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Is adsorption onto activated carbon a feasible drinking water treatment option for persistent and mobile substances?

Pia Schumann[1,2]*, Matthias Muschket[3], Daniel Dittmann[1], Luisa Rabe[1,2], Thorsten Reemtsma[3], Martin Jekel[2], Aki Sebastian Ruhl[1,2]

[1] German Environment Agency (UBA), Section II 3.3, Schichauweg 58, 12307 Berlin, Germany, pia.mc.schumann@campus.tu-berlin.de

[2] Technische Universität Berlin, Chair of Water Quality Control, Sekr. KF 4, Straße des 17. Juni 135, 10623 Berlin, Germany

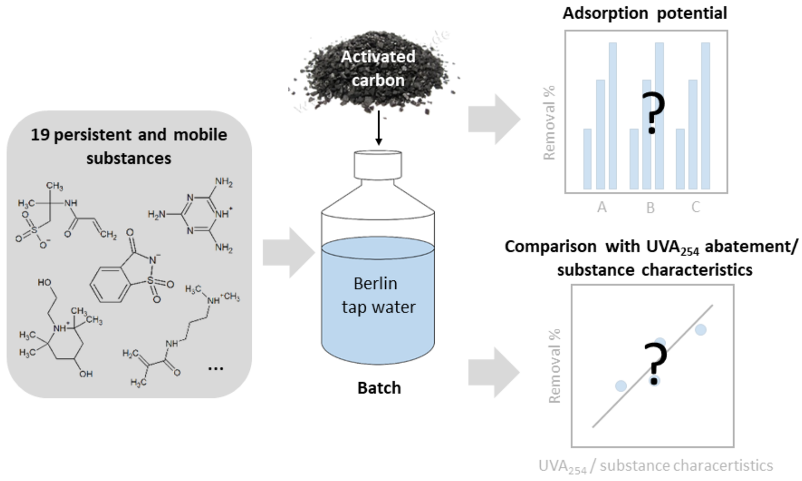
[3] Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig, Germany

* corresponding author

Highlights

- Adsorption potentials of 19 persistent and mobile candidates were assessed.
- Five substances were not/negligibly removed while other five were readily removed.
- Highly diverse adsorbability emphasizes need for substance specific solutions.
- UVA_{254} is a suitable surrogate for persistent and mobile candidate removal.
- No correlation was found for substance properties with adsorptive removals.

Graphical abstract



Abstract

Persistent and mobile (PM) substances among the organic micropollutants have gained increasing interest since their inherent properties enable them to enrich in water cycles. This study set out to investigate the potential of adsorption onto activated carbon as a drinking water treatment option for 19 PM candidates in batch experiments in a drinking water matrix with relevant target concentrations applying a microporous and a mesoporous activated carbon. Overall, adsorption of PM candidates onto activated carbon proved to be very variable and the extent of removal could not be directly related to molecular properties. At an activated carbon dose of 10 mg/L and 48 hours contact time, five (out of 19) substances were readily removed (≥ 80%), among them N-(3-(dimethylamino)-propyl)methacrylamide, which was investigated for the first time. For five other substances, no or negligible removal (< 20%) was observed, including 2-methyl-2-propene-1-sulfonic acid and 4-hydroxy-1-(2-hydroxyethyl)-2,2,6,6,-tetramethylpiperidine. For the former, current state of the art adsorption processes may pose a sufficient barrier. Additionally, substance specific surrogate correlations between removals and UVA_{254} abatements were established to provide a cheap and fast estimate for PM candidate elimination. Adsorption onto activated carbon could contribute significantly to PM substance elimination as part of multi barrier approaches, but assessments for individual substances still require clarification, as demonstrated for the investigated PM candidates.

Key words

Powdered activated carbon, emerging contaminants, organic micropollutants (OMP), trace organic compounds (TOrCs)

1. Introduction

Organic micropollutants (OMP) and their behaviors in the aquatic environment and in water treatment have been a topic in research for decades, and in recent years, persistent and mobile (PM) substances among OMP have attracted increasing interest (Hale et al., 2020a; Reemtsma et al., 2016). As PM substances are poorly biodegraded, photodegraded and removed by sorption processes, they are prone to penetrate through natural and technical barriers (Loos et al., 2013; Scheurer et al., 2017). PM substances belong to various substance classes and application fields such as pharmaceuticals, industrial chemicals, herbicides, and pesticides as well as their transformation products and therefore originate from multiple emission sources like households, agriculture, urban stormwater runoff, and industry (Reemtsma et al., 2016). Ineffective barriers alongside climatic changes are anticipated to favour PM substance enrichment in water cycles and consequently contamination of drinking water sources. In fact, numerous (potential) PM substances have been detected in the aquatic environment (Loos et al., 2010; Montes et al., 2022; Neuwald et al., 2021; Nödler et al., 2016; Schulze et al., 2019; Zahn et al., 2019) and even in drinking water (Scheurer et al., 2017; Zahn et al., 2016). To identify persistence for regulatory purposes, the use of the degradation half-life time in the environment as defined in the Annex XIII of REACH and applied in the PBT/vPvB assessment was proposed (Arp and Hale, 2019). In the same context, the pH-dependent octanol-water partition coefficient log D was suggested as a mobility indicator with substances having a $\log D < 4$ at a pH range of 4–9 considered mobile (Arp and Hale, 2019). However, there is an ongoing discussion about how to quantify the mobility of a substance in the scientific community: A commonly recognized quantitative definition (or quantification method) for a compound's mobility in the aquatic environment remains challenging (Hale et al., 2020b; Kalberlah et al., 2014; Sigmund et al., 2022).

The detection of mobile substances has long been limited by the capabilities of traditional chromatographic techniques such as gas chromatography and reversed-phase liquid chromatography. As analytics advanced, the spectrum of substances detected by liquid chromatography coupled with mass spectrometry extended to polar and very polar substances (Reemtsma et al., 2016). However, the analyses of very polar compounds continues to be a challenge and thus far, no analytical method appears to cover all mobile substances but different chromatography approaches (mixed-mode liquid chromatography, supercritical fluid chromatography, hydrophilic interaction liquid chromatography, gas chromatography, reversed-phase chromatography) rather seem to complement each other (Neuwald et al., 2021; Zahn et al., 2020).

The lack of appropriate analytical methods in the past, the vast number of (newly) detected compounds/ potential PM substances and the time and cost intensive field and laboratory studies required lead to the present knowledge gap on PM substances: Little is known about their toxic effects on the environment and human health, their fate in the aquatic environment and the efficiency of technical treatment options. Consequently, the precautionary principle should be applied to protect human health and the environment. Although minimizing emissions should be a priority, knowledge about remediation options is needed to counteract current and future contamination.

Adsorption onto activated carbon is an established water treatment technique eliminating a broad range of OMP (Jekel et al., 2015; Kennedy et al., 2015; Ternes et al., 2002) and therefore may be a suitable treatment option for PM substances. Although adsorption onto activated carbon is known for improved removals of hydrophobic OMP (Ridder et al., 2010), previous studies demonstrated removal of polar substances (Piai et al., 2019; Sperlich et al., 2017).

The removal potential of activated carbon depends on adsorbent characteristics, the water matrix as well as adsorbate characteristics. Since adsorption is a surface-related process, the surface area, pore size distribution and surface characteristics (of the adsorbent) play an important role in the selection of an appropriate activated carbon (due to size exclusion and kinetic limitations) (Aschermann et al., 2018; Dittmann et al., 2022; Piai et al., 2019). Previous studies linked adsorption behavior to electric charge, molecular weight, hydrophobicity, polarizability, aromaticity and the presence of H-bond donor/acceptor groups (Mailler et al., 2015; Ridder et al., 2010). Assessing the relationship between adsorbate characteristics and removal behavior may be useful to identify critical substances that may pass through the adsorption step of waterworks.

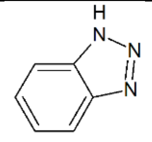
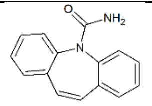
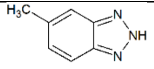
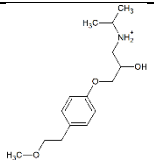
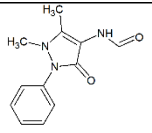
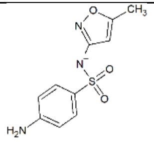
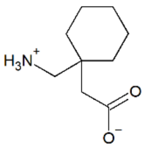
To obtain insight into the viability of adsorption onto activated carbon as a treatment option for PM substances, 19 potential PM substances, hereinafter referred to as PM candidates, were tested for their adsorption potential in batch experiments in equilibrium with one mesoporous and one microporous commercially available activated carbon. The selection of PM candidates was based on a monitoring in European water samples published by Schulze et al. (2019), where some PM candidates have been identified for the first time in surface waters or even drinking water. Three of the PM candidates, 2-acrylamido-2-methylpropane sulfonate (AAMPS), adamantan-1-amine (ATA) and trifluoromethanesulfonic acid (TFMSA), were among the 10 most frequently detected novel or scarcely investigated substances identified during a suspect screening by Neuwald et al. (2021) in samples of two river systems. The PM candidates chosen for this study were all characterized by a high polarity (median log D -1.4 at pH 7.5), a low molecular weight (median 186 g/mol) and were mostly charged (ionic or ionizable organic molecules) at the relevant pH. To put the adsorptive removal of the target substances into perspective and directly compare adsorption capacities, well-known OMP were tested as references. Based on their removals at economical carbon dosages, the PM candidates were classified according to their adsorption tendency. As UV_{254} absorbance measurement was proven to be a useful tool for OMP removal control (Altmann et al., 2014; Anumol et al., 2015), UVA_{254} abatement was compared with the removals of the PM candidates.

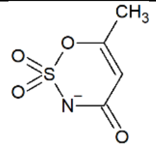
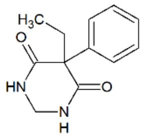
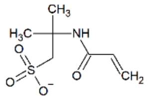
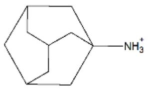
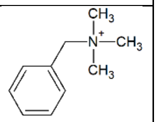
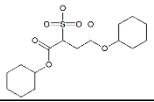
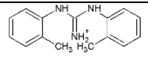
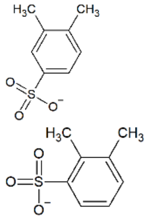
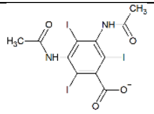
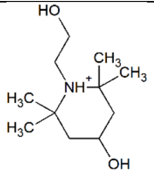
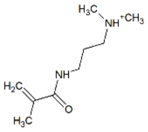
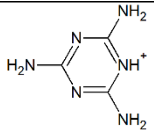
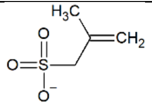
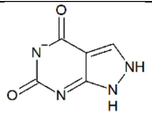
2. Materials and methods

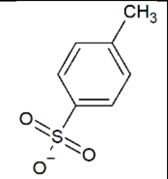
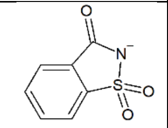
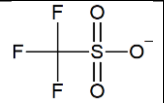
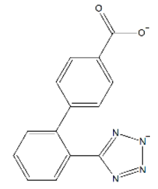
2.1. Investigated substances

In total, 25 substances were investigated in this study with abbreviations and relevant characteristics shown in Table 1. Nine substances were considered well-known OMP since their adsorption behavior has been studied widely (Zietzschmann et al. 2014, Altmann et al. 2014, Ruhl et al. 2015). The well-known substances acesulfame (ACE), benzotriazole (BTA) and primidone (PRI) were classified as PM candidates due to their characteristics. For the compounds log D, polarizability, maximum projection area and maximum projection diameter predicted values by Chemicalize (developed by ChemAxon) were used.

*Table 1: Overview of all investigated substances including abbreviations, CAS numbers and substance characteristics: log D (Chemicalize), molecular weights (MW), polarizability (Chemicalize), maximum projection area (Chemicalize), maximum projection diameter (Chemicalize), retention times (RT) in reversed-phase liquid chromatography (RPLC; details are provided in the SI chapter 2.4 RPLC method) and chemical structure. * both well-known OMP and PM candidates*

Substance	**Abbreviation**	**CAS**	**Substance class**	**log D at pH 8.2/ 8.3**	**MW (g/mol)**	**Polarizability ($Å^3$)**	**Maximum projection area ($Å^2$)**	**Maximum projection diameter (Å)**	**RT (min)**	**Structure**
well-known OMP										
Benzotriazole *	BTA	95-14-7	Industrial chemical	1.17/ 1.14	119.12	13.78	41.17	4.12	10. 78	
Carbamazepine	CBZ	298-46-4	Pharmaceutical	2.77	236.27	26.95	68.29	5.76	-	
5-Methyl-1H-benzotriazole	MBT	136-85-6	Industrial chemical	1.73/ 1.72	133.15	46.49	46.49	4.67	-	
Metoprolol	MTP	37350-58-6	Pharmaceutical	0.28/ 0.38	267.37	30.34	93.27	10.07	-	
Formylamino antipyrine	FAA	1672-58-8	Pharmaceutical metabolite	0.11	231.26	23.96	71.32	6.46	-	
Sulfamethoxazole	SMX	723-46-6	Antibiotic	-0.12/ -0.13	253.28	24.16	66.05	5.88	-	
Gabapentin	GAB	60142-96-3	Anticonvulsant	-1.28	171.24	18.62	50.59	4.99	-	

Acesulfame*	ACE	33665-90-6	Artificial sweetener	-1.49	163.15	13.45	41.97	4.15	7.48	
Primidone*	PRI	125-33-7	Anticonvulsant	1.12	218.25	23.07	60.88	5.40	11.75	
PM candidates										
2-acrylamido-2-methylpropane sulfonate	AAMPS	15214-89-8	Industrial chemical	-2.71	207.24	19.34	52.61	5.07	8.7	
Adamantan-1-amine	ATA	768-94-5	Pharmaceutical, industrial chemical	-0.93/ -0.85	151.25	18.50	43.33	4.14	9.94	
Benzyltrimethylammonium	BETMAC	14800-24-9	Industrial chemical	-2.25	150.24	19.20	53.39	5.15	7.24	
Dicyclohexyl sulfosuccinate	DCHSS	137361-04-7	Industrial chemical	0.42	362.44	35.05	90.25	8.11	-	
1,3-Di-o-tolylguanidine	DIOTOG	97-39-2	Industrial chemical	2.41/ 2.44	239.32	28.30	83.48	7.06	10.63	
Dimethylbenzenesulfonic acid (isomer mix)	DMBSA	25321-41-9 / 1300-72-7	Industrial chemical	-0.20	186.23/ 208.21	18.46 / 18.37	56.45 / 56.23	5.34 / 5.14	12.54	
Diatrizoic acid	DZA	117-96-4	Contrast agent	-0.64	613.91	38.98	88.94	6.58	8.5	
4-Hydroxy-1-(2-hydroxyethyl)-2,2,6,6,-tetramethylpiperidine	HHTMP	52722-86-8	Industrial chemical	-1.52/ -1.42	201.31	23.03	60.92	5.51	3.08	
N-(3-(dimethylamino)-propyl)methacrylamide	MAPMA	5205-93-6	Industrial chemical	-0.71/ -0.61	170.25	19.80	64.54	6.91	4.77	
Melamine	MEL	108-78-1	Industrial chemical	-1.88/ -1.80	126.12	11.18	43.64	4.38	1.32	
2-Methyl-2-propene-1-sulfonic acid	MPSA	3934-16-5	Industrial chemical	-2.21	136.17	12.56	39.52	4.30	6.07	
Oxipurinol	OXP	2465-59-0	Pharmaceutical metabolite	-3.33/ -3.37	152.11	12.72	46.19	4.64	9.93	

p-Toluenesulfonic acid	PTSS	104-15-4	Industrial chemical	-0.71	190.22	16.71	52.05	5.39	10.56	
Saccharine	SAC	81-07-2	Sweetener, pharmaceutical	-0.49	183.18	16.67	51.17	4.62	9.57	
Trifluoromethanesulfonic acid	TFMSA	1493-13-6	Industrial chemical	-1.23	150.08	7.58	29.78	3.58	3.55	
Valsartan acid (2'-(2H-tetrazol-5-yl)-[1,1'-biphenyl]-4-carboxylic acid)	VSA	164265-78-5	Pharmaceutical metabolite	-1.80/ -1.83	266.25	28.93	77.39	6.82	13.25	

2.2. Activated carbons

One microporous activated carbon (Hydraffin CC) and one mesoporous activated carbon (Epibon A, both Donau Carbon, Germany) based on coconut husk and lignite, respectively, were used for the batch experiments. Characteristics of the original granular activated carbons according to Aschermann et al. (2018; 2019) and Dittmann et al. (2022) are listed in Table 2. To obtain uniform adsorbents for evaluations in batch test (Freihardt et al. 2017), both granular activated carbons were pulverized (CryoMill, Retsch; used without cooling, 30 s, 30 Hz) prior to the experiments.

2.3. Batch experiments

Three batch experiments with pulverized activated carbon were conducted in 50 mL Berlin tap water spiked with OMP. An overview of the experiments is given in Table 3.

A first screening with two activated carbons aimed to assess the effect of the differing characteristics of the selected activated carbons on well-known OMP (experiment 1) and PM candidate (experiment 2) adsorption behaviour. Secondly, a comparison between the adsorptive removals of well-known OMP and selected PM candidates in equilibrium was conducted. For the following batch experiment 3, the favoured activated carbon was selected, additional PM candidates (DZA, OXP, VSA) were included, and the resolution of the applied activated carbon doses was increased.

Two mixed stock solutions (one for PM candidates and one for well-known OMP, both in ultrapure water) and one single-solute stock solution containing OXP (in ultrapure water and methanol) with concentrations of 10 mg/L of each analyte were used for spiking the initial target concentrations of 1 and 10 µg/L, respectively. Dissolved organic carbon (DOC) concentrations in experiment 3 were elevated compared to experiments 1 and 2 due to the methanol in the OXP stock solution. In previous studies, methanol was found to have no impact on the adsorption of OMP onto activated carbon (Kilduff et al; Mailler et al., 2016) and its impact on adsorption is therefore not further addressed in this study. Two activated carbon stock suspensions of 2 and 10 g/L, respectively, were used to apply the aimed activated carbon dose in the corresponding batches. A reference batch without activated carbon was prepared in parallel. After 48 h contact time on a horizontal shaker, the activated carbon was separated by membrane filtration (regenerated cellulose, 0.45 µm nominal pore diameter).

Table 2: Activated carbon characteristics: specific surface areas (SSA) determined with the BET method using N_2 isotherms (P/P_0 = 0.01–0.50), micropore percentage (V-t method with t layer thickness of carbon black), 4 V/A average pore size (Aschermann et al, 2018), point of zero charge (pH_{PZC}) (Aschermann et al, 2019), ash content, carbon content determined via surrogate analyses of the oxidative mass loss via thermogravimetric analysis (TGA), oxygen content and surface oxygen groups, both measured with TGA coupled to Fourier-transform infrared spectroscopy (TGA-FTIR) (Dittmann et al, 2022).

Activated carbon	Raw material	BET SSA (m^2/g)	Share of micropores (%)	Average pore size (Å)	Point of zero charge (pH_{PZC})	Ash content (wt%)	Carbon content (wt%)	Oxygen content (wt%)	Surface oxygen groups (µmol/g)					
									Carboxylic acids	Anhydrides	Lactones	Phenols & ethers	Carbonyls & quinones	Pyrones & chromenes
Hydraffin CC	Coconut husk	1140	95	16.8	9.5	7.1	86	4.7	297	143	n.d.	n.d.	n.d.	n.d.
Epibon A	Lignite	1030	67	24.1	8.1	14.7	80	1.8	37	35	34	90	267	265

2.4. Analytics

2.4.1. DOC and UVA_{254} analyses

DOC was analyzed via catalytic combustion on a varioTOC cube (elementar Analysensysteme, Germany). The UV absorbance at 254 nm (UVA_{254}) was measured by a dual beam spectral photometer (Lambda 12 UV-VIS, Perkin Elmer, Germany) using 10 mm quartz cuvettes (Hellma, Germany).

2.4.2. Well-known OMP analyses

The well-known OMP were analysed by liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). Thereby, the analytes were chromatographically separated by a reversed-phase XSelect HSS T3 XP column (2.1 × 50 mm column, Waters, USA). Subsequent compound detection was carried out by a triple quadrupole with electro spray ionization (TSQ Vantage, Thermo Fisher, USA). For each analyte two mass fragments were selected according to the DAIOS database (Wasserchemische Gesellschaft, Germany). The fragments with the largest peak areas and deuterated internal standards were used for quantification. Further details are described by Zietzschmann et al. (2019). Values below the limit of quantification (LOQ) of 0.1 µg/L were set to the LOQ value. The removal by activated carbon was calculated in comparison to the reference. Negative removals were set to 0%.

2.4.3. PM candidate analyses

2.4.3.1. Sample enrichment

All samples were enriched by azeotropic evaporation based on a slightly modified method of Schulze et al. (2020), as described in Neuwald et al. (2021). In short, four mL of sample was mixed with 21 mL acetonitrile and evaporated at 40°C under a gentle stream of nitrogen before reconstitution in 200 µL acetonitrile:water (90:10) to achieve a concentration factor of 20. The extract was centrifugated and the supernatant chemically analyzed.

Table 3: Overview of the batch experiments including experimental conditions and investigated substances.

Batch experiment	Activated carbon		Matrix				
	Activated carbon product	Activated carbon doses (mg/L)	DOC (mg/L)	UVA_{254} (m^{-1})	pH (-)	Substances	Aimed target concentration c_0 (µg/L)
1	Hydraffin CC, Epibon A	5, 10, 50, 100, 500	4.3	9.9	8.2	9 well-known OMP	1
2						13 PM candidates	
3	Hydraffin CC	1, 2, 5, 10, 15, 20, 50, 100	13.5	10.9	8.3	19 PM candidates	10

2.4.3.2. Instrumental analysis

For instrumental analysis by supercritical fluid chromatography coupled with high-resolution mass spectrometry (SFC-HRMS), an Acquity UPC2 system together with a Synapt GS2 quadrupole time-of-flight high-resolution mass spectrometer (both Waters, Milford, USA) were applied. Chromatographic separation was performed on an Acquity UPC^2 BEH column (100 x 3 mm, 1.7 µm, Waters). The gradient and eluent composition were taken from literature (Neuwald et al., 2021) and are given together with further details regarding SFC-HRMS in the SI, chapter 1.1 instrumental analyses by SFC-HRMS.

2.4.3.3. Calculation of removals and evaluation of matrix effects during instrumental analysis

Removals of the PM candidates were calculated using peak area ratios of target analytes before and after adsorption onto activated carbon due to a linear relation between analyte concentrations and peak areas that was confirmed by an external calibration curve prepared in ultra-pure solvent. However, the magnitude of signal suppression or enhancement ("matrix effects") of the target analytes during instrumental analysis by SFC-HRMS is potentially influenced by nonconstant concentrations of sample constituents ("matrix") before and after sample treatment with activated carbon. To exclude the influence of matrix effects on peak area ratios before and after sample treatment, matrix effects of all analytes were determined as described in the SI, chapter 1.2 Matrix effects.

Matrix effects leading to suppression or enhancement of the chromatographic signals of ACE, ATA, DMBSA, DCHSS, MPSA, HHTMP, SAC and TFMSA during chemical analysis by SFC-MS was recently published for method using a similar mobile phase and the same stationary phase in positive ionization mode as applied in this study (https://doi.org/10.1007/s00216-020-02722-5). Thus, matrix effects influencing the instrumental analysis of PM candidates were determined for all PM substances to assure that apparent removals during sample treatment with activated carbon are not exclusively resulting from signal suppression. Even if pronounced matrix effects between 76.3% for AAMPS and -80.3% for PTSS were found (SI, Figure SI1), only minor changes < 10% after sample treatment with activated carbon (SI, Figure SI2) were observed. With increasing amount of applied activated carbon, matrix effects increased in average about 6.1% (10 mg/L activated carbon), 7.8%

(50 mg/L activated carbon) and 9.3% (100 mg/L activated carbon) and thus only had a minor impact on received removals.

3. Results and Discussion

3.1. Comparing adsorptive removals of well-known OMP and PM candidates

In a first screening with two activated carbons testing a wide range of activated carbon doses (5–500 mg/L) for the removal of well-known OMP (experiment 1) as well as selected PM candidates (experiment 2), the former were removed as expected (Figure 1 A): CBZ, BTA, MBT and MTP known as well-adsorbing OMP were completely removed by both activated carbons applying a typical activated carbon dose of 10 mg/L or higher, while a dose of 50 mg/L activated carbon was necessary to reach 100% removal of FAA, SMX and PRI. Both ACE and GAB were poorly removed by both activated carbons exhibiting ≤ 35% elimination at a dose of 10 mg/L. Overall, increasing the activated carbon dose always resulted in improved removal of well-known OMP. In contrast, the removal of PM candidates appears to be more diverse, tending towards either none or high adsorptive removal (Figure 1 B): Three of the target substances, namely DIOTOG, MAPMA and BETMAC, indicate high affinities towards activated carbon with removals ≥ 89% already at the lowest dose (5 mg/L). In contrast, HHTMP, TFMSA and MPSA show none or negligible removal (≤ 11%) even for high activated carbon doses up to 100 mg/L.

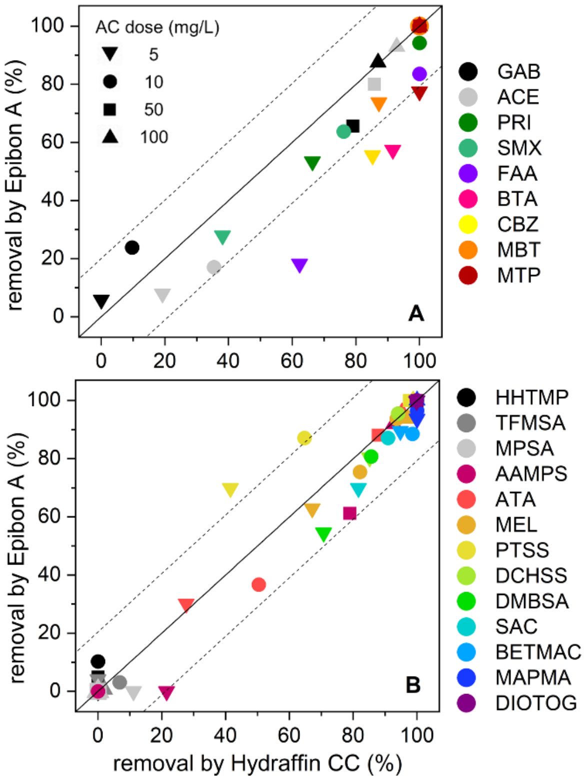


Figure 1: Direct comparison of removals of nine well-known OMP (A) and 13 PM candidates (B) by Hydraffin CC (x-axis) and Epibon A (y-axis) from tap water with initial concentrations of approx. 1 µg/L in batch experiments with 5, 10, 50 and 100 mg/L activated carbon (AC). Areas within dashed lines: similar removals (≤ 20% variation) by both activated carbons. Apparent negative removals were set to zero.

The strongly varying elimination potential of activated carbon for the PM candidates is emphasized in Figure 2, where the removal of four PM candidates (TFMSA, ATA, MEL, BETMAC) with a high occurrence in European water samples reported by Schulze et al. (2019) is shown in relation to the SMX removal. SMX was suggested as an indicator substance for moderate adsorption onto activated carbon (Jekel et al., 2015) and is frequently subject to monitoring and research (Benotti et al., 2009; Peng et al., 2011; Zhang et al., 2016). Overall, well-known OMP were eliminated on average by 80%, while PM candidates were removed considerably less by 63% on average, both at an activated carbon dose of 10 mg/L.

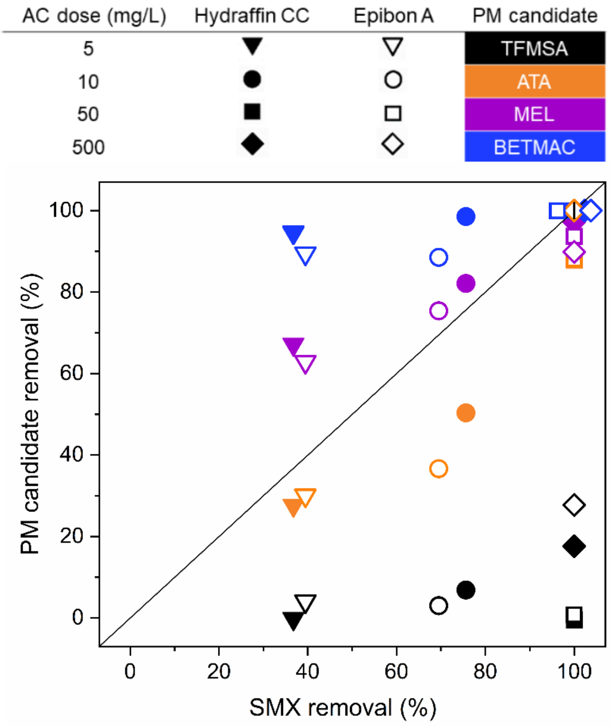


Figure 2: Removals of four PM candidates (TFMSA, ATA, MEL and BETMAC) in relation to the SMX removal in batch experiments (experiments 1 and 2) with two activated carbons and four activated carbon doses.

3.2. Removals of well-known OMP and PM candidates by Hydraffin CC and Epibon A

In Figure 1, A and B, the performance of the microporous Hydraffin CC and the mesoporous Epibon A for the removal of OMP and PM candidates (experiment 1 and 2, see Table 3) was compared. Thereby, an improved removal by at least 20% for one or more activated carbon doses was set as a benchmark for preferential adsorption as visualized by the dashed lines. Comparing the adsorptive removals, a total of 16 substances (HHTMP, TFMSA, MPSA, GAB, ACE, ATA, MEL, PRI, SMX, DCHSS, DMBSA, SAC, BETMAC, MAPMA, MBT, DIOTOG) showed a very similar affinity towards both activated carbon products accounting for more than 70% of all investigated substances. Only for five well-known OMP a distinctive tendency towards the microporous Hydraffin CC was identified: FAA > BTA > CBZ > MTP > AAMPS. This trend was visible only for the lowest activated carbon dose (5 mg/L) where competition with background organic matter is highest. Only one compound (PTSS) adsorbed preferentially to Epibon A.

One of the OMPs preferentially adsorbed by the microporous Hydraffin CC is BTA, the one with the lowest molecular mass (119 g/mol) (Figure 1). Also, Ruhl et al. (2014) observed the best performance for BTA removal to be of a coconut based activated carbon product (as Hydraffin CC) among eight different powdered activated carbons. The pore structure of an activated carbon influences the accessibility of its internal surface area. In theory, small compounds are anticipated to reach further into the porous structure and consequently adsorb better onto microporous activated carbons compared to high molecular-weight substances, which may be hindered by size exclusion (Jekel et al., 2015; Mestre et al., 2014). Previous analysis of Hydraffin CC revealed a high share of the total surface area located in the micropores with 95% compared to 64% of a macroporous activated carbon (Aschermann et al., 2018). However, larger molecules such as FAA, CBZ, MTP and AAMPS (207–267 g/mol) also adsorb well to Hydraffin CC. The higher BET surface of Hydraffin CC (Table 2) likely contributes to the improved adsorption properties of Hydraffin CC compared to Epibon A.

Apart from the evident beneficial physical properties of Hydraffin CC for the tested OMP, the adsorbents surface chemical properties contribute to the removal performance of individual organic compounds (Nielsen et al., 2014; Piai et al., 2019). Accordingly, the higher carbon content of Hydraffin CC compared to Epibon A (Table 2) has a positive effect on the adsorption capacity due to the increased number of available adsorption sites. Furthermore, at experimental pH (see Table 3), the activated carbons differ in their net surface charge due to their respective pH_{PZC} (see Table 2) enabling electrostatic attraction or repulsion of charged compounds. However, despite the positive net charge of Hydraffin CC, improved removal was mainly achieved for neutral compounds (BTA, CBZ, FAA) rather than for anionic compounds.

More specific bonding between a compound and the adsorbent may occur on functional groups: Particularly surface oxygen groups are known to play a key role for the affinity of OMP towards activated carbon (Dittmann et al., 2022). A relative high oxygen content and therefore, degree of functionalization is present in Hydraffin CC compared to Epibon A. Especially at pH 8.2/8.3 the pronounced amount of carboxylic acid groups provides moieties with negative charge in Hydraffin CC in contrast to its positive net surface charge. This may refer to a significant carbonate content interfering with the pH_{PZC}. However, coconut husk based activated carbons (as Hydraffin CC) contain increased amounts of phenol groups (Dittmann et al., 2022) that are known to chemically react with amide moieties of target compounds (Nielsen et al., 2014). Hence, the amide structure of AAMPS, FAA and CBZ is likely to cause enhanced adsorption by Hydraffin CC as affirmed by the obtained adsorption results.

3.3. Categorization of PM candidates

Based on the previous results, Hydraffin CC was tested for a wider range of activated carbon dosages adding also more OMPs to the test set (experiment 3, Table 3). The results are in line with the previous experiments albeit slightly lower removals (14% lower median removal, see Figure SI3) were achieved due to the higher initial PM substance concentration (Table 3).

Based on experiment 3, all investigated PM candidates were categorized according to their removals at a common activated carbon dose of 10 mg/L to assess the suitability of an adsorption step as a viable treatment option (Figure 3): As observed in the screening (experiment 2, Figure 1 B), the PM candidates exhibited a broad range of adsorbabilities onto activated carbon in equilibrium. At a practice-oriented activated carbon dose of 10 mg/L, nine substances adsorbed poorly (20–60%; VSA, PTSS, ATA, ACE) or very poorly (< 20%; DZA, AAMPS, HHTMP, MPSA, TFMSA) (Figure 3). The lowest removals were achieved for the sulfonic acids TFMSA and MPSA followed by HHTMP, all relatively small (150–201 g/mol) and very mobile (log D < -1.2) charged aliphatic compounds. These three substances do not achieve more than 50% removal even at an extensive dosage of activated carbon of 100 mg/L. Therefore, TFMSA, MPSA and HHTMP are likely to break through advanced drinking water treatment by activated carbon when present in the respective raw water. The short-chain perfluoroalkane sulfonic acid TFMSA was detected for the first time in European surface water, groundwater and bank filtrate by Schulze et al. (2019) at estimated concentrations of up to 1 µg/L. Following sampling campaigns including a variety of water samples such as surface and groundwater underlined these findings reporting TFMSA in 94% of all samples with a median concentration of 30 ng/L in Sweden (Björnsdotter et al., 2019) and concentrations > 1 µg/L in a wastewater influenced German surface water (Alb River) (Scheurer et al., 2022). The recent detection of TFMSA in the Arctic suggests that TFMSA is already ubiquitous in the aquatic environment (Björnsdotter et al., 2021).

Out of the 19 tested PM candidates, five (DCHSS, BETMAC, SAC, DMBSA and MEL) were moderately (60–80%) and five substances (DIOTOG, BTA, OXP, MAPMA, PRI) were readily removed achieving ≥ 80% removals at an activated carbon dose of 10 mg/L. Except for TFMSA, MPSA and HHTMP, a strong impact of the activated carbon dose on the adsorptive removals was observed. Consequently, further seven substances (DCHSS, BETMAC, SAC, DMBSA, MEL, VSA and PTSS, see Figure 3) reach good removals (≥ 80%) applying slightly higher activated carbon doses of 15 to 20 mg/L.

Overall, knowledge on PM substance removal by adsorption onto activated carbon is still limited: To our knowledge, this study is the first to address the adsorption potential of MAPMA, DCHSS, MPSA and HHTMP. While MPSA and HHTMP are hardly controllable by activated carbon adsorption, MAPMA and to some extent DCHSS, both industrial chemicals registered under REACH and used in adhesives and sealants amongst other consumer uses, indicate promising adsorption potentials. Furthermore, this study provides data regarding removability of AAMPS, ATA, BETMAC, DIOTOG, DMBSA and PTSS which are scarcely investigated, particularly in real water matrices. Interestingly, the removal of ATA and BETMAC in the present study exceeded recently reported eliminations in ultrapure water by Scheurer et al. (2022) by approx. 10% and 30%, applying the same activated carbon dosage (10 mg/L) and contact time (48 h). In contrast, AAMPS and PTSS showed enhanced removal by more than 50% in that study, which is in line with expectations due to the absence of competing background organic matter.

This study confirms that adsorption steps may be suitable options for the elimination of specific PM substances and should be considered when discussing appropriate treatment measures, especially since adsorption is already an established process with wide knowledge regarding operation and optimization. Typically, well adsorbable compounds are the target for an adsorption step: Thereby 80% removal of a specific compound or higher is a common elimination goal in advanced water treatment. This study shows that this can be well be reached for some of the PM candidates.

Removal of PM compounds by adsorption onto activated carbon can be further improved by increasing the activated carbon dose in case of a powdered activated carbon application or renewing granular activated carbon in a fixed-bed filter at lower throughputs. This may be necessary when regulatory concentration limits for specific compounds come into place and alternative treatment options are either lacking or even more cost and/or resource intensive. This is particularly relevant for substances that have been demonstrated to be toxic such as TFMSA, which was recently found to alter the liver lipid metabolism and gut microbiota of mice when exposed to low TFMSA concentrations (Zhou et al., 2020). However, further research is needed to investigate the role of kinetics and competing background organic matter, since they may hinder an economic application of activated carbon.

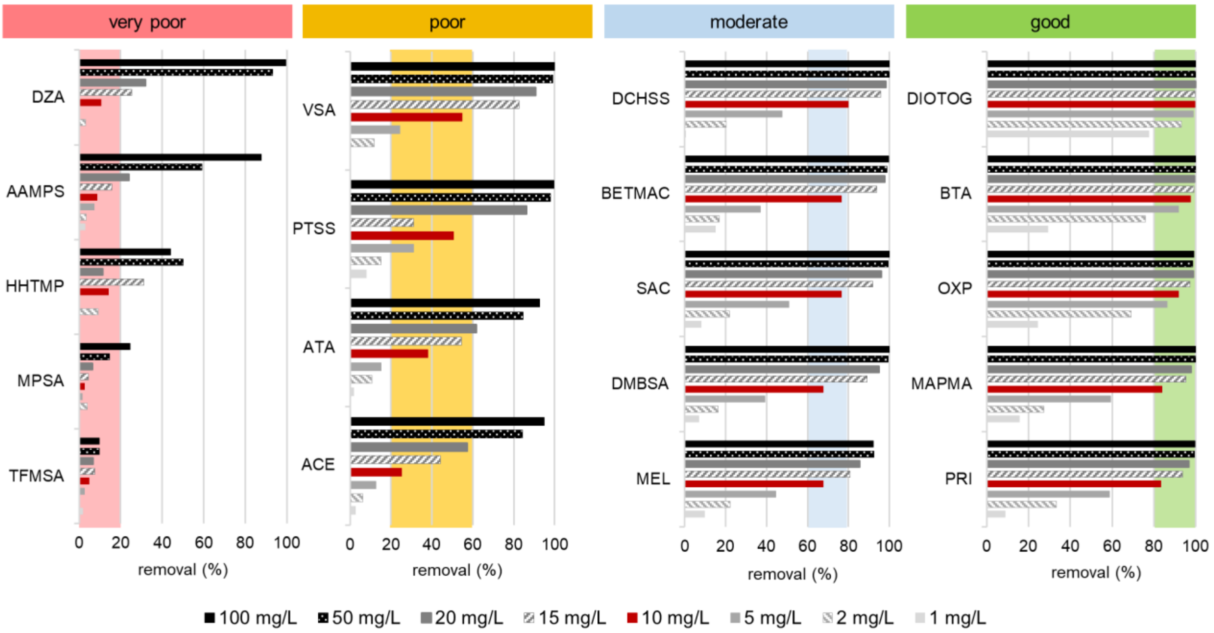


Figure 3: Removals of 19 PM candidates with Hydraffin CC in batch experiments (experiment 3, see Table 3) applying eight different activated carbon doses in spiked tap water (c_0≈10 µg/L) and 48 h contact time. PM candidates were classified into very poor (< 20%), poor (20–60%), moderate (60–80%) and good adsorptive removals (> 80%) by activated carbon according to an activated carbon dosage of 10 mg/L (red bar). Negative removals were not considered in this graph.

3.4. UVA$_{254}$ abatement as surrogate for PM candidate removals

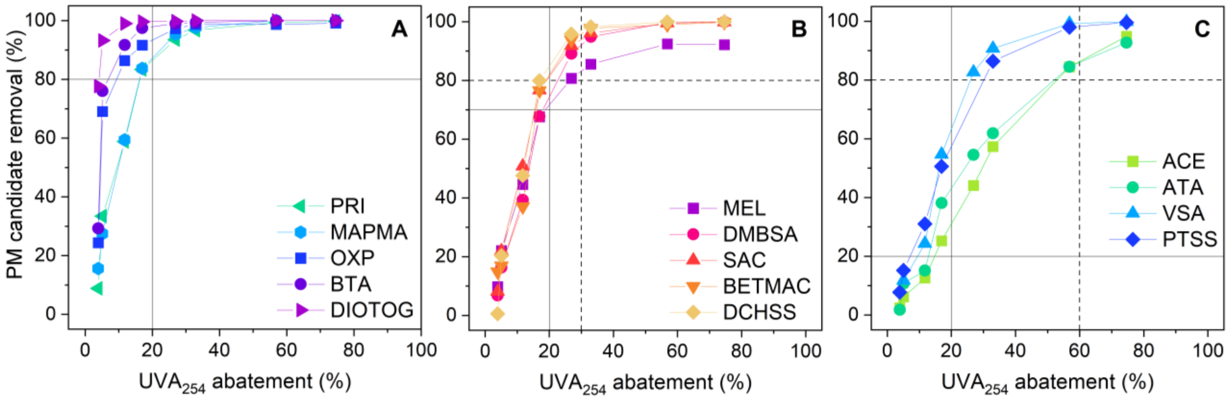


Figure 4: Correlation between PM candidate removals (c_0≈10 µg/L) and UVA$_{254}$ abatement in batch experiments with eight different activated carbon (Hydraffin CC) doses after 48 h contact time. PM candidates are grouped according to their adsorbability (Figure 3): A: good, B: moderate, C: poor. Solid lines indicate the PM candidate removals at 20% UVA$_{254}$ reduction. The UVA$_{254}$ abatements corresponding with 80% PM candidate removals are indicated as dashed lines.

In previous studies, UVA$_{254}$ abatement was reported to correlate with OMP eliminations by activated carbon and was therefore proposed as a surrogate (Anumol et al., 2015; Zietzschmann et al., 2014). This is of particular importance for very polar compounds since their determination remains challenging in analytics (Reemtsma et al., 2016). In this study, surrogate correlations (Figure 4) were established for the investigated PM candidates. A common elimination aim of 80% removal was reached at 20%, 30% and 60% UVA_{254} abatement for the well, moderately and poorly adsorbable compounds (Figure 4), respectively. Thus, UVA_{254} provides a cheap and fast estimate for the removals of the target compounds. This proves the broad applicability of the surrogate and justifies the use also for "new" OMP.

3.5. Correlation between removal by adsorption onto activated carbon and physico-chemical properties

To date, no reliable prediction of removal efficiencies of individual OMPs in specific water matrices is possible due to the complex processes that determine the interactions of adsorbent, adsorbate and water matrix (Kah et al., 2017; Ridder et al., 2010; Scheurer et al., 2022; Wang et al., 2021). A long-term research goal remains the identification of key characteristics of organic compounds that determine their affinities towards activated carbon. The most favorable characteristics are those that are both readily and quickly accessible and that allow predictions about the suitability of an adsorptive treatment for a specific compound without the need for time-consuming, labor-intensive, and costly experimental testing. Previous studies relating adsorption performance and log D in matrices without background organic matter obtained different results: While Ridder et al. (2010) demonstrated a clear trend between the increase in affinity of OMP for activated carbon and the increase in log D, no correlation was found in other studies (Alves et al., 2018; Piai et al., 2019; Scheurer et al., 2022).

Accordingly, the removals of all tested PM candidates (results from experiment 3, Table 3) applying a low, a medium and a high activated carbon dose (1, 10 and 50 mg/L) were compared with the predicted polarity indicator (log D), geometrical properties (projection area and projection diameter), the molecular mass and electric properties (polarizability) which have been related to adsorbability in the past (Piai et al., 2019; Ridder et al., 2010). Additionally, chromatographic information (retention time in RPLC) was selected to investigate a potential relation to adsorbability.

As shown in Figures 5 a–f no distinctive correlation with adsorptive removal was found for any of the parameters chosen for the correlation analysis in this study ($0.01 < R^2 < 0.28$). However, overall, the log D provides the highest R^2 range of 0.13–0.27. An overview of all determination coefficients R^2 received is given in Table SI3. This finding is supported by previous research connecting the relation between adsorption rates and log D with the nature of the test substances: hydrophilicity, a low molecular weight and/ or ionic or ionizable organic compounds, like all the PM candidates investigated in this study, translate into to less dominant hydrophobic partitioning and consequently poor correlations (Chen et al., 2007; Ridder et al., 2010; Westerhoff et al., 2005; Zwiener, 2007). However, these findings may be somewhat limited by the uncertainty of predicted log D data.

Since the experiments were carried out in real drinking water matrices, the different activated carbon dosages generate differing competition conditions with background organic matter: With increasing activated carbon dosages the adsorption competition decreases. It is noteworthy that even though general correlation is lacking, the log D correlation appears to be more relevant using low activated carbon dose, hence under most competing conditions. However, when general competition declines, other characteristics such as the geometrical properties, the interaction with a chromatographic column (RPLC) or the polarizability become more important since the R^2 increases with the applied activated carbon dose.

In conclusion, neither of the selected compound characteristics is suitable to solely describe the removability of the selected PM candidates by activated carbon adsorption. Hence, other substance characteristics as well as interactions with background organic matter significantly affect their adsorbability. Further studies focusing on multi-parameter approaches and/ or a larger set of PM substances are recommended to gain more insight into the relation between compound characteristics and adsorptive removals.

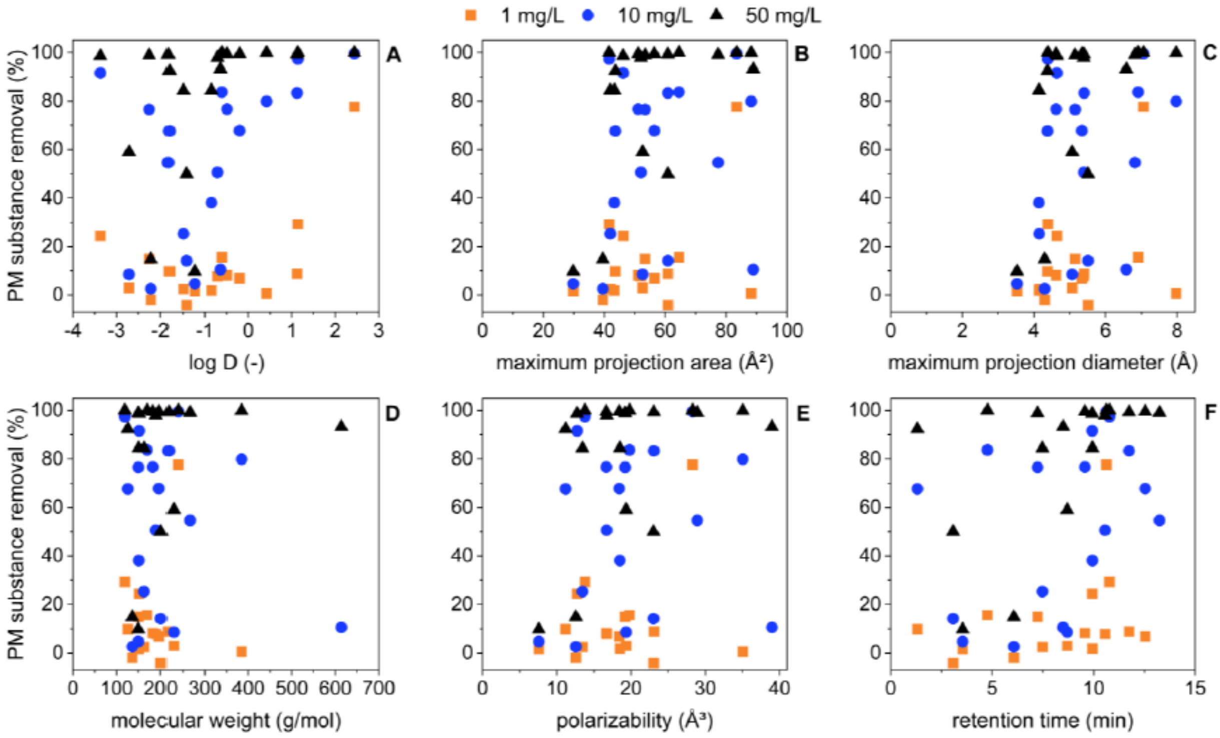


Figure 5: Relations between removals of PM candidate removal with activated carbon doses of 1 mg/L, 10 mg/L and 50 mg/L of Hydraffin CC in batch experiments (c_0≈10 µg/L, contact time: 48 h, pH: 8.3) and log D (A) maximum projection areas (B), maximum projection diameters (C), molecular weights (D), polarizabilities (E) and retention times in reversed phase liquid chromatography (details are provided in the SI chapter 2.3 RPLC method) (F). Numerical values are given in Table 1.

4. Conclusions

- The adsorption of 19 PM candidates onto activated carbon was investigated in batch experiments applying one microporous and one mesoporous activated carbon in a drinking water matrix.
- TFMSA, HHTMP and MPSA were not or very poorly removed independently of the applied activated carbon type and activated carbon dose. Here, the viability of other treatment options should be assessed.
- DIOTOG, BTA, OXP, PRI and MAPMA were readily removed which was indicated for MAPMA the first time. For these compounds, activated carbon adsorption may be a suitable treatment option even at the high level of competing background organic matter in Berlin tap water.
- The highly diverse elimination potentials emphasize the need for not only multi-barrier approaches and case specific treatment solutions but also the improvement of drinking water resource protection.

- UVA_{254} is a suitable and easy to measure surrogate for the substance specific adsorptive PM candidate removal, which proves its wide applicability and justifies its use also for newly detected OMP.
- Available substance characteristics, namely log D, projection area and diameter, molecular weight, polarizability or retention time in RPLC did not show useful relations to adsorptive removals.
- Adsorption onto activated carbon should be taken into account as an effective barrier for numerous PM substances even though high mobility implies poor removal.

Acknowledgements

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Supplementary materials

Supplementary data to this article can be found online at…

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