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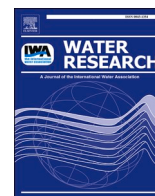
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# How properties of low molecular weight model competitors impact organic micropollutant adsorption onto activated carbon at realistically asymmetric concentrations

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## 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 to concisely examine 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  $\pi$ -interactions increased mDOM competitiveness, while  $\pi$ -interactions outweighed hydrophobic interactions. However,  $\pi$ -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 for 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; Guillosou 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., 2020), 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 contributing differently according to the pore size distribution of the applied activated carbons (Ebie et al., 2001;

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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., 2003b). Low molecular weight (LMW) DOM is the dominant site competitor against OMPs at equilibrium adsorption (Zietzschmann et al., 2014). 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 ( $\pi$ -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., 2003a; 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 elucidate the impacts of LMW mDOM characteristics on their competitiveness against OMP adsorption onto PAC, focusing on direct competition at realistically asymmetric concentrations ( $\text{DOC}/\text{OMP} \approx 500 \mu\text{g C}/\mu\text{g}$ ). 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 competitor adsorbates in PAC batch experiments (Table 1). The descriptors on the mDOM molecular structures/properties are given in Table 2; Log D and charge at pH 7 were derived from Chemicalize developed by ChemAxon (<https://chemicalize.com>). 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,

**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	<b>hydrophobicity</b> (by log D at pH7, from Chemicalize)
	hydroxyl groups	hexanol, hexanediol, hexanetriol	
phenols	double/triple bonds	pentanol, 4-penten-1-ol, 1-pentyn-5-ol	<b>aromaticity</b> aromatic ring activation/deactivation (by SUVA, experimentally determined)
	hydroxyl groups, on a cycloalkane	cyclohexanol, cyclohexanediol	
aromatic carboxylic acids	hydroxyl groups, on an aromatic ring	phenol, benzenediol, benzenetriol	
	carboxyl groups, on an aromatic ring	benzoic acid, phthalic acid, trimesic acid	

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  $>17 \text{ M}\Omega \cdot \text{cm}$ ,  $\text{DOC} < 0.2 \text{ mg/L}$ ) 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 ( $>1 \text{ g/L}$ ) for  $\geq 24 \text{ h}$ , to completely remove any adsorbable molecules; the PAC was subsequently removed by membrane filtration ( $0.2 \mu\text{m}$  cellulose nitrate membrane filter rinsed with ultra-pure water, Whatman, Germany). The target concentrations of the employed mDOMs were  $\sim 10 \text{ mg C/L}$  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.

### 2.2. PAC batch tests

PAC SAE Super (Norit, the Netherlands) was used in all experiments. The mesopore percentage of the selected PAC was  $\sim 50\%$  (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).

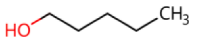
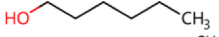
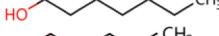
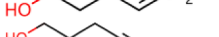
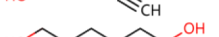
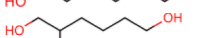

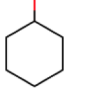
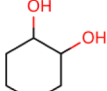
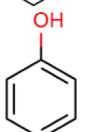
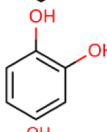
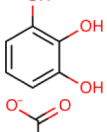
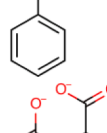
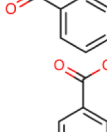
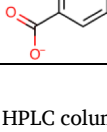
The applied PAC was dried in a drying cabinet at  $105 \text{ }^\circ\text{C}$  for  $\geq 24 \text{ h}$  and cooled in a desiccator before use. The six OMPs were spiked into the various mDOM solutions with  $20 \mu\text{g/L}$  of each OMP before PAC dosage. A 100 mL bottle-point method was used during PAC batch tests, with several PAC dosages (2.5–150 mg/L). The bottles were placed on a linear shaker to ensure completely turbulent mixing of PAC and sample solution. Samples for every PAC concentration were prepared in parallel, once for 30 min and once for 48 h adsorption time, to examine the adsorption competition at both non-equilibrium and equilibrium conditions. Samples were filtrated using a  $0.45 \mu\text{m}$  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),

**Table 2**

Molecular properties of competitive mDOM compounds. SUVA values were experimentally calculated while other parameters were from Chemicalize.

Name	Predominant species at pH 7 <sup>a</sup>	CAS #	MW (g/mol)	logD at pH7 <sup>a</sup>	Charge at pH7 <sup>a</sup>	SUVA <sup>b</sup> (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
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

equipped with a HSS T3 HPLC column (compound size 2.5  $\mu\text{m}$ , 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<sub>254</sub> 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<sub>254</sub> by DOC concentration (Weishaar et al., 2003).

#### 2.4. Evaluation of mDOM adsorption and competitiveness

To be able to compare 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., 2015). 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 Fig. 1 (original data in Fig. S1), in absence and presence of mDOM adsorbates, and with adsorption times of 0.5 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., 2016). 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., 2020), 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 48 h (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 benzotriazole 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.

#### 3.2. mDOM properties and competitiveness

To study the role of DOM functional groups in competitiveness with OMPs, Fig. 2 displays the impact of molecular characteristics on mDOM adsorption (indicated by DOC-PAC20%) and competitiveness (indicated by OMP-PAC80%) on OMP adsorption at 48 h. 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 length of alcohols (pentanol, hexanol and heptanol) on the related mDOM adsorption and competitiveness is shown in Fig. 2a. A clear positive relation between increasing alcohol chain length (C5 to C7) and increasing 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

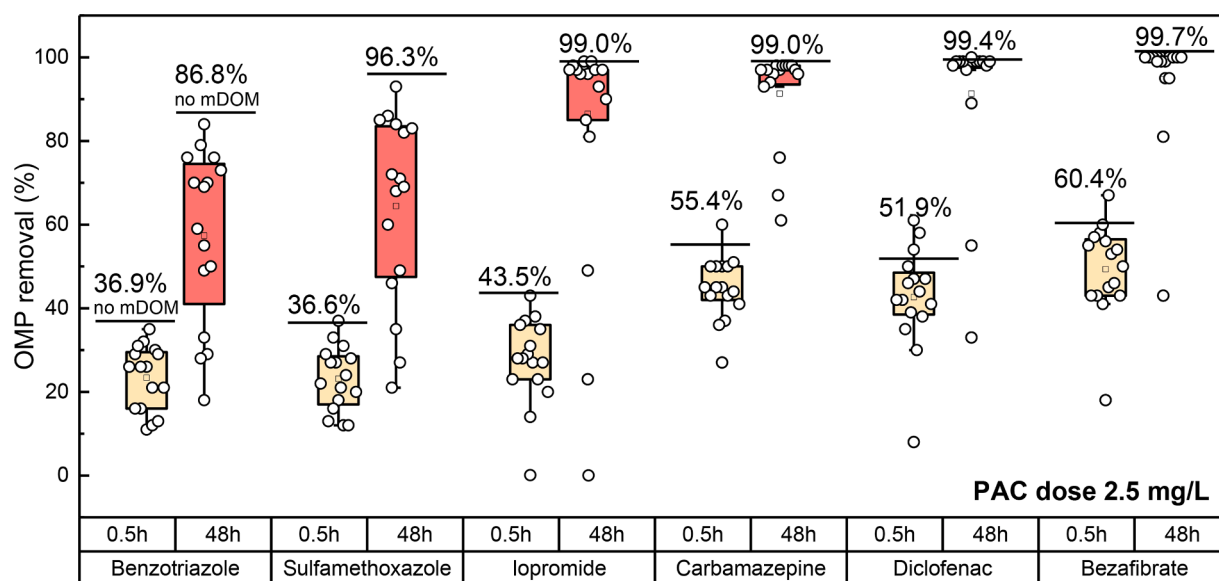
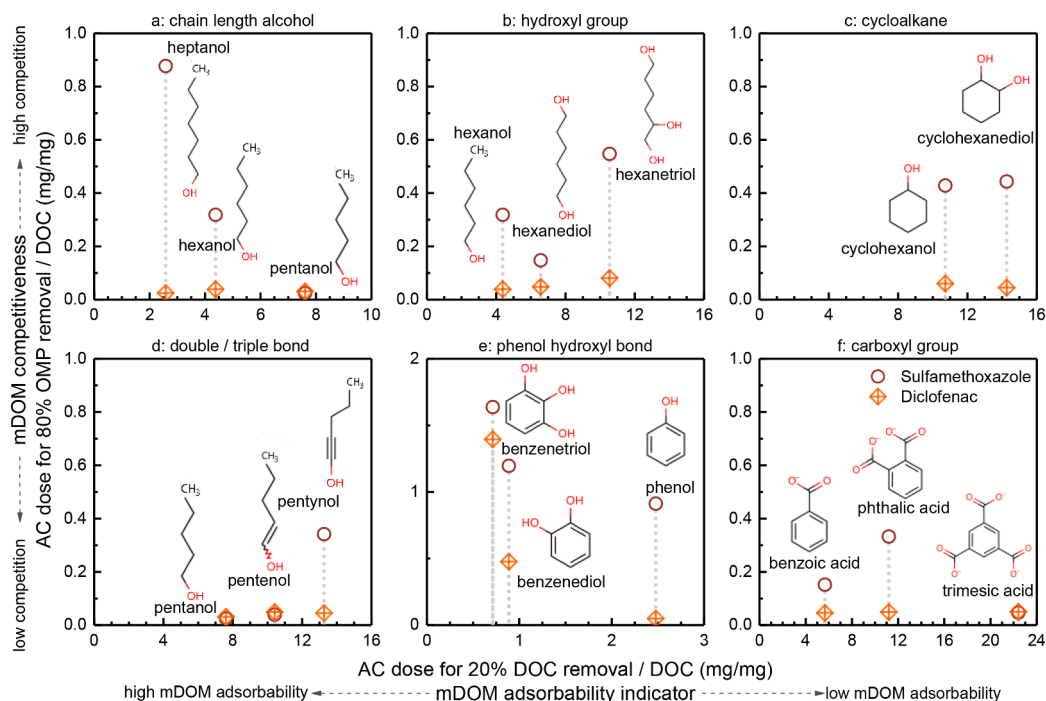


Fig. 1. OMP removals with 2.5 mg PAC/L in presence of all fifteen different mDOMs. The long solid reference lines above the boxes indicate the corresponding OMP removal without mDOM. Two adsorption times (0.5 and 48 h) were adopted. OMP removal data were presented as box plot (box, 25–75%; central point,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



**Fig. 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 Fig. S2. Note the different scales in subfigure e. Adsorption time was 48 h.

(OMP-PAC80%). As the most hydrophobic one ( $\log D = 2.14$ ) in the examined mDOM collection, heptanol induced remarkably strong competition against iopromide (Fig. 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 with 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  $\log D$  shows their increasing hydrophilicity with each additional hydroxyl group, while the alcohol adsorbability deteriorated (Fig. 2b,c). Compared with hexanol ( $\log D = 1.69$ ), cyclohexanol has a lower hydrophobicity ( $\log D = 1.28$ ), but it is higher than that of hexanediol ( $\log D = 0.63$ ). 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 cyclohexanediol 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.

### 3.2.2. $\pi$ -bonding effect in aliphatic mDOM

In aliphatic mDOM, double and triple bonds can facilitate interactions with the aromatic  $\pi$ -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 Fig. 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 in limited amount. Even though higher hydrophilicity makes pentenol and pentynol harder to remove from the water,  $\pi$ -interaction in adsorption processes may inhibit OMP adsorption (Belfort, 1979). All examined OMPs had aromatic structure, the observed stronger competition may thus be attributed to similar  $\pi$ -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  $\pi$ -interaction.

### 3.2.3. Hydrophobic and $\pi$ -bonding effect in aromatic mDOM

To examine the effect of  $\pi$ -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 (Figs. S3; cf. 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 similarly 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 (Fig. 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  $\pi$ -interactions on the PAC surface. Both effects reduced adsorbability of benzoic acids (Fig. 2f), which was lower than that of the phenols.

Corresponding competitiveness of aromatic mDOMs is also shown in Fig. 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  $\pi$ -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 Figs. 2e,f and S2e,f), indicate that  $\pi$ -interactions and hydrophobic effects were more important for mDOM competition against those OMPs than electrostatic interaction between mDOM/OMP/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., 2015).

### 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 Fig. 3. Aliphatic mDOM with a higher hydrophobicity had a higher adsorption affinity (R<sup>2</sup> = 0.49) (Fig. 3a), but no increasing trend for competitiveness was found (Figs. 3b,c and S4a–d). Aromatic mDOM compounds with log D > 0 at pH 7 had a 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, hydrophobic interactions (Tang et al., 2018). Accordingly, DOM fractionization on hydrophobicity/hydrophilicity appears inappropriate for competing DOM isolation and identification in practice

Aromaticity is defined to relate with the specific  $\pi$ -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  $\pi$ -electrons in carboxyl groups of phthalic/trimesic acid also contribute to SUVA increase in benzoic acid groups (despite their electron-withdrawing effect). Fig. 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

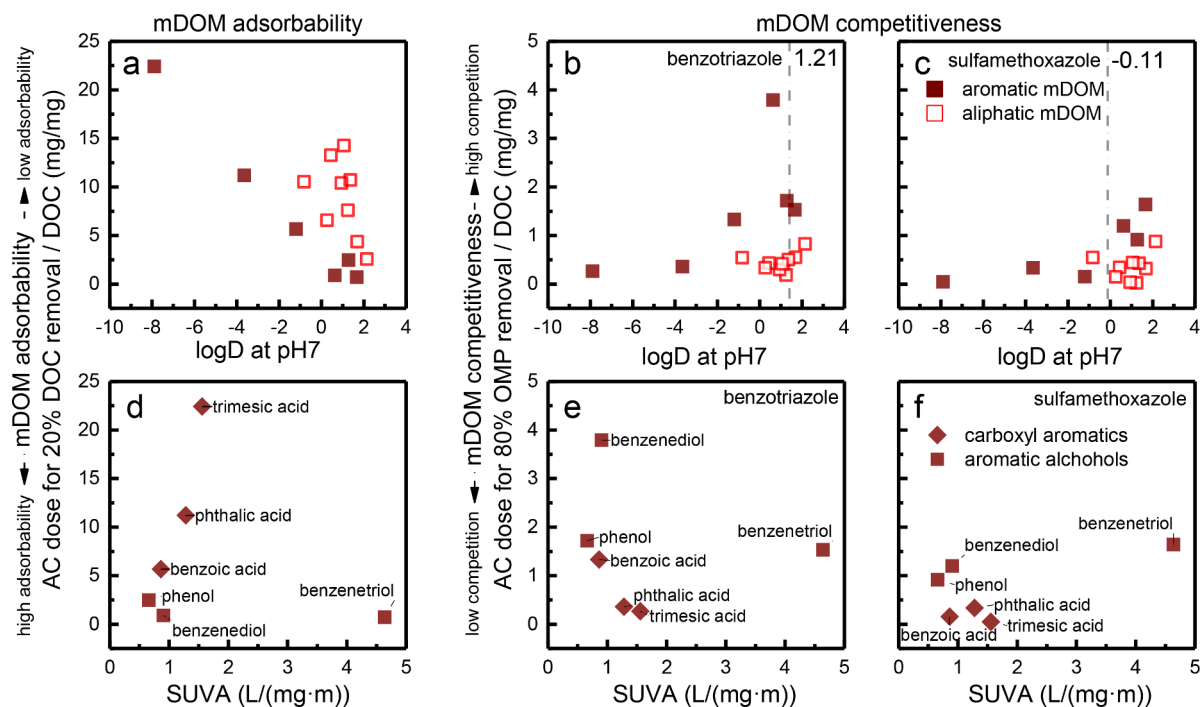


Fig. 3. mDOM adsorbability versus logD (a) and SUVA (d), and mDOM competitiveness versus logD and SUVA for benzotriazole (b,e) and sulfamethoxazole (c,f), respectively. Data for other four OMPs (iopromide, carbamazepine, diclofenac, bezafibrate) in Fig. S4. mDOM competitor names omitted in a–c due to 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 48 h.



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  $\pi$ -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 (48 h) in Fig. 4 (benzotriazole, sulfamethoxazole and diclofenac) and Fig. S5 (iopromide, carbamazepine and bezafibrate). Overall, mDOM adsorbability relates to mDOM competitiveness in most cases (cf. Fig. 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 ( $\mu\text{g/L}$ ), while mDOM concentrations ( $\sim 10 \text{ mg/L}$ ) were much higher. Even though mDOM is usually a weaker adsorbate than OMP (Fig. 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 (0.1–40 mg/L), they targeted for different adsorption 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.

Fig. 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 for their competitiveness. Different adsorption kinetics between mDOM and OMPs might be a reason for this circumstance. Fig. S8 compares mDOM adsorbability at 0.5 and 48 h. 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 0.5 h was observed as nearly

identical DOC-PAC20% values for weakly adsorbing mDOMs between 0.5 and 48 h. 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 prolong 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 0.5 than 48 h (Fig. 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.

To summarize the adsorbability impacts on competitive adsorption in this study, mDOM competitive adsorption against OMPs under large concentration asymmetry (concentration ratio was  $\sim 500 \mu\text{g DOC}/\mu\text{g OMP}$ ) is illustrated in Fig. 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 Fig. 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. The large area of little adsorption competition in Fig. 5 applies for the least adsorbable mDOMs competing against strongly adsorbable OMPs. When the concentration asymmetry is larger than the ratio ( $c(\text{mDOM})/c(\text{OMP}) \approx 500 \mu\text{g C}/\mu\text{g}$ ) in this case (e.g. OMPs in ng/L), stronger competition from mDOM might be expected (Newcombe et al., 2002). Hence concentration asymmetry between DOM and OMPs is suggested to be well quantified and discussed in the upcoming DOM competition studies.

DOM adsorbability, acting as a projection parameter here, may assist the further identification of LMW DOM competitors in real DOM-containing waters. Integrating hydrophobicity and aromaticity, DOM adsorbability could be a comprehensive parameter for evaluating aquatic DOM competition against OMPs in water treatment. By fractionizing DOM with different adsorbability before competition tests, competing LMW DOM fractions, responsible for competition against different OMPs, might be isolated, characterized and eventually targeted.

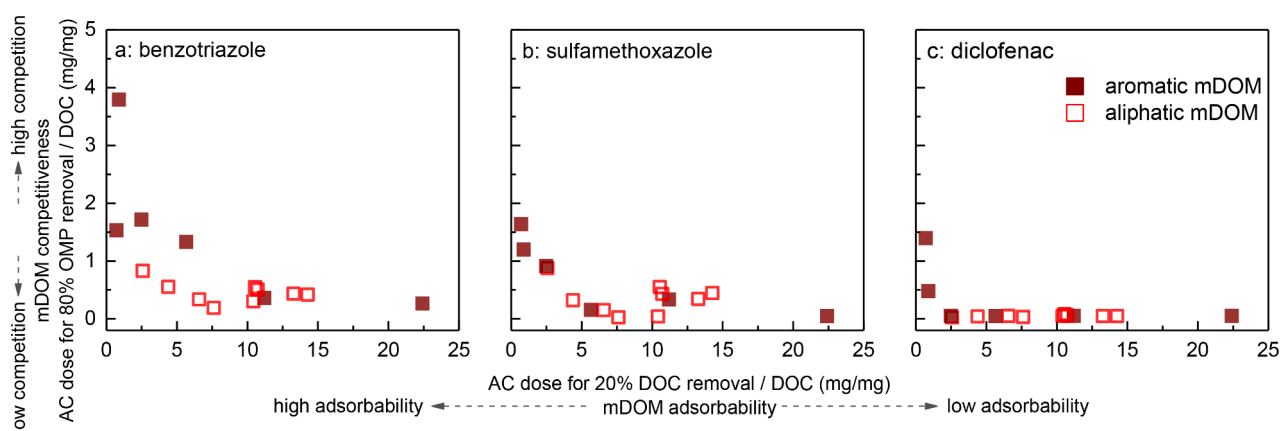


Fig. 4. mDOM adsorbability versus mDOM competitiveness for benzotriazole (a), sulfamethoxazole (b) and diclofenac (c), respectively. Data for other three OMPs (iopromide, carbamazepine and bezafibrate) in Fig. S5. The adsorption time was 48 h.

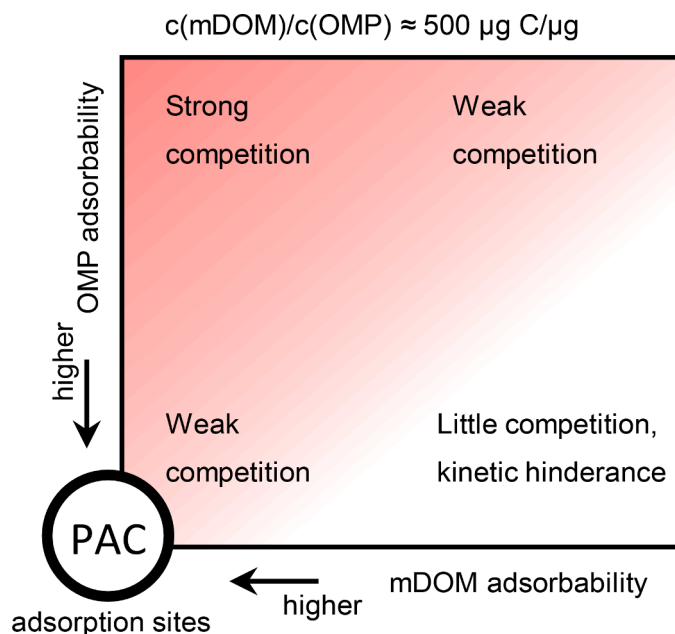


Fig. 5. Scheme diagram showing mDOM competitive adsorption against OMPs under concentration asymmetry (concentration ratio of mDOM and OMP  $\approx 500 \mu\text{g C}/\mu\text{g}$ ). mDOM adsorbability depicted against OMP adsorbability. Color regions meant mDOM competition against OMP with different 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  $\pi$ -interaction in adsorption competition.
- Rather than hydrophobicity ( $\log D$ ) 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 ( $\text{DOC-PAC}_{20\%} < 2.5 \text{ mg PAC}/\text{mg C}$ ) was a prerequisite for considerable competition against OMPs.
- At non-equilibrium adsorption (0.5 h), insufficient adsorption of strongly adsorbing mDOMs and sites pre-occupation by weak adsorbing mDOMs made DOM characteristics less important for competitiveness against OMPs than equilibrium state (48 h).
- A scheme was proposed to explain adsorption competition under large concentration asymmetry ( $c_{\text{mDOM}}/c_{\text{OMP}} \approx 500 \mu\text{g C}/\mu\text{g}$ ). 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.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2021.117443](https://doi.org/10.1016/j.watres.2021.117443).

#### References

- Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T., Ohno, K., 2010. Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated Carbon. *Water Res.* 44 (14), 4127–4136.
- Aschermann, G., Schroder, C., Zietzschmann, F., Jekel, M., 2019. Organic micropollutant desorption in various water matrices - activated carbon pore characteristics determine the reversibility of adsorption. *Chemosphere* 237, 124415.
- Belfort, G., 1979. Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions. solvophobic interaction approach and correlations of molar adsorptivity with physicochemical parameters. *Environ. Sci. Technol.* 13 (8), 939–946.
- Dean, J.R., 1998. *Extraction Methods For Environmental Analysis*. John Wiley Chichester.
- Deng, S., Bei, Y., Lu, X., Du, Z., Wang, B., Wang, Y., Huang, J., Yu, G., 2015. Effect of co-existing organic compounds on adsorption of perfluorinated compounds onto carbon nanotubes. *Front. Environ. Sci. Eng.* 9 (5), 784–792.
- Ding, L., Snoeyink, V.L., Marinas, B.J., Yue, Z.R., Economy, J., 2008. Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter. *Environ. Sci. Technol.* 42 (4), 1227–1231.
- Dittmann, D., Braun, U., Jekel, M., Ruhl, A.S., 2018. Quantification and characterisation of activated carbon in activated sludge by thermogravimetric and evolved gas analyses. *J. Environ. Chem. Eng.* 6 (2), 2222–2231.
- Ebie, K., Li, F., Azuma, Y., Yuasa, A., Hagishita, T., 2001. Pore distribution effect of activated carbon in adsorbing organic micropollutants from natural water. *Water Res.* 35 (1), 167–179.

- Edzwald, J.K., Becker, W.C., Wattier, K.L., 1985. Surrogate parameters for monitoring organic matter and THM precursors. *J. Am. Water Works Assoc.* 77 (4), 122–132.
- Endo, S., Grathwohl, P., Haderlein, S.B., Schmidt, T.C., 2009. Characterization of sorbent properties of soil organic matter and carbonaceous geosorbents using n-alkanes and cycloalkanes as molecular probes. *Environ. Sci. Technol.* 43 (2), 393–400.
- Ersan, G., Apul, O.G., Perreault, F., Karanfil, T., 2017. Adsorption of organic contaminants by graphene nanosheets: a review. *Water Res.* 126, 385–398.
- Fundneider, T., Alonso, V.A., Wick, A., Albrecht, D., Lackner, S., 2021. Implications of biological activated carbon filters for micropollutant removal in wastewater treatment. *Water Res.* 189.
- Guillosoy, R., Le Roux, J., Mailler, R., Pereira-Derome, C.S., Varrault, G., Bressy, A., Vulliet, E., Morlay, C., Nauleau, F., Rocher, V., Gasperi, J., 2020. Influence of dissolved organic matter on the removal of 12 organic micropollutants from wastewater effluent by powdered activated carbon adsorption. *Water Res.* 172.
- Hu, H.Y., Du, Y., Wu, Q.Y., Zhao, X., Tang, X., Chen, Z., 2016. Differences in dissolved organic matter between reclaimed water source and drinking water source. *Sci. Total Environ.* 133–142, 551–552.
- Jeirani, Z., Niu, C.H., Soltan, J., 2017. Adsorption of emerging pollutants on activated carbon. *Rev. Chem. Eng.* 33 (5), 491–522.
- Kah, M., Sigmund, G., Xiao, F., Hofmann, T., 2017. Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. *Water Res.* 124, 673–692.
- Kilduff, J.E., Karanfil, T., Weber, W.J., 1998. Competitive effects of nondisplaceable organic compounds on trichloroethylene uptake by activated carbon. I. thermodynamic predictions and model sensitivity analyses. *J. Colloid Interface Sci.* 205 (2), 271–279.
- Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003a. Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. *Water Res.* 37 (4), 773–784.
- Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003b. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Res.* 37 (20), 4863–4872.
- Lin, D., Xing, B., 2008. Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. *Environ. Sci. Technol.* 42 (19), 7254–7259.
- Ling, Y.H., Klemes, M.J., Steinschneider, S., Dichtel, W.R., Helbling, D.E., 2019. QSARs to predict adsorption affinity of organic micropollutants for activated carbon and beta-cyclodextrin polymer adsorbents. *Water Res.* 154, 217–226.
- Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A., Sillanpää, M., 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere* 83 (11), 1431–1442.
- Matsui, Y., Nakao, S., Taniguchi, T., Matsushita, T., 2013. Geosmin and 2-methylisoborneol removal using superfine powdered activated carbon: shell adsorption and branched-pore kinetic model analysis and optimal particle size. *Water Res.* 47 (8), 2873–2880.
- Matsui, Y., Yoshida, T., Nakao, S., Knappe, D.R., Matsushita, T., 2012. Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons. *Water Res.* 46 (15), 4741–4749.
- McMurry, J.E., 2011. *Organic Chemistry*. Cengage Learning.
- Nakayama, A., Sakamoto, A., Matsushita, T., Matsui, Y., Shirasaki, N., 2020. Effects of pre, post, and simultaneous loading of natural organic matter on 2-methylisoborneol adsorption on superfine powdered activated carbon: reversibility and external pore-blocking. *Water Res.*, 115992.
- Newcombe, G., Morrison, J., Hepplewhite, C., 2002. Simultaneous adsorption of MIB and NOM onto activated carbon. I. characterisation of the system and NOM adsorption. *Carbon* 40 (12), 2135–2146. N.Y.
- Pan, B., Lin, D., Mashayekhi, H., Xing, B., 2008. Adsorption and hysteresis of bisphenol A and 17 $\alpha$ -ethinyl estradiol on carbon nanomaterials. *Environ. Sci. Technol.* 42 (15), 5480–5485.
- Park, M., Wu, S.M., Lopez, I.J., Chang, J.Y., Karanfil, T., Snyder, S.A., 2020. Adsorption of perfluoroalkyl substances (PFAS) in groundwater by granular activated carbons: roles of hydrophobicity of PFAS and carbon characteristics. *Water Res.* 170.
- Piai, L., Dykstra, J.E., Adishakti, M.G., Blokland, M., Langenhoff, A.A.M., van der Wal, A., 2019. Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes. *Water Res.* 162, 518–527.
- Reemtsma, T., Berger, U., Arp, H.P., Gallard, H., Knepper, T.P., Neumann, M., Quintana, J.B., Voigt, P., 2016. Mind the gap: persistent and mobile organic compounds-water contaminants that slip through. *Environ. Sci. Technol.* 50 (19), 10308–10315.
- Swiss Confederation, 2016. Ordinance of the UVEK on the review of purification effects by measures for the elimination of organic micro-pollutants in wastewater treatment plants. Swiss Confederation.
- Tang, H., Zhao, Y., Shan, S., Yang, X., Liu, D., Cui, F., Xing, B., 2018. Theoretical insight into the adsorption of aromatic compounds on graphene oxide. *Environ. Sci. Nano* 5 (10), 2357–2367.
- To, P.C., Mariñas, B.J., Snoeyink, V.L., Ng, W.J., 2008. Effect of strongly competing background compounds on the kinetics of trace organic contaminant desorption from activated carbon. *Environ. Sci. Technol.* 42 (7), 2606–2611.
- Wang, Q., Zietzschmann, F., Yu, J., Hofman, R., An, W., Yang, M., Rietveld, L.C., 2020. Projecting competition between 2-methylisoborneol and natural organic matter in adsorption onto activated carbon from ozonated source waters. *Water Res.* 173, 115574.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37 (20), 4702–4708.
- Zhang, D., Pan, B., Wu, M., Zhang, H., Peng, H., Ning, P., Xing, B., 2012. Cosorption of organic chemicals with different properties: their shared and different sorption sites. *Environ. Pollut.* 160, 178–184.
- Zhang, X.X., Han, J.R., Zhang, X.R., Shen, J.M., Chen, Z.L., Chu, W., Kang, J., Zhao, S.X., Zhou, Y.Y., 2020. Application of fourier transform ion cyclotron resonance mass spectrometry to characterize natural organic matter. *Chemosphere* 260, 178–184.
- Zietzschmann, F., Aschermann, G., Jekel, M., 2016. Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents. *Water Res.* 102, 190–201.
- Zietzschmann, F., Mitchell, R.L., Jekel, M., 2015. Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption. *Water Res.* 84, 153–160.
- Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F., Jekel, M., 2014. Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater. *Water Res.* 65, 297–306.