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Important note
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Unraveling competition versus adsorbability of dissolved organic matter against organic micropollutants onto activated carbon

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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 is the impact of the OMP adsorbability and initial OMP concentration 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 [1,2]. Adsorption onto activated carbon is widely used for OMP abatement in water purification [3–5]. 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) [6–8]. DOM competition dramatically decreases OMP adsorption capacity through direct site competition or pore blocking [9]. As DOM is a multi-component mixture with unknown composition [10,11], the determination of DOM competitors from the bulk is important for the exploration of DOM competition mechanism, 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 [12–15], 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

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competitive against OMPs, either strongly or weakly [16,17]. However, in a previous study, we found that some model LMW organics were medium/poorly adsorbable but exerted no competition against OMPs [18]. 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 [19]. 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 [20], but the complicated interplay between OMPs and DOM fractions makes it difficult to describe the competitiveness of DOM fractions with varying adsorbability [20,21]. 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 [20,22]. 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 from coexisting, 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 at 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 from 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 ℃) 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%) [23], implicating a higher relevance of direct site competition rather than pore blockage [24]. The PAC was dried (at 105 ℃), 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 min. 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 in the experiments, due to their frequent occurrence in aquatic environments and their large difference in PAC absorbability, reported in earlier studies [12,20].

Adsorption isotherm test. OMP isotherm tests served for examining the overall competitiveness of DOM samples. Fig. 1 (top) displays the experimental procedures and aims of the conventional isotherm test. Table S1 provides details on examined waters, PAC doses, 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 Fig. 1). PAC doses (1–300 mg/L) were applied and adsorption was conducted on a shaker (120 rpm at 20℃) for 7 days (Iso2) [25]. 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).

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 (Fig. 1 bottom). In the 1st stage adsorption, varying adsorbable DOM fractions were removed by diverse PAC doses (marked as Asy1 in Fig. 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 [19]. 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 2nd stage adsorption dose here (Asy4), since (i) low PAC doses typically relate to the more pronounced competition against OMP adsorption [20], (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 Fig. S1), and (iii) the error for analyzing OMP removal was too high for lower PAC doses (<5 mg/L, cf. Fig. 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 of 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
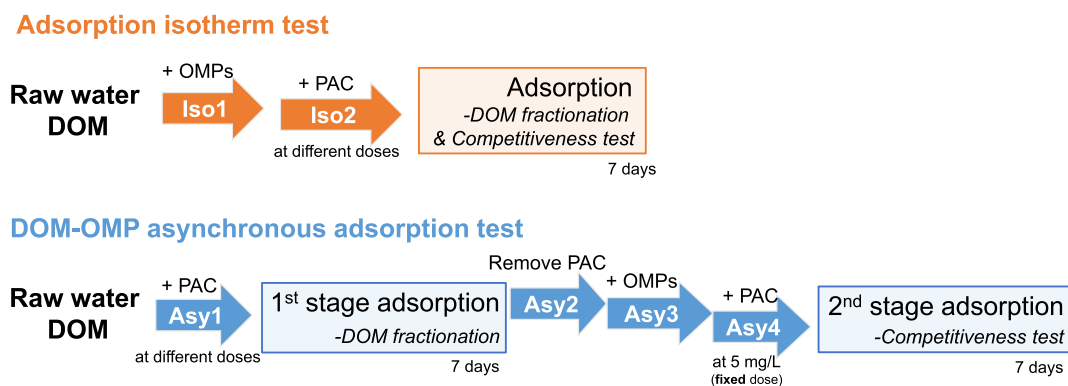
Adsorption isotherm test

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

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 (multiple 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 h 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 (1.7 μm 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 [19]. 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) [19].

$$q_e = \frac{1}{D_{PAC}}c_0 - \frac{1}{D_{PAC}}c_e \tag{1}$$

DOM adsorption analysis. To explain the removal of differently adsorbable DOM fractions during various PAC doses in isotherm tests and in 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 isotherm 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)·(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 [26,27].

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 ($K_{F,EBC}$, $1/n_{EBC}$) [28]. 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 $K_{F,EBC}$ (best fitted $K_{F,EBC}$ of OMP isotherm in untreated water, or K_F of OMP isotherm in DOM-free water) and $1/n_{EBC}$ (same as $1/n_F$ of OMP isotherm in DOM-free water) for each of the three OMPs, respectively [29]. 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 an 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 [28], 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. sample) 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 Fig. 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).

Fig. 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 (Fig. 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 [18,20,30]. However, from these results, it cannot be concluded if this stronger competition was (partially) attributed to the same amount of DOM competitors.

From Fig. 2 it can also be observed that $PAC_{200mg/L}$-treated DOM was competition-free, as the isotherms overlapped with, or partially exceeded, the ones 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 [18], 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) [18]. These preliminary results thus demonstrate that, also in natural water, an LMW adsorbable

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

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 [13,31,32]. Regarding the mechanism of competition-free adsorption, several adsorbates could complementarily occupy different sorption sites on the adsorbents [31,33]. 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 [19]. Moreover, some co-adsorbates could provide extra π-π interaction sites for OMPs [32,34], or even complex with OMPs [35], 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 [36–39]. This was also observed in our study, where 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
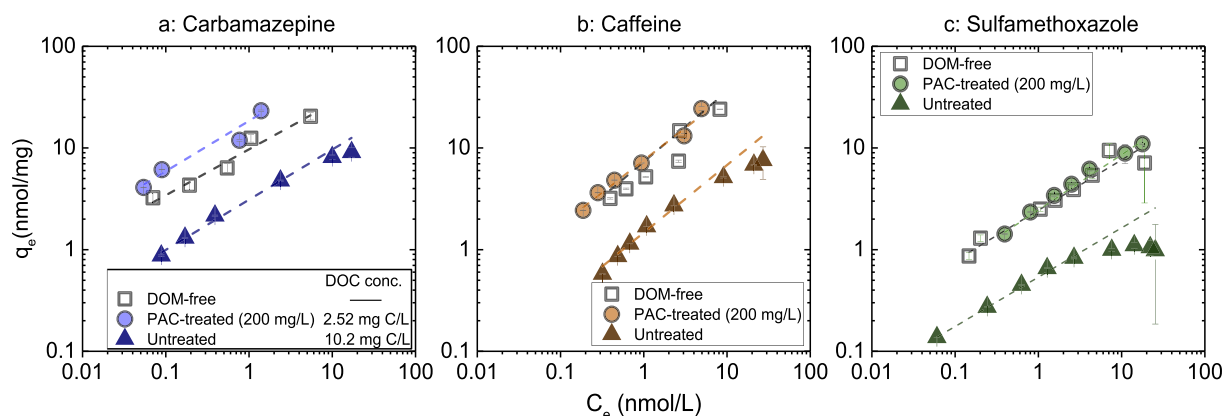

Fig. 2. Adsorption isotherms of three examined OMPs (carbamazepine, caffeine and sulfamethoxazole) in DOM-free water, untreated water of river Schie and $PAC_{200mg/L}$-treated water (Sept. sample). Freundlich model was applied to fit isotherms (Fitted results in Table 1). Error bars derived from experimental duplicates.

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 Fig. 3. In DOM-free water, the percentage removals of the three selected OMPs were all above 85% (most right data point in Fig. 3). However, in the untreated DOM-containing water, shown as $PAC_{0 mg/L}$ pretreatment points in Fig. 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.

DOM molecular weight analysis (see Fig. 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 [20,23].

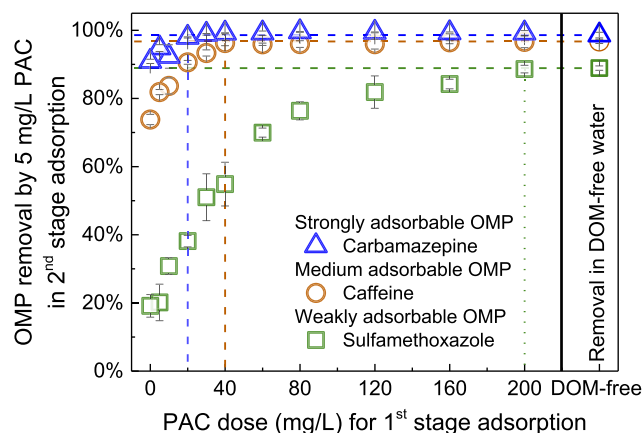The varying OMP adsorption in the 2nd stage adsorption is

illustrated in Fig. 4 using operating lines (scheme in Fig. 4a [40,41], and data applied in Fig. 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.

To relate DOM adsorbability to competitiveness against different OMPs, Fig. 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. Fig. 3). This resulted in a high percentage of non-competitive adsorbable DOM (~70%, cf. Fig. S3) and the percentage should be higher if the effect of MW was considered [27]. 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 (Fig. S3). 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) [21]. The stronger DOM competitiveness for weakly adsorbable OMPs was attributed not only to stronger inhibition by the same DOM sub-population [18], but also to a wider range of competitors.

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 Fig. 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. Fig. S4) [20,23]. From Fig. 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 (Fig. 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. Fig. 3). Note that
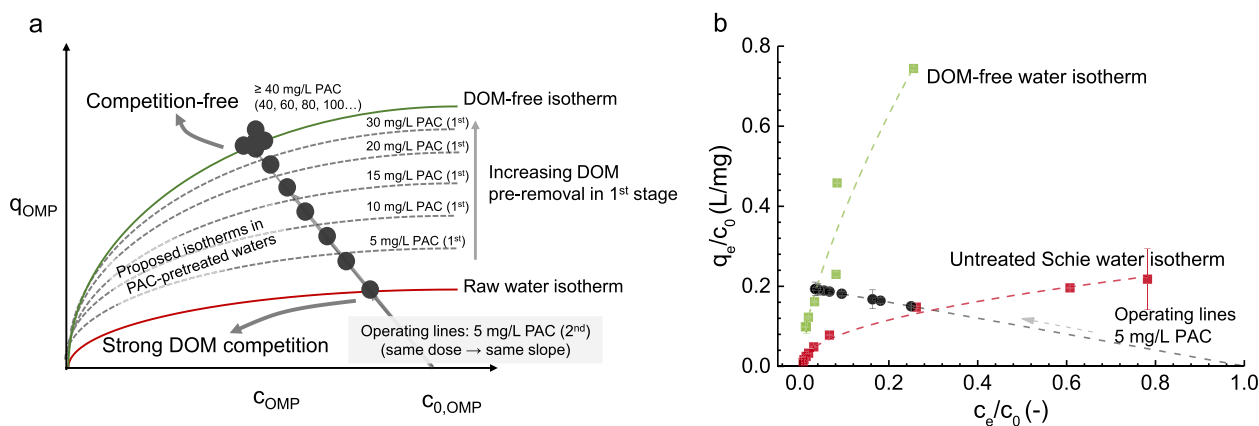

Fig. 3. Second stage OMP removals with 5 mg PAC/L after pre-DOM removal at variable first stage PAC doses for different OMPs, with horizontal dashed lines indicating OMP removals in DOM-free water, and vertical dashed lines indicating the first stage PAC doses required for full removal of competitive DOM, respectively. Error bars derived from experimental duplicates.

Fig. 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.
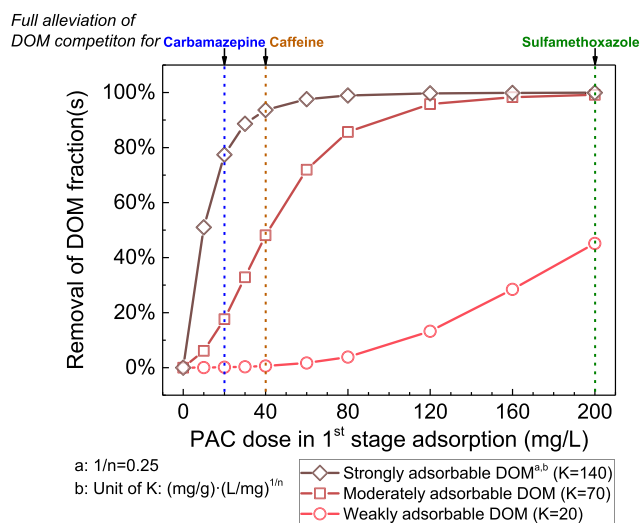

Fig. 5. The removals of the fictive DOM components at different first stage PAC doses, and the thresholds (required first stage PAC doses in pretreatment) for alleviating DOM competition against different OMPs (marked as vertical drop lines, also cf. Fig. 3). The removals of differently adsorbable DOM fractions were calculated using DOM adsorption analysis (K = 0, 20, 70, 140 (mg/g)·(L/mg)$^{1/n}$, 1/n = 0.25).

$c_{0,EBC}$ 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.

3.3. Impact of initial OMP concentration on DOM competitors

To illustrate the varying DOM competitors at different initial OMP concentrations, Fig. 7 relates the 2nd stage OMP percentage removals at different initial OMP concentrations to varying PAC pre-treatment doses in the 1st 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
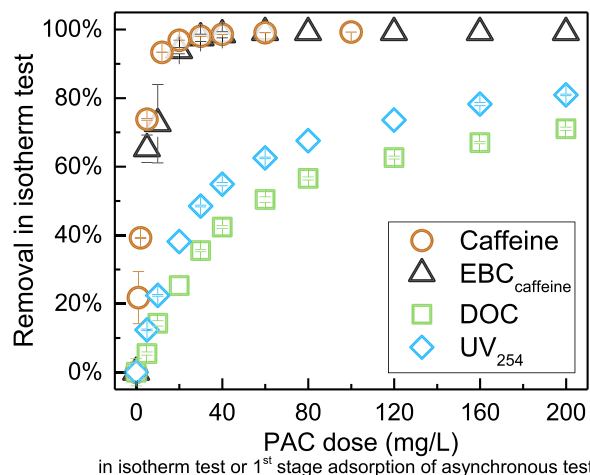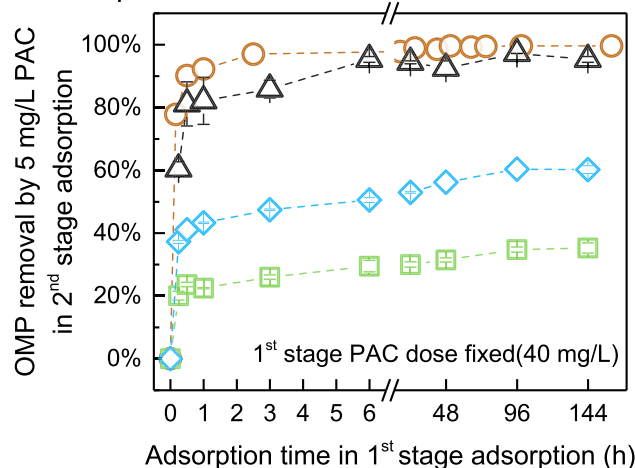

Fig. 6. The removal of DOM competitor (fictive–EBC, sum parameters including DOC and UV$_{254}$) in the first stage of DOM-OMP asynchronous adsorption as compared to removal of caffeine in isotherm/kinetic test in untreated water at (a) adsorption equilibrium; (b) adsorption kinetics with 40 mg PAC/L. 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).
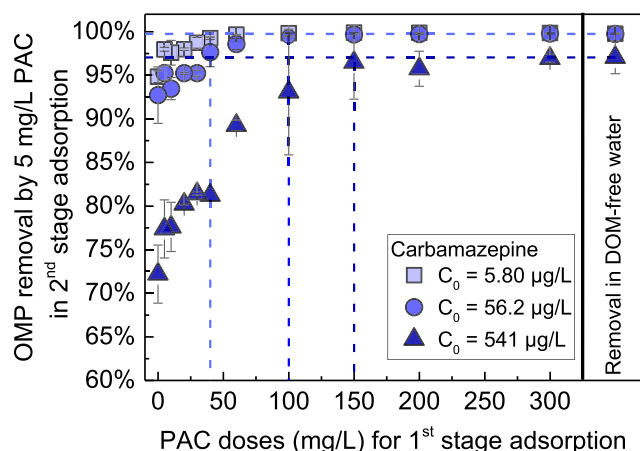
Fig. 7. Second stage removals of carbamazepine with 5 mg PAC/L after pre-DOM removal at variable first stage PAC doses for carbamazepine in different initial concentrations. Horizontal droplines showing averaged carbamazepine removals in DOM-free water, with vertical dashed droplines indicating competition alleviation achieved for carbamazepine in DOM-OMP asynchronous adsorption tests. Error bars derived from experimental duplicates.

removal percentages, whether or not DOM was present. But more importantly, the "adsorbable, non-competitive" was reproducible in the various DOM matrices (at 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. Fig. 7). The reason might be that OMP at higher concentrations also adsorb onto (energetically) less favorable adsorption sites that are still relatively favorable for some DOM molecules [42].

Again, EBCM was used to illustrate the impact of varying DOM competitors on OMP adsorption prediction, due to different initial OMP concentrations. In Fig. S5 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 [43]. 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 [44], ~ 30 μg/L for simetryn and ~ 1300 μg/L for asulam [21]), 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.

CRediT authorship contribution statement

Qi Wang: Investigation, Conceptualization, Methodology, Writing – original draft. **Frederik Zietzschmann:** Supervision, Conceptualization, Methodology, Writing – review & editing. **Roberta Hofman-Caris:** Supervision, Writing – review & editing. **Nan Jiang:** Investigation. **Jonas Schuster:** Investigation. **Zheng Wang:** Writing – review & editing. **Jianwei Yu:** Funding acquisition, Supervision, Writing – review & editing, Funding acquisition, Project administration. **Min Yang:** Supervision, Writing – review & editing, Project administration. **Luuk C. Rietveld:** Supervision, Conceptualization, Writing – review & editing.

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.

Acknowledgment

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.120942.

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