Science of the Total Environment 881 (2023) 163349

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Quantification of microplastics in wastewater systems of German industrial parks and their wastewater treatment plants

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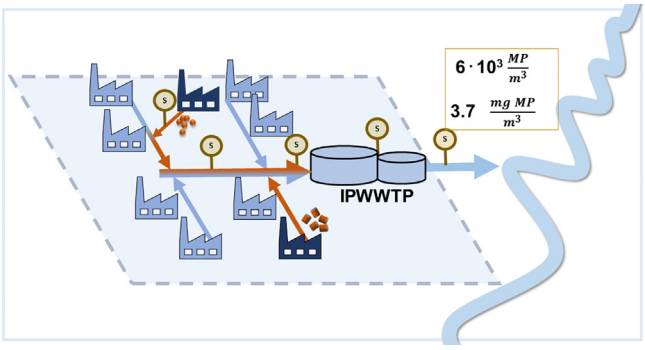
HIGHLIGHTS

- German industrial parks as MP emitters to the environment were researched in detail.
- Detection of mass- and number concentrations with a simultaneous sampling technique
- MP deriving from plastic producers is detectable throughout the wastewater system.
- Total MP numbers per day within IPWWTPs fluctuate greatly over time.
- In- and effluent MP concentrations of industrial and municipal WWTPs are comparable.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Kevin V Thomas

Keywords:
Microplastics
WWTP effluent
Industrial wastewater
Micropollutant
μ-Raman spectroscopy
Differential scanning calorimetry

ABSTRACT

Microplastics (MP) enter the aquatic environment via several pathways. Many research groups have focused on municipal discharge, while research on industrial sources is rare. This study provides one of the first insights into MP occurrence and distribution in the wastewater systems of industrial parks (IPs) and their wastewater treatment plants (IPWWTPs). The effluents from production plants as well as influent, effluent, and internal samples from the IPWWTPs were assessed. Sampling methods for parallel MP mass and number analyses were developed for varying conditions. The total item emissions of MP (≥ 10 μm) into the environment were analyzed using μ-Raman spectroscopy and ranged from $3 \cdot 10^2$ to $8 \cdot 10^4$ MP m^{-3}, with a median of $6 \cdot 10^3$ MP m^{-3} per IPWWTP. Masses analyzed using differential scanning calorimetry showed an MP mass discharge into the environment of 0.2 to 11 mg m^{-3} with a median of 3.7 mg m^{-3} per IPWWTP. MP item concentrations within an IPWWTP varied by two to three log levels over several days. Fibers were rare in all samples. Polymer types varied depending on the types of industrial sites and the production plants discharging into the IPWWTP. Within an IP, MP could be allocated to its dischargers, which could be useful for future regulatory requirements. Further research is needed to include different types of IPs producing various polymers and additional processing plants to expand this data set.

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http://dx.doi.org/10.1016/j.scitotenv.2023.163349
Received 1 February 2023; Received in revised form 22 March 2023; Accepted 3 April 2023
Available online 11 April 2023

Table 1
Production details of sampled plastics production plants.

Sampling site	Samples	Polymer produced	Product shape	Mean wastewater discharge (m^3·d)	Production
Plant A	n = 3	PVC	Powder	$1.4 \cdot 10^2$	Continuous
Plant B	n = 2	PE	Granules	Unknown[a]	Periodic
Plant C	n = 2	PE	Powder	$2.8 \cdot 10^2$	Continuous
Plant D	n = 3	PE	Powder	$4.8 \cdot 10^2$	Periodic

[a] No data available, because there are no measurement systems or estimations available from the site operators.

1. Introduction

Plastics are ubiquitous in the environment. They can be found in remote areas such as the deep sea and the Antarctic (Waller et al., 2017; Courtene-Jones et al., 2020), in every part of the environment (Schell et al., 2020), in animals, plants, and even human beings (Wang et al., 2019; Ragusa et al., 2021). Especially smaller plastic items might be of ecotoxicological relevance and tend to accumulate in the food chain (GESAMP, 2016). Therefore, all possible sources should be investigated to assess and identify effective methods to prevent and reduce plastics emissions into the environment. Plastic items smaller than 5 mm are called microplastics (MP) and can be divided into particles (MPP) and fibers (MPF).

As point sources for MP in the aquatic environment, municipal wastewater and municipal wastewater treatment plants (WWTPs) have mainly been studied so far (Habib et al., 2020; Iyare et al., 2020). However, wastewater is also produced by industrial activities such as plastics manufacturing and by processing companies which use water-intensive processes. In Germany, small plastics processing companies usually pretreat their wastewater and discharge it into municipal WWTPs, whereas large companies, mostly plastics producers, make use of the structural advantages of industrial parks (IPs) and their industrial wastewater treatment plants (IPWWTPs). The chemical industry in Germany, including polymer producers, is mainly housed in over 60 organized parks (VCI, 2012) which produce over 20 million tons of polymers every year (Federal Statistical Office of Germany, 2022). In Germany most IPs were not built in recent years but are the result of historical developments and have an individual infrastructure. This has led to very different settled industries and industrial wastewater compositions within IPs, as well as to equally diverse IPWWTPs.

There is a need for information about the MP emissions of industrial facilities (Ryberg et al., 2019). There are few studies, which are focusing on industries like plastic recycling (Umar et al., 2023) or textile industry (Chan et al., 2021). Most emission factors for assessing industrial MP emissions in wastewater systems are based on surveys or estimations based on production masses, rather than measurements (Lassen et al., 2015; Cole and Sherrington, 2016; Boucher et al., 2020). To date, little information is available which could be used to estimate MP distribution and the discharge of plastics producing and processing industries within IPs into the aquatic environment. This study is intended to provide data that can be used to further close this knowledge gap and give a more accurate picture of plastics emissions into the environment.

Two complementary methods for the analysis of MP numbers (μ-Raman spectroscopy) and masses (differential scanning calorimetry (DSC)) were used (Primpke et al., 2020). MP concentrations in the effluents of plastic production plants are presented. Influents and effluents of IPWWTPs were analyzed and the MP distributions within one IPWWTP examined.

2. Materials and methods

2.1. Sampling sites

The effluents of four different plastics production plants, each located in an IP, were analyzed. Plant A produces different kinds of polyvinylchloride (PVC), while plants B, C, and D produce polyethylene (PE) in different forms. The mean wastewater discharge of each plant in the IP sewage system ranges from 140 to 3600 m^3 per day, either as continuous discharge or periodically during polymer production cycles (see Table 1).

Apart from individual companies, the effluents of five IPs with a variety of plastics production and processing plants were sampled. The mean wastewater discharge per year and the wastewater treatment steps of each IPWWTP are similar, and most of the treated wastewater originates from industrial sources (see Table 2).

For a deeper insight into the distribution and occurrence of MP in the sewage system of industrial parks, samples of influents and partial influents were measured at IPWWTPs 1 and 2. The samples of partial influents were taken from the industrial wastewater sewage system at points with known indirect discharge from polymer production plants.

IPWWTP 5 was examined in depth using μ-Raman analysis, with four additional sampling points between treatment steps on nine sampling days in total. Retention times within the plant and the sewage network were taken into account. The structure of IPWWTP 5 is shown in Fig. 1 and can be described as follows: Wastewater is neutralized first, followed by primary sedimentation. The first two sampling points were influent and effluent of a denitrification step, which consists of five biologically activated continuous quartz sand filters (grain size 1–1.6 mm), each with a retention time of approx. 1.5 h and continuously circulated by four mammoth pumps. Sand and rinsing water are separated in the head of the mammoth pump, with the sand remaining in the filter and the rinsing water being pretreated in a settling tank/grit trap. Its effluent was chosen as the third sampling point. The effluents of grit traps and denitrification lead into a hydrolysis reactor, followed by anaerobic treatment within four high-rate reactors with internal recirculation (IC, granulated sludge, average loading rate 1.7 kg TOC·m^{-3} h^{-1}, 78 % TOC degradation). Its effluent was chosen as the fourth sampling point. A second influent (on average 23 % of the total effluent) from a cellulose processing plant, along with the effluent from the anaerobic treatment, leads into an aerobic treatment step (activated sludge). The last treatment step consists of a final clarifier whose effluent is released into a body of water.

Table 2
Sampled IPWWTPs with sampling points, wastewater treatment steps, percentage of treated municipal wastewater, and mean wastewater discharge.

Sampling site	Sampling points				Wastewater treatment steps		Treated municipal wastewater		Mean wastewater discharge
	Partial influent	Influent	Within IPWWTP	Effluent	Primary	Secondary	From municipalities	From employees[a]	(m^3 a^{-1})
IPWWTP 1	n = 2	n = 2	–	n = 1	Screening, settling, neutralization	Activated sludge (aerobic), sedimentation	–	3 %	$1.9 \cdot 10^6$
IPWWTP 2	n = 2	n = 2	–	n = 2	Screening, settling, neutralization	Activated sludge (aerobic), sedimentation	–	1 %	$1.4 \cdot 10^7$
IPWWTP 3	–	–	–	n = 3	Screening, neutralization, settling	Activated sludge (aerobic), sedimentation	–	3 %	$2.2 \cdot 10^7$
IPWWTP 4	–	–	–	n = 6	Screening, settling, neutralization, flocculation	Activated sludge (aerobic), sedimentation	10%[b]	2 %	$1.7 \cdot 10^7$
IPWWTP 5	–	–	n = 22	n = 6	Screening, neutralization, settling, filtration	IC, activated sludge (anaerobic, aerobic), sedimentation	–	3 %	$4.8 \cdot 10^6$

[a] The proportion of municipal wastewater treated by employees was estimated by calculating their water usage within each industrial park (DGNB (PUB), 2018; Baur et al., 2019).
[b] Maximum value, wastewater from nearby municipalities at irregular intervals.

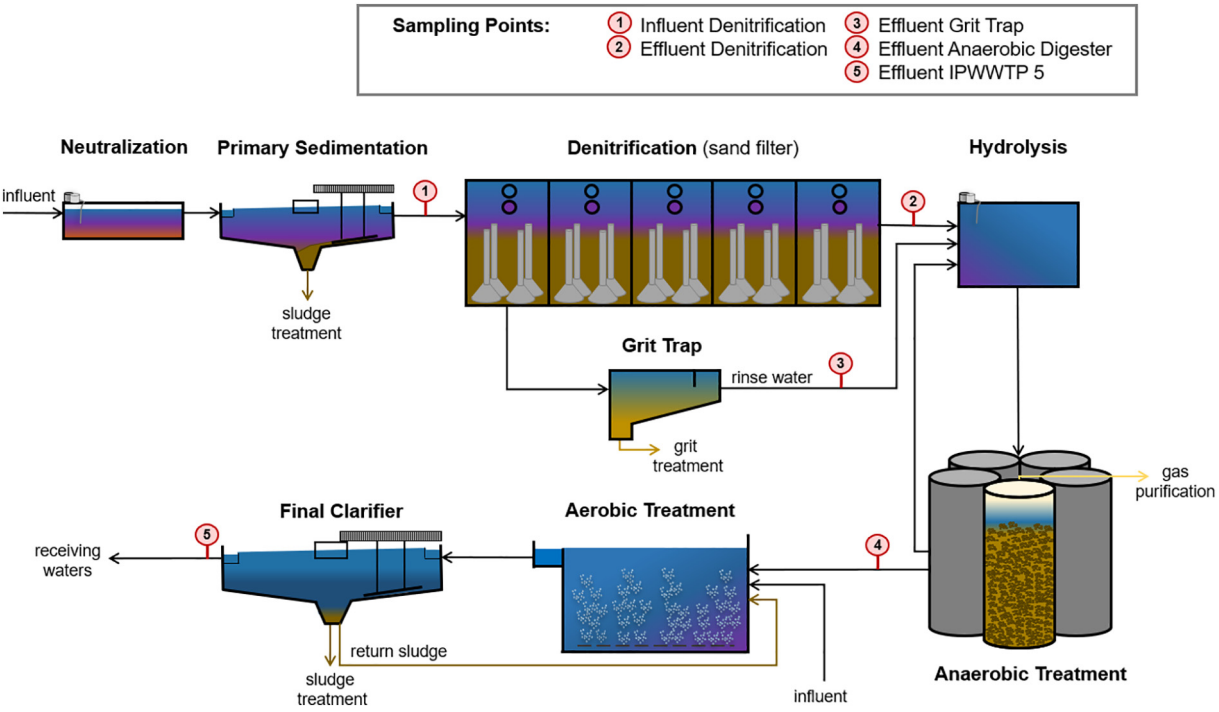

Fig. 1. Flow diagram of IPWWTP 5 with sampling points.

2.2. Sampling

A periodic (discontinuous) sampling was performed in accordance with DIN EN ISO 5667-1 (2007) at fixed time intervals, and the samples were subsequently combined into a composite sample. The sampling took place from 2018 to 2021. Wherever possible, three samples were taken from each site. As a rule, two methods were used depending on the amount of total suspended solids (TSS).

If the TSS was <30 mg l^{-1}, as is usual for all IPWWTP effluents, a volume-reducing sampling device with stainless-steel filters was used (see Fig. 2). This is a combination of the systems used by Wolff et al. (2019) and Bitter and Lackner (2020) to ensure parallel sampling for two different analysis methods. For μ-Raman analysis, a 10 μm cartridge filter with a stainless-steel membrane and housing (acuraScreen, Fuhr GmbH, Klein-Winternheim, Germany) was installed on the suction side of a centrifugal pump (VGX 9/10, SPECK Pumpen Verkaufsgesellschaft GmbH, Germany). Sample volumes were measured using a digital flow meter (Picomag, Endress + Hauser GmbH + Co. KG, Weil am Rhein, Germany). For DSC analysis, a second inlet hose was installed at the pump and three 9″ stainless-steel cartridge filters (Fuhr GmbH, Klein-Winternheim, Germany) with mesh sizes of 1000 μm, 100 μm, and 10 μm were installed in a cascade on the pressure side of the pump. Here, sample volumes were measured using a water meter (Hermann Pipersberg Jr. GmbH, Remscheid, Germany).

First, the filter system for DSC analysis was used for 5 min, then the filter for μ-Raman analysis was used for 1 min or until 20 l had been filtered. To prevent the formation of deposits between sampling intervals, the medium was pumped through the inlet and outlet hoses, bypassing the filters. In this time period, a 2 l glass bottle with a glass stopper was filled with 160 ml Wastewater as a sample for wastewater characterization. This was repeated every 10 min for up to 2 h. The filtered sample volumes ranged from 9 to 1000 l for μ-Raman analysis and from 64 to 2063 l for DSC analysis.

Before sampling, all hoses were connected to the pump and rinsed with the medium for 5 min to avoid contamination and MP loss through adsorption on the inner surfaces of the hoses.

If TSS > 30 mg l^{-1}, 2 h mixed samples were taken by an automatic sampler (WS312, Watersam GmbH & Co. KG, Balingen, Germany), or manually for 1 h or 2 h using 2 l glass bottles with glass plugs. Industrial influent samples, such as those described by (Shan et al., 2022), which might have been subject to large daily fluctuations, were taken as 24 h mixed samples. Due to safety regulations, effluent samples from production plants B and D had to be taken using different automatic samplers (Plant B: Ori mobil ex, ORI Abwassertechnik GmbH & Co. KG, Hille, Germany; Plant D: Ori NeMo Ex Solid Industrie, ORI Abwassertechnik GmbH & Co. KG, Hille, Germany). These automatic samplers contained sample-contacting parts made of polyvinylidene fluoride (PVDF) and PVC.

Before sampling, valves were pre-rinsed with wastewater for at least 2 min.

Besides the TSS concentration, the accessability of sampling points and flow rates influenced the choice of sampling method. For example, despite low TSS values, volume-reduced sampling at production Plant C was not possible and samples were taken manually because of a poorly accessible sampling point located on an outdoor scaffold for reactors. To quantify the contamination from atmospheric deposition during heavy rainfall, a second empty bottle was also opened and closed at the same time intervals during sampling and was prepared as a blank sample for μ-Raman spectroscopy (see Section 2.3).

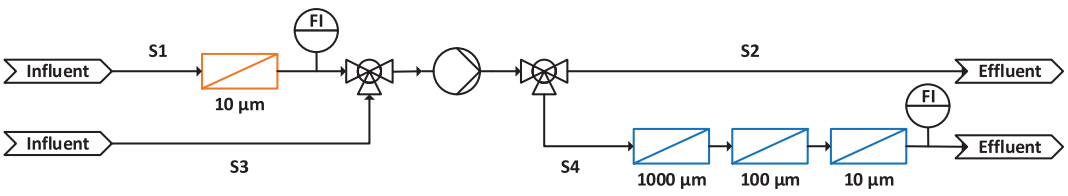

Fig. 2. Filtration for liquids TSS < 30 mg·l^{-1}, sampling for μ-Raman analysis (S1, S2), sampling for DSC analysis (S3, S4), and intermediate rinsing (S3, S2).

Sampling methods and sampled volumes for each sample are listed in Appendix A.

2.3. Sample preparation and analysis using μ-Raman spectroscopy

2.3.1. Sample preparation

IPWWTP 5 effluent samples nos. 1–3 were processed and analyzed as in Wolff et al. (2021). The effluent samples from plastics production Plant A have been published previously in Wolff et al. (2021); for this paper, the data were reviewed again and analyzed as outlined in Sections 2.3.5 and 2.3.6. All other samples were processed and analyzed as described below.

To eliminate organic matter in the sample matrix, an oxidative treatment was conducted as in Wolff et al. (2021). In the first step, the samples were treated with H_2O_2 (p.a. 50 %, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) for 24 h at 50 °C. For volume-reduced samples, the cartridge filter was treated in approx. 1 l H_2O_2. Liquid samples were filtered through a stainless-steel filter membrane with a pore width of 10 μm and a diameter of 47 mm (twilled weave, Spörl KG, Sigmaringendorf, Germany) with a vacuum filtration aperture before oxidation. In liquid samples with a very high concentration of solids, which could not be filtered onto the maximum of three filter membranes, solids settled in the bottle for 24 h. Then the supernatant was filtered, while settled solids remained in the bottle. In both cases (low and high concentrations of solids), the particles on the filter membranes were transferred back into the sampling bottle, and approx 0.3 l (lower solid concentration) or 0.5 l (higher solid concentration) of H_2O_2 were added, respectively. In the second step, the samples were transferred onto a stainless-steel filter membrane and treated with 0.3 l NaClO (12 % tech., Carl Roth GmbH & Co. KG, Karlsruhe, Germany) at room temperature for 6 d.

The density separation accelerated by centrifugation was performed as in Weber and Kerpen (2022) with a sodium polytungstate solution (ρ = 1.7 g·ml^{-1}, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) as the density separation agent.

Materials with sample contact (e.g. beakers and tweezers) were rinsed with n-hexane (HiPerSolv CHROMANORM, VWR, Radnor, PA, USA) from a syringe and purified water (Milli DI, Merck KGaA, Darmstadt, Germany) from a perfluoroalkoxy alkanes (PFA) squirt bottle to decrease particle losses at transfer steps (Wolff et al., 2021).

If the particle concentration in the sample was too high for analysis using μ-Raman spectroscopy (agglomerates, several layers of particles on the analysis filter), subsampling was performed as in Wolff et al. (2021). The percentage of aliquot per sample volume in each sample is stated in Appendix A.

2.3.2. Digital microscopy

Images of loaded analysis filters with a depth of field were made using a digital microscope (VHX-7000, Keyence, Osaka, Japan) at a magnification of 100×. The images were used to identify agglomerates and small particles adhering to larger ones. Because these agglomerated or adhering particles are not recognized by automatic particle detection (see Section 2.3.3), additional data acquisition points were placed manually according to the depth-of-field image.

2.3.3. μ-Raman spectroscopy

The measurements were taken using a μ-Raman spectroscope (DXR2xi, Thermo Fisher Scientific Inc., Waltham, MA, USA) with a front-illuminated EMCCD detector. The electron multiplier (EM) was turned off. All particles ≥ 10 μm on the filter were analyzed using the automatic particle detection feature of the instrumental software OMNICxi (v.2.3, Thermo Fisher Scientific Inc., Waltham, MA, USA). Each particle detected was analyzed with a laser wavelength of 785 nm, a laser power of 8 mW, and a total exposure time of 6.75 s (three repetitions of 2.25 s each). The objective used had a 20× magnification and a numerical aperture of 0.45. Spectra were recorded in the range of 50–3250 cm^{-1} with spectral autofocus in the range of 750–1750 cm^{-1} and a resolution of 5 cm^{-1}.

The spectra recorded were compared to the reference library P/N L60001 (S.T. Japan Europe GmbH, Cologne, Germany) using the OMNICxi and OMNIC software (v9.11.706, Thermo Fisher Scientific Inc., Waltham, MA, USA). Spectra were accepted if the match factor was ≥0.8. All spectra were manually checked by the same researcher for false positive or false negative results. The particle size was determined automatically using OMNICxi based on the longest diameter of a particle. On average, the particle diameter was overestimated by 15 μm by the instrument software. Therefore, a manual correction was undertaken. The length of fibers was measured manually.

2.3.4. Subsampling

Due to measurement settings and specifics of the instruments and software, the maximum number of acquisition points per sample was approximately 2500 per 24 h of measuring time. Where there were >2500 particles on the analysis filter, the minimum number of particles to be measured was determined as in Anger et al. (2018) (see Formula 1). Based on the evaluation of 25 samples and including a safety margin of 2 %, the proportion of MP particles to the total particles per analysis filter (P) was estimated at P = 5 %.

Number of particles required
(Anger et al., 2018)

$$n \geq \frac{P(1-P)}{\frac{e^2}{\sigma^2} + \frac{P(1-P)}{N}} \quad (1)$$

with $e = P * 0.01 = 0.005$

$\sigma = 1.65$

$N = number\ of\ particles\ on\ the\ analysis\ filter$

A retrospective data analysis proved that all samples that underwent this procedure contained an MP rate of ≥5 %. This means that the requirements set by Anger et al. (2018) were met.

2.3.5. Blank samples

For each sample set, a blank sample was taken simultaneously. Six procedural blanks (B1 - B6) in total were assessed by simulating the sample preparation, including all oxidative treatment, density separation, and transfer steps. Three separate blanks for the subsampling procedure were analyzed ($B_{sub}1$ - $B_{sub}3$), since subsampling was not necessary for all samples.

Contamination mitigation was conducted as in Weber et al. (2021). Detailed information is given in Appendix B.

2.3.6. Statistical analysis

Each analysis was treated as a separate calculation. Therefore, the limit of quantification (LOQ) was determined as follows (Formula 2) (DIN 32645, 2008).

Limit of quantification
(DIN 32645, 2008)

$$LOQ = \bar{x}_{blank} + 10 * SD_{blank} \quad (2)$$

with $\bar{x}_{blank}$: *arithmetic average of the blank values*

SD_{blank} : *standard deviation of the blank values*

The LOQ was determined for each polymer type independent of size fractions. Even for polymers with a zero-blank value, the minimum number of detected particles/fibers was set at n = 2 per analysis to be considered as significant above the LOQ. The LOQ of subsamples was determined in the same way as the LOQ for whole samples. If the result of a subsample was higher than the subsample's LOQ, it was extrapolated and compared to the total LOQ.

2.4. Sample preparation and analysis using DSC

Volume-reduced samples with different mesh sizes and liquid samples were processed as in Bitter and Lackner (2020). The crucible filling for

Table 3
Subsampling blank results and subsampling LOQ.

Polymer count		$B_{sub}1$	$B_{sub}2$	$B_{sub}3$	Mean subsampling blank (n = 3)	LOQ
MPP	PE	1	0	0	0.3 ± 0.6	6
	PP	1	0	0	0.3 ± 0.6	6

Table 4
Procedural blank results and LOQ for all procedural blanks.

Polymer or pigment count		B1	B2	B3	B4	B5	B6	Mean blank (n = 6)	LOQ
MPP	PE	4	7	9	6	9	6	6.8 ± 1.9	26
	PET	0	0	6	3	2	0	1.8 ± 2.4	26
	PP	1	1	1	1	0	1	0.8 ± 0.4	5
	PS	0	0	3	1	6	4	2.3 ± 2.4	27
	PVC	3	5	1	0	0	13	3.7 ± 5.0	53
Pigmented particles	CuPC	6	5	10	18	24	4	11.2 ± 8.1	92
	Red 214	0	0	1	1	0	0	0.3 ± 0.5	5
MPF	PET	2	0	0	0	2	4	1.3 ± 1.6	18
Pigmented fibers	CuPC	1	0	0	0	0	0	0.2 ± 0.4	4
	Indigo	1	0	0	0	0	0	0.2 ± 0.4	4

polymer analysis was also performed as in Bitter and Lackner (2020). For the analysis, a Netzsch DSC 214 Polyma (NETZSCH-Gerätebau GmbH, Selb, Germany) was used. The analysis, including LOQ, was performed as in Bitter and Lackner (2021) with a recovery rate of 93 %, which was included in the polymer mass calculation. IPWWTP 5 effluent samples nos. 1–3 have been published previously in Bitter and Lackner (2020).

Methods of contamination avoidance for both analysis techniques are described in Appendix B.

3. Results and discussion

3.1. Blanks for μ-Raman spectroscopy

Both subsampling and procedural blanks were low and had a low amount of variations. Thus, despite a high safety factor, the LOQ was low as well (see Tables 3 and 4). While only one subsampling blank contained one PE and polypropylene (PP) particle each, in the procedural blanks there was a higher variation in common polymers such as polystyrene (PS), polyethylene terephthalate (PET), PE, PP, and PVC, along with three different types of pigmented particles. The source of pigmented particles and MPP could be cross-contamination, while MPF and the pigmented fibers probably originated from clothing. Copper phtalocyanine (CuPC) was detected in the tap water of the laboratory (Weber et al., 2021). Because the tap water was used for cleaning laboratory equipment, the source of those particles could be tap water.

3.2. MP in industrial parks

3.2.1. MP in effluents from plastics production plants

Samples of four plastic production plant effluents were analyzed; however, methodological limitations meant that not all samples could be analyzed using both analytical methods. Plant A produces PVC, so no sample could be analyzed using DSC analysis. The matrix of Plant D is not suited to μ-Raman analysis, due to non-separable particles causing interference signals.

Fig. 3 shows the results obtained using μ-Raman spectroscopy. The effluent samples from PVC production Plant A contained 2–4 · 10^5 MPP m^{-3}, 94 % of which fell within a size range between 10 to <100 μm. In PE production, Plant B, with total concentrations of 8 · 10^5 and 13 · 10^5 MPP m^{-3}, 61 % of the particles were 100 to <500 μm in size, while 6 % were larger particles ranging from 500 to <5000 μm in size. This could be related to the fact that it was the only sampled plant producing both granules and process residues resulting from underwater cutting. The sample from the second PE production facility, Plant C, at 8.2 · 10^5 MPP m^{-3} showed similar MPP concentrations to those from Plant B, but had a higher number of smaller particles, with 47 % ranging from 50 to <100 μm and 40 % being 10 to <50 μm in size. Mainly the polymer types produced by the plant were found. It should also be noted that plastics used in the automatic samplers for the effluents from Plants B and D were not found in the samples.

MP mass concentrations in the samples from Plant D varied from 0.5 g MP m^{-3} to 4.5 g MP m^{-3} (see Fig. 4). Product changes occurred during sampling, which could have resulted in high MP mass concentration measurements. In Plants A and C, lower mass concentrations from 0.4 to 0.8 g MP m^{-3} were detected. It was possible to separate the polymer types PE, both high density (PE-HD) and low density (PE-LD), using DSC analysis (Bitter and Lackner, 2021), but in PE production Plants B, C, and D only PE-HD was found. Only in Plant C was a second MP type, 1 % PP, detected using DSC analysis, and was also found with μ-Raman analysis.

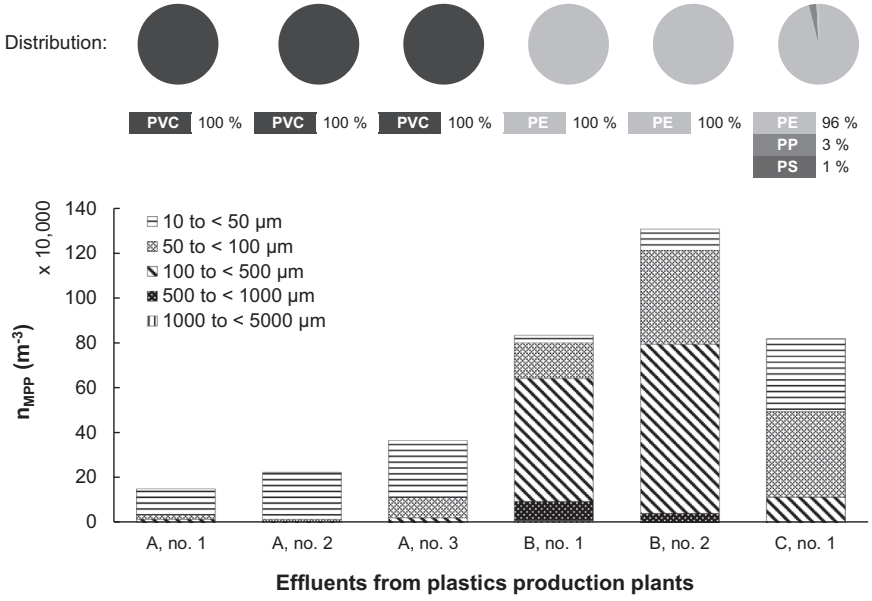

Fig. 3. MPP per cubic meter showing the polymer and size distribution of six samples of effluents from three plastics production plants.

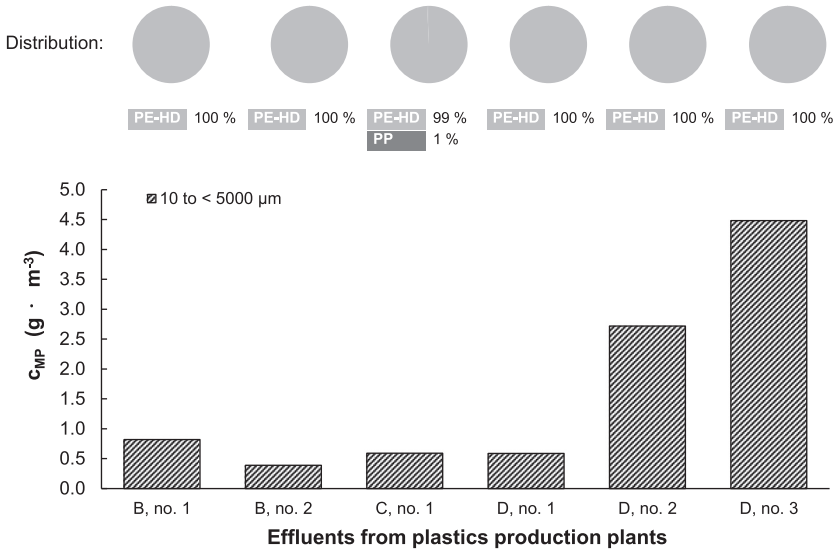

Fig. 4. MP mass per cubic meter in the size range from 10 to <5000 µm, showing the polymer distribution in effluents from three plastics production plants.

As expected, both analysis methods detected the plant-produced polymers, particularly as MPP. Only in plastics production Plant C were different types of MP found using both analysis techniques. In the blank taken while sampling Plant C (see Section 2.2), $6 \cdot 10^2$ PE MPP were found, which amounts to 0.08 % of PE counts in the actual sample. The PE particles in this blank sample could be due to PE powder from the air and dust from the surrounding scaffolding being washed into the bottle by rainfall (see Section 2.2). Two PP particles were also found in the blank, amounting to 0.01 % of PP counts in the sample, whereas PS particles could be found in the sample but not in the blank. This indicates another source for PP and PS in the effluent sample. These may have originated in plastic materials installed in Plant C, such as pipes (Zhang et al., 2021), seals, or foreign objects.

3.2.2. MP in influents to IPWWTPs

The MP polymer types measured in partial influents matched the products of the discharging polymer production plants, as indicated in Fig. 5. In the sampled partial influent to IPWWTP 1, PVC- and PS-producing production plants discharged wastewater into the sewage system. An additional PS-producing plant discharged wastewater into the total influent of IPWWTP 1; this partial influent was not sampled, but may be responsible for a shift in MP distribution from 8 % PS and 92 % PVC particles in the partial influent to 98 % PS and 2 % PVC particles in the total influent to IPWWPT 1. In a partial influent to IPWWTP 2, PE- and polyamide (PA) -producing production plants discharged wastewater into the sewage system. However, PA was not analyzed using µ-Raman, since it is not resistant to the chemicals used for sample preparation (Wolff et al., 2019). Another PS production plant discharged wastewater into IPWWTP 2, with its polymers being detectable in the total influent. The MP distributions in the total influent to IPWWTP 2 varied from 92 % PS and 8 % PE particles to 33 % PS and 67 % PE particles, due to varying production processes and flow rates of discharged wastewater.

Most MPP had a small diameter, with 94 % of MPP measuring 10 to <100 µm overall. No MPF were found. The particle concentrations in the two partial influents varied by four log levels between $4–9 \cdot 10^4$ MPP m^{-3} and $1–3 \cdot 10^7$ MPP m^{-3}, respectively. The influent concentrations

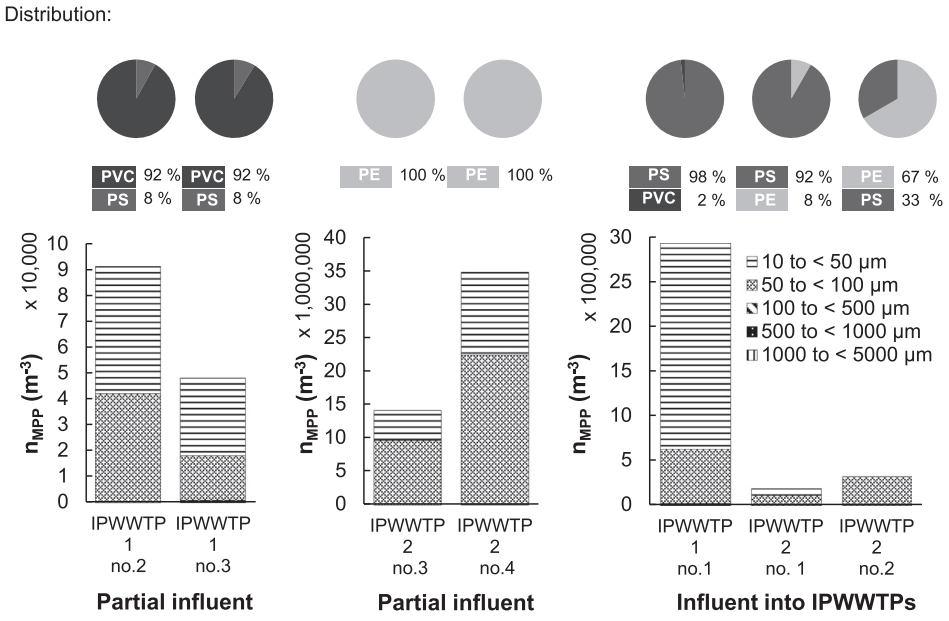

Fig. 5. MPP counts per cubic meter with polymer and size distribution in seven samples of (partial) influents into two different IPWWTPs.

ranged around 2–5 · 10^5 MPP m^{-3} at IPWWTP 2 and 3 · 10^6 MPP m^{-3} at IPWWTP 1. These concentrations are similar to those in municipal influents, where comparable studies have reported 2 · 10^3–2 · 10^7 MP m^{-3}, including a high amount of MPF (Magni et al., 2019; Simon et al., 2018).

Non-removable black particles caused a sample loss due to photolysis during the μ-Raman analysis of a second IPWWTP 1 influent sample. These black particles are suspected to be activated carbon, which is a known component of IPWWTP 1's influent due to its industrial application in wastewater discharging plants.

Also, for four samples, the MP/TSS ratio was too low for DSC analysis, with the exception of one sample from the influent to IPWWTP 1, where 6 mg MP m^{-3} consisting of PE-HD was found. Two samples of partial influent to IPWWTP 2 contained 1.3–7.0 · 10^3 mg MP m^{-3} consisting of PE-LD, PE-HD, and PA 12. Because of differences in the oxidative treatment in the two analysis methods (see Sections 2.3.1, 2.4) it was possible to measure PA using DSC analysis but not μ-Raman analysis in these samples.

Although no representative numbers of samples were analyzed, the traceability of MP to the types of polymer production plants in IPs can be assumed based on these data. Detailed pathways of MP in an industrial sewage system with defined discharge routes should be investigated in further studies. This would improve representative sampling methods for different locations, concentrations, flow rates, and preparation for samples with high TSS concentrations.

3.2.3. MP in effluents from IPWWTPs

In effluents from five IPWWTPs, a variation from 7 · 10^2 to 8 · 10^4 MPP m^{-3} with a median of 6 · 10^3 MPP m^{-3} was found. As shown in Fig. 7A, fluctuations occur among and within IPWWTPs, especially IPWWTP 5. MPF were only analyzed in three samples from IPWWTP 5, consisting of PP and PET, mainly longer than 100 μm. One sample was taken during heavy rainfall and contained only MPF and no MPP. In comparison, analyses of 15 German municipal WWTP effluents have shown MP concentrations in a similar range, from 10^1 to 10^4 MP m^{-3}, including a high amount of MPF (Wolff et al., 2019; Mintenig et al., 2017; Roscher et al., 2021; Wolff et al., 2021).

>72 % of the detected MPP ranged from 10 to <50 μm, while 22 % measured from 50 to <100 μm and only few MPP (6 %) ranged from 100 to <500 μm. Likewise, in German municipal WWTP effluents, MPP < 100 μm were most commonly reported (70 % MPP: 20 to <100 μm (Mintenig et al., 2017); 96 % MPP: 10 to <100 μm (Wolff et al., 2019); 93 % MPP: 15 to <100 μm (Roscher et al., 2021)).

Only MPP of common polymers were detected (Fig. 7B). The distribution was specific to each IPWWTP. For instance, only PE particles were found in effluents from IPWWTP 3. In contrast, effluents from IPWWTP 4 mainly contained PVC, PS, PP, sometimes PE, and rarely PET particles.

Yearly total discharges were extrapolated based on the wastewater volumes of each plant (Table 2) and ranged from 2 · 10^9 MP to 1 · 10^{12} MP with a median of 7 · 10^{10} MP per IPWWTP and year. Researchers using comparable sampling, processing, and analysis techniques sampled 25 municipal WWTPs in Europe and Australia and extrapolated yearly total discharges (Fig. 6). The yearly total discharges of IPWWTPs shown here are comparable to the upper third of yearly total discharges from municipal WWTPs.

It must be noted that in samples from IPWWTP 3, 4, and all samples from IPWWTP 5, particles with a pigment spectrum were analyzed. As the authors' own experience suggests, sometimes a high pigment concentration in particles leads to an undetected polymer spectrum. In these samples, 1 · 10^2–1 · 10^4 pigmented particles per m^3, mainly consisting of copper phthalocyanine, were measured and could mask MPP. All pigmented items found are listed in Appendix A. In addition, losses of MP due to sampling preparation and detection must be taken into account (Weber and Kerpen, 2022). Therefore, all MP concentration data given should be considered as minimum concentrations.

The effluents from four IPWWTPs analyzed using DSC showed that the mass concentrations of total MP ranged between 0.2 and 10.8 mg m^{-3}, with a median of 3.7 mg m^{-3} (see Fig. 8A). Overall, most MP masses (55 %) were detected in the smallest size range sampled, at 10 to

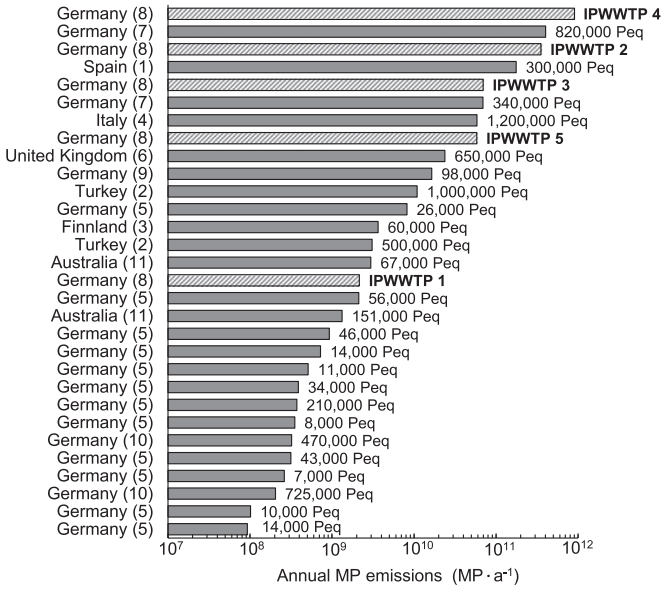

Fig. 6. Annual MP emissions from WWTPs with its population equivalent (Peq) from studies with comparable sampling, preparation, and analysis, in the following described as (number) study; analysis method, smallest measurable particle: (1) Edo et al. (2020), FTIR, 25 μm; (2) Gündoğdu et al. (2018), Raman, 55 μm; (3) Lares et al. (2018), FTIR/Raman, 25 μm; (4) Magni et al. (2019), FTIR, 10 μm; (5) Mintenig et al. (2017), FTIR, 20 μm; (6) Murphy et al. (2016), FTIR, 65 μm; (7) Roscher et al. (2021), FTIR, 11 μm; (8) this study, 10 μm, Raman; (9) Wolff et al. (2019), Raman, 10 μm; (10) Wolff et al. (2021), Raman, 10 μm; (11) Ziajahromi et al. (2017), FTIR, 25 μm.

<100 μm; on average, 26 % of all MP masses were analyzed in the size range of 100 to <1000 μm and only five samples showed MP masses in the size range from 1000 to 5000 μm, with an overall proportion of 19 %. As a detection method for semi-crystalline MP, DSC is comparable to other mass-based methods (Becker et al., 2020). The mass concentrations measured were in the same order of magnitude as the values from German municipal WWTPs presented in Roscher et al. (2021) and Primpke et al. (2020), which were analyzed using pyrolysis gas chromatography. Estimated daily MP emissions into the environment ranged from 3.2 to 646 g

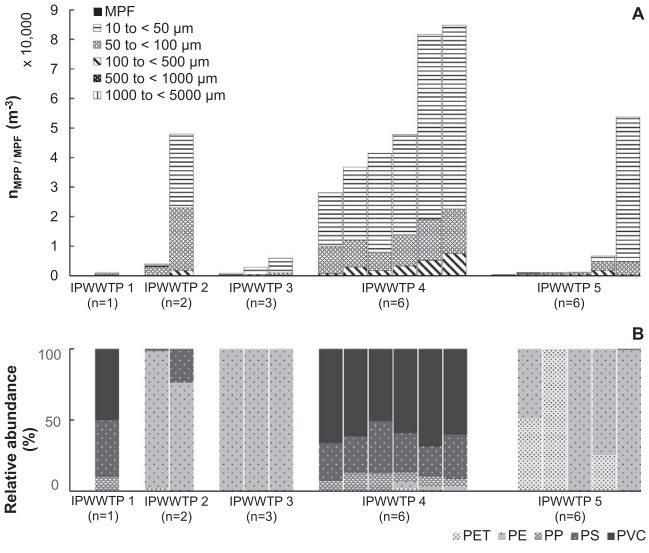

Fig. 7. μ-Raman spectroscopy analysis of five different effluents from IPWWTPs. A) MPP/MPF counts per cubical meter with a size distribution, B) relative abundance of MPP polymer distribution.

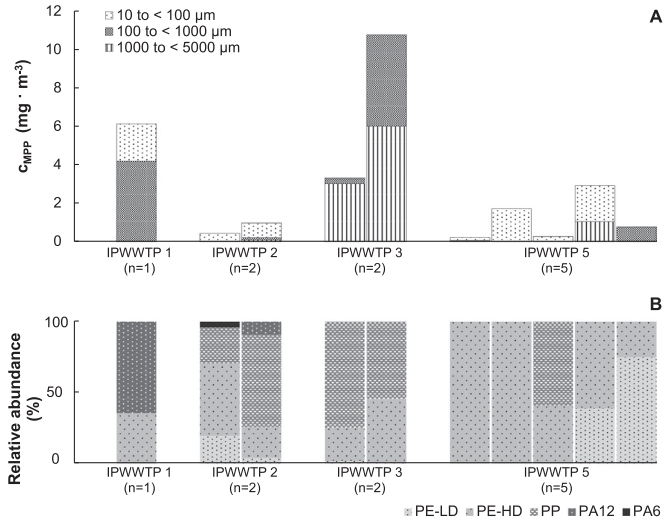

Fig. 8. DSC analysis of four different effluents from IPWWTPs. A) MP mass per cubical meter with a size distribution, B) relative abundance of MP polymer distribution.

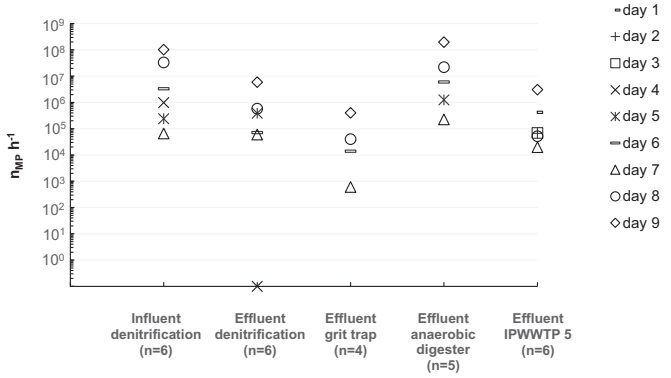

Fig. 10. Total MP number per hour discharged on different days from IPWWTP 5 sampling points.

d^{-1} with a median of 29 g d^{-1}, which can be compared to the four municipal WWTPs sampled and analyzed using DSC analysis by Bitter et al. (2022), with MP emissions of 4.5 to 117 g d^{-1}.

In every sample, PE-LD was found, PE being the most common polymer overall (see Fig. 8B). In IPWWTPs 1 and 2, PA was found, and in three out of four sampled IPWWTPs, PP was present.

Despite simultaneous sampling for µ-Raman and DSC analysis, polymer abundances differed. Under µ-Raman analysis PP items were found only in IPWWTP 1, but PP masses were only detected with DSC analysis in IPWWTPs 2 and 3. Also, PET items were detected in samples from IPWWTPs 2 and 5, but no PET mass was analyzed using DSC analysis. This illustrates the need for different approaches in the discussion of mass and particle number analysis, due to factors such as varying emphasis on particle sizes, required sample volumes, and sample preparation-related deviations. To this end, Primpke et al. (2020) have highlighted the complementarity of mass and particle analysis in greater detail.

3.2.4. MP distribution in IPWWTP 5

The relative abundances of MPF and MPP size ranges and polymer types in IPWWTP 5 are shown in Fig. 9. In the effluent, mainly PE, PET, and a few PS particles were found. In contrast, the polymers PE, PET, PP, PVC, a large number of PS particles, and, in exceptional cases, polymers such as PC, polyphenylene ether (PPE), polyphenylene sulfide (PPS), and phenoxy resin were found at sampling points one to four. No trends were apparent in polymer distribution along the sampling points. High levels of PS within the plant and which were not found in the effluent appeared to have been removed by the aerobic treatment and final clarifier. The concentrations of PE and PET in the total effluent may have been increased by the second influent of a cellulose processing plant which could not be sampled separately. Likewise, an increase in these polymers could be due to a release

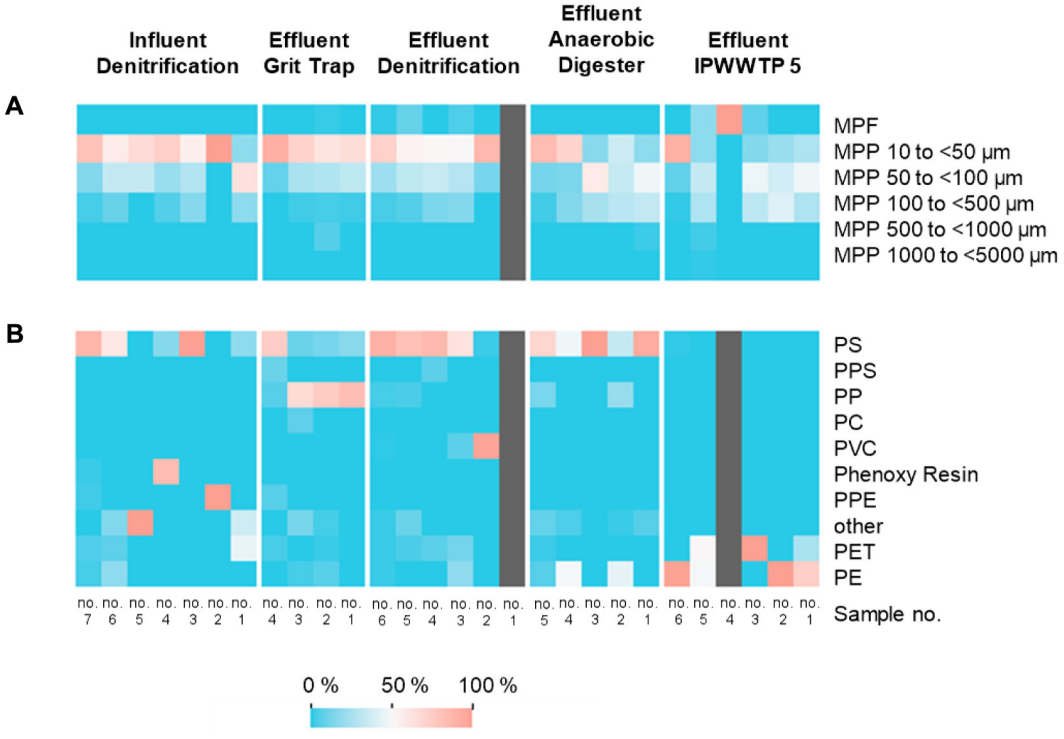

Fig. 9. Heat map showing relative abundance (A) of MPP in different size ranges and MPF at the IPWWTP 5 sampling points, (B) of MPP polymer types at the IPWWT 5 sampling points.

from the PE pipe system (Zhang et al., 2021) or the abrasion of other plastic compounds at the plant. MPF with a length > 100 μm were found mainly in the total effluent and denitrification effluent. At every sampling point, most frequently MPP ranging from 10 to <500 μm (99.9 % on total average) were detected, with a large amount of MPP ranging from 10 to <50 μm (76.8 % on total average) found at sampling points one to four and slightly larger particles measuring up to 10 to <1000 μm in diameter found in grit trap effluents. High forces and abrasion within the sand filter did not seem to have a significant effect on MPP sizes.

The effluent concentrations showed a high variation in particle number concentrations (see Fig. 7). To obtain a better understanding of MP behavior and removal rates within IPWWTP 5, total MP numbers per hour were extrapolated based on the wastewater flow rate during sampling. Fig. 10 shows the results per sampling point and sampling day. At one sampling point, the total MP number per hour sometimes differed by up to four log units between sampling days, but trends within a sample day across treatment steps were apparent. In the sand filter denitrification process, MP seemed to be removed at rates of 94–100 %, with two outliers at day 5 (−61 %) and day 7 (10 %). Overall, this is comparable to the results obtained by Wolff et al. (2021). Even the grit traps seemed to have an additional benefit in reducing MP numbers in the rinse water, with a median of $3 \cdot 10^6$ MP m^{-3} lower effluent concentration compared to the sand filter denitrification effluent. This treated rinse water and denitrification effluent made up the inlet for the hydrolysis and anaerobic treatment. In the anaerobic digester effluent, MP numbers per hour were 1–2 log units higher than in the inlet within a sampling day.

As several studies have shown, MP in municipal WWTPs mostly end up in sewage sludge (Horton et al., 2021; Salmi et al., 2021; Lares et al., 2018) and even nanoplastics can attach to the surface of biomass (Fu et al., 2018; Feng et al., 2018). MP may be included or attached to the biomass in question and may also accumulate in the anaerobic digesters, as Maliwan et al. (2021) reported for membrane bioreactors. The TSS load in the effluent from the reactors was 2.6 ± 0.5 higher on average when compared to the inlet during sampling. It was possible to buffer peak loads of MP before sampling using the reactors; they could be released again with a time delay. Likewise, the granulated sludge might have been heavily loaded with MP prior to reactor filling. Generally, sludge from paper mill WWTPs is used for the inoculation of these reactors, which takes place only once every few years. Due to the robustness of the data, it is more likely that an external release of MP into the anaerobic treatment is responsible for high MP loads in its outlet. Therefore the analysis of added chemicals, such as the dosage of NaOH during hydrolysis, should be taken into account. Further research is needed to fully understand the behavior and occurrence of MP in anaerobic granulated sludge reactors.

The second influent from a cellulose processing plant into the aerobic treatment step (see Section 2.1) could not be sampled because of poor accessability. Despite of 23 % unknown influent, the results showed that aerobic treatment and a final clarifier had a major impact, with an average removal rate between the anaerobic digester effluent and the IPWWTP 5 total effluent of 96 % on days 7, 8, and 9. This underlines the impact of these treatment steps for MP removal within WWTPs. Here, activated sludge proposes as sink for MPs. Sludge from the primary sedimentation and final clarifier are treated together in a dehydration and then incineration, as it is state of the art for sludges from IWWTPs in Germany.

This data presented, based on 2 h sampling, seems to fit present total MP numbers per hour and their distribution over several days within an IWWTP. However, to further monitor inconsistent MP concentrations, it would be useful to determine the size and polymer distributions in a larger number of samples within a day or 24 h samples over a longer period of time.

There are a multitude of factors which have an impact on MP discharge by IPWWTPs into the environment, such as polymer production or processing plants and their production schedules within the IP, installed treatment steps, retention times within the IPWWTP, and additional influents. The data from this study are meant to be a first step in understanding this complex situation. To fully understand MP emissions by IPWWTPs, further research and long-term studies are needed.

4. Future research perspectives and recommendations

- Mass and particle analysis are complementary and should be conducted simultaneously. Due to the varying requirements of each type of analysis, simultaneous sampling and sample preparation for the two methods should be standardized to generate comparable data across research groups. This is especially necessary in the case of challenging sampling locations within industrial sites, where temperatures, pH values, conductivities, or solids contents can vary greatly from those in municipal sampling situations.
- In the anaerobic digester examined here, MP concentrations in the effluent were higher than in the influents. Possible reasons for this should be investigated.
- MP concentrations within IPWWTPs fluctuate greatly from day to day. Further research is highly recommended to determine the degree of fluctuation.
- The initial analysis indicates that within IPs, MP in the wastewater system can be allocated to its dischargers. This could be relevant to future regulatory requirements. More extensive sampling within several IPs is needed for confirmation.
- To the authors' knowledge, research on Industrial MP emissions into the aquatic environment from plastics industries located in IPs is scarce. Further research is required to assess their overall impact on MP emissions into the environment in detail.

5. Conclusion

- It is confirmed that in the plastics production plants sampled in this study, the polymers produced generally occur as MP in the discharged wastewater.
- The initial analysis indicates that within IPs, MP in the wastewater system can be allocated to its dischargers. This could be relevant to future regulatory requirements. More extensive sampling within several IPs is needed for confirmation.
- Total MP numbers per day within IPWWTPs fluctuate greatly over time.
- Influent analysis data for MP are scarce, but the data that exist indicate that MP particle concentrations in influents to IPWWTPs and municipal WWTPs are similar.
- MP effluents emitted into the environment from IPWWTPs have MP particle and mass concentrations comparable to those of municipal WWTPs. There are fewer IPWWTPs in Germany (approximately 60, according to VCI (2012)) than municipal WWTPs (approximately 9166, according to Schmidt et al. (2020)). However, an IPWWTP's total amount of MP emissions per year is comparable to that of some municipal WWTPs described in the literature. This leads to the conclusion that IPWWTPs might be a significant point source for local aquatic ecosystems. But industrial MP emissions may not make a large overall contribution to the small role of WWTPs as source of plastics emitted into the environment when compared to major sources, such as weathered mismanaged waste or tire abrasion (Bertling et al., 2018).

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.163349.

CRediT authorship contribution statement

Luisa Barkmann-Metaj: Conceptualization, Methodology, Validation, Formal analysis, Resources, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **Felix Weber:** Validation, Resources, Investigation, Writing – review & editing. **Hajo Bitter:** Resources, Investigation, Writing – review & editing. **Sebastian Wolff:** Resources, Investigation, Writing – review & editing. **Susanne Lackner:** Writing – review & editing, Funding acquisition.

Jutta Kerpen: Writing – review & editing, Funding acquisition. **Markus Engelhart:** Writing – review & editing, Supervision, Funding acquisition.

Data availability

Data is included in the appendix.

Declaration of competing interest

The authors declare that they have no conflicts of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Acknowledgments

The authors would like to thank the companies involved for allowing access and for their cooperation.

Funding

This work was part of the EmiStop project, funded by Germany's Federal Ministry of Education and Research (BMBF) as part of the "Plastics in the Environment - Sources•Sinks•Solutions" initiative within the BMBF "Research for Sustainable Development" (FONA3) framework program with grant number 02WPL1444A-E.

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