



Semi-crystalline microplastics in wastewater plant effluents and removal efficiencies of post-treatment filtration systems

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ABSTRACT

Microplastics (MPs) are ubiquitous in the environment and have been found in every environmental compartment. Wastewater and wastewater treatment plants (WWTPs) have been identified as possible point sources contributing to the emission of microplastic particles (MPP) into the aquatic environment. So far, MPP in wastewater effluents have mainly been analyzed by spectroscopic methods resulting in concentrations as number per volume. In this study, we present mass concentrations in the secondary effluents of four German municipal WWTPs, removal efficiencies of seven post-treatment systems and the resulting load emissions. Differential Scanning Calorimetry (DSC) was used for the analysis of semi-crystalline MPs. The concentrations of secondary effluents ranged from 0.1 to 19.6 $\mu\text{g L}^{-1}$. Removal efficiencies > 94% were found for a microfiltration membrane (MF), two cloth types of a pile cloth media filter (PCMF), a micro strainer, a discontinuous downflow granulated activated carbon filter (GAC) and a powdered activated carbon (PAC) stage with clarifier and rapid sand filtration. A rapid sand filter (RSF) at WWTP B showed a removal efficiency of 82.38%. Only a continuous upflow GAC filter at WWTP C proved to be unsuitable for MP removal with an average removal efficiency of 1.9%.

Introduction

Since the invention of plastics and their mass production in the 1950s, the worldwide production has risen exponentially to 368 MT in 2019 (PlasticsEurope, 2020). Today plastics occupy almost every aspect of our day-to-day lives (Hale et al., 2020). Consequently, reports of plastic emissions go back to the early 1970s and have risen significantly in the past 15 years (Carpenter et al., 1972; Zhang et al., 2020). Today plastic particles < 5 mm, commonly referred to as microplastics (MPs), are found in every environmental compartment from the deep sea (Van Cauwenberghe et al., 2013) to surface waters (Kernchen et al., 2022; Mani et al., 2019), soils (Piehl et al., 2018; Zhou et al., 2020) and the atmosphere (González-Pleiter et al., 2021). The ubiquity of MPs in a variety of sizes, shapes and colours coincide with reports of a corresponding ecotoxicity. Adverse effects are greatest when MPs are mistaken for food and ingested by fauna (Duncan et al., 2019; Wright et al., 2013), but also include possible transport or leaching of persistent organic micropollutants (Koelmans et al., 2014; Schrank et al., 2019) and internalization into cells (Ramsperger et al., 2022). Recently, plastic

particles > 700 nm have also been detected in samples of human blood (Leslie et al., 2022).

In an effort to pinpoint possible sources of and pathways for MPs into the environment, wastewater treatment plants (WWTPs) have come into focus (Sun et al., 2019). A few studies have reported elevated numbers of MPs in the vicinity of WWTPs (Klein et al., 2015; Mora-Teddy and Matthaei, 2020) which highlights the need to investigate current treatment technologies with the respective effluent qualities including further treatment possibilities. Plants with primary, conventional aerobic sludge and secondary treatment have already been reported to reduce the number of MPs by up to 99% (Carr et al., 2016; Yuan et al., 2021; Ziajahromi et al., 2021). However, even with low effluent concentrations, WWTPs can release significant numbers of microplastic particles (MPP) into the environment because of high volumetric flows, especially in urban areas (Leslie et al., 2017; Murphy et al., 2016).

In the last 20 years tertiary treatment systems have come into focus to tackle increasing problems of phosphorous concentrations (Fundneider et al., 2020), micropollutants (Fundneider et al., 2021) and antibiotic resistant bacteria (Alexander et al., 2016; Fundneider et al.,

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2019). Depending on specific treatment needs, process alternatives include precipitation/flocculation, adsorption or oxidation and disinfection, but rely largely on surface or depth filtration (Metcalf et al., 1991). These processes were originally designed for other purposes than MP removal. Still, various studies have shown that post-treatment processes also reduce the numbers of MPP, albeit with different sampling and analysis methods resulting in varying rates: A dissolved air flotation and an oxidation ditch were found to remove 95% (Talvitie et al., 2017) and 53.6% of MPP (Lv et al., 2019), respectively. Micro strainers were found to remove 89.7% (Simon et al., 2019) and 40 - 98.5% (Talvitie et al., 2017). Rapid sand filters showed removal efficiencies of 75.49% (Bayo et al., 2020), 97% (Talvitie et al., 2017) and 99.2% - 99.9% (Wolff et al., 2021). A pile cloth media filter (PCMF) was found to remove 97% (Mintinig et al., 2017) and membrane bioreactors (MBR) removed MPP by 79.01% (Bayo et al., 2020), 82.1% (Lv et al., 2019), 99.4% (Lares et al., 2018) and 99.9% (Talvitie et al., 2017).

On the one hand, MP removal rates based on the numbers and concentrations of particles measured by spectroscopic methods in effluents are necessary to evaluate possible ecotoxicological effects. On the other hand, it has been pointed out that mass concentrations are vital to estimate correct loads, to pinpoint significant sources (Norwegian Environment Agency Miljødirektoret, 2014) or for monitoring and regulatory purposes (Braun et al., 2020). Several thermoanalytical tools are available and have been used for MP measurements in environmental samples (Dierkes et al., 2019; Eisentraut et al., 2018; Nuelle et al., 2014; Okoffo et al., 2020). In wastewater samples, mass concentrations have been extrapolated from imaging data (Olesen et al., 2019; Simon et al., 2018) or parts of the studied particles ($> 500 \mu\text{m}$) have been weighed (Rasmussen et al., 2021). Recently, Roscher et al. (2022) reported the quantification of the sample fraction $< 500 \mu\text{m}$ in the effluent of a WWTP.

Differential Scanning Calorimetry (DSC) is an analytical tool to examine phase transitions in polymers and is widely applied in material sciences. The method has been adapted to environmental samples such as wastewater (Bitter and Lackner, 2021) by measuring the heat flux occurring in the melting process of semi-crystalline polymers. Although amorphous polymers cannot be detected, the mass of thermoplastic particles can be quantified directly (Majewsky et al., 2016) without the need for estimation from two-dimensional data on particle shape and equivalent diameter. The method is comparatively easy and has been successfully used to identify and quantify reference materials (Becker et al., 2020; Rodríguez Chialanza et al., 2018) and for the quantification of semi-crystalline MPs in industrial wastewaters (Bitter and Lackner, 2020).

In this study, we examined mass concentrations of semi-crystalline MPs measured via DSC in secondary effluents of four German wastewater treatment plants. In addition, seven post-treatment processes for phosphorous or micropollutant removal were analyzed. The investigation focused on the suitability of these systems to also remove MPP without any adaptation of the operation or design. Their efficiencies for MPP removal were also evaluated.

Materials and methods

Sampled sites

From April 2017 until December 2020, four German municipal WWTPs were sampled. At each site the secondary effluent and different post-treatment filtration systems were analyzed.

WWTP A is built for a population equivalent (PE) of 70,000 people with an average dry weather flow of $10,300 \text{ m}^3 \text{ d}^{-1}$. It is equipped with primary, biological and secondary treatment as well as phosphorous removal by iron chloride coagulation. Submerged drain pipes in the secondary clarifiers facilitate the discharge of the final effluent. Two pilot plants for further phosphorous and micropollutant removal were examined:

- (i) A pile cloth media filter (PCMF) with a PES-14 and a UFH-12 pile cloth media, successively. The fabric is woven with a multi-dimensional structure, consisting of a filter-active pile fiber layer and a non-filter-active backing fabric. The pile fibers layer is made of polyethylene terephthalate (PET) for PES-14 and PET and polyamide 6 (PA6) for UFH-12. The backing of both pile cloths was woven from PET and polypropylene (PP).
- (ii) A membrane filter (MF) with a $0.1 \mu\text{m}$ pore size was operated parallel to the PCMF. Details on the pilot plants and their operation are readily available in Fundneider et al. (2020).

WWTP B has a size of 45,000 PE and an average volumetric flow of $4200 \text{ m}^3 \text{ d}^{-1}$. The plant includes primary, biological, secondary and tertiary treatment with chemical coagulation. The effluent of the secondary clarifiers flows over toothed weirs and on to a multi-layer rapid sand filter (RSF). The filter was built in 1995 in an effort to reduce concentrations of the total suspended solids (TSS) and phosphorous in the effluent. It consists of six chambers, each with a filter area of 9.45 m^2 and three layers. Theoretically, the top layer is 80 mm high and has a grain size of 4.5 - 8 mm. The second layer consists of sand with a grain size diameter of 0.7 - 1.3 mm and is 620 mm high. The bottom layer consists of expanded slate with a grain size of 1.4 - 2.5 mm.

WWTP C has a size of 32,000 PE, an average volumetric flow of $4900 \text{ m}^3 \text{ d}^{-1}$. The plant includes primary, biological and secondary treatment with toothed weirs for the effluent overflow as well as chemical coagulation. Here, a micro strainer and a continuous upstream granulated active carbon filter (cont. GAC \uparrow), both pilot-scale, were examined. The fabric of the micro strainer was made of PET and had a pore size of $10 \mu\text{m}$.

WWTP D handles wastewater of 725,000 PE with primary, biological, secondary and tertiary treatment and has an average volumetric flow of $87,000 \text{ m}^3 \text{ d}^{-1}$. The secondary effluent flows over toothed weirs onto iron chloride coagulation for phosphorous removal and a full scale powdered activated carbon (PAC) stage with a clarifier (CF) and a dual-layer RSF. The top layer of the latter is 400 mm high and consists of anthracite with a grain size 1.4 - 2.5 mm, the bottom layer is 600 mm high and contains sand with a grain size of 0.7 - 1.3 mm. At the time of sampling, one of the RSF columns was used as a GAC pilot plant for the comparison of micropollutant removal.

All post-treatment systems examined in this study, except the sand filter at WWTP B, were built to reduce the concentration of micropollutants in the wastewater effluent or as a part of such a process. No specific MPP removal had been considered in the planning or design of the systems.

Sampling method

At each site, samples were taken from shafts, valves or tanks depending on the accessibility and ensuring representability. At plant A, the PCMF was operated parallel to the MF. Effluent of both plants flowed into open plastic storage tanks within a tent. The effluent of the membrane filter was used as blank value and the mean concentration subtracted from the mean concentration of the PCMF.

Every sample was taken continuously over two hours using centrifugal pumps with a stainless steel impeller (GPN 1500, Nowax S.r.l., Italy) and stainless steel cartridge filters with $1000 \mu\text{m}$, $100 \mu\text{m}$ and $10 \mu\text{m}$ mesh sizes (Fuhr GmbH, Klein-Winternheim, Germany and Wolftechnik Filtersysteme GmbH & Co. KG, Weil der Stadt, Germany). Combined with a steel screen in front the pump, the particulate matter of each sample was separated into the size fractions $1000 - 5000 \mu\text{m}$, $100 - 1000 \mu\text{m}$ and $10 - 100 \mu\text{m}$. Filters from Fuhr GmbH were installed into stainless steel casings while filters from Wolftechnik Filtersysteme GmbH & Co. KG had casings made of PP and styrene-acrylonitrile resin (SAN). For the latter, blank values were measured to rule out possible sample contamination.

The sampled volumes were measured using a water meter (Hermann

Pipersberg jr. GmbH, Remscheid, Germany) or a magnetic inductive flowmeter (Siemens AG, Munich, Germany) and ranged from 2.04 to 8.74 m³ (see Table S1). Connecting pipes were made of polyvinyl chloride (PVC) or silicone and gaskets were made of polytetrafluoroethylene (PTFE) or rubber to prevent contamination with relevant semi-crystalline polymers.

Sample processing and analysis

For every sample fraction, the cartridge filter was rinsed thoroughly to remove the particulate matter. A 100 µm metal sieve (Retsch GmbH, Haan, Germany) was used to filter the size fraction 1000 – 5000 µm, the other two were poured into glass bottles. Polycarbonate membrane filters (5 µm pore size, $\phi = 47$ mm, Nuclepore™, Track-etched, Whatman™, GE Healthcare UK Limited, England) were used for subsequent volume reduction.

To reduce the amount of particulate matter, the following steps were applied as needed:

- Wet oxidation with hydrogen peroxide solution (50%, VWR International GmbH, Darmstadt, Germany) at 50 °C over 24 h
- Wet oxidation with sodium hypochlorite solution (6 – 14% Cl₂, VWR International GmbH, Darmstadt, Germany) at room temperature
- Density separation with zinc chloride solution ($\rho = 1.8$ g cm⁻³) and a Thermo Scientific™ X3 centrifuge (Fischer Scientific GmbH, Schwerte, Germany) operated at 660 G

This was followed by further filtration and rinsing. After drying and weighing the residual particles on 5 µm polycarbonate membrane filters, crucibles (Concavus® aluminum pan, 30/40 mL, $\phi = 5$ mm, NETZSCH-Gerätebau GmbH, Selb, Germany) were filled for polymer analysis. A recovery rate was determined for every person handling samples in the lab which was incorporated into the calculation of the resulting concentration values. An R 160 P precision scale (Sartorius AG, Göttingen, Germany) was used for weight measurements. For every sample fraction

a maximum of 10 crucibles were filled for measurement.

The quantification of polymers was carried out using Differential Scanning Calorimetry (DSC; Netzsch DSC 214 Polyma, Netzsch-Gerätebau GmbH, Selb, Germany). The analysis was based on measuring melting enthalpies and therefore only allowed the analysis of semi-crystalline thermoplastics. Each thermogram of extracted particles was searched for melting peaks. Any presenting melting peaks were analyzed for the peak melting temperature to identify a polymer. Afterwards, the integration of the peak area resulted in a polymer mass. The applied temperature program, and information on matrix effects and accuracy can be found in Bitter and Lackner (2021). In the present study, the five polymers low-density polyethylene (PE-LD), high-density polyethylene (PE-HD), PP, PA6 and PET were quantified in the different effluents. The analyzed concentrations of each polymer was added up to create an MP sum concentration of a sample.

Removal efficiencies of post-treatment systems were calculated by comparing effluent and influent concentrations. If the concentrations were below the limit of quantification (LOQ), the threshold value was used for the calculation of the removal. The LOQ in mg is readily available (see previous paragraph) and divided by sample volumes at specific samples dates to create an LOQ in µg L⁻¹ for every sample fraction. The MP load removal efficiencies were calculated with volumetric flow values of respective sampling days recorded by the WWTPs. MP load emissions into the aquatic environment were calculated for final effluents of systems in regular operation not including pilot plants.

Results

The measured MP concentrations at the four sampled WWTPs are shown in Fig. 1. Bars indicate mean concentrations of secondary effluent and whiskers the standard deviation. At WWTP A, an average concentration of 10.8 ± 7.2 µg L⁻¹ was measured in the secondary effluent, WWTP B showed a lower average concentration of 5.3 ± 1.2 µg L⁻¹. WWTP C displayed the lowest concentration of 0.7 ± 0.6 µg L⁻¹ and at WWTP D a concentration of 9.4 ± 4.1 µg L⁻¹ was measured. The highest

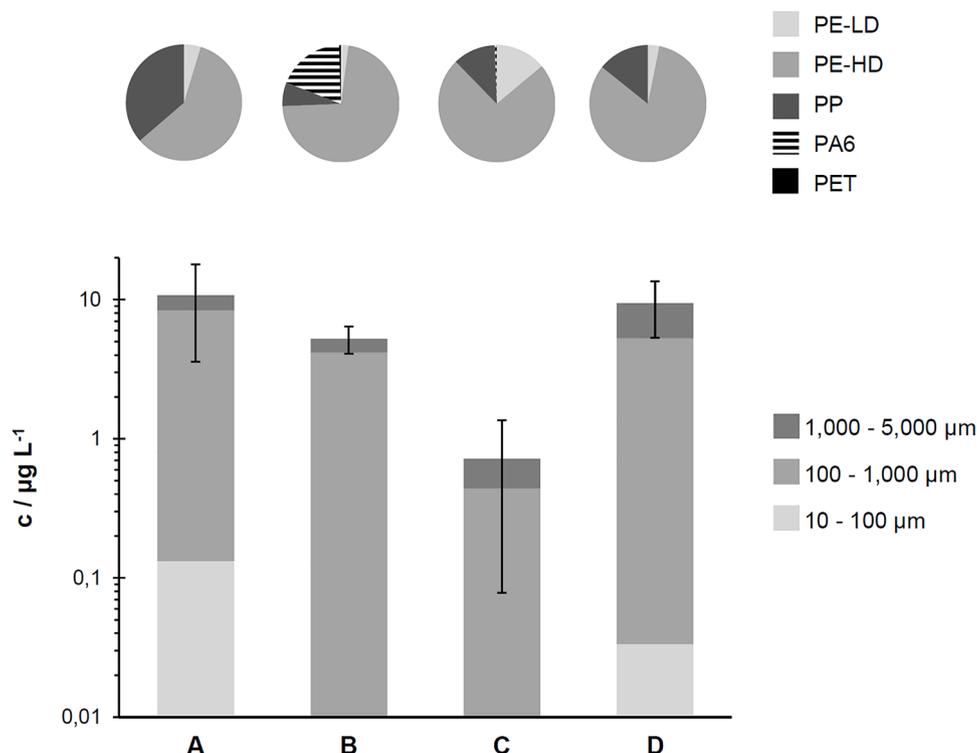


Fig. 1. Mean concentration of MPP in the secondary effluents of WWTPs A-D. Size fractions and polymer types are indicated by greyscales; whiskers indicate standard deviation of mean total value; pie charts indicate mean composition of the effluent.

single value of 19.6 $\mu\text{g L}^{-1}$ was measured at WWTP A, the lowest of 0.1 $\mu\text{g L}^{-1}$ at WWTP C. As shown by the greyscales, 99 to 100% of the measured mass of MPP are found in the size ranges > 100 μm . The size range 10 – 100 μm accounted for up to 1%, if measured at all.

The pie charts show the mean composition of the measured MPs. At WWTP A, 4.8% PE-LD, 58.9% PE-HD and 36.3% PP were found. Also at WWTP B, PE-HD accounted for the largest fraction with 72.2% with all other detectable polymers making up the rest, with 18.6% PA6, 6.5% PP and 0.5% PET. A similar fraction of PE-HD was detected at WWTP C with 73.8%, however, the further distribution of the polymer fractions showed a slightly different composition with 13.9% PE-LD, 11.8% PP, 0.5% PA6 and < 0.1% PET were found. The effluent of WWTP D had a similar composition as WWTP A with a different distribution between the polymers. This wastewater was dominated by PE-HD with 82.6% and also contained 3.1% PE-LD, and 14.3% PP. Overall, the effluent MP concentrations were all in the low $\mu\text{g L}^{-1}$ -range consisting of > 80% PE-LD, PE-HD and PP.

Figs. 2 and 3 compare the influent and effluent concentrations as well as the removal efficiencies in the seven post-treatment systems. At WWTP A, two different pile cloth media types of a PCMF were examined. PES-14 showed a removal efficiency of 98.87% with an average influent concentration of 9.9 $\mu\text{g L}^{-1}$. UFH-12 resulted in a 99.99% removal efficiency with an average influent concentration of 2.0 $\mu\text{g L}^{-1}$. The MF showed an average influent concentration of 12.2 $\mu\text{g L}^{-1}$. An average concentration of 0.67 $\mu\text{g L}^{-1}$ was still detectable in the effluent of the MF,

with MPP in the size ranges of 100 – 1000 μm and 1000 – 5000 μm . No MPP were found in the size range of 10 – 100 μm . Separate analyses, however, showed that the membrane and the set-up were fully functioning and intact (Fundneider et al., 2020). Therefore, the removal efficiency was set at 100% and the measured MP concentration was used as a blank for the PCMF. At WWTP B, the RSF showed a removal of 82.38% with an average influent concentration of 5.3 $\mu\text{g L}^{-1}$. The continuous upflow GAC filter at WWTP C was only able to remove 1.9% of the MPP with an average influent concentration of 0.5 $\mu\text{g L}^{-1}$. A micro strainer mounted on disk filters showed a removal efficiency of 94.63% with an average influent concentration of 1.0 $\mu\text{g L}^{-1}$. Two of the three effluent values were below the LOQ. At WWTP D, the discontinuous downflow GAC filter delivered a removal efficiency of 99.56% with an average influent concentration of 6.7 $\mu\text{g L}^{-1}$. Lastly, a full-scale PAC-system with clarifier and an RSF showed a removal of 97.15% with an average influent concentration of 9.4 $\mu\text{g L}^{-1}$.

Fig. 3 shows individual measurements as effluent over influent concentrations. Values are given in Table S1. The removal efficiency of the MF (100%) is not included due to the logarithmic scale. It shows the removal efficiencies on each sampling day and shows that all but one effluent concentrations were < 1 $\mu\text{g L}^{-1}$. It also shows the influent concentrations and highlights the low values for the micro strainer and the continuous upflow GAC filter at WWTP C.

The removal efficiencies of individual polymers are shown as a heat map in Fig. 4. Systems with a removal efficiency > 94% do not show

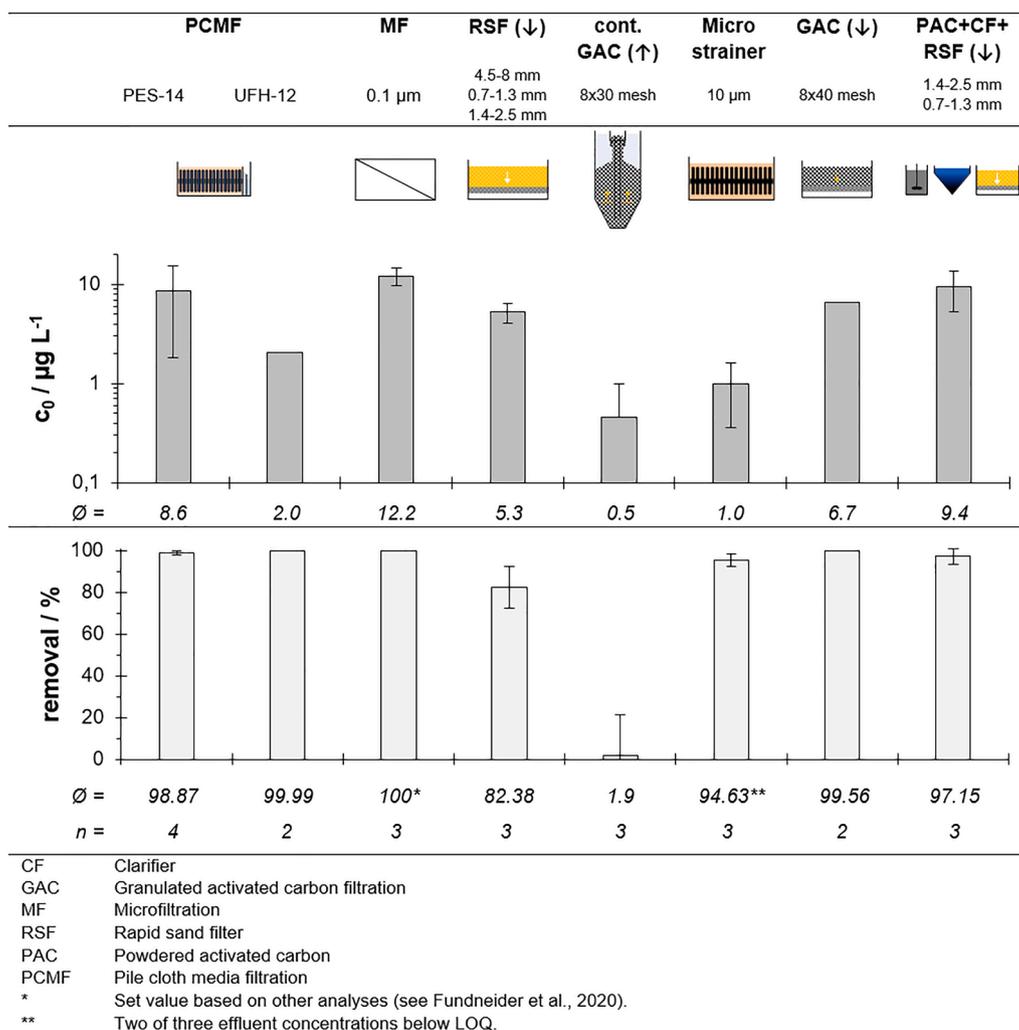


Fig. 2. Removal efficiencies of MPP by seven post-treatment systems with influent concentrations, mean values and number of samples. Whiskers indicate standard deviation.

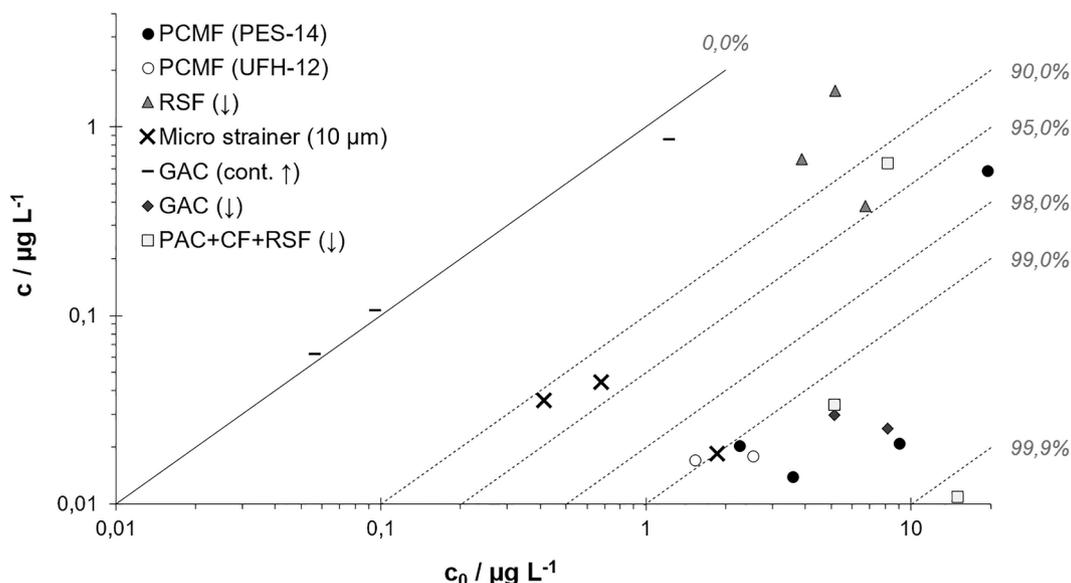


Fig. 3. Effluent over influent concentrations of individual sampling days from six post-treatment systems. Visualizations are given for 0, 90, 95, 98, 99 and 99.99% removal.

PCMF: pile cloth media filter, RSF: rapid sand filter, PAC: powdered activated carbon, CF: clarifier, GAC: granulated activated carbon. Membrane filter (MF: 0.1 µm) removal efficiency of 100% not shown due to logarithmic scale.

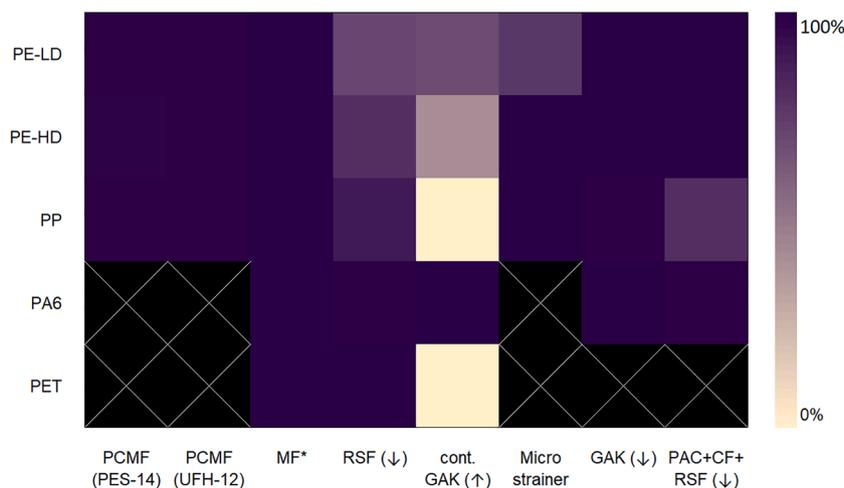


Fig. 4. Removal efficiencies of individual polymers by post-filtration systems. Crossed out field: Polymer was measured neither in the influent nor in the effluent. * Values for removal efficiency of MF based on separate analyses (see above).

clear trends of a dependency on the polymer types. The RSF removed PA6 and PET better than PE-LD, PE-HD and PP. The continuous upflow GAC filter did not remove PET and PP particles, showed a mid-range removal efficiency for PE-LD and PE-HD and a high removal efficiency for PA6. In addition, the polymer types used for the manufacturing of the pile layer (PET or PET/PA6) of the pile cloth media as well as the fabric of the micro strainer (PET) were not found in their effluents.

The average MP loads in the secondary effluent and the average removal of post-treatment systems are given in Table 1, as well as the load emissions into the environment. All post-treatment systems except the continuous upflow GAC filter removed significant MP loads. WWTP A and C showed an average load of 116.74 g d⁻¹ and 4.77 g d⁻¹ in the secondary effluent, respectively. WWTP B showed an average load of 4.49 g d⁻¹ in the effluent of the RSF. WWTP D showed an average load of 50.42 g d⁻¹ in the effluent of the PAC system. Population-related emissions of 0.10 mg PE⁻¹ d⁻¹, 0.15 mg PE⁻¹ d⁻¹ and 0.07 mg PE⁻¹ d⁻¹ are in the same range for WWTPs B, C and D, respectively. WWTP A stands out with an emission of 1.67 mg PE⁻¹ d⁻¹.

Table 1

Average MP values for loads in secondary effluent, post-treatment removal and emissions of WWTPs into environment.

WWTP	Post-treatment system	Effluent secondary clarifier	Post-treatment removal	Emissions into environment*	
		[mg PE ⁻¹ d ⁻¹]	[mg PE ⁻¹ d ⁻¹]	[mg PE ⁻¹ d ⁻¹]	[g d ⁻¹]
A	PCMF (PES-14)	2.17	2.12	1.67	116.74
	PCMF (UFH-12)	0.33	0.33		
	MF	1.76	1.76		
B	RSF (↓)	0.69	0.59	0.10	4.49
C	GAC (cont. ↑)	0.05	0.01	0.15	4.77
	Micro strainer	0.24	0.23		
D	GAC (↓)	1.51	1.51	0.07	50.42
	PAC+CF+RSF (↓)	1.40	1.33		

* values calculated for systems in regular operation, not including pilot plants.

Discussion

MP analysis

Previously, mostly spectroscopic methods were used to examine municipal WWTP effluents (Elkhatib and Oyanedel-Craver, 2020). Fourier transform infrared (FTIR) spectroscopy can identify MPP down to 10 μm (Möller et al., 2020). Here, characteristic vibrational spectra of functional groups enable the identification of MPP, including particle number, size and chemical composition. A drawback of the method is that particles containing a high amount of black carbon are most likely undetectable due to the high absorption of infrared radiation. Raman spectroscopy uses vibrational spectra of specific chemical bonds to identify particles and their polymer type (Käppler et al., 2016). It has better spatial resolution, allowing the detection of particles down to 1 μm (Ivleva et al., 2017). However, the method is sensitive to fluorescence from natural organic matter or certain clay minerals (Braun et al., 2020). The results of both spectroscopic methods are given in numbers of MPP per sample volume generating important information for ecotoxicological studies. Disadvantages include the need for highly purified samples and long measurement times, making the overall sample processing and analysis costly and time consuming. As a result, only small sample sizes are usually analyzed. Sample sizes < 100 L are common in wastewater studies (Bretas Alvim et al., 2020; Elkhatib and Oyanedel-Craver, 2020; Sun et al., 2019) and cannot be regarded as representative of WWTP effluents which include diurnal, weekly and monthly fluctuations of both contaminants and volumes.

Another approach with shorter analysis times are thermoanalytical methods. Mostly gas chromatography–mass spectrometry (GC–MS) either coupled to pyrolysis (Py) (Nuelle et al., 2014) or thermal extraction and desorption (TED) (Dümichen et al., 2015) have been applied so far. Both methods identify characteristic substances after the thermal decomposition of a sample which are then used for the quantification of polymers. Py-GC-MS analyzes samples in the μg -range and therefore needs a sample purification similar to spectroscopic methods. Recently, mass concentrations of 0.3 – 3.8 $\mu\text{g L}^{-1}$ for the MP fraction < 500 μm in a WWTP effluent were reported using this method (Roscher et al., 2022). TED-GC–MS uses larger crucibles with sample sizes in the mg-range. Environmental samples need purification to increase the ratio of MPP within a sample but interference from matrix substances is less an issue (Braun et al., 2020). This method has been used to examine MPP from different rivers and a biogas plant (Dümichen et al., 2017) as well as particles from tire wear in environmental samples (Eisentraut et al., 2018).

Using DSC, only semi-crystalline polymers can be quantified. Thus, any resulting MP concentration is potentially lower than the total value of MPs, taking into account polymers without crystalline fractions. PVC, polyurethane (PUR) and polystyrene (PS) are examples of amorphous polymers produced in large quantities and found frequently in wastewaters. However, PE, PP and PET accounted for the majority of production in the plastic industry (PlasticsEurope, 2020) and commonly constitute the largest fraction of MPP abundance in municipal wastewaters (Lv et al., 2019; Mintenig et al., 2014; S.M. 2017; Roscher et al., 2022; Wolff et al., 2019). An advantage of the DSC analysis is its simplicity and the short measurement time (~2 h). The method is also not as prone to interference from matrix substances as shown in Bitter and Lackner (2021) and the comparatively high LOQ reduces the risk of contamination during the processing of samples in the lab. Although it potentially necessitates large sample volumes in wastewater effluents. The effectiveness in comparison to other thermoanalytical methods was proven in an interlaboratory trial (Becker et al., 2020).

Secondary effluents

MP concentrations of secondary effluents at four WWTPs were analyzed with values ranging from 0.1 to 19.6 $\mu\text{g L}^{-1}$. This proves the

validity of the DSC analyses for the purpose of determining MP loads in WWTP effluents, as the values fit in the range of concentrations reported with other methods: A median MP concentration of 16 $\mu\text{g L}^{-1}$ was reported for ten Danish WWTPs by extrapolating from spectroscopic data (Vollertsen and Hansen, 2017). Thereafter, 0.5 – 11.9 $\mu\text{g L}^{-1}$ were measured by for MPP the size of 10 – 500 μm with a similar method (Simon et al., 2018) and 0.3 – 3.8 $\mu\text{g L}^{-1}$ were determined for MPP also the size of 10 – 500 μm by py-GC-MS (Roscher et al., 2022). This confirms the range of MP concentrations found here for WWTPs that include primary clarification, biological treatment and secondary clarification. However, in this study, the possibility of undetected amorphous MPP remains which would increase the reported values, especially from industrial discharge. Lv et al. (2019) measured a higher average concentration of 168 \pm 20 $\mu\text{g L}^{-1}$ in the effluent of an oxidation ditch, most likely due to the different design of the plant.

This study shows that not only the drainage area has an impact on the MP emissions, but also the post-treatment systems (see next subchapter) as well as possibly the design of the secondary clarifier: WWTP A showed the highest average MP concentrations in the secondary effluent. At the time of sampling, a visible circulation was transporting small amounts of particulate matter from the separation zone to the top of the clear water zone. After the sampling period, the inlet structure of the clarifier was modified to optimize the influent of the sludge into the sedimentation and to break up the resulting circulation, increasing the hydraulic capacity, reducing the effluent TSS (Fundneider, 2020) and likely changing MP concentrations.

Average MP loads from 0.05 $\text{mg PE}^{-1} \text{d}^{-1}$ to 2.17 $\text{mg PE}^{-1} \text{d}^{-1}$ were found in the secondary effluents, which are in the same range as the values given in literature. Simon et al. (2018) estimated 0.56 $\text{g capita}^{-1} \text{a}^{-1}$ in Denmark and Conley et al. (2019) calculated 0.34 – 0.68 $\text{g capita}^{-1} \text{a}^{-1}$ in Charleston, South Carolina. These values translate to 1.53 $\text{mg PE}^{-1} \text{d}^{-1}$ and 0.93 – 1.86 $\text{mg PE}^{-1} \text{d}^{-1}$, respectively. While these numbers help to improve future models on MP mass fluxes, the significance of WWTPs as point sources for MPP into aquatic environments still remains a point of discussion. The non-population-related MP loads of 4.77 g d^{-1} at WWTP C to 116.74 g d^{-1} at WWTP A also show that WWTPs without tertiary treatment can indeed be significant point sources, even though the amount of MPs originating from non-point sources or littered plastic waste might be higher. Estahbanati and Fahrenfeld (2016) suggest an influence on environmental emissions of MPs as well by comparing numbers of MPP in rivers upstream and downstream of four WWTPs.

In addition, studies investigating MPP in stormwater retention ponds suggest that this can also be a significant pathway for MPP into the environment (Liu et al., 2019; Olesen et al., 2019). Launay et al. (2016) examined micropollutants and showed that stormwater discharges can carry a significant fraction of the load emissions into the environment. Equipping stormwater discharges with technical particle-retention systems, comparable to the ones investigated in this study could therefore reduce MP emissions significantly, although the technical feasibility and economical expenses would need to be evaluated.

Altogether, more research is needed to understand the fluctuations of effluent concentrations in comparison to weather conditions, stormwater discharge and the type of urban discharge systems.

Post-treatment systems

WWTPs face rising concerns relating to the quality of receiving water bodies, such as phosphorous concentrations, micropollutants and antibiotic resistant bacteria. Rogowska et al. (2020) summarized the occurrence of micropollutants measured in treated wastewater, showing maximum concentrations from 1.00 to 37.14 $\mu\text{g L}^{-1}$ for 95 of 100 compounds, which is roughly the same concentration range as MPs found in secondary effluents (see previous subchapter). These findings can necessitate tertiary treatment systems for WWTP effluents. Although those treatment systems are not developed or designed with the intention of removing MPP, they often include surface or depth filtration

steps which suggest a synergetic removal of MPs. Hence, we examined seven different post-treatment systems to further understand the fate of MPP in WWTP effluents: a PCMF, an MF, an RSF, a micro strainer, a continuous upflow GAC, a discontinuous downflow GAC and a full scale PAC-stage including a clarifier and an RSF.

An MF pilot plant was operated to reduce TSS, phosphorous concentrations as well as bacteria and genes. Contrary to our findings, no measurable MPP in the effluent were expected due to findings of Fundneider et al. (2020), where the MF was reported to be intact and fully functioning. As all measured MPP were found in the size ranges $> 100 \mu\text{m}$, it is very unlikely that they passed through the membrane. Additionally, the samples were taken out of the open effluent storage tank and therefore the measured MPP could be attributed to contamination from the surrounding plant site. The concluded removal efficiency of 100% is higher than numbers reported for MF in Bayo et al. (2020), Lares et al. (2018), Lv et al. (2019) and Talvitie et al. (2017).

Two different cloth types of the PCMF were examined. The PES-14 and the UFH-12 pile cloth media showed a removal of 98.87% and 99.99%, respectively. Mintenig et al. (2017) reported a slightly lower removal efficiency of 97% for a PA2-13 pile cloth media (pile layer made of PA6). Low numbers of PET fibres were found in the effluent which would likely amount to a mass concentration below the LOQ of the DSC method applied here. We found low concentrations of PE-LD, PE-HD and PP in the effluents, but neither PA nor PET which are used to produce the pile cloth media.

While the majority of systems showed removal efficiencies of $> 94\%$, the RSF showed an average removal of 82.38%. This is lower than the 97% reported in Talvitie et al. (2017) and the 99.2 – 99.9% reported in Wolff et al., (2021) and higher than the efficiency of 79.01% reported in Bayo et al. (2020). The reason for the comparatively low removal, is most likely the lack of maintenance on the filter. A visual inspection after sampling showed that the filter beds had been reduced significantly and no new sand had been added. The higher removal efficiency of PET and PA6 versus PP, PE-HD and PE-LD are likely due to stochastic distribution and not an indication of a different filtration performance of polymer types.

A micro strainer showed a removal efficiency of 94.63%. It has to be noted, that two of three effluent values were below the LOQ. To calculate the removal, the LOQ threshold values were used. The overall result is likely influenced by the low influent concentrations found in the secondary effluent. We expect the removal efficiency to be closer to 98.5% reported for filter 2 in Talvitie et al. (2017) if examined with a higher influent concentration. Simon et al. (2018) reported a lower removal efficiency of 89.7% of MPP, but conceded that the results suggested a compromised operation. MPP were removed independently of their polymer types and no PET was found in the effluent. This differs from the findings in Talvitie et al. (2017) where PET fibres were found in the effluent of both filters. While the fabric of the micro strainer in this study is made of PET, Talvitie et al. (2017) did not specify the polymers of the investigated filters.

The continuous upflow GAC filter was the only system studied which has to be classified as inadequate for MP removal. This is most likely due to the continuous internal circulation of GAC in the filter column. During the washing of the filter material, the MPP can be returned to the filter surface with the recycled GAC and transported to the effluent due to the upflow process. PA6 was removed at a higher percentage than the other polymer types, which is most likely due to its low influent concentrations. The differences between the remaining polymers are likely stochastic and would present differently with higher sample numbers.

Both, a full scale PAC stage and a GAC filter showed high removal efficiencies of 97.15 and 99.56%, respectively. Polymer types had no measurable impact on the removal.

The full-scale RSF and PAC stage significantly lowered the MP load of the secondary effluent. The same should be true for scaled-up systems of the PCMF, MF, micro strainer and discontinuous downflow GAC filter. The continuous upflow GAC filter did not remove MP loads significantly.

Rasmussen et al. (2021) reported an MP load of 0.7 kg d^{-1} in the effluent of a full-scale micro strainer system, translating to $0.89 \text{ mg PE}^{-1} \text{ d}^{-1}$ with a PE of 790,000. This population-related value is similar to the effluents of WWTP B and D which both include tertiary treatment.

Conclusions

This study presents mass concentrations of semi-crystalline MPs in effluents of four German WWTPs. All measurements were performed using DSC, providing a fast and comparatively easy tool to analyze semi-crystalline MPP. MP concentrations in effluents of secondary clarifiers were found to be in the low $\mu\text{g L}^{-1}$ -range, which is in accordance with other studies, proving the usefulness of DSC for the determination of MP concentrations in WWTP effluents.

The implementation of post-treatment processes designed for other micropollutants showed in most cases a very good removal of MPs independent of polymer types. Only a continuous upflow GAC filter showed poor removal rates and a rapid sand filter showed a less satisfactory removal rate of 82%. All the other systems included functioning filtration and showed removal efficiencies $> 94\%$. Based on those results, we can state that post-treatment systems, which contain either (discontinuous) depth or surface filtration, efficiently remove MPP on top of their original treatment purpose and significantly reduce MP loads of secondary effluents.

Overall, these findings help to better understand the fate of MPP in wastewater effluents and mass fluxes of MPP into the environment.

CRediT authorship contribution statement

Hajo Bitter: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **Leonie Krause:** Investigation, Resources, Writing – review & editing. **Franziska Kirchen:** Resources, Writing – review & editing. **Thomas Fundneider:** Conceptualization, Validation, Resources, Data curation, Writing – review & editing, Visualization, Funding acquisition. **Susanne Lackner:** Validation, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is given in supplementary material.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.wroa.2022.100156](https://doi.org/10.1016/j.wroa.2022.100156).

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