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1	Impact of different DOM size fractions on the desorption of		
2	organic micropollutants from activated carbon		
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8	Delft, Netherlands		
9			
10	Highlights		
11	• Organic micropollutant (OMP) desorption batch tests with 3 activated carbons (AC)		
12	• Low (lmw) and high molecular weight (hmw) DOM fractions used as background		
13	matrix		
14	• Effects on OMP desorption extent are similar for lmw- and hmw-DOM fraction		
15	• Macroporous AC shows enhanced desorption of OMP, independent of DOM		
16	composition		
17	• Microporous AC shows irreversible OMP adsorption, independent of DOM		
18	composition		
19			

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20 Abstract

21 Whereas the adsorption of organic micropollutants (OMP) onto activated carbon (AC) is 22 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 23 24 desorption from AC was examined. By different pre-treatments of a raw drinking water, a 25 high molecular weight (hmw) and a low molecular weight (lmw) DOM solution were 26 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 27 28 were conducted in parallel with three AC of different pore structures (microporous, 29 mesoporous/balanced, macroporous). The tests were evaluated with respect to the extent of 30 OMP adsorption and its reversibility, which represents the potential extent of OMP 31 desorption. In terms of OMP adsorption, the lmw-DOM fraction induced a higher competitive 32 effect on OMP adsorption in comparison to the hmw-DOM fraction. In terms of their impact 33 on OMP desorption extent, both fractions led to very similar results. In case of the 34 macroporous AC, both DOM fractions induce an enhanced OMP desorption that can be 35 attributed to displacement effects in both cases. For the microporous AC, an increased 36 irreversibility of OMP adsorption was found in both cases, which shows that DOM adsorption 37 prevents OMP desorption, independently of the size of the adsorbed DOM compounds. 38 Whereas results from this study as well as from former studies indicate that this effect might 39 be induced by permanent pore blockages by adsorbed DOM, further results show that there 40 could be more complex DOM interactions that lead to the decreased desorption in case of 41 microporous AC. Nonetheless, the very similar impact of the different DOM fractions on the 42 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 porestructure of the used AC.

45

46 Keywords

47 activated carbon, organic micropollutants, desorption, adsorption, drinking water, dissolved48 organic matter

49

50 1. Introduction

51 The application of activated carbon (AC) is a promising method for the removal of organic 52 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, 53 54 Zietzschmann et al. 2016b). This removal is caused by the adsorption of the compounds onto 55 the AC surface. Due to the rather weak binding forces that occur in this process, it is often 56 assumed to be reversible (Crittenden et al. 2005, Worch 2012), which means that already 57 adsorbed compounds can also desorb again. In terms of water treatment, desorption of target 58 compounds, such as OMP, during the process is undesired as it leads to increased effluent 59 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 60 61 displacement by other better adsorbing compounds (competitive adsorption). Especially, 62 granular AC filters might be affected by desorption as the AC remains much longer in the

63 system than the treated water. This allows the AC surface to be continuously loaded as well as64 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 65 affected by the extent of desorption and the corresponding desorption kinetics. It has been 66 shown that the extent of OMP desorption under real conditions can be strongly influenced by 67 68 the adsorption of background dissolved organic matter (DOM). The actual effect of DOM on 69 desorption depends on the AC pore structure. For macroporous AC, DOM adsorption 70 aggravates the concentration reversal-driven desorption of OMP, whereas microporous AC 71 show stronger irreversibility effects and, thus, lower desorption (Aschermann et al. 2018). 72 It is known that different DOM size fractions can generally adsorb onto AC, e.g. larger humic 73 compounds as well as low molecular weight compounds (Velten et al. 2011). Different 74 studies show that the adsorption of these different fractions affects OMP adsorption, as they 75 lead to different competitive effects. Several studies indicate that low molecular weight 76 compounds induce higher competitive effects compared to larger DOM constituents and lead 77 to lower adsorptive OMP removal (Hu et al. 2016, Zietzschmann et al. 2014). It is assumed 78 that smaller DOM compounds lead to direct competition on adsorption sites, whereas larger 79 compounds decrease OMP adsorption as they block the AC pores and, thus, reduce adsorption 80 capacity (Li et al. 2003a, Li et al. 2003b). However, a clear attribution of these effects to the different DOM fractions is still missing. 81

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

86 could explain the different effects of DOM that were observed in a previous study

87 (Aschermann et al. 2018).

Bue 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.

94 The results will help to estimate the desorption behavior of different waters with different or 95 varying DOM composition, which would provide beneficial information for water utilities to 96 estimate potential desorption effects in their system.

97

98 2. Material and Methods

99 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.

106 These powdered AC samples were characterized in a previous study (Aschermann et al. 2018)

107 with respect to their pore structure (cf. Supporting Information). Based on the relative

108 differences in their pore size distribution, which can be reflected by the average pores size,

109 they can be classified as microporous (Hydraffin CC, average pore size: 1.7 nm), mesoporous

110 (Epibon A, average pore size: 2.4 nm) and macroporous (HK 1200, average pore size:

111 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

113 tested AC in a qualitative manner.)

114 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

116 the indirect titration method (Sontheimer et al. 1988). This method is described in the

117 Supporting Information more detailed. The resulting pH_{pzc} are 9.5 (Hydraffin CC), 8.1

118 (Epibon A) and 3 (HK 1200), respectively.

119

120 2.2. Organic micropollutants

121 Five substances were studied in the experiments, which represent typical OMP:

122 carbamazepine, diclofenac, 4-formylaminoantipyrine, sulfamethoxazole (all Sigma Aldrich,

123 Germany) and iomeprol (Dr. Ehrenstorfer, Germany). They were initially prepared as single

124 stock solutions with a concentration of 20 mg/L and then mixed in a stock solution with

125 concentrations of 2 mg/L of each OMP. From this mixed stock solution certain amounts were

126 taken to spike particular experimental solutions.

128 2.3. Experimental solutions

129 Experiments were conducted with different background solutions, which were used as 130 adsorption (spiked) and as desorption (unspiked) solution. These solutions were prepared 131 from Berlin drinking water (taken from laboratory tap after adequate flushing). This raw 132 water was also used for previous desorption studies (Aschermann et al. 2018). With the goal 133 of preparing a low molecular weight (lmw) DOM solution and a high molecular weight 134 (hmw) DOM solution, the water was treated in two different ways. These pre-treatment steps are schematically shown in Figure 1. 135 For the preparation of the lmw-DOM solution, 90 mg/L Al^{3+} was added as AlCl₃ solution. 136 137 Under stirring the pH was adjusted to a value of 6 by adding NaOH to form flocks. After 138 additional slow stirring the formed flocks were removed by 0.45 µm filters (Th. Geyer GmbH 139 & Co. KG, Germany). The filtrated solution was transferred to a SIMAtec LSta80 bench scale 140 filtration unit with a TS40 nanofiltration membrane (TriSep, USA) with a molecular weight 141 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 142 143 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.

148

149 The hmw-DOM solution was prepared by use of the same membrane filtration unit under the 150 same operating conditions, by filtering the raw drinking water using a NP010 nanofiltration 151 membrane (Microdyn-Nadir, Germany, MWCO ~ 1000 daltons (Machado et al. 2016)). The 152 resulting concentrate (at 80% recovery) was collected. 153 Both concentrate samples were diluted to a goal DOC level of 5 mg/L. Therefore, a salt 154 solution with a similar ionic composition as the raw drinking water was used. The detailed 155 composition of this solution can be found in the Supporting Information. The resulting pH 156 values were 7.3 (hmw-DOM-solution) and 7.6 (lmw-DOM solution), respectively. The 157 concentrations of the analyzed OMP in both prepared solutions were below the respective

158 limit of quantification (LoQ) of the used analytical method (see 2.5).

160 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.

167

168 **2.4.1.** Desorption batch tests with simultaneous adsorption of DOM and OMP

169 Batch tests were conducted, which simulated a decrease of the OMP inflow concentration in 170 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 $\sim 50 \ \mu g/L$ 171 172 ("adsorption solution"), were filled into centrifuge flasks (175 mL, Falcon, USA). Certain 173 amounts (between 250 and 1000 µL) of the AC stock suspensions were added to the 174 individual flask to obtain the above-indicated AC doses. After a contact time of 48 hours on a 175 horizontal shaker the AC was separated by centrifugation, 95 mL AC-free adsorption solution 176 were drawn off and replaced by 100 mL unspiked desorption solution (with OMP 177 concentrations below the limit of quantification). Subsequently, the batches were shaken for 178 another 48 hours, which could be identified as adequate contact time to achieve equilibrium 179 conditions (Aschermann et al. 2018). Adsorption and desorption samples were immediately 180 filtrated using 0.45 µm regenerated cellulose membrane filters (Chromafil Xtra, Macherey-181 Nagel, Germany). A detailed description of the experimental procedure can be found 182 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).

187 **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 ~ $50 \mu g/L$ 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.

195

196 2.5. Analytics

197 High performance liquid chromatography coupled with tandem mass spectrometry (HPLC-198 MS/MS) was used for measurements of OMP concentrations, following a method established 199 previously (Altmann et al. 2015, Zietzschmann et al. 2016a). An XSelect HSS T3 column (2.1 200 * 50 mm, Waters, USA) with 2.5 µm particle size was used for separation. Mobile phases 201 were ultra-pure water with 0.1 vol.-% formic acid (HPLC grade, Sigma Aldrich, Germany) 202 and pure methanol (HPLC grade, J.T. Baker, USA), pumped with a flow rate of 0.5 mL/min 203 and with a linear gradient. After electrospray ionization in positive mode the formed ions 204 were analyzed with a triple quadrupole mass spectrometer TSQ Vantage (Thermo Scientific,

205 USA). For substance identification the characteristic ratio of two mass fragments were used, which were chosen according to DAIOS database provided by Zweckverband 206 207 Landesversorgung (Stuttgart, Germany). Concentrations were determined using the more 208 abundant fragment, in combination with deuterated internal standards (Toronto Research 209 chemicals, Canada) and after data evaluation with Xcalibur 2.1 software (Thermo Scientific). 210 Calibration levels (9 in total) were between 0.01 and 55 µg/L. The limits of quantification 211 (LoQ) of this method are 0.05 μ g/L (for carbamazepine and sulfamethoxazole) and 0.1 μ g/L 212 (for diclofenac, 4-formylaminoantipyrine and iomeprol), respectively. LoQ were chosen as 213 the calibration level at which the less abundant fragment ion (qualifier) had a signal to noise 214 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 CO₂.
UV_{254nm} was measured with a Lambda 12 photospectrometer (Perkin-Elmer, USA) with 10
mm Spurasil quartz cuvettes (Hellma, Germany).

219 For further characterization of organic carbon composition, selected samples were analyzed 220 with liquid chromatography coupled with an online organic carbon detector (LC-OCD, DOC-221 Labor Dr. Huber, Germany), using a HW50S size exclusion column (Toyopearl, Japan). 222 According to Huber et al. (2011) molecular weight calibration was performed using 223 Suwannee river humic and fulvic acid from the International Humic Substances Society 224 (IHSS). Data processing was conducted using the software ChromCalc (DOC-Labor Dr. 225 Huber, Germany). DOM can be generally classified into different sub-fractions by means of 226 the resulting LC-OCD chromatogram (in order of increasing elution time): biopolymers (macromolecular compounds, such as polysaccharides and proteins); humic substances; 227

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.

231

232

2.6. Calculations and data evaluation

233 The AC loadings with OMP after adsorption and desorption were calculated using mass 234 balances. The resulting equations according to the experimental procedure can be found 235 elsewhere (Aschermann et al. 2018). The loadings were plotted against the respective OMP 236 equilibrium concentrations after the adsorption and desorption phase, respectively, to obtain 237 adsorption and desorption isotherms. A comparison of the relative position of the 238 corresponding adsorption and desorption isotherms was used to make qualitative statements 239 about the desorption extent of OMP. Therefore, the entire curves were evaluated (not single 240 data points).

241 As explained and illustrated elsewhere (Aschermann et al. 2018) the error in loading calculation strongly rises with decreasing differences between the initial OMP concentration, 242 243 the OMP concentration after adsorption and the OMP concentration after desorption. To 244 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 245 246 OMP after adsorption was above 25%. This constraint (plus the non-consideration of data 247 points with concentrations below the LoQ) resulted in adsorption and desorption isotherms, 248 which partly consisted of less than seven data points (which would ideally result from the 249 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) $ (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		

260 concentrations of the two prepared solutions are very similar and in the range of the raw

261 water. Thus, the solutions are comparable in terms of its quantitative DOM composition.

263 Table 1: DOC, UV_{254nm} and SUVA of the prepared experimental solutions and the raw water

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

264 (Berlin drinking water).

265

In terms of UV_{254nm} the solutions show differences after their specific pre-treatment in 266 267 comparison to the raw water. Related therewith, also the SUVA values are different. The 268 hmw-DOM solution shows an increased SUVA in comparison to the raw water, which 269 indicates a higher aromaticity of the DOM (Weishaar et al. 2003). Furthermore, an increasing 270 SUVA can also be related to a relative increase of humic compounds of higher molecular 271 weight (Huber et al. 2011). As the hmw-DOM solution results from the concentrate of the 272 nanofiltration process (MWCO: 1000 Da), this can be explained by the retention of aromatic 273 humic compounds by the membrane, resulting in an accumulation of this DOM fraction in the 274 concentrate. The lmw-DOM shows a decreased SUVA in comparison to the original raw 275 water indicating a removal of aromatic compounds in this case. This can be attributed to the 276 pre-treatment by flocculation, which leads to decreased SUVA values (Archer and Singer 277 2006, Volk et al. 2000).

- 278 For further characterization of the prepared solutions LC-OCD measurements were
- 279 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).

291



292

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

296 The normalized chromatogram of the lmw-DOM solution shows a clear shift of DOM size 297 composition to lower molecular weight compounds in comparison to the raw water. Its 298 maximum (at ~ 48 min) is not in the range of humic compounds, but in the range of building 299 blocks. Furthermore, low molecular weight acids and neutrals show a higher relative 300 abundance in comparison to the raw water, as resulting from the pre-treatment of the lmw-301 DOM solution. Flocculation with aluminum salts leads to a removal especially of higher 302 molecular weight DOM (Davis and Gloor 1981). Lower molecular weight compounds like 303 building blocks and low molecular weight acids and neutrals are not or less removed during 304 flocculation and were concentrated during nanofiltration. These DOM fractions show a higher 305 appearance in waste water treatment plant effluent DOM in comparison to drinking water 306 DOM (Zietzschmann et al. 2016a). The lower abundance of humic compounds is in 307 accordance with the decreased SUVA of this solution.

308 The normalized signal of the hmw-DOM solution shows generally a very similar 309 chromatogram in comparison to the raw water. This indicates that the DOM composition did 310 not change due to nanofiltration. This would imply that both, higher molecular weight humic 311 substances as well as lower molecular weight compounds are not affected by size exclusion 312 during the membrane treatment and, thus, could pass the nanofiltration membrane. Based on 313 the MWCO of this membrane (1.000 Da), an enrichment of high molecular weight 314 compounds and, thus a higher percentage of humic substances could be expected as this was 315 also reported in a previous fractionation study with the same membrane (Zietzschmann et al. 316 2014). This can actually not be seen in Figure 2. This can be explained by an enrichment of 317 more hydrophobic compounds in the concentrate, expressed by the increased SUVA of the 318 hmw-DOM solution. It was shown elsewhere that a higher hydrophobicity of compounds 319 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.

324 Despite an overlapping size range between the two prepared fractions, the hmw-DOM and 325 lmw-DOM solution show clear differences in their DOM size composition and can be used to 326 represent rather high molecular weight compounds and low molecular weight compounds, 327 respectively.

328

329 3.2. Adsorption of DOM

330 Figure 3 shows the DOC removal in the lmw-DOM and the hmw-DOM solution after 331 adsorption for all three tested AC. In both cases, the Epibon A shows the highest DOC 332 removal and the Hydraffin CC shows the lowest removal. The same trend was also seen for 333 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 334 335 pore size distribution. Although the given average AC pore sizes (see section 2.2) differ by 336 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 337 less than 0.8 nm, Pelekani and Snoeyink (1999) reported strongly different DOM adsorption 338 339 of these AC products, with lower DOM removal in case of the AC with a lower average pore 340 size and a narrow pore size distribution. Accordingly, the microporous Hydraffin CC shows 341 the lowest the DOC removal in this study. On the other hand, also the chemical properties of 342 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 343 344 can induce electrostatic repulsion of negatively charged DOM. This can explain the lower 345 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 346 347 both positively charged at the pH of both solutions, which is assumed to benefit the 348 adsorption of negatively charged DOM. However, the strong differences between these two 349 AC indicate that the DOM adsorption is rather impacted by the pore size distribution than by 350 the surface charge of the AC.

351 Furthermore, for all AC the DOC removal in the lmw-DOM and the hmw-DOM solution is 352 generally very similar. Thus, both fractions are comparable concerning their adsorbability. 353 Different studies that fractionated organic matter from waste water treatment plant effluents in 354 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 355 356 similarity of lmw- and hmw-DOM adsorption is likely induced by a combination of size 357 effects and aromatic/hydrophobic interactions. On the one hand, different studies (Kilduff et 358 al. 1996, Schreiber et al. 2005) report an increasing DOM adsorption with decreasing 359 molecular weight of the organic compounds, which would generally favor the removal of the 360 lmw-DOM compounds. On the other hand, more aromatic DOM shows higher adsorbability 361 in comparison to more aliphatic DOM, due to increased interactions with the AC (Schreiber et 362 al. 2005). This would favor the removal of compounds of the hmw-DOM solution, which has 363 a higher SUVA compared to the lmw-DOM solution. Since both mechanisms operate exactly 364 opposed for the lmw- and hmw-DOM solutions, respectively, barely any difference in DOM 365 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.

371



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

375

376 3.3. Effects of different DOM size fractions on OMP desorption

377 The following results originate from batch tests, where the AC was firstly loaded

378 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

383 representative OMP here. The isotherms of all other tested compounds can be found in the384 Supporting Information.

385



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

391 It can be seen that the position of the desorption isotherms in comparison to their respective 392 adsorption isotherms are different for the three tested AC. In the case of the microporous AC 393 Hydraffin CC the desorption isotherms are strongly shifted to the left in comparison to the 394 adsorption isotherms, in both tested waters. This indicates a strong irreversible adsorption of 395 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.

402 The desorption isotherms of the macroporous HK 1200 are located below the corresponding 403 adsorption isotherms. This shows an increased desorption of carbamazepine and diclofenac 404 from this AC. Also for this AC, experiments under pure water conditions result in rather 405 congruent OMP adsorption and desorption isotherms (Aschermann et al. 2018), which 406 illustrates that the shift of the desorption isotherm observed in the current study can be 407 attributed to DOM effects. Furthermore, additional experiments where the desorption solution 408 consisted of pure water instead of the respective DOM solution illustrate this effect more 409 detailed (corresponding isotherms of carbamazepine in SI (Figure S7)). As shown in Figure 410 S7, desorption under pure water conditions (following a simultaneous adsorption of OMP and 411 the respective DOM fraction) leads to superimposing adsorption and desorption isotherms in 412 case of the HK 1200, which illustrates completely reversible OMP adsorption (in case of both 413 DOM fractions). Thus, it can be assumed that in this case, no/reduced pore blockage effects 414 occur during the adsorption phase. This allows OMP to desorb as a result of the reversed 415 concentration gradient. In the experiments corresponding to Figure 4 and 5, the loaded AC 416 (after the adsorption phase) gets in contact with 'fresh' DOM in the desorption phase. This 417 leads to an additional adsorption of DOM compounds during the desorption phase as the 418 initial DOM concentration is above the equilibrium DOM concentration at the end of the 419 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).

427



429 Figure 5: Adsorption and desorption isotherms of carbamazepine ($c_0 = 37.4 \mu g/L$) and diclofenac 430 ($c_0 = 41.6 \mu g/L$) for all tested activated carbons after adsorption and desorption in the lmw-DOM 431 solution.

433 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 434 435 indicates displacement effects, similar to those described for HK1200. Also in this case, the 436 desorption isotherm is shifted to the bottom/right, when DOM is present during the desorption 437 phase (Figure 4/5 vs. Figure S7). However, the desorption isotherms move closer to the 438 corresponding adsorption isotherms and partly cross them for increased loadings. This 439 indicates reduced displacement as well as partial pore blockages, which prevent the 440 desorption of OMP.

441 The results generally show that a higher AC pore size results in a higher OMP desorption 442 extent, which can be explained by different DOM interactions: pore blockage effects for 443 microporous AC on the one hand and displacement effects for macroporous AC. As discussed 444 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 445 446 similarities between the Hydraffin CC and the Epibon A would be expected due to their rather 447 similar values, especially in comparison with the HK 1200. However, these two AC 448 (Hydraffin CC and Epibon A) act quite different in terms of OMP desorption (as shown in 449 Figure 4 and 5). Furthermore, the exemplary shown compounds, carbamazepine and 450 diclofenac, also differ in their charge. Whereas carbamazepine is uncharged over a wide pH 451 range, diclofenac is negatively charged at a neutral pH (Suriyanon et al. 2013). Thus, stronger 452 differences in the desorption behavior of these compounds would be expected, if the AC 453 surface charge would be a dominating factor in terms of OMP adsorption/desorption. 454 However, both compounds actually show very similar results for the particular AC, 455 underlining the dominating role of the AC pore structure with respect to OMP desorption in 456 the presence of DOM.

457 All these described effects can be seen in a similar manner for the used raw water 458 (Aschermann et al. 2018). Furthermore, the course of the desorption isotherms in comparison 459 to the adsorption isotherms is very similar for the lmw-DOM solution and the hmw-DOM 460 solution for the respective AC. No differences in the OMP desorption behavior can be seen in 461 the two different solutions. This indicates that both solutions do not differ in their effects on 462 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. 463 464 The lmw-DOM solution contains a relatively low percentage of humic substances, the hmw-465 DOM solution contains relatively low percentages of low molecular weight compounds. It is 466 known that the ratio of OMP and (unfractionated) DOM (Knappe et al. 1998) and of OMP 467 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 468 469 DOM fractions would also lead to different impacts on OMP desorption. As latter cannot be 470 observed, generally similar effects of the fractions examined here can be assumed. Thus, these 471 effects are not induced by DOM compounds of a certain size, but by both, smaller and larger 472 compounds.

473 Based on this, it seems likely that model compounds that are often used for different DOM

474 fractions do not reflect the real behavior of DOM. For example, Li et al. (2003b) inferred that

475 low molecular weight DOM induces displacement effects as the model compound 1,4-

476 dichlorobenzene did this. The current results of the lmw-DOM show that such a conclusion

477 from model compounds cannot readily be drawn.

479 3.4. Effects of DOM size on adsorption of organic micropollutants

480 Figure 4 and Figure 5 also allow a comparison of the adsorption isotherms of carbamazepine 481 and diclofenac in both tested solutions. As the respective OMP concentrations as well as the 482 DOC in both solutions were very similar (and, thus, also the OMP/DOC ratio), the isotherms 483 are directly comparable (Knappe et al. 1998, Zietzschmann et al. 2016a). For all tested AC the 484 respective adsorption isotherm in the lmw-DOM solution (Figure 5) is below the 485 corresponding isotherm in the hmw-DOM solution (Figure 4). This indicates a higher 486 competitive effect in the lmw-DOM solution leading to a lower OMP adsorbability. This 487 confirms previous results which identified smaller DOM compounds to be more competitive 488 towards OMP adsorption than larger compounds (Hu et al. 2016, Zietzschmann et al. 2014, 489 Zoschke et al. 2011). However, in these studies the increased competition effect of smaller 490 compounds is referred to a direct competition on adsorption sites between these compounds 491 and OMP, which was, thus, identified as the major competition effect. In comparison, the 492 weaker competitive effects of larger compounds were referred to pore blockage effects. The 493 current results of the desorption experiments show that such a classification is not possible as 494 both fractions lead to very similar effects.

495

496 3.5. Influence of DOM preloading on OMP adsorption

497 For further identification of the described effects, batch experiments with a sequential
498 adsorption phase were conducted. In this case, the AC was pre-loaded with the particular
499 DOM fraction (OMP concentration < LoQ) prior to the adsorption of OMP. The resulting

adsorption isotherms of carbamazepine in comparison to the isotherms after simultaneous



501 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.

506

507 The isotherms in the case of the sequential adsorption are located below the ones after 508 simultaneous adsorption in nearly all cases. The same effect can also be seen for diclofenac 509 (shown in the Supporting Information). Thus, the pre-loading with both, hmw- and lmw-510 DOM, leads to a decreased adsorption of OMP. A similar effect could also be seen for 511 unfractionated drinking water DOM (Aschermann et al. 2018). It indicates a lower availability 512 of adsorption sites due to the pre-loading, which can be referred to AC pore blockages and, 513 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).

517 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, 518 519 was determined for sequential and simultaneous adsorption (with an averaged n in both cases 520 for each AC and each background solution). The ratio of these two K_F values can be used as a 521 parameter for the comparison of simultaneous/sequential adsorption. It can be seen that pre-522 loading with DOM leads to a stronger decrease of OMP adsorption with higher microporosity 523 of the AC, for both tested solutions. Thus, microporous AC are more affected by pore 524 blockages as macroporous AC (as it was also the case for unfractionated drinking water DOM 525 (Aschermann et al. 2018)). Similar effects were also seen in preloading experiments by Li et 526 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.

532 Due to these observations, it can be assumed that the DOM composition does not significantly 533 influence the desorption behavior of OMP in real AC applications. Thus, effects in terms of 534 desorption behavior might be independent of the DOM size composition of different waters. 535 This indicates that the effects that were seen for one specific drinking water (Aschermann et 536 al. 2018) might be transferable also to other real waters with different composition. 537

538 **3.6.** Influence of DOM preloading on OMP desorption in pure water

539 In this experimental series, the tested AC were brought into contact with pure water,

540 subsequent to sequential loading with DOM and OMP. The resulting desorption isotherms of

541 carbamazepine after sequential adsorption in the lmw-DOM and the hmw-DOM solution,

542 respectively, can be found in Figure 7.

543



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

549 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 550 551 substances into these pores. Thus, the subsequently added OMP are expected to adsorb in 552 pores that are not blocked. By conducting a desorption step in pure water and, thus, without 553 further interactions between the adsorbed OMP and other water constituents, desorption from 554 these unblocked adsorption sites is expected to be driven only by the reversal of the OMP 555 concentration gradient, and should proceed without interference by DOM. Under these 556 conditions the OMP adsorption is expected to be highly or completely reversible 557 (Aschermann et al. 2018).

558 However, only the macroporous HK 1200 shows a completely reversible adsorption, 559 illustrated by the superimposing isotherms (excluding one outlying data point for the lmw-560 DOM solution). The desorption isotherms in case of the microporous Hydraffin CC and the 561 mesoporous Epibon A are shifted to the left in comparison to their corresponding adsorption 562 isotherms (excluding one outlying data point in case of Epibon A (lmw-DOM)). This 563 characterizes the irreversibility of OMP adsorption under these conditions, especially for the 564 microporous Hydraffin CC. These results are very similar to the results of the experiment, 565 where the respective AC were simultaneously loaded with OMP and the respective DOM 566 fraction, followed by a desorption phase in pure water (see Figure S7 in the Supporting 567 Information). Thus, the OMP desorption behavior is independent from adsorption sequence of 568 OMP and DOM as simultaneous and sequential adsorption lead to the same effects. 569 This contradicts the expected results described above. It indicates that the idea of static and 570 permanent pore blockages might be too simple to completely describe the effects of DOM 571 during OMP adsorption and desorption. Possible explanations for the observed results would 572 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

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.

607

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