Impact of different DOM size fractions on the desorption of organic micropollutants from activated carbon

Aschermann, Geert; Neubert, Lino; Zietzschmann, Frederik; Jekel, Martin

DOI
10.1016/j.watres.2019.05.039

Publication date
2019

Document Version
Accepted author manuscript

Published in
Water Research

Citation (APA)
Aschermann, G., Neubert, L., Zietzschmann, F., & Jekel, M. (2019). Impact of different DOM size fractions on the desorption of organic micropollutants from activated carbon. *Water Research*, *161*, 161-170. https://doi.org/10.1016/j.watres.2019.05.039

Impact of different DOM size fractions on the desorption of organic micropollutants from activated carbon

Geert Aschermann[a)*)], Lino Neubert[a)], Frederik Zietzschmann[a) b)], Martin Jekel[a)]

*Corresponding author, e-mail: geert.aschermann@tu-berlin.de

[a)] Technische Universität Berlin, Chair of Water Quality Control, KF 4, Str. des 17. Juni 135, 10623 Berlin, Germany

[b)] Delft University of Technology, Department Water Management, P.O. Box 5048, 2600GA Delft, Netherlands

Highlights

- Organic micropollutant (OMP) desorption batch tests with 3 activated carbons (AC)
- Low (lmw) and high molecular weight (hmw) DOM fractions used as background matrix
- Effects on OMP desorption extent are similar for lmw- and hmw-DOM fraction
- Macroporous AC shows enhanced desorption of OMP, independent of DOM composition
- Microporous AC shows irreversible OMP adsorption, independent of DOM composition

Abstract

Whereas the adsorption of organic micropollutants (OMP) onto activated carbon (AC) is relatively well studied, little is known about potential OMP desorption effects, especially in real waters. In this study, the impact of different fractions of drinking water DOM on OMP desorption from AC was examined. By different pre-treatments of a raw drinking water, a high molecular weight (hmw) and a low molecular weight (lmw) DOM solution were prepared. These solutions were used as background matrix in AC adsorption/desorption batch tests, simulating a drop of the OMP inflow concentration to a fixed-bed adsorber. The tests were conducted in parallel with three AC of different pore structures (microporous, mesoporous/balanced, macroporous). The tests were evaluated with respect to the extent of OMP adsorption and its reversibility, which represents the potential extent of OMP desorption. In terms of OMP adsorption, the lmw-DOM fraction induced a higher competitive effect on OMP adsorption in comparison to the hmw-DOM fraction. In terms of their impact on OMP desorption extent, both fractions led to very similar results. In case of the macroporous AC, both DOM fractions induce an enhanced OMP desorption that can be attributed to displacement effects in both cases. For the microporous AC, an increased irreversibility of OMP adsorption was found in both cases, which shows that DOM adsorption prevents OMP desorption, independently of the size of the adsorbed DOM compounds. Whereas results from this study as well as from former studies indicate that this effect might be induced by permanent pore blockages by adsorbed DOM, further results show that there could be more complex DOM interactions that lead to the decreased desorption in case of microporous AC. Nonetheless, the very similar impact of the different DOM fractions on the reversibility of OMP adsorption indicates that the potential extent of desorption is similar in

different waters (with different DOM composition) and primarily depending on the pore structure of the used AC.

Keywords

activated carbon, organic micropollutants, desorption, adsorption, drinking water, dissolved organic matter

1. Introduction

The application of activated carbon (AC) is a promising method for the removal of organic micropollutants (OMP), in drinking water treatment as well as in advanced waste water treatment (Boehler et al. 2012, Westerhoff et al. 2005, Zietzschmann et al. 2016a, Zietzschmann et al. 2016b). This removal is caused by the adsorption of the compounds onto the AC surface. Due to the rather weak binding forces that occur in this process, it is often assumed to be reversible (Crittenden et al. 2005, Worch 2012), which means that already adsorbed compounds can also desorb again. In terms of water treatment, desorption of target compounds, such as OMP, during the process is undesired as it leads to increased effluent concentrations. Desorption of adsorbed OMP can generally be induced by a) a reversal of the concentration gradient (e.g. due to decreased influent concentrations) and b) by the displacement by other better adsorbing compounds (competitive adsorption). Especially, granular AC filters might be affected by desorption as the AC remains much longer in the system than the treated water. This allows the AC surface to be continuously loaded as well as the influent water composition to change over the course of a filter run.

Generally, it can be assumed that the desorption behavior of a compound in AC filters is affected by the extent of desorption and the corresponding desorption kinetics. It has been shown that the extent of OMP desorption under real conditions can be strongly influenced by the adsorption of background dissolved organic matter (DOM). The actual effect of DOM on desorption depends on the AC pore structure. For macroporous AC, DOM adsorption aggravates the concentration reversal-driven desorption of OMP, whereas microporous AC show stronger irreversibility effects and, thus, lower desorption (Aschermann et al. 2018).

It is known that different DOM size fractions can generally adsorb onto AC, e.g. larger humic compounds as well as low molecular weight compounds (Velten et al. 2011). Different studies show that the adsorption of these different fractions affects OMP adsorption, as they lead to different competitive effects. Several studies indicate that low molecular weight compounds induce higher competitive effects compared to larger DOM constituents and lead to lower adsorptive OMP removal (Hu et al. 2016, Zietzschmann et al. 2014). It is assumed that smaller DOM compounds lead to direct competition on adsorption sites, whereas larger compounds decrease OMP adsorption as they block the AC pores and, thus, reduce adsorption capacity (Li et al. 2003a, Li et al. 2003b). However, a clear attribution of these effects to the different DOM fractions is still missing.

In terms of adsorption, both effects, direct competition and pore blocking, lead to the same result: a lower adsorption capacity. In terms of desorption, it has to be assumed that these effects have different impacts. Direct competition would increase desorption due to displacement, whereas pore blocking would decrease desorption due to steric hindrance. This could explain the different effects of DOM that were observed in a previous study (Aschermann et al. 2018).

Due to these potentially different effects it is necessary to understand which DOM fractions induce these effects. Thus, it is the goal of the current study to use adsorption and desorption batch tests to identify the impact of different DOM size fractions on OMP desorption. These tests were conducted (i) in the presence of differing DOM size fractions to understand their effects, and (ii) with different AC products to evaluate the impact of different pore size distributions.

The results will help to estimate the desorption behavior of different waters with different or varying DOM composition, which would provide beneficial information for water utilities to estimate potential desorption effects in their system.

2. Material and Methods

2.1. Activated carbons

Three commercial activated carbons (AC) were used for lab batch experiments: Hydraffin CC, Epibon A (both Donau Carbon, Germany) and HC HK 1200 (CSC, Germany). The granular products were pulverized on a Pulverisette mill (Fritsch, Germany) and sieved (Retsch, Germany) to obtain powdered activated carbon with particle sizes below 63 µm. Before usage the AC material were dried at 105°C overnight and stored in a desiccator until experimental usage.

These powdered AC samples were characterized in a previous study (Aschermann et al. 2018) with respect to their pore structure (cf. Supporting Information). Based on the relative differences in their pore size distribution, which can be reflected by the average pores size, they can be classified as microporous (Hydraffin CC, average pore size: 1.7 nm), mesoporous (Epibon A, average pore size: 2.4 nm) and macroporous (HK 1200, average pore size: 3.3 nm) products. (Note that this classification is not based on the definition of micro-, meso-, and macropores by IUPAC, but should reflect the differences in the pore structures among the tested AC in a qualitative manner.)

Furthermore, the pH, at which the surface of the particular AC has equal amounts of negative and positive charges (referred to as point of zero charge) (pH_{pzc}), was determined according to the indirect titration method (Sontheimer et al. 1988). This method is described in the Supporting Information more detailed. The resulting pH_{pzc} are 9.5 (Hydraffin CC), 8.1 (Epibon A) and 3 (HK 1200), respectively.

2.2. Organic micropollutants

Five substances were studied in the experiments, which represent typical OMP: carbamazepine, diclofenac, 4-formylaminoantipyrine, sulfamethoxazole (all Sigma Aldrich, Germany) and iomeprol (Dr. Ehrenstorfer, Germany). They were initially prepared as single stock solutions with a concentration of 20 mg/L and then mixed in a stock solution with concentrations of 2 mg/L of each OMP. From this mixed stock solution certain amounts were taken to spike particular experimental solutions.

2.3. Experimental solutions

Experiments were conducted with different background solutions, which were used as adsorption (spiked) and as desorption (unspiked) solution. These solutions were prepared from Berlin drinking water (taken from laboratory tap after adequate flushing). This raw water was also used for previous desorption studies (Aschermann et al. 2018). With the goal of preparing a low molecular weight (lmw) DOM solution and a high molecular weight (hmw) DOM solution, the water was treated in two different ways. These pre-treatment steps are schematically shown in Figure 1.

For the preparation of the lmw-DOM solution, 90 mg/L Al^{3+} was added as $AlCl_3$ solution. Under stirring the pH was adjusted to a value of 6 by adding NaOH to form flocks. After additional slow stirring the formed flocks were removed by 0.45 µm filters (Th. Geyer GmbH & Co. KG, Germany). The filtrated solution was transferred to a SIMAtec LSta80 bench scale filtration unit with a TS40 nanofiltration membrane (TriSep, USA) with a molecular weight cut-off (MWCO) of 200 to 300 daltons (according to manufacturer data). The solution was filtrated in cross-flow mode with an applied pressure of 35 bar. Filtration was stopped at a recovery of 80 percent. The resulting concentrate was collected.

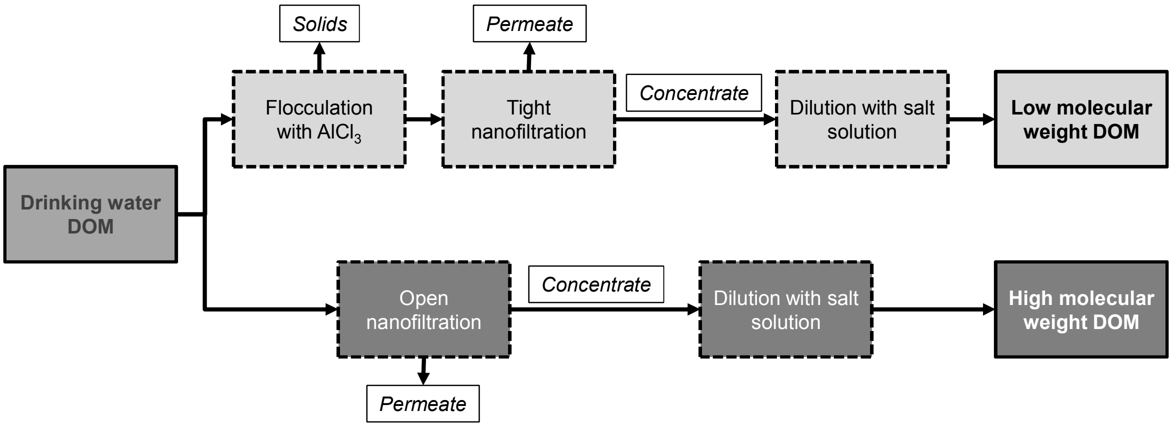

Figure 1: Schematic description of preparation procedure for the low molecular weight and the high molecular weight DOM solutions.

The hmw-DOM solution was prepared by use of the same membrane filtration unit under the same operating conditions, by filtering the raw drinking water using a NP010 nanofiltration membrane (Microdyn-Nadir,Germany, MWCO ~ 1000 daltons (Machado et al. 2016)). The resulting concentrate (at 80% recovery) was collected.

Both concentrate samples were diluted to a goal DOC level of 5 mg/L. Therefore, a salt solution with a similar ionic composition as the raw drinking water was used. The detailed composition of this solution can be found in the Supporting Information. The resulting pH values were 7.3 (hmw-DOM-solution) and 7.6 (lmw-DOM solution), respectively. The concentrations of the analyzed OMP in both prepared solutions were below the respective limit of quantification (LoQ) of the used analytical method (see 2.5).

2.4. Experimental procedure

Different laboratory batch experiments were conducted with the three activated carbon products in parallel. Therefore, AC stock suspensions (0.8 and 5 g/L) were prepared with ultra pure water. Prior to the experiments, the suspensions were degassed and subsequently homogenized with a magnetic stirrer. Every single experimental series consisted of seven batches with different doses of the respective AC (also meaning that no replicates were prepared). The doses were 50, 30, 14, 8, 4, 3 and 2 mg/L AC.

2.4.1. Desorption batch tests with simultaneous adsorption of DOM and OMP

Batch tests were conducted, which simulated a decrease of the OMP inflow concentration in an AC system during an ongoing treatment process. Therefore, for each batch 100 mL of a solution, which was previously spiked with OMP to a concentration level of ~ 50 µg/L ("adsorption solution"), were filled into centrifuge flasks (175 mL, Falcon, USA). Certain amounts (between 250 and 1000 µL) of the AC stock suspensions were added to the individual flask to obtain the above-indicated AC doses. After a contact time of 48 hours on a horizontal shaker the AC was separated by centrifugation, 95 mL AC-free adsorption solution were drawn off and replaced by 100 mL unspiked desorption solution (with OMP concentrations below the limit of quantification). Subsequently, the batches were shaken for another 48 hours, which could be identified as adequate contact time to achieve equilibrium conditions (Aschermann et al. 2018). Adsorption and desorption samples were immediately filtrated using 0.45 µm regenerated cellulose membrane filters (Chromafil Xtra, Macherey-Nagel, Germany). A detailed description of the experimental procedure can be found elsewhere (Aschermann et al. 2018).

Additional experiments, generally following the same procedure, were conducted that also consisted of simultaneous adsorption of DOM and OMP (as described above). However, in these experiments the desorption solution was pure water (not the respective DOM solution).

2.4.2. Desorption batch tests with sequential adsorption of DOM and OMP

For sequential adsorption, equivalent AC doses were added to the unspiked lmw-DOM and hmw-DOM solutions, respectively. After 48 hours contact time a certain volume of the OMP stock solution was added to each individual batch to achieve again concentrations of ~ 50 µg/L in the respective batches. Subsequently, the batches were shaken for another 48 hours. AC was then separated as described above and 100 mL desorption solution were added, which was pure water in this case. The contact time during the desorption phase was 72 hours for these experiments.

2.5. Analytics

High performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) was used for measurements of OMP concentrations, following a method established previously (Altmann et al. 2015, Zietzschmann et al. 2016a). An XSelect HSS T3 column (2.1 * 50 mm, Waters, USA) with 2.5 µm particle size was used for separation. Mobile phases were ultra-pure water with 0.1 vol.-% formic acid (HPLC grade, Sigma Aldrich, Germany) and pure methanol (HPLC grade, J.T. Baker, USA), pumped with a flow rate of 0.5 mL/min and with a linear gradient. After electrospray ionization in positive mode the formed ions were analyzed with a triple quadrupole mass spectrometer TSQ Vantage (Thermo Scientific, USA). For substance identification the characteristic ratio of two mass fragments were used, which were chosen according to DAIOS database provided by Zweckverband Landesversorgung (Stuttgart, Germany). Concentrations were determined using the more abundant fragment, in combination with deuterated internal standards (Toronto Research chemicals, Canada) and after data evaluation with Xcalibur 2.1 software (Thermo Scientific). Calibration levels (9 in total) were between 0.01 and 55 µg/L. The limits of quantification (LoQ) of this method are 0.05 µg/L (for carbamazepine and sulfamethoxazole) and 0.1 µg/L (for diclofenac, 4-formylaminoantipyrine and iomeprol), respectively. LoQ were chosen as the calibration level at which the less abundant fragment ion (qualifier) had a signal to noise ratio of ≥3.

DOC was determined with a varioTOC Cube (elementar Analysensysteme, Germany) using high-temperature catalytic combustion and non-dispersive infrared detection of formed CO_2. UV_{254nm} was measured with a Lambda 12 photospectrometer (Perkin-Elmer, USA) with 10 mm Spurasil quartz cuvettes (Hellma, Germany).

For further characterization of organic carbon composition, selected samples were analyzed with liquid chromatography coupled with an online organic carbon detector (LC-OCD, DOC-Labor Dr. Huber, Germany), using a HW50S size exclusion column (Toyopearl, Japan). According to Huber et al. (2011) molecular weight calibration was performed using Suwannee river humic and fulvic acid from the International Humic Substances Society (IHSS). Data processing was conducted using the software ChromCalc (DOC-Labor Dr. Huber, Germany). DOM can be generally classified into different sub-fractions by means of the resulting LC-OCD chromatogram (in order of increasing elution time): biopolymers (macromolecular compounds, such as polysaccharides and proteins); humic substances;

building blocks (breakdown products of humic substances); low molecular weight acids; low molecular weight neutrals (Huber et al. 2011). An exemplary chromatogram including these fractions is shown in the Supporting Information.

2.6. Calculations and data evaluation

The AC loadings with OMP after adsorption and desorption were calculated using mass balances. The resulting equations according to the experimental procedure can be found elsewhere (Aschermann et al. 2018). The loadings were plotted against the respective OMP equilibrium concentrations after the adsorption and desorption phase, respectively, to obtain adsorption and desorption isotherms. A comparison of the relative position of the corresponding adsorption and desorption isotherms was used to make qualitative statements about the desorption extent of OMP. Therefore, the entire curves were evaluated (not single data points).

As explained and illustrated elsewhere (Aschermann et al. 2018) the error in loading calculation strongly rises with decreasing differences between the initial OMP concentration, the OMP concentration after adsorption and the OMP concentration after desorption. To minimize the impact of analytical errors on the course of the resulting isotherms, only those data pairs were considered for the depiction in isotherms, where the removal of the respective OMP after adsorption was above 25%. This constraint (plus the non-consideration of data points with concentrations below the LoQ) resulted in adsorption and desorption isotherms, which partly consisted of less than seven data points (which would ideally result from the seven batches per experimental series).

For modeling the adsorption isotherms the Freundlich equation was used in a pseudo single-solute fashion (e.g. Meinel et al. (2016)). By using the linearized form (Eq. (1)) the Freundlich coefficient K_F and the Freundlich exponent n were determined.

$$\log(q) = n * \log(c) + \log(K_F) \qquad (1)$$

where q is the loading and c is the liquid phase concentration of a certain compound.

3. Results and Discussion

3.1. Characteristics of DOM fractions

Table 1 shows the qualitative and quantitative characteristics of the prepared DOM solutions in comparison to the original raw water (Berlin drinking water). As intended, the DOC concentrations of the two prepared solutions are very similar and in the range of the raw water. Thus, the solutions are comparable in terms of its quantitative DOM composition.

Table 1: DOC, UV_{254nm} and SUVA of the prepared experimental solutions and the raw water (Berlin drinking water).

	DOC [mg L^{-1}]	UV_{254nm} [m^{-1}]	SUVA [L $mg^{-1}m^{-1}$]
Raw water	4.7	10.7	2.3
hmw-DOM	5.1	15.5	3.0
lmw-DOM	4.8	9.0	1.9

In terms of UV_{254nm} the solutions show differences after their specific pre-treatment in comparison to the raw water. Related therewith, also the SUVA values are different. The hmw-DOM solution shows an increased SUVA in comparison to the raw water, which indicates a higher aromaticity of the DOM (Weishaar et al. 2003). Furthermore, an increasing SUVA can also be related to a relative increase of humic compounds of higher molecular weight (Huber et al. 2011). As the hmw-DOM solution results from the concentrate of the nanofiltration process (MWCO: 1000 Da), this can be explained by the retention of aromatic humic compounds by the membrane, resulting in an accumulation of this DOM fraction in the concentrate. The lmw-DOM shows a decreased SUVA in comparison to the original raw water indicating a removal of aromatic compounds in this case. This can be attributed to the pre-treatment by flocculation, which leads to decreased SUVA values (Archer and Singer 2006, Volk et al. 2000).

For further characterization of the prepared solutions LC-OCD measurements were conducted. Figure 2 shows the normalized chromatograms of the organic carbon (OC) signal.

In this case, all data points of the chromatogram are divided by the maximum signal of the respective chromatogram. Thus, the maximum signal value represents 100%. Using these normalized curves, qualitative DOM size compositions of the different solutions can be compared.

The raw water chromatogram shows its maximum in the range of humic compounds (retention time ~ 42 min) which is the dominant DOM fraction of this water. The nominal average molecular weight of this fraction was determined to be 895 g/mol. Furthermore, building blocks (retention time ~ 47 min) as well as low molecular weight acids and neutrals (retention time > 50 min) appear to a lower percentage. Biopolymers (with an expected retention time between 30 and 40 minutes) are not present. This composition is typical for drinking waters (Zietzschmann et al. 2016a).

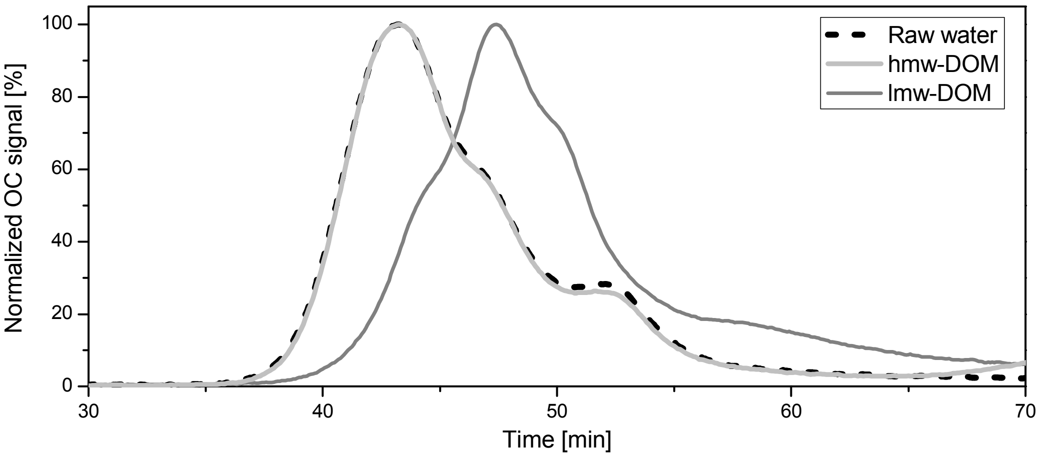

Figure 2: Normalized LC-OCD chromatograms of the used raw water (Berlin drinking water) and the prepared DOM fractions.

The normalized chromatogram of the lmw-DOM solution shows a clear shift of DOM size composition to lower molecular weight compounds in comparison to the raw water. Its maximum (at ~ 48 min) is not in the range of humic compounds, but in the range of building blocks. Furthermore, low molecular weight acids and neutrals show a higher relative abundance in comparison to the raw water, as resulting from the pre-treatment of the lmw-DOM solution. Flocculation with aluminum salts leads to a removal especially of higher molecular weight DOM (Davis and Gloor 1981). Lower molecular weight compounds like building blocks and low molecular weight acids and neutrals are not or less removed during flocculation and were concentrated during nanofiltration. These DOM fractions show a higher appearance in waste water treatment plant effluent DOM in comparison to drinking water DOM (Zietzschmann et al. 2016a). The lower abundance of humic compounds is in accordance with the decreased SUVA of this solution.

The normalized signal of the hmw-DOM solution shows generally a very similar chromatogram in comparison to the raw water. This indicates that the DOM composition did not change due to nanofiltration. This would imply that both, higher molecular weight humic substances as well as lower molecular weight compounds are not affected by size exclusion during the membrane treatment and, thus, could pass the nanofiltration membrane. Based on the MWCO of this membrane (1,000 Da), an enrichment of high molecular weight compounds and, thus a higher percentage of humic substances could be expected as this was also reported in a previous fractionation study with the same membrane (Zietzschmann et al. 2014). This can actually not be seen in Figure 2. This can be explained by an enrichment of more hydrophobic compounds in the concentrate, expressed by the increased SUVA of the hmw-DOM solution. It was shown elsewhere that a higher hydrophobicity of compounds induces a shift of the LC-OCD signal towards longer retention times, since hydrophobic/aromatic compounds are usually retained longer on the employed LC column (Ruhl and Jekel 2012). This would imply that the hmw-DOM solution contains larger size DOM compounds than the raw water, but that the effect is masked by increased interactions and retardation of the compounds with the LC column.

Despite an overlapping size range between the two prepared fractions, the hmw-DOM and lmw-DOM solution show clear differences in their DOM size composition and can be used to represent rather high molecular weight compounds and low molecular weight compounds, respectively.

3.2. Adsorption of DOM

Figure 3 shows the DOC removal in the lmw-DOM and the hmw-DOM solution after adsorption for all three tested AC. In both cases, the Epibon A shows the highest DOC removal and the Hydraffin CC shows the lowest removal. The same trend was also seen for untreated drinking water (Aschermann et al. 2018). Thus, the pre-treatment did not change the affinity of the DOM towards a certain AC. On the one hand, this affinity is affected by the AC pore size distribution. Although the given average AC pore sizes (see section 2.2) differ by less than 2 nm, which might seem to be similar, differences in this range can strongly impact the DOM adsorption. By testing different AC fibers that differed in their average pore size by less than 0.8 nm, Pelekani and Snoeyink (1999) reported strongly different DOM adsorption of these AC products, with lower DOM removal in case of the AC with a lower average pore size and a narrow pore size distribution. Accordingly, the microporous Hydraffin CC shows the lowest the DOC removal in this study. On the other hand, also the chemical properties of the AC, which determine their surface charge, can affect the DOM adsorption (Bjelopavlic et al. 1999). Due to its low pH_{pzc} of 3 the HK 1200 is negatively charged at a neutral pH, which can induce electrostatic repulsion of negatively charged DOM. This can explain the lower DOM removal of the HK 1200 in comparison to the Epibon A, despite the wider pore size distribution of the HK 1200. The Epibon A (pH_{pzc}: 8.1) and the Hydraffin CC (pH_{pzc}: 9.5) are both positively charged at the pH of both solutions, which is assumed to benefit the adsorption of negatively charged DOM. However, the strong differences between these two AC indicate that the DOM adsorption is rather impacted by the pore size distribution than by the surface charge of the AC.

Furthermore, for all AC the DOC removal in the lmw-DOM and the hmw-DOM solution is generally very similar. Thus, both fractions are comparable concerning their adsorbability. Different studies that fractionated organic matter from waste water treatment plant effluents in a similar way showed a higher affinity of low molecular weight compounds towards AC than bigger DOM compounds (Hu et al. 2016, Zietzschmann et al. 2014). In the present study the similarity of lmw- and hmw-DOM adsorption is likely induced by a combination of size effects and aromatic/hydrophobic interactions. On the one hand, different studies (Kilduff et al. 1996, Schreiber et al. 2005) report an increasing DOM adsorption with decreasing molecular weight of the organic compounds, which would generally favor the removal of the lmw-DOM compounds. On the other hand, more aromatic DOM shows higher adsorbability in comparison to more aliphatic DOM, due to increased interactions with the AC (Schreiber et al. 2005). This would favor the removal of compounds of the hmw-DOM solution, which has a higher SUVA compared to the lmw-DOM solution. Since both mechanisms operate exactly opposed for the lmw- and hmw-DOM solutions, respectively, barely any difference in DOM adsorption can be constituted.

The similar removals at the same AC doses in combination with the very similar initial DOC values (Table 1) also show that the DOC loadings of the lmw-DOM and the hmw-DOM after adsorption can be expected to be quantitatively very similar in the different experiments for the different tested AC products. Thus, a good comparability of the results is given in terms of the potentially observable qualitative effects of these fractions on OMP ad- and desorption.

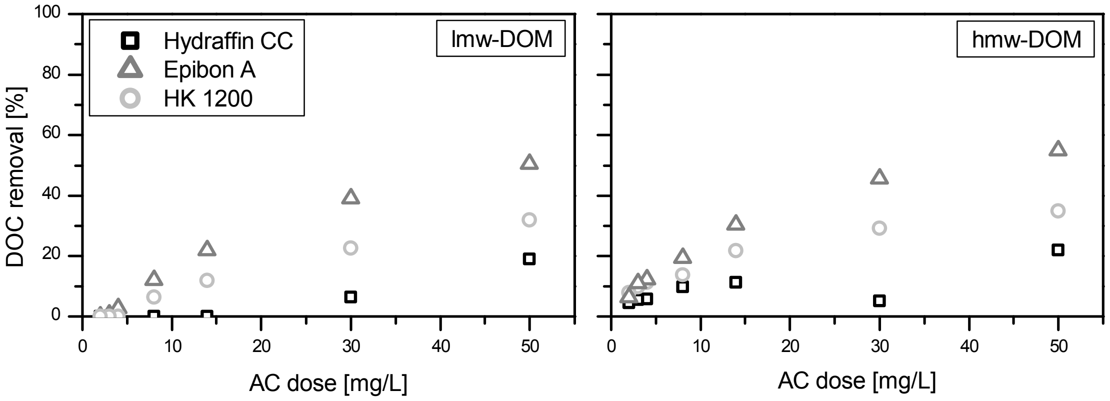

Figure 3: DOC removal over activated carbon dose in lmw-DOM (left) and hmw-DOM (right) solutions for the three tested activated carbons.

3.3. Effects of different DOM size fractions on OMP desorption

The following results originate from batch tests, where the AC was firstly loaded simultaneously with OMP and the respective DOM fraction, followed by a desorption phase in the respective unspiked DOM solution (see section 2.4.1). The resulting desorption isotherms of carbamazepine and diclofenac in both, the hmw-DOM and lmw-DOM solutions, as compared to the respective adsorption isotherms are shown in Figure 4 and Figure 5. As all tested compounds showed generally a similar behavior, these two substances are used as representative OMP here. The isotherms of all other tested compounds can be found in the Supporting Information.

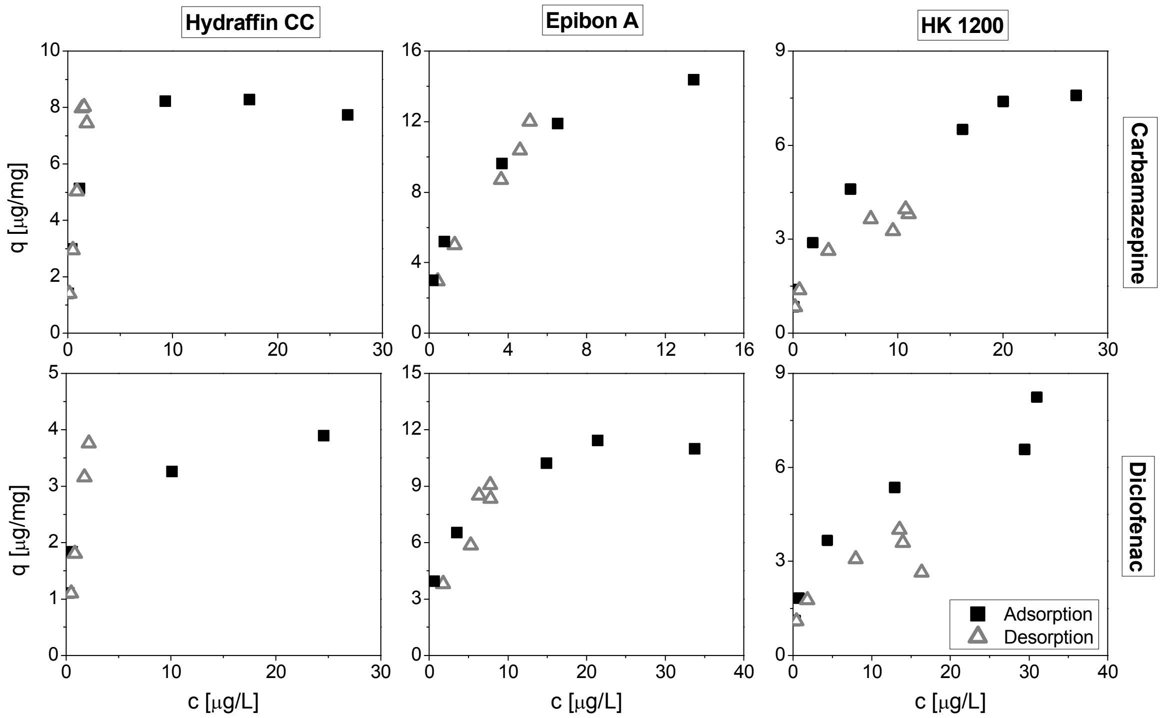

Figure 4: Adsorption and desorption isotherms of carbamazepine ($c_0 = 42$ µg/L) and diclofenac ($c_0 = 55.7$ µg/L) for all tested activated carbons after adsorption and desorption in the hmw-DOM solution.

It can be seen that the position of the desorption isotherms in comparison to their respective adsorption isotherms are different for the three tested AC. In the case of the microporous AC Hydraffin CC the desorption isotherms are strongly shifted to the left in comparison to the adsorption isotherms, in both tested waters. This indicates a strong irreversible adsorption of carbamazepine and diclofenac. Under pure water conditions the respective corresponding adsorption and desorption isotherms are rather congruent, indicating a highly/completely reversible adsorption (Aschermann et al. 2018). Thus, the additional adsorption of DOM affects the desorption of OMP and leads to a higher irreversibility of the OMP adsorption in case of the Hydraffin CC. This could be referred to pore blockages by DOM compounds during the adsorption phase, in the lmw-DOM as well as in the hmw-DOM solution, preventing the subsequent desorption of adsorbed OMP by steric hindrance.

The desorption isotherms of the macroporous HK 1200 are located below the corresponding adsorption isotherms. This shows an increased desorption of carbamazepine and diclofenac from this AC. Also for this AC, experiments under pure water conditions result in rather congruent OMP adsorption and desorption isotherms (Aschermann et al. 2018), which illustrates that the shift of the desorption isotherm observed in the current study can be attributed to DOM effects. Furthermore, additional experiments where the desorption solution consisted of pure water instead of the respective DOM solution illustrate this effect more detailed (corresponding isotherms of carbamazepine in SI (Figure S7)). As shown in Figure S7, desorption under pure water conditions (following a simultaneous adsorption of OMP and the respective DOM fraction) leads to superimposing adsorption and desorption isotherms in case of the HK 1200, which illustrates completely reversible OMP adsorption (in case of both DOM fractions). Thus, it can be assumed that in this case, no/reduced pore blockage effects occur during the adsorption phase. This allows OMP to desorb as a result of the reversed concentration gradient. In the experiments corresponding to Figure 4 and 5, the loaded AC (after the adsorption phase) gets in contact with ′fresh′ DOM in the desorption phase. This leads to an additional adsorption of DOM compounds during the desorption phase as the initial DOM concentration is above the equilibrium DOM concentration at the end of the adsorption phase. This secondary DOM adsorption is shown in the Supporting Information, where the DOC removal after the desorption phase for the three AC in the respective DOM solution is illustrated. As no/reduced blockages occur, the additionally adsorbing DOM compounds can enter the AC pores and displace adsorbed OMP, which leads to an increased desorption. This is illustrated by the shift of the desorption isotherm to the bottom/right in comparison to the corresponding adsorption isotherm (Figure 4/5), but also in comparison to the equivalent desorption isotherm, when no DOM is present during the desorption (Figure 4/5 vs. Figure S7).

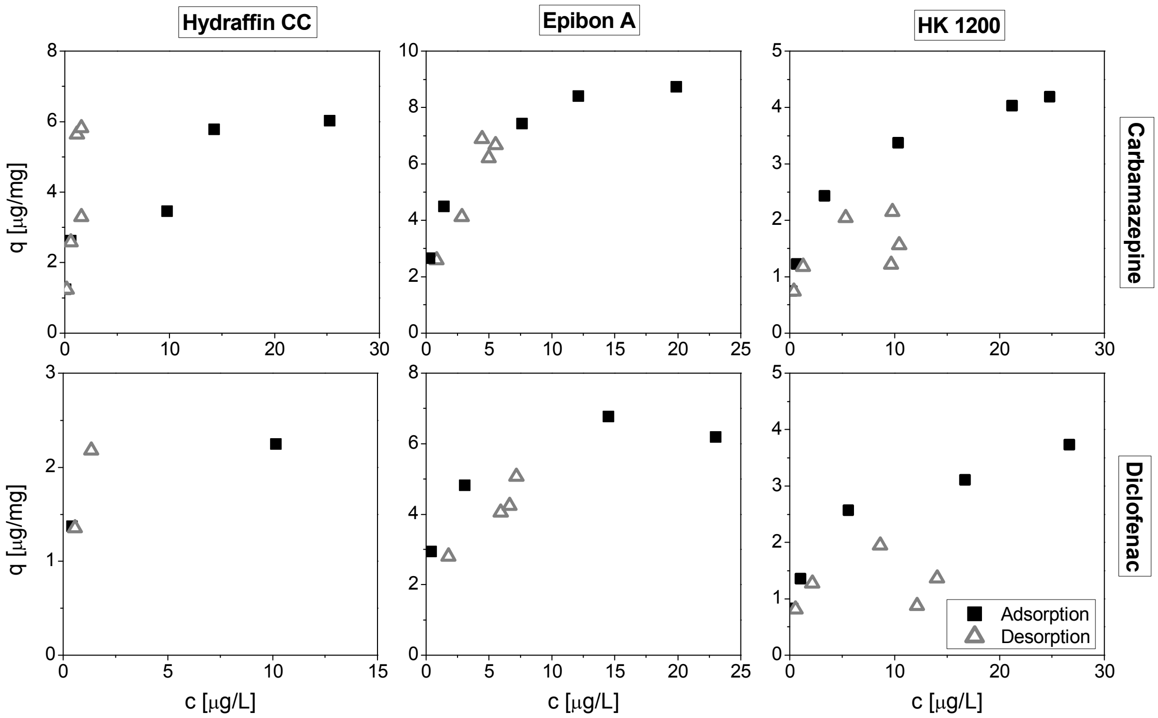

Figure 5: Adsorption and desorption isotherms of carbamazepine ($c_0 = 37.4$ µg/L) and diclofenac ($c_0 = 41.6$ µg/L) for all tested activated carbons after adsorption and desorption in the lmw-DOM solution.

For the mesoporous AC Epibon A, both described effects can be seen. For lower AC loadings the desorption isotherms are located below the corresponding adsorption isotherms, which indicates displacement effects, similar to those described for HK1200. Also in this case, the desorption isotherm is shifted to the bottom/right, when DOM is present during the desorption phase (Figure 4/5 vs. Figure S7). However, the desorption isotherms move closer to the corresponding adsorption isotherms and partly cross them for increased loadings. This indicates reduced displacement as well as partial pore blockages, which prevent the desorption of OMP.

The results generally show that a higher AC pore size results in a higher OMP desorption extent, which can be explained by different DOM interactions: pore blockage effects for microporous AC on the one hand and displacement effects for macroporous AC. As discussed above, the tested AC also differ in their surface charge, which might also affect the OMP adsorption/desorption in the presence of DOM. Nonetheless, based on the pH_{pzc}, higher similarities between the Hydraffin CC and the Epibon A would be expected due to their rather similar values, especially in comparison with the HK 1200. However, these two AC (Hydraffin CC and Epibon A) act quite different in terms of OMP desorption (as shown in Figure 4 and 5). Furthermore, the exemplary shown compounds, carbamazepine and diclofenac, also differ in their charge. Whereas carbamazepine is uncharged over a wide pH range, diclofenac is negatively charged at a neutral pH (Suriyanon et al. 2013). Thus, stronger differences in the desorption behavior of these compounds would be expected, if the AC surface charge would be a dominating factor in terms of OMP adsorption/desorption. However, both compounds actually show very similar results for the particular AC, underlining the dominating role of the AC pore structure with respect to OMP desorption in the presence of DOM.

All these described effects can be seen in a similar manner for the used raw water (Aschermann et al. 2018). Furthermore, the course of the desorption isotherms in comparison to the adsorption isotherms is very similar for the lmw-DOM solution and the hmw-DOM solution for the respective AC. No differences in the OMP desorption behavior can be seen in the two different solutions. This indicates that both solutions do not differ in their effects on OMP desorption. Both assumed DOM effects, pore blockages and OMP displacement, occur in a very similar way. Figure 2 shows that the DOM sizes in the two solutions partly overlap. The lmw-DOM solution contains a relatively low percentage of humic substances, the hmw-DOM solution contains relatively low percentages of low molecular weight compounds. It is known that the ratio of OMP and (unfractionated) DOM (Knappe et al. 1998) and of OMP and DOM fractions (Zietzschmann et al. 2016a) generally strongly affects the adsorption behavior of OMP. Therefore, it can be expected that different ratios of OMP and certain DOM fractions would also lead to different impacts on OMP desorption. As latter cannot be observed, generally similar effects of the fractions examined here can be assumed. Thus, these effects are not induced by DOM compounds of a certain size, but by both, smaller and larger compounds.

Based on this, it seems likely that model compounds that are often used for different DOM fractions do not reflect the real behavior of DOM. For example, Li et al. (2003b) inferred that low molecular weight DOM induces displacement effects as the model compound 1,4-dichlorobenzene did this. The current results of the lmw-DOM show that such a conclusion from model compounds cannot readily be drawn.

3.4. Effects of DOM size on adsorption of organic micropollutants

Figure 4 and Figure 5 also allow a comparison of the adsorption isotherms of carbamazepine and diclofenac in both tested solutions. As the respective OMP concentrations as well as the DOC in both solutions were very similar (and, thus, also the OMP/DOC ratio), the isotherms are directly comparable (Knappe et al. 1998, Zietzschmann et al. 2016a). For all tested AC the respective adsorption isotherm in the lmw-DOM solution (Figure 5) is below the corresponding isotherm in the hmw-DOM solution (Figure 4). This indicates a higher competitive effect in the lmw-DOM solution leading to a lower OMP adsorbability. This confirms previous results which identified smaller DOM compounds to be more competitive towards OMP adsorption than larger compounds (Hu et al. 2016, Zietzschmann et al. 2014, Zoschke et al. 2011). However, in these studies the increased competition effect of smaller compounds is referred to a direct competition on adsorption sites between these compounds and OMP, which was, thus, identified as the major competition effect. In comparison, the weaker competitive effects of larger compounds were referred to pore blockage effects. The current results of the desorption experiments show that such a classification is not possible as both fractions lead to very similar effects.

3.5. Influence of DOM preloading on OMP adsorption

For further identification of the described effects, batch experiments with a sequential adsorption phase were conducted. In this case, the AC was pre-loaded with the particular DOM fraction (OMP concentration < LoQ) prior to the adsorption of OMP. The resulting adsorption isotherms of carbamazepine in comparison to the isotherms after simultaneous adsorption are shown in Figure 6.

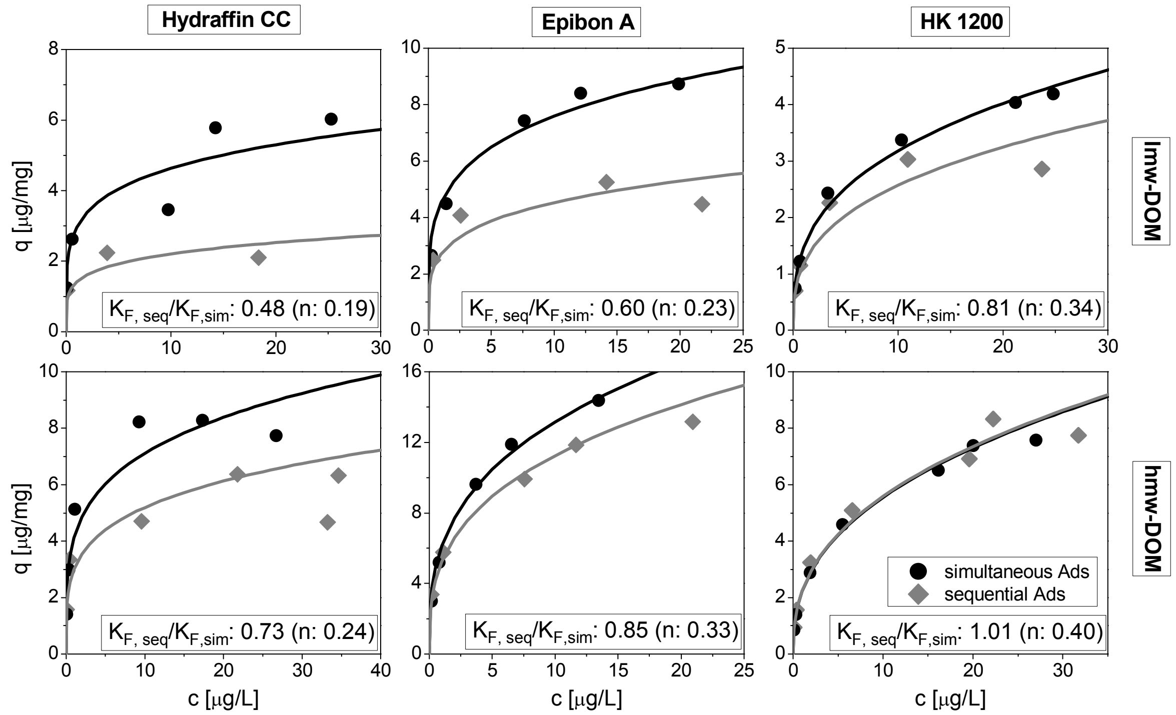

Figure 6: Adsorption isotherms of carbamazepine (with modeling after Freundlich) for all tested AC after simultaneous and sequential adsorption of DOM and OMP in the lmw-DOM (top) and hmw-DOM (bottom) solutions.

The isotherms in the case of the sequential adsorption are located below the ones after simultaneous adsorption in nearly all cases. The same effect can also be seen for diclofenac (shown in the Supporting Information). Thus, the pre-loading with both, hmw- and lmw-DOM, leads to a decreased adsorption of OMP. A similar effect could also be seen for unfractionated drinking water DOM (Aschermann et al. 2018). It indicates a lower availability of adsorption sites due to the pre-loading, which can be referred to AC pore blockages and, thus, a steric hindrance for OMP to enter these pores. Vice versa, it seems likely that pore blocking can also prevent the release of OMP that are adsorbed in deeper parts of the respective pore and, thus, can explain the irreversibility of OMP adsorption in certain cases (Figure 4 and Figure 5).

To quantify the changes in OMP adsorption between simultaneous and sequential adsorption the isotherms were fitted with the Freundlich equation. K_F, as parameter for the adsorbability, was determined for sequential and simultaneous adsorption (with an averaged n in both cases for each AC and each background solution). The ratio of these two K_F values can be used as a parameter for the comparison of simultaneous/sequential adsorption. It can be seen that preloading with DOM leads to a stronger decrease of OMP adsorption with higher microporosity of the AC, for both tested solutions. Thus, microporous AC are more affected by pore blockages as macroporous AC (as it was also the case for unfractionated drinking water DOM (Aschermann et al. 2018)). Similar effects were also seen in preloading experiments by Li et al. (2003a).

Furthermore, both solutions lead to similar decreases in adsorptions after preloading (with slightly higher decreases in the case of the lmw-DOM solution). This indicates again that both, lmw-DOM and hmw-DOM, can block AC pores. Thus, pore blockage is not a matter of molecular size and can also be induced by smaller DOM compounds. This can explain why both solutions lead to the same effects in terms of OMP desorption.

Due to these observations, it can be assumed that the DOM composition does not significantly influence the desorption behavior of OMP in real AC applications. Thus, effects in terms of desorption behavior might be independent of the DOM size composition of different waters. This indicates that the effects that were seen for one specific drinking water (Aschermann et al. 2018) might be transferable also to other real waters with different composition.

3.6. Influence of DOM preloading on OMP desorption in pure water

In this experimental series, the tested AC were brought into contact with pure water, subsequent to sequential loading with DOM and OMP. The resulting desorption isotherms of carbamazepine after sequential adsorption in the lmw-DOM and the hmw-DOM solution, respectively, can be found in Figure 7.

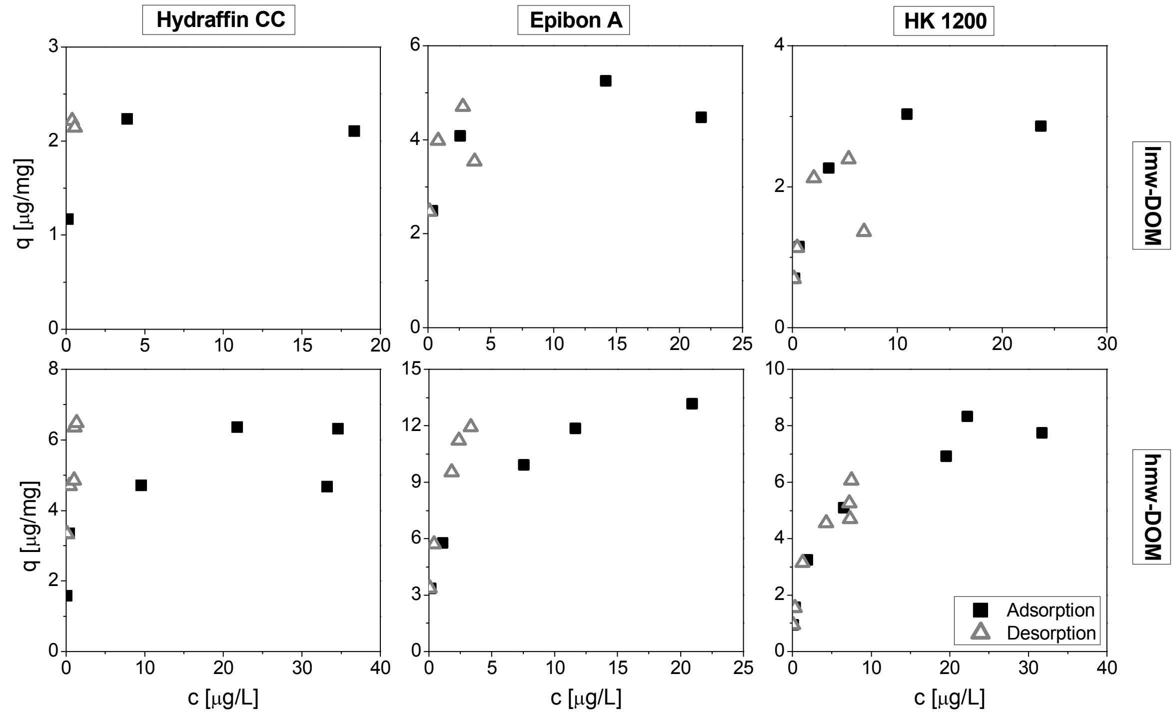

Figure 7: Adsorption and desorption isotherms of carbamazepine for all tested activated carbons after sequential adsorption in the lmw-DOM solution (top, c_0 = 35.2 µg/L) and the hmw-DOM (bottom, c_0 = 47.3 µg/L) solution, respectively, and desorption in pure water.

Based on the previous findings, it could be assumed that the preloading with DOM leads to permanent blockages of the AC pores, which sterically hinders a further transport of substances into these pores. Thus, the subsequently added OMP are expected to adsorb in pores that are not blocked. By conducting a desorption step in pure water and, thus, without further interactions between the adsorbed OMP and other water constituents, desorption from these unblocked adsorption sites is expected to be driven only by the reversal of the OMP concentration gradient, and should proceed without interference by DOM. Under these conditions the OMP adsorption is expected to be highly or completely reversible (Aschermann et al. 2018).

However, only the macroporous HK 1200 shows a completely reversible adsorption, illustrated by the superimposing isotherms (excluding one outlying data point for the lmw-DOM solution). The desorption isotherms in case of the microporous Hydraffin CC and the mesoporous Epibon A are shifted to the left in comparison to their corresponding adsorption isotherms (excluding one outlying data point in case of Epibon A (lmw-DOM)). This characterizes the irreversibility of OMP adsorption under these conditions, especially for the microporous Hydraffin CC. These results are very similar to the results of the experiment, where the respective AC were simultaneously loaded with OMP and the respective DOM fraction, followed by a desorption phase in pure water (see Figure S7 in the Supporting Information). Thus, the OMP desorption behavior is independent from adsorption sequence of OMP and DOM as simultaneous and sequential adsorption lead to the same effects.

This contradicts the expected results described above. It indicates that the idea of static and permanent pore blockages might be too simple to completely describe the effects of DOM during OMP adsorption and desorption. Possible explanations for the observed results would be that (i) pore blocking DOM partly act like a kind of valve (e.g. due to changes in their molecular conformation), which allow OMP to enter the deeper parts of the pore, but not to leave pores or (ii) there are partial interactions between adsorbed DOM and OMP when less adsorption sites are available due to pore blockages, which are irreversible and prevent OMP from desorption.

Thus, further research is necessary to get a deeper understanding of DOM effects on OMP adsorption and desorption, which can then also describe the effects observed on sequential adsorption of DOM and OMP, followed by desorption in pure water.

4. Conclusion

By conducting adsorption and desorption batch tests with different size fractions of drinking water DOM, it was found that

- low molecular weight DOM compounds lead to a stronger competition effect on OMP adsorption onto AC, which confirms the results of previous studies.
- low molecular weight and high molecular weight DOM compounds have very similar effects on the extent of OMP desorption and can both, increase as well as decrease OMP desorption.
- for both fractions the actual effect on OMP desorption is depending on the pore size distribution of the used AC. For a microporous AC, both DOM fractions lead to a decrease of desorption, whereas in case of a macroporous AC both fractions increase desorption.
- preloading AC with the different DOM fractions leads to decreased adsorbability of OMP especially for microporous AC. This indicates pore blockage effects that can be

induced by both, low molecular weight and high molecular weight DOM compounds, which also could explain the similar desorption effects of these fractions.

- OMP adsorption after DOM preloading is also irreversible in case of micro- and mesoporous AC. Whereas previous outcomes can be explained by the assumption of a static and permanent blockage of AC pores by DOM, the present results contradict this concept. They indicate rather complex interactions between DOM and AC that lead to the partly irreversible adsorption of OMP. Thus, further research is required to fully understand DOM effects on OMP ad- and desorption.

The very similar effects of different DOM fractions on desorption show that these effects are independent of the DOM size composition. This indicates, that waters with different DOM composition still might lead to very similar effects in terms of desorption. It is especially the pore characteristics of the used AC that affect the effect of DOM on OMP desorption.

5. Acknowledgements

This study was part of the research training group Urban Water Interfaces (UWI) (GRK 2032/1), funded by the German Research Foundation (DFG). We thank Dr. Gesine Götz and Christina Selge from the Chair of Environmental Process Engineering (Technische Universität Berlin) as well as Ulrike Förster, Jutta Jakobs, Katharina Kutz, Katrin Noack for their assistance in the lab.

6. References

Altmann, J., Zietzschmann, F., Geiling, E.L., Ruhl, A.S., Sperlich, A. and Jekel, M. (2015) Impacts of coagulation on the adsorption of organic micropollutants onto powdered activated carbon in treated domestic wastewater. Chemosphere 125, 198-204.

Archer, A.D. and Singer, P.C. (2006) Effect of SUVA and enhanced coagulation on removal of TOX precursors. Journal (American Water Works Association) 98(8), 97-107.

Aschermann, G., Zietzschmann, F. and Jekel, M. (2018) Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption. Water Research 133, 123-131.

Bjelopavlic, M., Newcombe, G. and Hayes, R. (1999) Adsorption of NOM onto activated carbon: Effect of surface charge, ionic strength, and pore volume distribution. Journal of Colloid and Interface Science 210(2), 271-280.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A. and Siegrist, H. (2012) Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. Water Science and Technology 66(10), 2115-2121.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J. and Tchobanoglous, G. (2005) Water Treatment - Principles and Design (2nd Edition), John Wiley & Sons, Hoboken, USA.

Davis, J.A. and Gloor, R. (1981) Adsorption of dissolved organics in lake water by aluminum oxide. Effect of molecular weight. Environmental Science & Technology 15(10), 1223-1229.

Hu, J., Shang, R., Heijman, B. and Rietveld, L. (2016) Influence of activated carbon preloading by EfOM fractions from treated wastewater on adsorption of pharmaceutically active compounds. Chemosphere 150, 49-56.

Huber, S.A., Balz, A., Abert, M. and Pronk, W. (2011) Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). Water Research 45(2), 879-885.

Kilduff, J.E., Karanfil, T. and Weber, W.J. (1996) Competitive interactions among components of humic acids in granular activated carbon adsorption systems: Effects of solution chemistry. Environmental Science & Technology 30(4), 1344-1351.

Knappe, D.R.U., Matsui, Y., Snoeyink, V.L., Roche, P., Prados, M.J. and Bourbigot, M.M. (1998) Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters. Environmental Science & Technology 32(11), 1694-1698.

Li, Q., Snoeyink, V.L., Mariñas, B.J. and Campos, C. (2003a) Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. Water Research 37(20), 4863-4872.

Li, Q.L., Snoeyink, V.L., Mariaas, B.J. and Campos, C. (2003b) Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. Water Research 37(4), 773-784.

Machado, M.T.C., Trevisan, S., Pimentel-Souza, J.D.R., Pastore, G.M. and Hubinger, M.D. (2016) Clarification and concentration of oligosaccharides from artichoke extract by a sequential process with microfiltration and nanofiltration membranes. Journal of Food Engineering 180, 120-128.

Meinel, F., Zietzschmann, F., Ruhl, A.S., Sperlich, A. and Jekel, M. (2016) The benefits of powdered activated carbon recirculation for micropollutant removal in advanced wastewater treatment. Water Research 91, 97-103.

Pelekani, C. and Snoeyink, V.L. (1999) Competitive adsorption in natural water: Role of activated carbon pore size. Water Research 33(5), 1209-1219.

Ruhl, A.S. and Jekel, M. (2012) Elution behaviour of low molecular weight compounds in size exclusion chromatography. Journal of Water Supply: Research and Technology - Aqua 61(1), 32-40.

Schreiber, B., Brinkmann, T., Schmalz, V. and Worch, E. (2005) Adsorption of dissolved organic matter onto activated carbon - the influence of temperature, absorption wavelength, and molecular size. Water Research 39(15), 3449-3456.

Sontheimer, H., Crittenden, J.C. and Summers, R.S. (1988) Activated carbon for water treatment, DVGW-Forschungsstelle, Engler-Bunte-Institut, Universitat Karlsruhe (TH).

Suriyanon, N., Punyapalakul, P. and Ngamcharussrivichai, C. (2013) Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials. Chemical Engineering Journal 214, 208-218.

Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H.P., von Gunten, U., Boller, M. and Meylan, S. (2011) Characterization of natural organic matter adsorption in granular activated carbon adsorbers. Water Research 45(13), 3951-3959.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G. and LeChevallier, M. (2000) Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. Water Research 34(12), 3247-3257.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R. and Mopper, K. (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology 37(20), 4702-4708.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environmental Science & Technology 39(17), 6649-6663.

Worch, E. (2012) Adsorption Technology in Water Treatment, Fundamentals, Processes, and Modeling., De Gruyter, Berlin, Boston.

Zietzschmann, F., Aschermann, G. and Jekel, M. (2016a) Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents. Water Research 102, 190-201.

Zietzschmann, F., Stutzer, C. and Jekel, M. (2016b) Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater - Aligning breakthrough curves and capacities. Water Research 92, 180-187.

Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F. and Jekel, M. (2014) Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater. Water Research 65, 297-306.

Zoschke, K., Engel, C., Bornick, H. and Worch, E. (2011) Adsorption of geosmin and 2-methylisoborneol onto powdered activated carbon at non-equilibrium conditions: Influence of NOM and process modelling. Water Research 45(15), 4544-4550.