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Original Research

How aromatic dissolved organic matter differs in competitiveness against organic micropollutant adsorption

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ABSTRACT

Activated carbon is employed for the adsorption of organic micropollutants (OMPs) from water, typically present in concentrations ranging from ng L^{-1} to μg L^{-1}. However, the efficacy of OMP removal is considerably deteriorated due to competitive adsorption from background dissolved organic matter (DOM), present at substantially higher concentrations in mg L^{-1}. Interpreting the characteristics of competitive DOM is crucial in predicting OMP adsorption efficiencies across diverse natural waters. Molecular weight (MW), aromaticity, and polarity influence DOM competitiveness. Although the aromaticity-related metrics, such as UV_{254}, of low MW DOM were proposed to correlate with DOM competitiveness, the method suffers from limitations in understanding the interplay of polarity and aromaticity in determining DOM competitiveness. Here, we elucidate the intricate influence of aromaticity and polarity in low MW DOM competition, spanning from a fraction level to a compound level, by employing direct sample injection liquid chromatography coupled with ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry. Anion exchange resin pre-treatment eliminated 93% of UV_{254}-active DOM, predominantly aromatic and polar DOM, and only minimally alleviated DOM competition. Molecular characterization revealed that nonpolar molecular formulas (constituting 26% PAC-adsorbable DOM) with medium aromaticity contributed more to the DOM competitiveness. Isomer-level analysis indicated that the competitiveness of highly aromatic LMW DOM compounds was strongly counterbalanced by increased polarity. Strong aromaticity-derived π-π interaction cannot facilitate the competitive adsorption of hydrophilic DOM compounds. Our results underscore the constraints of depending solely on aromaticity-based approaches as the exclusive interpretive measure for DOM competitiveness. In a broader context, this study demonstrates an effect-oriented DOM analysis, elucidating counterbalancing interactions of DOM molecular properties from fraction to compound level.

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1. Introduction

Adsorption onto activated carbon (AC) is widely applied in water treatment to limit the potential health concerns from organic micropollutants (OMPs) [1–3]. However, the efficiency of OMP removal is hindered by competitive adsorption with the widely distributed dissolved organic matter (DOM). This obstacle arises due to the distinct competitiveness of DOM originating from diverse sources and compositions, presenting a significant challenge in water treatment efficacy [4,5]. Achieving a comprehensive isolation of competitive components for different DOM samples is experimentally unfeasible. However, examining how molecular characteristics influence DOM competitiveness can enhance our comprehension of the heterogeneous OMP adsorptive removal from various natural waters.

DOM molecular weight is a key characteristic for the competitiveness against OMPs, as the low molecular weight (LMW) DOM can easily access micropores of adsorbents where OMPs (with usually relatively small molecular sizes) mainly adsorb [4,6–8]. Regarding the role of aromaticity on DOM competitiveness, the actual interpretation of OMP adsorption studies is partly contradictory. The ultraviolet absorbance of LMW DOM (LMWUV), a surrogate for LMW aromatic DOM, can indicate DOM competitiveness in both natural waters and ozonated waters, as ozonation yields LMW DOM but decreases the corresponding competitiveness by degrading LMW aromatics [9,10]. When aligning the OMP breakthrough curves from drinking water and treated wastewater, LMWUV outperformed other bulk parameters like dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), and the concentration of LMW organics (LMWOC) [11]. However, DOM remained highly competitive against OMPs even after a strong decrease in aromaticity induced by anion exchange resin (AER) or coagulant *pre*-treatments [12–14]. In these studies, removing aromatic DOM did not decrease DOM competitiveness, contrasting the preference for UV_{254}-active DOM in activated carbon adsorption. This indicates that other physicochemical characteristics of DOM, like polarity, may also drive DOM competitiveness. Some aromatic DOM compounds may also be polar through other functional groups: highly polar DOM functionalities (e.g., carboxylic acids) can induce hydrophilic hindrance for the adsorption of aromatics at adsorbent surfaces, which typically involve π-π interactions at specific molecular configurations [15–17]. Therefore, we hypothesize that besides aromaticity, the polarity of DOM is also an important driver for competitive adsorption; however, the relative importance of both DOM characteristics is currently unknown.

To simultaneously characterize individual DOM molecules for their molecular weight, aromaticity, and polarity, Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is a promising tool [18,19]. Ultrahigh-resolution MS enables the refinement of DOM compound characterization, transitioning from fraction to compound level. This approach mitigates the uncertainty associated with the indirect method of analyzing highly hydrophobic DOM fractions through size-exclusion chromatography [12,20]. Using FT-ICR-MS for molecular characterization, molecular formulas can be assigned to mass peaks, allowing the calculation of molecular descriptors like degree of saturation (H/C) and oxygenation (O/C). Moreover, a formula-centric approach provides a detailed characterization of aromaticity for individual DOM molecules through the carboxyl-accounted unsaturation state, denoted as the aromaticity index (AI_{mod}), offering a more precise characterization than UV-based characterization at the bulk/fractionated DOM level [21,22]. Simultaneously, the nominal carbon oxidation state (NOSC) indicates DOM polarity [23]. Consequently, individual molecule aromaticity and polarity across MW ranges can be related to the adsorption and competitiveness of various DOM fractions, thus largely expanding the view of DOM fractionation studies that often only focus on one particular DOM bulk property (e.g., MW or polarity) at a time. By adding reversed-phase liquid chromatography (RPLC) to FT-ICR-MS, the DOM characteristics can even be studied at the isomer level, where RPLC elution time serves as a supplementary indicator of DOM compound polarity [24]. Moreover, additional fractionation during typical FT-ICR-MS sample processing (i.e., solid phase extraction) can be avoided by directly injecting water samples in RPLC-FT-ICR-MS [25].

Rather than the isolation of competitive components, the objective of this study was to resolve how aromatic DOM (of variable MW) differs in competitiveness against OMPs due to counterbalancing effects by polarity, using DOM fractionations coupled with molecular-level characterization by RPLC-FT-ICR-MS. We employed powdered activated carbon (PAC) and AER *pre*-treatments to remove different aromatic DOM fractions. We characterized the competitiveness of the remaining DOM fractions using OMP adsorption tests and the DOM properties via RPLC-FT-ICR-MS analysis. (For clarity, note that our approach involves two adsorption steps, the 1st step using AER or PAC *pre*-treatment for aromatic DOM removal and the 2nd step using PAC only for testing the effect of the *pre*-treatments on competitive OMP-DOM adsorption; cf. Fig. 1.) Overall, our processing scheme aimed to reveal if high aromaticity was sufficient for high DOM competitiveness. Grouping the removal of DOM compounds (based on FT-ICR-MS peak intensities) into MW ranges allows for allocating the varying impacts of DOM aromaticity and polarity on DOM competition. Moreover, we applied RPLC elution time to assess the polarity of DOM isomers, thus illustrating the counterbalancing effect of polarity on aromatic DOM competition. Unraveling the superimposed effects of different DOM molecular properties with respect to competition against OMPs in activated carbon adsorption, this research may advance robust monitoring and abatement technologies for DOM competition.

2. Materials and methods

2.1. Water samples

A water sample from river Schie (Delft, the Netherlands; sampled on September 2nd, 2020, in dry weather) was used. This sample is considered representative of other surface water DOM, which typically has a large proportion of aromatic and polar compounds [26–28] and was used to exemplify the different competitive properties of aromatic DOM compounds. The general water parameters are given in Table S1. In addition, the adaptable applicability of DOM-OMP competition in different various aquatic environments (natural waters/wastewaters) has been reported in numerous investigations [5,8,29–33].

Both for post-sampling and pre-batch tests, the water sample was filtered by 0.45 μm polyethersulfone membrane filters (Millipore, rinsed with ultrapure water) to remove suspended solids and minimize the bioactivity during batch adsorption. Additionally, inorganic-amended ultrapure water was prepared for the reference "competition-free" scenario of OMP adsorption. The ion composition of inorganic-amended water was similar to that of untreated river water (Table S2).

2.2. OMPs

Caffeine, sulfamethoxazole, and carbamazepine (from Sigma-Aldrich) were selected as exemplary OMPs for this study, covering a log D polarity range from −0.55 to 2.95 (cf. Table S3),

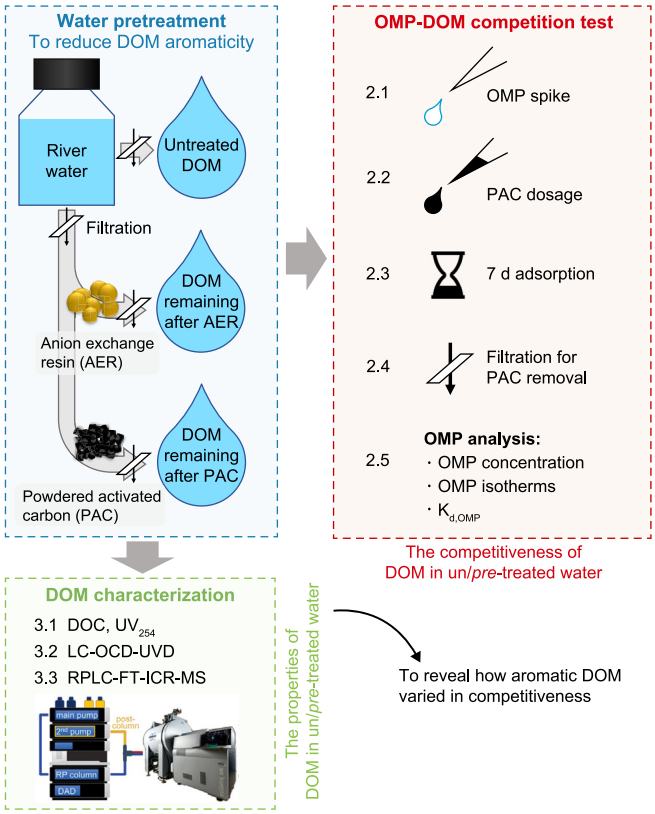


Fig. 1. Experimental scheme of water *pre*-treatment with anion exchange resin (AER) and powdered activated carbon (PAC), OMP-DOM competitiveness test in un/*pre*-treated waters, and DOM characterization from bulk to molecular level. Further experimental details can be found in Table S4.

being either neutral or anionic at pH 7 [34], resulting in contrasting adsorbabilities on activated carbon [9,12,35]. No positively charged OMPs were considered in this research, as their adsorption is generally less affected by DOM competition. The electrostatic attraction between positively charged OMPs (e.g., atenolol and erythromycin) and DOM constituents was observed to enhance adsorption [20].

2.3. Adsorbents

A strongly basic, granular Cl-form AER (Lewatit 8071, Bayer, UK) was used for AER *pre*-treatment. This choice was based on its high performance in removing negatively charged DOM, which is usually highly aromatic, especially from surface water [12]. Resin samples were rinsed with sodium chloride solution (~1 mol L^{-1}) and ultrapure water before use. The employment of AER in the Cl-form demonstrated the successful elimination of negatively charged DOM with minimal alteration in solution pH (from 7.81 to 7.93) and a slight rise in conductivity (from 930 to 1010 μs cm^{-1}). A negligible pH or ionic composition shift is unlikely to affect OMP adsorption significantly, similar to prior findings where the addition of $FeCl_3$ had little impact on OMP adsorption [36].

A mesoporous PAC (SAE Super, Norit, Netherlands; ~50% pore volume for mesopores) was selected for batch adsorption tests, including PAC *pre*-treatment and the characterization of DOM competitiveness using OMP-DOM competition tests, since DOM pore blockage generally plays a subordinate role in adsorption on mesoporous PAC while direct site competition is more pronounced [37]. Furthermore, since SAE Super is extensively utilized in water treatment across European nations, this investigation into DOM competition enhanced its relevance to real-world water treatment scenarios, rendering the study more comparable and applicable to other OMP adsorption investigations [5,38,39]. PAC samples were rinsed with ultrapure water, dried at 105 °C overnight, and degassed in a vacuum for preparing PAC stock suspensions at 4 and 20 g L^{-1}. Homogenization by 0.5 h stirring was applied before dosing PAC (using pipettes).

2.4. Water pre-treatments

Fig. 1 gives an overview of the DOM *pre*-treatment and competitiveness tests. To investigate the role of aromaticity in DOM competitiveness, AER and PAC *pre*-treatments, respectively, were employed to reduce the DOM aromaticity, and thus, less aromatic DOM fractions were generated. AER *pre*-treatment involved a high dose (15 mL L^{-1}) and 60 min contact time [12]. PAC *pre*-treatment used various PAC doses (from 5 to 200 mg L^{-1}, ten doses in total) for seven days (Table S4). To clarify the context further, PAC doses were associated with the names of PAC-pretreated waters. For example, the water *pre*treated with 200 mg L^{-1} of PAC is referred to as $PAC_{200\ mg\ L^{-1}}$-*pre*treated water.

2.5. OMP-DOM competition test

After removing the adsorbents used for *pre*-treatment, the DOM competitiveness was assessed by an OMP spike (~6 μg L^{-1}) and subsequent PAC adsorption experiments. Note that the objectives of the two PAC adsorption processes were different: The PAC adsorption in *pre*-treatment was intended to remove aromatic DOM, while the PAC adsorption in the OMP-DOM competition test was intended to test the effects of the preceding AER/PAC *pre*-treatments on OMP adsorption *after* aromatic DOM removal.

Concerning the PAC adsorption in the OMP-DOM competition test, OMP adsorption (onto PAC) isotherm tests revealed the competitiveness of the DOM remaining in solution by juxtaposing DOM-free water, untreated water, AER-*pre*treated water, and $PAC_{200\ mg\ L^{-1}}$-*pre*treated water (Table S4). In addition, for PAC-*pre*treated waters (with ten PAC concentration levels), a fixed PAC dose (5 mg L^{-1}) was applied in the competitiveness test. All PAC adsorption tests were conducted as 100 mL batches on a shaker (120 rpm) for seven days at 20 °C. To prepare the glassware, a preheating step at 450 °C for 4 h was employed, effectively eliminating any residual organics and ensuring sterilization. Subsequently, aliquots for OMP and DOM analysis were prepared using 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), respectively. Over seven days, negligible biodegradation occurred, evidenced by <1% UV_{254} reduction (0.299–0.296 cm^{-1}).

2.6. OMP partition coefficients on PAC and OMP quantification

The partition coefficients of OMPs on activated carbon ($K_{d,OMP}$) at $PAC_{5\ mg\ L^{-1}}$ (i.e., a fixed number of total adsorption sites) were determined by dividing the solid-phase OMP loadings on the activated carbon with the liquid-phase OMP concentrations at equilibrium adsorption. The OMP concentrations were determined using high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS, Xevo TQ-S-micro, Waters), coupled with an ACQUITY UPLC BEH C18 column (1.7 μm particle size, 2.1 × 50 mm, Waters, USA). A qualitative analysis was performed with two daughter ions of OMPs, and deuterated internal standards were used for OMP quantification (details in Text S1).

2.7. 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, ~28 min, >20000 g mol^{-1}; humics, ~39 min, ~1000 g mol^{-1}; building blocks, ~42 min, 300–500 g mol^{-1}; LMW humics and acids, ~46 min, <350 g mol^{-1}; LMW neutrals, ~49 min, <350 g mol^{-1}) of examined DOM samples [40].

2.8. RPLC-FT-ICR-MS measurement

DOM samples for FT-ICR-MS measurements were prepared as experimental triplicates without an OMP spike. Samples were directly injected without further sample preparation onto a C18 reversed-phase column (ACQUITY HSS T3, 1.8 μm, 100 Å, 150 × 3 mm, Waters, Milford, MA, USA 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 [41]. The LC setup includes a dual pump setup supplying a post-column counter gradient as described in Han et al. [41] and Jennings et al. [24]. 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 separating the matrix from the DOM and, hence, direct injection of water samples at their native concentrations. The LC system was hyphenated with an 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 counter gradient stabilizes the solvent composition of the ESI source to 50% MQW/50% MeOH and facilitates the ionization of the most polar DOM fractions. FT-ICR mass spectra were acquired in full profile broadband mode (147–1000 m/z) with 0.8 s ion accumulation time and two megaword data size (mass resolution: 231 000 @ 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 elution time and to facilitate data processing, an averaged mass spectrum between 10 and 15.8 min (338 individual mass spectra) was generated. Mass peaks with a signal-to-noise (S/N) ratio > 4 were considered in averaged spectra, and the average mass spectra were internally recalibrated with a mass list of known DOM masses using DataAnalysis (version 5.0, Bruker Daltonics). Later, eluting DOM was excluded from the spectral averaging step due to a few large mass peaks in the spectra > 15.8 min (cf. Fig. S1).

2.9. FT-ICR-MS data processing

In-house software was used with a well-organized workflow for reproducible data processing (Fig. S2). Molecular formulas were assigned to m/z values in averaged mass spectra using 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}. 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. [42] and element probability rules proposed by Kind and Fiehn [43]. Recent inter-laboratory comparisons have provided evidence on the reproducibility aspect of various software tools used in the biogeochemical interpretation of FT-ICR-MS data. The findings suggest that the reproducibility across different data processing tools in this context is notably high [44]. To enhance the reusability and reproducibility by other researchers, the dataset is available along with the paper (https://doi.org/10.48758/ufz.12409).

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. Molecular formulas from the blank-corrected triplicate treatments were merged into a single molecular formula list comprising only molecular formulas present in at least two out of three replicates. Due to low intensity and/or larger-than-average mass errors in some replicate measurements, up to one of the three triplicates was excluded before generating the final formula list (Table S5).

Three molecular descriptors, derived from the element composition of molecular formulas, were used as parameters linking DOM properties to DOM adsorbability/competitiveness: Aromaticity (using modified aromaticity index (AI_{mod}) in equation (1)) to describe π-π interaction [22], polarity (using nominal carbon oxidation state (NOSC) in equation (2)) to describe hydrophilic hindrance for adsorption, and formula mass, as a proxy of pore accessibility [24]. A comparison of independent samples (before/after *pre*-treatment) was performed with the Mann-Whitney *U* test. To align with the LC-OCD results, DOM compounds (<350 Da) were defined as LMW DOM in this study.

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

$$NOSC = 4 - \frac{4C + H - 3N - 2O - 2S}{C} \quad (2)$$

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 *pre*-treatment from untreated water (i.e., DOM adsorbed on PAC/AER). The mass peak intensity in the solution after treatment was considered as the fractional part of the respective DOM compound remaining after PAC/AER *pre*-treatment (for specific adsorbent doses). Raw mass peak intensities were found to be superior to normalized intensities (Fig. S3) while maintaining a good relationship between DOC concentrations and the sum peak intensity in the averaged spectrum (Fig. S4) [24]. Only molecular formulas with an intensity difference of >5% were considered as DOM compounds that could (at least partially) sorb on adsorbents.

To assess the distribution and average polarity of isomers contributing to individual molecular formulas, extracted ion chromatograms (EIC) were generated from raw LC-MS data using a mass window of 5 ppm. Based on the EIC data, an intensity-weighted average elution time (AET) for individual molecular formulas was calculated to describe the mean polarity of the examined isomers. EIC data were smoothed using a Savitzky-Golay filter ($n = 31$, three cycles) for visualization. AET was calculated based on the intensity distribution of each molecular formula, within the elution time ranging from 10.0 to 15.8 min to match the elution time used for averaging the spectra.

To visualize how aromatic DOM varies in competitiveness, molecular features in PAC-adsorbed DOM (during *pre*-treatment) were classified into two components of distinct competitiveness using the intersection of merged formula lists of two DOM samples. Specifically, both DOM *remaining* after AER *pre*-treatment and DOM *adsorbed* onto $PAC_{40\ mg\ L^{-1}}$ (i.e., 40 mg PAC L^{-1}) were characterized

as highly competitive DOM, but had a substantial difference in the molecular composition (cf. section 3.2). It was previously found that AER *pre*-treatment does not mitigate DOM competition against OMPs [12], highlighting the potential of AER to remove poorly competitive DOM. Therefore, merging findings from AER and $PAC_{40\ mg\ L^{-1}}$ *pre*-treatments allow for exploring how PAC-adsorbed DOM varied in competitiveness. Therefore, through an intersection of their molecular formulas, DOM adsorbed onto $PAC_{40\ mg\ L^{-1}}$ was further classified into two types: DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment (representing the strongly competitive fraction) and DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ but not detected after AER *pre*-treatment (representing the poorly competitive fraction).

A semi-quantitative comparison among the adsorbed DOM ($PAC_{40\ mg\ L^{-1}}$) molecular formulas regarding their adsorption behavior was performed based on the removal percentages [45]. It should be noted that the molecular formulas with a low peak intensity ($<10^5$ in untreated DOM) were not included in this comparison, as the intensity in the treated sample may be below the detection limits (S/N = 4), leading to an overestimation of removal. The relationship between peak intensity and removal is shown in Fig. S5. The calculated removal was always below 100% due to the inherent instrumental detection limit.

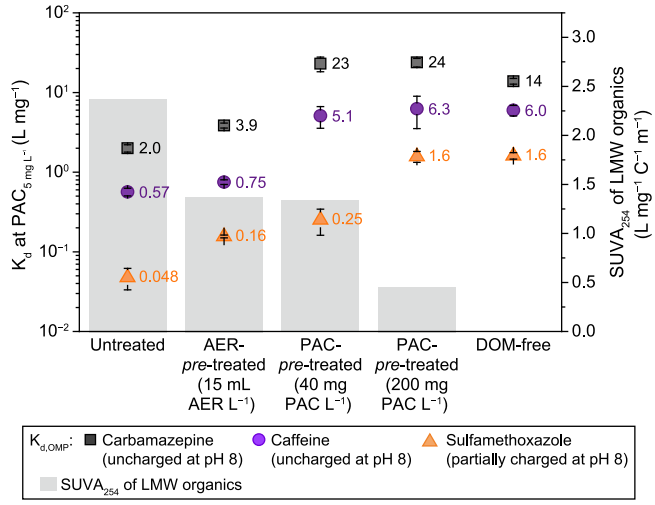
To assess the competitiveness of different isomers in strongly competitive DOM (adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment), selected molecular formulas (peak intensity rank < 1000, removal < 100% for $PAC_{40\ mg\ L^{-1}}$, $PAC_{200\ mg\ L^{-1}}$, and AER *pre*-treatment) were used to calculatethe removal of DOM isomers with different elution time.

3. Results and discussion

3.1. OMP-DOM competition following partial removal of aromatic DOM

The effects of AER and PAC *pre*-treatments on the competitiveness of DOM against OMPs are shown via PAC-water partition coefficients (K_d) of the OMPs (Fig. 2), along with bulk DOM characteristics. Compared to DOM-free water, the K_d values of carbamazepine, caffeine, and sulfamethoxazole in untreated river water were 14%, 9%, and 3%, respectively. The decrease of OMP removal was more pronounced for hydrophilic caffeine (log D = −0.55) and sulfamethoxazole (log D = 0.03) in contrast to hydrophobic carbamazepine (log D = 2.95). Numerous studies conducted in various wastewater and natural water environments have shown that hydrophilic OMPs face greater vulnerability to interference from DOM competition during activated carbon adsorption [5,8,29–32].

AER *pre*-treatment led to a high DOM removal from the river water (75% DOC, 93% UV_{254}-active DOM), but the increase in OMP K_d values was only small (carbamazepine, from 2.0 to 3.9; caffeine, from 0.57 to 0.75; sulfamethoxazole, from 0.048 to 0.16, respectively), and their adsorption isotherms were close to the isotherms in untreated water (Fig. S6). Adsorption isotherm tests revealed strong adsorbability of the remaining DOM after AER *pre*-treatment (Fig. S7), implying the inefficiency of AER pretreatment in reducing DOM competition, aligning with a previous investigation employing other AER and PAC products [12]. These findings underscore the ongoing challenge of insufficient DOM competition reduction for AER *pre*-treatment. In contrast, the PAC *pre*-treatment at a dose of 40 mg L^{-1} only resulted in a moderate DOM removal (42% in DOC, 53% for UV_{254}), while the OMP K_d values increased substantially for carbamazepine (from 2.0 to 23) and caffeine (from 0.57 to 5.1). This confirms that the DOM competition against carbamazepine and caffeine was almost completely alleviated by PAC *pre*-treatment, in



	Untreated	AER-*pre*-treated (15 mL AER L^{-1})	PAC-*pre*-treated (40 mg PAC L^{-1})	PAC-*pre*-treated (200 mg PAC L^{-1})	DOM-free
DOC (mg C L^{-1})	10.00	2.27	5.86	2.52	-
LMWOC (mg C L^{-1})	1.96	1.32	0.90	0.32	-
UV_{254} (cm^{-1})	0.297	0.021	0.135	0.049	-
$LMWUV_{254}$ (cm^{-1})	0.047	0.018	0.012	0.002	-

Fig. 2. Partition coefficients (K_d) of carbamazepine, caffeine, and sulfamethoxazole between solid phase (PAC) and liquid phase in the examined waters at $PAC_{5\ mg\ L^{-1}}$ (i.e., 5 mg PAC L^{-1}) along with $SUVA_{254}$ of LMW organics (grey bars), and DOC concentrations for the bulk DOM or LMW organics (LMWOC), as well as UV_{254} and $LMWUV_{254}$ (table). Note: $PAC_{5\ mg\ L^{-1}}$ refers to the second stage adsorption to assess the competitiveness of remaining DOM in *pre*treated waters (AER-*pre*treated, $PAC_{40\ mg\ L^{-1}}$-*pre*treated, and $PAC_{200\ mg\ L^{-1}}$-*pre*treated, respectively).

accordance with the markedly reduced adsorption capacity for remaining DOM post-PAC *pre*-treatment (Fig. S7). The higher K_d of carbamazepine in PAC-*pre*treated water than in DOM-free water, may be attributed to the complexation with weakly adsorbing hydrophilic DOM [46–49]. In contrast to the neutral OMPs, competition against negatively charged sulfamethoxazole was reduced less strongly by $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment and a higher PAC *pre*-treatment dose (200 mg L^{-1}) was required to alleviate the DOM competition in the subsequent OMP-DOM competition test (cf. Fig. S8).

The OMP adsorption was further compared to six bulk DOM and LMW DOM parameters (DOC, UV_{254}, $SUVA_{254}$, LMWOC, LMWUV, and $SUVA_{254}$ of LMW organics; Fig. S9). No clear linear relationship was found with any of the six parameters except between LMWOC and K_d of sulfamethoxazole (in log scale), suggesting that neither optical nor size-based bulk parameter can fully explain different DOM competitiveness against various OMPs in AER- and PAC-treated water. This is in contrast to previous results, which suggested that the amount of (UV-active) LMW DOM could serve as an indicator of DOM competitiveness [5,10,11]. Here, we found that DOM remaining after AER *pre*-treatment was much more competitive than DOM remaining after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment, although both resulting DOM samples had a similar $SUVA_{254}$ of the respective LMW fractions (~40% of the untreated water; cf. Fig. 2 and LC-OCD/LC-UV chromatogram in Fig. S10). This indicates that highly aromatic DOM fractions were preferentially removed by both *pre*-treatment processes. However, the AER-removed aromatic DOM was much less competitive than the PAC-removed aromatic DOM. This can be explained by different aromatic DOM fractions targeted by AER and PAC, as the remaining DOM varied largely regarding competitiveness. Consequently, aromaticity may not be

the main driver of DOM competitiveness in PAC treatment. In fact, polarity likely also plays an important role in the competitive adsorption of DOM against OMPs, as both aromaticity-induced π-π interactions and (a)polarity-induced hydrophobic interactions are key driving forces of DOM competitive adsorption [50].

3.2. Molecular characteristics of aromatic DOM after pre-treatments

To understand which fraction of aromatic DOM was removed by PAC and AER *pre*-treatments, respectively, FT-ICR-MS was used to characterize the molecular mass, aromaticity, and polarity of DOM before and after the *pre*-treatments. 7352 molecular formulas were assigned to FT-ICR-MS derived mass peaks in the untreated sample, with CHNO compounds accounting for 46%, followed by CHO (33%), CHNOS (11%), and CHOS (10%) (Table S6). After *pre*-treatment with PAC or AER, the number of assigned formulas and the total spectrum intensity decreased linearly according to the decreasing DOC concentrations (Fig. S4). Higher removal for CHNO compounds was achieved through PAC *pre*-treatment (55% for $PAC_{40\ mg\ L^{-1}}$ and 60% for $PAC_{200\ mg\ L^{-1}}$) than that through AER *pre*-treatment (46%) (Table S6, also cf. Figs. S11 and S12). Similarly, stronger adsorption of CHNO compounds has been found on a hydrophobic resin [51], implying a stronger interaction of nitrogen-containing DOM compounds during adsorption.

The DOM removal by $PAC_{40\ mg\ L^{-1}}$, and AER was further examined using molecular descriptors (AI_{mod} vs. molecular mass, Fig. 3; NOSC vs. AI_{mod}, Fig. S13; NOSC vs. molecular mass, Fig. S14). The intensity-averaged mass-to-charge ratio (m/z_{wa}) decreased only slightly from 401 to 387 Da ($p < 0.001$, Mann-Whitney *U* test, cf. Table S6) after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment. A more pronounced decrease in molecular mass from 401 to 327 Da ($p < 0.001$) was observed after AER *pre*-treatment. 97% of the molecular formulas with $m/z > 500$ Da were undetected after AER *pre*-treatment (Fig. 3d), which is in agreement with the high removal of humics (~1000 g/mol) and building blocks (~300–500 g mol^{-1}) observed with LC-OCD (cf. Fig. S10) [12]. As ion exchange is the dominant mechanism of DOM removal in AER *pre*-treatment [52–54], the high removal of HMW DOM by AER was possibly attributed to the higher likelihood of large DOM molecules having more accessible anionic functional groups (e.g., carboxylic acid groups) and lower solubility [53,55–58].

AI_{mod} describes the average (un)saturation state of carbon in a molecule and is associated with the aromaticity of DOM compounds and the potential for π-π interactions in adsorption processes [22]. Overall, 53% of LMW DOM compounds (<350 Da) were fully removed after AER *pre*-treatment, with a higher share (82%) for highly aromatic LMW DOM compounds ($AI_{mod} > 0.5$). In contrast, $PAC_{40\ mg\ L^{-1}}$ removed only 35% of LMW DOM compounds completely and only 54% of highly aromatic LMW DOM compounds. As a consequence, $AI_{mod,wa}$ (intensity-averaged AI_{mod}) decreased significantly from 0.32 to 0.23 ($p < 0.001$) after AER *pre*-

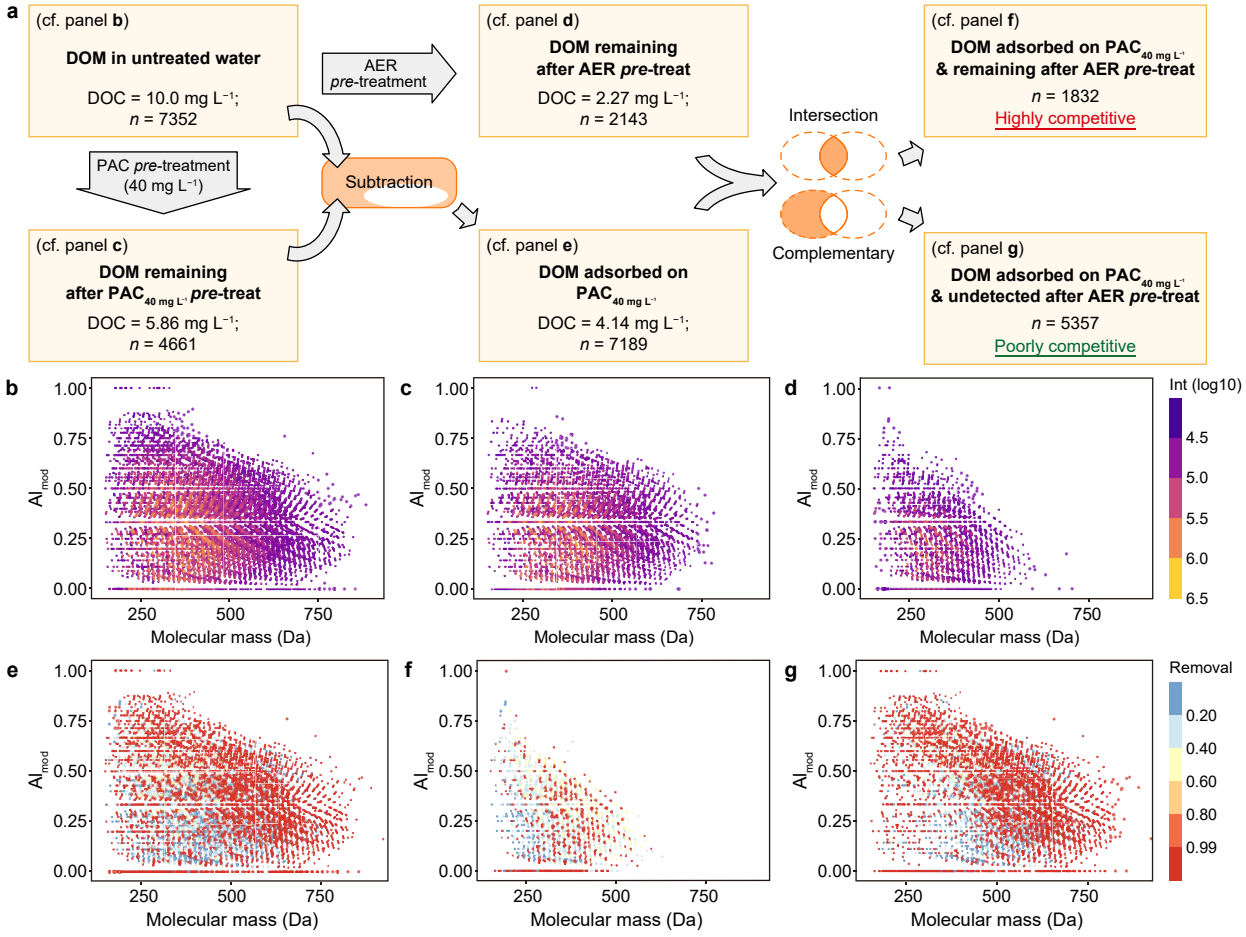


Fig. 3. **a**, Scheme illustrating data analysis for associating DOM competitiveness with FT-ICR-MS-derived DOM characteristics. **b**–**g**, AI_{mod} versus molecular mass for molecular formulas in untreated DOM (**b**), DOM remaining after $PAC_{40\ mg\ L^{-1}}$ (**c**) or AER *pre*-treatment (**d**), DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ (**e**), DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment (**f**), and DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and undetected after AER *pre*-treatment (**g**). The numbers (*n*) and DOC concentrations are provided in panel a, in correspondance with the other panels.

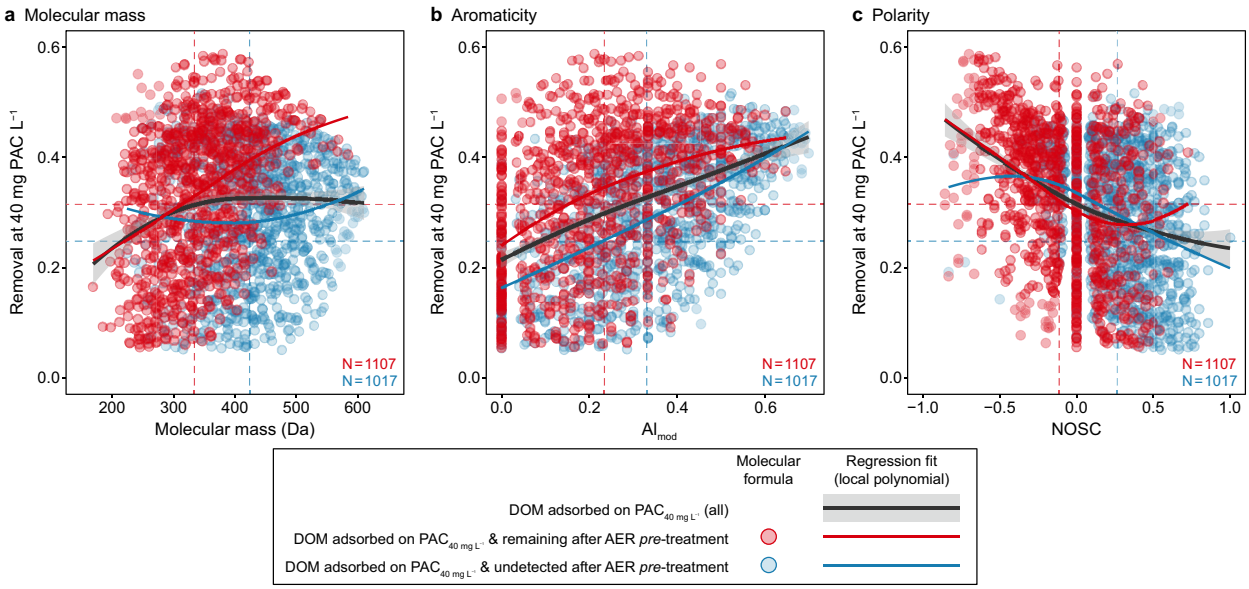


Fig. 4. Removed fraction (based on FT-ICR-MS intensities) of two types of DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$, remaining (red) or undetected (blue) after AER *pre*-treatment vs. molecular mass (**a**), modified aromaticity index (AI_{mod}, **b**), and polarity (in NOSC, **c**). Data are displayed with local polynomial regression fits with 95% confidence interval (black for all $PAC_{40\ mg\ L^{-1}}$-adsorbed compounds). Mean molecular mass, AI_{mod}, NOSC, mean removal (dashed lines), and the number of molecular formulas (N) are provided. Note: the compounds undetected after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment (100% removal) and molecular formulas with peak intensity < 10^5 in the untreated DOM sample are not included.

treatment, and to just 0.31 ($p < 0.001$) after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment.

The strong removal of highly aromatic DOM during AER *pre*-treatment only resulted in a minimal reduction in DOM competitiveness (cf. Fig. 2), indicating that neither low $SUVA_{254}$ nor low AI_{mod} of LMW DOM suffices to explain the high competitiveness of DOM remaining after AER *pre*-treatment. Again, this indicates that aromaticity apparently is less of a predominant driver of competitiveness than previously thought. In this case, the role and degree of hydrophilic hindrance determined by the molecule polarity and its potential to override aromaticity-driven π-π interactions must also be considered.

NOSC accounts for the average oxidation state of carbon in a molecule, which is linked to the polarity of DOM compounds and is usually associated with hydrophobic interactions in DOM sorption [23,41]. Molecular formulas in DOM remaining after AER *pre*-treatment mostly had NOSC values < 0.5, suggesting that polar DOM components (with high NOSC) were preferentially removed. In contrast to AER, $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment resulted in strong adsorption of non-polar DOM compounds with low NOSC values (<0; Fig. S13). Total ion chromatograms derived from RPLC-FT-ICR-MS indicate that DOM compounds with, on average, stronger retention on the C_{18} column were preferentially removed by $PAC_{40\ mg\ L^{-1}}$ (Fig. S15). Higher average elution time, in turn, correlates with lower NOSC values of DOM compounds (Fig. S16), confirming the general applicability of NOSC as a polarity indicator. AER favored adsorption of polar DOM while PAC adsorbed more nonpolar DOM. This may explain why DOM remaining after AER *pre*-treatment exhibited comparable competitiveness as untreated DOM. These results suggest that the nonpolar DOM compounds may substantially contribute to DOM competition via PAC adsorption site occupation through hydrophobic interactions.

3.3. PAC-adsorbed DOM compounds with divergent competitiveness

$PAC_{40\ mg\ L^{-1}}$ *pre*-treatment substantially alleviated the competition between the remaining DOM and OMPs in the subsequent PAC competitive adsorption step (cf. Fig. 2); therefore the DOM adsorbed onto $PAC_{40\ mg\ L^{-1}}$ likely includes the most competitive DOM fraction (Fig. 3e). However, *all* DOM compounds (i.e., independently of molecular mass and/or AI_{mod}) detected in the original river water appeared to be (completely or partially) adsorbed on $PAC_{40\ mg\ L^{-1}}$ ($n = 7190$ or 98%, Fig. 3e). Together with the limited DOC removal (42% for $PAC_{40\ mg\ L^{-1}}$ treatment), this confirms the nonspecific nature of DOM adsorption onto PAC [10,59]. In contrast, the high aromatic DOM removal and poor alleviation of DOM competition during AER *pre*-treatment indicate that the adsorbable (aromatic) DOM features highly vary in DOM competitiveness. The removability of DOM features by AER was a good examination of low DOM competitiveness. In contrast to the PAC *pre*-treatment, the AER *pre*-treatment was more selective (and more efficient) in DOM removal while removing the poorly competitive DOM fraction (Fig. 2). Therefore, the results from AER and $PAC_{40\ mg\ L^{-1}}$ *pre*-treatments were combined to unravel how PAC-adsorbed DOM varied in competitiveness (Fig. 3d–g). The molecular formula-based intersection of $PAC_{40\ mg\ L^{-1}}$-adsorbed DOM and DOM remaining after AER *pre*-treatment revealed DOM components with a greater impact on DOM competitiveness, being non-polar but also of low aromatic character, representing ~26% of all molecular formulas in $PAC_{40\ mg\ L^{-1}}$-absorbable DOM (Fig. 3f). This highly competitive fraction was less aromatic and less polar than the poorly competitive fraction. The most aromatic features adsorbed strongly on both PAC and AER but appear as poorly competitive compounds, possibly due to simultaneous high polarity (Fig. 3g and Fig. S13f). This is remarkable, as (higher) polarity and (higher) aromaticity are often found to be connected in aqueous DOM molecular characteristics, ensuring solubility in water [55,60]. This connection, however, elucidates why $SUVA_{254}$ and AI_{mod} alone cannot fully explain DOM competitiveness.

As NOSC is a polarity indicator calculated from molecular formulas only, it does not account for the potential dissociation of ionizable groups, with dissociation typically leading to a further increase in actual polarity and hydrophilic hindrance on adsorbents [24]. DOM dissociation can strongly inhibit the competitiveness of

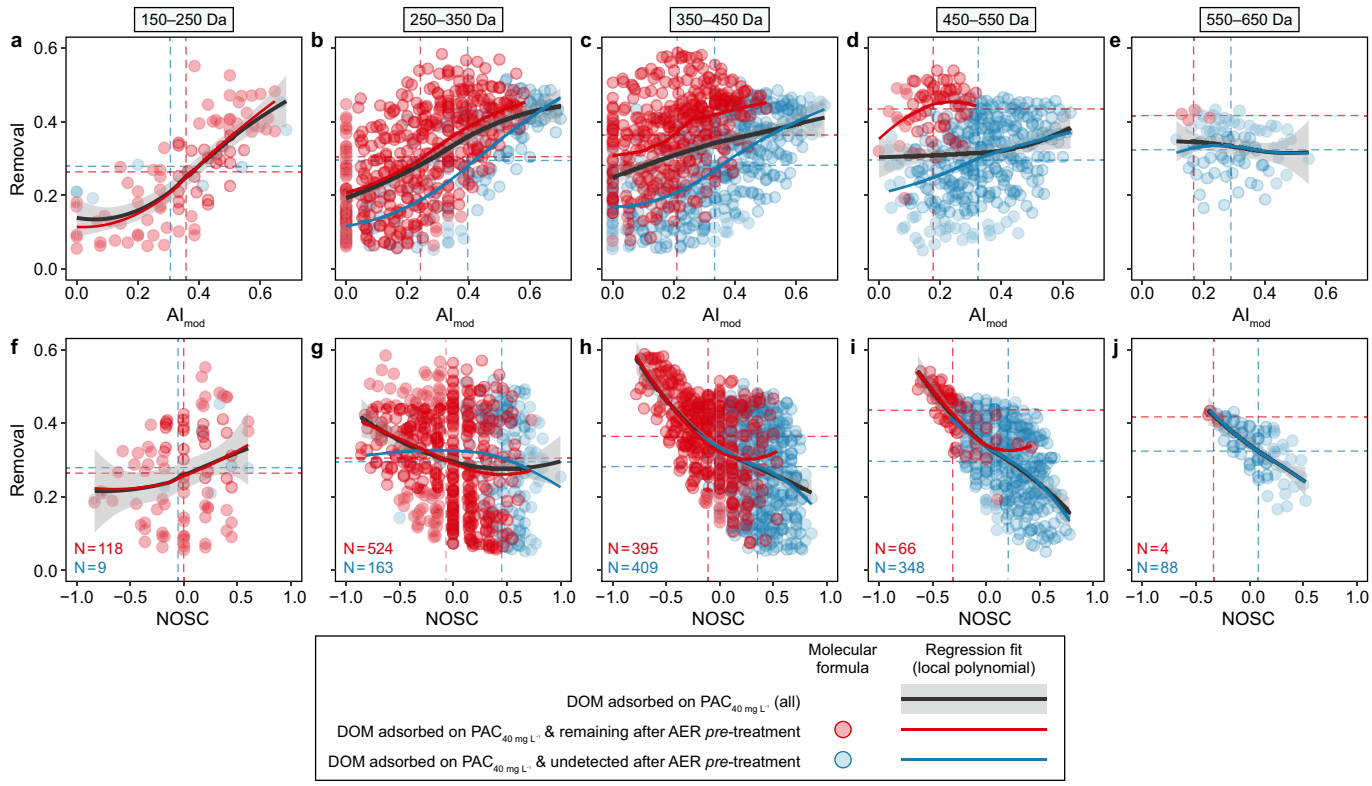


Fig. 5. Removed fraction (based on FT-ICR-MS intensities) of DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining (red) or undetected (blue) after AER *pre*-treatment plotted vs. AI_{mod} (**a**–**e**) or NOSC (**f**–**j**) for different mass ranges: 150–250 Da (**a**, **f**), 250–350 Da (**b**, **g**), 350–450 Da (**c**, **h**), 450–550 Da (**d**, **i**), and 550–650 Da (**e**, **j**). Local polynomial regression fits with 95% confidence interval, mean AI_{mod} or NOSC, and the number of molecular formulas (N) are provided. Note: the compounds undetected after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment (100% removal) and molecular formulas with peak intensity < 10^5 in untreated DOM samples are not included.

aromatic DOM, especially against uncharged OMPs (i.e., carbamazepine and caffeine); undissociated 2,4-dichlorophenol and 4-chloroaniline are competitive against nonionic naphthalene, while dissociation at neutral pH makes them non-competitive [61].

Although the fractionation-based DOM molecular characterization cannot chemically isolate the competitive DOM fraction at this point, our results highlight the limitation of aromaticity and the importance of polarity in understanding DOM competitiveness. Identifying an "accurate" molecular composition of a concise competitive fraction within the physico-chemical continuum of natural DOM may never be possible because competitive DOM — by its very nature — will always cover a *certain range* of structures and molecular properties.

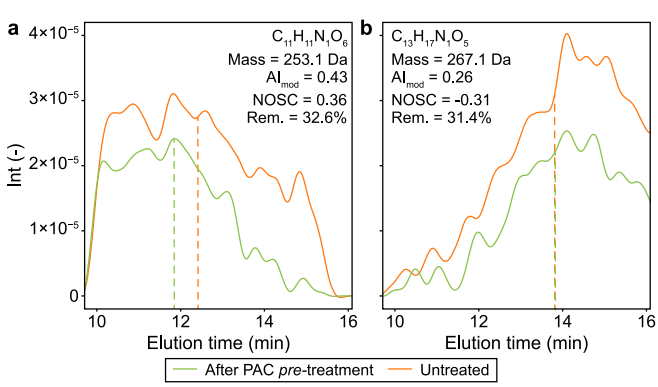


Fig. 6. EICs and AETs (dashed lines) of two molecular formulas with comparable removal, before and after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment: **a**, $C_{11}H_{11}N_1O_6$; **b**, $C_{13}H_{17}N_1O_5$.

3.4. Joint impact of aromaticity and polarity on DOM competitive adsorption

To analyze how molecular characteristics affect DOM competitive adsorption, $PAC_{40\ mg\ L^{-1}}$-adsorbable molecular formulas are intersected with molecular formulas that remained after AER *pre*-treatment (red colored in Fig. 4, strongly competitive) and molecular formulas that were undetected after AER *pre*-treatment (blue colored in Fig. 4, weakly competitive) with respect to their FT-ICR-MS derived molecular descriptors (MW, AI_{mod}, NOSC). Not considering undetected molecular formulas after PAC *pre*-treatment, the removal of DOM compounds detectable after PAC *pre*-treatment was found with up to 59% and 91% intensity loss for 40 and 200 mg L^{-1} PAC, respectively (Fig. 4 and Fig. S9). As the common view of DOM adsorption is that it is enhanced by higher MW/aromaticity or lower polarity, we tested the relationship between MW/aromaticity/polarity and adsorption for the two DOM fractions.

DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment (i.e., the strongly competitive fraction) was characterized by lower mean MW (327 Da vs. 457 Da) and also a higher mean removal during $PAC_{40\ mg\ L^{-1}}$ adsorption (Fig. 4a) as compared to the DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and undetected after AER (i.e., the less competitive fraction). Similar to MW, the higher adsorption on $PAC_{40\ mg\ L^{-1}}$ for the strongly competitive fraction corresponded to a lower mean AI_{mod}. In contrast to the common perception, our results indicate that DOM competitive adsorption was only partly driven by (high) MW and (high) aromaticity.

Nonetheless, within the fraction of DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment (i.e., the

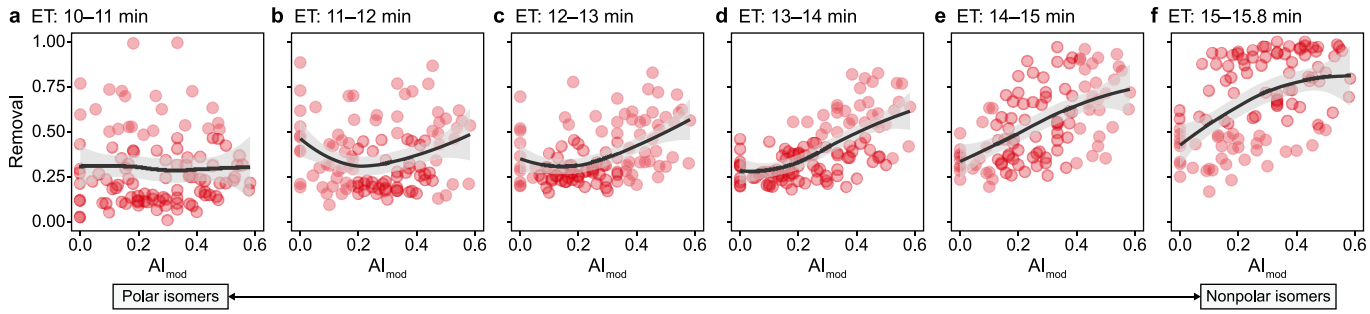


Fig. 7. Removed isomers with different elution time (ET) in DOM adsorbed on $PAC_{40\ mg\ L^{-1}}$ and remaining after AER *pre*-treatment (red dots) plotted vs. AI_{mod}. Note: all panels relate to the same molecular formulas and the shown removals were calculated as averaged intensity decrease over the indicated elution time range in each panel. Local polynomial regression was used, with a 95% confidence interval, for data analysis.

strongly competitive fraction), higher MW correlated to higher removal (Fig. 4a). Likewise, a positive relationship was found between AI_{mod} and DOM removal for both DOM fractions (Fig. 4b), while a negative relationship was found for NOSC and DOM removal (Fig. 4c). This corroborates that neither DOM aromaticity nor DOM polarity alone are sufficient descriptors for competition.

To better understand this observation, DOM removal was further assessed in several MW ranges and plotted against AI_{mod} and NOSC (Fig. 5). For the LMW DOM (molecular mass < 350 Da), aromaticity positively correlated with the DOM removal after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment but gradually diminished with the increase of MW. In contrast, DOM removal by PAC was negatively correlated with polarity (expressed as NOSC) in the high MW fractions (MW > 350 Da). These results extend previous knowledge where adsorbability and competitiveness of LMW DOM model compounds (<200 Da) were mainly described by their aromaticity and less so by their hydrophobicity [17].

Our observations point towards better steric access of unsaturated/aromatic structures in LMW DOM during adsorption, whereas aromatic rings are possibly located more centrally in HMW DOM molecules, leading to more steric hindrance during surface adsorption [17,62]. In fact, LMW DOM components with high AI_{mod} were categorized as poorly competitive due to their high AER removability (Fig. 5b–d), which may be attributed to the higher mean polarity of such compounds (NOSC > 0.4, Fig. 5g–h and Fig. S17). The possible dissociation of polar functional groups of such unsaturated compounds limits their competitiveness towards high-energy PAC adsorption sites [61]. Highly aromatic DOM can only be soluble in water if they carry polar functional groups [55,60], and completely non-polar aromatics (e.g., condensed aromatics, a prototype of ideal DOM competitors), are rarely present in natural water [27]. With the possibility of using non-extracted DOM with direct injection RPLC-FT-ICR-MS, the most polar and non-polar fractions of DOM become accessible, expanding our view on DOM competition.

3.5. Isomer-resolved PAC adsorption decodes the interrelation between polarity and aromaticity

Up to now, only isomer-averaged molecular characteristics have been discussed concerning their OMP competitiveness. To further elucidate how polarity counterbalances the effect of aromaticity, individual DOM compounds were analyzed with respect to their chromatographic behavior during HPLC. The EICs of highly competitive DOM (i.e., molecular formulas characterized as adsorbable in $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment and as remaining after AER *pre*-treatment) were examined (Fig. 6). Molecular formulas (each with a distinct mass and corresponding AI_{mod} value) eluting at different elution times can be associated to isomers of varying polarity [41]. Intensity-weighted AET was used to characterize the mean polarity of all isomers of a respective molecular formula in untreated/*pre*treated DOM samples, and lower AETs correspond well with the higher (isomer-averaged) polarity of molecular formulas described by NOSC (Fig. S16).

As an example, a DOM compound with molecular formula $C_{13}H_{17}N_1O_5$ showed uniform intensity loss across polar and nonpolar isomers after PAC adsorption, leading to only marginal AET changes (Fig. 6b). In contrast, $C_{11}H_{11}N_1O_6$ (with similar average removal, but higher AI_{mod} & NOSC values and lower AET as compared to $C_{13}H_{17}N_1O_5$) showed preferential removal of low polarity isomers after approx. 13.5 min by the $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment (as indicated by the loss in EIC intensity, Fig. 6a), suggesting pronounced variability in the adsorption potential of isomers of highly aromatic DOM (based on AI_{mod}). This observation on the isomer level is reflected by the contrasting effect of bulk molecular aromaticity and polarity on DOM adsorption (Fig. 4).

To comprehensively assess the effect of aromaticity on isomer adsorption, the removal of DOM isomers was evaluated at different elution time ranges and plotted against AI_{mod} (Fig. 7). For nonpolar isomers (elution time: 12–15.8 min) of molecular formulas with higher aromaticity, a high removal after $PAC_{40\ mg\ L^{-1}}$ *pre*-treatment was observed. In contrast, polar isomers (elution time: 10–12 min) demonstrated minimal influence of aromaticity on their removal. This observation provides direct evidence for how increased polarity largely compensates the π-π interaction introduced by aromatic moieties and that aromaticity alone is not sufficient to explain the sorption behavior on PAC.

Based on the isomer resolution of RPLC-FT-ICR-MS, we conclude that only the non-polar isomers of aromatic compounds are strongly adsorbing on PAC and likely remain after AER treatment (due to a lack of ionizable groups). Concerning the number of detected molecular formulas, it is this relatively small fraction of DOM compounds that appears to be the main driver of DOM competition against OMPs (Fig. 3 and Fig. S12). Overall, the combination of effect-driven multiple DOM fractionations and molecular/isomer-level resolution via RPLC-FT-ICR-MS analysis enabled us to depict how aromaticity and polarity influence DOM competitive adsorption collectively and resolve contradictory observations on the bulk DOM level. Due to the nature of DOM as a continuum of molecular properties, this kind of polarity-aromaticity interaction can be expected for the competitive adsorption of all kinds of natural water DOM, maybe more or less pronounced depending on its source. In water treatment, a simultaneous reduction in DOM aromaticity and increased DOM polarity (e.g., by ozonation) could effectively control DOM competition against OMPs in activated carbon adsorption [9,10].

4. Conclusion

In our study, we observed that both $PAC_{40\ mg\ L^{-1}}$ and AER *pre*-treatment resulted in a comparable decrease in the $SUVA_{254}$ of LMW DOM. However, the remaining DOM after AER *pre*-treatment exhibited substantially greater competitiveness than the remaining DOM after PAC *pre*-treatment. AER was selective towards the removal of highly aromatic, polar compounds, whereas PAC treatment exhibited a preference for nonpolar compounds. These findings suggest that aromatic DOM (as measured by UV_{254}) was not essentially competitive against OMPs in adsorption.

Furthermore, the chemical features of PAC-adsorbed DOM were classified into two distinct components. This classification was achieved through a molecular formula-based intersection between $PAC_{40\ mg\ L^{-1}}$-adsorbed DOM, and DOM remaining after AER *pre*-treatment. The DOM component composed of highly aromatic, polar compounds displayed lower competitiveness compared to the less aromatic and less polar component, potentially due to hydrophilic hindrance.

While both higher aromaticity and lower polarity individually improved DOM adsorption, aromaticity played a dominant role in the adsorption of LMW DOM (<350 Da). However, as DOM molecular weight increased, the significance of aromaticity decreased and was replaced by polarity as an important driver. Further characterization of LMW DOM isomers revealed that the positive effect of aromaticity on isomer adsorption was only observed for nonpolar DOM isomers (later eluted), confirming that stronger aromaticity-derived π-π interaction cannot enhance the adsorption for hydrophilic DOM compounds. This study illustrates the counterbalancing effect of aromaticity and polarity in understanding the competitive adsorption of DOM and highlights the limitations of relying solely on aromaticity or UV_{254}-based methods as the sole interpretive metric.

CRediT authorship contribution statement

Qi Wang: Investigation, Formal Analysis, Conceptualization, Methodology, Writing - Original Draft. **Oliver J. Lechtenfeld:** Investigation, Formal Analysis, Software, Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing. **Luuk C. Rietveld:** Conceptualization, Resources, Supervision, Writing - Review & Editing. **Jonas Schuster:** Investigation, Formal Analysis, Writing - Review & Editing. **Mathias Ernst:** Methodology, Resources, Supervision, Writing - Review & Editing. **Roberta Hofman-Caris:** Conceptualization, Supervision, Writing - Review & Editing. **Jan Kaesler:** Investigation, Formal Analysis, Software, Writing - Review & Editing. **Chunmiao Wang:** Visualization, Writing - Review & Editing. **Min Yang:** Resources, Supervision, Writing - Review & Editing, Funding Acquisition, Project Administration. **Jianwei Yu:** Conceptualization, Supervision, Writing - Review & Editing, Funding Acquisition, Project Administration. **Frederik Zietzschmann:** Conceptualization, Methodology, Formal Analysis, Visualization, Supervision, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ese.2024.100392.

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