.6%) in the DOM sorbed on PAC$_{40mg/L}$ and in the DOM remaining after AER pretreatment (54.0 %), suggesting an important role of N-containing molecules in OMP competition, which has not been found in literatures.

## 3.4 Impact of molecular properties on competitiveness

To further analyze the FTICR-MS-based molecular characteristics (MW, $AI_{mod}$, NOSC) with respect to DOM adsorbability/competitiveness, the removal of two types of DOM sorbed on $PAC_{40mg/L}$ (i.e., $PAC_{40mg/L}$-sorbable and remaining/undetected after AER treatment) was compared side-by-side with respect to their FTICR-MS-based molecular descriptors (MW, $AI_{mod}$, NOSC, Figure 3). Incomplete removal (5% < mass peak intensity loss < 100%) of DOM compounds was found in a continuum up to 58.8% and 91.1% intensity loss for 40 mg/L and 200 mg/L PAC, respectively (Figures 3 and S-8). Overall stronger sorption on $PAC_{40mg/L}$ was observed for molecular formulas that were unaffected by the AER treatment, compared to molecular formulas that were fully eliminated by AER. This was probably a result of the DOM dissociation, as discussed before. Higher MW was mostly beneficial for DOM adsorption (Figure 3a), as larger DOM molecules can interact with multiple PAC adsorption sites (Kah et al., 2017). However, the higher average mass observed for the DOM sorbed on $PAC_{40mg/L}$ and undetected after AER pretreatment (457.37 Da) (compared to 327.08 Da for DOM remaining after AER pretreatment, Figure 3a) did not result in a higher removal during $PAC_{40mg/L}$ adsorption. A considerably more positive, effect was found for $AI_{mod}$ (compared to MW) on DOM removal (Figure 3b). The higher averaged $AI_{mod}$ of $PAC_{40mg/L}$-sorbed compounds that remained after AER pretreatment, did not result in a higher removal as compared to components of $PAC_{40mg/L}$-sorbed compounds that were undetected after AER pretreatment. Polarity, indicated by a relatively higher NOSC of DOM sorbed on $PAC_{40mg/L}$ and undetected after AER pretreatment, probably contributed to a stronger DOM dissociation potential,

inhibiting the hydrophobic interaction with the PAC surface and counterbalancing the merits
of stronger π-π interaction and multiple adsorption sites, brought by higher MW and $AI_{mod}$.
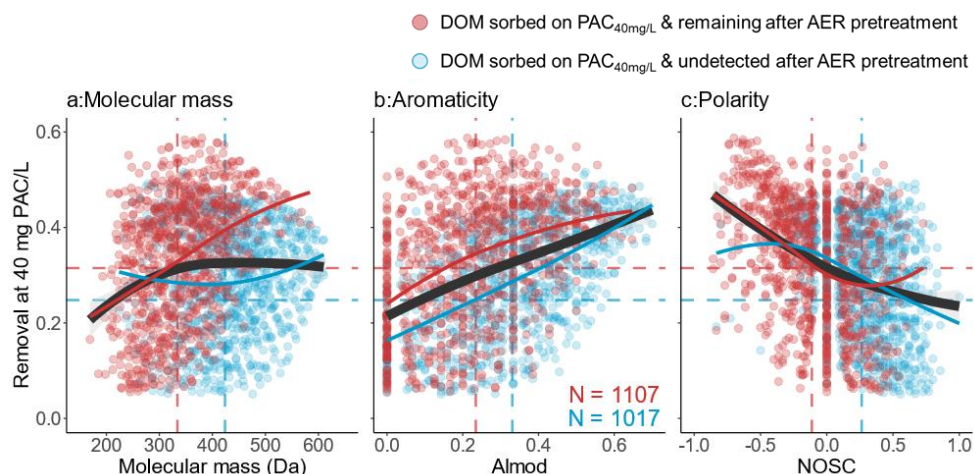


**Figure 3** *Removals of two types of DOM sorbed on $PAC_{40mg/L}$, remaining (red) or undetected (blue)
after AER pretreatment vs molecular mass (a); aromaticity index ($AI_{mod}$) (b); polarity (in NOSC) (c),
with local polynomial regression fits with 95% confidence interval (black for all $PAC_{40mg/L}$-sorbed
compounds), and averaged molecular mass, $AI_{mod}$, NOSC, averaged removal (dashed lines), and the
number of molecular formulas (N) included. Note that the compounds undetected after $PAC_{40mg/L}$
pretreatment (100% removal) and molecular formulas with peak intensity $< 10^5$ in untreated DOM
sample not included.*

DOM removal was further assessed in several MW subranges and plotted against $AI_{mod}$ and
NOSC (Figure 4). Aromaticity was well correlated with the removal of LMW DOM components
(MW < 350 Da) in $PAC_{40mg/L}$ adsorption, but its influence gradually diminished for DOM
compounds with increasing MW until it reached an indistinguishable level. The key impact

factor on DOM adsorbability transited from aromaticity to polarity as MW increased, aligned with a previous study where the authors suggested a dominance of π-π interactions over hydrophobicity in determining LMW DOM (< 200 Da) adsorbability and competitiveness (Wang et al., 2021). Moreover, the present study suggests a lower impact of aromaticity for higher MW DOM compounds, likely because aromatic groups are located more centrally in HMW DOM molecules, causing reduced π-π interactions with PAC surfaces due to steric hindrance (Shevchenko and Bailey, 1996; Wang et al., 2021).
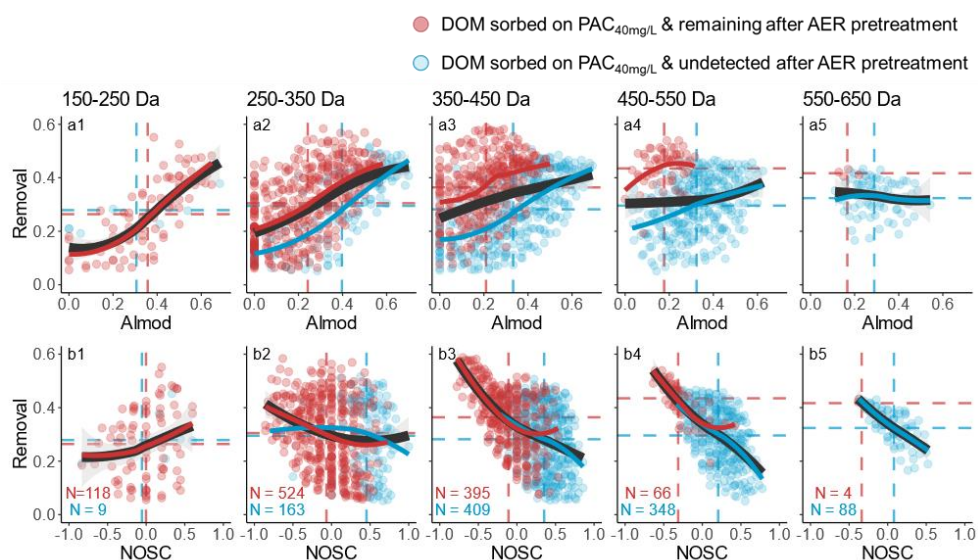


*Figure 4* *Removals of PAC$_{40mg/L}$-sorbable formulas are plotted vs AI$_{mod}$ (a1-a5) and NOSC (b1-b5) in different mass ranges, with AER-noneliminated DOM in red and AER-eliminated DOM in blue. Local polynomial regression fits with 95% confidence interval, averaged AI$_{mod}$ or NOSC, and the number of molecular formulas (N) included. Note that the compounds undetected after PAC$_{40mg/L}$ pretreatment (100% removal) and molecular formulas with peak intensity < 10$^5$ in untreated DOM sample not included.*

Overall, the steeper slopes of the regression lines (Figure 4a1-a4) for the adsorption of highly competitive DOM (i.e., remaining after AER pretreatment, red) than of all $PAC_{40mg/L}$-sorbed DOM (black), indicate a strong influence of aromaticity on competitive DOM, while the influence was underestimated without excluding the DOM dissociation effects (mild slopes for all $PAC_{40mg/L}$-sorbed DOM). For similar removal of $PAC_{40mg/L}$-sorbed DOM with different AER treatability (remaining/undetected after AER pretreatment), higher $AI_{mod}$ is required for the less competitive DOM (i.e., undetected after AER pretreatment).

Regarding the molecular configuration, DOM remaining after AER pretreatment had fewer carboxyl groups and more phenolic/quinonyl groups explaining their lower AER removability. Different from carboxyl groups, phenolic/quinonyl groups have a positive contribution to the π-interaction and enhance the DOM adsorbability and competitiveness of DOM compounds (Deng et al., 2015). By contrast, some DOM components with high $AI_{mod}$ were also removed after AER pretreatment (thus categorized as poorly competitive) (Figure 4a2-a4), and their polarity was generally much higher (Figure S12). Strong dissociation of such polar unsaturated compounds (probably carboxyl-rich for all isomers) probably limited their competitiveness towards high-energy PAC adsorption sites, while being moderately adsorbable.

In terms of elemental composition, DOM components containing heteroatoms (i.e., CHNO and CHOS) were found to be more adsorbed than CHO components onto activated carbon (Figure S13), whereas removed to a lesser extent than CHO components by AER (Figure S14). CHNO components were the major contributors (68.2%) to aromatic molecules (with $AI_{mod} \geq 0.5$) within the highly competitive DOM (i.e., DOM sorbed on $PAC_{40mg/L}$ and remaining after AER

pretreatment; Figure S15). N-containing aromatics may enhance the DOM adsorbability competitiveness through stronger electrostatic attraction (positively charged N-containing functional groups and negatively charged O-containing functional groups), enhanced π- π interactions and H-bonds (dipole-dipole H-bond) (Hai Nguyen et al., 2017). Additionally, basic functional groups (ketone, pyrone, and chromene) have been found to be important for the adsorption (competition not assessed) of sulfur-containing compounds (Huang et al., 2020b).

## 3.5 Effect of aromaticity and polarity on isomer adsorption

So far only descriptors of (isomer)-averaged molecular formulas were associated with the DOM competition. Therefore, LC data were further used to disentangle the relationship between polarity/aromaticity and the adsorbability of highly competitive DOM (i.e., DOM sorbed on $PAC_{40mg/L}$ and remaining after AER pretreatment), as displayed in Figure 5. The AETs were found to associate well with the overall polarity of molecular formulas described by NOSC (Figure S11), whereas the AET shift after $PAC_{40mg/L}$ pretreatment indicated selective adsorption of DOM isomers with distinct polarity.

DOM compounds with a molecular formula $C_{11}H_{11}N_1O_6$ (with relatively high $AI_{mod}$, NOSC, and early AET) were preferentially removed (as indicated by the loss in EIC intensity, cf. Figure 5) after 13.5 min due to the $PAC_{40mg/L}$ treatment. In contrast, $C_{13}H_{17}N_1O_5$ (with similar removal, yet lower NOSC value) showed uniform PAC adsorption (EIC intensity decrease) with regard to isomers. Overall, the AETs of DOM compounds with high $AI_{mod}$ considerably decreased after $PAC_{40mg/L}$ treatment, suggesting that nonpolar isomers (later eluted in RPLC) were preferentially adsorbed on PAC. For DOM components with high aromaticity and high polarity,

an increasing number of possible isomers (a simplified instance, 1 isomer for $C_3H_8$, 2 isomers for $C_3H_6$, 5 isomers for $C_3H_6O$) with varying polarity could be expected, although there is one NOSC for a specific molecular formula. This finding elucidates that the selective adsorption of apolar isomers is the way how aromaticity counterbalances the impact of polarity on DOM adsorbability, and that nonpolar isomers with, formula-wise, high aromaticity and polarity are also important competitors against OMPs. The potentials of tandem mass spectrometry (MS/MS) or nuclear magnetic resonance spectroscopy (NMR) should be explored in future research to examine these indications (Leyva et al., 2022).
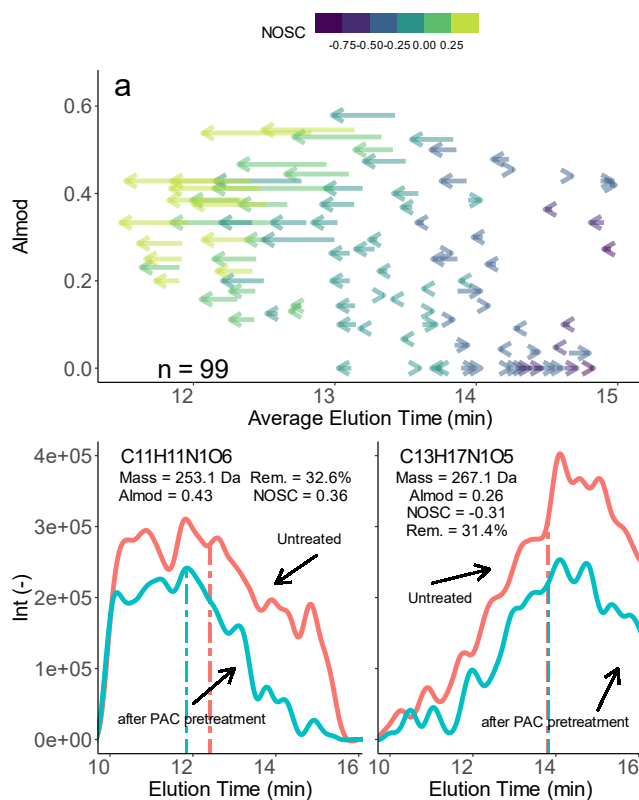
*Figure 5* *Aromaticity index ($AI_{mod}$) plotted vs the change of average elution time (AET) of some high-intensity molecular formulas from DOM (partially) sorbed on $PAC_{40mg/L}$ remaining after AER pretreatment (a), arrows point from the AET of untreated DOM sample to that of $PAC_{40mg/L}$-sorbed DOM sample (a). EICs of two molecular formulas $C_{11}H_{11}N_1O_6$, b) and $C_{13}H_{17}N_1O_5$, c) with comparable removal illustrating the change of AETs (dash lines, based on elution time 10-15.8 min) after $PAC_{40mg/L}$ treatment.*

## 3.6 Environmental implications

From the results of this study, it can be concluded that aromaticity is more influential for the competitive adsorption of LMW DOM, whereas the impact is outweighed by polarity for HMW

DOM. When, in practice, conventional DOM surrogates, such as $UV_{254}$ and $SUVA_{254}$, are measured the aromaticity of HMW DOM has more weight than LMW DOM, and therefore, these surrogates are not necessarily related to DOM competitiveness.

In addition, it was found in this study that the competitiveness of some aromatic LMW DOM with high polarity (hydrophilicity) was limited, due to the strong dissociation, from high polarity. This could explain the limitation of UV absorbance of LMW DOM to predict the DOM competitiveness for a standard humic/fulvic substances with highly unsaturated and ionizable DOM (Wang et al., 2020), but feasible for predicting DOM competitiveness of natural waters and ozonated waters (Matsui et al., 2012; Wang et al., 2020; Zietzschmann et al., 2016a), as the hydrophobicity and aromaticity decreased simultaneously during ozonation (Von Sonntag and Von Gunten, 2012).

Apart from competition alleviation by removing strongly adsorbable DOM, that competes against all examined OMPs, weakly adsorbable DOM is also necessary to control, due to its competitiveness against polar OMPs (sulfamethoxazole here). As the OMPs with poor adsorbability usually raise more concerns for the effluent quality (Reemtsma et al., 2016), the strategies to alleviate DOM competition may therefore vary for differently adsorbable OMPs. E.g., an ozone-induced elevation of DOM polarity might have little effect to control the number of potential competitors against polar sulfamethoxazole, whereas considerably reducing the concentration of DOM competitors against strongly adsorbable, hydrophobic OMPs (Zietzschmann et al., 2015b). Thus maximizing adsorbable DOM removal appropriately would benefit the adsorption of OMPs across a wide range of adsorbability. E.g., boosting the removal of HMW DOM and weakly adsorbable LMW DOM by coagulation or AER

pretreatment could alleviate the competition against weak adsorbable OMP (Hu et al., 2014; Matsui et al., 1999). Strongly competitive DOM (hydrophobic, aromatic LMW DOM) could be well abated through ozonation at a higher DOC-specific ozone dose (for coagulation/AER-treated water).

# Supporting information

***Text S1*** *OMP quantification with LC-MS/MS.*

High performance liquid chromatography combined with tandem mass spectrometry (LC-MS/MS) was employed to quantify OMPs in this study. Ultrapure water and acetonitrile (LC-MS grade, Biosolve, France) phases, both acidified with 0.1 % LC-MS grade formic acid (Biosolve, France), were applied as mobile phases on an ACQUITY UPLC® BEH C18 (1.7μm particle size, 2.1x50 mm, Waters, Ireland) column, at a flow rate of 0.35 ml/min. Tandem mass spectrometry was conducted on a Xevo TQ-S micro (Waters, USA), equipped with electrospray ionization in positive modes. Two daughter ions from the mother ion were combined for detecting each OMP and quantification was performed with deuterated internal standards. Data evaluation was conducted with TargetLynx.

***Table S1*** *Ionic concentrations in Schie water.*

|  | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | $Cl^-$ | $SO_4^{2-}$ | $NO_3^-$ | $HCO_3^-$ |
|---|---|---|---|---|---|---|---|---|
| **Concentration** (mmol/L) | 1.79 | 0.68 | 3.08 | 0.32 | 3.21 | 0.48 | 0.03 | 4.01 |

***Table S2*** *Replicate DOM characteristics and FT-ICR MS derived molecular composition before and after anion exchange resin (AER) and/or powdered activated carbon (PAC) pretreatment.*

| Sample name | Replicate | Treatment | DOC (mg C/L) | $UV_{254}$ (1/cm) | $SUVA_{254}$ (L·m⁻¹·mgC⁻¹) | CHO | CHNO | CHNOS | CHOS | m/z (wa)a | H/C (wa) | O/C (wa) | N/C (wa) | S/C (wa) | DBE (wa) | DBE-O (wa) | AImod (wa) | NOSC (wa) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | 10.05 | 0.296 | 2.95 | 2503 (32.0%) | 3574 (45.6%) | 973 (12.4%) | 780 (10.0%) | 442 | 1.22 | 0.59 | 0.043 | 0.010 | 10.16 | -0.50 | 0.32 | 0.12 |
| Untreated DOM | 2 | - | 10.04 | 0.297 | 2.96 | 2470 (31.8%) | 3530 (45.4%) | 990 (12.7%) | 778 (10.0%) | 442 | 1.22 | 0.59 | 0.043 | 0.010 | 10.11 | -0.53 | 0.32 | 0.11 |
| | 3 | | 9.91 | 0.297 | 3.00 | 2496 (32.0%) | 3567 (45.7%) | 968 (12.4%) | 763 (9.8%) | 443 | 1.22 | 0.59 | 0.043 | 0.010 | 10.16 | -0.52 | 0.32 | 0.11 |
| DOM remaining after PAC40mg/L pretreatment | 1 | 40 mg/L PAC | 6.01 | 0.14 | 2.33 | 1972 (34.9%) | 2506 (44.3%) | 553 (9.8%) | 616 (10.9%) | 451 | 1.28 | 0.65 | 0.040 | 0.010 | 10.12 | -1.10 | 0.31 | 0.15 |
| | 2 | | 6.05 | 0.135 | 2.23 | 1887 (34.7%) | 2423 (44.5%) | 542 (10.0%) | 584 (10.7%) | 447 | 1.29 | 0.65 | 0.041 | 0.010 | 10.01 | -1.15 | 0.31 | 0.15 |
| DOM remaining after PAC200mg/L pretreatment | 1 | 200 mg/L PAC | 2.46 | 0.047 | 1.91 | 1153 (41.9%) | 1135 (41.2%) | 154 (5.6%) | 303 (11.0%) | 440 | 1.33 | 0.71 | 0.040 | 0.010 | 9.68 | -1.69 | 0.30 | 0.23 |
| | 2 | | 2.48 | 0.049 | 1.98 | 1090 (44.0%) | 987 (39.8%) | 126 (5.1%) | 272 (11.0%) | 439 | 1.35 | 0.72 | 0.038 | 0.010 | 9.54 | -1.80 | 0.30 | 0.22 |
| DOM remaining after AER pretreatment | 1 | 15 mL/L AER | 2.22 | 0.021 | 0.95 | 788 (29.2%) | 1453 (53.8%) | 207 (7.7%) | 245 (9.1%) | 353 | 1.38 | 0.47 | 0.068 | 0.009 | 7.14 | -0.17 | 0.23 | -0.21 |
| | 3 | | 2.28 | 0.021 | 0.92 | 733 (29.2%) | 1340 (53.3%) | 192 (7.6%) | 239 (9.5%) | 354 | 1.38 | 0.47 | 0.068 | 0.009 | 7.14 | -0.12 | 0.22 | -0.22 |

| Sample name | Replicate | Treatment | DOC (mg C/L) | UV254 (1/cm) | SUVA$_{254}$ (L·m$^{-1}$·mgC$^{-1}$) | CHO | CHNO | CHNOS | CHOS | m/z (wa)a | H/C (wa) | O/C (wa) | N/C (wa) | S/C (wa) | DBE (wa) | DBE-O (wa) | AImod (wa) | NOSC (wa) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DOM remaining after AER and PAC10mg/L pretreatment | 1 | 15 mL/L AER+ | 1.22 | 0.007 | 0.57 | 533 (33.9%) | 794 (50.5%) | 104 (6.6%) | 132 (8.4%) | 347 | 1.46 | 0.51 | 0.066 | 0.009 | 6.71 | -0.60 | 0.21 | -0.23 |
| | 3 | 10 mg/L PAC | 1.33 | 0.007 | 0.53 | 514 (33.4%) | 770 (50.1%) | 106 (6.9%) | 140 (9.1%) | 353 | 1.46 | 0.50 | 0.066 | 0.010 | 6.85 | -0.54 | 0.21 | -0.23 |

a, wa means averaged values weighted by peak intensity.

b, Formula intensities from Untreated DOM sample.

**Table S3** *Average DOM characteristics and FT-ICR MS derived molecular composition before and after anion exchange resin (AER) and/or powdered activated carbon (PAC) pretreatment.*

| Sample name | Treatment | DOC (mg C/L) | UV$_{254}$ (1/cm) | SUVA$_{254}$ (L·m$^{-1}$·mgC$^{-1}$) | CHO | CHNO | CHNOS | CHOS | m/z (wa)[a] | H/C (wa) | O/C (wa) | N/C (wa) | S/C (wa) | DBE (wa) | DBE-O (wa) | AI$_{mod}$ (wa) | NOSC (wa) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Untreated DOM | - | 10.00 | 0.297 | 2.97 | 2450 (33.3%) | 3361 (45.7%) | 797 (10.8%) | 744 (10.1%) | 400.61 | 1.13 | 0.55 | 0.04 | 0.009 | 9.21 | -0.48 | 0.32 | 0.10 |
| DOM remaining after PAC$_{40mg/L}$ pretreatment | 40 mg/L PAC | 5.86 | 0.135 | 2.30 | 1728 (37.1%) | 2109 (45.2%) | 310 (6.7%) | 514 (11.0%) | 386.68 | 1.15 | 0.58 | 0.03 | 0.008 | 8.61 | -1.06 | 0.31 | 0.12 |
| DOM remaining after PAC$_{200mg/L}$ pretreatment | 200 mg/L PAC | 2.52 | 0.049 | 1.94 | 998 (46.7%) | 851 (39.8%) | 58 (2.7%) | 231 (10.8%) | 366.84 | 1.15 | 0.62 | 0.03 | 0.007 | 8.00 | -1.63 | 0.30 | 0.19 |
| DOM remaining after AER pretreatment | 15 mL/L AER | 2.27 | 0.021 | 0.93 | 681 (31.8%) | 1157 (54.0%) | 103 (4.8%) | 202 (9.4%) | 326.88 | 1.32 | 0.45 | 0.06 | 0.007 | 6.61 | -0.19 | 0.23 | -0.23 |
| DOM remaining after AER and PAC$_{10mg/L}$ pretreatment | 15 mL/L AER+ 10 mg/L PAC | 1.26 | 0.007 | 0.56 | 455 (37.2%) | 624 (51.0%) | 39 (3.2%) | 106 (8.7%) | 309.47 | 1.36 | 0.47 | 0.06 | 0.007 | 6.02 | -0.64 | 0.21 | -0.23 |

| Sample name | Treatment | DOC (mg C/L) | UV$_{254}$ (1/cm) | SUVA$_{254}$ (L·m$^{-1}$·mgC$^{-1}$) | CHO | CHNO | CHNOS | CHOS | m/z (wa)[a] | H/C (wa) | O/C (wa) | N/C (wa) | S/C (wa) | DBE (wa) | DBE-O (wa) | AI$_{mod}$ (wa) | NOSC (wa) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DOM sorbed on PAC$_{40mg/L}$ and remaining after AER pretreatment [b] | - | - | - | - | 605 (33.0%) | 1019 (55.6%) | 50 (2.7%) | 158 (8.6%) | 327 | 1.32 | 0.46 | 0.058 | 0.006 | 6.63 | -0.23 | 0.22 | -0.22 |
| DOM sorbed on PAC$_{40mg/L}$ and undetected after AER pretreatment [b] | - | - | - | - | 1789 (33.4%) | 2269 (42.4%) | 735 (13.7%) | 564 (10.5%) | 457 | 1.01 | 0.58 | 0.039 | 0.012 | 11.16 | -0.22 | 0.35 | 0.29 |

a, wa means averaged values weighted by peak intensity.

b, Formula intensities from Untreated DOM sample.
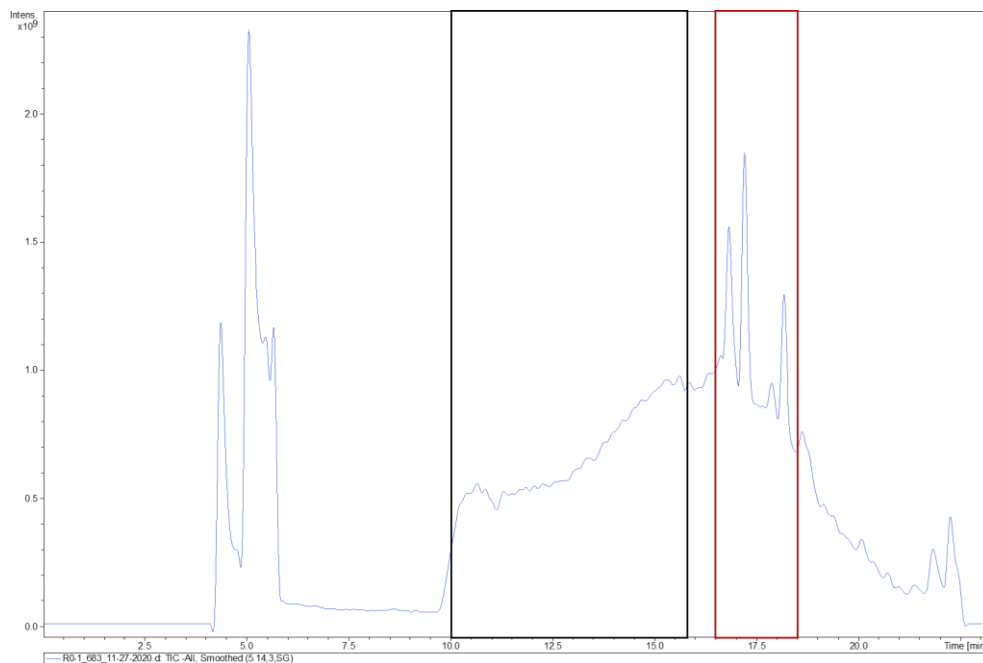
**Figure S1** *Total ion chromatogram (TIC) of untreated water sample. The time range to derive formula-average spectrum (10.0-15.8 min, marked in black), and large mass peaks (possible contaminants, >15.8 min, marked in red). Archived from DataAnalysis.*
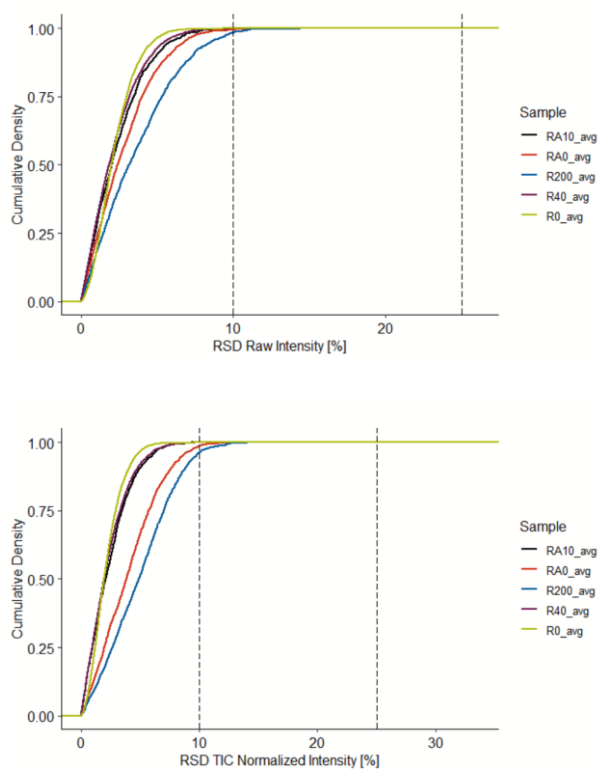
***Figure S2*** *Intensity reproducibility for averaged replicates, shown as cumulative density plots of relative standard deviation (RSD) of two quantification methods (top: raw peak intensity, bottom: normalized intensity with total ion chromatogram (TIC)).*
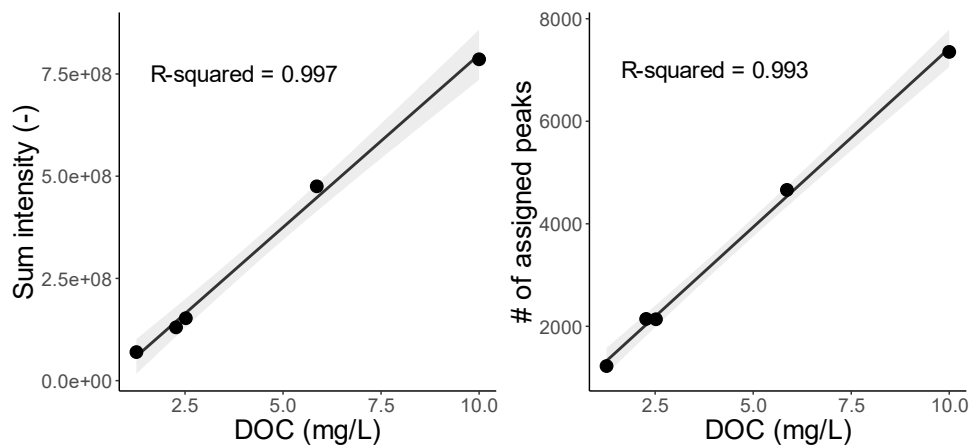
***Figure S3*** *Sum intensity (left), number (#) of assigned peaks (right) versus DOC concentrations of examined DOM samples. Linear regression fits with 95% confidence interval and respective R²values included.*
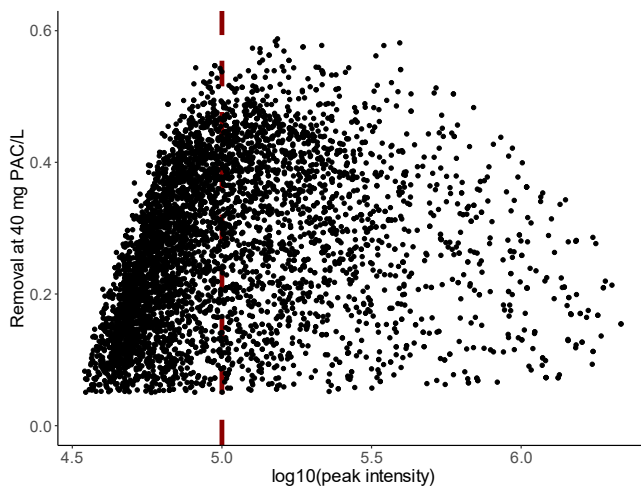


***Figure S4*** *Percentage removal by PAC$_{40mg/L}$ treatment vs. peak intensity (in log scale) of molecular formulas. The threshold of peak intensity (>$10^5$) for the semi-quantitative analysis indicated (red dashed line).*
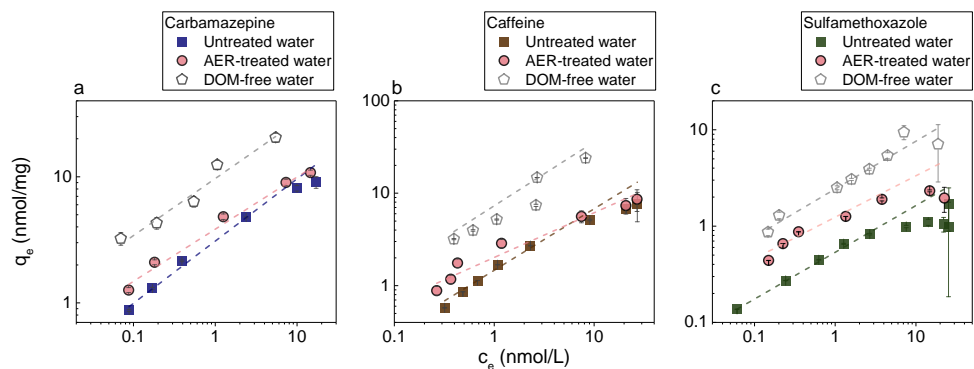
***Figure S5*** *Adsorption isotherms of three examined OMPs (carbamazepine, caffeine and
sulfamethoxazole) in DOM-free water, untreated water of river Schie and AER-treated water.
Freundlich model was applied to fit isotherms.*
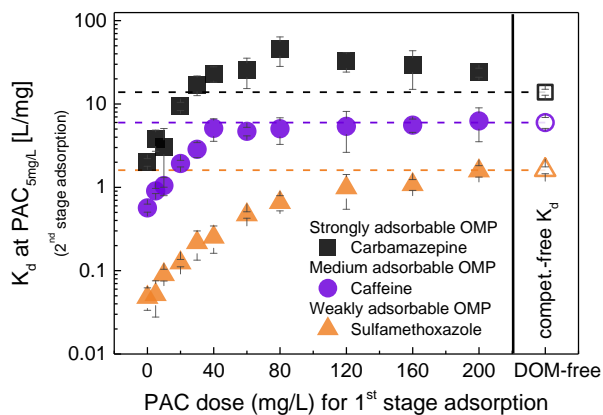


***Figure S6*** *OMP partition coefficients ($K_d$) between solid phase (PAC) and liquid phase in the PAC-
treated waters at $PAC_{5mg/L}$ (i.e.,5 mg PAC/L, the second stage adsorption).*
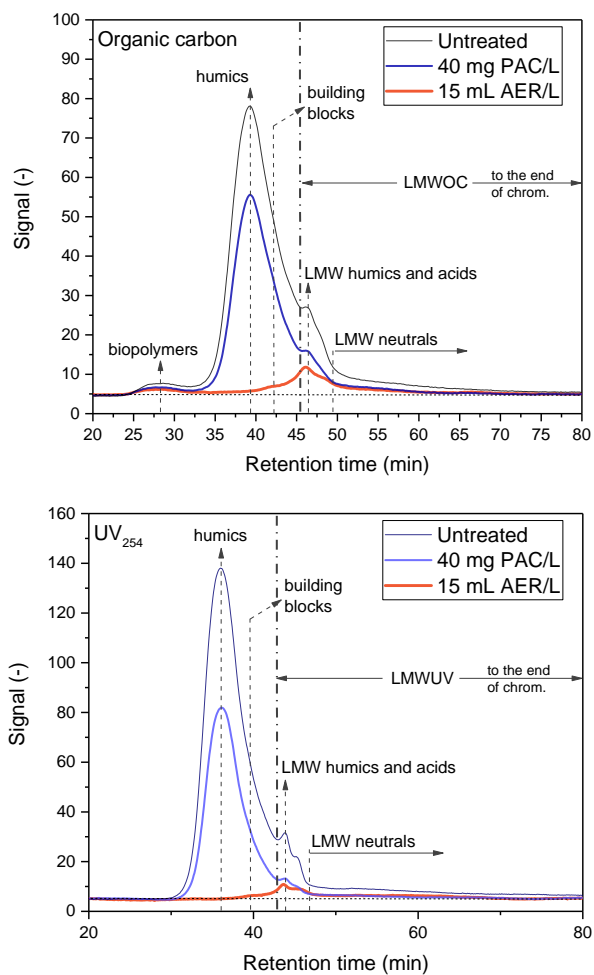
**Figure S7** *LC-OCD (a)/ LC-UV (b) chromatograms of the untreated DOM, DOM remaining after PAC$_{40mg/L}$ water and AER-treated water.*
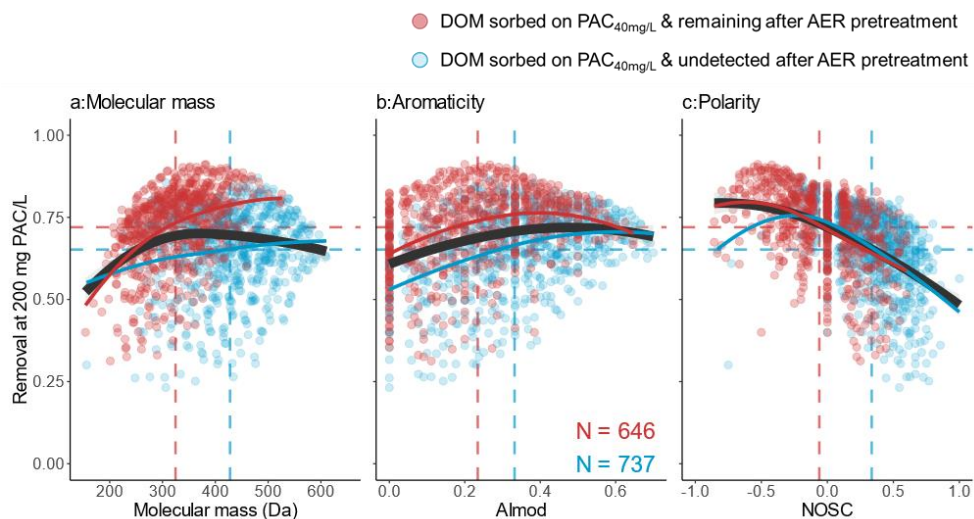
***Figure S8*** *Removals of two types of PAC$_{200mg/L}$-sorbed DOM, remaining (red) or undetected (blue)
after AER pretreatment vs molecular mass (a); aromaticity index (AI$_{mod}$) (b); polarity (in NOSC) (c),
with local polynomial regression fits with 95% confidence interval (black for all PAC$_{40mg/L}$-sorbed
compounds), and averaged molecular mass, AI$_{mod}$, NOSC, averaged removal (dashed lines), and the
number of molecular formulas (N) included. Note that the compounds undetected after PAC$_{40mg/L}$
pretreatment (100% removal) and molecular formulas with peak intensity < 10$^5$ in untreated DOM
sample not included.*
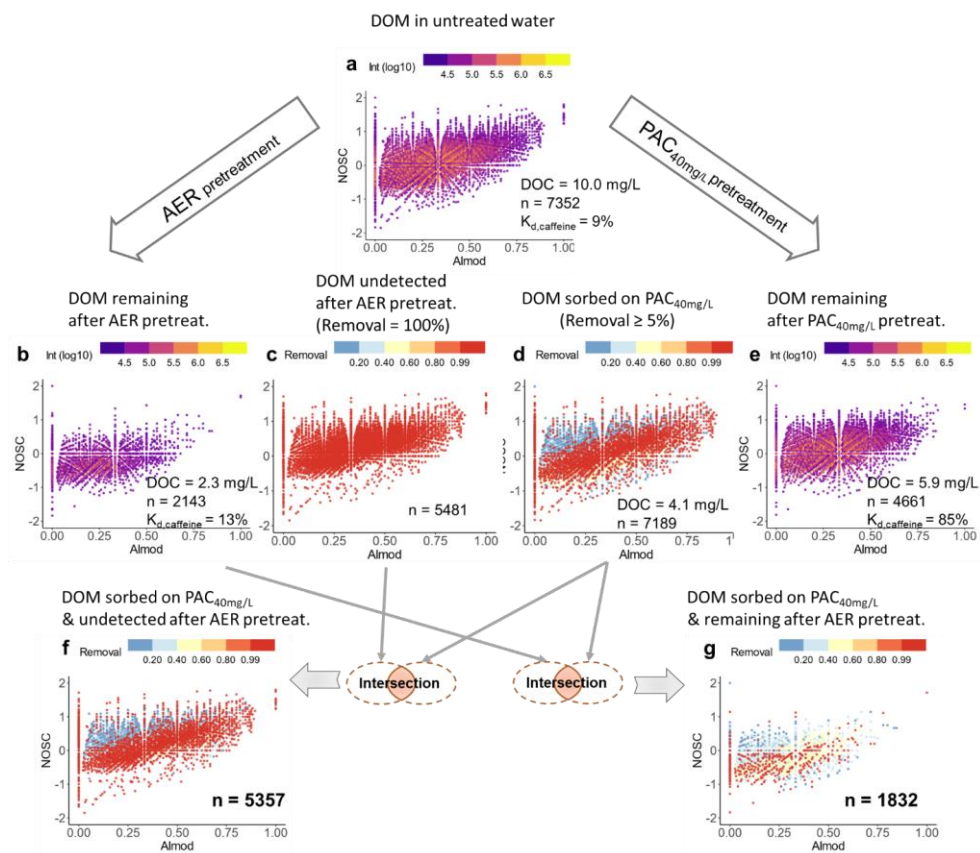
*Figure S9* FT-ICR MS derived polarity (expressed with NOSC) versus modified aromaticity index (AI_mod) for molecular formulas in untreated DOM (a), DOM remaining after AER/PAC_40mg/L pretreatment (b, c), PAC-sorbable DOM (40 mg/L PAC; d), and types of PAC-adsorbable DOM (e). Mean NOSC and molecular mass (dashed lines), the number of molecular formulas (N) detected in each sample, the respective DOC concentrations (a-d), and relative partitioning of caffeine (K_d,caffeine) as compared to DOM-free water (a-c) are indicated.
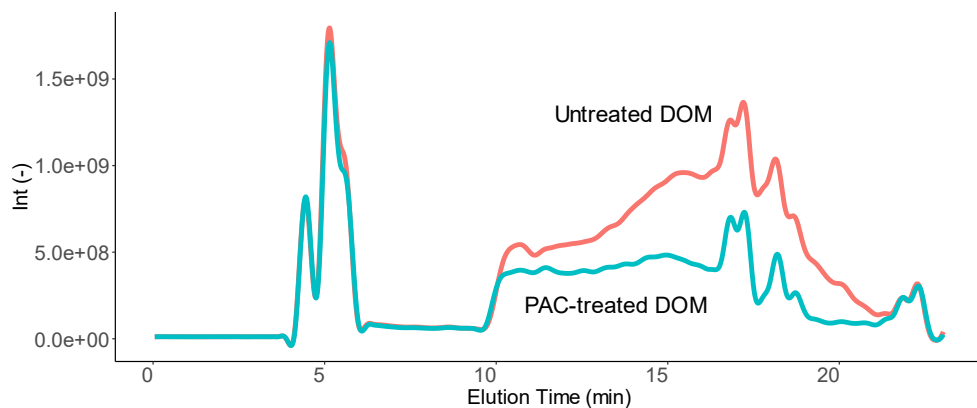
***Figure S10*** *Total ion chromatogram (TIC) for untreated DOM and remaining DOM after PAC$_{40mg/L}$ pretreatment.*
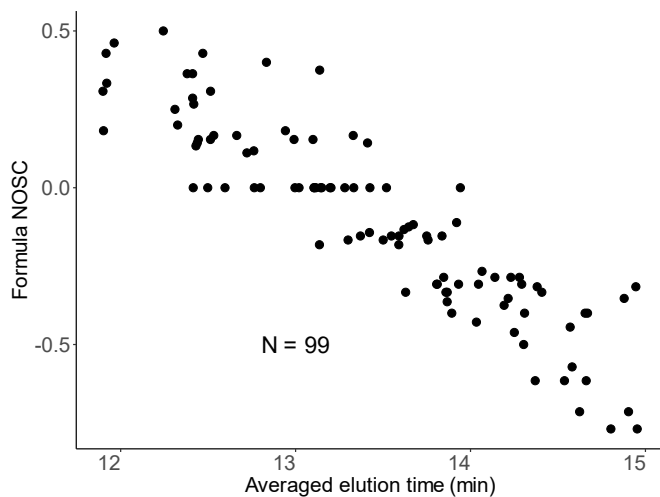


***Figure S11*** *Formula NOSC versus averaged elution time (AET) of DOM that sorbed on PAC$_{40mg/L}$ and remaining after AER pretreatment; low intensity peaks (rank >1000, in untreated sample) omitted.*
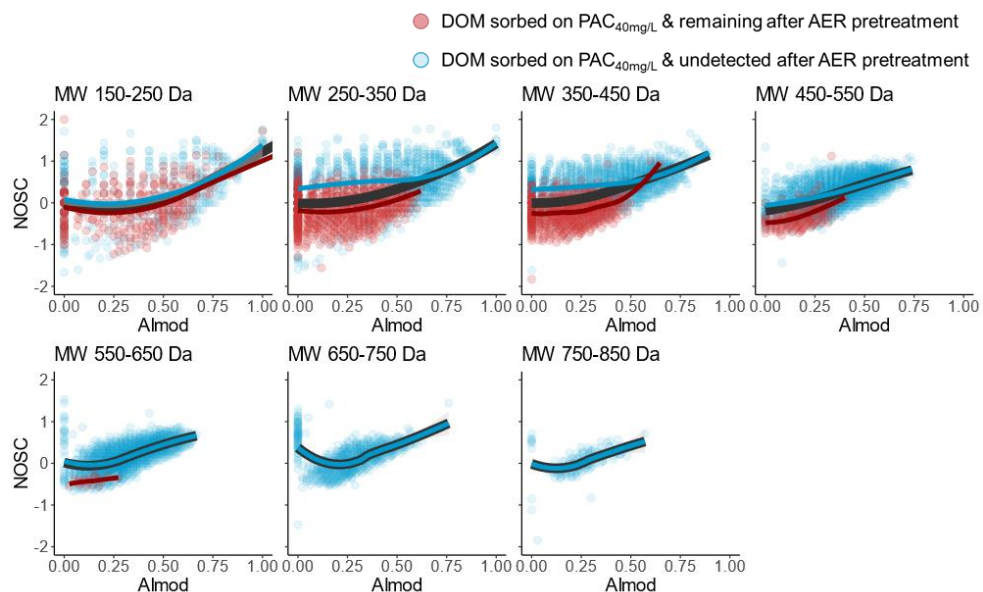
**Figure S12** *FT-ICR MS derived polarity (expressed with NOSC) versus modified aromaticity index (AI$_{mod}$) for molecular formulas in two types of PAC$_{40mg/L}$-sorbed DOM (remaining after AER pretreatment, red; undetected after AER pretreatment, blue).*
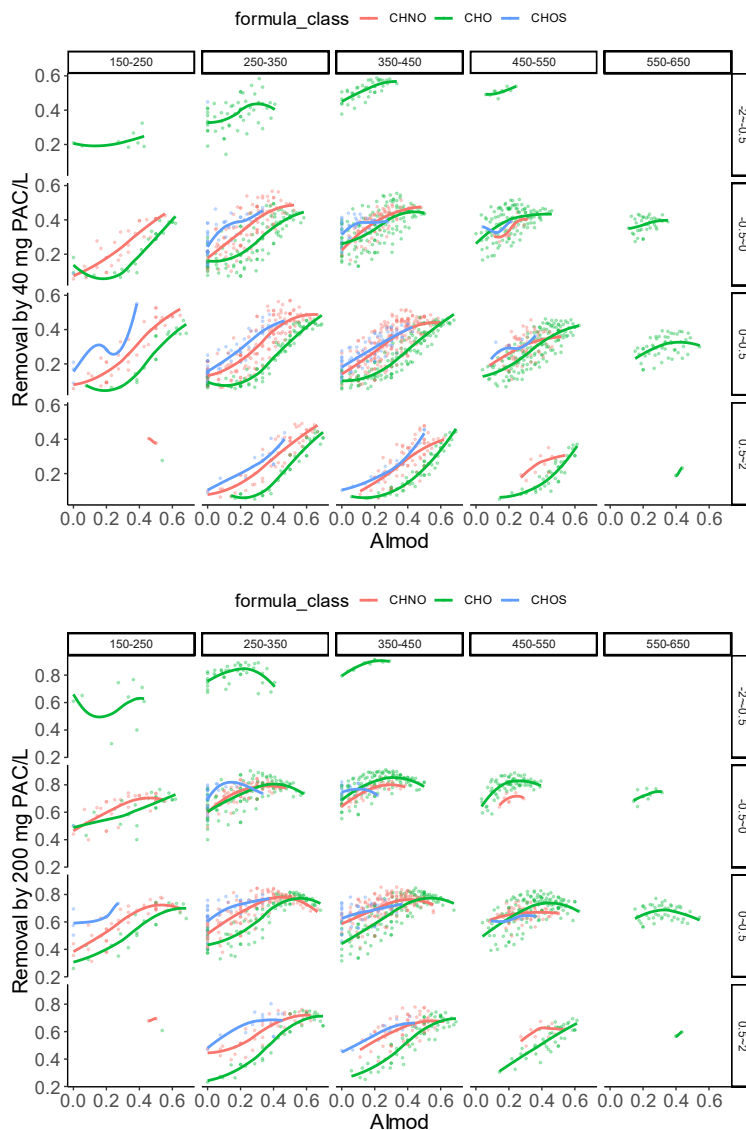
***Figure S13*** *Removals of PAC-sorbed DOM in different formula classes vs aromaticity index (AImod)
in different MW and NOSC ranges (40 mg PAC/L, top; 200 mg PAC/L, bottom). Local polynomial
regression fits with 95% confidence interval included. Note that the undetected formulas after PAC
pretreatment (100% removal) and molecular formulas with insufficient quantification condition
(peak intensity < 10⁵ in untreated DOM sample) not included.*
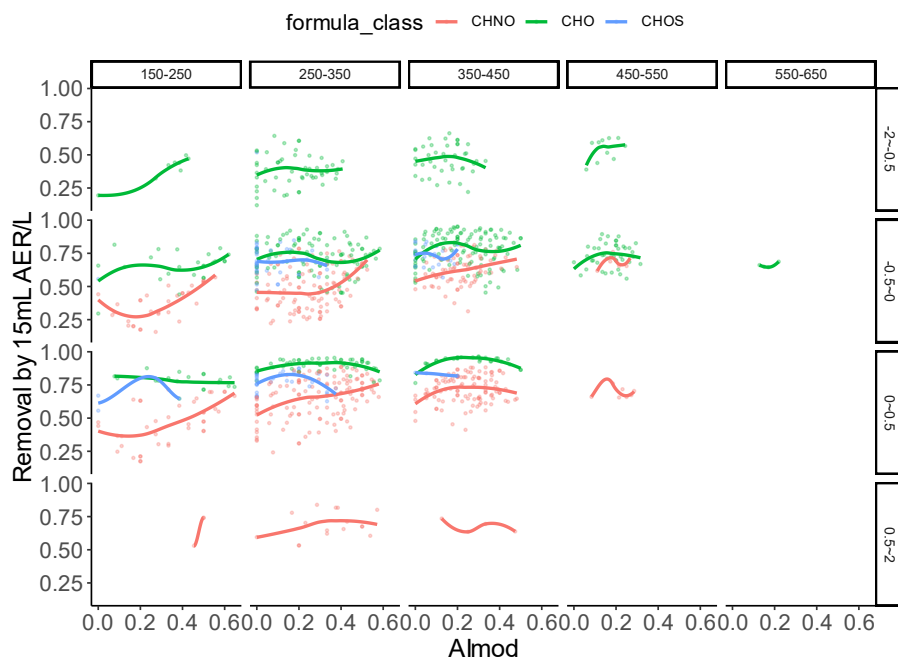
***Figure S14*** *Removals of AER-sorbed DOM in different formula classes vs aromaticity index ($AI_{mod}$) in different MW and NOSC ranges. Local polynomial regression fits with 95% confidence interval included. Note that the undetected formulas after AER pretreatment (100% removal) and molecular formulas with insufficient quantification condition (peak intensity < $10^5$ in untreated DOM sample) not included.*
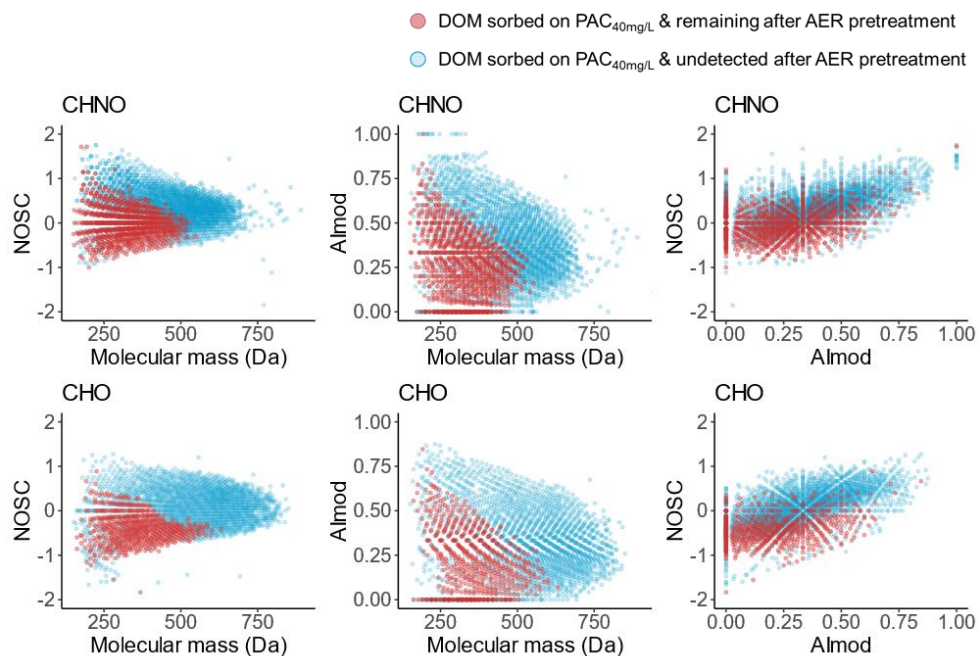
**Figure S15** *CHNO (top) and CHO (bottom) compounds sorbed on PAC$_{40mg/L}$. Polarity (expressed as NOSC) vs molecular mass (left); aromaticity index (AI$_{mod}$) vs molecular mass (mid); Polarity (expressed as NOSC) vs aromaticity index (AI$_{mod}$) (right).*

# Chapter 5

# Projecting competition between 2-methylisoborneol and natural organic matter in adsorption onto activated carbon from ozonated source waters
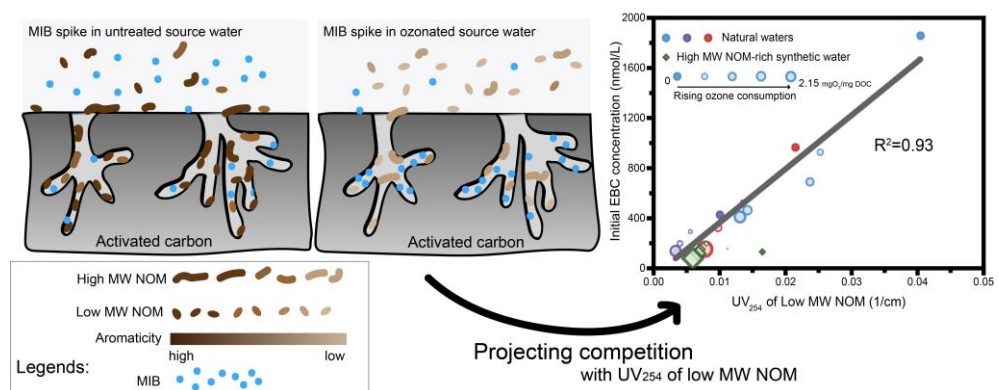
## Abstract

Though the ozone-activated carbon process has been widely applied for drinking water purification, little is known about how ozone-modified natural organic matter (NOM) competes with micropollutants in activated carbon adsorption. In this study, three natural waters and one synthetic water (standard humics solution) with highly heterogeneous NOM compositions were employed to investigate the interference of ozonated NOM with the adsorption of 2-methylisoborneol (MIB). Analysis using liquid chromatography with online carbon and $UV_{254}$ detection (LC-OCD-UVD) revealed that ozonation led to various disintegration patterns of macromolecules in NOM, and UV absorbance was reduced markedly for nearly all NOM fractions. Powdered activated carbon (PAC) adsorption experiments showed that increasing ozone consumption coincided with reducing NOM competition against MIB in the three natural waters, as expressed by the fitted initial concentrations of the equivalent background compound ($c_{0,EBC}$). In the synthetic water, in contrast, competition increased under low/moderate specific ozone consumptions and then decreased with further elevation of ozone consumptions. Regarding the significance on affecting ozonated NOM interference, aromaticity reduction outweighed the formation of low molecular weight (LMW) organics in most cases, enhancing MIB adsorption capacity. However, the disintegration of the humics fraction with larger molecular weight (1,103 g/mol, as compared to 546-697 g/mol in three natural waters) into smaller, more competitive fractions caused the observed initial deteriorated MIB adsorption in synthetic water. A superior correlation between $c_{0,EBC}$ and the UV absorbance of LMW organics ($R^2$=0.93) over concentrations of LMW organics underlined the importance of the aromatic properties in competitive adsorption projection for ozone pretreated natural waters. Furthermore, the change of relative concentration of UV absorbing compounds during ozonation could help estimate the decrease of $c_{0,EBC}$, which could be a promising tool for waterworks to adjust PAC doses for MIB removal in ozonated waters.

## 1. Introduction

2-methylisoborneol (MIB), odorous at a concentration as low as 10 ng/L (Matsui et al., 2014), occurs in up to 50% of lake/reservoir waters in China (Wang et al., 2019a). Conventional treatment and ozonation perform poorly on MIB removal (Peter and Von Gunten, 2007; Zoschke et al., 2011), wherefore powdered activated carbon (PAC) adsorption or ozone-biological activated carbon (BAC) combinations are often the methods of choice (Guo et al., 2016; Newcombe et al., 2002b). However, adsorption interference by coexisting natural organic matter (NOM) results in high PAC doses or short service times for carbon filters (Summers et al., 2013). The interference mechanisms are direct competition for internal adsorption sites and pore blockage with macromolecules (Li et al., 2003c). Direct competition is the dominant factor for low molecular weight (LMW) NOM molecules, with aromatic NOM inducing stronger competitive effects (Hu et al., 2014; Zietzschmann et al., 2014b). In $O_3$-BAC treatment, ozonation prior to adsorption may affect NOM characteristics, e.g. by hydrophilizing hydrophobic compounds, breakage of larger NOM constituents, or decreasing the aromatic content of the NOM (Lamsal et al., 2011; Song et al., 2010). The reduction in aromaticity and hydrophobicity of organics will reduce the competitive adsorption by NOM (Lerman et al., 2013), while the formation of small molecules from the breakage of larger NOM constituents may act in the other direction (Newcombe et al., 2002b). It was revealed that ozonation of wastewater treatment plant (WWTP) effluent positively alleviates the NOM interference with micropollutants, due to concomitantly decreasing aromaticity/hydrophobicity (Zietzschmann et al., 2015b). However, the origins and compositions of NOM in surface waters are much different from those in WWTP (Gonsior et al., 2011; Nam and Amy, 2008), which would exert an influence on the oxidation and adsorption behaviors of NOM and thus the competition with MIB.

To describe the competitive adsorption, the concentrations of LMW organic carbon (LMWOC) and UV absorbance of LMW organics (LMWUV), which could be measured by liquid chromatography with online OC and ultraviolet absorbance detection (LC-OCD-UVD), have been suggested as two important parameters (Zietzschmann et al., 2016c). On the other hand, the equivalent background compound model (EBCM) (Najm et al., 1991) has been used to project required PAC doses or GAC breakthrough curves for MIB removal in surface waters by indicating the competing NOM fraction of the targeted compound (Crittenden et al., 2012; Matsui et al., 2012). A relatively good correlation was mentioned

between LMWOC/LMWUV and EBC (Matsui et al., 2012). However, it is not clear if the two parameters could still be valid to describe the competing NOM in ozonated waters.

Therefore, the present study aims at elucidating the effects of ozonation on the interference behaviors of NOM to the MIB adsorption on activated carbon and projecting the corresponding adsorption interference with MIB. Three natural surface waters with diverse DOC, specific ultraviolet absorbance (SUVA), molecular weight distribution, and one synthetic water prepared with high molecular weight humics solution were employed to represent largely heterogenous NOM. LC-OCD-UVD and Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) were applied to characterize NOM fractions, and the EBCM was used to estimate the initial concentrations of competing NOM. The results of this study will be helpful for waterworks to deal with highly varying characteristics and concentrations of competing NOM in ozonation-adsorption stages.

## 2. Materials and Methods

### 2.1 Natural waters and synthetic water

Three raw waters were sampled in October 2018 from Mopanshan reservoir (MPS) in Harbin, Jinze reservoir (JZ) in Shanghai and Shiyan reservoir (SY) in Shenzhen, China. At the sampling time, no odor problems were identified in the reservoirs and the concentrations of MIB were lower than 10 ng/L. In addition, synthetic water was prepared by dissolving Suwannee River humic acids (SHA) from IHSS in ultrapure water. SHA is an isolation product from Suwannee River in South Georgia, USA, impacted by peat deposits and decomposing vegetation (Averett et al., 1994). The solution was stored in dark for 72 h to allow the humic solution to expand fully. Inorganic ions were amended to imitate the ionic background of natural waters for the SHA water and organic-free water (Table S1). To exclude the impacts of suspended solids on the subsequent treatment process, all raw waters were filtered by a 0.45 μm membrane (142mm, Supor-450, Pall Co.); the corresponding water parameters are listed in Table 2.

### 2.2 Ozonation procedures and PAC batch tests

Filtered waters were ozonated with a bench-scale ozonation setup equipped with an ozone generator (OS-1N, Mitsubishi Electric Co., Japan), with $O_2$ fed directly from an oxygen

generator (FY3, Beijing North Star Yaao, China). Ozone was bubbled into 2 L of the stirred filtrate in a glass jar. With ozone production rate ranging from 130 to 200 mg/h of ozone producer (same for ozonation of each water), the contact time of ozonation varied within 3-40 minutes according to the target dosage in four examined waters. The concentrations of ozone in inflow gas and exhaust gas were determined by iodimetry. The specific ozone consumption was calculated by the difference of the inflow and exhaust ozone by the water volume, divided by the concentration of dissolved organic carbon (DOC) of the respective ozonated water samples.

MIB was spiked in ozonated waters to comparable concentrations of 500 ng/L, using MIB stock solutions at 10 mg/L. The stock solutions were prepared by diluting the as-bought stock solution (10 g/L in methanol, Sigma Aldrich) with ultrapure water. PAC batch tests were then conducted with the raw and ozonated waters. PAC (SAE Super, Norit, Netherlands) was washed, dried and cooled in a desiccator, suspended in ultrapure water at 4 g/L, and stored overnight for full wetting. More information about the carbon properties is explained in Table S4 and Figure S6. Different volumes of stirred stock suspension were pipetted to 100 mL batches of the MIB-spiked waters (PAC dose range from 0-100mg/L, details in Table S2), which were put on a shaker under 160 rpm for 48 h, whereupon the batches were filtered through 0.45 μm polyether sulfone membrane filters.

## 2.3 Analytical methods

The MIB concentrations were determined using a solid phase micro-extraction (SPME) method coupled with gas chromatography-mass spectrometry (GC-MS, QP2010Plus, Shimadzu, Japan) (Liang et al., 2005). SPME was performed using an automated device (Combi PAL GC Multi-Function Autosampler, CTC Analytics, Switzerland). 2-isopropyl-3-methoxypyrazine (Supelco, USA) was added to each sample as an internal standard (80 ng/L) and the calibration range of MIB was from 8 to 640 ng/L.

Bulk $UV_{254}$ was measured by a UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan). DOC was determined using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Three-dimensional fluorescence spectrum analysis was conducted by a Fluorescence Spectrophotometer F-7000 (HITACHI, Japan).

NOM fractions of raw waters, ozonated waters and corresponding ones after adsorption, were analyzed by liquid size exclusion chromatography on a HW50S column (Toyopearl, Japan) coupled with LC-OCD-UVD (Model 9, DOC-Labor Huber, Germany) (Huber et al., 2011). All LC-OCD chromatograms were analyzed and fractionated quantitative results were obtained using automated integration with manually adjusted time frames for each fraction in the ChromCALC software (DOC-Labor Huber). ChromCALC automatically allocates aromatic LMW humic acids, as a part of LMW acids, to the humics fraction. However, considering the impact on micropollutant adsorption, LMW humic acids were assigned into LMW acids here, and the expression of "LMW humics and acids" was adopted. For both LMWOC and LMWUV integration, the local minimum between the building blocks and the LMW humics and acids was used as the left integration limit; as the right integration limit, the baseline at the end of the chromatogram was used, as indicated in Figure 1 (Zietzschmann et al., 2016c). The number averaged MW ($\overline{M}_n$) of humic substances fraction was calculated automatically in ChromCALC by the number of molecules $n$ and molar mass $M$ (Eq. 1). The MW was calibrated with humic acid (HA) and fulvic acid (FA) standards from IHSS (Eq. 2). Accordingly, retention time $t_r$ (min) and matching coefficients (A and B) from calibration with IHSS HA and FA were utilized (Huber et al., 2011).

$$\overline{M_n} = \frac{\sum_i (n_i \times M_i)}{\sum_i n_i} \qquad \text{..........................................(Eq. 1)}$$

$$MW = \exp\left(-\frac{t_r - A}{B}\right) \text{............................................(Eq. 2)}$$

The molecular characterization for LMW organics was performed by using FTICR-MS. A Bruker SolariX FT-ICR-MS equipped with a 15.0 T superconducting magnet was applied in this study. Details about extraction, measurement and data analysis are given in the Supporting Information.

## 2.4 Modeling for competing NOM analysis

The EBC model (EBCM) (Najm et al., 1991), based on the ideal adsorbed solution theory (IAST), as a fictive two-component competitive adsorption model was fitted to the experimental data for all batch-tested waters. The EBCM allocates all observed adsorption competition against a micropollutant (here MIB) in real water to one competing component, the EBC, which is characterized by Freundlich isotherm parameters ($K_{F,EBC}$, $1/n_{EBC}$) and an

initial concentration $c_{0,EBC}$. To increase comparability between the EBCM fitting results for different waters, global $K_{F,EBC}$ and $1/n_{EBC}$ were used for all waters, so that $c_{0,EBC}$ was the only fitting parameter and could therefore be easily correlated to water quality parameters (Zietzschmann et al., 2016a). For each PAC dose, our algorithm searches for the best suiting $q_{MIB}$ and $q_{EBC}$ using the two criteria of the EBC equations (Eqs. 3 & 4), calculates the corresponding $c_{MIB}$ and $c_{EBC}$, and determines the corresponding error for each $j$ in the minimization equation (Eq. 5). The algorithm finds the lowest value of *Min*, i.e., the best suiting set of EBC parameters, by trying various parameter combinations. Global $K_{F,EBC}$ and $1/n_{EBC}$ were calculated by averaging over the water-individual parameters; using the global parameters, we fitted a second time while only varying $c_{0,EBC}$.

$$c_{0,MIB} - d \times q_{MIB} - \frac{q_{MIB}}{q_{MIB}+q_{EBC}}\left(\frac{n_{MIB}q_{MIB}+n_{EBC}q_{EBC}}{n_{MIB}K_{F,MIB}}\right)^{n_{MIB}} = 0 \dots\dots\dots\dots\dots(\text{Eq. 3})$$

$$c_{0,EBC} - d \times q_{EBC} - \frac{q_{EBC}}{q_{MIB}+q_{EBC}}\left(\frac{n_{MIB}q_{MIB}+n_{EBC}q_{EBC}}{n_{EBC}K_{F,EBC}}\right)^{n_{EBC}} = 0 \dots\dots\dots\dots\dots(\text{Eq. 4})$$

where $d$ is the activated carbon dose, and $c_{i,0}$ are the initial concentrations, $q_i$ are the loadings, $1/n_i$ are the Freundlich exponents, and $K_{F,i}$ are the Freundlich coefficients of MIB and the EBC, respectively; units are molar.

$$Min = \frac{1}{N} \times \sum_{j=1}^{N}\left(\frac{|(c_{MIB,meas}-c_{MIB,mod})j|}{c_{MIB,meas}} + \frac{|(q_{MIB,meas}-q_{MIB,mod})j|}{q_{MIB,meas}}\right) \dots\dots\dots\dots(\text{Eq. 5})$$

where *Min* is the minimization term, $N$ is the number of data points (PAC doses), $c$ and $q$ are the liquid phase concentrations and PAC loading, respectively, and indices *meas* and *mod* refer to measured and modeled data, respectively.

In addition, we calculated an error margin for $c_{0,EBC}$, by adopting the uncertainty ranges of our MIB analysis (±5%) and error margins of the PAC dosage (±5%) into the c0,EBC fitting procedure, as similarly outlined in a previous publication (cf. SI of Zietzschmann et al., 2016).

## 3. Results and discussion

### 3.1 Raw water characterization

The pH, DOC concentrations, $UV_{254}$, SUVA and $\overline{M}_n$ of the examined waters are shown in Table 2 in ascending SUVA. Their DOC concentrations ranged from 1.39 mg/L in the SY water to 5.29 mg/L in MPS water; the SUVA values ranged from 2.16 to 6.26 L/(mg·m). The SUVA of anthropogenically influenced waters (JZ and SY) was lower than the humic-rich waters (MPS and SHA). $\overline{M}_n$ ranged from 546 to 697 g/mol in natural waters and 1,103 g/mol in synthetic SHA water. The highest aromaticity and $\overline{M}_n$ of SHA was due to its resin isolation, during which most neutral and hydrophilic fractions with lower SUVA were discarded (Thurman and Malcolm, 1981). For fluorescence pattern, both MPS and SHA waters had typical humic-like peaks, while JZ and SY waters shared similar protein-rich peaks (fluorescence characterization in Figure S1), but their fluorescence intensities were considerably different.

**Table 2** *Basic water parameters of the four examined waters.*

|  | pH | DOC (mg/L) | SUVA (L/(mg · m)) | $\overline{M}_n^*$ (g/mol) |
|---|---|---|---|---|
| Shiyan (SY) | 7.84 | 1.39 | 2.16 | 546 |
| Jinze (JZ) | 7.76 | 3.57 | 2.72 | 596 |
| Mopanshan (MPS) | 7.14 | 5.29 | 3.63 | 697 |
| Suwannee river humics (SHA)** | 7.08 | 4.06 | 6.26 | 1103 |

$^*$ $\overline{M}_n$: Number-average molar mass of humics fraction.

$^{**}$Inorganic salts were introduced to simulate the natural water (Table S1).

The LC-OCD chromatograms of the tested waters are shown in Figure 1, also presenting chromatograms normalized by maximum intensity of each sample for easier comparison on varying DOC concentrations. NOM could be divided into fractions including biopolymers (>20000 g/mol, ~13 min retention time), humics (~1000 g/mol, 17~22 min), building blocks (sub-units of humics, 300~500 g/mol, ~23 min), LMW humics and acids (<350 g/mol, ~27 min), LMW neutrals (<350 g/mol, >29 min) (Huber et al., 2011).
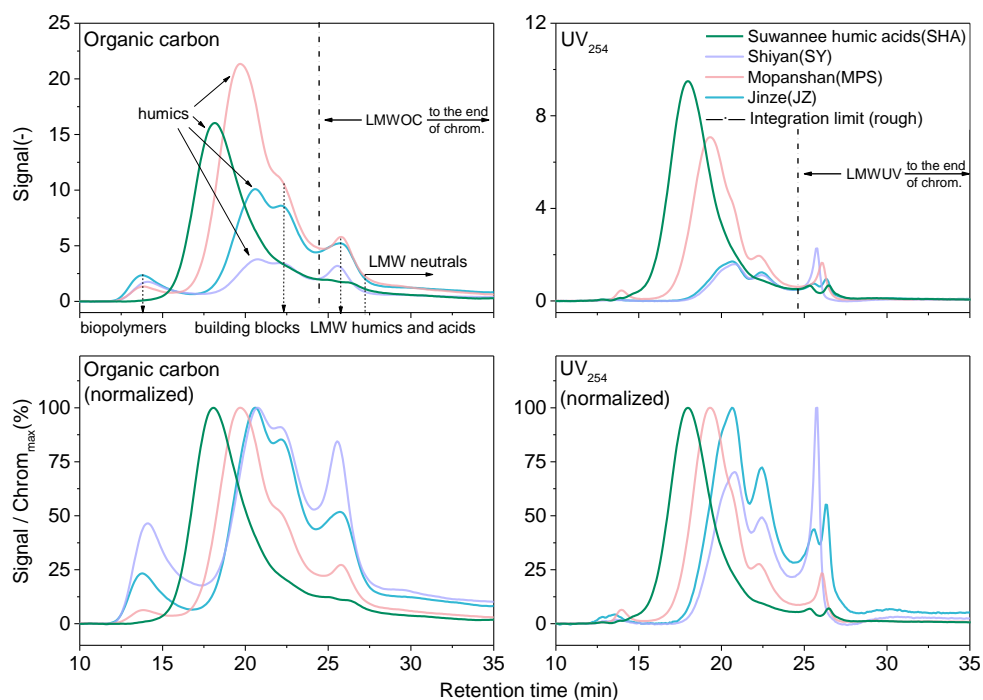
*Figure 1* LC-OCD absolute (top) and normalized (bottom) organic carbon (left) and UV₍254₎ (right) chromatograms of the examined waters, with approximate position of integration limit and integration range for concentrations of low molecular weight organic carbon (LMWOC) and UV absorbance of LMW organics (LMWUV); the exact position of integration limit followed the local minimum between building blocks and LMW humics and acids.

Within the examined waters, SY and JZ waters contained the largest proportion of LMW compounds including LMW humics and acids, and LMW neutrals. The MW of their humics fractions was comparatively small, as indicated by a longer retention time ($\sim$21 min). The corresponding UVD chromatograms were similar to the OCD chromatograms. The highest measured value in SY water was LMW humics and acids, suggesting higher aromaticity of LMW NOM (Altmann et al., 2016a). The MPS water contained a low percentage of biopolymers but a larger proportion of humics with a comparatively big $\overline{M}_n$ (697 g/mol), indicating relatively low anthropogenic influence in the upstream regions (Huber et al., 2011; Wang et al., 2013b). The highest percentage of aromatic humics fraction was observed

in SHA water. The $\overline{M}_n$ and SUVA of SHA were the highest among all examined aquatic NOM according to an investigation by Huber (Huber et al., 2011), which could help examine the behavior of aromatic macromolecules (>1000 g/mol) in ozonation with little impact by LMW fractions in the current study.

## 3.2 Impacts of ozonation on NOM fractions

The OCD chromatograms of the examined waters within a specific ozone consumption range from 0 to 2.84 mg $O_3$/mg DOC are shown in Figure 2 (fractionated quantitative results in Figure S4). Ozonation led to the disintegration of the macromolecules (biopolymers and humics) with increasing peaks of lower molecular weight fractions (Altmann et al., 2014; Von Sonntag and Von Gunten, 2012), but it is interesting to find the different variation patterns of NOM fractions displayed in different waters. SHA water experienced the most obvious reduction of humics and increase in building blocks and LMW humics and acids, with only slight changes of these fractions in JZ and SY waters. The greater increase in building blocks in SHA water may be related to the larger size of the humics precursors, as shown by a considerable reduction in the $\overline{M}_n$ of the humics in SHA water, from 1103 g/mol in raw water to 601 g/mol under an ozone consumption of 2.84 mg $O_3$/mg DOC (Table S3). By contrast, $\overline{M}_n$ values only varied within narrower ranges in ozonated natural waters (Table S3). An apparent reduction of humics was also observed in MPS water, but the accumulation of LMW fractions did not occur, possibly attributed to the strong mineralization as indicated by the conspicuous decrease of DOC during ozonation (Figure 2C).
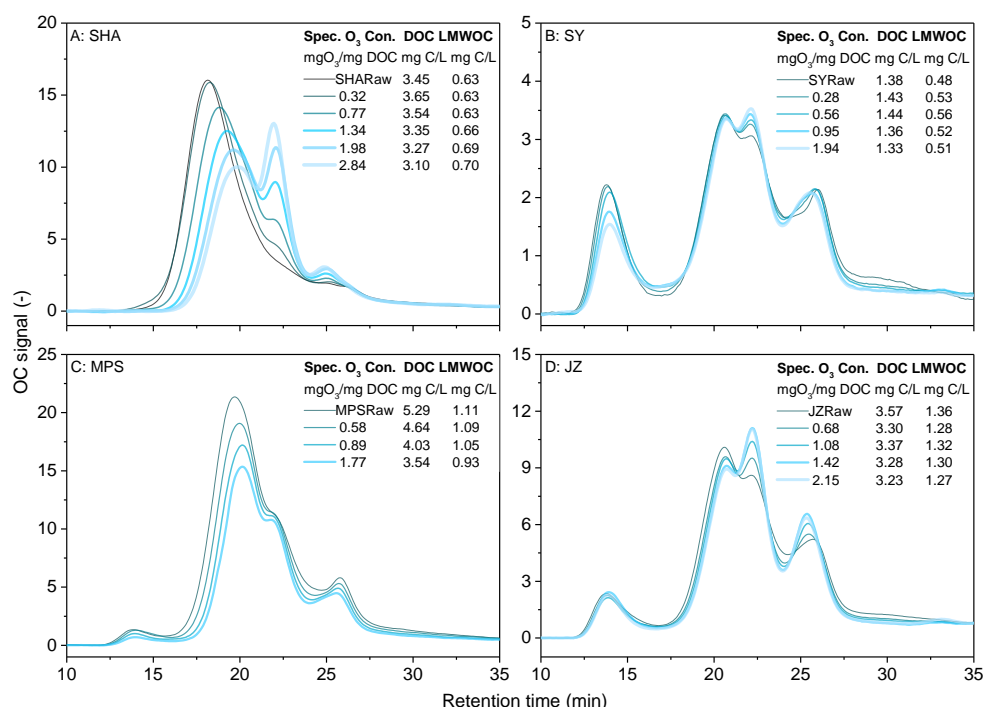
**Figure 2** *LC-OCD chromatograms of the examined waters after varying ozonation; the specific ozone consumptions (mg O₃/mg DOC), DOC of bulk organics and LMW organics (mg C/L) are indicated by the legends. Note the different y-axis scales in four chromatograms.*

The UVD diagrams of the ozonated waters exhibited an overall reduction of UV absorbance for most of the fractions (Figure S3). Although the DOC reduction differs significantly in the four examined waters, the decrease pattern of chromophores in organic matter, indicated by UV, is more similar. Only a mild increase in building blocks peak (~22 min) was observed in SHA ozonated water, caused by the strong shift of the humics peak; this was also supported by the declining absorbance in the fractionated quantitative results (Figure S5A). At the same time, the aromaticity of all fractions was reduced by ozonation in the natural waters (Figure S5), independent of the size of fractions. Though the formation of new LMW unsaturated/aromatic compounds was often observed in previous studies (Phungsai et al., 2019; Reemtsma and These, 2005), ozonation would lead to the overall decrease for medium and low MW fractions (Van der Helm et al., 2009). Only slight increments were observed, in terms of UV absorbance of LMW humics and acids, during ozonation of SHA

water (cf. Figure S5A); this could not be observed in ozonated natural waters or wastewaters without such a large proportion of aromatic humics (cf. Figure 1) (Van der Helm et al., 2009; Zietzschmann et al., 2015b).

## 3.3 Interference of ozonated NOM with MIB adsorption

MIB adsorption experiments were conducted in the four examined waters pre-ozonated under a specific ozone consumption range between 0 and 2.84 mg $O_3$/mg DOC (see isotherms in Figure S2). In comparison with the batch in organic-free water, 25 - 95% of MIB adsorption capacity was lost for all the NOM-containing samples. As shown in Figure 3, the MIB adsorption capacity in JZ raw water was the lowest, followed by MPS, SY and SHA waters. Accordingly, the highest value of $c_{0,EBC}$ (1858 nmol/L, cf. Figure 4) in JZ raw water was discovered and $c_{0,EBC}$ was in reverse order with MIB adsorption capacity. It is interesting that the $c_{0,EBC}$ of JZ raw water was over a magnitude larger than that of SHA raw water ($c_{0,EBC}$ = 132 nmol/L) though they had similar DOC. In this respect, NOM interference was not reflected by conventional bulk organic parameters like DOC and bulk $UV_{254}$, underlining the limitation of using these global parameters in explaining the NOM interference on adsorption (Newcombe et al., 2002b; Zietzschmann et al., 2014b). For SHA water, the extremely low $c_{0,EBC}$ indicated the adsorption sites occupied by the SHA might be different from those by MIB. It was reported that the large humics are normally adsorbed on the surface of activated carbon (Ando et al. 2010), while MIB is reported to be mainly associated with the micropores (Yu et al., 2007). Also, the ionizable character induced by resin isolation procedures (elution at low pH, the neutrals and bases fractions discarded), might have accounted for the reported lower adsorption and interference at neutral pH (Hu et al., 2014; Matsui et al., 2012; McCreary and Snoeyink, 1980). The stronger competitive effects in JZ and MPS were likely related to relatively high LMWOC/LMWUV (cf. Figure 1 and Figure 3).
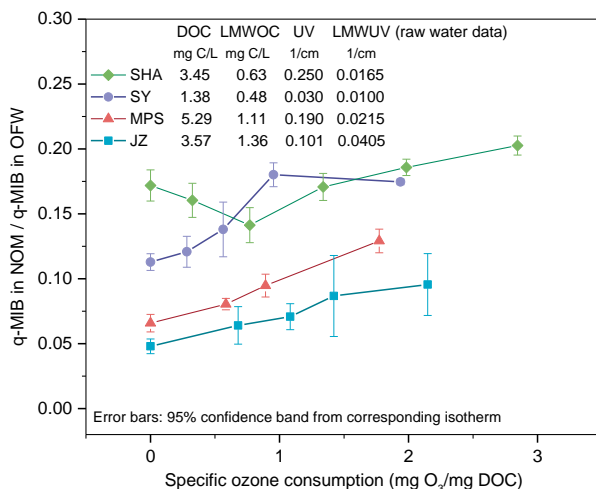
**Figure 3** *Ratio of MIB adsorption capacity (at $c_{eq,MIB} \approx 0.3$ nmol/L, isotherms in Figure S2) in NOM-containing samples to that in organic-free water (OFW) over specific ozone consumptions (mg $O_3$/ mg DOC) in the tested ozonated waters, with basic water parameters of raw waters in the legend including DOC (mg C/L), LMWOC (mg C/L), UV (1/cm) and LMWUV (1/cm); error bars based on 95% confidence band of MIB adsorption isotherm.*

Regarding the ozonation impacts, it was found that decreasing NOM competition against MIB adsorption in general occurred with increasing ozone consumption for SY, MPS and JZ waters (except for an insignificant increase in SY at the highest ozone consumption), similar to a previous study with wastewater (Zietzschmann et al., 2015b). In contrast, an increase in adsorption competition occurred at low/moderate specific ozone consumptions ($\leqslant 0.77$ mg $O_3$/mg DOC) in SHA water, while the competition declined at higher specific ozone consumptions. This is the first time to find a different interference behavior of SHA water under mild ozonation, which might be associated with the enhanced pore accessibility due to the breakage of large humics.

Figure 4 illustrates the NOM loading variation on activated carbon and the corresponding $c_{0,EBC}$ from EBCM-fitting at a specific carbon dose (16.5±2.5 mg PAC/mg DOC, cf. Table S2) under different ozone consumptions. Compared with untreated samples, the NOM loading

after ozonation experienced notable drops, 20-55% at similar specific ozone consumptions of 2 mg $O_3$/ mg DOC, for the three surface waters (Matsui et al., 1999); by contrast, the $c_{0,EBC}$ declined more significantly (64-68%). On the other hand, the reduction in NOM loading was higher for smaller organics than for the humics/building blocks fractions despite the increase of LMWOC concentrations, suggesting the important effect of the decreased affinity of LMW NOM, the suspected competing NOM, towards activated carbon due to the destruction of aromaticity by ozonation. In short, the NOM loading on PAC only partly reflected the competitiveness of the corresponding NOM (Zietzschmann et al. 2014).

In contrast to the natural waters, the humic-rich SHA water exhibited a quite different adsorption and interference behavior and it is a valuable instance for elucidating counteracting ozonation impacts on humics fraction in adsorption interference, the descending aromaticity and also declining $\overline{M}_n$ (Table S3). In general, the NOM loading and $c_{0,EBC}$ shared the same variation trend during ozonation. Under mild ozonation ($\leqslant$ 0.77 mg $O_3$/mg DOC), the enhanced loading of humics fraction, induced by higher pore accessibility from $\overline{M}_n$ reduction, was the main positive contributor to the elevated NOM loading (Figure 4). More pores might be occupied or blocked by smaller aromatic humics and therefore MIB adsorption was restricted. This could not be easily avoided using PAC like SAE Super with abundant secondary micropores and narrow mesopores (data in Table S4 and Figure S6) as these pores are susceptible to the adsorption or blockage of aromatic humics with lower molecular weight, in line with previous studies (Li et al., 2003c; Newcombe et al., 1997). For higher ozone consumptions (1.34-2.84 mg $O_3$/mg DOC), aromaticity reduction was dominant and NOM adsorbability decreased, just like the ozonation in three natural waters. Hence, scavenging the organic chromophores both in macromolecules and small molecules is the distinct advantage of ozonation to restrict the formation of competing NOM in both synthetic and natural waters, and the increment of competing NOM should also be concerned where MW of humics fraction is high in source waters.
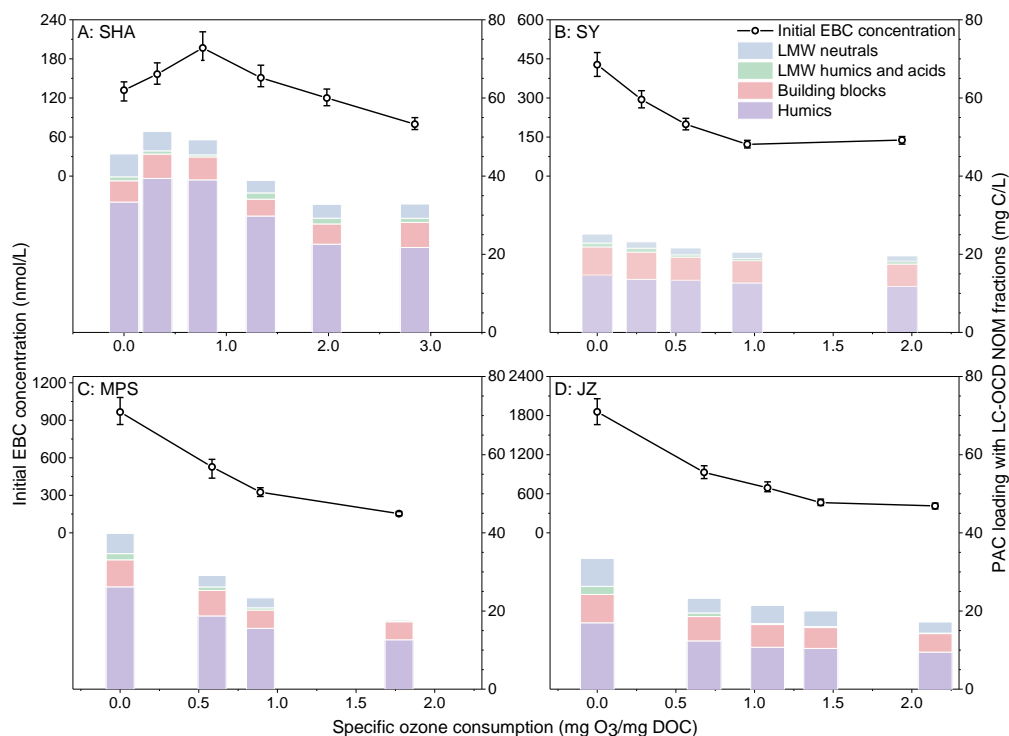
*Figure 4* *Variations of initial EBC concentrations ($c_{0,EBC}$, nmol/L) for MIB and NOM loading (mg C/g) on activated carbon with different fractions, at specific carbon dose (16.5±2.5 mg PAC/mg DOC, cf. Table S2), in dependence of specific ozone consumptions (mg $O_3$/mg DOC) in the examined waters.*

## 3.4 LMWUV as the key indicator for competitive adsorption

The $c_{0,EBC}$ for MIB are plotted versus LMWOC concentrations and LMWUV absorbance in Figure 5 No overall relation between $c_{0,EBC}$ and LMWOC concentrations occurred in all examined samples (Figure 5A). Instead, the LMWUV exhibited a good relation with $c_{0,EBC}$ in natural waters (Figure 5B, $R^2$=0.93, SHA excluded). This appears to contrast with previous studies where LMWOC was also suggested to explain $c_{0,EBC}$ in manifold waters (drinking waters, surface waters, wastewater treatment plant effluents) (Matsui et al., 2012; Zietzschmann, 2016). However, these studies did not induce NOM changes by pre-treatment like ozonation but used only the original natural waters. The results of the current study demonstrated that LMW aromatic organics should be the key NOM fraction reflecting the competitiveness of natural water NOM compounds against MIB. The superiority of LMWUV over LMWOC is that it not only incorporates the *concentration* of suspected competing NOM

but, more importantly, also the *character* (aromaticity/adsorbability). The correlation in Figure 5B thus helps to project $c_{0,EBC}$ (or, more generally, prospective adsorption competition) for MIB in both natural waters and ozonated waters with a wide range of specific consumptions (0~2 mg $O_3$/mg DOC), and simplifies the determination of required PAC doses.



(A)                                    (B)
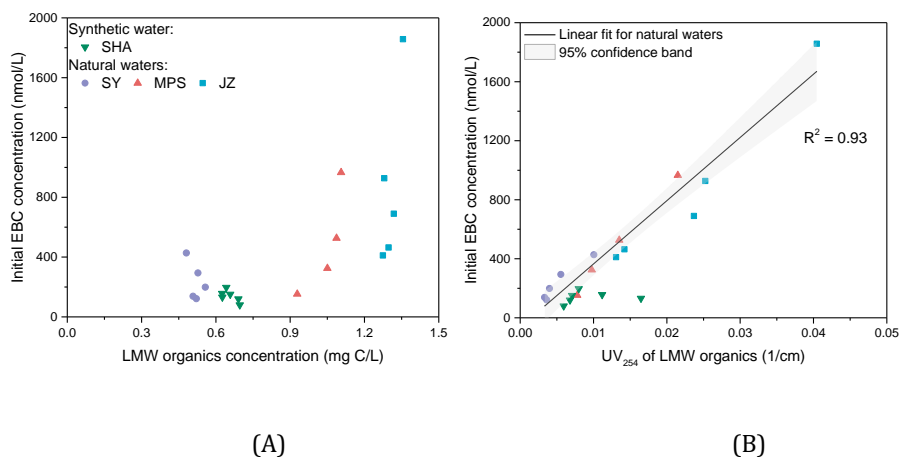
**Figure 5** *Fitted initial EBC concentrations ($c_{0,EBC}$) for MIB vs LC-OCD LMW organic carbon (A) and UV (B) in the differently ozonated natural/synthetic waters. Note that the synthetic water (SHA) is excluded in the correlation for natural waters.*

From a mechanistic point of view, the counteracting effects of competing NOM concentration and NOM aromaticity are quite difficult to quantify clearly, complicating a comprehensive evaluation of ozonation effects on NOM-MIB competition. In previous studies, resin fractionation of NOM has been reported to explain the competitive effect (Lerman et al. 2013). Hydrophobic acids and neutrals were found to be primary competitors while the hydrophilic fraction showed little competition. However, each resin isolation may contain NOM fractions with different sizes and strongly variable UV absorbances, distributed over the range of LC-OCD chromatograms (Bolto et al., 1999; Kennedy et al., 2005). Similar wide distributions were also observed after ultrafiltration/nanofiltration fractionization (Newcombe et al., 2002a; Zietzschmann et al., 2014b). Therefore, tracing the changing LMWUV with LC-OCD-UVD can have better performance to describe the competing

NOM and give overall estimations for $c_{0,EBC}$. In Figure S7 and S8, further results on LMW organics characterization in JZ water by FTICR-MS reveals that both ozonation and adsorption had preferential performance in reducing the relative abundance of compounds with low O/C value or low H/C value, covering the area reported correlating with UV absorbance, facilitating our LMWUV projection (Lavonen et al., 2015). The high similarity of ozonation and adsorption in removing components in LMW organics also helps confirm the alleviation effect of ozonation on subsequent MIB adsorption in NOM-containing waters.

From a practical point of view, estimating NOM adsorption competition variations against MIB through monitoring LMWUV via LC-OCD is still difficult for most waterworks. In our study, the degradation of LMWUV and online measurable bulk UV were similar during ozonation of individual natural waters (cf. Figure S5), making bulk UV a potentially feasible practical parameter for inferring LMWUV variations. The remaining percentage of $c_{0,EBC}$ ($c_{0,EBC}$ in ozonated water/ $c_{0,EBC}$ in raw water) for MIB is depicted over the remaining percentage of bulk UV absorbance ($UV_{254}$ in ozonated water/ $UV_{254}$ in raw water) in Figure 6, showing a well-established relationship between these two parameters (similar $R^2$ as when using LMWUV, cf. Figure 5B). In practical application, the change of $c_{0,EBC}$ after ozonation can be well indicated by bulk UV accompanied with only one batch-test for evaluation of the initial competition behavior in unozonated water. These two estimation methods from both mechanistic and practical perspectives may provide more scientific grounds for the reported application to use bulk UV serving as a simple and robust parameter for micropollutants removal (Altmann et al., 2016a; Ziska et al., 2016).
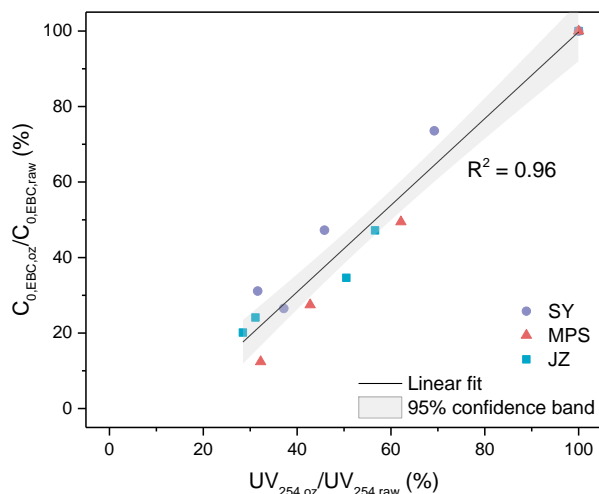
**Figure 6** *Degradation of $c_{0,EBC}$ ($C_{0,EBC,oz}$ /$C_{0,EBC,raw}$, $c_{0,EBC}$ in ozonated water/ $c_{0,EBC}$ in raw water) for MIB depicted over the change of bulk $UV_{254}$ ($UV_{254,oz}$ /$UV_{254,raw}$, $UV_{254}$ in ozonated water/ $UV_{254}$ in raw water) during ozonation of the three natural waters.*

## 4. Conclusions

-   Variable ozonation of three natural waters and an IHSS standard humics solution (Suwannee river humic acids, SHA) resulted in highly heterogeneous NOM with strong variability of the corresponding competitive adsorption against MIB onto PAC. Ozone-induced accumulation of LMW organics was strongly impacted by the molecular weight of humics and DOC mineralization. On the other hand, NOM UV absorbance clearly decreases for nearly all fractions with increasing ozone consumptions.

-   NOM adsorption competitiveness against MIB decreased with increasing ozonation intensity in natural waters. By contrast, SHA NOM ozonation caused increased NOM adsorption and competition against MIB unexpectedly for low/moderate ozone consumptions, likely due to increased pore accessibility or blockage by humics with lower molecular weight. For higher ozone consumptions, this effect was outweighed by the competition-alleviating UV absorbance reduction and NOM adsorbability and

competitiveness decline in SHA water. In this respect, SHA NOM behaved differently than NOM from the three natural waters.

- $c_{0,EBC}$ of the EBCM correlated well with LMWUV (synthetic water excluded), underlining the predictability of adsorption competition against MIB in ozonated natural waters and the relevance of incorporating LMW properties into estimating approaches (as opposed to only using LMWOC). Further characterization with FTICR-MS showed that LMW organics with similar molecular properties (low O/C value or low H/C value, covering the area related to UV) were preferentially removed both in ozonation and adsorption.

- Waterworks could use bulk UV to infer $c_{0,EBC}$, and thus optimize the required PAC doses, since LMWUV quantification via LC-OCD is usually not practically feasible, nor available in online measurements.

# Supporting information

## SI1 Ionic concentrations in some adsorption batches.

***Table S3*** *Ionic concentrations in organic-free water and SHA synthetic water.*

|  | Molar concentration [mmol/L] |
| --- | --- |
| $CaCl_2$ | 1 |
| $NaHCO_3$ | 0.5 |
| $MgCl_2 \cdot 6H_2O$ | 0.2 |
| $NaCl$ | 0.3 |
| $Na_2SO_4$ | 0.1 |
| $KNO_3$ | 0.1 |

## SI2 Applied PAC doses in batch tests.

***Table S4*** *Absolute and DOC-relative PAC doses in batch experiments.*

| SHA | | SY | | MPS | | JZ | | Comments |
|---|---|---|---|---|---|---|---|---|
| c [mg/L] | c/DOC [mg/mg] | c [mg/L] | c/DOC [mg/mg] | c [mg/L] | c/DOC [mg/mg] | c [mg/L] | c/DOC [mg/mg] | |
| 1 | 0.25 | 1 | 0.72 | 2 | 0.38 | 1 | 0.28 | |
| 2 | 0.49 | 2 | 1.44 | 5 | 0.95 | 2 | 0.56 | |
| 3 | 0.74 | 3 | 2.16 | 8 | 1.51 | 4 | 1.12 | |
| 4 | 0.99 | 4 | 2.88 | 10 | 1.89 | 6 | 1.68 | |
| 5 | 1.23 | 5 | 3.60 | 15 | 2.84 | 10 | 2.80 | |
| 6 | 1.48 | 8 | 5.76 | 20 | 3.78 | 15 | 4.20 | |
| 7 | 1.72 | 11 | 7.91 | 30 | 5.67 | 22 | 6.16 | |
| 15 | 3.69 | 15 | 10.79 | 50 | 9.45 | 30 | 8.40 | |
| 50 | 12.32 | 25 | 17.99 | 100 | 18.90 | 50 | 14.00 | NOM loading data shown in Figure 4 |

## SI3 Three-dimensional fluorescence spectrum analysis of examined waters.

Figure S1 displays the three-dimensional fluorescence spectrum analysis for examined water. It shows that the fluorescence intensities of JZ water, which had been diluted five times with pure water before analysis, were still much higher than other water samples without dilution. As previously reported, a fluorescence with Ex/Em of 250-260/380-480 corresponds to humic and/or fulvic materials. The second region with Ex/Em of 300-370/400-480 relates to the humic acid-like materials (Her et al., 2003; Świetlik et al., 2004). The fluorescence with excitation at 220-280 nm and emission at 300-381 nm is commonly described as having arisen protein-like from the aromatic amino acids, or as protein constituents. The fluorescence with Ex/Em of 220-237 nm/275-310 nm and the Ex/Em of 270-280 nm/300-330 nm is tyrosine-like organic matter, while with Ex/Em of 220-237 nm/330-381 nm corresponds to tryptophan-like materials (Yamashita et al., 2003).

As indicated in Figure S1(A) and (C) that the humic-like peaks took the most part of the organic matter in SHA and MPS water. Meanwhile, the tyrosine-like and protein-like materials were the main parts of organic matter for SY and JZ water (Figures S1(B) and (D)). The diversity of fluorescence patterns benefits the analysis of the role of fluorescence in the evaluation of MIB adsorption competition.
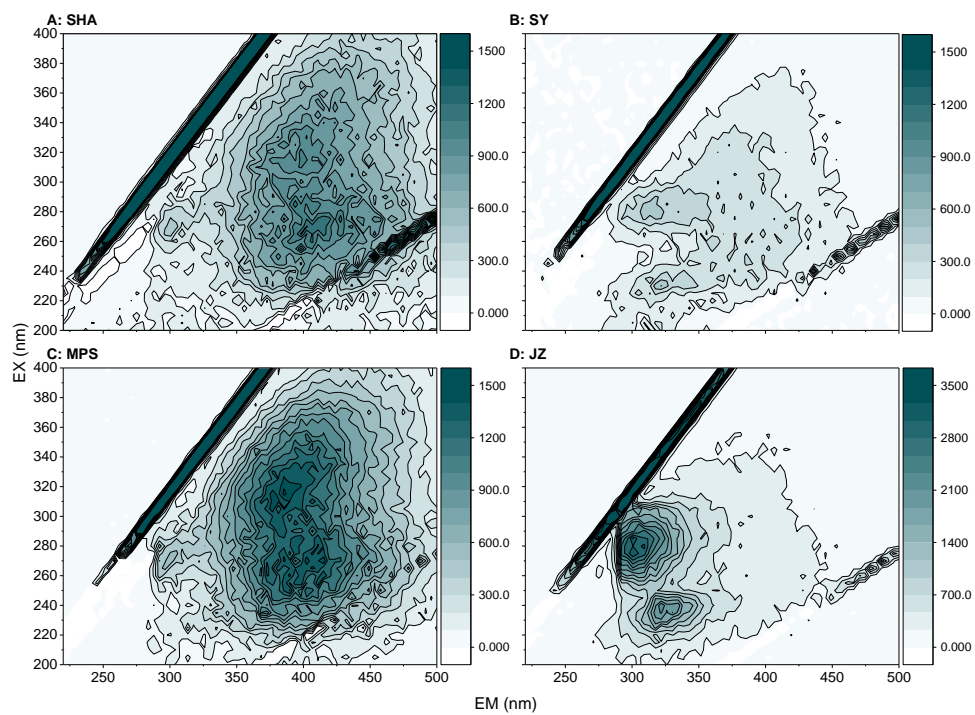
***Figure S1*** *The three-dimensional fluorescence spectrum analysis for the organic matter in SHA (A), SY (B), MPS(C) and JZ (D) waters. Note that the special color scales in subfigure D.*

*MIB adsorption isotherms.*
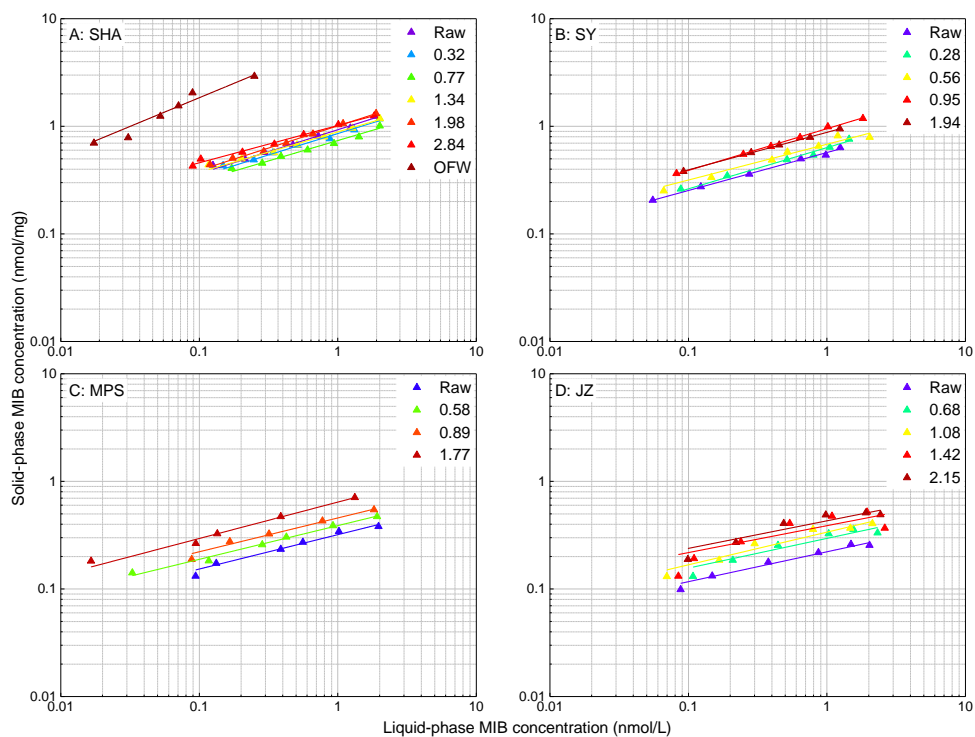


**Figure S2** *MIB adsorption isotherms in raw, ozonated and organic-free (OFW) waters. Initial MIB concentrations were comparable concentrations of 500 ng/L. The legends indicate the specific ozone consumptions (mg $O_3$/mg DOC).*

## SI4 The effect of ozonation on LC-OCD chromatograms.
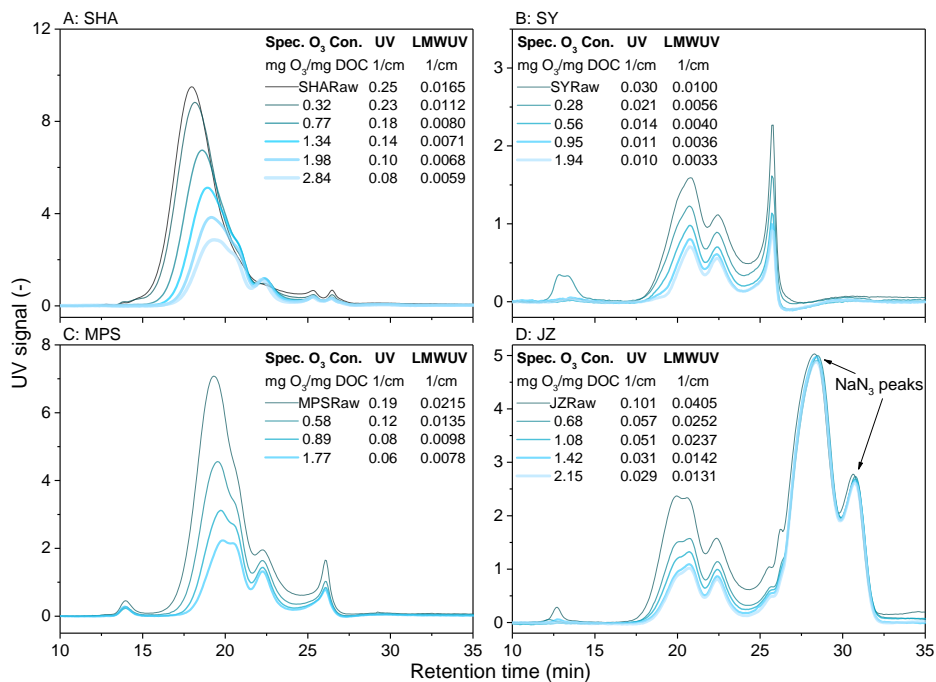


***Figure S3*** *LC-UVD chromatograms (at 254 nm) of the examined waters after varying ozonation; the specific ozone consumptions (mg O₃/mg DOC), UV of bulk organics and LMW organics (1/cm) are indicated by the legends. The NaN₃ was used to preserve the samples for LC-OCD measurements and the corresponding peaks were shown here and corrected in quantification results (Figure S5). Note the different y-axis scales in top and bottom chromatograms.*

## SI5  Fractionized results: ozonation impacts on NOM fractions.
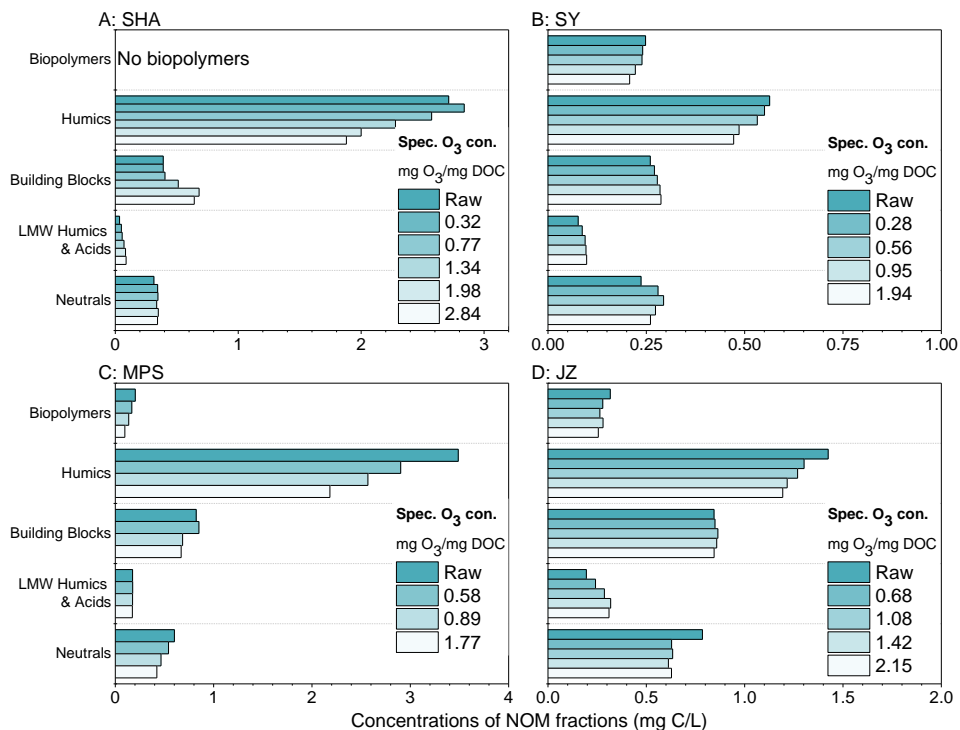


**Figure S4** *The effect of ozonation on concentrations of NOM fractions (mg C/L) in examined waters. Note the different scales in subfigures.*
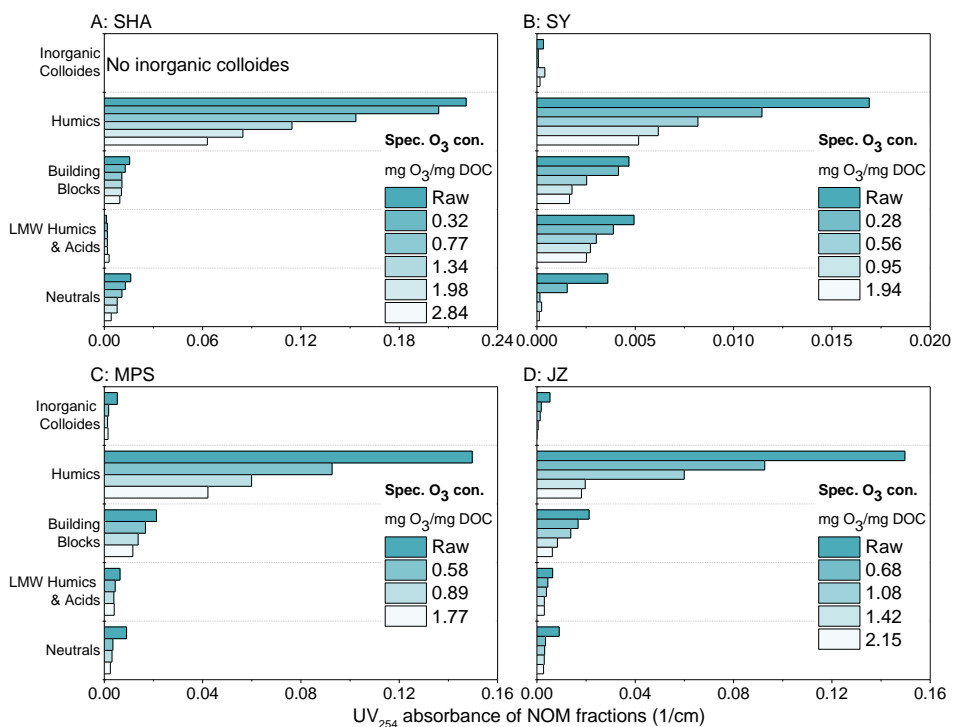
***Figure S5*** *The effect of ozonation on UV absorbance of NOM fractions (1/cm) in examined waters. Note the different scales in subfigures.*

## SI6 Characterization of ozonated humics fraction.

*Table S5* *Molecular and aromatic characteristics of humics fraction in raw and differently ozonated waters.*

|  | Specific $O_3$ consumption [mg $O_3$/mg DOC] | $\overline{M}_n$ of humics fraction [g/mol] | SUVA of humics fraction [L/(mg · m)] |
|---|---|---|---|
| SHA | 0.00 | 1103 | 8.16 |
|  | 0.32 | 1088 | 7.27 |
|  | 0.77 | 844 | 5.96 |
|  | 1.34 | 733 | 5.02 |
|  | 1.98 | 693 | 4.23 |
|  | 2.84 | 601 | 3.34 |
| SY | 0.00 | 546 | 2.74 |
|  | 0.28 | 521 | 1.95 |
|  | 0.56 | 521 | 1.52 |
|  | 0.95 | 506 | 1.16 |
|  | 1.94 | 503 | 0.92 |
| MPS | 0.00 | 697 | 4.29 |
|  | 0.58 | 684 | 3.19 |
|  | 0.89 | 627 | 2.33 |
|  | 1.77 | 586 | 1.93 |
| JZ | 0.00 | 596 | 3.25 |
|  | 0.68 | 586 | 2.26 |
|  | 1.08 | 579 | 1.76 |
|  | 1.42 | 564 | 1.41 |
|  | 2.15 | 564 | 1.30 |

## SI7 PAC Characterization.

Carbon properties of selected PAC (SAE Super) were determined from Ar gas-physisorption isotherms measured with an Autosorb iQ Station 2 (Quantachrome, USA). Prior to the measurement, PAC sample were degassed at 105 °C. The overall results are indicated in Table S and Figure S6.

***Table S6*** *Pore characteristics of PAC (Norit SAE Super).*

| B.E.T. surface [m²/g] | Total pore volume [cm³/g] | Primary micropores <0.8 nm [cm³/g] | Secondary micropores 0.8-2 nm [cm³/g] | Mesopores 2-50 nm [cm³/g] | Average pore diameter [nm] |
|---|---|---|---|---|---|
| 1122 | 0.74 | 0.15 | 0.22 | 0.37 | 2.807 |



***Figure S6*** *Pore size distribution of PAC with DFT and BJH methods. Note the break within the x-axis and different scales in two subfigures.*

## *SI8 Ultrahigh Resolution Mass Spectrometry characterization of low molecular weight NOM*

**Methods:** Sample enrichment and desalination were performed with solid phase extraction (Dittmar et al., 2008). In short, water samples (2L) were acidified with HCl to pH 2 and pumped through the SPE cartridges (Bond Elute PPL, 1 g/6 mL). The cartridges were rinsed with 6 mL of pure methanol (MS grade) and 0.01 M HCl before use. Then, the cartridges were rinsed with 6 mL of 0.01 M HCl for the complete removal of residual salts, and then dried under a gentle stream of nitrogen. Elution was performed by eluting with three cartridge volumes (18 mL) of methanol at a flow rate of 5 mL/min. The eluted DOM samples were then lyophilized and stored in the dark at -18℃. These dried samples were eventually re-dissolved in 1:1 MeOH:$H_2O$.

Mass spectra were acquired using a Bruker SolariX FT-ICR-MS equipped with a 15.0 T superconducting magnet. ESI ion source was used and the ESI needle voltage was set to -3.8 kV and time-domain data sets were coadded with 256 acquisitions and one hundred mass spectra were averaged per sample. The lower mass limit was set to m/z 150 Da and the upper mass limit to m/z 1000 Da, respectively. The spectra were first externally calibrated using a linear calibration based on sodium formate (10 mM) in 50% isopropyl alcohol. Internally calibration was also conducted with ~50 molecular formulas with a set of normal NOM reference materials. Only Peaks of LMW organics(≤350 Da) with a signal-to-noise ratio (S/N) > 3 and mass error ≤1 ppm were used to further identify $C_{5-40}H_{10-50}O_{0-20}$ molecular formulas using Bruker Data Analysis software. Further restrictions were performed with elemental ratios of H/C ≤ 2.2 and O/C ≤ 1.0. In the data analysis of CHO formulas, double bond equivalents per carbon (DBE/C) and degree of oxidation of organic compounds (OSc) were calculated for more information.

$$DBE/C = \frac{C - \frac{H}{2} + 1}{C}$$

$$OSc = \frac{(H \times 1) - (O \times 2)}{C}$$

**Results and discussion:** As shown in Figure S7, In the process of ozonation, the intensity maximum area of NOM molecules in JZ water moves slightly from an O/C value of 0.5 in the

original isolates to a value of 0.6 at 1.76 mg of O3/mg of DOC, implying the preferential removal of compounds with a low O/C ratio and elevated oxygen content of the ozonation products (These and Reemtsma 2005). The complete removal of some molecules with low O/C ratio and formation of high O/C ones facilitates the increased average oxidation state of NOM in JZ water, while $O_3$ reaction with high O/C-NOM is less preferential (cf. Figure S8A). In Figure S8A, the percentage reduction of relative abundance for paired peaks located in two analyses (raw water& ozonated water / raw water & water after adsorption) was depicted in van Krevelen plot. Ozonation and adsorption share a wide overlap zone in van Krevelen diagram for preferential removal. Ozonation and adsorption reduce the relative abundance of compounds with O/C < 0.4 or H/C < 0.8 at a similar level (shown as a similar bubble size), implying ozonation could assist to remove highly-absorbable compounds on activated carbon. These results help to provide more descriptors for competing NOM. In Figure S8B, ozonation and adsorption preferably removed molecules with lower OSc values with the same double bond equivalents per carbon (DBE/C). MIB is also a compound with low OSc and low DBE/C (DBE/C = 0.18, OSc = -1.72), close to the preferential removal area of activated carbon adsorption (DBE/C < 0.5, OSc < -0.5). Compared with ozonation, as the pretreatment for micropollutants adsorption, coagulation was reported to be much less effective (Altmann et al. 2015, Zoschke et al. 2011). One reason is that coagulation had limited removal of LMW fractions (Zoschke et al. 2011) and the removable fraction for coagulation was mostly oxidized molecules with high O/C value (Zhang et. al 2012, Lavonen et. al. 2015), significantly differing from strongly absorbable components on activated carbon.
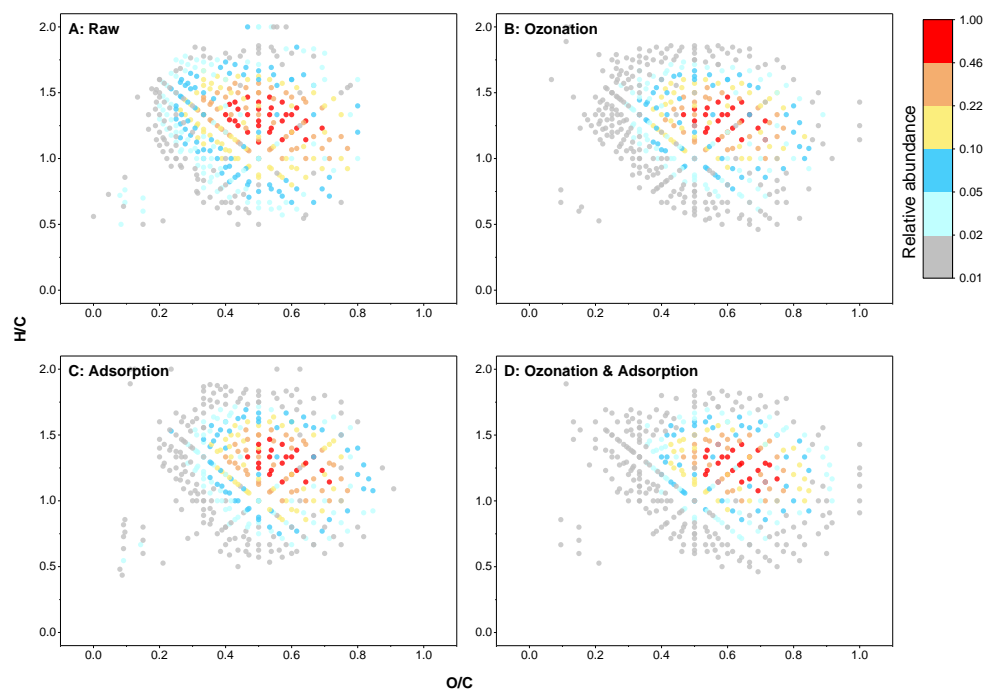
***Figure S7*** *van Krevelen diagram of CHO formulas (MW < 350 g/mol) identified in differently treated JZ water: (A) raw water; (B) Ozonated water (1.76 mg O₃/DOC); (C) Adsorption-treated water (50 mg/L PAC dose); (D) Adsorption-treated (50 mg/L PAC dose) ozonated water (1.76 mg O₃/DOC).*
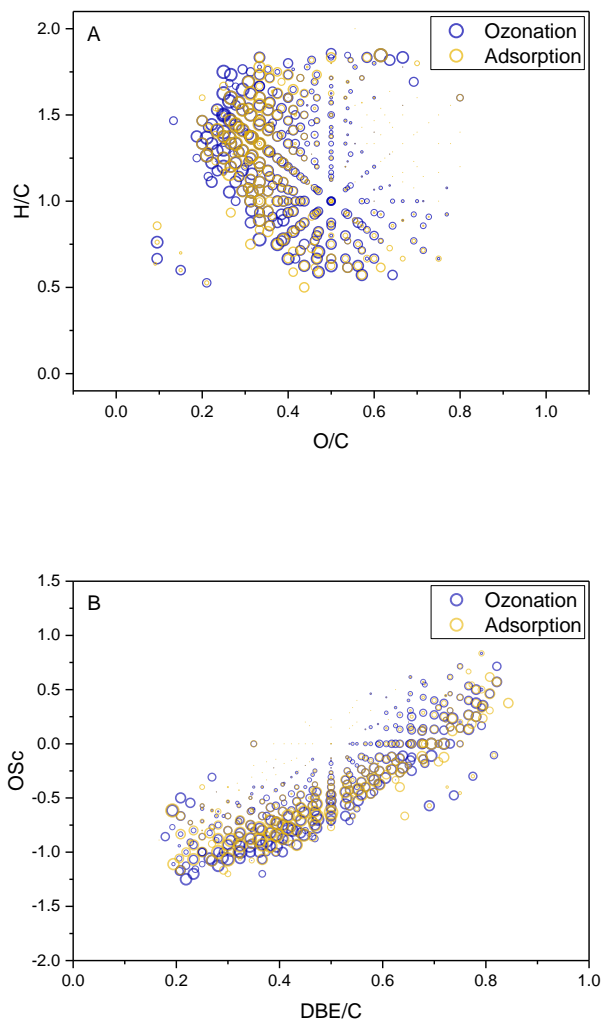
**_Figure S8_** _van Krevelen plot (a) and OSc against DBE/C plot (b) of change of LMW organics during ozonation and adsorption in JZ water. The bubble size represents the reduction in relative abundance (blue bubble = ozonation, red bubble = adsorption)._

# Chapter 6
# Conclusions and Outlook

# 1. Conclusions

A study was conducted on relevant characteristics of low molecular weight (LMW) dissolved organic matter (DOM) competitors against organic micropollutants (OMPs) in activated carbon adsorption. Within LMW DOM, the effects of a series of physico-chemical molecular properties like hydrophobicity, aromaticity and dissociation, as well as a more bulk characteristic like adsorbability, on the competitiveness against a variety of OMPs were explored. In addition, proper DOM surrogates for different surface waters in the presence/absence of ozonation pretreatment were discussed to project DOM competitiveness. The conclusions with respect to the research questions raised in Chapter 1 are as follows:

**How do properties of model LMW DOM impact OMP adsorption onto activated carbon at environmentally relevant (asymmetric) concentrations?**

Batch tests with fifteen LMW model DOM compounds (mDOM) were conducted to study the effect of hydrophobicity, aromaticity (or other unsaturated structures), and adsorbability on competitive adsorption against OMPs with various characteristics. π-π interaction of unsaturated structures (benzene ring, double/triple bond) enhanced mDOM competitiveness, compared to the mDOMs with similar hydrophobicity or adsorbability, implying its importance in adsorption competition. In contrast, higher hydrophilicity of carboxylic aromatics, induced by mDOM dissociation at neutral pH, strongly limited the adsorbability and competitiveness. Overall, mDOM adsorbability was found to be an overall indicator for mDOM competitiveness, rather than hydrophobicity (logD) and aromaticity (SUVA), which could indicate overall mDOM competitiveness.

**What is the impact of OMP concentration and adsorbability on competitive adsorption with DOM in natural water?**

Based on the previous findings, natural water DOM was fractionated by adsorbability using PAC treatment, and the competitiveness of the remaining DOM was tested. It was revealed that adsorbable but non-competitive DOM also existed in the natural water matrix, and that some weakly adsorbable DOM (including part of the LMW fraction) did not compete for the

adsorption sites against OMPs. The amount of DOM competitors was dependent on the target OMP, decreasing with increasing OMP adsorbability. The moderately adsorbable DOM fraction had variable roles, serving as competitors against weakly adsorbable OMPs, but was non-competitive against strongly adsorbable OMPs. The adsorption of carbamazepine was even higher in the presence of some weakly adsorbable DOM than in DOM-free water, and complexation might be the reason for the enhanced adsorption instead of competition. The different initial OMP concentrations (from ~6 µg/L to ~500 µg/L) varied concentration asymmetries between DOM and OMPs. The stronger competition was found in batches with a higher OMP concentration, as more weakly adsorbable DOM participated in the competitive adsorption of activated carbon against OMPs at high concentrations, where more adsorption sites (with lower energy) were occupied by OMPs. These low-energy adsorption sites are usually not preferred by OMPs at lower concentrations but still relatively favorable for some DOM molecules.

## What is the interplay between molecular weight, aromaticity, and polarity of natural water DOM in competitive adsorption against OMPs?

The competitive DOM against natural OMPs was further identified at a molecular level by FTICR-MS, comparing DOM characteristics after two types of pretreatments (PAC and AER). The AER-sorbable DOM (mostly negatively charged), the fraction less relevant for DOM competition, contained mostly molecular formulas with high polarity, highlighting the relevance of high hydrophobicity (low polarity) in DOM competition. The impact of aromaticity on DOM adsorbability and competitiveness was more prominent for molecular formulas in the LMW DOM range, while this dominance was outweighed by polarity with respect to DOM compounds with higher MW. The reason might be that central aromatic structures in HMW compounds hardly interact with PAC surface due to steric hindrance. Integrated with the knowledge from the mDOM study presented **in Chapter 2**, it could be concluded that, aromaticity and hydrophobicity are indispensable properties for competitive DOM, high competitiveness cannot be achieved with a deficiency in one of them. In addition, a high hydrophobicity could be indicated by the low polarity of molecular formulas or a few dissociated species in ambient pH.

**How do decreased DOM aromaticity and accumulated LMW DOM influence the competition of various ozonated waters, with a large difference in DOM molecular size distribution (Chapter 5)?**

In **Chapter 5** the examination of the influence of ozonation on DOM competitiveness in three natural waters and one standard humics solution was reported. The concentration of LWM DOM in ozonated waters was relevant to the cleavage of HMW DOM and mineralization of LMW DOM, but the DOM hydrophobicity and aromaticity were simultaneously reduced by pre-ozonation. Consequently, the adsorbability of LMW DOM in natural waters was substantially diminished, although LMW organics accumulated in the ozonated waters. In addition, the ozone-induced cleavage of aromatic macromolecules in the standard humics' solution did not result in a largely intensified competition against OMP, implying that reduced aromaticity was more important than LMW DOM accumulation for DOM competition in ozonated surface waters. To project the DOM competitiveness of ozonated waters, the LMWOC (concentrations of LMW organics, measured by LC-OCD) was not valid as an indicator, due to the undifferentiated weakly/no adsorbable LMW DOM (probably non-competitors) produced during ozonation. As DOM aromaticity and hydrophobicity were reduced simultaneously during the ozonation, the LMWUV (UV absorbance of LMW organics, measured by LC-OCD) exhibited a more feasible correlation in fourteen untreated/ozonated surface waters.

**Overall conclusion**

In this thesis, it was demonstrated that DOM competition does not originate equally from all adsorbable DOM fractions. Some weakly adsorbable (LMW) DOM occupied PAC adsorption sites without reducing OMP removal. The amount of DOM competitors and the level of competitiveness are dependent on the OMP characteristics and the initial OMP concentrations. The characteristics of competitive DOM are presented in Figure 1. With similar micropore accessibility (i.e., LMW), high hydrophobicity is a precondition for high DOM competitiveness, which is indicated by a high log D (only available for model DOM compounds) or low dissociation at ambient water pH (i.e., low negative charge, for natural water DOM). Moreover, through π-π interactions, aromaticity could elevate DOM

adsorbability (for compounds with similar hydrophobicity) and enhance DOM competitiveness (for compounds with similar adsorbability). However, simply inspecting DOM aromaticity (e.g., by SUVA) without considering DOM MW and hydrophobicity, is also not sufficient to determine the competitiveness. For raw waters and ozonated waters (simultaneously decreasing DOM hydrophobicity and aromaticity and MW), assessing the LMWUV for the bulk LMW organics proved useful to project the competitiveness of surface water DOM.
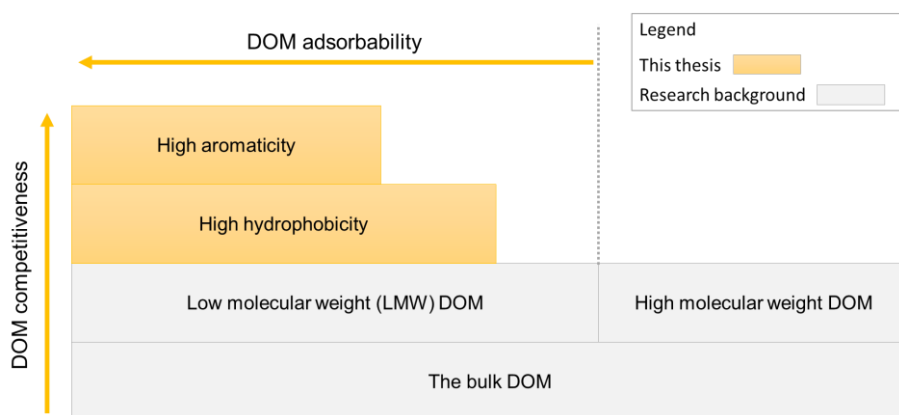


**Figure 1** The relationship of key characteristics of competitive DOM and the corresponding chapters.

## 2. Outlook and recommendations for future research

### 2.1 Improve OMP adsorption in natural water

The results of this study imply that the translation from (LMW) DOM adsorbability to competitiveness is related to the characteristics and adsorbability of each respective OMP. Hydrophilic OMPs with lower PAC adsorbability would usually have to compete for the adsorption sites with nearly all adsorbable LMW DOM, whereas only with a small percentage of adsorbable LMW DOM for hydrophobic OMP. Therefore, it is necessary to reduce DOM competition or boost OMP removal with combined treatment.

To alleviate the DOM competition, especially for direct site competition, ozonation was found to be an effective pretreatment and to degrade a broad range of OMPs at the same

time. However, in practical ozone dosages (e.g., 0.5-0.7 mg $O_3$/mg DOC), the decrease in DOM competitiveness is not large. The reason is that the HMW DOM, usually in higher concentration than LMW DOM, consume a large percentage of oxidants during ozonation with little alleviation effect towards DOM competition. One ideal treatment is to selectively oxidize the LMW DOM and OMPs, with little impact from HMW DOM, in a heterogeneous catalytic system, where only LMW DOM can penetrate the pore system of catalysts and be oxidized. However, it is still hard to manufacture a material that works as a molecular sieve and is coated with oxidation catalysts in the pore structure. Coagulation before ozonation-activated carbon, a commonly-used treatment train, already effectively removes HMW DOM (Zoschke et al., 2011), increasing the specific ozone dose for the remaining LMW DOM. Higher OMP removal in ozonation and subsequent adsorption (due to low competition) could therefore be expected.

Another alternative is to couple activated carbon adsorption with dense membrane filtration (e.g., reverse osmosis). Dense membrane filtration is effective in rejecting hydrophilic OMPs of which the removal by activated carbon is strongly interfered by DOM competitors, while being less effective to reject some hydrophobic OMPs, opposite to the preference for activated carbon or other carbonaceous materials. Preliminary attempts have been explored to use the combination (membrane-activated carbon); either separate modules working in series/parallel (Konradt et al., 2021; Schoonenberg Kegel et al., 2010), or coating the membrane surface with carbon material (Li et al., 2021; Tagliavini and Schäfer, 2018), would be beneficial for the OMP abatement in water treatment. Further research should focus on increasing the robustness of membrane materials in OMP removal, and optimizing the design (e.g., sequence, applied materials, operational parameters) for the combined treatment.

## 2.2 OMP adsorption prediction in different waters

As discussed in Chapter 1, based on batch adsorption experiments, adsorptive $UV_{254}$ removal is helpful to infer PAC-induced OMP removals in practice. However, a direct prediction of DOM competitiveness from the DOM characteristics of different waters, without any adsorption experiments, is still not fully realized. DOM, coexisting with target OMPs, is highly heterogeneous in composition and various pretreatments also strongly change the DOM composition. Therefore, the primary need in competitive adsorption studies is to

understand how heterogeneous DOM compositions alter the DOM competition against different OMPs, with a quantitative description of the corresponding impact. From this thesis, it is concluded that HMW DOM and LMW hydrophilic DOM with weak PAC affinity, although PAC adsorbable, are mostly irrelevant to site competition against OMPs (Zietzschmann et al., 2014b). Bulk DOM parameters (DOC, UV$_{254}$) and LMWOC are therefore less suitable for a direct DOM competitiveness prediction. LMWUV is the best surrogate so far and could be applied in the prediction in non-ozonated and ozonated surface waters, by converting LMWUV into the concentrations of fictive DOM competitors initialized by IAST-EBCM and subsequently DOM isotherms in different waters. However, LMWUV were found not to be feasible to predict the DOM competitiveness in PAC-pretreated water and AER-treated water, because the poorly competitive hydrophilic aromatics (also UV-active) were selectively removed (by AER pretreatment) or remained (by PAC pretreatment). Further research should focus on more advanced DOM surrogates (e.g., fluorescence-based) that could assess the richness of LMW hydrophobic aromatics in different waters.

## 2.3 Future study on DOM competition in GAC filters

Regarding the OMP removal prediction in GAC filters, the monitoring of LMWUV breakthrough is the most up-to-date solution to relate to OMP breakthrough in different waters (Zietzschmann et al., 2016c). Direct prediction of OMP breakthrough curves is more difficult, due to the insufficient knowledge of the non-simultaneous adsorption of LMW DOM competitors and OMPs in GAC filters, of which the competition mechanism is different from the competition during PAC treatment (and batch tests), and should thus be further studied. The DOM preloading on GAC is non-simultaneous for different DOM fractions, which is different from the PAC adsorption process. Weakly adsorbable DOM fractions occupy the high-energy sites first, whereafter the strongly adsorbable DOM fractions are adsorbed, followed by the OMPs. In the present study, it was found that weakly adsorbable DOM was not competitive with OMPs in PAC adsorption, but it is not clear how these non-competitive DOM substances modify virgin GAC surfaces and influence the adsorption of subsequent strongly adsorbable DOM and OMPs, as well as the GAC service time. The availability of adsorption sites on minerals (kaolinite and gibbsite) has been recently found to decrease during sequential DOM sorption (five repeated loading), and the surface charge was modified simultaneously in the initial DOM loading process (Chen et al., 2022). Further knowledge on GAC filters could be obtained by simulating the continuous DOM adsorption

into sequential DOM adsorption with increasing DOM adsorbability across multiple adsorption stages (i.e., weakest adsorbable DOM first, strongest adsorbable DOM last).

# Summary

To eliminate organic micropollutants (OMPs) from (surface) water, activated carbon adsorption is a cost-effective technology to remove a broad range of OMPs without producing any byproducts. However, co-existing dissolved organic matter (DOM), at much higher concentrations (mg C/L) than OMPs (ng/L-μg/L), inducing adsorption competition, can interfere with OMP removal. Direct site competition and pore blocking are two DOM competition mechanisms, and low molecular weight (LMW) DOM has been recognized as the major competitor in the site competition against OMPs. However, the insights into DOM molecular properties are limited with regard to DOM competition. Therefore, the objective of this research was to relate (LMW) DOM properties to the competitiveness against OMPs, clarify the mechanism of direct site competition, and explore a useful DOM surrogate to predict DOM competitiveness.

Model DOM compounds (mDOMs) could be described individually and more accurately with molecular properties than a complex, real DOM matrix in water. To elucidate the impact of LMW DOM characteristics (hydrophobicity/polarity and aromaticity) on DOM competitiveness, fifteen model compounds (mDOM), differed in functional groups (hydroxyl, phenol, carboxyl groups, etc.), were used to represent several elemental structures of LMW DOM. By temporarily occupying adsorption sites prior to OMPs, LMW mDOM was found to be more competitive to inhibit OMP adsorption kinetics than OMP adsorption equilibrium. Although OMPs were more preferentially adsorbed onto activated carbon than mDOM, the large concentration asymmetry (~500 μg DOC/μg OMP) made a few mDOM compounds exert strong competition against OMPs. The mDOM competitiveness increased when compounds were more hydrophobic and more aromatic, whereas π-π interactions were more important to determine mDOM competitiveness than hydrophobic interaction for LMW mDOM compounds. As an integrated indicator, mDOM adsorbability, defined by mDOM adsorption capacity, was considered better to associate with mDOM competitiveness than hydrophobicity and aromaticity individually. The competition was found to be strong between strongly adsorbable mDOM and weakly adsorbable OMPs, where weakly adsorbable mDOM could even co-adsorb with strongly adsorbable OMPs with little to no competition.

To relate DOM adsorbability to competitiveness in natural waters, a two-stage adsorption procedure was designed to differentiate the adsorption of DOM fractions and OMPs by removing variously adsorbable DOM fractions with activated carbon pretreatment and

analyzing the competitiveness of the remaining DOM fractions. Our results demonstrated that adsorbable (LMW) DOM was not necessarily competitive against OMPs. In addition, an increasing amount of DOM competitors was observed against the weaker adsorbable OMPs, compared to their stronger adsorbable counterparts. Similarly, more DOM competitors were identified at high initial OMP concentrations, due to the increased loading of OMPs on activated carbon, highlighting the variable roles (varying competitiveness/ complementary adsorption) of differently adsorbable DOM fractions in competition.

To elucidate the role of molecular weight (MW), polarity and aromaticity in DOM competition from a natural DOM with a complex molecular composition, activated carbon and anion exchange resin (AER) pretreatment served for differentiating competitive DOM from natural DOM. Ultrahigh-resolution Fourier transform mass spectrometry was employed for the DOM analysis at the molecular level. A large percentage of molecular formulas in untreated DOM was PAC-absorbable (97.8% for 40 mg PAC/L), while ~75% of PAC-absorbable formulas were considered poorly competitive, since these molecular formulas were not detected in DOM remaining after AER pretreatment that was highly competitive. The semi-quantitative analysis revealed that aromaticity was the dominant factor for LMW DOM adsorbability and competitiveness. In contrast, with higher MW, the competitiveness of an increasing number of aromatic DOM compounds was diminished due to strong dissociation induced by relatively high polarity.

Finally, the interference of ozone-modified NOM with the adsorption of 2-methylisoborneol (MIB, an odorous OMP) was studied in three natural waters and one standard humics solution in order to study how ozonation influences the competitiveness of DOM with different MW distributions. In the three natural waters, it was found that reducing NOM competition against MIB was found to coincide with increasing ozone consumption. The cleavage of the macromolecules in a standard humics solution, with larger molecular weight and higher aromaticity than the humics in natural waters, only induced a slightly stronger competition under low/moderate ozone consumptions. Overall, the declined aromaticity outweighed the produced LMW DOM in the competitiveness of DOM against MIB in ozonated natural waters. The UV absorbance of the LMW DOM was better correlated with the competitiveness of ozonated/non-ozonated waters than the LMW DOM concentration itself, underlining the role of LMW hydrophobic aromatics in competitive adsorption prediction.

From this thesis, it could thus be concluded that the DOM competition against OMPs is not ubiquitous for all (adsorbable, LMW) DOM fractions. The amount of DOM competitors, as well as their competitiveness, strongly varies with to OMP adsorbability and the initial OMP concentrations (i.e., the concentration asymmetry). For LMW DOM, aromaticity was a key characteristic to promote DOM competitiveness, while the high polarity reduced the DOM competitiveness by DOM dissociation (and thus high hydrophilicity/polarity). To project the competitiveness of ozonated DOM of which the hydrophobicity and aromaticity were simultaneously diminished, LMWUV can then be a handy DOM surrogate instead of LMW DOM concentration itself.

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Qi Wang

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# Curriculum Vitae

## Personal information:

Qi Wang (王齐) was born in Beijing, China, on August 1th, 1994. He had his four years' bachelor study at the Beijing University of Civil Engineering and Architecture, majoring in Environmental Sciences. In 2016, he started his master and doctoral program in the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, working on the topic of the organic micropollutant (OMP) control in drinking water treatment. From February, 2018 to April 2018, he was a visiting researcher at TU Delft under the supervision of Prof. Luuk Rietveld. Since then, he focused his research on how various DOM properties influence the OMP adsorption, working under the supervisory team from the Netherlands (Frederik Zietzschmann, Roberta Hofman-Caris and Luuk Rietveld). His PhD career, at TU Delft, formally began in February 2020, the initial stage of the COVID-19 crisis. When continuing his adsorption experiments in the Waterlab of the TU Delft, the collaboration network was further expanded to German research institutes (Helmholtz Centre for Environmental Research, and Hamburg University of Technology).

## Publication list:

1.**Wang, Q.**, Zietzschmann, F., Yu, J., Hofman, R., An, W., Yang, M. and Rietveld, L.C. 2020. Projecting competition between 2-methylisoborneol and natural organic matter in adsorption onto activated carbon from ozonated source waters. Water Research 173, 115574.

2. **Wang, Q.**, Raja-Louisa M., Hofman, R., Yu, J., An, W., Yang, M., Rietveld, L.C. and Zietzschmann, F. 2021. How properties of low molecular weight model competitors impact organic micropollutant adsorption onto activated carbon at realistically asymmetric concentrations. Water Research, 117443.

3. **Wang, Q.**, Zietzschmann, F., Hofman, R. Jiang N.., Schuster J., Wang Z., Yu, J., Yang, M., Rietveld, L.C. Unraveling competition versus adsorbability of dissolved organic matter against organic micropollutants onto activated carbon. Separation and Purification Technology, 120942.

4. **Wang, Q.**, Lechtenfeld O. J., Rietveld, L.C, Yu, J., Yang M., Schuster J., Ernst M., Hofmann R., Kaesler J., Zietzschmann F. The interplay between molecular weight, aromaticity, and polarity of DOM in competitive adsorption against OMPs. In preparation

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