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ORIGINAL PAPER

Effects of organic matter in drinking water and wastewater on micropollutant adsorption to activated carbon

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Abstract

Improving the removal of micropollutants from wastewater effluent is crucial to protect surface water quality. This can be achieved by applying adsorption to granular activated carbon. However, activated carbon filters used for wastewater treatment have a shorter lifetime than filters used for drinking water production. It was assessed whether this is related exclusively to the higher organic matter concentration in wastewater effluent, compared to drinking water, or also to organic matter characteristics. Influent of activated carbon filters from a drinking water plant and wastewater effluent were used as organic matter sources, and their effect on micropollutant affinity for activated carbon and adsorption rate was compared at the same dissolved organic carbon concentrations. Organic matter characterization (excitation–emission matrices and parallel factor—PARAFAC—analysis) and fractionation methods, based on size and hydrophobicity, were combined to assess the relevance of specific components that affect micropollutant removal. The results show that both organic matter concentration and composition determine their effect on micropollutant affinity for activated carbon and adsorption rate. The affinity of micropollutants for activated carbon is more reduced in the presence of organic matter from wastewater effluent. Adsorption rate is lower in the presence of organic matter originating from drinking water plants at levels around 10 mg/L, compared to wastewater effluent. One PARAFAC component is more abundant in drinking water organic matter and is likely responsible for this effect. This knowledge supports the development of strategies to overcome bottlenecks on the application of activated carbon filters in water treatment.

Keywords Adsorption affinity · Adsorption kinetics · Effluent organic matter · Organic matter characterization

Introduction

Granular activated carbon (GAC) filtration is an important technology to remove micropollutants from water. This technology has been applied for decades in drinking water production and, more recently, also in post-treatment of wastewater effluent (Meinel et al. 2015; Benstoem et al. 2017). The latter application is limited by the shorter lifetime of GAC and a faster breakthrough of micropollutants in GAC filters in wastewater treatment plants (WWTPs) compared to drinking water treatment plants (DWTPs) (Altmann et al. 2016). This difference has been attributed to the higher concentrations of dissolved organic matter (DOM) in wastewater effluent and a negative impact of DOM on micropollutant removal (Altmann et al. 2016). However, it remains unknown whether the shorter lifetime of GAC in WWTPs is also related to the different DOM characteristics in wastewater effluent and surface water used for drinking water production.

DOM is a heterogeneous and complex mixture of molecules that can be characterized based on their size and chemical composition. One method to characterize DOM is based on fluorescence spectroscopy, generating excitation–emission matrices (EEMs), which are used to identify the presence of humic-like and protein-like compounds in DOM. Fluorescence-based methods are fast, sensitive and cheap (Bieroza et al. 2009), and have been proposed in several studies as a monitoring technique for water quality

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to predict the total organic carbon removal and the formation of trihalomethanes (Bieroza et al. 2009), DOM biodegradability (Hudson et al. 2008; Goffin et al. 2018) and micropollutant removal (Guillossou et al. 2021). Shimabuku et al. (2017) used EEMs and fluorescence index (ratio of emission intensity 450 nm/500 nm at 370 nm excitation) to infer DOM influence on micropollutant adsorption. These authors concluded that the fluorescence index correlates with the molecular weight of DOM and consequently also with the DOM impact on micropollutant removal by GAC. EEMs can be combined with parallel factor (PARAFAC) analysis to decompose these matrices in different organic matter components. Comparing the components obtained in the PARAFAC model with databases and previous studies gives only indirect information about the chemical nature of the different components in DOM (Murphy et al. 2014). Alternatively, DOM composition can be studied based on membrane and resin fractionation methods, which separate DOM based on size and hydrophobicity (Drewes and Croue 2002; Gijn et al. 2022). Contrary to PARAFAC analysis, these methods provide direct information about the composition of DOM in a sample, with the disadvantage of being more labour-intensive.

Both the chemical composition and the size of DOM molecules affect the extent at which DOM interferes with micropollutant adsorption to GAC. Previous research has shown that the molecular weight of DOM is the most important descriptor for the impact of DOM on micropollutant adsorption. The low molecular weight (LMW) fraction of DOM (<1 kDa) competes more strongly with micropollutants for adsorption sites (Shimabuku et al. 2017), reducing their removal to a larger extent than other DOM fractions. Yet, DOM chemical composition also plays a role on micropollutant adsorption. Wang et al. (2021) used model compounds to represent LMW DOM with different functional groups. The authors observed that the presence of aromatic rings and double/triple bonds increase competitiveness of DOM, even if its hydrophobicity or adsorbability are low.

This study addresses a knowledge gap regarding the shorter lifetime of GAC filters in WWTPs, compared to DWTPs, and its relation to DOM concentration and composition in these two water streams. DOM in drinking water sources and wastewater effluent contains similar fractions, but has small differences. Drinking water sources, such as surface water, contain refractory DOM including humic substances. Wastewater effluent also contains this refractory fraction, but also soluble microbial products and more easily degradable carbon, which are not detected in surface water (Drewes and Croue 2002). The knowledge on the different impacts of DOM originating from drinking water or wastewater effluent on micropollutant adsorption provided in this study can help developing strategies to increase the lifetime of GAC filters in wastewater treatment plants. Two different DOM sources were used: influent of GAC filters from a DWTP and wastewater effluent. The effect of DOM from these two sources on micropollutant adsorption affinity for GAC and adsorption rate was compared. Furthermore, DOM was characterized using a combination of EEMs coupled with PARAFAC analysis and two DOM fractionation methods. To the best of the author's knowledge, this is the first study to combine fractionation and fluorescence-based methods to improve our understanding of the chemical composition of different DOM components identified on PARAFAC models. Our results provide insight into the groups present in DOM from drinking water sources and wastewater effluent and how they impact micropollutant adsorption. The research has been carried out at Environmental Technology, Wageningen University in 2021.

Materials and methods

Micropollutants and granular activated carbon

Eight micropollutants were selected for this study (Table 1) based on their frequent detection in Dutch domestic wastewater effluent and their poor biodegradability (Margot et al. 2015; Thiebault 2020; Paíga et al. 2021; Zhao et al. 2021; Gijn et al. 2022). This selection included compounds with negative, positive and neutral charge at neutral pH. Stock solutions of micropollutants were prepared in acetonitrile or methanol and stored at −20 °C.

GAC (AquaSorb K-CS), a microporous GAC (Piai et al. 2019), was obtained from Jacobi®. The GAC pre-treatment included: (1) sieving to obtain particles with a diameter between 0.5 mm and 0.85 mm; (2) rinsing with demineralized water for one hour to remove impurities; and (3) drying at 105 °C before storage. Immediately before the

Table 1 Molecular weight and charge of micropollutants used in this study

	Molecular weight (g/mol)	Charge at pH 7.0
Benzotriazole	119	Neutral (Margot et al. 2013)
Carbamazepine	236	Neutral (Margot et al. 2013)
N,N-diethyl-meta-toluamide (DEET)	191	Neutral (Wei et al. 2018)
Furosemide	331	Negative (Cho et al. 2021)
Mecoprop	215	Negative (Margot et al. 2013)
Pyrimethanil	199	Positive ("Chemicalize", n.d.)
Sulfamethoxazole	253	Negative (Margot et al. 2013)
Trimethoprim	290	Neutral–positive (Margot et al. 2013)

experiments, GAC was boiled in demineralized water for 20 min to remove entrapped air from the pores.

Dissolved organic matter

Sources and pre-treatment

Two different sources of DOM were used in the micropollutant adsorption experiments: (1) domestic wastewater effluent collected in a dry period from a WWTP in Bennekom (the Netherlands), abbreviated as WWef, and (2) influent of GAC filters from a DWTP using surface water as intake water, operated by Evides Water Company, located in Kralingen (the Netherlands), abbreviated as infGAC. The treatment steps that precede the GAC filters in the DWTP are coagulation/flocculation, sedimentation, rapid sand filtration in double-layer anthracite–sand filters and UV irradiation.

InfGAC was concentrated and WWef was diluted to obtain different dissolved organic carbon (DOC) concentrations. The infGAC originally contained 2.7 mg DOC/L (low DOC level) and was concentrated by nanomembrane filtration to approx. 10.6 mg/L DOC (high DOC level), using a dNF40 membrane and a Mexplorer portable filter (NX filtration, the Netherlands). The nanofiltration was done at a flow rate of 70 L/h at a transmembrane pressure of 3 bar. The concentrated stream was then diluted to approx. 5.9 mg DOC/L (medium DOC level) with demineralized water. WWef containing originally 9.8 mg DOC/L (high DOC level) was diluted with demineralized water to concentrations of 3.2 and 6.1 mg DOC/L, corresponding to the low and medium DOC levels, respectively. These solutions were stored at 4 °C in glass bottles wrapped in aluminium foil until further use.

Dissolved organic matter fractionation and characterization

DOM in infGAC and WWef was characterized using EEMs combined with PARAFAC analysis. PARAFAC analysis was conducted using the software RStudio (1.4.1106) and the StaRdom package (Pucher et al. 2019) to decompose the EEMs. Data pre-processing included: (1) correction of inner filter effects by calculating correcting factors with the samples' absorbance spectra, according to the procedure described in Muprhy et al. (2013); (2) removal of Rayleigh scatter and interpolation of removed scatter areas; and (3) normalization of each EEM to its total signal. The fluorescence index (McKnight et al. 2001) was calculated in staRdom. Model fit was evaluated by split-half analysis. Tucker's congruency coefficient and excitation and emission loadings of different models tested in the split-half analysis are shown in Table S1 and Fig. S1, respectively. The modelling process started with preliminary PARAFAC model development and was repeated several times until a suitable number of components were identified and a stable model was obtained. After determining the appropriate number of components, their loadings in each sample were calculated. Finally, the obtained spectra of the components were compared with previous studies on OpenFluor to interpret the modelling results.

DOM in WWef was fractionated based on hydrophobicity (resin fractionation) and size (membrane fractionation). Additionally, effluent from 4 other WWTPs (WWef2-5) in the Netherlands (Bath, Ede, Epe and Nieuwveen) was also fractionated. Details about the resin and membrane fractionation procedures are described elsewhere (Gijn et al. 2022). Table 2 shows an overview of the different DOM sources used, and the experiments and/or analysis in which they were incorporated.

Adsorption experiments

Micropollutant adsorption experiments (kinetics and isotherms) were performed in batches with both DOM sources (WWef and infGAC) at 3 different DOC levels (low, medium and high). Adsorption isotherms were also performed in demineralized water as a control. A total of 25 mg of GAC was added to glass bottles containing 50 mL of DOM source or demineralized water and the micropollutant mixture. All experiments were buffered with 10 mM of phosphate buffer. The bottles were closed with butyl rubber stoppers and aluminium caps and wrapped in aluminium foil to prevent micropollutant photodegradation. The bottles were incubated at 20 °C in an orbital shaker mixed at 120 rpm. GAC load was calculated based on the difference between the micropollutant initial and final concentration.

For micropollutant adsorption kinetics, initial micropollutant concentration was 2 µM and samples were taken on days 2, 4, 7, 8, 10, 12, 14 and 18. In this set of experiments, the bottles contained sodium azide (100 mg/L) to inhibit biodegradation.

For isotherms, a total of 8 different initial micropollutant concentrations were used, ranging from 0.05 to 2.5 µM. Bottles were sampled on day 14, except infGAC with high DOC level, which was sampled on day 17. Results were fit to the Freundlich equation (Eq. 1) using a nonlinear

Table 2 Overview of streams used as dissolved organic matter source and experiments/analysis in which they were incorporated

	Micropollutant adsorption experiments	Dissolved organic matter fractionation	PARAFAC analysis
infGAC	X		X
WWef	X	X	X
WWef2-5		X	X

optimization method as suggested by Tran et al. (2017), starting from the linearized form of the model (Eq. 2).

$$q_e = K_f c_e^{\frac{1}{n}} \quad (1)$$

$$\log q_e = \frac{1}{n}\log c_e + \log K_f \quad (2)$$

where q_e is the micropollutant load on GAC (µmol/g) at equilibrium, K_f is the adsorption Freundlich constant (µmol /g)(L/ µmol)$^{1/n}$, c_e is the micropollutant concentration at equilibrium (µmol /L) and n is the Freundlich intensity parameter (dimensionless).

In this set of experiments, no biological inhibitor was used to avoid the influence of this inhibitor on the affinity of the micropollutants for GAC. In a separate set of experiments, it was observed that biodegradation was negligible in this experimental setup due to the low biodegradability of the selected compounds and relatively short incubation time (Table S2). Therefore, micropollutant removal due to biodegradation during the adsorption isotherm experiments could be neglected. An adsorption isotherm of DOM, without spiked micropollutants, was performed in a similar setup using 100 mL of WWef at its original concentration (15 mg DOC/L), with varying GAC amounts from 10 to 100 mg.

Micropollutant and DOM adsorption was also assessed in a laboratory-scale GAC filter. The filter was made of a glass cylinder with 2.6 cm internal diameter and 20 cm length. The bed height was 10 cm, and the remaining volume was permanently filled with influent. The filter influent consisted of WWef spiked with micropollutants at a concentration of approximately 1 µM. The influent flow rate was 3.5 mL/min, resulting in an empty bed contact time (EBCT) of 15 min, which is within the practical range applied in full-scale GAC filters as, for example, used in DWTPs (Kennedy et al. 2015). Regular backwash with tap water was performed weekly for 5 min at a flow rate of 3 – 6 L/h.

Analytical methods

Micropollutant concentration was measured using an ultra-high-pressure liquid chromatography (ExionLC™ Series UHPLC, Sciex, USA) equipped with a triple quad mass spectrometer (SCIEX Triple Quad™ 5500 + System, Sciex, USA) according to the method described in Gijn et al. (2022). The limit of quantification was 50 ng/L for all micropollutants, which corresponds to 0.15 to 0.42 nmol/L depending on the micropollutant. The linearity of calibration curves was 0.98 or higher.

Fluorescence measurements were taken using quartz cuvettes and a fluorometer (Luminescence Spectrometer LS50B, PerkinElmer, USA) with emission wavelengths ranging from 280 to 550 nm with an interval of 0.5 nm and excitation wavelengths ranging from 220 to 450 nm with an interval of 5 nm. Excitation wavelengths up to 250 nm were identified as outliers and excluded from the PARAFAC analysis. Slit width for both emission and excitation wavelengths was 5 nm, and the scanning speed was 1300 nm/min. UV–Vis absorbance scan was measured in a 1 cm quartz cuvette using a spectrophotometer (Cary 4000, Agilent, USA) with a wavelength range from 230 to 700 nm.

DOC was measured by a SHIMADZU total organic carbon analyser TOC-L CPH/CPN using a non-purgeable organic carbon method. The sample was pre-treated in the instrument by adding concentrated acid to convert all the inorganic forms of carbon into CO_2, and the CO_2 was flushed away by CO_2-free synthetic air. After that, the sample was injected into a tube filled with a catalyst and kept at 720 °C, where the remaining organic carbon was converted to CO_2 and then measured with a non-dispersive infrared detector. The limit of quantitation was 2 mg/L.

Results and discussion

Impact of DOM on micropollutant affinity for GAC

Micropollutant adsorption isotherms were conducted in three water matrices: infGAC and WWef at three DOC levels and in demineralized water. As expected, micropollutant affinity coefficient (K_f) reduced with increasing DOC concentrations (Fig. 1 and Table S3). Increasing DOC levels from low to medium resulted in a decrease of K_f values from 1 to 63%, depending on the micropollutant. Further increasing the DOC level from medium to high resulted in a further decrease of K_f values from 45% to almost 100%. Of the tested micropollutants, benzotriazole was the micropollutant affected the least by the presence of DOM. Similar results have been reported in previous studies, showing a limited influence of organic matter on adsorption of benzotriazole (Zietzschmann et al. 2014). This can be related to the fact that the reduced availability of adsorption sites due to DOM adsorption might be compensated by benzotriazole adsorption to the DOM itself. Increased adsorption of benzotriazole to soil in the presence of humic acids has been reported and attributed to additional adsorption sites created by the humic acids sorbed to soil (Wu et al. 2020). It is hypothesized that the same mechanism could have happened in the present experiments, given the prevalence of humic acids in the DOM used in this study (see Sect. 3.3). At DOC concentrations below 10 mg/L, the affinity of micropollutants for GAC was generally lower in WWef than in infGAC, indicating that WWef contains higher concentrations of competing

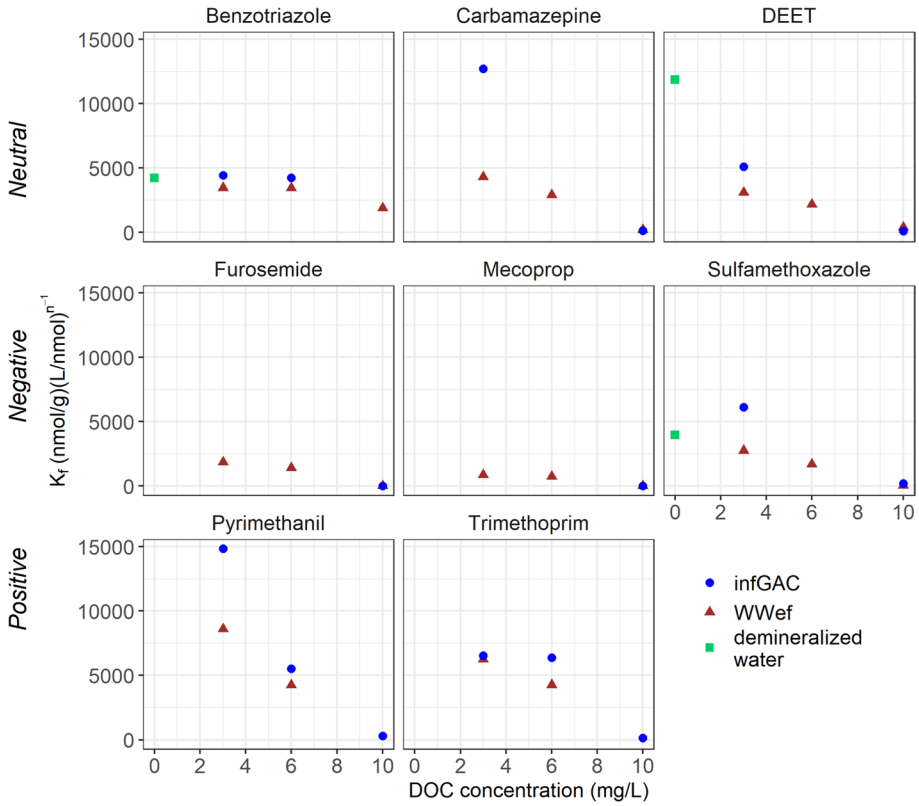

Fig. 1 Freundlich affinity coefficient (K_f) of micropollutants of different charges for GAC at different initial DOC concentrations in three matrices: demineralized water, influent of GAC filters from a drinking water treatment plant (infGAC) and wastewater effluent (WWef). K_f values for experimental curves that could not be fitted to the Freundlich equation ($R^2 < 0.70$) are not displayed

DOM than infGAC. At relatively high DOC concentrations, K_f values were similar for both infGAC and WWef.

Negatively charged micropollutants showed the lowest K_f values already at the low (~ 3 mg/L) and medium (~ 6 mg/L) DOC level (Fig. 1). A stronger impact of DOM on the adsorption of negatively charged micropollutants has been reported in different studies (Margot et al. 2013; Guillossou et al. 2020) and is related to the overall negative charge of the activated carbon surface upon adsorption of DOM (Newcombe 1994). However, it is not clear whether the low K_f value for the negatively charged micropollutants is due to the impact of DOM or also to their inherent low affinity for GAC. As the Freundlich equation did not fit to the adsorption isotherm in demineralized water for most micropollutants ($R^2 < 0.7$), it is not possible to compare the K_f in the absence and presence of DOM for all micropollutants.

Furthermore, the adsorption of micropollutants was assessed in a laboratory-scale GAC filter treating WWef spiked with micropollutants. After 87 days (approx. 8,300 bed volumes), the lowest breakthrough levels were observed for positively charged micropollutants, followed by the neutral micropollutants (Fig. S2). One exception to this trend was benzotriazole, which showed values comparable to the positively charged micropollutants, despite being a neutral molecule. As expected, the relative micropollutant concentration (effluent–influent ratio) at the end of the experiment was in agreement with the adsorption affinities observed in the batch experiments. Furosemide, mecoprop and sulfamethoxazole had the lowest removal in the filter and the lowest K_f values. Benzotriazole, trimethoprim and pyrimethanil had the highest removal in the filter and the highest K_f values (Fig. 1 and S2). These results are in agreement with other studies on the removal of micropollutants using activated carbon (Zhiteneva et al. 2020; Betsholtz et al. 2021; Wang et al. 2022).

Impact of DOM on micropollutant adsorption rate

Micropollutant adsorption rate in infGAC and WWef with different DOC levels was measured. After 14 days, micropollutant adsorption reached or was very close to an equilibrium (Fig. S3). As an indication of adsorption rate, the ratios of GAC load on day 7 (half way through the experiment) and day 14 (final day of the experiment) were compared. The closer this ratio is to 1, the faster the adsorption. In general, lower ratios of GAC load at day 7 to GAC load at day 14 were obtained with increasing DOC levels, indicating that micropollutant adsorption rate correlated negatively with the DOC concentration (Fig. 2). Interestingly, the largest difference for WWef was observed when going from the low (~ 3 mg/L) to the medium (~ 6 mg/L) DOC level, and the adsorption rates were similar at the medium and high DOC levels (10 mg/L). This might indicate that, at the medium DOC level, the GAC is already close to saturation with the

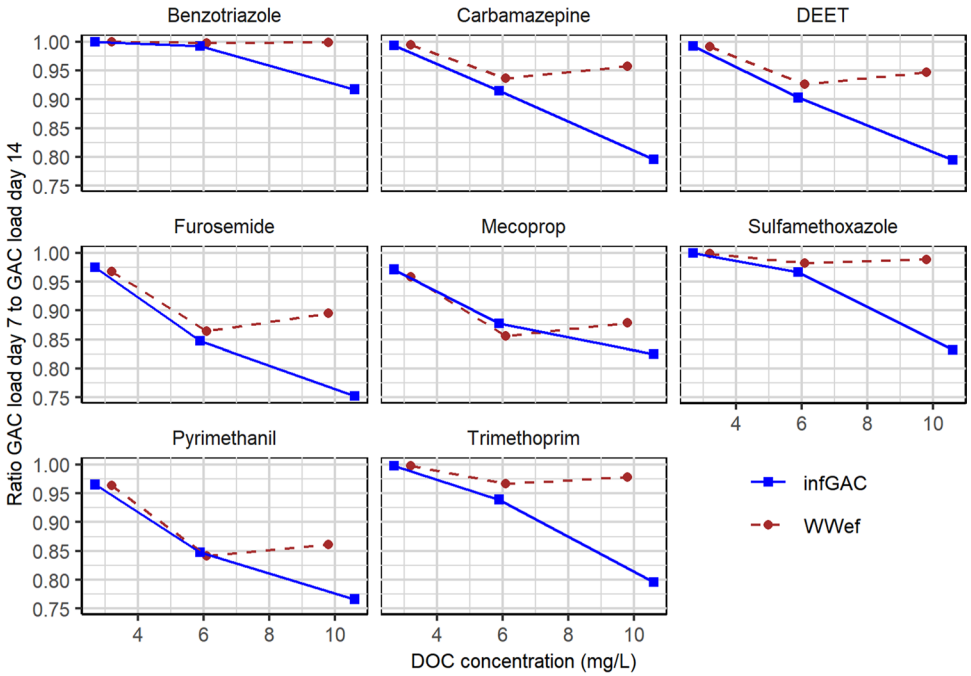

Fig. 2 Ratio GAC load on day 7 to GAC load on day 14 for different initial DOC concentrations in influent of GAC filters from a drinking water treatment plant (infGAC) and wastewater effluent (WWef)

fraction of DOM that contributes to reducing the micropollutant adsorption rate. A different trend was observed for infGAC, where increasing DOC levels from medium to high resulted in a strong reduction of the adsorption rate. As expected, no correlation between micropollutant charge and impact of DOM on adsorption rate was observed, given that adsorption rate is limited by diffusion which correlates more with the size of a molecule, rather than to its charge (Piai et al. 2019).

As expected, a decreasing trend in adsorption rate with increasing micropollutant size (indicated by their molecular weight) was observed, especially at the medium and high DOC levels (Fig. 3). Interestingly, at the high DOC level, the effect of DOM on adsorption rate was stronger with infGAC than with WWef. Such a large difference between both DOM sources was not observed when assessing their effect on micropollutant affinity for GAC. These results show that certain components of the DOM in infGAC, not present in WWef, have a strong impact on micropollutant adsorption rate, but not on micropollutant affinity for GAC.

Dissolved organic matter characterization

DOM in both matrices (infGAC and WWef) was characterized in terms of absorbance and fluorescence. WWef has a higher specific UV_{254} absorbance (SUVA) (Fig. 4a) in all

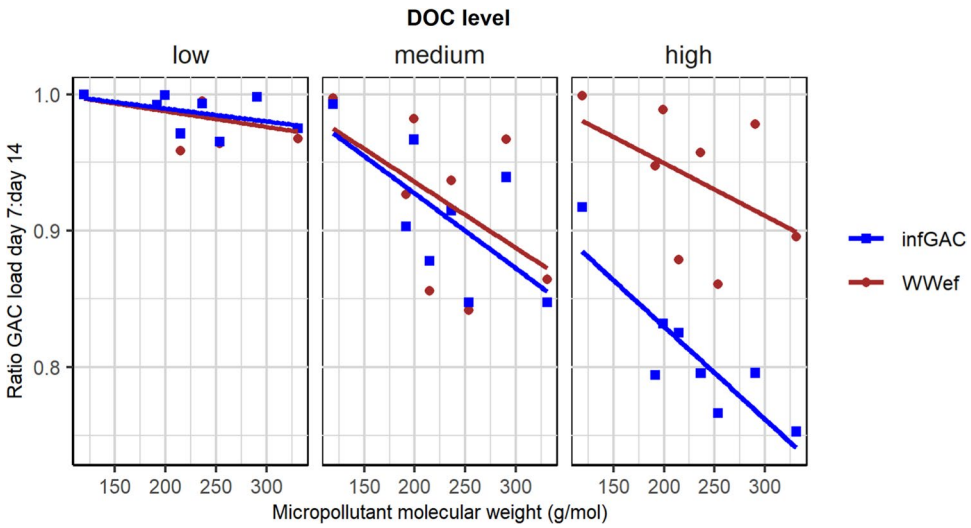

Fig. 3 Ratio GAC load on day 7 to GAC load on day 14 for different initial DOC levels in influent of GAC filters from a drinking water treatment plant (infGAC) and wastewater effluent (WWef)

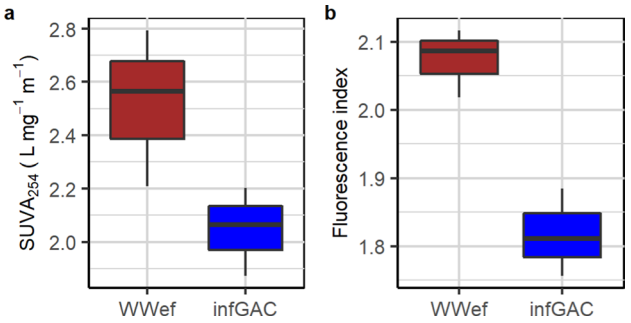

Fig. 4 Specific UV_{254} absorbance ($SUVA_{254}$) (**a**) and fluorescence index (**b**) of influent of GAC filters from a drinking water treatment plant (infGAC) and wastewater effluent (WWef)

DOC levels, indicating a higher degree of aromaticity in the organic matter present in this matrix (Weishaar et al. 2003). Moreover, WWef has a higher fluorescence index (Fig. 4b), an index that correlates negatively with the molecular weight of DOM (Shimabuku et al. 2014); hence, fluorescent DOM in WWef is composed of smaller molecules than DOM in infGAC.

A PARAFAC analysis was performed to decompose the EEMs of all samples in their underlying components. A stable model was obtained when using 4 PARAFAC components (C1 to C4) (Fig. S4). Components C1, C2, C3 and C4 yielded, respectively, 23, 24, 100 and 1 matches on OpenFluor using 0.95 as minimum excitation and emission similarity score. The excitation and emission maxima and matches on OpenFluor are presented in Table 3. No tryptophan- or tyrosine-like peaks were detected in the EEMs.

The loading of these PARAFAC components in the DOM matrices was assessed. C3 has a relatively high loading (33% to 39%) in infGAC, whereas it shows no loading in the WWef samples used in the micropollutant adsorption experiments (Fig. 5). All other components have an absolute and relative higher loading in WWef than in infGAC. A higher loading of C3 in infGAC is therefore the main difference between these two water streams, suggesting that C3 is the component responsible for the higher reduction of micropollutant adsorption rate observed for infGAC at the high DOC level (Fig. 3). The remaining components are likely responsible for the reduced adsorption affinity of micropollutants for GAC in WWef at low and medium DOC levels.

It is known that DOM adsorbability is the most important factor determining its impact on micropollutant adsorption (Wang et al. 2022). An adsorption isotherm with WWef was performed to assess the absorbability of the different PARAFAC components. The absolute loading of all PARAFAC components decreased with increasing GAC dose,

Table 3 PARAFAC components, their corresponding excitation and emission maxima, and characteristics according to references matched on OpenFluor

Component	Excitation maxima (nm)	Emission maxima (nm)	Characteristics
C1	< 250, 345	435	Ubiquitous humic-like component from terrestrial sources (Peleato et al. 2017; Yang et al. 2019)
C2	< 250, 395	480	Terrestrial humic-like (Peleato et al. 2017; Weigelhofer et al. 2020)
C3	255	420	Humic-like (Gonçalves-Araujo et al. 2015; Lambert et al. 2017)
C4	325	395	UV-A humic-like, low molecular weight (Kothawala et al. 2012)

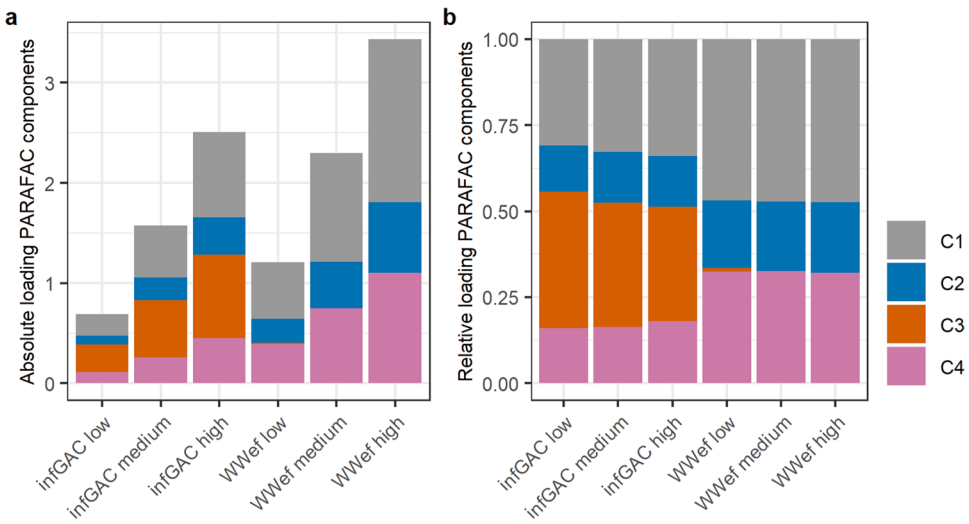

Fig. 5 Absolute (**a**) and relative (**b**) loading of PARAFAC components in influent of GAC filters from a drinking water treatment plant (infGAC) and wastewater effluent (WWef) at different DOC levels (low ~ 3 mg DOC/L, medium ~ 6 mg DOC/L and high ~ 10 mg DOC/L)

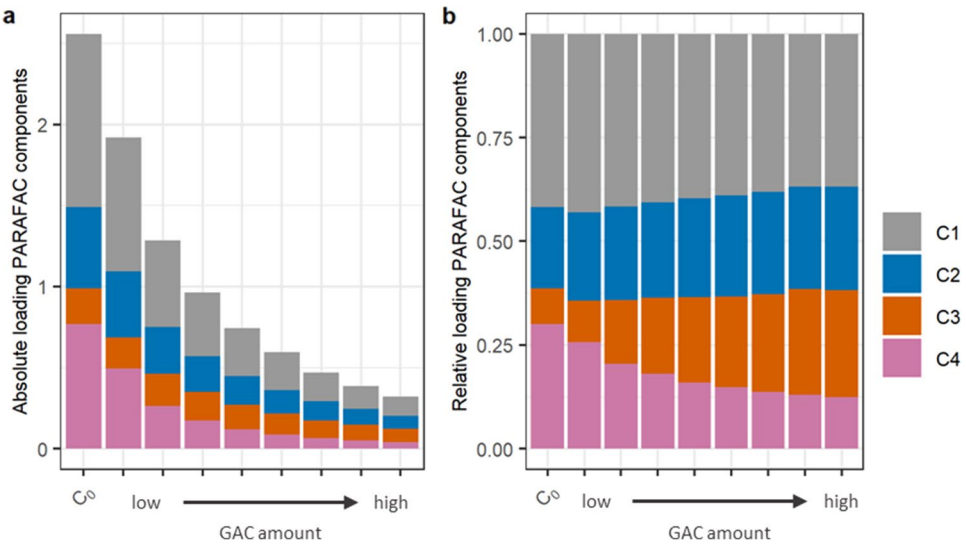

Fig. 6 Absolute (**a**) and relative (**b**) loading of PARAFAC components in adsorption isotherm of wastewater effluent (WWef). C_0 corresponds to initial loading (before addition of GAC)

showing that all PARAFAC components contain adsorbable DOM, although not to the same extent. The order in which the absolute loading of each component decreases is C4 > C1 > C2 > C3 (Fig. 6a), which corresponds to their adsorbability to GAC. Since C3 and C2 are the components that adsorb the least to GAC, their relative loading increases at increasing GAC doses (Fig. 6b). The relative loading of C3 increases the most, i.e. 200% when comparing the lowest and the highest GAC dose, whereas the relative loading of C2 increases by 27%. The relative loading of C1 and C4 decrease with increasing GAC dose by 22% and 59%, respectively.

Interestingly, C3 is the component with the lowest affinity for GAC and yet has a strong impact on micropollutant adsorption rate. One possible explanation is that C3 forms complexes with the micropollutants studied, reducing their diffusion rate in the GAC. A similar finding has been reported by Guillossou et al. (2020), who observed that adsorption of some micropollutants to powder activated carbon was negatively impacted by the presence of effluent DOM only in the first 30 min of adsorption, but sufficient contact time (72 h) resulted in a similar removal as in the absence of DOM. The authors proposed that this effect is a result of the formation of DOM–micropollutant complexes that diffuse slower than free micropollutants. Another explanation proposed by Guillossou et al. (2020) and also applicable to the present study is the blockage of GAC pores by DOM. The infGAC has larger molecules than WWef, as indicated by a lower fluorescence index, and C3 is a component present in infGAC at higher loadings than in WWef. Therefore, it is hypothesized that C3 contains DOM of relatively large molecular weight, which by adsorbing to GAC also decreases the diffusion of micropollutants without impacting their affinity for GAC. Since C3 contains weakly adsorbable DOM, only a high DOC concentration can an effect on micropollutant adsorption rate; hence, this is only observed at the highest DOC loading. Similar results have been reported by Shimabuku et al. (2017), who showed a negative correlation between fluorescence index of DOM (at 4 mg DOC/L) and tortuosity of GAC. The authors concluded that large molecular weight DOM (identified by a low fluorescence index) experiences size exclusion effects and affects micropollutant removal due to pore blockage, and not due to direct competition for adsorption sites.

The order of adsorbability of each PARAFAC component in the WWef adsorption isotherm corresponded also to their order of adsorbability in the laboratory-scale GAC filter (Fig. S5). All PARAFAC components were present in the filter effluent from day 1 onwards, indicating that none of the fractions were adsorbable to GAC and/or that the EBCT was too short, resulting in high levels of mass transfer limitation in the film layer around the GAC particles. Each PARAFAC component corresponds to a mixture of different molecules sharing similar fluorescing properties. Hence, each component contains molecules with different degrees of adsorbability and non-adsorbable molecules, which would explain the immediate breakthrough of all components. Nevertheless, the relatively short EBCT (15 min) can still affect adsorption of DOM with lower diffusion rates, i.e. larger molecules of DOM, limiting their adsorption in the filter. This supports the hypothesis that C3 contains a significant fraction of relatively large molecules, resulting in a higher level of breakthrough (62%) than the other components already at the beginning of the experiment.

Dissolved organic matter fractionation

Information about the chemical nature of PARAFAC components can be obtained by comparing their EEMs with previous research, characterizing DOM from different sources

and of different types (Murphy et al. 2014). However, this strategy provides only indirect information about the chemical nature of PARAFAC components. To gain more insight into the molecular size and hydrophobicity of each PARAFAC component, DOM in effluent from 5 different WWTPs was fractionated using membrane and resin fractionation methods and the loading of each PARAFAC component in these fractions was assessed.

After resin fractionation, the relative loading of hydrophobic fractions of DOM was enriched in C3, especially the hydrophobic neutrals, whereas the loading of the hydrophilic fraction was reduced (Fig. 7). This was unexpected since C3 is the least adsorbable of the 4 PARAFAC components and hydrophobic DOM is supposed to adsorb better to GAC than hydrophilic DOM (Jamil et al. 2019). The enrichment of C3 in hydrophobic fractions is another indication that the lower adsorbability of C3 to GAC is due to size exclusion effects and not due to low hydrophobicity. C3 was also the component that presented the highest variance in terms of loading in the 5 WWTPs (Fig. 7b). However, its enrichment in the hydrophobic fractions and reduced loading in the hydrophilic fraction was consistent across the 5 WWTPs. Also unexpected is the fact that the components with higher adsorbability, C1 and C4, are enriched in the hydrophilic fraction, even though hydrophilicity is in general negatively correlated with affinity for GAC (Jamil et al. 2019). These results reveal the complexity of organic matter composition and the need to further understand the connection between the different characterization and fractionation methods used to monitor water quality.

PARAFAC components could not be completely separated with resin fractionation, i.e. all fractions contained all components, although at different relative loadings. Similar results were obtained by He and Hur (2015), who observed that the source of DOM influenced which PARAFAC components were more abundant in each resin fraction.

The loading of the 4 PARAFAC components in two membrane fractions with a cut-off between 1 and 10 kDa and smaller than 1 kDa was also calculated. No large differences were observed in the relative loading of PARAFAC components in each fraction, except that the LMW fraction (< 1 kDa) was enriched in C4 (Fig. 8a). This finding can explain why C4 is the most adsorbable of the PARAFAC components. LMW DOM is known to adsorb well to GAC and compete more strongly with micropollutants (Zietzschmann et al. 2014). The higher abundance of C4 in WWef than in infGAC explains why micropollutant affinity for GAC (indicated by the K_f values) was generally lower in WWef at low and medium DOC levels. At high DOC levels, the difference between the micropollutant affinity for GAC in these two streams becomes smaller, likely because at high DOC concentrations other components of the DOM also become stronger competitors with micropollutants.

A large variance was observed for the loading of C3 among the 5 effluents analysed, making it difficult to draw conclusions regarding the prevalent molecular size of the DOM in this component. For WWTPs 3 and 5, C3 was enriched in the larger DOM fraction (between 1 and 10 kDa), which would be in line with the hypothesis that this component is responsible for the reduced adsorption kinetics of micropollutants due to its large size. However, in the other WWTPs, C3 was as abundant in both fractions or slightly reduced in the larger fraction. This inconsistency could be related to the high variance of relative loading of C3 in the WWTP effluent samples (ranging between 0.07 and 0.32).

The results presented in this study provide insight into the specific groups of compounds in DOM that affect micropollutant removal with GAC by using fractionation and fluorescence-based methods. Whereas fractionation methods

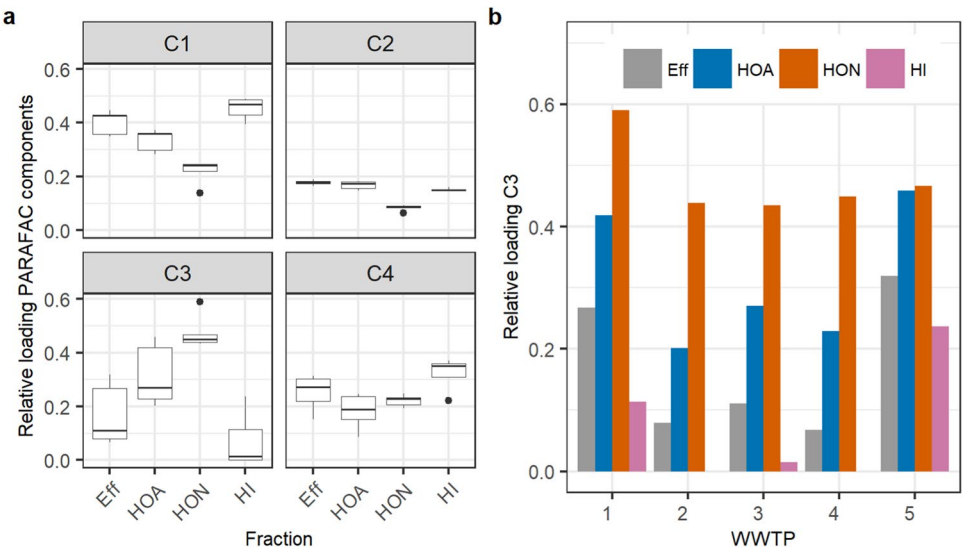

Fig. 7 Relative loading of PARAFAC components in wastewater effluent from 5 WWTPs before (Eff) and after resin fractionation (**a**) and relative loading of PARAFAC component C3 for each WWTP individually (**b**). HOA: hydrophobic acids; HON: hydrophobic neutrals; HI: hydrophilics

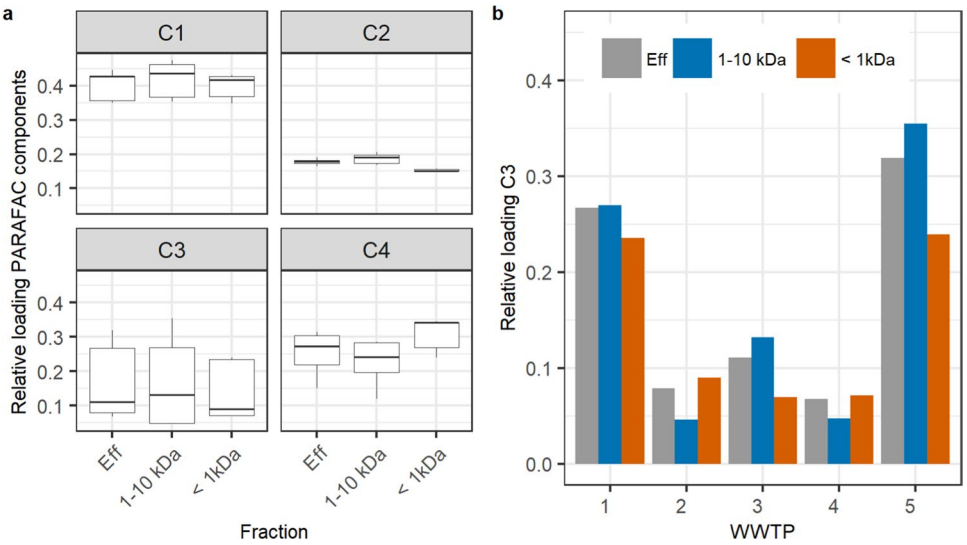

Fig. 8 Relative loading of PARAFAC components in wastewater effluent from 5 WWTPs before (raw effluent) and after membrane fractionation (**a**) and PARAFAC component C3 for each WWTP individually (**b**)

are labour-intensive and not suitable for routine measurements, fluorescence-based methods are relatively cheap, fast and suitable for monitoring purposes and routine measurements. We propose to expand the approach of combining these methods to a larger number of WWTP effluents and to influent of GAC filters from different DWTPs. This will help elucidating the chemical properties of the components identified in the PARAFAC analysis and will expand the applicability of fluorescence methods to predict micropollutant removal with GAC filters.

Conclusion

Both DOM concentration and composition determine its effect on micropollutant affinity for GAC and their adsorption rate. A stronger effect of DOM originating from WWTP effluent on micropollutant affinity was observed, compared to DOM originating from DWTPs. These results showed that the lower lifetime of GAC in post-treatment of WWTP effluent is related not only to the relatively higher DOM concentration, but also to the DOM composition. Furthermore, a stronger effect of DOM from DWTPs than from WWTPs at DOC levels around 10 mg/L was observed with respect to micropollutant adsorption rate. One PARAFAC component (C3) was more abundant in drinking water DOM and was identified as potentially responsible for reducing the rate of micropollutant adsorption. These novel findings are relevant for transferring GAC-based technologies from drinking water to wastewater treatment. Nevertheless, the reduced adsorption rate was observed only at DOC levels higher than occurring in GAC filters in DWTPs; hence, such a strong reduction in micropollutant adsorption rate is not expected in DWTPs.

In this study, different methods of DOM characterization (EEM + PARAFAC) and DOM fractionation were combined. This combination showed the relevance of specific groups of compounds in DOM that affect micropollutant removal with GAC. Expanding this strategy to study a larger number of WWTPs and DWTPs can help to stablish a correlation between cheap and simple characterization methods, such as EEMs, and more labour-intensive fractionation techniques. This allows a better understanding of the chemical composition of DOM components identified in PARAFAC analysis, expanding the applicability of fluorescence methods and their usefulness to predict micropollutant removal with GAC.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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