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DOI

[10.1016/j.watres.2020.115574](https://doi.org/10.1016/j.watres.2020.115574)

Publication date

2020

Document Version

Final published version

Published in

Water Research

Citation (APA)

Wang, Q., Zietzschmann, F., Yu, J., Hofman, R., An, W., Yang, M., & Rietveld, L. C. (2020). Projecting competition between 2-methylisoborneol and natural organic matter in adsorption onto activated carbon from ozonated source waters. *Water Research*, 173, Article 115574. <https://doi.org/10.1016/j.watres.2020.115574>

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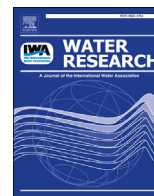
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Projecting competition between 2-methylisoborneol and natural organic matter in adsorption onto activated carbon from ozonated source waters

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ARTICLE INFO

Article history:

Received 1 October 2019

Received in revised form

28 January 2020

Accepted 30 January 2020

Available online 4 February 2020

Keywords:

Activated carbon

Ozonation

Competitive adsorption

Natural organic matter

MIB

ABSTRACT

Though the ozone-activated carbon process has been widely applied for drinking water purification, little is known about how ozone-modified natural organic matter (NOM) competes with micropollutants in activated carbon adsorption. In this study, three natural waters and one synthetic water (standard humics solution) with highly heterogeneous NOM compositions were employed to investigate the interference of ozonated NOM with the adsorption of 2-methylisoborneol (MIB). Analysis using liquid chromatography with online carbon and UV₂₅₄ detection (LC-OCD-UV₂₅₄) revealed that ozonation led to various disintegration patterns of macromolecules in NOM, and UV absorbance was reduced markedly for nearly all NOM fractions. Powdered activated carbon (PAC) adsorption experiments showed that increasing ozone consumption coincided with reducing NOM competition against MIB in the three natural waters, as expressed by the fitted initial concentrations of the equivalent background compound ($C_{0,EBC}$). In the synthetic water, in contrast, competition increased under low/moderate specific ozone consumptions and then decreased with further elevation of ozone consumptions. Regarding the significance on affecting ozonated NOM interference, aromaticity reduction outweighed formation of low molecular weight (LMW) organics in most cases, enhancing MIB adsorption capacity. However, disintegration of the humics fraction with larger molecular weight (1,103 g/mol, as compared to 546–697 g/mol in three natural waters) into smaller, more competitive fractions caused the observed initial deteriorated MIB adsorption in synthetic water. A superior correlation between $C_{0,EBC}$ and the UV absorbance of LMW organics ($R^2 = 0.93$) over concentrations of LMW organics underlined the importance of the aromatic properties in competitive adsorption projection for ozone pretreated natural waters. Furthermore, the change of relative concentration of UV absorbing compounds during ozonation could help estimate the decrease of $C_{0,EBC}$, which could be a promising tool for waterworks to adjust PAC doses for MIB removal in ozonated waters.

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1. Introduction

2-methylisoborneol (MIB), odorous at a concentration as low as

10 ng/L (Matsui et al., 2014), occurs in up to 50% of lake/reservoir waters in China (Wang et al., 2019). Conventional treatment and ozonation perform poorly on MIB removal (Peter and Von Gunten, 2007; Zoschke et al., 2011), wherefore powdered activated carbon (PAC) adsorption or ozone-biological activated carbon (BAC) combinations are often the methods of choice (Guo et al., 2016; Newcombe et al., 2002b). However, adsorption interference by coexisting natural organic matter (NOM) results in high PAC doses

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or short service times for carbon filters (Summers et al., 2013). The interference mechanisms are direct competition for internal adsorption sites and pore blockage with macromolecules (Li et al., 2003). Direct competition is the dominant factor for low molecular weight (LMW) NOM molecules, with aromatic NOM inducing stronger competitive effects (Hu et al., 2014; Zietzschmann et al., 2014). In O₃-BAC treatment, ozonation prior to adsorption may affect NOM characteristics, e.g. by hydrophilizing hydrophobic compounds, breakage of larger NOM constituents, or decreasing the aromatic content of the NOM (Lamsal et al., 2011; Song et al., 2010). The reduction in aromaticity and hydrophobicity of organics will reduce the competitive adsorption by NOM (Lerman et al., 2013), while the formation of small molecules from the breakage of larger NOM constituents may act in the other direction (Newcombe et al., 2002b). It was revealed that ozonation of wastewater treatment plant (WWTP) effluent positively alleviates the NOM interference with micropollutants, due to concomitantly decreasing aromaticity/hydrophobicity (Zietzschmann et al., 2015). However, the origins and compositions of NOM in surface waters are much different from those in WWTP (Gonsior et al., 2011; Nam and Amy, 2008), which would exert an influence on the oxidation and adsorption behaviors of NOM and thus the competition with MIB.

To describe the competitive adsorption, the concentrations of LMW organic carbon (LMWOC) and UV absorbance of LMW organics (LMWUV), which could be measured by liquid chromatography with online OC and ultraviolet absorbance detection (LC-OCD-UVD), have been suggested as two important parameters (Zietzschmann et al., 2016b). On the other hand, the equivalent background compound model (EBCM) (Najm et al., 1991) has been used to project required PAC doses or GAC breakthrough curves for MIB removal in surface waters by indicating the competing NOM fraction of the targeted compound (Crittenden et al., 2012; Matsui et al., 2012). Relatively good correlation was mentioned between LMWOC/LMWUV and EBC (Matsui et al., 2012). However, it is not clear if the two parameters could still be valid to describe the competing NOM in ozonated waters.

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

2. Materials and methods

2.1. Natural waters and synthetic water

Three raw waters were sampled in October 2018 from Mopanshan reservoir (MPS) in Harbin, Jinze reservoir (JZ) in Shanghai and Shiyao reservoir (SY) in Shenzhen, China. At the sampling time, no odor problems were identified in the reservoirs and the concentrations of MIB were lower than 10 ng/L. In addition, synthetic water was prepared by dissolving Suwannee river humic acids (SHA) from IHSS in ultrapure water. SHA is an isolation product from Suwannee River in South Georgia, USA, impacted by peat deposits and decomposing vegetation (Averett et al., 1994). The

solution was stored in dark for 72 h to allow the humic solution to expand fully. Inorganic ions were amended to imitate the ionic background of natural waters for the SHA water and organic-free water (Table S1). To exclude the impacts of suspended solids on subsequent treatment process, all raw waters were filtered by a 0.45 μm membrane (142 mm, Supor-450, Pall Co.); the corresponding water parameters are listed in Table 1.

2.2. Ozonation procedures and PAC batch tests

Filtered waters were ozonated with a bench-scale ozonation setup equipped with an ozone generator (OS-1N, Mitsubishi Electric Co., Japan), with O₂ fed directly from an oxygen generator (FY3, Beijing North Star Yaa, China). Ozone was bubbled into 2 L of the stirred filtrate in a glass jar. With ozone production rate ranging from 130 to 200 mg/h of ozone producer (same for ozonation of each water), the contact time of ozonation varied within 3–40 min according to the target dosage in four examined waters. The concentrations of ozone in inflow gas and exhaust gas were determined by iodimetry. The specific ozone consumption was calculated by the difference of the inflow and exhaust ozone by the water volume, divided by the concentration of dissolved organic carbon (DOC) of the respective ozonated water samples.

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

2.3. Analytical methods

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

Bulk UV₂₅₄ was measured by a UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan). DOC was determined using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Three-dimensional fluorescence spectrum analysis was conducted by a Fluorescence Spectrophotometer F-7000 (HITACHI, Japan).

Table 1
Basic water parameters of the four examined waters.

	pH	DOC	SUVA	(\bar{M}_n) ^a
Units	–	mg C/L	L/(mg·m)	g/mol
Shiyao (SY)	7.84	1.39	2.16	546
Jinze (JZ)	7.76	3.57	2.72	596
Mopanshan (MPS)	7.14	5.29	3.63	697
Suwannee river humics (SHA) ^b	7.08	4.06	6.26	1103

^a (\bar{M}_n): Number-average molar mass of humics fraction.

^b Inorganic salts were introduced to simulate the natural water (Table S1).

NOM fractions of raw waters, ozonated waters and corresponding ones after adsorption, were analyzed by liquid size exclusion chromatography on a HW50S column (Toyopearl, Japan) coupled with LC-OCD-UVD (Model 9, DOC-Labor Huber, Germany) (Huber et al., 2011). All LC-OCD chromatograms were analyzed and fractionized quantitative results were obtained using automated integration with manually adjusted time frames for each fraction in the ChromCALC software (DOC-Labor Huber). ChromCALC automatically allocates aromatic LMW humic acids, as a part of LMW acids, to the humics fraction. However, considering the impact on micropollutant adsorption, LMW humic acids were assigned into LMW acids here, and the expression of "LMW humics and acids" was adopted. For both LMWOC and LMWUV integration, the local minimum between the building blocks and the LMW humics and acids was used as left integration limit; as right integration limit, the baseline at the end of the chromatogram was used, indicated in Fig. 1 (Zietzschmann et al., 2016b).

The number averaged MW (\bar{M}_n) of humic substances fraction was calculated automatically in ChromCALC by the number of molecules n and molar mass M (Eq. (1)). The MW was calibrated with humic acid (HA) and fulvic acid (FA) standards from IHSS (Eq. (2)). Accordingly, retention time t_r (min) and matching coefficients (A and B) from calibration with IHSS HA and FA was utilized (Huber et al., 2011).

$$\bar{M}_n = \frac{\sum_i (n_i \times M_i)}{\sum_i n_i} \quad (1)$$

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

The molecular characterization for LMW organics was performed by using FTICR-MS. A Bruker Solarix FT-ICR-MS equipped

with a 15.0 T superconducting magnet was applied in this study. Details about extraction, measurement and data analysis are given in the Supporting Information.

2.4. Modeling for competing NOM analysis

The EBC model (EBCM) (Najm et al., 1991), based on the ideal adsorbed solution theory (IAST), as a fictive two-component competitive adsorption model was fitted to the experimental data for all batch-tested waters. The EBCM allocates all observed adsorption competition against a micropollutant (here MIB) in a real water to one competing component, the EBC, which is characterized by Freundlich isotherm parameters ($K_{F,EBC}$, $1/n_{EBC}$) and an initial concentration $c_{0,EBC}$. To increase comparability between the EBCM fitting results for different waters, global $K_{F,EBC}$ and $1/n_{EBC}$ were used for all waters, so that $c_{0,EBC}$ was the only fitting parameter and could therefore be easily correlated to water quality parameters (Zietzschmann et al., 2016a). For each PAC dose, our algorithm searches for the best suiting q_{MIB} and q_{EBC} using the two criteria of the EBC equations (Eqs. (3) and (4)), calculates the corresponding c_{MIB} and c_{EBC} , and determines the corresponding error for each j in the minimization equation (Eq. (5)). The algorithm finds the lowest value of Min , i.e. the best suiting set of EBC parameters, by trying various parameter combinations. Global $K_{F,EBC}$ and $1/n_{EBC}$ were calculated by averaging over the water-individual parameters; using the global parameters, we fitted a second time while only varying $c_{0,EBC}$.

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

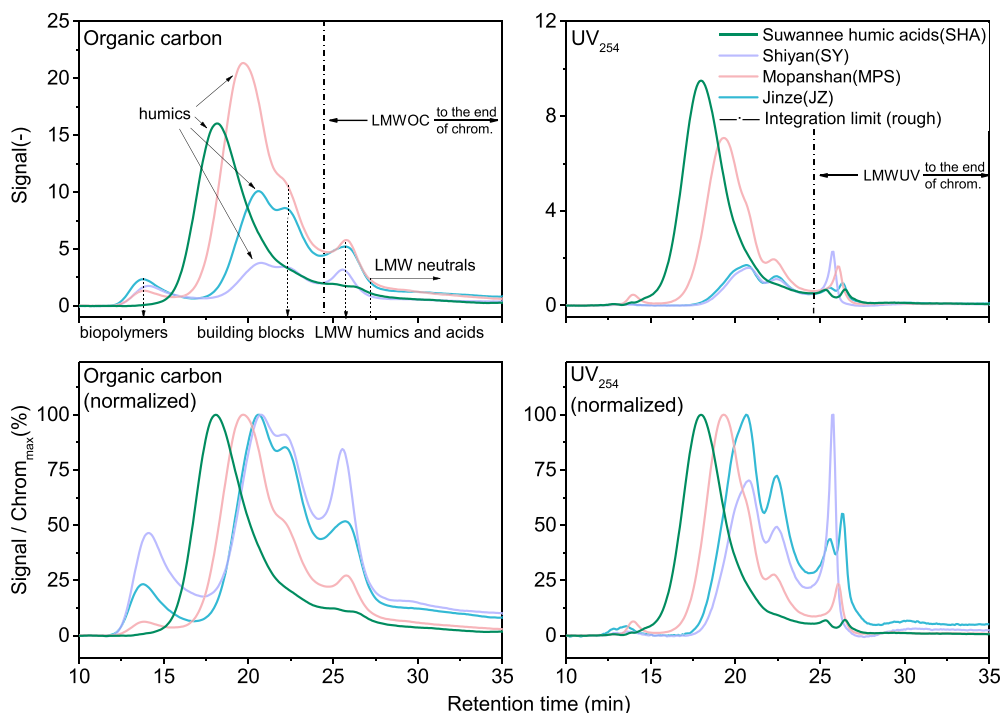


Fig. 1. LC-OCD absolute (top) and normalized (bottom) organic carbon (left) and UV₂₅₄ (right) chromatograms of the examined waters, with approximate position of integration limit and integration range for concentrations of low molecular weight organic carbon (LMWOC) and UV absorbance of LMW organics (LMWUV); exact position of integration limit followed the local minimum between building blocks and LMW humics and acids.

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

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

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

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

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

3. Results and discussion

3.1. Raw water characterization

The pH, DOC concentrations, UV₂₅₄, SUVA and (\bar{M}_n) of the examined waters are shown in Table 1 in ascending SUVA. Their DOC concentrations ranged from 1.39 mg/L in the SY water to 5.29 mg/L in MPS water; the SUVA values ranged from 2.16 to 6.26 L/(mg·m). The SUVA of anthropogenically influenced waters (JZ and SY) was lower than the humic-rich waters (MPS and SHA). (\bar{M}_n) ranged from 546 to 697 g/mol in natural waters and 1,103 g/mol in synthetic SHA water. The highest aromaticity and (\bar{M}_n) of SHA was due to its resin isolation, during which most neutral and hydrophilic fractions with lower SUVA were discarded (Thurman and Malcolm, 1981). For fluorescence pattern, both MPS and SHA waters had typical humic-like peaks, while JZ and SY waters shared similar protein-rich peaks (fluorescence characterization in Fig. S1), but their fluorescence intensities were considerably different.

The LC-OCD chromatograms of the tested waters are shown in Fig. 1, also presenting chromatograms normalized by maximum intensity of each sample for easier comparison on varying DOC concentrations. NOM could be divided into fractions including biopolymers (>20000 g/mol, ~13 min retention time), humics (~1000 g/mol, 17–22 min), building blocks (sub-units of humics, 300–500 g/mol, ~23 min), LMW humics and acids (<350 g/mol, ~27 min), LMW neutrals (<350 g/mol, >29 min) (Huber et al., 2011).

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

2013; Huber et al., 2011). The highest percentage of aromatic humics fraction was observed in SHA water. The (\bar{M}_n) and SUVA of SHA were the highest among all examined aquatic NOM according to investigation of Huber (Huber et al., 2011), which could help examining the behavior of aromatic macromolecules (>1000 g/mol) in ozonation with little impact by LMW fractions in the current study.

3.2. Impacts of ozonation on NOM fractions

The OCD chromatograms of the examined waters within a specific ozone consumption range from 0 to 2.84 mg O₃/mg DOC are shown in Fig. 2 (fractionized quantitative results in Fig. S4). Ozonation led to disintegration of the macromolecules (biopolymers and humics) with increasing peaks of lower molecular weight fractions (Von Sonntag and Von Gunten, 2012; Zietzschmann et al., 2015), but it is interesting to find the different variation patterns of NOM fractions displayed in different waters. SHA water experienced the most obvious reduction of humics and increase in building blocks and LMW humics and acids, with only slight changes of these fractions in JZ and SY waters. The greater increase in building blocks in SHA water may be related to the larger size of the humics precursors, as shown a considerable reduction in the (\bar{M}_n) of the humics in SHA water, from 1103 g/mol in raw water to 601 g/mol under an ozone consumption of 2.84 mg O₃/mg DOC (Table S3). By contrast, (\bar{M}_n) values only varied within narrower ranges in ozonated natural waters (Table S3). An apparent reduction of humics was also observed in MPS water, but the accumulation of LMW fractions did not occur, possibly attributed to the strong mineralization as indicated by the conspicuous decrease of DOC during ozonation (Fig. 2C).

The UVD diagrams of the ozonated waters exhibited overall reduction of UV absorbance for most of the fractions (Fig. S3). Although the DOC reduction differs significantly in four examined waters, the decrease pattern of chromophores in organic matter, indicated by UV, is more similar. Only a mild increase in building blocks peak (~22 min) was observed in SHA ozonated water, caused by the strong shift of the humics peak; this was also supported by the declining absorbance in the fractionized quantitative results (Fig. S5A). At the same time, the aromaticity of all fractions was reduced by ozonation in the natural waters (Fig. S5), independent of the size of fractions. Though the formation of new LMW unsaturated/aromatic compounds was often observed in previous studies (Phungsai et al., 2019; These and Reemtsma, 2005), ozonation would lead to the overall decrease for medium and low MW fractions (Van der Helm et al., 2009). Only slight increments were observed, in terms of UV absorbance of LMW humics and acids, during ozonation of SHA water (cf. Fig. S5A); this could not be observed in ozonated natural waters or wastewaters without such a large proportion of aromatic humics (cf. Fig. 1) (Van der Helm et al., 2009; Zietzschmann et al., 2015).

3.3. Interference of ozonated NOM with MIB adsorption

MIB adsorption experiments were conducted in the four examined waters pre-ozonated under a specific ozone consumption range between 0 and 2.84 mg O₃/mg DOC (see isotherms in Fig. S2). In comparison with the batch in organic-free water, 25–95% of MIB adsorption capacity was lost for all the NOM-containing samples. As shown in Fig. 3, the MIB adsorption capacity in JZ raw water was the lowest, followed by MPS, SY and SHA waters. Accordingly, the highest value of $c_{0,EBC}$ (1858 nmol/L, cf. Fig. 4) in JZ raw water was discovered and $c_{0,EBC}$ was in reverse order with MIB adsorption capacity. It is interesting that the $c_{0,EBC}$ of JZ raw water was over a magnitude larger than that of SHA raw

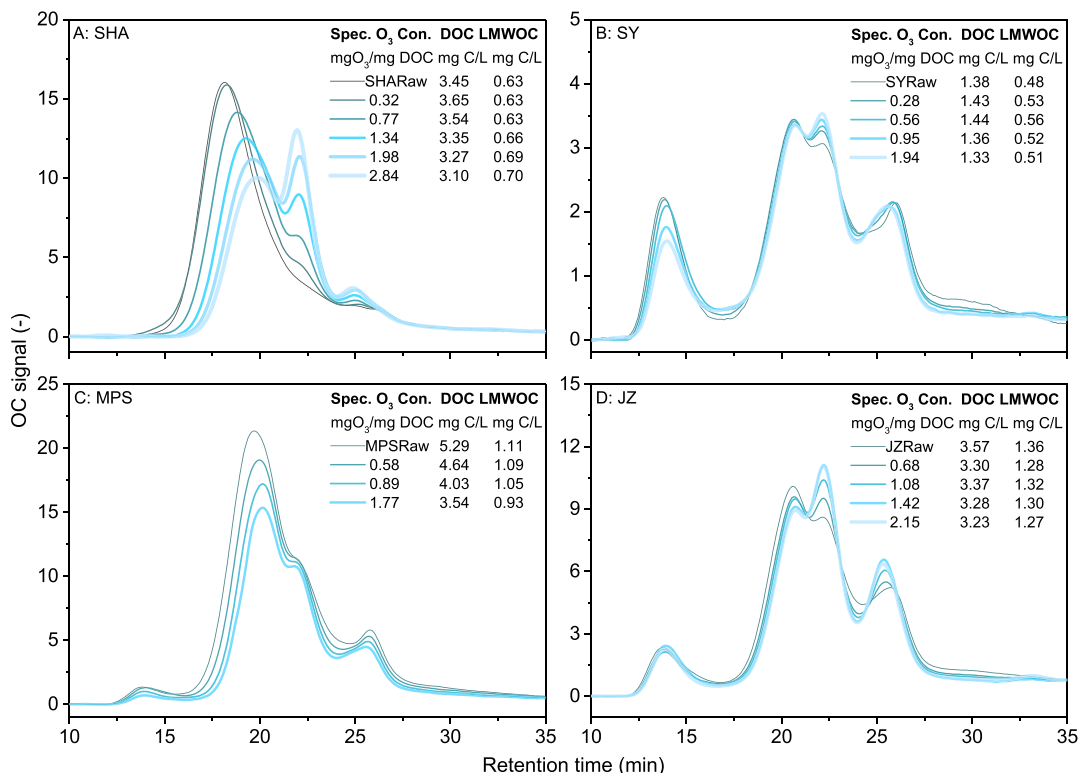


Fig. 2. LC-OCD chromatograms of the examined waters after varying ozonation; the specific ozone consumptions (mg O₃/mg DOC), DOC of bulk organics and LMW organics (mg C/L) are indicated by the legends. Note the different y-axis scales in four chromatograms.

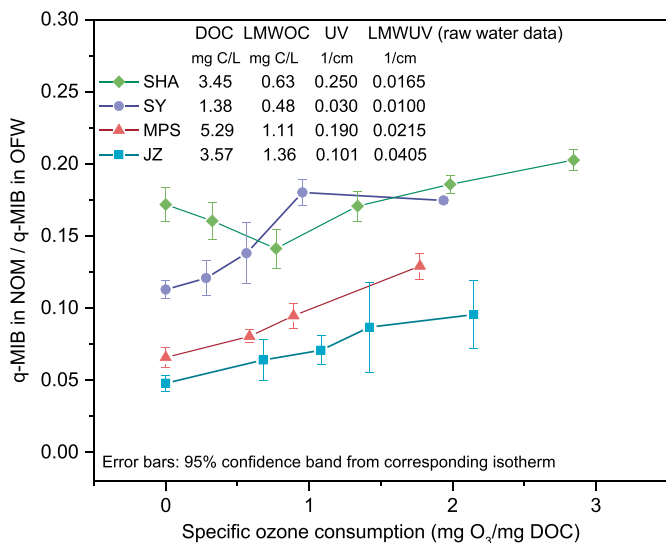


Fig. 3. Ratio of MIB adsorption capacity (at $c_{0,EBC} \approx 0.3$ nmol/L, isotherms in Fig. S2) in NOM-containing samples to that in organic-free water (OFW) over specific ozone consumptions (mg O₃/mg DOC) in the tested ozonated waters, with basic water parameters of raw waters in the legend including DOC (mg C/L), LMWOC (mg C/L), UV (1/cm) and LMWUV (1/cm); error bars based on 95% confidence band of MIB adsorption isotherm.

water ($c_{0,EBC} = 132$ nmol/L) though they had similar DOC. In this respect, NOM interference was not reflected by conventional bulk organic parameters like DOC and bulk UV₂₅₄, underlining the limitation of using these global parameters in explaining the NOM interference on adsorption (Newcombe et al., 2002b; Zietzschmann

et al., 2014). For SHA water, the extremely low $c_{0,EBC}$ indicated the adsorption sites occupied by the SHA might be different from those by MIB. It was reported that the large humics are normally adsorbed on the surface of activated carbon (Ando et al., 2010), while MIB is reported to be mainly associated with the micropores (Yu et al., 2007). Also, the ionizable character induced by resin isolation procedures (elution at low pH, the neutrals and bases fractions discarded), might have accounted for the reported lower adsorption and interference at neutral pH (Hu et al., 2014; Matsui et al., 2012; McCreary and Snoeyink, 1980). The stronger competitive effects in JZ and MPS were likely related to relatively high LMWOC/LMWUV (cf. Figs. 1 and 3).

Regarding the ozonation impacts, it was found that decreasing NOM competition against MIB adsorption in general occurred with increasing ozone consumption for SY, MPS and JZ waters (except for an insignificant increase in SY at the highest ozone consumption), similar with a previous study with wastewater (Zietzschmann et al., 2015). In contrast, an increase in adsorption competition occurred at low/moderate specific ozone consumptions (≤ 0.77 mg O₃/mg DOC) in SHA water, while the competition declined at higher specific ozone consumptions. This is the first time to find a different interference behavior of SHA water under mild ozonation, which might be associated with the enhanced pore accessibility due to the breakage of large humics.

Fig. 4 illustrates the variation of PAC loading with NOM fractions and the corresponding $c_{0,EBC}$ from EBCM-fitting at specific carbon dose (16.5 ± 2.5 mg PAC/mg DOC, cf. Table S2) under different ozone consumptions. Compared with untreated samples, the NOM loading after ozonation experienced notable drops, 20–55% at similar specific ozone consumptions of 2 mg O₃/mg DOC, for the three surface waters; by contrast, the $c_{0,EBC}$ declined more significantly (64–68%). On the other hand, the reduction in

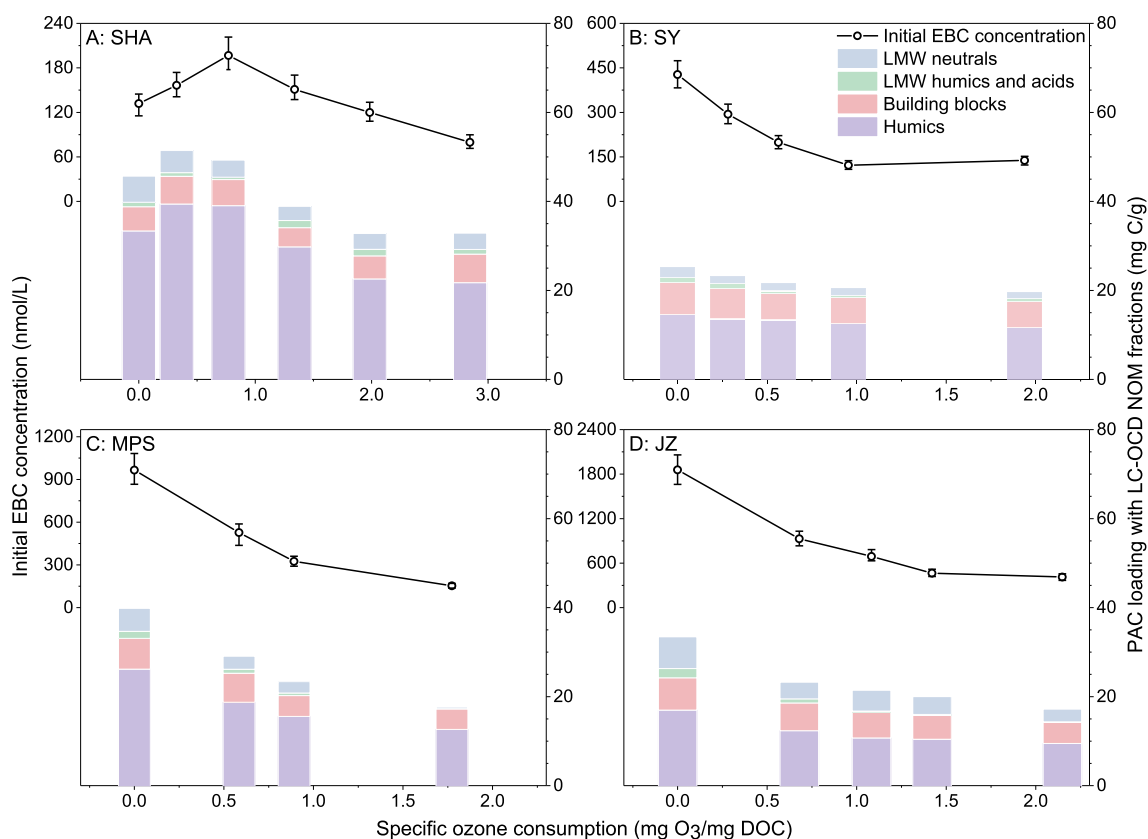


Fig. 4. Variations of initial EBC concentrations ($c_{0,EBC}$, nmol/L) for MIB and PAC loading with LC-OCD NOM fractions (mg C/g), at specific carbon dose (16.5 ± 2.5 mg PAC/mg DOC, cf. Table S2), in dependence of specific ozone consumptions (mg O₃/mg DOC) in the examined waters.

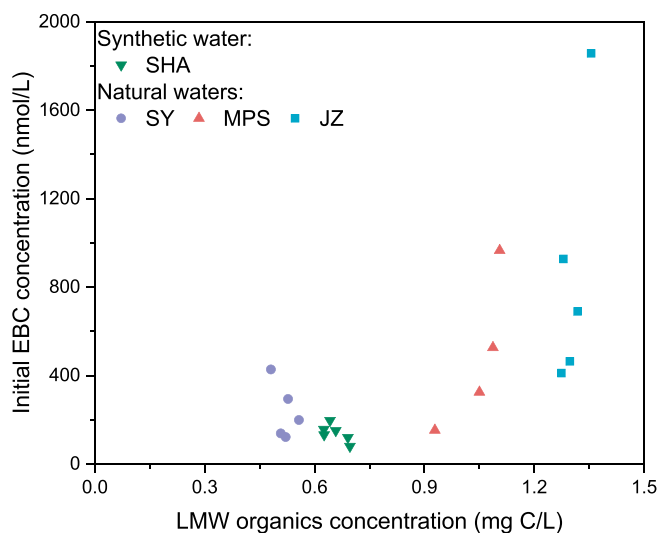
NOM loading was higher for smaller organics than for the humics/building blocks fractions despite the increase of LMWOC concentrations, suggesting the important effect of the decreased affinity of activated carbon due to the destruction of aromaticity by ozonation. In short, the NOM loading on PAC only partly reflected the competitiveness of the corresponding NOM (Zietzschmann et al., 2014).

In contrast to the natural waters, the humic-rich SHA water exhibited a quite different adsorption and interference behavior and it is a valuable instance for elucidating counteracting ozonation impacts on humics fraction in adsorption interference, the descending aromaticity and also declining (\bar{M}_n) (Table S3). In general, the NOM loading and $c_{0,EBC}$ shared the same variation trend during ozonation. Under mild ozonation (≤ 0.77 mg O₃/mg DOC), the enhanced loading of humics fraction, induced by higher pore accessibility from (\bar{M}_n) reduction, was the main positive contributor to the elevated NOM loading (Fig. 4). More pores might be occupied or blocked by smaller aromatic humics and therefore MIB adsorption was restricted. This could not be easily avoided using PAC like SAE Super with abundant secondary micropores and narrow mesopores (data in Table S4 and Fig. S6) as these pores are susceptible to the adsorption or blockage of aromatic humics with lower molecular weight, in line with previous studies (Li et al., 2003). For higher ozone consumptions (1.34–2.84 mg O₃/mg DOC), aromaticity reduction was dominant and NOM adsorbability decreased, just like the ozonation in three natural waters. Hence, scavenging the organic chromophores both in macromolecules and small molecules is the distinct advantage of ozonation to restrict the formation of competing NOM in both synthetic and natural waters, and the increment of competing NOM should also be concerned where MW of humics fraction is high in source waters.

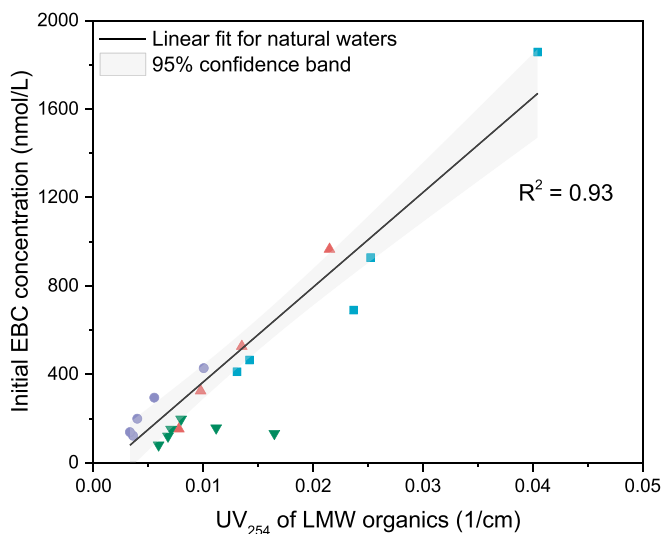
3.4. LMWUV as the key indicator for competitive adsorption

The $c_{0,EBC}$ for MIB are plotted versus LMWOC concentrations and LMWUV absorbance in Fig. 5. No overall relation between $c_{0,EBC}$ and LMWOC concentrations occurred in all examined samples (Fig. 5A). Instead, the LMWUV exhibited a good relation with $c_{0,EBC}$ in natural waters (Fig. 5B, $R^2 = 0.93$, SHA excluded). This appears to contrast with previous studies where LMWOC was also suggested to explain $c_{0,EBC}$ in manifold waters (drinking waters, surface waters, wastewater treatment plant effluents) (Matsui et al., 2012; Zietzschmann, 2016). However, these studies did not induce NOM changes by pre-treatment like ozonation but used only the original natural waters. The results of the current study demonstrated that LMW aromatic organics should be the key NOM fraction reflecting the competitiveness of natural water NOM compounds against MIB. The superiority of LMWUV over LMWOC is that it not only incorporates the concentration of suspected competing NOM but, more importantly, also the character (aromaticity/adsorbability). The correlation in Fig. 5B thus helps to project $c_{0,EBC}$ (or, more generally, prospective adsorption competition) for MIB in both natural waters and ozonated waters with a wide range of specific consumptions (0–2 mg O₃/mg DOC), and simplifies the determination of required PAC doses.

From a mechanistic point of view, the counteracting effects of competing NOM concentration and NOM aromaticity are quite difficult to quantify clearly, complicating a comprehensive evaluation of ozonation effects on NOM-MIB competition. In previous studies, resin fractionation of NOM has been reported to explain the competitive effect (Lerman et al., 2013). Hydrophobic acids and neutrals were found to be primary competitors while the hydrophilic fraction showed little competition. However, each resin



(A)



(B)

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

isolation may contain NOM fractions with different size and strongly variable UV absorbances, distributed over the range of LC-OCD chromatograms (Bolto et al., 1999; Kennedy et al., 2005). Similar wide distributions were also observed after ultrafiltration/nanofiltration fractionization (Newcombe et al., 2002a; Zietzschmann et al., 2014). Therefore, tracing the changing LMWUV with LC-OCD-UVD can have better performance to describe the competing NOM and give overall estimations for $c_{0,EBC}$. In Figs. S7 and S8, further results on LMW organics characterization in JZ water by FTICR-MS reveals that both ozonation and adsorption had preferential performance in reducing the relative abundance of compounds with low O/C value or low H/C value, covering the area reported correlating with UV absorbance, facilitating our LMWUV projection (Lavonen et al., 2015). The high similarity of ozonation

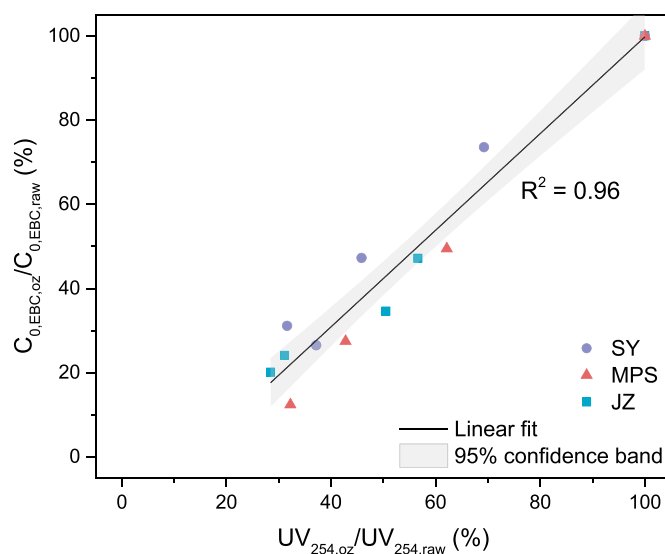


Fig. 6. Degradation of $c_{0,EBC}$ ($c_{0,EBC,oz}/c_{0,EBC,raw}$, $c_{0,EBC}$ in ozonated water/ $c_{0,EBC}$ in raw water) for MIB depicted over the change of bulk UV_{254} ($UV_{254,oz}/UV_{254,raw}$, UV_{254} in ozonated water/ UV_{254} in raw water) during ozonation of the three natural waters.

and adsorption in removal components in the LMW organics also helps confirming the alleviation effect of ozonation on subsequent MIB adsorption in NOM-containing waters.

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

4. Conclusions

- Variable ozonation of three natural waters and an IHSS standard humics solution (Suwannee river humic acids, SHA) resulted in highly heterogeneous NOM with strong variability of the corresponding competitive adsorption against MIB onto PAC. Ozone-induced accumulation of LMW organics were strongly impacted by the molecular weight of humics and DOC mineralization. On the other hand, NOM UV absorbance clearly decreased for nearly all fractions with increasing ozone consumptions.
- NOM adsorption competitiveness against MIB decreased with increasing ozonation intensity in natural waters. By contrast, SHA NOM ozonation caused increased NOM adsorption and competition against MIB unexpectedly for low/moderate ozone consumptions, likely due to increased pore accessibility or blockage by humics with lower

molecular weight. For higher ozone consumptions, this effect was outweighed by the competition-alleviating UV absorbance reduction and NOM adsorbability and competitiveness decline in SHA water. In this respect, SHA NOM behaved differently than NOM from the three natural waters.

- $c_{0,EBC}$ of the EBCM correlated well with LMWUV (synthetic water excluded), underlining the predictability of adsorption competition against MIB in ozonated natural waters and the relevance of incorporating LMW properties into estimating approaches (as opposed to only using LMWOC). Further characterization with FTICR-MS showed that LMW organics with similar molecular properties (low O/C value or low H/C value, covering the area related with UV) were preferentially removed both in ozonation and adsorption.
- Waterworks could use bulk UV to infer $c_{0,EBC}$, and thus optimize the required PAC doses, since LMWUV quantification via LC-OCD is usually not practically feasible, nor available in online measurements.

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.

Acknowledgements

This work was supported by the Major Science and Technology Program for Water Pollution Control and Treatment, China (No. 2017ZX07207004) and National Key Research and Development Program of China (No. 2018YFE0204100). We must thank Dr. Stefan A. Huber and Mr. Sebastian Straub, from DOC-Labor and Ms. Aijun Zhang from the Institute of Seawater Desalination and Multipurpose Utilization for their valuable laboratory assistance on LC-OCD measurement and analysis. Norit Company is also gratefully acknowledged for providing PAC samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115574>.

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