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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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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

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
23 real waters. In this study, the impact of different fractions of drinking water DOM on OMP
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
27 tests, simulating a drop of the OMP inflow concentration to a fixed-bed adsorber. The tests
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

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

45

46 **Keywords**

47 activated carbon, organic micropollutants, desorption, adsorption, drinking water, dissolved
48 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
53 treatment (Boehler et al. 2012, Westerhoff et al. 2005, Zietzschmann et al. 2016a,
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
60 concentration gradient (e.g. due to decreased influent concentrations) and b) by the
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 as
64 the influent water composition to change over the course of a filter run.

65 Generally, it can be assumed that the desorption behavior of a compound in AC filters is
66 affected by the extent of desorption and the corresponding desorption kinetics. It has been
67 shown that the extent of OMP desorption under real conditions can be strongly influenced by
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
81 different DOM fractions is still missing.

82 In terms of adsorption, both effects, direct competition and pore blocking, lead to the same
83 result: a lower adsorption capacity. In terms of desorption, it has to be assumed that these
84 effects have different impacts. Direct competition would increase desorption due to
85 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).

88 Due to these potentially different effects it is necessary to understand which DOM fractions
89 induce these effects. Thus, it is the goal of the current study to use adsorption and desorption
90 batch tests to identify the impact of different DOM size fractions on OMP desorption. These
91 tests were conducted (i) in the presence of differing DOM size fractions to understand their
92 effects, and (ii) with different AC products to evaluate the impact of different pore size
93 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**

100 Three commercial activated carbons (AC) were used for lab batch experiments: Hydriffin
101 CC, Epibon A (both Donau Carbon, Germany) and HC HK 1200 (CSC, Germany). The
102 granular products were pulverized on a Pulverisette mill (Fritsch, Germany) and sieved
103 (Retsch, Germany) to obtain powdered activated carbon with particle sizes below 63 μm .

104 Before usage the AC material were dried at 105°C overnight and stored in a desiccator until
105 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-,
112 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
115 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.

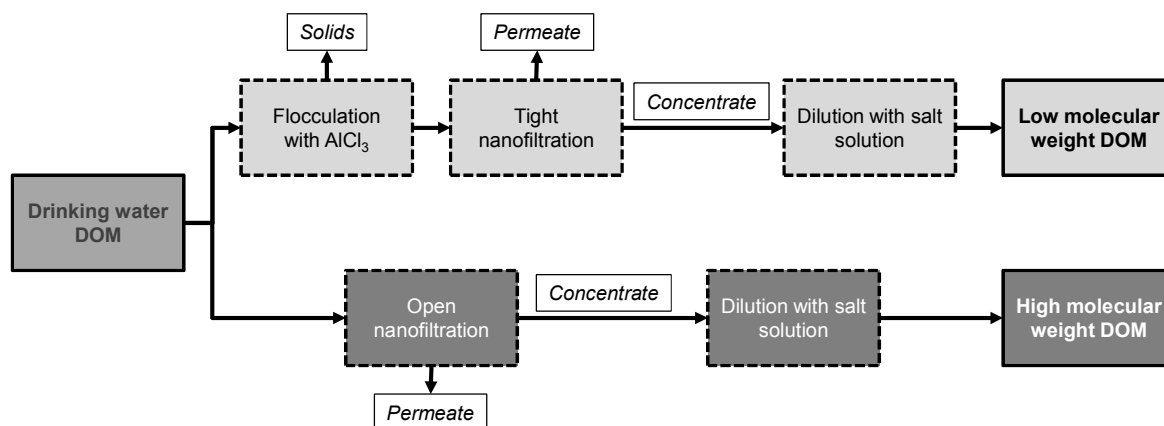
127

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
135 are schematically shown in Figure 1.

136 For the preparation of the lmw-DOM solution, 90 mg/L Al^{3+} was added as $AlCl_3$ solution.
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
142 filtrated in cross-flow mode with an applied pressure of 35 bar. Filtration was stopped at a
143 recovery of 80 percent. The resulting concentrate was collected.

144



145

146 **Figure 1: Schematic description of preparation procedure for the low molecular weight and the**
 147 **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).

159

160 **2.4. *Experimental procedure***

161 Different laboratory batch experiments were conducted with the three activated carbon
162 products in parallel. Therefore, AC stock suspensions (0.8 and 5 g/L) were prepared with ultra
163 pure water. Prior to the experiments, the suspensions were degassed and subsequently
164 homogenized with a magnetic stirrer. Every single experimental series consisted of seven
165 batches with different doses of the respective AC (also meaning that no replicates were
166 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
171 solution, which was previously spiked with OMP to a concentration level of ~ 50 µg/L
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).

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

186

187 **2.4.2. Desorption batch tests with sequential adsorption of DOM and OMP**

188 For sequential adsorption, equivalent AC doses were added to the unspiked lmw-DOM and
189 hmw-DOM solutions, respectively. After 48 hours contact time a certain volume of the OMP
190 stock solution was added to each individual batch to achieve again concentrations of ~
191 50 µg/L in the respective batches. Subsequently, the batches were shaken for another 48
192 hours. AC was then separated as described above and 100 mL desorption solution were
193 added, which was pure water in this case. The contact time during the desorption phase was
194 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,
206 which were chosen according to DAIOS database provided by Zweckverband
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 µg/L (for carbamazepine and sulfamethoxazole) and 0.1 µg/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 .

215 DOC was determined with a varioTOC Cube (elementar Analysensysteme, Germany) using
216 high-temperature catalytic combustion and non-dispersive infrared detection of formed CO₂.
217 UV_{254nm} was measured with a Lambda 12 photospectrometer (Perkin-Elmer, USA) with 10
218 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
227 (macromolecular compounds, such as polysaccharides and proteins); humic substances;

228 building blocks (breakdown products of humic substances); low molecular weight acids; low
229 molecular weight neutrals (Huber et al. 2011). An exemplary chromatogram including these
230 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
242 calculation strongly rises with decreasing differences between the initial OMP concentration,
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
245 data pairs were considered for the depiction in isotherms, where the removal of the respective
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).

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

$$253 \quad \log(q) = n * \log(c) + \log(K_F) \quad (1)$$

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

255

256 **3. Results and Discussion**

257 **3.1. Characteristics of DOM fractions**

258 Table 1 shows the qualitative and quantitative characteristics of the prepared DOM solutions
259 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.

262

263 **Table 1: DOC, UV_{254nm} and SUVA of the prepared experimental solutions and the raw water**
 264 **(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

265

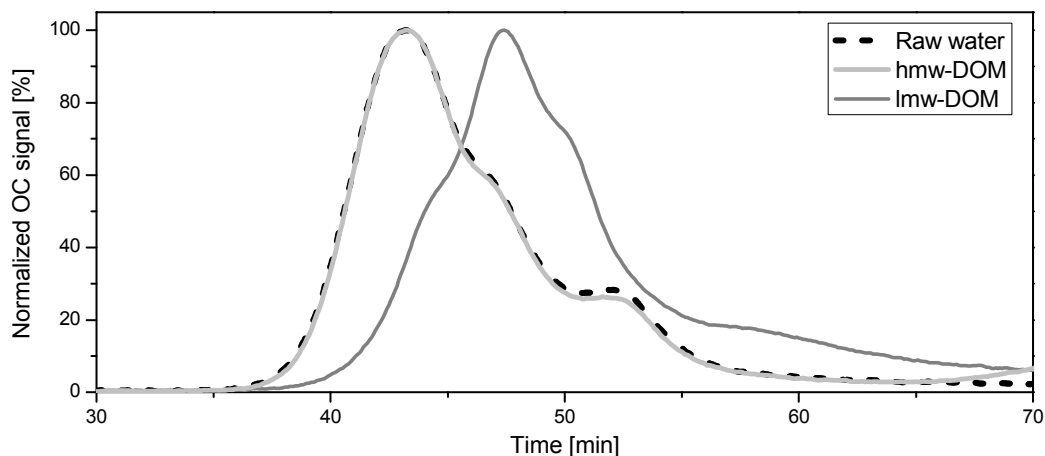
266 In terms of UV_{254nm} the solutions show differences after their specific pre-treatment in
 267 comparison to the raw water. Related therewith, also the SUVA values are different. The
 268 hmw-DOM solution shows an increased SUVA in comparison to the raw water, which
 269 indicates a higher aromaticity 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.

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

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

291



292

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

295

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

320 hydrophobic/aromatic compounds are usually retained longer on the employed LC column
321 (Ruhl and Jekel 2012). This would imply that the hmw-DOM solution contains larger size
322 DOM compounds than the raw water, but that the effect is masked by increased interactions
323 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**

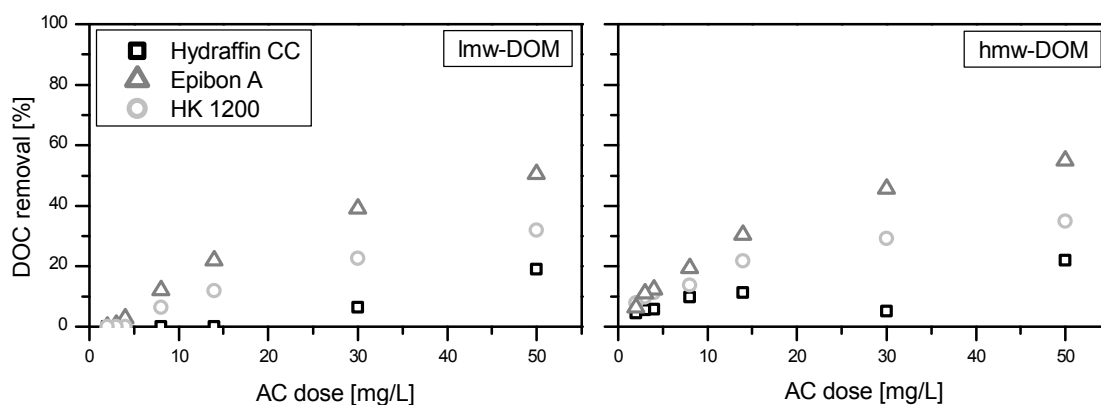
330 Figure 3 shows the DOC removal in the lmw-DOM and the hmw-DOM solution after
331 adsorption for all three tested AC. In both cases, the Epibon A shows the highest DOC
332 removal and the Hydriffin CC shows the lowest removal. The same trend was also seen for
333 untreated drinking water (Aschermann et al. 2018). Thus, the pre-treatment did not change the
334 affinity of the DOM towards a certain AC. On the one hand, this affinity is affected by the AC
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
337 the DOM adsorption. By testing different AC fibers that differed in their average pore size by
338 less than 0.8 nm, Pelekani and Snoeyink (1999) reported strongly different DOM adsorption
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 Hydriffin 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

343 al. 1999). Due to its low pH_{pzc} of 3 the HK 1200 is negatively charged at a neutral pH, which
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
346 distribution of the HK 1200. The Epibon A (pH_{pzc} : 8.1) and the Hydraffin CC (pH_{pzc} : 9.5) are
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
355 bigger DOM compounds (Hu et al. 2016, Zietzschmann et al. 2014). In the present study the
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.

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

371



372

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

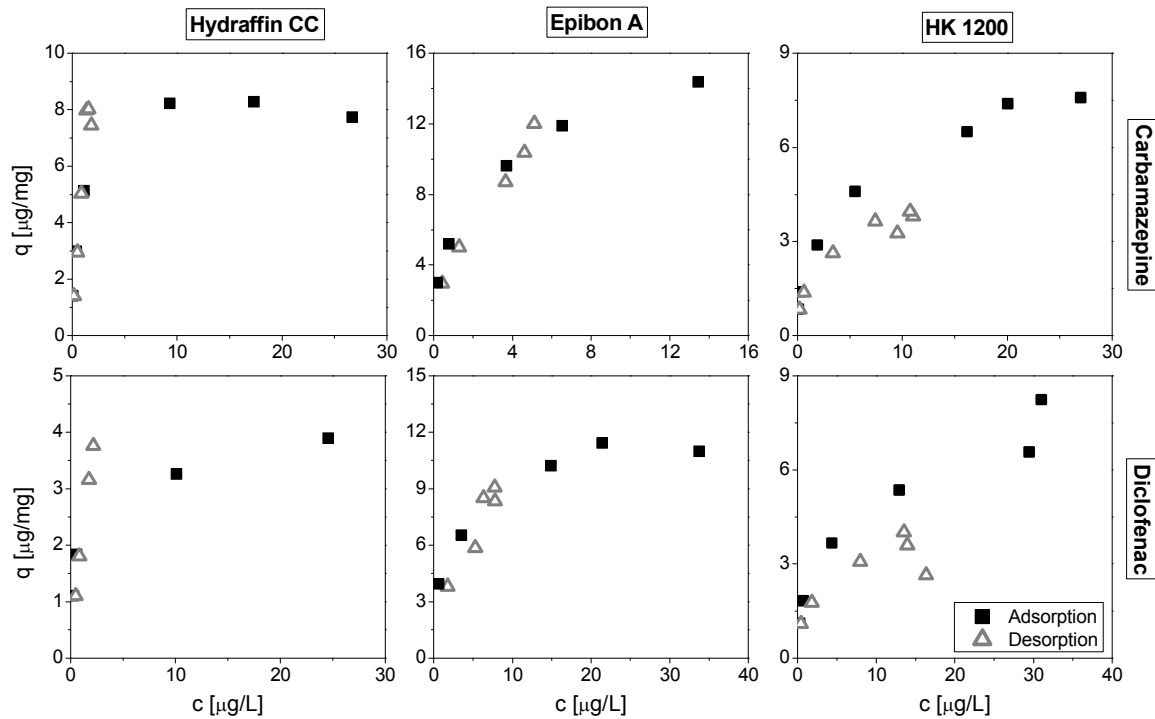
375

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
379 in the respective unspiked DOM solution (see section 2.4.1). The resulting desorption
380 isotherms of carbamazepine and diclofenac in both, the hmw-DOM and lmw-DOM solutions,
381 as compared to the respective adsorption isotherms are shown in Figure 4 and Figure 5. As all
382 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 the
384 Supporting Information.

385



386

387 **Figure 4: Adsorption and desorption isotherms of carbamazepine ($c_0 = 42 \mu\text{g/L}$) and diclofenac**
388 **($c_0 = 55.7 \mu\text{g/L}$) for all tested activated carbons after adsorption and desorption in the hmw-**
389 **DOM solution.**

390

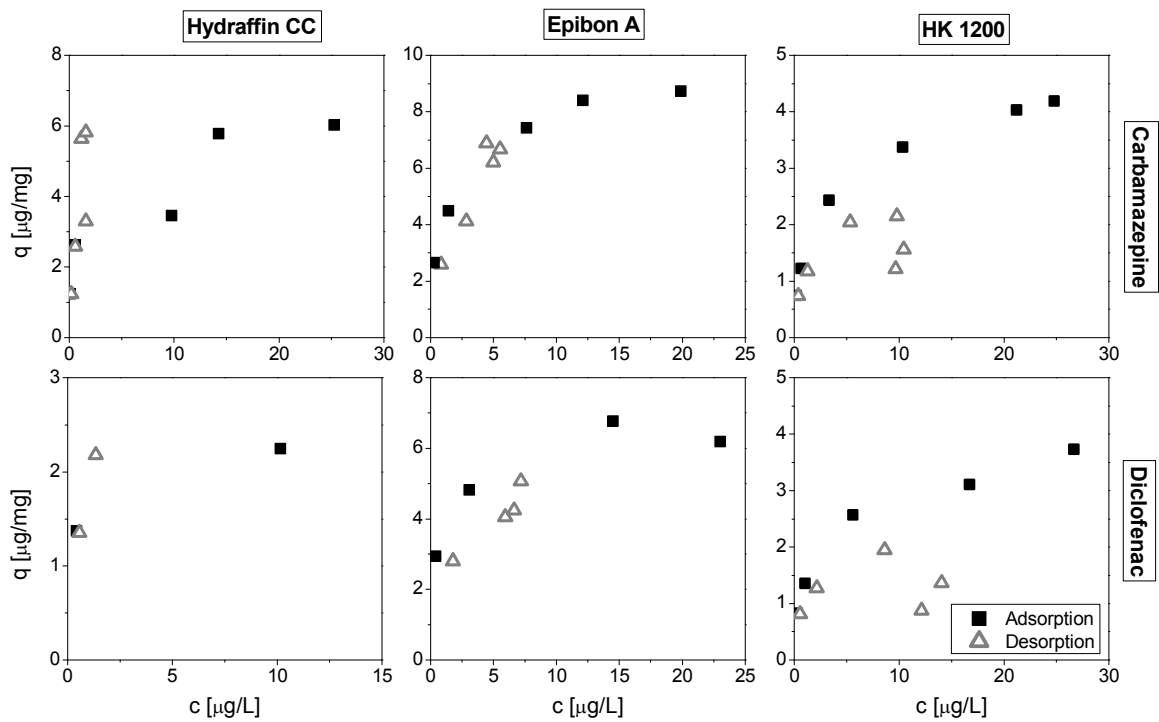
391 It can be seen that the position of the desorption isotherms in comparison to their respective
392 adsorption isotherms are different for the three tested AC. In the case of the microporous AC
393 Hydriffin CC the desorption isotherms are strongly shifted to the left in comparison to the
394 adsorption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

396 adsorption and desorption isotherms are rather congruent, indicating a highly/completely
397 reversible adsorption (Aschermann et al. 2018). Thus, the additional adsorption of DOM
398 affects the desorption of OMP and leads to a higher irreversibility of the OMP adsorption in
399 case of the Hydraffin CC. This could be referred to pore blockages by DOM compounds
400 during the adsorption phase, in the lmw-DOM as well as in the hmw-DOM solution,
401 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,

420 where the DOC removal after the desorption phase for the three AC in the respective DOM
 421 solution is illustrated. As no/reduced blockages occur, the additionally adsorbing DOM
 422 compounds can enter the AC pores and displace adsorbed OMP, which leads to an increased
 423 desorption. This is illustrated by the shift of the desorption isotherm to the bottom/right in
 424 comparison to the corresponding adsorption isotherm (Figure 4/5), but also in comparison to
 425 the equivalent desorption isotherm, when no DOM is present during the desorption (Figure
 426 4/5 vs. Figure S7).

427



428

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

432

433 For the mesoporous AC Epibon A, both described effects can be seen. For lower AC loadings
434 the desorption isotherms are located below the corresponding adsorption isotherms, which
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
445 adsorption/desorption in the presence of DOM. Nonetheless, based on the pH_{pzc} , higher
446 similarities between the Hydrffin 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 (Hydrffin 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
463 in a very similar way. Figure 2 shows that the DOM sizes in the two solutions partly overlap.
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
468 behavior of OMP. Therefore, it can be expected that different ratios of OMP and certain
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.

478

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

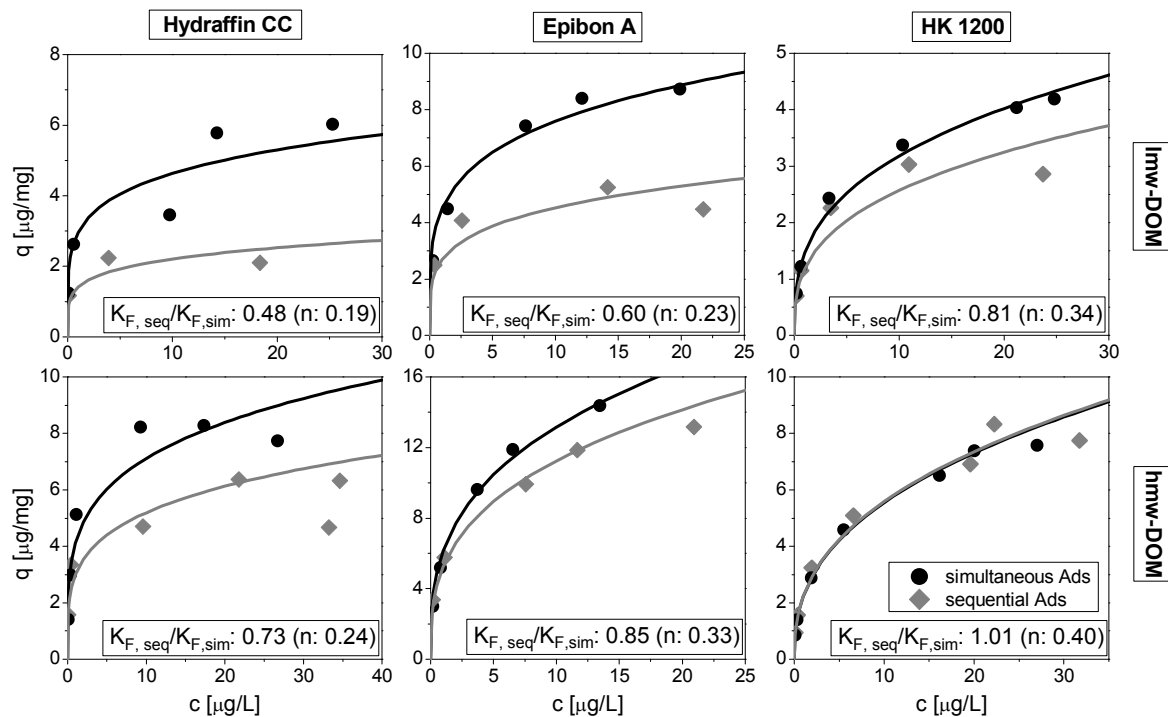
480 Figure 4 and Figure 5 also allow a comparison of the adsorption isotherms of carbamazepine
481 and diclofenac in both tested solutions. As the respective OMP concentrations as well as the
482 DOC in both solutions were very similar (and, thus, also the OMP/DOC ratio), the isotherms
483 are directly 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

500 adsorption isotherms of carbamazepine in comparison to the isotherms after simultaneous
 501 adsorption are shown in Figure 6.



502
 503 **Figure 6: Adsorption isotherms of carbamazepine (with modeling after Freundlich) for all tested**
 504 **AC after simultaneous and sequential adsorption of DOM and OMP in the lmw-DOM (top) and**
 505 **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

514 blocking can also prevent the release of OMP that are adsorbed in deeper parts of the
515 respective pore and, thus, can explain the irreversibility of OMP adsorption in certain cases
516 (Figure 4 and Figure 5).

517 To quantify the changes in OMP adsorption between simultaneous and sequential adsorption
518 the isotherms were fitted with the Freundlich equation. K_F , as parameter for the adsorbability,
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).

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

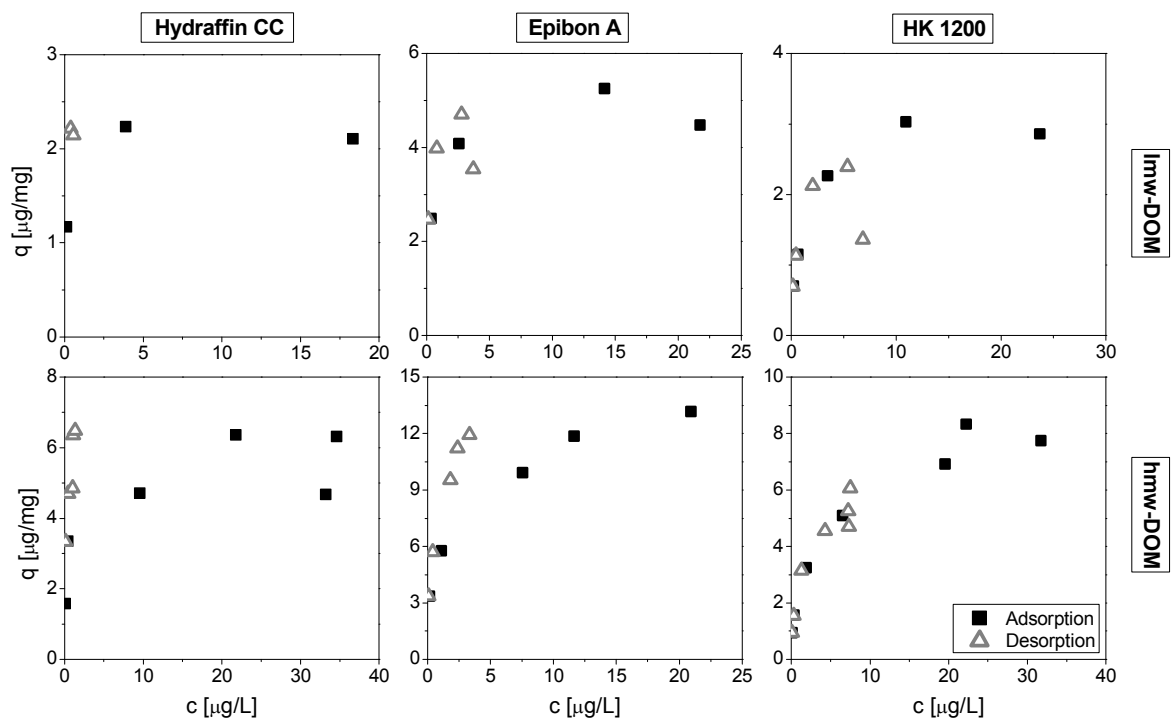
532 Due to these observations, it can be assumed that the DOM composition does not significantly
533 influence the desorption behavior of OMP in real AC applications. Thus, effects in terms of
534 desorption behavior might be independent of the DOM size composition of different waters.
535 This indicates 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



544

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

548

549 Based on the previous findings, it could be assumed that the preloading with DOM leads to
550 permanent blockages of the AC pores, which sterically hinders a further transport of
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 Hydrffin 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 Hydrffin 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

573 molecular conformation), which allow OMP to enter the deeper parts of the pore, but not to
574 leave pores or (ii) there are partial interactions between adsorbed DOM and OMP when less
575 adsorption sites are available due to pore blockages, which are irreversible and prevent OMP
576 from desorption.

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

580

581 **4. Conclusion**

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

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

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

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

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

607

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614

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