This is the accepted manuscript version of the contribution published as:

Schumann, P., Müller, D., Eckardt, P., **Muschket, M.**, Dittmann, D., Rabe, L., Kerst, K., Lerch, A., **Reemtsma, T.**, Jekel, M., Ruhl, A.S. (2023): Pilot-scale removal of persistent and mobile organic substances in granular activated carbon filters and experimental predictability at lab-scale *Sci. Total Environ.* **884**, art. 163738

The publisher's version is available at:

https://doi.org/10.1016/j.scitotenv.2023.163738

1	Pilot-Scale Removal of Persistent and Mobile Organic Substances in Granular
2	Activated Carbon Filters and Experimental Predictability at Lab-Scale
3	Pia Schumann ^{*1,2} , Dario Müller ^{4,5} , Paulina Eckardt ² , Matthias Muschket ³ , Daniel Dittmann ¹ , Luisa
4	Rabe ^{1,2} , Kristin Kerst ⁴ , André Lerch ⁴ , Thorsten Reemtsma ³ , Martin Jekel ² , Aki Sebastian Ruhl ^{1,2}
5	*corresponding author
6	¹ German Environment Agency (UBA), Section II 3.3, Schichauweg 58, 12307 Berlin, Germany,
7	pia.mc.schumann@campus.tu-berlin.de
8	² Technische Universität Berlin, Chair of Water Quality Control, Sekr. KF 4, Straße des 17. Juni 135,
9	10623 Berlin, Germany
10	³ Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig, Germany
11	⁴ Technische Universität Dresden, Chair of Process Engineering in Hydro Systems, Institute of Urban
12	and Industrial Water Management, 01062 Dresden, Germany
13	⁵ Kommunale Wasserwerke Leipzig, Johannisgasse 7/9, 04103 Leipzig, Germany
14	Highlights
15	• Breakthrough behavior of 9 out of 17 target substances in pilot filter observed
16	• 5 out of 9 substances reach complete breakthrough < 20,000 BV
17	• Economic removal of 5 substances (e.g. melamine) in GAC fixed-beds
18	Lab-scale experiments are suitable for conservative breakthrough prediction
19	Reduction of knowledge gap on PM substances in activated carbon filters
~ ~	

.

20

_ ...

.

21 Graphical abstract



22

23 Abstract

24 Present knowledge about the fate of persistent and mobile (PM) substances in drinking water 25 treatment is limited. Hence, this study assesses the potential of fixed-bed granular activated carbon 26 (GAC) filters to fill the treatment gap for PM substances and the elimination predictability from lab-27 scale experiments. Two parallel pilot filters (GAC bed height 2 m, diameter 15 cm) with different GAC 28 were operated for 1.5 years (ca. 47,000 BV throughput) alongside rapid small-scale column tests 29 (RSSCT) designed based on the proportional diffusivity (PD) and the constant diffusivity (CD) 30 approaches. Background dissolved organic matter (DOM) and a set of 17 target substances were 31 investigated, among them 2-acrylamido-2-methylpropane sulfonate (AAMPS), adamantan-1-amine 32 (ATA) and trifluoromethanesulfonic acid (TFMSA). Nine substances were predominantly present in the drinking water used as pilot filter influent (frequencies of detection above 80%, median 33 34 concentrations 0.003–1.868 µg/L) and their breakthrough behaviors could be observed: TFMSA was 35 not retained at all, four substances including AAMPS and ATA reached complete breakthrough below

36 20,000 BV, three compounds were partially retained until the end of operation and oxypurinol was 37 retained completely. The comparable PM candidate and DOM removal performances of both GAC 38 aligns with their very similar surface characteristics and elemental compositions. The agreement of 39 results between RSSCT with the pilot-scale filters were substance specific and no superior RSSCT 40 design could be identified. However, CD-RSSCT provide a conservative removal prediction for most 41 studied compounds. Melamine (MEL) adsorption was significantly underestimated by both RSSCT 42 designs. Using the criterion of a carbon usage rate (with respect to 50% breakthrough) below 43 25 mg_{GAC}/L_{water} for an economic retention by fixed-bed GAC filters, five (out of nine) substances met 44 the requirement.

45 Key words

46 emerging contaminants, trace organic chemicals (TOrC), rapid small-scale column tests (RSSCT),
47 organic micropollutants (OMP), polar contaminants

48 **1. Introduction**

49 The group of persistent and polar and thus mobile substances (PM substances) among organic 50 micropollutants (OMP) is receiving increasing interest by researchers and regulators: Their intrinsic 51 properties imply limitations in their elimination by conventional and advanced water treatment and 52 they might ultimately appear in drinking water (Reemtsma et al., 2016). Consequently, persistent, 53 mobile, and toxic as well as very polar and very mobile substances have been categorized as 54 substances of very high concern by the European Commission (European Commission, 2020). 55 However, a common definition of "persistence" and "mobility" is yet missing and is controversially 56 discussed in scientific and regulatory communities (Hale et al., 2020b; Sigmund et al., 2022).

57 Since PM substances are a heterogeneous group of anthropogenic chemicals defined only by their 58 properties, they belong to various substance classes such as industrial chemicals, pharmaceuticals 59 and pesticides (Arp and Hale, 2019). Hence, PM substances are released into the environment by a large variety of human activities: Industrial production, agriculture, traffic, human consumption and many more lead to point or diffuse source emissions into the aquatic environment. The risk for accumulation in water cycles and contamination of drinking water sources is especially high in partially closed water cycles, like in urban areas (Hale et al., 2020a; Jekel et al., 2015; Pal et al., 2014). It is well established from a variety of studies, that PM substances are widely present in European drinking water sources (Neuwald et al., 2022; Scheurer et al., 2022; Schulze et al., 2019), which calls for action to protect drinking water and ultimately environmental and human health.

67 Widespread advanced drinking water treatment options suited for OMP elimination are ozonation 68 and adsorption onto activated carbon. Comparing both treatment options, adsorption has the 69 advantage of removing target compounds instead of transforming them into more and largely 70 unknown compounds (Gulde et al., 2021; Peyrelasse et al., 2022). In activated carbon applications, 71 fixed-bed filter using granular activated carbon (GAC) are a state-of-the-art drinking water treatment 72 option for taste and odor elimination as well as OMP removal with a broad knowledge base for 73 scientists, regulators, and operators (Worch, 2021). Even though the inherent polarity of PM 74 substances is expected to cause poor removals by adsorption onto activated carbon, previous results 75 indicated partially promising elimination potentials by an adsorption step (Schumann et al., 2023).

Different activated carbons differ in raw materials and activation processes resulting in divers commercially available products. Their physical and chemical properties deviate highly between products and even batches of the same product, which consequently leads to varying selectivities and treatment efficiencies (Ania and Bandosz, 2005; Dittmann et al., 2022; Nielsen et al., 2014). To link the adsorption behavior of an activated carbon product to its characteristics, comprehensive adsorbent analyses is crucial. Thus, this study comprises comprehensive GAC analysis including GAC surface characteristics and elemental composition.

Rapid small-scale column tests (RSSCT) are cost and time effective lab-scale experiments aiming to
simulate the breakthrough behavior of the respective target compounds in fixed-bed filters and
consequently replace laborious pilot plant studies or extensive kinetic and isotherm studies in

preparation for model-based breakthrough prediction. Two down-scaling approaches are commonly
used to design RSSCT: The proportional diffusivity (PD) approach assuming equal intraparticle
diffusion coefficients, and the constant diffusivity (CD) approach concluding a proportional relation
of the intraparticle diffusion coefficient and the particle size (Crittenden et al., 1986; Crittenden et al., 1987).

91 Based on their occurrence in European surface waters, 17 target substances were selected (Neuwald 92 et al., 2021; Neuwald et al., 2022; Schulze et al., 2019). Among them 2-acrylamido-2-methylpropane 93 sulfonate (AAMPS), adamantan-1-amine (ATA) and trifluoromethanesulfonic acid (TFMSA) ranking 94 within the ten most frequently detected compounds in a suspect screening for PM substances of 95 German surface water samples by Neuwald et al. (2021). All investigated substances are polar with 96 log D ranging from -2.86 to 1.27 (median -1.35) at pH 7.5, relatively small with molecular weights 97 between 84 and 614 g/mol (median 158 g/mol). In addition, the majority of the substances studied 98 are either ionic or ionizable and occur predominantly as charged species at environmental pH. Not 99 all target compounds have yet been subjected to systematic persistence testing and are therefore 100 referred to hereafter as PM candidates. However, their presence in water cycles suggests low 101 biodegradability under environmental conditions.

102 To fill the knowledge gap on the extent to which PM substance can be removed by adsorption on GAC 103 filters under realistic conditions, pilot studies over 1.5 years accompanied by RSSCT were carried 104 out. Thereby, this study aims (a) to explore PM candidate occurrences, concentration levels and 105 seasonal changes in conventionally treated (bank filtration, aeration, flocculation, and rapid sand 106 filtration) finished drinking water, (b) to investigate simultaneous adsorption of 17 PM candidates 107 with very different chemical properties in the presence of dissolved organic matter (DOM) in GAC 108 fixed-bed filters in both pilot-scale and lab-scale taking into account the influence of GAC 109 characteristics, and (c) to assess the transferability of RSSCT breakthrough onto large scale 110 applications and identify the appropriate scale-up approach for the target substances. To our 111 knowledge, this is the first study to specifically focus on the fate of PM substances in GAC fixed-bed filters and therefore seeks to contribute to closing the knowledge gap on PM substance behavior inadvanced drinking water treatment.

114 **2. Materials and methods**

115 **2.1. Activated carbons and carbon characterization**

116 In both pilot and laboratory scale, two commercially available GAC (both 8 x 30 mesh) were used: 117 The lignite based AquaSorb 5000 (AS 5000, Jacobi, Germany) and the bituminous based HCR+1 118 (Carbon Service & Consulting, Germany). The selection was based on a preliminary GAC screening 119 described in short in the supporting information (SI, section 1.1). In the screening comparing nine 120 different commercial GAC products, large differences in removal performances were revealed: The 121 removal between the GAC products applying the same contact time and activated carbon dose 122 differed by 30±21% on average, which emphasizes on the importance of the selection of an 123 appropriate GAC for a specific purpose. For the pilot filters, the two best-performing GAC were 124 selected.

The specific surface area (SSA) and the pore structures were determined via N_2 adsorption isotherms ($n \ge 3$) using an AutoSorb-1-MP device (Quantachrome, USA). Further details are provided in the SI (section 1.2).

Both the ash content and the carbon content were determined via surrogate analyses of the oxidative
mass losses by thermogravimetric analysis (TGA) using a thermobalance TGA/DSC 3+ from Mettler
Toledo (USA). Additionally, evolved gas analysis by Fourier-transform infrared spectroscopy (TGAFTIR, Thermo Fisher Scientific, USA) was applied to quantify the oxygen content as well as the surface
oxygen groups according to Dittmann et al. (2022).

X-ray fluorescence spectroscopy (XRF) was conducted to characterize the inorganic elemental
composition applying a Spectro XEPOS III with the software X-LabPro 5.1/TurboQuant (Spectro
Analytical Instruments, Germany) (Dittmann et al., 2022). For TGA, TGA-FTIR and XRF analyses, the

activated carbons were pulverized using a ball mill (CryoMill, Retsch, Germany; 30 s with 30 Hz) and
washed with ultrapure water (2 h contact time on a horizontal shaker).

138 The point of zero charge (pH_{PZC}) of both GAC, the pH of the solution at which the net surface charge

is zero, was determined based on the indirect titration method by Sontheimer et al. (1988) further

140 described in the SI (section 1.3).

141 **2.2. Investigated PM candidates**

In the present study, 17 PM candidates were investigated. The nine PM candidates frequently detected in the water used as pilot plant influent are listed in Table 1. The remaining eight substances are characterized in Table SI3. Due to analytical challenges, OXP was excluded from the RSSCT experiments.

146Table 1: Overview of the nine frequently detected PM candidates in the pilot plant influent (frequency of detection147 $(FOD) \ge 80\%$) including abbreviations, CAS numbers, log D values, pKa values, molecular weights (MW;148Chemicalize) and structure. * prediction of log D and pka values by Chemicalize (https://chemicalize.com/),149developed by ChemAxon.

SubstanceAbbre viationCASSubstance class		log D at pH 7.3/ 7.9 *	MW (g/mol)	pKa *	Structure		
2-acrylamido-2- methylpropane sulfonate	AAMPS	15214-89- 8	Industrial chemical	-2.71	207.24	-0.96 -0.19	
Acesulfame	ACE	33665-90- 6	Artificial sweetener	-1.49	163.15	3.02	
Adamantan-1-amine	АТА	768-94-5	Pharmaceutica l intermediate, industrial chemical	-1.42 / -1.14	151.25	10.71	NH [*] 3
Diatrizoic acid	DZA	117-96-4	Contrast agent	-0.63	613.91	2.17	
Melamine	MEL	108-78-1	Industrial chemical	-2.38 / -2.09	126.12	9.56	

Oxypurinol	ОХР	2465-59-0	Pharmaceutica l metabolite	-2.70 / -3.15	152.11	2.09 6.25	
Primidone	PRI	125-33-7	Anticonvulsant	1.12	218.25	11.50	H ^o H ^o H ^z H
Trifluoromethanesulfoni c acid	TFMSA	1493-13-6	Industrial chemical	-1.23	150.08	-3.43	F 0 F
Valsartan acid (2'-(2H- tetrazol-5-yl)-[1,1'- biphenyl]-4-carboxylic acid)	VSA	164265- 78-5	Pharmaceutica l metabolite	-1.13 / -1.66	266.25	-1.45 4.03	

150

151 **2.3. Water quality**

152 The pilot plant and the RSSCT were fed with drinking water from a full-scale waterworks. The 153 upstream drinking water treatment consisted in bank filtration, aeration, flocculation, and rapid sand 154 filtration. Table 2 indicates the water characteristics as dissolved organic carbon (DOC) 155 concentrations, ultraviolet absorbance at 254 nm (UVA₂₅₄) and pH values of all influents. The mean 156 water temperature of the pilot plant influent was 13.7 ± 1.9 °C while the lab experiments were 157 carried out at room temperature (approx. 25 °C). For the RSSCT, the influents were spiked with the 158 PM candidates (Table 1) with target concentrations of 2 µg/L each (resulting PM candidate 159 concentrations are given in Table SI4). Concentrations of ions are provided in Table SI5. The influent 160 water for the RSSCT was collected from the waterworks and stored at 4°C until use.

Table 2: Water quality including dissolved organic carbon (DOC) concentrations, ultraviolet light absorbance at
254 nm (UVA₂₅₄) and pH values.

	DOC (mg/L)	UVA ₂₅₄ (m ⁻¹)	pH (-)
Pilot plant	2.2 ± 0.2	4.9 ± 0.4	7.9 ± 0.4
RSSCT-CD	2.4 ± 0.2	4.9 ± 0.2	7.3 ± 0.3
RSSCT-PD	2.3 ± 0.3	4.8 ± 0.2	7.3 ± 0.3

164 **2.4. Pilot plant set-up and sampling**

Two fixed-bed GAC filters were operated in parallel for about 1.5 years corresponding to a total throughput of approx. 47,000 bed volumes (BV). One filter was filled with HCR+1 and one with AS5000. Details on the pilot plant set-up, dimensions and operation conditions are provided in Figure SI4 and Table 3. Both GAC were used as received.

169 The filter influent and both effluents were sampled weekly until approx. 20,000 BV and then 4-

170 weekly until the end of operation. All sampling locations of the GAC filters are indicated in Figure SI4.

171 Temperatures and pH values were measured on-site directly after sampling. All samples were then

- stored at 4°C until further analyses. Both filters were backwashed after 48 and 69 days of operation,
- 173 respectively.

174 Table 3: Dimensions and operational conditions of the pilot plant and the RSSCT.

	Pilot plant		RSSCT				
Parameter	455000	HCR+1	C	D	PD		
	A35000		AS5000	HCR+1	AS5000	HCR+1	
Empty bed contact time 15 min		8.3 s	6.8 s	86.3 s	78.4 s		
Particle diameter d _P	e ter d _P 1200 μm 1320 μm		115 μm				
Column diameter	15 cm		7.2 mm				
Bed volume 35 L		0.81 mL	0.74 mL	0.81 mL	0.74 mL		
Flow rate	141	L/h	5.7 ml/min		0.52 mL/min		
Filter velocity	8.0 m/h		8.4 m/h		0.8 m/h		
Reynolds number4.85.7		0.48	0.52	0.04	0.05		

175

176 **2.5. RSSCT set-up and dimensioning**

The RSSCT were designed to directly represent the pilot filter. The downscaling based on the constant diffusivity (CD) approach and the proportional diffusivity (PD) approach by Crittenden et al. (1986; 1987) with x=0 for the CD approach and x=1 for the PD approach in Eq. 1.

$$\frac{EBCT_{RSSCT}}{EBCT_{pilot}} = \left(\frac{d_{RSSCT}}{d_{pilot}}\right)^{2-x}$$
(1)

180 The equation directly relates the empty bed contact time (EBCT) of the pilot filter EBCT_{pilot} and the 181 granule diameter of the GAC used in the pilot filter d_{pilot} to the EBCT of the RSSCT EBCT_{RSSCT} and the 182 particle diameter of the GAC fraction used in the RSSCT d_{RSSCT}. The Reynolds minimum criterion was 183 applied to attain sufficient similarity between the mass transfer conditions in the pilot plant and the 184 CD-RSSCT, while minimizing the amount of water needed to depict a throughput of 100.000 BV. 185 Accordingly, Remin was determined according to Eq. 2 where Sc is the Schmidt number (with SC=1371 186 in this RSSCT set-up) (Kearns et al., 2020; Summers et al., 2014). The Reynolds numbers of the CD-187 RSSCT were kept above Re_{min} (with Re_{min}=0.36 in this RSSCT set-up).

$$Re_{min} = \frac{500}{Sc} \tag{2}$$

In the interest of feasible hydraulic pressure losses, PD-RSSCT were dimensioned equal to the CDapproach, and the flow rates were adjusted. The dimensions and operational conditions of the pilot
plant and both RSSCT approaches are summarized in Table 3.

191 In preparation for the RSSCT, both GAC were manually ground (Pulverisette, Fritsch GmbH, 192 Germany) and subsequently sieved (Retsch, Germany) to yield the particle size fraction of 90-193 140 µm. 300 mg of GAC per RSSCT were soaked in ultrapure water, degassed and washed to remove 194 dust and thus avoid clogging. The RSSCT were conducted in glass columns with a diameter of 7.2 mm. 195 Thereby, glass pearls, glass wool and glass filters fixed the activated carbon filter bed. The columns 196 were operated in downstream mode using peristaltic pumps (Ismatec, Germany). Sampling was 197 carried out by a fraction collector (2211 Superrac, LKB Bromma, Austria) combined with a peristaltic 198 pump.

199 **2.6**

2.6. Curve fitting and calculations

Breakthrough curves were fitted with a MATLAB script according to the S-shaped Eq. 3 where c/c_0 is the relative effluent concentration and BV treated throughput. Fitting outputs a, b and d are summarized alongside the determination coefficient R² in Table SI6. R² was between 0.94 and 1.00 for all RSSCT breakthrough curves and between 0.26 and 0.95 for the pilot plant breakthroughcurves.

$$\frac{c}{c_0} = \frac{d}{(1 + \exp(a - b * BV))}$$
(3)

205 Carbon usage rates at a respective PM candidate breakthrough of 50% (CUR_{50%}) were calculated 206 based on Eq. 4 where ρ_b is the apparent bed density of the respective activated carbon and BV_{50%} is 207 the throughput in bed volumes until the concentration in the effluent reaches 50% of the influent 208 concentration.

$$CUR_{50\%} = \frac{\rho_b}{BV_{50\%}}$$
(4)

The apparent capacity K*50% of a specific GAC at a respective PM candidate breakthrough of 50% was determined according to Eq. 5 developed by Corwin and Summers (2011). Accordingly, K*10% and K*20% correspond to a PM candidate breakthrough of 10% and 20%, respectively.

$$K^* 50\% = \frac{BV_{50\%}}{\rho_b}$$
(5)

212 **2.7. PM candidate analyses**

213 **2.7.1. Instrumental analysis**

214 Chemical analysis of water samples of the pilot plant was performed by LC-MS/MS using an Agilent 215 1260 Infinity series HPLC system (Agilent Technologies, Waldbronn, Germany) coupled to a QTRAP® 216 5500 mass spectrometer (AB Sciex, Darmstadt, Germany), all controlled by Analyst® 1.6.2 software. 217 Chromatographic separation was performed in reversed-phase mode on an Atlantis T3 column (100 218 x 2.1 mm, 3 µm particle size, Waters) at a flow rate of 0.3 mL/min. The column temperature was set 219 to 35°C. The injection volume was 50 μ L. The applied mobile phase gradient is given in Table SI7. 220 Authentic reference standards of the target analytes were purchased from various suppliers, all listed 221 in Table SI8.

Mass spectrometric analysis was carried out in positive and negative ion multiple reaction monitoring (MRM) mode. The MRM transitions of compounds were optimized by direct infusion of authentic reference standards and are displayed in Table SI9.

Analysis of RSSCT samples was conducted with a modified reversed-phase LC-MS/MS method
described in detail by Zeeshan et al. (2023, under review).

227

2.7.2. Quantification

228 Signal integration was carried out using the software Multiquant 3.0.3 (AB Sciex, Darmstadt, 229 Germany). Signal suppression or enhancement of target analytes during MS analysis by "matrix 230 effects" were equally pronounced in chemical analysis of pristine groundwater and samples of the 231 influent and effluents of the GAC pilot filters. Thus, for quantification of analytes without authentic 232 isotope labelled internal standards, an external, matrix matched calibration using pristine 233 groundwater was performed to ensure accurate quantification under consideration of matrix effects 234 in pilot plant samples. Target analytes with available internal standards were quantified by the 235 internal standard method.

236

2.7.3. Method validation – instrumental and calibration blanks

237 Instrumental background contamination was evaluated by chromatographic separation runs 238 without an injection into the LC-MS/MS system. No instrumental background contamination was 239 observed. For analysis of "calibration blanks", 50 µL of none-spiked pristine groundwater, that was 240 used to prepare the external, matrix matched calibration, was injected into the LC-MS/MS system. In 241 case of background contamination by target analytes within the groundwater, corresponding signal 242 areas were subtracted from signal areas of calibration standards before fitting of the calibration 243 curve. The external, matrix matched calibration was freshly prepared before each measurement. Calibration blanks were observed in some cases for HHTMP, BTA, PTSS, BDMA, DPG, MEL and VSA. 244

245 **2.7.4. Method validation - quantification limits**

The limit of quantification (LOQ) was defined as the lowest spike concentration showing a signal in the chromatogram with $S/N \ge 10$ and deviating less than 20% from the external, matrix matched linear fitted calibration curve. The resulting LOQ varied slightly between frequently prepared external, matrix matched calibration curves. An overview of the average LOQ (median) is given in Table SI10.

251

2.8. Background dissolved organic matter (DOM) analyses

252 Background dissolved organic matter (DOM) breakthroughs in the pilot filters were quantified via 253 DOC measurements in influent and effluents. Concentrations of DOC were quantified by catalytic 254 combustion using a varioTOC cube (elementar Analysensysteme, Germany). The background DOM 255 composition in the drinking water before and after treatment with activated carbon was 256 characterized by size exclusion chromatography (HW50S column, Toyopearl, Japan) with continuous 257 organic carbon and organic nitrogen detection (LC-OCD-OND, model 8, DOC-Labor Huber, Germany; 258 OND data not shown here). Thereby, typically five DOC fractions are separated (Huber et al., 2011): 259 biopolymers (31-45 min), humic substances (HS, 45-49 min), building blocks (49-53.5 min), low 260 molecular weight (LMW) acids and HS (53.5–58 min) and LMW neutrals (> 58 min). Samples taken after approx. 4500 BV and 10500 BV were analyzed via LC-OCD-OND. The UVA₂₅₄ was determined 261 262 with a dual beam spectral photometer (Lambda 12 UV-VIS, Perkin Elmer, Germany) in 10 mm quartz 263 cuvettes (Hellma, Germany).

264 **3. Results and Discussion**

265 **3.1. Activated carbon characteristics**

Comparing both activated carbons, AS5000 offers the higher BET specific surface area (Table 4) by
 more than 100 m²/g. Albeit, both BET specific surface areas range within typical and relatively high
 adsorbent specific values (Worch, 2021). Their similar share of micropores of 62% and 66% for

AS5000 and HCR+1, respectively, as well as the shape of their N₂ adsorption isotherms (Figure SI5) make them typical representatives of mesoporous activated carbons (Aschermann et al., 2018). The mesoporous structure of AS5000 and HCR+1 might be favourable for specific adsorbate/adsorbent interactions, which are likely for polar target compounds, as functional groups exclusively occur in larger pores, i.e. in large micropores and in mesopores (Nielsen et al., 2014).

274 Table 4: Characteristics of the GAC used in the pilot plant and the RSSCT.

	BET SSA (m²/g)	Share of micropores (%)	Bulk density (kg/m³)	pH _{PZC}	Carbon content (wt%)	Ash content (wt%)	Oxygen content (wt%)
AquaSorb 5000	1090	62	369	9.1	83.5	11.8	1.31
HCR+1	980	66	403	9.3	84.0	11.2	1.58

275

276 Lignite or bituminous coal based activated carbon products are typically characterized by lower 277 surface oxygen group levels comprised by mainly carbonyl and pyrone functionalities (Dittmann et 278 al., 2022) as found for AS5000 and HCR+1: Pyrones and/or chromenes dominate the surface 279 chemistry with more than 50% share of the total surface oxygen groups (Figure 1). Along with 280 carbonyls and quinones as well as phenols and ethers, they account for 88% of all oxygen containing 281 functionalities (for both activated carbons). Depending on the dominant adsorption mechanism, 282 oxygenated functional groups might enhance the adsorption of OMP significantly: Adsorption of 283 compounds relying on π - π dispersive interactions decreases with increasing oxygen containing 284 surface groups, like previously reported for carbamazepine (Dittmann et al., 2020). In contrast, 285 molecules binding primarily via hydrogen bonding profit from increasing surface oxygen group 286 levels as described for PFOS by Barbosa et al. (2020). The activated carbons AS5000 and HCR+1 287 contain overall low amounts of surface oxygen groups and therefore potentially promote adsorption 288 based on π - π interactions. Additionally, both activated carbons comprise low total oxygen 289 contents below 2% (Table 4). Low total oxygen contents indicate an overall low surface 290 hydrophilicity of an activated carbon (Ridder et al., 2010).



291

292 Figure 1: Surface oxygen groups in μmol/g of AS5000 and HCR+1 with respective schematic chemical structures.

293 Depending on the prevailing pH, the functional groups on an activated carbon surface can be 294 protonated or deprotonated. The tipping point pH_{PZC}, where the net positive surface charge at lower 295 pH changes to a net negative surface charge at higher pH, was basic with pH_{PZC} above pH 9 for both 296 AS5000 and HCR+1 (Table 4) as reported previously for lignite and bituminous based activated 297 carbons (Aschermann et al., 2019; Dittmann et al., 2022; Lorenc-Grabowska and Gryglewicz, 2007). 298 The basic pH_{PZC} of both GAC is in accordance with the low prevalence of acidic functional groups 299 (carboxylic acids, anhydrides and lactone groups) and the relatively high amounts of basic functional 300 groups such as pyrones chromenes on the activated carbons surfaces. Since the pH of the investigated 301 drinking water was below the pH_{PZC} in all experiments (Table 2), the surfaces of both adsorbents 302 were mainly protonated and therefore carrying a net positive charge. In theory, the charge of an 303 adsorbent's surface has a major influence on charged target compounds compared to neutral ones 304 (Worch, 2021), as most of the investigated compounds are negatively charged (Table 1). Hence, 305 anionic species among the PM candidates may have an advantage in preferential adsorption due to 306 electrostatic attraction.

The most abundant inorganic elements of both activated carbons are Al, Si and Fe with individual shares above 10%, which together represent more than 80% of the total inorganic elements detected by XRF (Figure SI6). Even though the ash content was previously reported not to be linked to the inorganic elemental composition (Dittmann et al., 2022), both are very similar for AS5000 and
HCR+1 emphasizing their overall resemblance.

In summary, the activated carbons are surprisingly similar in the analyzed properties. This suggests similar adsorption capacities and substance selectivities of both GAC. Since the selection was based on a screening with a variety of GAC products (SI section 1.1.), these characteristics are presumably beneficial for the adsorption of the tested PM candidates.

316 **3.2. DOM breakthrough**

317 The DOC concentrations in effluents of both GAC filters increase sharply, reaching 39% and 36% DOC 318 removal at 10,000 BV for AS5000 and HCR+1, respectively, and approaching complete breakthrough 319 after ca. 42,000 BV (Figure 2A). Background DOM is a site-specific multi-component mixture of 320 unknown naturally occurring organic water constituents that may be a target for elimination in 321 drinking water treatment to reduce taste and odor. However, in adsorption processes targeting OMP, 322 simultaneous DOM adsorption is a drawback mainly due to two interfering mechanisms: Background 323 DOM effectively reduces the adsorption capacity of an activated carbon by direct adsorption site 324 competition and by pore clogging (Ebie et al., 2001).

325 The UVA₂₅₄ in both effluents increases similarly to DOC concentrations, reaching 55% and 50% 326 removal at 10,000 BV by AS5000 and HCR+1, respectively, and finally stabilizes at about 15% 327 removal after a throughput of ca. 37,000 BV (Figure 2B). Comparing DOC removal and UVA254 328 abatement throughout the pilot plant runtime, a typical pattern emerges: UVA₂₅₄ breakthrough is less 329 steep due to the improved adsorbability of UV₂₅₄ absorbing DOC constituents. Furthermore, effluent 330 UVA₂₅₄ stabilization indicates biodegradation to less UV₂₅₄ absorbing compounds as described previously by Sperlich et al. (2017), which is sustained by the DOC breakthrough at a similar 331 332 throughput. Also, ongoing adsorption of highly adsorbable DOC fractions may cause the levelling of 333 UVA₂₅₄ abatement by the GAC filters.

334 The overall retention of DOC and UVA₂₅₄ in both pilot filters was comparable: Previous studies 335 reported approx. 25% lower DOC removals at 10,000 BV under similar operational conditions but 336 with higher DOC concentrations (ca. 4–5 mg/L) (Sperlich et al., 2017; Ullberg et al., 2021). In a full-337 scale GAC adsorber investigated by Merle et al. (2020), earlier complete DOC breakthrough occurred 338 for similar operation conditions but four-fold lower DOC influent concentrations at a specific 339 throughput of ca. 90 m³_{water}/kg_{GAC} compared to ca. 110 m³_{water}/kg_{GAC} in this study. Likewise, both GAC 340 filters retained UV₂₅₄ absorbing compounds very effectively: 25% of the influent UVA₂₅₄ was reached 341 after ca. 28,000 BV compared to ca. 10,000 BV in the pilot plant studied by Sperlich et al. (2017). Both 342 DOC and UVA₂₅₄ measurements do not allow a distinction in the performance of both activated 343 carbons in terms of DOM retention.



Figure 2: DOC concentrations (A) and UVA₂₅₄ (B) in pilot plant influent and effluents as a function of the
throughout in BV.

344

However, a closer look into the adsorption of specific DOC fractions revealed by LC-OCD analyses indicates differences in the GAC products (Figure 3): AS5000 achieves overall higher removals of all fractions, particularly at the lower throughput of 4,500 BV when the GAC is still loaded to a small extent. In detail, preferential removals by AS5000 increased with molecular size and was highest for humic substances and building blocks, exceeding removals of HCR+1 by 20% and 16%, respectively, at 4,500 BV. As the GAC continues to load with background DOM, this effect declines and the removals of all fractions by AS5000 levels approx. 5% above those of HCR+1. The higher total BET SSA and the
slightly lower share of micropores (Table 4) likely contributed to the preferential removal of larger
DOM fractions by AS5000.

With respect to the removal of specific DOC fractions (measured by LC-OCD), their respective retention decreases with increasing molecular size as found in previous research (Ullberg et al., 2021; Wang et al., 2021; Weber, 2004; Zietzschmann et al., 2014): At a throughput of 10,500 BV, LMW neutrals are the best adsorbed fraction with 54% and 47% retention by AS5000 and HCR+1, respectively, which exceeds the retention of humic substances by a factor of two (Figure 3B).



361

362 Figure 3: A: LC-OCD chromatograms of influent and both pilot filter effluents at 4,500 BV and 10,000 BV

363 throughput including DOC fraction limits. B: Removal of DOC fractions at 4,500 BV and 10,000 BV throughput in

- 364 %. BV: bed volumes; LMW: low molecular weight; HS: humic substances.
- 365

3.3. PM candidate occurrences

Due to the long-term pilot plant operation, a comprehensive picture of the prevalence of the monitored PM candidates in the drinking water used as pilot plant influent was attained: Out of the 17 regularly measured PM candidates, two substances were not detected at all (CG and BETMAC), five substances were detected rarely (BDMA, HHTMP, MAPMA, MPSA, SAC) with frequencies of detection (FOD) between 5% and 29%, and PTSS was detected in 75% of all samples. In total, nine
substances were predominantly present in all samples (FOD > 80%) with decreasing median
concentrations in the following order: MEL > OXP > DZA > VSA > ACE > PRI > AAMPS > ATA > TFMSA.
Five of these PM candidates (AAMPS, DZA, MEL, PRI and VSA) were found in all samples. Overall,
median concentrations of all occurring PM candidates ranged from 0.003 to 1.868 µg/L. An overview
of the occurrences of all PM candidates including frequencies of detection and median concentrations
is given in Table SI11.

Throughout the pilot plant operation time of more than one year, distinct seasonal changes were observed for five substances (Figure 4): While elevated concentrations during spring and summer (April to September) were identified for AAMPS, VSA and PRI, concentrations of MEL peaked later in the months from Juli to September. In contrast, OXP reached its highest concentrations during winter. For TFMSA and ATA, pronounced concentration peaks were observed in spring 2020.

382

3.4. PM candidate breakthrough

383 The PM candidates vary strongly in their retention by the GAC fixed-bed filters: TFMSA is adsorbed 384 negligibly, reaching complete breakthrough before a throughput of 5,000 BV. The poor removal of 385 TFMSA was previously observed in activated carbon batch experiments (Scheurer et al., 2022). The 386 PM candidates AAMPS, ATA, ACE and DZA were retained moderately by both GAC filters: The 387 adsorption capacities of both adsorbents were reached slightly earlier for AAMPS and ATA at ca. 388 15,000 BV compared to ca. 20,000 BV for ACE and DZA (Figure 4 and 6). Interestingly, four of the five 389 least adsorbing PM candidates (TFMSA, AAMPS, ACE, DZA) carry a negative charge at experimental 390 pH: Even though the negative charge might enable interactions with protonated functional groups 391 on the activated carbon surfaces (Table 4), their high polarity (log D values between -2.71 and -0.63), 392 their relatively small size (Table 1) and secondary interactions with negatively charged functional 393 groups, e.g. deprotonated carboxylic functional groups, appear to govern their low adsorption. In 394 contrast to the negatively charged AAMPS, ACE and DZA, ATA occurs predominantly cationic,

395 potentially undergoing electrostatic repulsion due to the alkaline pH_{PZC} of both GAC (Table 4). 396 Another common key characteristic is the aliphatic structure of the poorly to moderately retained 397 PM candidates (TFMSA, AAMPS, ACE, ATA) except for DZA: For these substances, adsorbent 398 interactions rely on electrostatic attraction/ repulsion and hydrogen bonding, even though their 399 small size (molecular weights between 150 and 207 g/mol) limits specific bonding. Since DZA 400 contains an aromatic ring, a higher adsorption capacity is expected here. However, the symmetrically 401 arranged iodine atoms in the DZA molecule may shield de aromatic ring and thereby inhibit π - π 402 interactions (Bartels et al., 2023). Consequently, when TFMSA, AAMPS, ATA, ACE and DZA occur in 403 drinking water sources, additional treatment steps are necessary to prevent drinking water 404 contamination, since typical GAC adsorber operation times exceed 20,000 BV. This is particularly 405 relevant, because TFMSA, ATA and AAMPS are frequently detected water contaminants according to 406 several recent surveys of surface waters, groundwater and bankfiltrate in Germany, hinting towards 407 a widespread presence in drinking water sources (Neuwald et al., 2021; Neuwald et al., 2022; 408 Scheurer et al., 2022). Additionally, TFMSA, ATA and AAMPS were identified as high priority PM 409 candidates based on FOD and novelty in a Europe-wide survey of water samples by Schulze et al. 410 (2019). Previous studies underline the potential of ATA to reach drinking water: Concentrations of 411 6.5–18 ng/L (median concentrations) and 4.8–38.1 ng/L were detected in drinking water samples in 412 China (Xue et al., 2020) and Japan (Simazaki et al., 2015), respectively.

413 Promising results were obtained for three PM candidates: For VSA, PRI and MEL only partial 414 breakthrough was observed reaching approx. 70%, 60% and 5% of the influent concentration after 415 ca. 47,000 BV, respectively (Figure 4). The removal of VSA is likely enhanced by biodegradation, as 416 observed previously (Sperlich et al., 2017). Interestingly, MEL appears to "slip through" during early 417 pilot plant operation: Before 4,000 BV, a breakthrough of up to 34% of the influent concentration 418 was observed. Since this phenomenon occurs in both effluents, analytical errors are excluded. 419 Enhanced retention of MEL with increasing throughput suggests beneficial changes in the conditions 420 for MEL retention with increasing filter throughput. At experimental pH, MEL occurs mainly in its

421 positive form according to structure-based predictions by Chemicalize (developed by ChemAxon), 422 and consequently, may have to overcome electrostatic repulsion since the charge of both activated 423 carbon surfaces is the same (Table 4). However, experimental results indicate the prevalence of non-424 charged MEL at neutral pH (Hynes et al., 2020; Sal'nikov et al., 2009), which contradicts the 425 hypothesis and emphasizes the uncertainty of predicted molecular characteristics. With increasing 426 throughput (and time), the initially fresh GAC loads with background DOM, which forms a coating 427 and thereby changes the physical properties of the GAC surface (Weber, 2004) which may be 428 beneficial for MEL uptake. Since MEL is a compound frequently used in coatings and materials, 429 leaching from pilot plant materials could be a plausible reason for elevated effluent concentrations 430 during the start-up period of the pilot plant. The long-term retention of MEL in both GAC filters may 431 be partly due to biotransformation: Microorganisms capable of MEL degradation were isolated from 432 wastewater treatment plants of MEL or MEL precursor processing industries (El-Sayed et al., 2006; 433 Wang et al., 2014), and Piai et al. (2022) achieved prolonged activated carbon filter runtimes for MEL 434 adsorption by using activated carbon, which has been inoculated with MEL degrading biomass. 435 However, MEL was found to be persistent in biologically active sand columns (Zeeshan et al., 2023, 436 under review), in batch tests applying biologically active activated carbon (Piai et al., 2020) and 437 during activated sludge treatment (An et al., 2017; Xu et al., 2013). As previous research indicates 438 moderate to good adsorptive removal of MEL in batch tests (Piai et al., 2019; Piai et al., 2020; 439 Schumann et al., 2023), it is likely that adsorption accounts for a major part of the elimination in the 440 current pilot study. The surprisingly high adsorption potential of MEL in alkaline solutions despite 441 its high polarity was recently attributed to the capability of the unprotonated MEL species to not only 442 bond to the activated carbon surface but also to interconnect with neighbouring MEL molecules via 443 hydrogen bonding (Hynes et al., 2020).



444

Figure 4: PM candidate influent (black) and effluent concentrations (blue: AS5000; red: HCR+1) of the pilot plant
throughout the complete operation time including month indication. LOQ are indicated with dashed lines for PM
candidates with concentrations close to the LOQ.

Finally, OXP was not detected in either effluent and was thus 100% eliminated until the end of operation. This aligns with previous results, reporting more than 80% removal after approx. 39,000 BV in a pilot filter fed with drinking water (Sperlich et al., 2017) and effective removals by full-scale drinking water treatment including activated carbon filtration (Funke et al., 2015). As OXP is negatively charged, electrostatic attraction may play a vital role in its removal. Furthermore, all well retained PM candidates (VSA, MEL, PRI, OXP) contain aromatic rings that enable π - π interactions with the activated carbon structure. This confirms the identified surface properties of both AS5000

455 and HCR+1, which favor π - π interactions due to their comparably low amounts of functional 456 groups.In this study, MEL and OXP were identified as PM candidates with by far the highest 457 concentrations in the influent, with median concentrations of 1.87 μ g/L and 1.60 μ g/L and FODs of 458 100% and 84%, respectively (Table SI11). Both PM candidates are known to be present in drinking 459 water (Funke et al., 2015; Rüdel et al., 2020; Zhu and Kannan, 2020), which suggests at least partial 460 passage of conventional drinking water treatment. Likewise, prior studies noted limited removal 461 efficiencies for MEL and OXP by ozonation (Sangjung and Ihnsup, 2015; Sauter et al., 2021). However, 462 as demonstrated, activated carbon adsorption provides a suitable advanced treatment alternative to 463 protect drinking water.

464 The calculated throughput until 50% breakthrough in the pilot filter decreased in the following 465 order: PRI > VSA > ACE > DZA > AAMPS > ATA > TFMSA (Table SI6). The observed adsorbabilities 466 align for the most part with results in previous batch experiments (Schumann et al., 2023 under 467 revision). Thereby, the sequence of adsorbability in a drinking water matrix is the same except for 468 ATA, which shows lower than expected removals in the GAC filters in this study. While ATA removal 469 exceeds AAMPS, DZA and ACE adsorbability applying 10 mg/L powdered activated carbon in a batch 470 at equilibrium, the latter three are retained longer in the pilot-scale GAC filters. The obvious 471 difference in batch and fixed-bed experiments is the ongoing adsorption competition with 472 background DOM, which might be the reason for lower adsorption capacities in fixed-bed GAC filters 473 for ATA.

474 **3.5. Suitability of RSSCT for breakthrough prediction**

The relative breakthrough of background DOM, measured as DOC, and of UV₂₅₄ absorbing substances among DOM in the pilot filter and both RSSCT designs match each other almost perfectly as depicted in Figure 5 for AS5000. Both CD-RSSCT an PD-RSSCT directly reflect the relative breakthrough and therefore serve as prediction tools for large-scale DOM breakthrough.



479

480 Figure 5: Relative DOC (A) and UVA₂₅₄ (B) breakthrough in the pilot filter and both RSSCT designs (PD and CD)
481 with AS5000.

482 To assess the predictability of large-scale PM candidate breakthrough in GAC fixed-bed filters from 483 lab-scale experiments, the relative breakthrough curves obtained in PD-RSSCT and CD-RSSCT were 484 plotted with the pilot plant results for direct comparison (Figure 6): Here, it was possible to draw on 485 results from eight PM candidates that were closely monitored in the pilot plant as well as in the 486 RSSCT. As the same trends were visible in both GAC filters, breakthrough curves are only shown for 487 AS5000 while breakthrough curves for HCR+1 are provided in the SI Figure SI7. The breakthrough 488 behavior in both RSSCT corresponds largely with the pilot filter results, except for MEL. In contrast 489 to the pilot filter, where relative MEL concentrations did not exceed 5% until the end of operation 490 (ca. 47,000 BV), 90% breakthrough in the RSSCT was reached after approx. 47,400 BV, by the latest. 491 A recent study by Piai et al. (2022) of MEL adsorption in a fixed-bed filter using a coconut shell based 492 activated carbon (AcquaSorbTM K-CS, Jacobi) and a comparable EBCT but in the absence of 493 background DOM, complete breakthrough was reached at a 10-fold lower throughput (approx. 494 5,500 BV) than in the present study. The strong variation in MEL retention by the latter study, the

495 RSSCT and the pilot filters may be linked to the differences of experimental temperature: MEL 496 adsorption was reported to increase with decreasing temperature (Piai et al., 2020). Hence, the lower 497 temperature in the waterworks is likely to have contributed to the improved removal in the pilot 498 filter. Biodegradation of MEL in the long-term operated pilot-scale filters may be a plausible cause 499 for improved MEL removals. However, biodegradation of MEL in fixed-bed GAC filters was 500 exclusively observed in experiments using GAC, which was inoculated with activated sludge 501 containing MEL degrading microorganisms (Piai et al., 2022). In contrast, batch experiments with 502 used GAC from a drinking water plant, no biodegradation occurred (Piai et al., 2020). Equal to the 503 pilot filters, TFMSA does not adsorb in the RSSCT.



Figure 6: Relative effluent concentrations and fitted curves of AAMPS, ACE, ATA, DZA, MEL, PRI, TFMSA and VSA
in the pilot plant and both RSSCT approaches (PD and CD) for AS5000 (HCR+1: Figure SI7).

The apparent capacities K* for ATA, PRI, DZA, VSA, ACE and AAMPS were calculated with respect to a relative breakthrough of 10%, 20% and 50% to compare the adsorbent/adsorbate system specific K* between pilot filters and RSSCT (K*50%, Figure 7). The overall difference between lab-scale K*50%, taking into account both RSSCT designs and GAC, is 33 ± 25% on average. Thereby, the RSSCT design resulting in the best fit to the corresponding pilot filter is substance specific: While the CD- 512 RSSCT yield good analogies for PRI and DZA, breakthroughs of ACE and AAMPS align with PD-RSSCT 513 breakthroughs. For these substances, not only the K*50% is similar, but also the shape of the 514 breakthrough curve: The total mean variation of the K*10%, K*20% and K*50% of the respective 515 RSSCT and the pilot filter was below 25% for at least one GAC (Table SI6). The slope of the 516 breakthrough curve reflects the extent of the mass transfer zone spreading in the fixed-bed filter. A 517 long mass transfer zone indicates low adsorption kinetics, as found for the comparably large PRI and 518 VSA (218 g/mol and 266 g/mol, respectively), with an absolute difference between the throughput 519 at 10% and 50% breakthrough of 10,000 BV and 25,000 BV (Figure 6).

520 VSA breakthrough in the pilot filter does not coincide with either RSSCT approach. For VSA, 521 breakthrough occurs in the following sequence with increasing K*50%: CD-RSSCT < pilot filters < 522 PD-RSSCT. Biodegradation processes in fixed-bed GAC adsorbers are likely to cause a shift of the 523 breakthrough curves towards higher throughputs as observed by Piai et al. (2022) who compared 524 sole adsorption with simultaneous biodegradation and adsorption in a GAC filter.

In contrast to previous works (Corwin and Summers, 2010; Kempisty et al., 2022), there was no consistent RSSCT overprediction of target substance removal associated with GAC fouling in the large-scale filters. Schaefer et al. (2020) ascribed this phenomenon to surface-near adsorption at early breakthrough, which may play a role for the adsorption of ATA in the present study.

A generally superior RSSCT design for the present case could not be identified. However, the CD-RSSCT approach provides a conservative prediction tool for the investigated PM candidate breakthrough with the exception of ATA, as the results indicate either coinciding pilot filter retention or earlier breakthrough and a lower adsorption capacity (Figure 6 and SI6).



533

Figure 7: Apparent capacity K* and CUR at a specific PM candidate breakthrough of 50% of ATA, PRI, DZA, VSA,
ACE and AAMPS in the pilot plant and both RSSCT approaches (PD and CD) for AS5000 (blue) and HCR+1 (red).

To evaluate the economic viability of GAC filters for a specific target substance in practice, the CUR is often applied. The CUR indicates the treated water volume until a specific treatment target, e.g., 50% elimination (CUR_{50%}), is reached. Adopting the criterion of a CUR₅₀ below 25 mg_{GAC}/L_{water} for feasible full-scale GAC treatment, as recently proposed by Kempisty et al. (2022) for PFAS, the following PM candidates in the pilot filters meet the requirement (Figure 7): ACE, VSA, PRI, MEL and OXP (for the latter two substances, CUR_{50%} could not be determined since they did not reach 50% breakthrough throughout the operation time).

543 **4.** Conclusions

The present study addresses the breakthrough behavior of PM candidates in GAC filters from drinking water, taking into account results from both lab-scale and pilot-scale experiments. Nine out of 17 investigated PM candidates were prevalent in the drinking water used as pilot filter influent with FOD above 80 % and median concentrations of 0.003–1.868 µg/L. The observed adsorption capacities in the pilot filters varied strongly: TFMSA was not retained, for four PM candidates 549 (AAMPS, ATA, ACE and DZA) the pilot filters represented a short-term barrier, reaching complete 550 breakthrough below 20,000 BV, three PM candidates (MEL, VSA, PRI) are partially removed until the 551 end of operation time of 47,000 BV and OXP was eliminated by 100% throughout the complete 552 operation time. Both tested GAC exhibit largely identical adsorption capacities owing to their very 553 similar characteristics identified by comprehensive activated carbon characterization. Predictions of 554 large-scale breakthrough from PD-RSSCT and CD-RSSCT was substance specific and no superior 555 RSSCT design could be identified. However, the CD-RSSCT provides a conservative removal 556 prediction for most studied compounds (except for ATA). MEL adsorption was significantly 557 underestimated by both RSSCT designs. Based on the criterion of CUR_{50} below 25 mg_{GAC}/L_{water} to 558 evaluate economic full-scale feasibility, GAC filtration provides an effective and economic barrier in 559 drinking water treatment for five out of the nine PM candidates studied, namely ACE, VSA, PRI, MEL 560 and OXP.

561 Acknowledgements

562 The authors thank the German Ministry for Education and Research (BMBF, Bonn) for funding the 563 project "Persistente mobile organische Chemikalien in der aquatischen Umwelt (PROTECT)" (FKz: 564 02WRS1495 A/D/E) and both Jacobi and Carbon Service & Consulting for supplying the GAC. The 565 UBA expresses its gratitude towards Silke Pabst and Fanny Kohn-Eberle for their support in chemical 566 analysis, Leon Saal for the LC-OCD data tool as well as Ina Janthur, René Sahm and Bonny Haueisen 567 for IC analysis. The UFZ gratefully acknowledges Bettina Seiwert and Petra Keil for their support with 568 the chemical analysis. Furthermore, the authors thank Ulrike Förster, Jutta Jakobs, Katharina Kutz, 569 Gisela Sosna and Katrin Noack from Technische Universität Berlin for their assistance in the lab and 570 Maike Mai for GAC surface analysis.

571 **References**

572 An H, Li X, Yang Q, Wang D, Xie T, Zhao J et al. The behavior of melamine in biological wastewater

573 treatment system. Journal of hazardous materials 2017;322(Pt B):445–53.

Ania CO, Bandosz TJ. Importance of structural and chemical heterogeneity of activated carbon
surfaces for adsorption of dibenzothiophene. Langmuir the ACS journal of surfaces and colloids
2005;21(17):7752–9.

Arp HPH, Hale SE. REACH: Improvement of guidance methods for the identification and assessment
 of PMT/vPvM substances: Final Report. Dessau-Roßlau: Umweltbundesamt; 2019.

579 Aschermann G, Neubert L, Zietzschmann F, Jekel M. Impact of different DOM size fractions on the

desorption of organic micropollutants from activated carbon. Water research 2019;161:161–70.

581Aschermann G, Zietzschmann F, Jekel M. Influence of dissolved organic matter and activated carbon

582 pore characteristics on organic micropollutant desorption. Water research 2018;133:123–31.

583 Barbosa MO, Ribeiro RS, Ribeiro ARL, Pereira MFR, Silva AMT. Solid-phase extraction cartridges with

- 584multi-walled carbon nanotubes and effect of the oxygen functionalities on the recovery efficiency
- of organic micropollutants. Scientific reports 2020;10(1):22304.
- Bartels Y, Jekel M, Putschew A. Can reductive deiodination improve the sorption of iodinated X-ray
 contrast media to aquifer material during bank filtration? Chemosphere 2023:138438.
- Corwin CJ, Summers RS. Scaling trace organic contaminant adsorption capacity by granular activated
 carbon. Environmental science & technology 2010;44(14):5403–8.

590 Corwin CJ, Summers RS. Adsorption and desorption of trace organic contaminants from granular

activated carbon adsorbers after intermittent loading and throughout backwash cycles. Water
research 2011;45(2):417–26.

- 593 Crittenden J, Berrigan J, Hand D. Design of Rapid Small-Scale Adsorption Tests for a Constant
 594 Diffusivity. Washington, D.C; 1986. EPA/600/J-86/133.
- 595 Crittenden JC, Berrigan JK, Hand DW, Lykins B. Design of Rapid Fixed-Bed Adsorption Tests for 596 Nonconstant Diffusivities. Journal of Environmental Engineering 1987;113(2):243–59.
- 597 Dittmann D, Eisentraut P, Goedecke C, Wiesner Y, Jekel M, Ruhl AS et al. Specific adsorption sites and
- 598 conditions derived by thermal decomposition of activated carbons and adsorbed carbamazepine.
- 599 Scientific reports 2020;10(1):6695.

- Dittmann D, Saal L, Zietzschmann F, Mai M, Altmann K, Al-Sabbagh D et al. Characterization of
 activated carbons for water treatment using TGA-FTIR for analysis of oxygen-containing
 functional groups. Appl Water Sci 2022;12(8).
- Ebie K, Li F, Azuma Y, Yuasa A, Hagishita T. Pore distribution effect of activated carbon in adsorbing
 organic micropollutants from natural water. Water research 2001;35(1):167–79.
- 605 El-Sayed WS, El-Baz AF, Othman AM. Biodegradation of melamine formaldehyde by Micrococcus sp.
- strain MF-1 isolated from aminoplastic wastewater effluent. International Biodeterioration &
 Biodegradation 2006;57(2):75–81.
- 608 European Commission. Chemicals Strategy for Sustainability Towards a Toxic-Free Environment,
- 609 2020. https://eur-lex.europa.eu/legal-content/DE/TXT/?uri=COM:2020:667:FIN (accessed
 610 December 12, 2022).
- Funke J, Prasse C, Lütke Eversloh C, Ternes TA. Oxypurinol A novel marker for wastewater
 contamination of the aquatic environment. Water research 2015;74:257–65.
- Gulde R, Rutsch M, Clerc B, Schollée JE, Gunten U von, McArdell CS. Formation of transformation
 products during ozonation of secondary wastewater effluent and their fate in post-treatment:
- From laboratory- to full-scale. Water research 2021;200:117200.
- Hale SE, Arp HPH, Schliebner I, Neumann M. Persistent, mobile and toxic (PMT) and very persistent
 and very mobile (vPvM) substances pose an equivalent level of concern to persistent,
 bioaccumulative and toxic (PBT) and very persistent and very bioaccumulative (vPvB)
 substances under REACH. Environ Sci Eur 2020a;32(1).
- Hale SE, Arp HPH, Schliebner I, Neumann M. What's in a Name: Persistent, Mobile, and Toxic (PMT)
- and Very Persistent and Very Mobile (vPvM) Substances. Environmental science & technology
 2020b;54(23):14790-2.
- 623 Huber SA, Balz A, Abert M, Pronk W. Characterisation of aquatic humic and non-humic matter with
- 624 size-exclusion chromatography--organic carbon detection--organic nitrogen detection (LC-OCD-
- 625 OND). Water research 2011;45(2):879–85.

626	Hynes L, Montiel G, Jones A, Riel D, Abdulaziz M, Viva F et al. Melamine adsorption on carbon
627	materials: impact of carbon texture and surface chemistry. Mater. Adv. 2020;1(2):262–70.
628	Jekel M, Dott W, Bergmann A, Dünnbier U, Gnirß R, Haist-Gulde B et al. Selection of organic process
629	and source indicator substances for the anthropogenically influenced water cycle. Chemosphere

630 2015;125:155-67.

631 Kearns J, Dickenson E, Knappe D. Enabling Organic Micropollutant Removal from Water by Full-Scale

Biochar and Activated Carbon Adsorbers Using Predictions from Bench-Scale Column Data.
Environmental Engineering Science 2020;37(7):459–71.

Kempisty DM, Arevalo E, Spinelli AM, Edeback V, Dickenson ERV, Husted C et al. Granular activated
carbon adsorption of perfluoroalkyl acids from ground and surface water. AWWA Water Science
2022;4(1).

637 Lorenc-Grabowska E, Gryglewicz G. Adsorption characteristics of Congo Red on coal-based
638 mesoporous activated carbon. Dyes and Pigments 2007;74(1):34–40.

Merle T, Knappe DRU, Pronk W, Vogler B, Hollender J, Gunten U von. Assessment of the breakthrough
of micropollutants in full-scale granular activated carbon adsorbers by rapid small-scale column
tests and a novel pilot-scale sampling approach. Environ. Sci.: Water Res. Technol.
2020;6(10):2742–51.

Neuwald I, Muschket M, Zahn D, Berger U, Seiwert B, Meier T et al. Filling the knowledge gap: A
suspect screening study for 1310 potentially persistent and mobile chemicals with SFC- and
HILIC-HRMS in two German river systems. Water research 2021;204:117645.

646 Neuwald IJ, Hübner D, Wiegand HL, Valkov V, Borchers U, Nödler K et al. Occurrence, Distribution,

and Environmental Behavior of Persistent, Mobile, and Toxic (PMT) and Very Persistent and Very

648 Mobile (vPvM) Substances in the Sources of German Drinking Water. Environmental science &

649 technology 2022;56(15):10857–67.

650 Nielsen L, Biggs MJ, Skinner W, Bandosz TJ. The effects of activated carbon surface features on the

reactive adsorption of carbamazepine and sulfamethoxazole. Carbon 2014;80:419–32.

- Pal A, He Y, Jekel M, Reinhard M, Gin KY-H. Emerging contaminants of public health significance as
 water quality indicator compounds in the urban water cycle. Environment international
 2014;71:46–62.
- Peyrelasse C, Jacob M, Lallement A. Multicriteria Comparison of Ozonation, Membrane Filtration, and
 Activated Carbon for the Treatment of Recalcitrant Organics in Industrial Effluent: A Conceptual
- 657 Study. Environ. Process. 2022;9(1).
- Piai L, Blokland M, van der Wal A, Langenhoff A. Biodegradation and adsorption of micropollutants
 by biological activated carbon from a drinking water production plant. Journal of hazardous
 materials 2020;388:122028.
- Piai L, Dykstra JE, Adishakti MG, Blokland M, Langenhoff AAM, van der Wal A. Diffusion of hydrophilic
- organic micropollutants in granular activated carbon with different pore sizes. Water research
 2019;162:518–27.
- Piai L, Langenhoff A, Jia M, Wilde V de, van der Wal A. Prolonged lifetime of biological activated carbon
 filters through enhanced biodegradation of melamine. Journal of hazardous materials
 2022;422:126840.
- Reemtsma T, Berger U, Arp HPH, Gallard H, Knepper TP, Neumann M et al. Mind the Gap: Persistent
 and Mobile Organic Compounds-Water Contaminants That Slip Through. Environmental science
 & technology 2016;50(19):10308–15.
- Ridder DJ de, Villacorte L, Verliefde ARD, Verberk JQJC, Heijman SGJ, Amy GL et al. Modeling
 equilibrium adsorption of organic micropollutants onto activated carbon. Water research
 2010;44(10):3077–86.
- Rüdel H, Körner W, Letzel T, Neumann M, Nödler K, Reemtsma T. Persistent, mobile and toxic
 substances in the environment: a spotlight on current research and regulatory activities. Environ
 Sci Eur 2020;32(1).

- 676 Sal'nikov YI, Boos GA, Ryzhkina IS, Fattakhov SG, Chmutova GA, Zaripova GR. Melaphen, malamine, 677 and bis(hydroxymethyl)phosphinic acid. Acid-base properties and behavior in the presence of 678 some metal cations. Russ J Gen Chem 2009;79(6):1074-9.
- 679 Sangjung L, Ihnsup H. The analysis of melamine and the removal efficiencies in the advanced 680 oxidation process (AOP) and granular activated carbon (GAC) processes. Desalination and Water
- 681 Treatment 2015;53(6):1565-77.
- 682 Sauter D, Dabrowska A, Bloch R, Stapf M, Miehe U, Sperlich A et al. Deep-bed filters as post-treatment 683 for ozonation in tertiary municipal wastewater treatment: impact of design and operation on 684 treatment goals. Environ. Sci.: Water Res. Technol. 2021;7(1):197-211.
- 685 Schaefer CE, Nguyen D, Culina VM, Guelfo J, Kumar N. Application of Rapid Small-Scale Column Tests
- 686 for Treatment of Perfluoroalkyl Acids Using Anion-Exchange Resins and Granular Activated 687 Carbon in Groundwater with Elevated Organic Carbon. Ind. Eng. Chem. Res. 2020;59(38):16832-7.
- 688
- 689 Scheurer M, Sandholzer A, Schnabel T, Schneider-Werres S, Schaffer M, Börnick H et al. Persistent 690 and mobile organic chemicals in water resources: occurrence and removal options for water 691 utilities. Water Supply 2022;22(2):1575-92.
- 692 Schulze S, Zahn D, Montes R, Rodil R, Quintana JB, Knepper TP et al. Occurrence of emerging 693 persistent and mobile organic contaminants in European water samples. Water research 694 2019;153:80-90.
- 695 Schumann P, Muschket M, Dittmann D, Rabe L, Reemtsma T, Jekel M et al. Is adsorption onto activated 696 carbon a feasible drinking water treatment option for persistent and mobile substances? Water 697 research 2023:119861.
- 698 Sigmund G, Arp HPH, Aumeier BM, Bucheli TD, Chefetz B, Chen W et al. Sorption and Mobility of
- 699 Charged Organic Compounds: How to Confront and Overcome Limitations in Their Assessment.
- 700 Environmental science & technology 2022;56(8):4702–10.

- Simazaki D, Kubota R, Suzuki T, Akiba M, Nishimura T, Kunikane S. Occurrence of selected
 pharmaceuticals at drinking water purification plants in Japan and implications for human health.
 Water research 2015;76:187–200.
- Sontheimer H, Crittenden J, Summers RS. Activated carbon for water treatment. Karlsruhe:
 Universität Karlsruhe; 1988.
- Sperlich A, Harder M, Zietzschmann F, Gnirss R. Fate of Trace Organic Compounds in Granular
 Activated Carbon (GAC) Adsorbers for Drinking Water Treatment. Water 2017;9(7):479.
- Summers R, Knappe D, Reinert A, Fotta M, Mastropole A, Corwin C et al. Evaluation of Available Scaleup Approaches for the Design of GAC Contactors; 2014.
- 710 Ullberg M, Lavonen E, Köhler SJ, Golovko O, Wiberg K. Pilot-scale removal of organic micropollutants
- and natural organic matter from drinking water using ozonation followed by granular activated
 carbon. Environ. Sci.: Water Res. Technol. 2021;7(3):535–48.
- Wang H, Li J, Hu A, Qin D, Xu H, Yu C-P. Melaminivora alkalimesophila gen. nov., sp. nov., a melaminedegrading betaproteobacterium isolated from a melamine-producing factory. International
 journal of systematic and evolutionary microbiology 2014;64(Pt 6):1938–44.
- Wang Q, Mitchell R-L, Hofman R, Yu J, Yang M, Rietveld LC et al. How properties of low molecular
 weight model competitors impact organic micropollutant adsorption onto activated carbon at
 realistically asymmetric concentrations. Water research 2021;202:117443.
- Weber WJ. Preloading of GAC by natural organic matter in potable water treatment systems:
 Mechanisms, effects and design considerations. Journal of Water Supply: Research and
 Technology-Aqua 2004;53(7):469–82.
- Worch E. Adsorption Technology in Water Treatment: De Gruyter; 2021.
- Xu S, Zhang Y, Sims A, Bernards M, Hu Z. Fate and toxicity of melamine in activated sludge treatment
 systems after a long-term sludge adaptation. Water research 2013;47(7):2307–14.
- 725 Xue M, Wu H, Liu S, Huang X, Jin Q, Ren R. Simultaneous determination of 44 pharmaceutically active
- compounds in water samples using solid-phase extraction coupled with ultra-performance liquid

- 727 chromatography-tandem mass spectrometry. Analytical and bioanalytical chemistry
 728 2020;412(1):203-22.
- Zeeshan M, Schumann P, Pabst S, Ruhl AS. Transformation of potentially persistent and mobile
 organic micropollutants in column experiments. Heliyon 2023.
- 731 Zhu H, Kannan K. Occurrence and distribution of melamine and its derivatives in surface water,
- drinking water, precipitation, wastewater, and swimming pool water. Environmental pollution
- 733 (Barking, Essex 1987) 2020;258:113743.
- 734 Zietzschmann F, Worch E, Altmann J, Ruhl AS, Sperlich A, Meinel F et al. Impact of EfOM size on
- competition in activated carbon adsorption of organic micro-pollutants from treated wastewater.
- 736 Water research 2014;65:297–306.