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Efficacy of activated carbon filtration and ozonation to remove persistent and mobile substances – a case study in two wastewater treatment plants

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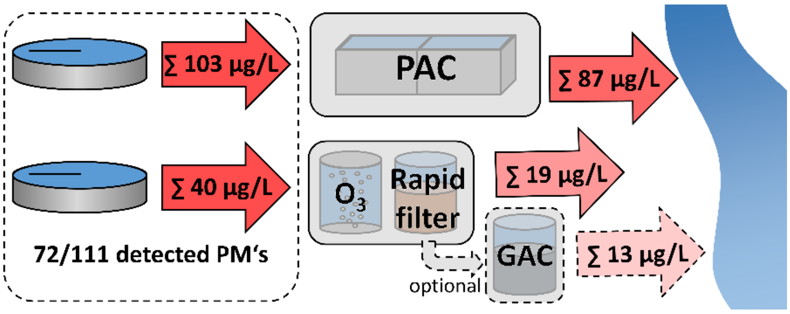
Keywords

benzotriazole, melamine, 1,3 diphenylguanidine, valsartanic acid, guanylurea

Graphical Abstract



Abstract

Persistent and mobile (PM) substances are able to spread quickly in the water cycle and were thus identified as potentially problematic for the environment and water quality. If also toxic (PMT) or very persistent and very mobile (vPvM) their regulation under REACH as substances of very high concern is foreseen. Yet, knowledge on the effectiveness of advanced wastewater treatment in removing PM-substances from WWTP effluents is limited to few rather well-known chemicals. The occurrence and behavior of 111 suspected and known PM-substances was investigated in two wastewater treatment plants employing either powdered activated carbon (PAC, full-scale) or ozonation with subsequent sand/anthracite filtration (pilot-scale) and an additional granular activated carbon (GAC) filtration was investigated. 72 of the 111 PM-substances analyzed were detected at least once in the secondary effluent of either wastewater treatment plant, resulting in total concentrations of 104 µg/L and 40 µg/L, respectively. While PAC removed 32 % of PM-substances well, the total PM burden in the effluent was only reduced from 103 µg/L to 87 µg/L. Ozonation and the subsequent sand/anthracite filtration was able to reduce the PM burden in wastewater from 40 µg/L to 19 µg/L, showing a higher removal efficacy than PAC in this study. The additional GAC filtration further reduced the total PM-concentration to 13 µg/L. Among the investigated PM-chemicals detected were constituents of ionic liquids: The anion hexafluorophosphate was one of few chemicals that was detected in effluent concentrations > 1 µg/L and could not be removed by the processes studied, showing that for some chemicals preventive actions may be required.

Introduction

The chemical industry is estimated to produce more than 70000 chemical products (Rogowska et al., 2020), with a rising trend, as registrations under REACH have increased by roughly 50 % within the last four years (European Chemicals Agency). These chemicals may pose a risk for the aquatic environment and eventually drinking water, once emitted. Conventional waste water treatment plants (WWTPs), including biological treatment, are capable of removing a large number of these chemicals from household and industrial waste water. However, for chemicals that are persistent and thus degrade only slowly in the environment (Cousins et al., 2019), other treatment options are required. The European Water Framework Directives propose that “Member States shall ensure the necessary protection for the bodies of water [...] in order to reduce the treatment required in the production of drinking water” (European Commission, 2000, European Commission, 2008, European Commission, 2013). Therefore, advanced wastewater treatment is increasingly applied to improve effluent quality (Altmann et al., 2014, Lim et al., 2022). In 2016, the Swiss water protection law imposed the implementation of advanced waste water treatment methods for large WWTPs (> 80.000 population equivalents) and WWTPs close to particularly polluted waters (Bundesversammlung der Schweizerischen Eidgenossenschaft, 1991). The German Environment Agency has proposed upgrading WWTPs similarly to the Swiss law in 2015 (Umweltbundesamt, 2015). Most commonly, conventional WWTPs are upgraded with either activated carbon (AC) treatment steps or ozonation facilities commonly followed by biologically active filtration. With climate change resulting in longer dry periods, the need for direct or indirect water reuse will increase (Tortajada et al., 2020), while water levels in surface and groundwater drop, decreasing the effect of dilution along the water cycle. In such a water stressed environment the effective removal of anthropogenic chemicals becomes even more important, further increasing the need for effective wastewater treatment.

Advanced treatment has proven successful for many pharmaceuticals and personal care products (PCPs) that only showed limited removal through biological treatment (Bolong et al., 2009, Kovalova et al., 2013, Margot et al., 2013, Pistocchi et al., 2022). However, the effectiveness of these technologies for the broad majority of persistent and mobile (PM) substances is still in question. Recent regulatory actions, such as the introduction of persistent, mobile and toxic (PMT) and very persistent and very mobile (vPvM) substances under REACH, as well as further ongoing regulatory (Neumann et al., 2019, European Commission, 2021) and scientific (Reemtsma et al., 2016, Sigmund et al., 2022) discussions have drawn attention to PM-substances. They are expected to adsorb only poorly onto natural sorbents or be transformed by microorganisms, and thus advanced treatment processes are essential to limit their spread throughout the water cycle. Availability of monitoring data regarding their removal in WWTPs is only available for a few well-known chemicals, such as ethylenediaminetetraacetate (EDTA) (Reemtsma et al., 2006) or 1,4-dioxane (Stepien et al., 2014), benzotriazole (Weiss et al., 2006, Farré et al., 2008) or acesulfame (Scheurer et al., 2009, Rizzo et al., 2019). Multiple preparative and chromatographic techniques, such as hydrophilic interaction chromatography (HILIC), mixed-mode liquid chromatography (MMLC), supercritical fluid chromatography (SFC), capillary electrophoresis (CE) or ion chromatography (IC) (Montes et al., 2017, Höcker et al., 2020, Knoll et al., 2020, Schulze et al., 2020, Zahn et al., 2020) have been used for the analysis of PM-substances, but neither of these methods are extensively used for monitoring or screening purposes hampering the availability of data.

To gain more insight into the effectiveness of advanced wastewater treatment for PM-substances, this study investigated the fate of 111 known and suspected PM-substances during water treatment with AC (WWTP 1) and by ozonation followed by sand/anthracite filtration (WWTP 2) with an optional subsequent GAC filtration as advanced treatment options. This data is used to assess the efficacy of these advanced treatment technologies for the removal of PM-substances from wastewater. Additionally, PM-substances with high concentrations in the secondary and advanced treatment effluents of these WWTPs were identified, which may contribute to prioritization of PM-substances for future research activities, the inclusion in monitoring campaigns, or regulatory efforts. HILIC and SFC were utilized to cover this large set of polar and often difficult to analyze PM-substances. Analyte selection was based on a thorough evaluation of chemical property and use data of REACH chemicals

(Schulze et al., 2018) and extended by the findings of a suspect screening (Neuwald et al., 2021). In particular a wide range of ionic liquid (IL) constituents was included since these chemicals were recently identified as a novel class of water contaminants (Neuwald et al., 2020).

Materials and methods

PM-analytes

In total, 111 PM-substances were monitored. Structural, physicochemical and analytical information, as well as information on the used standard material are presented in Table S 1. 65 PM-substances were analyzed with HILIC and 46 compounds were analyzed with SFC. Already existing target methods were extended by PM-substances identified in a previous suspect screening (Neuwald et al., 2021), including a variety of ILs based on literature research and availability of standards. Analytes of known behavior in advanced treatment were used as indicator substances.

Samples

Two representative WWTPs, both with large population equivalents of more than 700,000, were selected for this monitoring and sampled in two periods. WWTP 1 employed powdered AC (PAC) as advanced treatment. Fourteen 24-hour mixed samples of secondary WWTP effluent and effluent of the advanced treatment were taken from 25th until 31st January and 19th until 25th July 2021. The continuously added AC was Jacobi MP23 with a dosage of 10 g/m^3 and a mean contact time of 30 minutes. Further details on operational parameters are shown in Table S 2 and S 3.

In WWTP 2 (Sauter et al., 2021), a pilot plant that was operated with ozonation and subsequent filtration, eight 24-hour mixed samples of WWTP effluent of secondary treatment, effluent after ozonation and rapid (sand/anthracite) filtration (RF 1), and effluent of an additional subsequent rapid GAC filtration (RF 2) were sampled from 1st until 4th and 15th until 18th March 2021. In the second sampling, the filter speed of the rapid filter was increased (Table S 6). The ozone dose was 0.8 mg/mg dissolved organic carbon (DOC) with a contact time of > 15 minutes. Further operational parameters, as well as constitution and dimensions of the rapid filters are presented in Table S 4 and S 5. A scheme of secondary and advanced treatment of each WWTP is presented in Figure S 1.

All samples were taken in wide-mouth glass bottles (LABSOLUTE®, Th. Geyer, Renningen, Germany), stored at 4°C under exclusion of light, and processed within 8 weeks.

Sample preparation

Multi-layer SPE and evaporative concentration

The multi-layer solid-phase extraction (mlSPE) and evaporative concentration (EC) protocol is based on Köke et al. (Köke et al., 2018) and was further modified as mentioned in Neuwald et al. (Neuwald et al., 2022). For details see Text S 1.

Azeotropic evaporative concentration

Enrichment by azeotropic evaporative concentration (AEC) was performed according to a modified protocol by Schulze et al. (Schulze et al., 2020). Details see Text S 1.

Analytical methods

HILIC-MS/MS

The applied liquid chromatography (LC) system was a Shimadzu Nexera X2, containing a degassing unit, four pumps, an autosampler, a communication module and a column oven (Shimadzu, Kyoto, Japan). The tandem mass-spectrometry (MS/MS) instrument was a QTrap 5500 (AB Sciex, Darmstadt, Germany) with electrospray ionization (ESI). The HILIC column used was an Acquity UPLC BEH Amide 1.7 µm, 2.1 x 100 mm (Waters, Milford, MA, USA), heated to 30 °C. MS analysis was performed in multiple reaction monitoring (MRM) mode. Chromatographic and MS settings are presented in Text S 2 and Table S 7.

SFC-MS/MS

The used SFC-MS/MS instrument was an Acquity UPC^2 system coupled to a Xevo TQ-XS MS/MS equipped with an ESI source (all from Waters, Milford, MA, USA). The column used was an Acquity

UPC^2 BEH 1.7 µm, 3.0 x 100 mm (Waters, Milford, MA, USA). During instrumental analysis, pure acetonitrile (ACN): water (H_2O) (90:10, v/v) was injected between each sample to avoid carryover. Additionally, a mixture containing 1 µg/L of all target analytes in pure ACN:H_2O (90:10, v/v) was injected every 50 runs to allow for MS sensitivity correction. Chromatographic and MS settings for each analyte are presented in Text S 2 and Table S 7.

Quality control

Analysis and validation in HILIC-MS/MS measurements

For HILIC measurements, the following quality control measures were performed: A mix standard containing all PM-substances analyzed was injected at least three times per sample batch to monitor for intensity and retention time shifts. The difference in calculated concentration of quantifier and qualifier was less than 20 % for analytes containing two transitions. For quality control, 30 % of mlSPE samples and 15 % of EC samples were used to determine recovery and matrix effects. Instrumental limit of quantification (LOQ) of each PM-substance was determined by a signal to noise ratio of 10 in the external calibration (12 calibration points, weighting of calibration regression line 1/x) and limit of determination (LOD) corresponds to LOQ/3. Since matrix effects of PM-substances are often strongly varying between samples (Müller et al., 2020), they were determined for each sample individually by splitting the aliquot after reconstitution and spiking one part with the PM analyte mix. Both matrix effects and recovery were considered in calculating analyte concentrations in the WWTP samples. For each batch enriched via mlSPE and EC, a procedural blank, consisting of ultrapure H_2O, was processed in parallel to the WWTP samples and blank signals were subtracted from the respective sample signal, if present. About 10 % of the samples were enriched in duplicate with mlSPE and EC to assess reproducibility. Equations for calculation of recovery, matrix effects and removal efficacies are presented in Text S 3. Validation parameters and duplicates are shown in Table S 8 and S 9.

Analysis and validation in SFC-MS/MS measurements

For SFC measurements, the following quality control measures were performed: For each batch two procedural blanks (ultrapure ACN) were processed in parallel to the WWTP samples and occurring blank signals were subtracted from the respective sample signal, if present. Target peaks with less than 2-fold areas in the extracts of the WWTP samples compared to the mean area of the procedural blanks were discarded. Apparent recoveries (sREs) were determined to account for matrix effects and recovery losses and applied for calculating analyte concentrations. For WWTP 1, sREs were determined in the July samples and applied to the January samples while for WWTP 2, all samples were used for individual sRE determination. To this end, pure and spiked water samples (addition of 10 µL of all target analytes) were concentrated by AEC. LOQ was derived by considering sREs, concentration factor and the lowest calibration point showing a signal in the chromatogram that deviates less than 25% from the external calibration curve (7 calibration points, weighting of calibration regression line 1/x). The LODs correspond to LOQ/3. For equations, see Text S 4. Results from validation are shown in Table S 8.

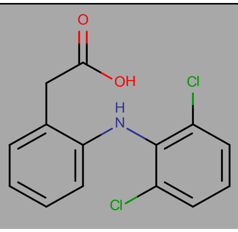
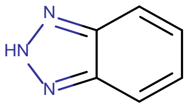
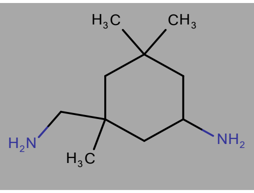
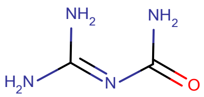
Results and discussion

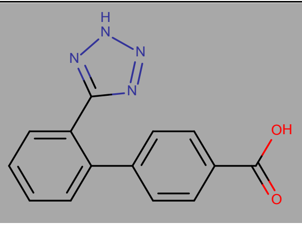
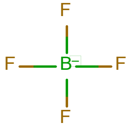
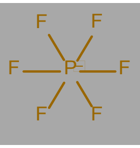
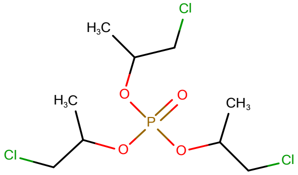
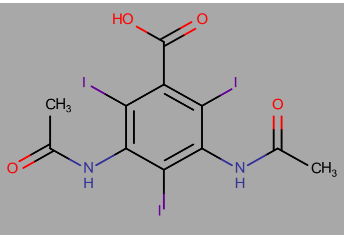
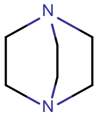
Occurrence and concentrations of PM-chemicals in secondary effluent

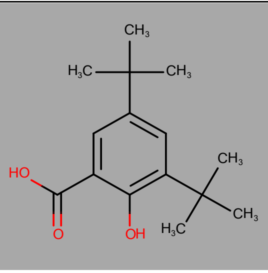
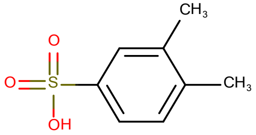
In this monitoring, 111 PM-substances were analyzed in two WWTPs after secondary wastewater treatment and after consecutive advanced treatment steps, either AC filtration or ozonation followed by sand/anthracite filtration (RF 1) with two sample series over a period of seven and four days, respectively. Individual concentrations are presented in Table S 10. Values of detected PM-substances that were between LOD and LOQ were included in the following calculations to increase statistical significance. In total, 72 PM-substances were detected more than once in the effluent of the WWTPs with 47 occurring in both WWTPs and 25 only detected in one of them. For 12 of the detected PM-substances the median concentration exceeded 1 µg/L (Table 1). 6/12 of these PM-substances are well-known and have been investigated in WWTPs before, 4/12 are emerging contaminants for which data exists but is still scarce and for 2/12 of these high-concentration PM-substances this is the first quantitative data in any compartment of the water cycle.

The well-known PM-substances, such as diclofenac (DCF), benzotriazole (BTA), guanylurea (GUA), valsartan acid (VSA), tris-2-chloroisopropyl phosphate (TCPP) and diatrizoic acid (DZA) have frequently been detected in WWTP effluent before, and concentrations reported herein are in line with previous studies (see Table 1 and S 11 and S 12) (Reemtsma et al., 2006, Rosal et al., 2010, Tran et al., 2018). For the emerging PM-contaminants isophoronediamine (IPDAM), 1,4-diazabicyclooctane (DABCO), 3,5-di-tert-butylsalicylic acid (DTBSA) and dimethylbenzenesulfonic acid (DMBSA) (Schulze et al., 2019, Neuwald et al., 2022, Tisler et al., 2022), no information on occurrence in effluent of secondary treatment is available yet. The two novel PM-substances, which have only recently been identified as environmental contaminants (Neuwald et al., 2021), are tetrafluoroborate (BF4, only detected in WWTP 1) and hexafluorophosphate (PF6) with median concentrations of 4.0 and 3.4 µg/L respectively. For these two inorganic chemicals, this is the first quantitative data in wastewater treatment plants. For WWTP 1, only data from July was considered (see next chapter).

Table 1: Structure, median concentration after effluent of secondary treatment and advanced treatment, frequency of detection (FOD), removal efficacy, and availability of quantitative data for the PM-substances detected with median concentrations > 1 µg/L in the effluent of secondary treatment. Data presented for WWTP 2 is from effluent samples of RF 1 (sand/anthracite filtration).

Substance	**Abbr.**	**Structure**	**Median conc. effluent sec. treatment (µg/L) WWTP 1/2**	**Median conc. effluent adv. treatment (µg/L) WWTP 1/2**	**FOD (%) WWTP 1/2**	**Median removal (%) WWTP 1/2**	**Availability of quantitative data**	**Literature**
diclofenac	DCF		10.4 / 7.98	n.d. / 0.055	86 / 100	100 / 99	well-known	(Petrović et al., 2003) (Jekel et al., 2015)
benzotriazole	BTA		32.5 / 4.46	12.1 / 1.92	100 / 100	62 / 57	well-known	(Herrero et al., 2014) (Careghini et al., 2014) (Farré et al., 2008) (Weiss et al., 2006)
isophoronediamine	IPDAM		5.91 / n.d.	0.77 / n.d.	100 / N/A	87 / N/A	emerging contaminant, quantitative data available	(Schulze et al., 2019)
guanylurea	GUA		10.5 / 3.33	1.29 / 3.04	100 / 100	88 / 9	well-known	(Scheurer et al., 2012) (Trautwein et al., 2011)

valsartan acid	VSA		2.55 / 5.82	1.58 / 2.23	100 / 100	38 / 62	well-known	(Nödler et al., 2013) (Margot et al., 2013) (Castro et al., 2019)
tetrafluoroborate	BF4		4.03 / n.d.	5.39 / n.d.	100 / N/A	-34 / N/A	Novel, no quantitative data available	(Neuwald et al., 2021)
hexafluorophosphate	PF6		11.3 / 2.90	11.9 / 3.28	100 / 100	-5/ -13	Novel, no quantitative data available	(Neuwald et al., 2021)
tris-2-chloroisopropyl phosphate	TCPP		1.77 / 1.88	n.d. / 0.47	71 / 100	100 / 75	well-known	(Luo et al., 2014) (Loos et al., 2013)
diatrizoic acid	DZA		6.51 / 1.36	6.66 / 1.39	100 / 100	-2 / -2	well-known	(Kovalova et al., 2013) (Scheurer et al., 2011)
1,4-diazabicyclooctane	DABCO		1.33 / 1.76	1.25 / n.d.	100 /100	6 / 100	emerging contaminant, quantitative data available	(Schulze et al., 2019) (Neuwald et al., 2022)

3,5-di-tert-butylsalicylic acid	DTBSA		1.47 / 0.023	1.23 / 0.025	100 / 50	16 / -9	emerging contaminant, quantitative data available	(Schulze et al., 2019)
dimethylbenzene-sulfonic acid	DMBSA		2.25 / 1.16	0.67 / 0.22	100 / 100	70 / 81	emerging contaminant, quantitative data available	(Schulze et al., 2019) (Tisler et al., 2022)

Removal efficacy of activated carbon and ozone as advanced treatment technologies

To address the knowledge gap on the effectiveness of AC and ozonation to remove PM-substances we investigated the PAC step in WWTP 1 and the ozonation followed by rapid sand/anthracite filtration in WWTP 2. The obtained removal efficacies were categorized as follows: good/well removal with > 70 %, medium removal between 30 and 70 % and no removal with ± 30 %. Values between -30 and -100 % are classified as inconclusive, while values < -100 % are categorized as formation.

Powdered activated carbon (WWTP 1)

For the PAC treatment at WWTP 1 the January and July samples were inconsistent, with January samples showing much lower removal for many analytes. The median removal of the analyzed chemicals was 29 % and 42 %, respectively, individual removal efficacies are shown in Figure 1. Since the removal of the well-studied compounds during the January sampling was significantly lower than described in literature (see Table S 11) it was assumed that the PAC step of the WWTP operated not optimally during the first sampling period. For more information on January samples refer to Text S 5 and Figure S 3. In contrast, the median quotient of the spectral absorption coefficient at 254 nm (SAC_{254}) between biological effluent and PAC effluent, which acts as a general indicator for the removal of chemicals with aromatic systems, remained almost constant (0.62 ± 0.025 1/m July vs. 0.68 ± 0.070 1/m January), which may indicate that adsorption of PM-substances is more strongly affected by changing operational conditions or influent quality than the removal of bulk organic matter. However, this was only observed in one sampling campaign in one WWTP and systematic studies with varying operating conditions will be required for confirmation and to identify the conditions most strongly affecting removal of PM-chemicals.

In the July samples, removal efficacies by AC for 11 of 13 well-known substances were within the range reported in literature (Table S 11), indicating good comparability to other WWTPs employing similar advanced treatment, and is thus the sampling that will be discussed herein after. 58 PM-substances were detected in total in the effluent of secondary treatment, 31 of them with a concentration above 0.1 µg/L. The median removal efficacy of these substances was 50 % with narrow interquartile ranges (q1-q3) indicating stable removal throughout the one-week sampling period (see Figure S 3). The detected PM-substances were evenly distributed throughout the three removal categories (Figure 1). Despite 1/3 of the PM chemicals showing good removal efficacies the total sum of detected PM-substances was only reduced from 103 to 87 µg/L, which was caused by the poor removal of many high concentration PM-substances. Interestingly, cyanuric acid (CYA) was not detected in the secondary effluent and showed formation during PAC treatment. CYA is formed from other triazines, such as MEL, atrazine or ametryn, (Seffernick et al., 2016). Since recirculation of used PAC from the sedimentation basin back in to the contact basin promotes biological processes (Zietzschmann et al., 2019), formation of CYA from such precursors may occur in this step.

Almost 2/3 of detected PM-substances were not well removed from the secondary effluent by PAC. Many factors affect the sorption behavior of chemicals, among others their charge state, molecular structure and size, and pKa. The most commonly used proxy is the octanol-water coefficient logD. Kovalova et al. (Kovalova et al., 2013) concluded that sorption of compounds with a logD > 2 is much more likely than for compounds with a logD < 2. The scatterplot of logD calculated for pH 7.5 of all detected PM-substances in WWTP 1 against their removal (Figure S 5) shows that this set of analytes investigated herein follows the trend proposed in the literature.

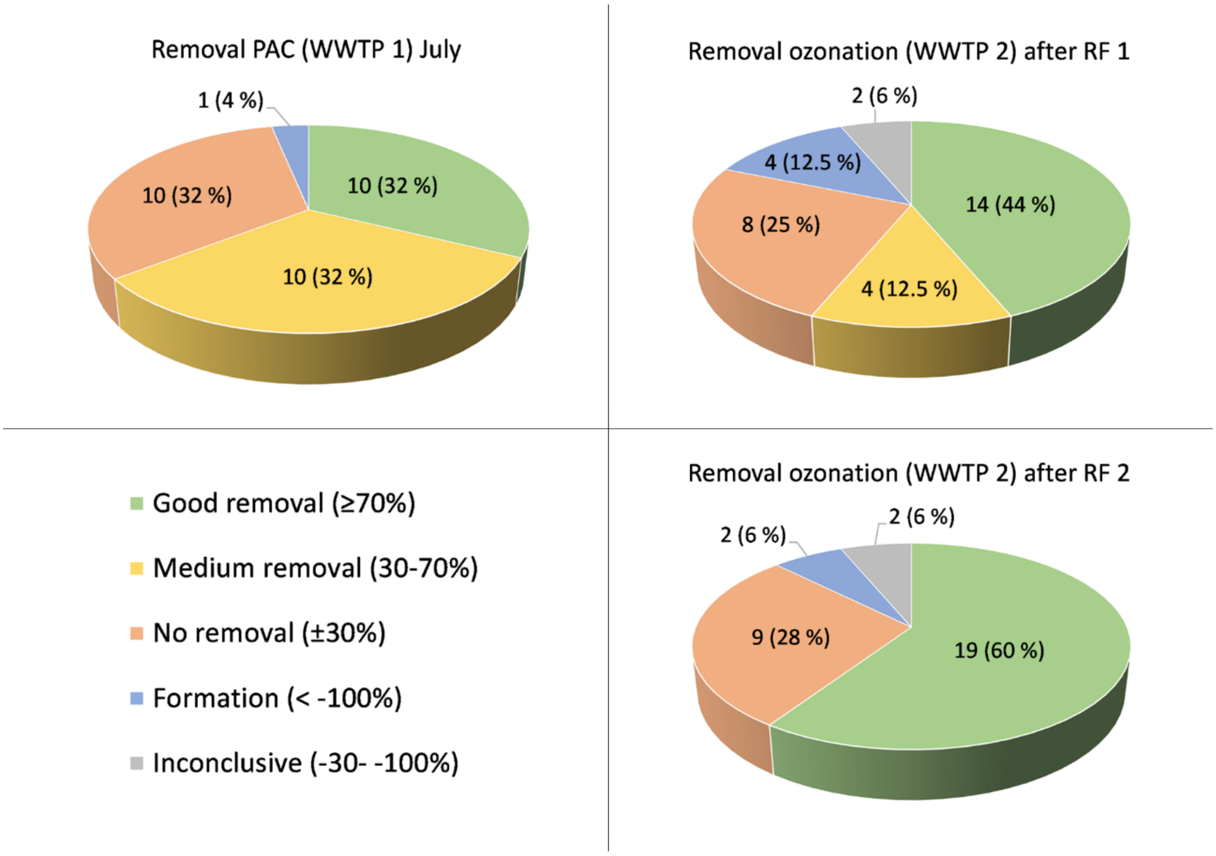


Figure 1: Pie chart of removal efficacies of the detected PM-substances > 0.1 µg/L for PAC samples of WWTP 1 in July (n=7 samples for PAC influent and effluent) and ozonation samples of WWTP 2 after RF 1 (sand/anthracite rapid filter; upper chart) and RF 2 (additional GAC filtration; lower chart) (n=4 for ozonation influent, effluent and RF 1 and 2) merged for both sampling campaigns.

Ozonation and sand/anthracite filtration (WWTP 2)

In the effluent of WWTP 2 (RF 1), 61 of the 111 PM-substances were detected. As far as these chemicals have been studied before, their removal in both sampling campaigns agreed to literature (Table S 12). Thus, the results of both sampling campaigns were combined. For the 32 PM-substances with concentrations above 0.1 µg/L, the median removal was 57 %. The total concentration of all detected PM-substances was reduced from 40 to 19 µg/L. 14 substances were assigned a good removal, four medium removal and twelve no removal or formation. A recent study determined similar magnitudes of concentration reduction during ozonation for potentially persistent and mobile substances using nontarget screening (Gollong et al., 2022).

Electron-rich functional groups exhibit a high affinity to ozone are C=C double bonds, such are dissociated phenols, anilins, thiophenols, deprotonated thiols and tertiary amines. Of the 14 PM-substances with good removal in ozonation at WWTP 2, twelve contain at least one such moiety, while all of the PM-substances with no distinct removal did either not contain a functional group that is prone to ozonation or whose functional groups are in close proximity to electron-withdrawing groups, with one exception (GUA). Thus, removal efficacies for PM-substances by ozonation generally followed the observed trends from literature (von Sonntag et al., 2012, Kovalova et al., 2013).

Comparison of removal efficacies for PM-chemicals with pharmaceuticals and personal care products

The main driver for the implementation of advanced treatment at municipal WWTPs was to increase the removal of PCPs and pharmaceuticals. Therefore, Figure 2 presents a comparison of literature data on removal of PM-substances (n = 72) versus PCPs and pharmaceuticals (n = 94) within the AC and ozonation step (Hollender et al., 2009, Kovalova et al., 2013, Margot et al., 2013, Ruhl et al., 2014, Pang et al., 2020). As PCPs and pharmaceuticals may also be PM, nine substances were present in both datasets. Nervertheless, the data shows that their average removal for AC was about twice as high as found for PM-substances in this study. The median logD at pH 7.4 of the PM-substances tested herein is -0.58 while the median logD of the PCPs and pharmaceuticals from literature is 0.38, making adsorption to AC of the latter groups more likely. For ozonation, removal is not dependent on hydrophilicity but on the presence of electron-rich structural moieties. This might be the reason why the difference in removal by ozone is less pronounced for pharmaceuticals and PCPs from literature and PM-substances in this study. However, the conclusions of PM-substances likely being less readily removed compared to PCPs and pharmaceuticals should be taken with caution, since literature data for PCPs and pharmaceuticals and the obtained monitoring data may only be partially comparable.

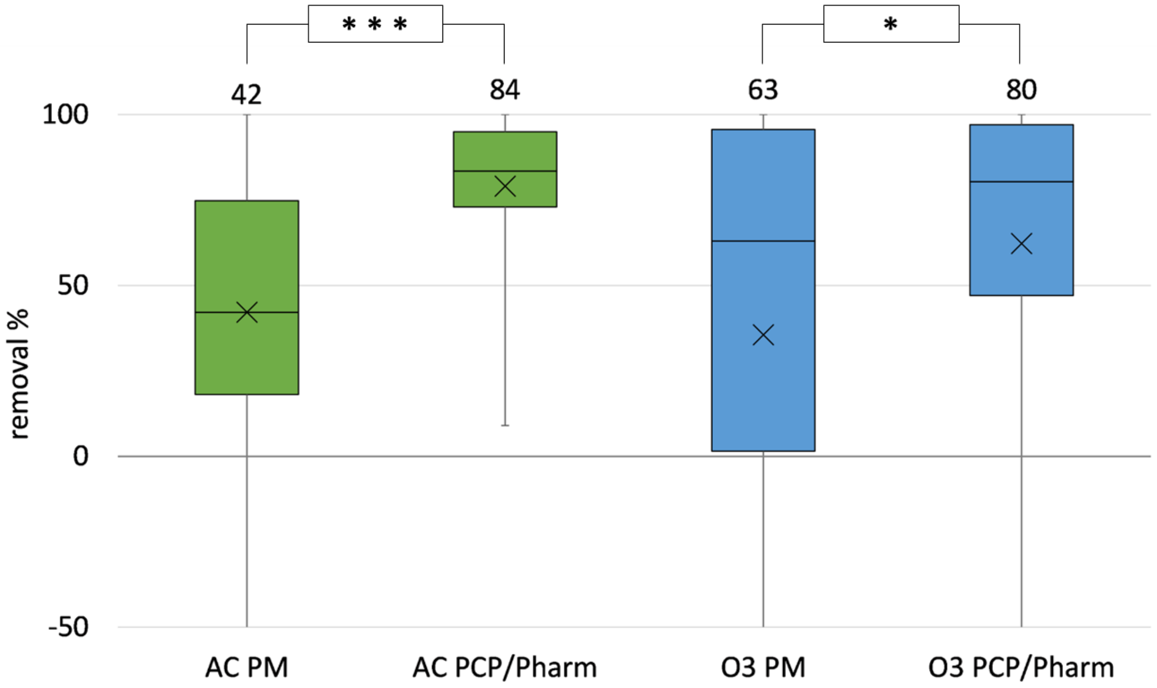


*Figure 2: Comparison of removal efficacies for PM-substances from this study (n=72) and personal care products (PCPs) and pharmaceuticals from literature (n=94) after the activated carbon or ozonation step in each WWTP. The box describes the 25-75 % interquartile range, whiskers mark minimum and maximum removal, mean is indicated by 'x', and the median by a line. ***: p-value of T-test < 0.005, *: p-value of T-test < 0.05.*

Comparison of PAC and Ozonation followed by rapid filtration

Since adsorption onto AC and ozonation are only partially effective against PM-substances it is interesting to assess their level of complementarity and whether a combination of both treatment techniques may result in a significant additional reduction of the PM-burden in treated municipal wastewater. Figure 3 presents a scatterplot of removal efficacies for 40 PM-substances detected in both WWTPs. About two thirds of the PM-substances (65 %) can be well removed by at least one of the two investigated treatment methods. Only five of the PM-substances that were present in both WWTPs were not removed by either of the two advanced treatment methods, two of them exceeding median concentrations of 1 µg/L.

Interestingly, 13 of the 17 PM-substances that are well removed by PAC also showed good removal by ozonation and subsequent filtration. Twelve of these compounds were already removed to a large extent by ozonation itself, while the remaining PM-substance was removed by the subsequent filtration stage in WWTP 2. Vice versa, only 13 of the 23 PM-substances well-removed by ozonation were also well removed during PAC. This is further evidence that the application of ozonation in advanced wastewater treatment may remove PM-substances more effectively than adsorption onto AC. On the other hand, the drawback of ozonation is the inherent formation of transformation products (TPs). Since the polarity of chemicals commonly increases upon transformation the formation of TPs that are PM may play a significant, yet not thoroughly investigated role during wastewater treatment with ozone (Hübner et al., 2015, Seiwert et al., 2021). A recent study in an advanced treatment pilot plant found that 1/3 of TPs formed during ozonation were not removed by subsequent filtration through sand/anthracite and GAC (Gollong et al., 2022), further highlighting the potential for the formation of highly polar TPs. While, neither the number of WWTPs nor the number of samples of this study is large enough for generalized conclusions and differences in the wastewater matrix of both WWTPs may complicate comparisons the data is consistent and in agreement with expectations: AC as an at least partially polarity driven process seems less effective in the removal of PM-substances than ozonation.

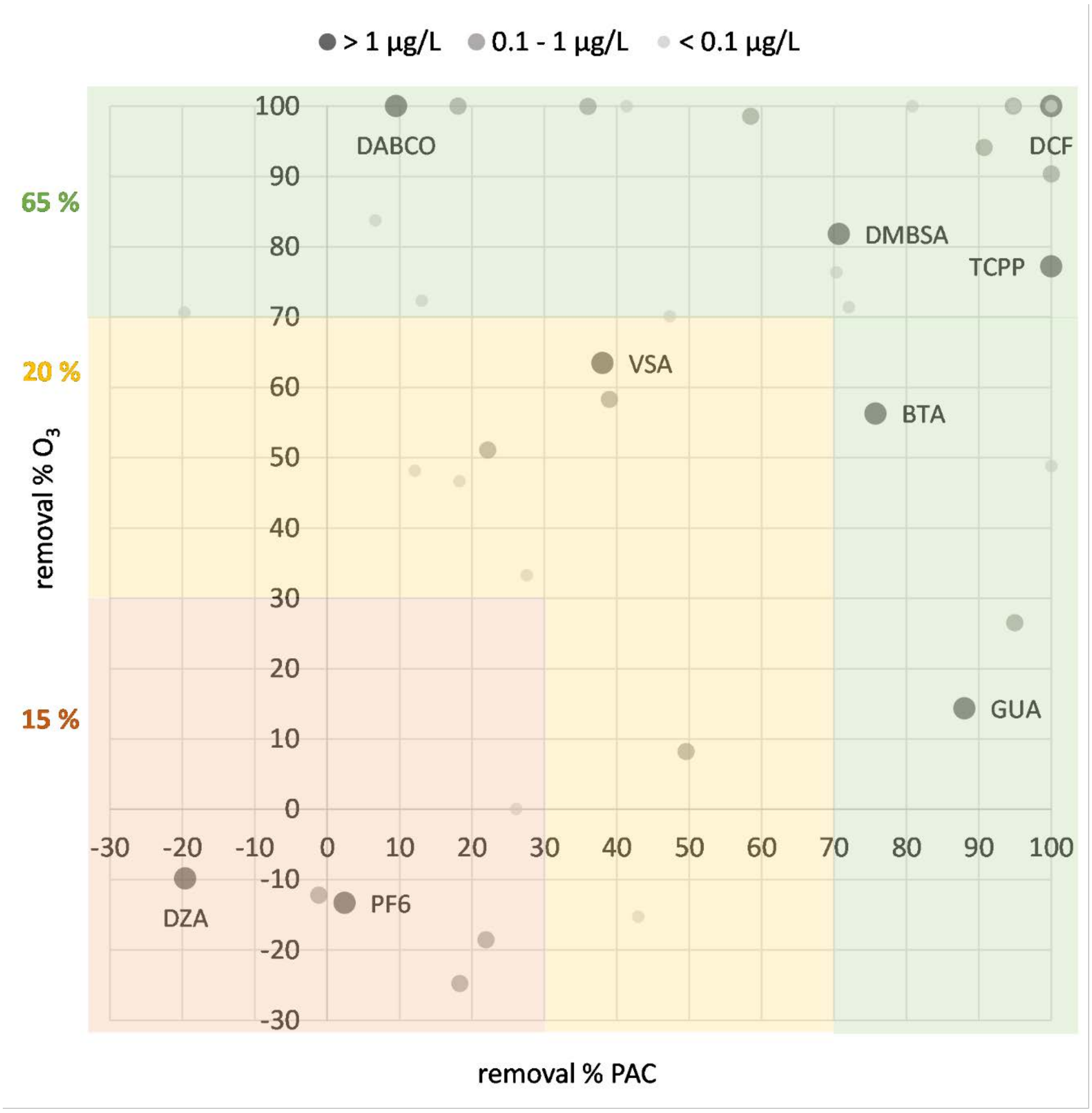


Figure 3: Scatterplot of removals during PAC treatment (WWTP 1) and ozonation and sand/anthracite filtration (WWTP 2, RF 1) for PM-substances detected in both WWTPs. Green area marks good removal (> 70 %), yellow area marks medium removal (30-70 %) and red area marks substances with no distinct removal (± 30 %). The colored numbers show the percentages of substances in the green, yellow and red area. BTA: Benzotriazole, DABCO: 1,4-Diazabicyclo[2.2.2]octane, DCF: Diclofenac, DMBSA: Dimethylbenzenesulfonic acid, DZA: Diatrizoic acid, GUA: Guanlyurea, PF6: Hexafluorophosphate, TCPP: Tri-(2-chloroisopropyl)phosphate, VSA:Valsartan acid.

Ozonation and rapid filtration followed by GAC filtration for PM-removal

AC filtration and ozonation followed by rapid filtration (RF 1) are the two commonly used advanced treatment options for wastewater. Despite the above-discussed benefits of linking ozone and AC treatment, a combination of both processes is typically not considered for full-scale plants due to economic reasons. In the pilot plant setup of WWTP 2 the combination of ozonation, rapid filtration through sand/anthracite and subsequent GAC filtration (RF 2) was explored as the most sophisticated option. Implementation of the additional GAC step led to good removal of 19 PM-substances instead of 14 (Figure 1), further reducing the total effluent concentration of PM-substances from 19 µg/L (RF 1) to 13 µg/L (RF 2, 40 µg/L in secondary effluent). The main driver of this improved performance is the enhanced removal of some high concentration substances like BTA (from 56% after RF 1 to 86% removal after RF 2) and DTBSA (formed during ozonation and 49% removal after RF 2, Figure S 6). Consequently, it was shown that at least in this pilot plant the combination of ozonation, rapid filtration (RF 1) and GAC filtration (RF 2) can further reduce the PM concentration in WWTP effluent. However, even the combination of both methods is only partially effective and full-scale applications would result in an increased effort.

The PM-burden in the effluent of advanced treatment

With neither treatment technology nor the combination of both enabling a complete removal of the high concentration PM-substances present in the secondary effluent, chemicals with high concentrations in the effluent of advanced treatment need to be prioritized for a more detailed investigation. Figure 4 presents the removal for PM-substances with concentrations > 0.1 µg/L during advanced treatment in WWTP 1 and WWTP 2, including their effluent concentrations in secondary and advanced effluent. Removal efficacies for all detected PM-substances and sampling campaigns are shown in Figure S 3 and S 4 and Table S 13.

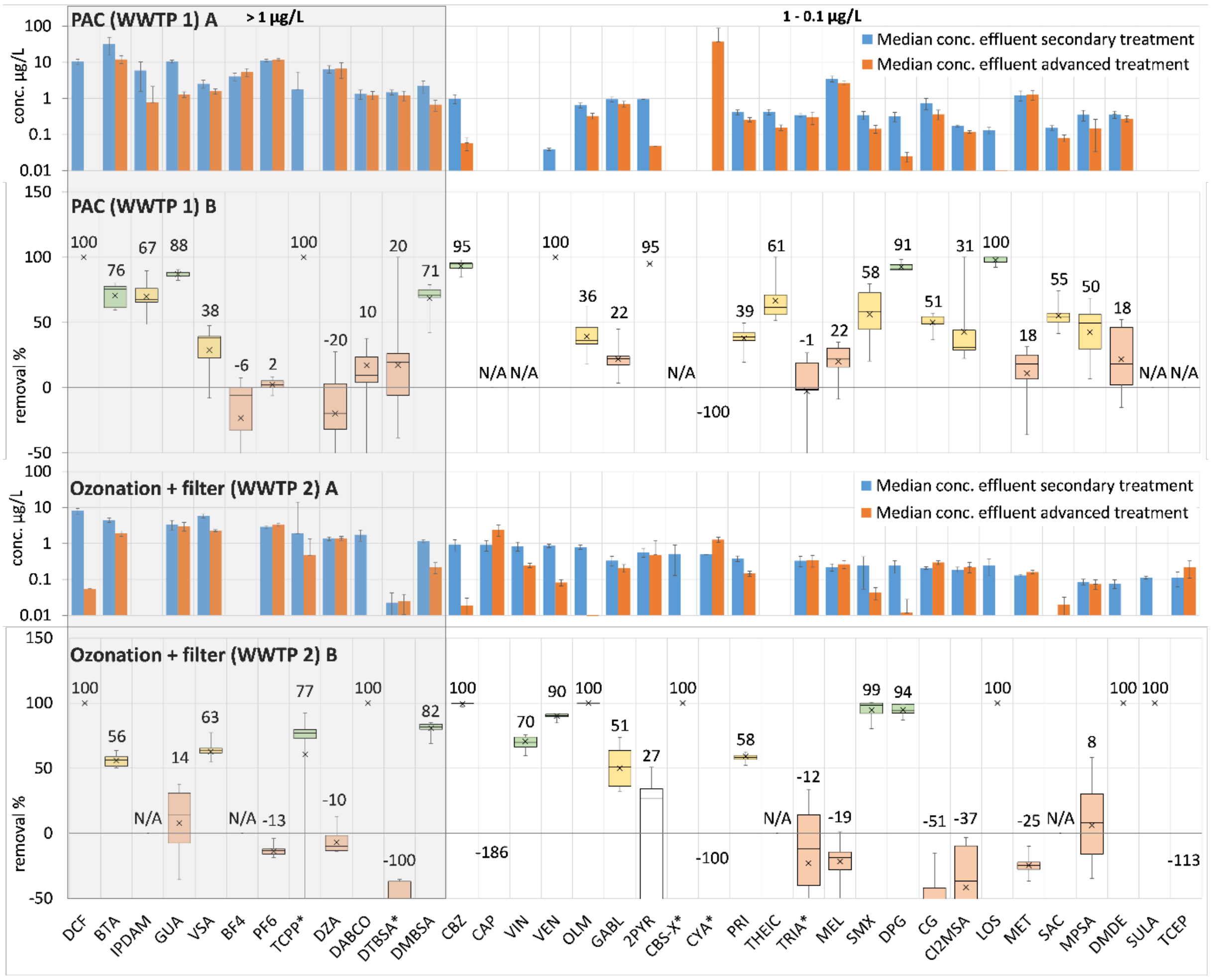


Figure 4: (A) Median concentrations in the effluent of secondary and advanced treatment of WWTP 1 and 2 and (B) boxplot of removal efficacy of the detected PM-substances in WWTP 1 and 2 samples (B, July only for WWTP 1) with cutoff at - 50 %. The box describes the 25-75 % interquartile range, whiskers mark minimum and maximum removal, mean is indicated by 'x', and the median by a line. Substances with N/A were not detected in the effluent of secondary treatment. PM-substances without a color are not assigned a removal to due to their strong variation between positive and negative removal. PM-substances marked with a star indicate a mean concentration below LOQ. Figure S 3 and S 4 show the complete y-axis range and all detected PM-substances over all four sampling campaigns.

Of the 12 PM-substances detected with concentrations > 1µg/L DCF, BTA, GUA, TCPP, DABCO, and DBMSA were well removed with at least one of the two investigated treatments. For DCF, BTA, GUA and VSA, removal by AC and ozonation was already shown elsewhere (Table S 11 and S 12). To the best of our knowledge, literature data on removal of DABCO and DMBSA in advanced treatment of full-scale WWTPs is not available. For TCPP, there are indications that removal by AC and ozonation is possible in principle (Sun et al., 2018, Wang et al., 2018). However, even for well-removed PM-substances, incomplete removal may result in discharge into the aquatic environment if initial concentrations are sufficiently high. This is evident for BTA and GUA for which effluent concentrations are still in the 1 µg/L range even though they are removed by more than 70 %. BF4, PF6, DZA and DTBSA did not show any significant removal with either treatment option. DZA is already known for its poor removal during ozonation and AC filtration (Margot et al., 2013), while literature data on removal is not available for BF4, PF6 and DTBSA. All three chemicals are anions which often results in a reduced sorption tendency to activated carbon. DTBSA has an aromatic ring, which may imply reactivity with ozone, however, the electron-density of the aromatic ring is reduced by the presence of a sulfonate group and the bulky tertiary butyl groups may act as a stearic hinderance against an attack of ozone.

Of the 24 PM-substances that were detected in the effluent of the WWTP with a concentration range of 0.1 - 1 µg/L, 11 were well removed with at least one of the two advanced treatments, among them scarcely investigated compounds, such as the industrial chemicals 2,2'-([1,1'-biphenyl]-4,4'-diylbis(ethene-2,1-diyl))dibenzenesulfonate (CBS-X), 2,2-dimorpholinyldiethylether (DMDE) and the tire leachable 1,3-diphenylguanidine (DPG). Seven PM-substances showed medium removal, 1,2,4-triazole (TRIA), melamine (MEL), metformin (MET) were not removed and CYA showed formation with both treatment options. Recently identified environmental contaminants, such as trifluoromethanesulfonic acid (TFMSA), bromochloromethanesulfonic acid (BrClMSA), tris(pentafluoroethyl)trifluorophosphate (FAP) and bis(trifluoromethanesulfonyl)imide (NTF2) were also not removed in this study (Figure S 3 and S 4). Consequently, either because of their high concentrations and incomplete removal or their ability to pass advanced treatment almost unimpaired, these PM-substances may be considered for future monitoring activities.

Two of the high concentration PM-substances not removed during advanced wastewater treatment in this study, namely BF4 and PF6, are inorganic anions used in ILs. An- and cations of ILs were recently identified as novel class of environmental contaminants (Neuwald et al., 2021, Maculewicz et al., 2022). Since their annual growth rate for patent applications is estimated at 10% with increasing tendency (Shiflett, 2020), it seems likely that IL emissions will grow in coming years. Besides these two high concentration IL constituents other IL anions and cations, such as tetramethylammonium (TMAM), tetrabutylammonium (TBAM), hexadecyltrimethylammonium (HTMAM), 1-ethyl-4-methylpyridinium (EMP), 1-butylpyrdinium (BP), benzyltrimethylammonium (BETMAC), 1-allyl-2-aminopyridinium (AAP), tributylmethylphosphonium (TBMP), tributylmethylammonium (TBMAM), tetraphenylborate (TPB), 1-butyl-4-methylpyridinium (BMP), NTF2, 1-methyl-3-octylimidazolium (MOIM) and FAP were detected even after advanced wastewater treatment with effluent concentrations between 12 µg/L and 0.1 ng/L. Many investigations regarding removability of IL components are limited to laboratory experiments and are not verified in full scale processes (Mrozik et al., 2012, Mena et al., 2022) or focused on single substance classes (Pati et al., 2020). In general, the removal of IL cations ranged from complete removal to medium removal by either PAC or ozonation and filtration. In contrast, the detected IL anions, which were all fluorinated, did not show any significant removal with either advanced treatment method.

The total molar concentrations of the IL anions determined in this study (54.5 nmol/L) exceeded the total molar concentration of the detected cations (1.0 nmol/L) more than 50-fold. This observation may have four causes: (1) IL cations might be more prone to sorption to sludge (Amde et al., 2015) or biological transformation than anions and thus already removed in preceding treatment steps. This, however, may be accompanied by the release of yet unknown IL TPs. (2) There are much more IL cations on the market than anions, increasing the chance of omission during analyte selection. (3) In the applications most strongly contributing to these findings anions may be paired with inorganic cations like Li^+ rather than with organic cations. (4) BF4 and PF6, the two most prominent IL anions in this study, may have other yet unknown sources that contribute to their occurrence in municipal wastewater.

For many of the PM-substances occurring at high concentration (> 0.1 µg/L) that are not completely removed (e.g. BF4, PF6, DZA, MEL, IPDAM, BTA, CYA) environmental or human health effects are only partially known. MEL has been proven to be toxic to kidneys in humans and animals (Brown et al., 2007, Chen, 2009) and may be toxic to reproduction (Huang et al., 2018). In combination with CYA, nephrotoxic effects are increased (Brown et al., 2007). First studies have shown that DZA may induce cytotoxicity (Ward, 2019). However, toxic effects have been determined at concentrations at two or more orders of magnitude higher than the concentrations detected within this study. For ILs, several laboratory experiments have shown that anions, among others BF4 and PF6, play a minor role regarding toxicity compared to their respective cations (Goncalves et al., 2021). Contrarily, for BTA, genetic alterations have been observed in invertebrates, even at the concentrations detected in this study (double-digit µg/L range), and indications for endocrine disruption have been determined in vertebrates (Shi et al., 2019). However, even when laboratory experiments are available, systemic effects, mixture toxicity, and the consequences of long-term exposure are difficult to assess and often elude standard toxicity testing.

Conclusion

- Advanced treatment with either PAC or ozonation appears to be an additional, yet only partially effective barrier against PM-substances to reduce their discharge by treated municipal wastewater. PAC treatment and ozonation with sand/anthracite filtration of WWTP effluent reduced the total PM load from 103 to 87 µg/L and from 40 to 19 µg/L, respectively. The combination of ozonation, sand/filtration and subsequent GAC filtration in a pilot-scale application further reduced the total PM concentration from 40 to 13 µg/L. While ozonation was more effective in this study, it also brings the risk of an increased formation of mobile transformation products.
- The only partial efficacy of established advanced wastewater treatment methods for the removal of PM-substances shows that there is a need for alternative treatment technologies for high priority PM-chemicals. Even if such more specialized methods are not widely applicable applications at known point sources (e.g. industrial WWTPs) may reduce the PM burden in receiving waters.

- The ionic liquid anions BF4 and PF6 were among the highest concentrations (>1 µg/L) in the effluent of advanced treatment. Other fluorinated anions, such as NTF2 and FAP which fall under the OECD definition of per- and polyfluorinated alkyl substances were not removed by advanced treatment as well. Combined with the rapid growth of the ILs market, fluorinated IL anions may represent a relevant novel class of contaminants that potentially accumulate in the aquatic environment. Additionally, the large discrepancy between IL anions and cations (anions showed a 50-fold higher molar concentration) hints at severe knowledge gaps in the occurrence and fate of IL cations in wastewater treatment.
- For high-concentration PM-substances, particularly without effective removal options, prevention might be required. The foreseen implementation of mobility criteria within REACH is a first step in this direction.

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