Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy

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ABSTRACT

Samples from the secondary clarifier effluent of a waste water treatment plant (serving 98500 inhabitants) were analyzed to determine the microplastics (MP) emission.

The samples were collected using a stainless steel centrifugal pump and filtered through a 10 μm stainless steel cartridge filter. Microplastics particles (MPPs) and microplastics fibers (MPFs) were recovered by chemical and physical sample purification. To remove natural organic matter, the samples were first subjected to oxidative treatment with H2O2 and NaClO. Inorganic materials were subsequently removed by density separation in ZnCl2 (ρ = 1.9 g/cm3) using a centrifuge. Special centrifuge tubes were developed for this purpose. Sample analysis was performed on a Si filter by Raman micro-spectroscopy. Particles with a diameter (dp) ≥ 10 μm were analyzed.

The results were differentiated by dry and wet weather samples. On average, 5900 MPPs m⁻³ were identified in the effluent on wet weather days compared to 3000 MPPs m⁻³ on dry weather days. Most of the MPPs detected were in the 30 μm < dp < 100 μm size range. The MPFs ranged between 100 μm and 1000 μm in length. While most of the MPFs were of PET origin, the MPPs consisted mainly of PET, PP, PE and PS.

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1. Introduction

Plastics have been mass-produced for more than sixty years. Their high durability on exposure to the most diverse media and environmental conditions combined with their versatile manufacturing methods and applications have made plastics highly attractive materials in our modern society (Ehrenstein and Pongratz, 2007). Since 1950 world production of plastics has been continuously expanding (PlasticsEurope, 2009, 2018).

There are manifold pathways by which plastics are introduced into the environment. Plastics enter the water cycle through wind entrainment, urban surface runoff1 or improper disposal practices and ultimately end up in the sea (Dris et al., 2015). Estimates for 2010 show that up to 12.7 million tonnes of plastics entered the oceans through riverine inputs worldwide (Jambeck et al., 2015). MP is ubiquitous in marine ecosystems and many inland waters (Wu et al., 2018). Plastics input into the environment through anthropogenic sources is substantial and still increasing.

Under the influence of abiotic (e.g. UV radiation) and biotic processes (biodegradation), plastic items break down into increasingly smaller particles (Ojeda et al., 2011; Andrady, 2011), forming secondary MP. MP have been defined as synthetic organic polymer particles with a size of <5 mm. Particles <1 mm are sometimes referred to as small MPPs. There is no standard definition (Moore, 2008; Browne et al., 2008; Miklos et al., 2016). The lower size boundary for MPPs is 100 nm. Particles smaller than 100 nm are classified as nanoparticles (ISO/TS 80004–2:2015). Primary MP include particles that are purposefully manufactured in the required sizes for use as fillers or abrasives in paints and toothpaste (Lassen et al., 2015).

From ecotoxicological aspects, MP are a source of concern as they can be mistaken for food and ingested by marine organisms (Thompson et al., 2004; Browne et al., 2008; Setälä et al., 2014). Studies have demonstrated that organic pollutants are sorbed to plastics at concentrations multiple times higher than in natural sediments (Teuten et al., 2007). Once ingested, additives contained in or pollutants sorbed onto plastics can be released again in

1 Surface runoff to the sewer system during precipitation events.
organisms (Batel et al., 2016). In vertebrates and invertebrates, MP ingestion can lead to reduced growth and fecundity, physical damage to the digestive tract through intestinal blockage, impaired enzyme production and adverse effects on the hormone level, etc. (Wright et al., 2013).

Currently, many research groups are engaged in the analysis of MP in surface waters, sediments, living organisms, food and hygiene products. In many MP studies, light microscopy was used for sample analysis. A comparison of the visually identified MPPs and MPFs with analysis results from FTIR and Raman spectroscopy has shown that up to 70% of the finds are false positives (Hidalgo-Ruz et al., 2012; Lenz et al., 2015). The reliability of visual identification methods decreases significantly in particular for MPPs <100 μm (Lenz et al., 2015). Analysis by FTIR spectroscopy reaches detection limits of down to 20 μm (Loder et al., 2012). Raman microspectroscopy can identify particles down to 1 μm in size (Ivleva et al., 2017) and pyrolysis GC-MS allows the polymer types of particles > 100 μm to be identified (Dekiff et al., 2014). So far, there are very few studies using Raman or FTIR spectroscopy for MP analysis in waste water.

Therefore in the present work an analysis method was developed to determine the MP concentration in the secondary clarifier effluent of a municipal waste water treatment plant (WWTP) using Raman microspectroscopy. The effluent sample from the secondary clarifier was concentrated on a stainless steel cartridge filter. Subsequent sample processing involved oxidative treatment to decompose natural organic matter present following density separation to remove inorganic material.

There are several different approaches to density separation. The common feature is the use of a salt solution with high density (e.g. ZnCl2, NaI, sodium polytungstate etc.) to separate MP from inorganic particles. In some studies, a separation funnel is used for separation (Mintenig et al., 2017; Vollertsen et al., 2017) and in other studies a centrifuge is used (Carr et al., 2016; Ziajahromi et al., 2017; Gündoğdu et al., 2018). When using a separation funnel, especially small particles are adsorbed at the glass wall of the thin outlet. Using a centrifuge it is not possible to quantitatively transfer MP by simply decanting. Within the scope of this study, the method of centrifugation was further developed. By using flexible centrifuge tubes made of silicone, quantitative transfer of MP is possible. Therfore the silicone tubing is being pinched off and then decanted. Adsorbed MP can be rinsed off multiple times, subsequently.

2. Materials and methods

2.1. Equipment and materials

To minimize sample contamination through airborne fibers/particles, virtually all work steps were conducted in a laminar flow box (MSC Advantage 12, Thermo Fisher Scientific Inc., USA). Contamination through plastic tools/materials was minimized by using glass and stainless steel equipment with the following exceptions:

- polyethylene (PE)/polypropylene (PP) (original chemical containers)
- polycarbonate (PC) (filter membrane for water and chemicals filtration)
- acrylonitrile butadiene rubber (NBR) and polytetrafluoroethylene (PTFE) (pump seal)
- silicone (pump inlet hose, filter gasket, centrifuge tubes)
- perfluoroalkoxy polymer resin (PFA) (squit bottle)

NBR, PTFE, PFA and PC do not count among the plastics normally encountered in municipal waste water (Mintenig et al., 2017) and were therefore not considered in the analyses. As the use of silicone was unavoidable, silicone was not considered either. PE and PP were analyzed because all chemicals were filtered through an 0.6 μm fiberglass filter (MN85/70 BF, Macheray-Nagel GmbH & Co. KG, Germany) and an 8 μm polycarbonate filter (TETP 04700, Merck KGaA, Germany) prior to use in order to remove particulate contaminants. The polycarbonate filter was used to retain glass fibers entrained from the fiberglass filter.

The equipment and materials used were rinsed with filtered deionized water prior to use. Rinses with filtered deionized water and n-hexane (HiPerSolv CHROMANORM, VWR, USA) were carried out after each work step to ensure quantitative recovery of the MPPs. Because of its non-polar properties, n-hexane lends itself to the removal of adhering particles from surfaces. Preliminary trials with fluorescent tracer particles (Cospheric LLC, USA) had shown that particles < 20 μm can be quantitatively transferred by rinsing with hexane. This is not possible with water.

The deionized water was produced in a reverse osmosis unit (OS 3050, H + E GmbH, Germany) and then filtered using the same method as for the other chemicals employed (see above).

2.2. Sampling

The water samples were collected in the secondary clarifier effluent launder at the WWTP operated by the Rüsselsheim/Raunheim Sewerage and Water Board (serving 98,500 inhabitants, effluent rate: approx. 10,000 m³/d). The WWTP consists of a mechanical treatment stage and a biological stage comprising upstream denitrification, nitrification and biological phosphorus removal.

During the period of November 2017 to January 2018, seven grab samples were collected. The sampling apparatus (Fig. 1) consisted of a centrifugal pump (VGX 9/10, SPECK Pumpen Verkaufsgesellschaft GmbH, Germany) and a 10 μm cartridge filter (acuraScreen, Fuhr GmbH, Germany), both made of stainless steel, a stainless steel housing and a silicone hose (Techniplaza GmbH, Germany). The sample collection setup was adapted from the sampling procedure reported by Mintenig et al., 2017.

The cartridge filter was installed under laboratory conditions in the laminar flow box before sampling to prevent airborne contamination. The samples were collected on three dry weather and four wet weather days (Table 1). Prior to sampling, the pump was rinsed via a bypass (rinsing loop) for 3 min. Since the total amount of microplastics in the wastewater effluent is very low compared to the amount of inorganic or natural organic solids, the maximum possible amount of water was filtered. The filtered water volume was measured by a flow meter installed in the filter effluent line and was about 100 L on average (between 40 and 200 L). After sampling, the apparatus was thoroughly rinsed with tap water for 10 min followed by rinsing with 50 L deionized water.

2.3. Sample processing

2.3.1. Chemical purification

To obtain reliable results, the MP must be isolated from the sample matrix as completely as possible. While inorganic components can hide MP on the used silicon (Si) filter (see 2.3.2), organic material may lead to interfering fluorescence signals in Raman spectroscopy. Removal of organic material, e.g., activated sludge flocs and algae, was accomplished by treatment with oxidizing chemicals:

After sampling, the residual water in the cartridge filter housing was filtered through a disk-shaped stainless steel filter (Spörk KG, Germany) (same specifications as the mesh of the stainless steel cartridge filter) using an all-glass vacuum filter (Merck KGaA,
Germany). The loaded stainless steel filter cartridge was removed from the housing, placed into a 2 L beaker together with the stainless steel filter disk and treated with H₂O₂ (c = 50%, pure grade, Bernd Kraft GmbH, Germany) at 50°C for 24 h. Both filters were then rinsed and removed.

Next, the sample was filtered through a stainless steel filter disk (Fig. 2, left). The loaded filter was transferred to a 1 L beaker and treated with 400 ml NaClO (c = 12%, technical grade, Carl Roth GmbH + Co. KG, Germany) at room temperature for 6 days. The prepared sample was passed through another stainless steel filter disk for further concentration (Fig. 2, right).

### Table 1

| Sample no. | V_sample [L] | t_retention [h] | Classification |
|------------|--------------|-----------------|----------------|
| 1          | 84           | 51              | Dry weather    |
| 2          | 214          | 45              |                |
| 7          | 100          | 41              |                |
| 4          | 90           | 31              |                |
| 6          | 96           | 28              |                |
| 3          | 100          | 27              | Wet weather    |
| 5          | 41           | 16              |                |

**2.3.2. Density separation**

Inorganic particles (e.g. sand, glass, etc.) were removed by centrifugation (Sigma 3–16 L) in a ZnCl₂ solution (p = 1.9 g/cm³, pure grade, Carl Roth GmbH + Co. KG, Germany).

Using an ultrasonic cleaner (S 100 H, Elma Schmidbauer GmbH, Germany), the sample matrix was separated from the stainless steel filter disk and transferred to silicone centrifuge tubes (in-house construction, Fig. 3) that had been specifically developed for this purpose. Silicone tubes offer the advantage that they can be pinched off above the level of the heavy fraction at the bottom. Therefore there is no risk of mixing the light fraction with the inorganic fraction at the tube bottom while pouring out the tube. Floating MP were recovered from the supernatant by decanting and multiple rinsing with n-hexane by using a glass syringe (Fortuna Optima, 20 ml, Poulten & Graf GmbH, Germany).

The isolated MP were transferred to a Si filter (Smartmembranes GmbH, Germany) with a pore size of 10 µm and an area of 1 cm². Silicon was selected as a substrate because its Raman signals does not mask the polymer spectra of interest and it does not produce interfering fluorescence (Kappler et al., 2015), thus facilitating identification of the polymers. Other advantages of Si filters are the smooth surface and the uniform filter pores. To reduce the filtration area, a stainless steel funnel (in-house construction) was used for sample transfer to the Si filter (Fig. 3). The funnel reduces the diameter from 47 mm to 8 mm.

### 2.4. Raman microspectroscopy

Analysis was conducted using a Raman microspectrometer (DXR2xi, Thermo Fisher Scientific Inc., USA). Before scanning the sample with a 785 nm laser, an optical image was generated at 100× magnification. Other spectroscopy parameters selected were
a laser power of 20 mW, an exposure time of 0.025 s and a repetition rate of 10. The recorded spectral data were compared with the reference spectral library (ST Japan) by the instrument software (OMNIXi, Thermo Fisher Scientific Inc., USA) and read out as a chemical image. Identified MP are colour-coded by the software. To reduce the analysis time, a cross-shaped mapping area (see Mintenig et al., 2017) was analyzed. This sub-area represented 32% of the total filter area and was extrapolated to the total filter area for evaluation. MPPs/MPFs lying only partly in the mapping area were counted proportionally. All identified MPPs and MPFs were measured. For the determination of the MPP diameter, a mean value was determined from a minimum of two lengths each.

2.5. Method validation

2.5.1. Recovery rate

To quantify the sample losses during sample processing, the recovery rates were determined for the 90–106 μm and 250–300 μm size classes. For this purpose, spherical PE particles (Cospheric LLC, USA) of a defined diameter were counted before sampling and placed into the cartridge filter housing. Sampling, sample processing and analysis were carried out as described in 2.2–2.4. Recovery rates were determined for both the total filter area and the extrapolated cross-shaped sub-area (see 2.4). To find out if the chosen sub area represents the number of MP, the recovery rates of the MPP on the whole filter area and on the cross-shaped (extrapolated to the whole area) were compared. Due to their shape and specific colour, the particles can be readily identified and enumerated. No recovery rates were determined for microplastic fibers (MPFs).

2.5.2. Blanks

Sample contamination cannot be completely ruled out during the individual steps of the analysis procedure. Sources of contamination include airborne particles and fibers, contamination of the lab equipment, chemicals and the rinse water used. To quantify the contamination during the steps of the analysis procedure, the process was simulated without sample matrix. The blank determined covers analysis procedure as described in 2.3 and 2.4. This includes the use of all chemicals and other materials. Cleaned filters (stainless steel cartridge filters and stainless steel filter disks) were used for this purpose. The blank determination was carried out as a single determination.

2.5.3. Chemical resistance of plastics

Granulates of different polymers (Table 2) were exposed to H2O2 and NaClO as well as ZnCl2 and n-hexane to test them for their chemical resistance. The 7-day oxidative treatment of the samples produced very good results (Fig. 2). A shorter exposure period proved to be insufficient in preliminary trials. Reliable identification of the polymers depends on as complete a destruction of the organic polymers as possible.

3. Results and discussion

3.1. Sampling

The analyses described in this study relate to grab samples. Due to the high fraction of natural organic matter, the maximum filterable water volume was low and varied between 40 and 200 L. Under these conditions, it is difficult to collect composite samples. For the samples to be representative, composite samples are needed. Qualified grab samples could be a solution to improve the representativeness of the samples as against grab samples. Grab samples are unsuitable for determining diurnal and weekly MP concentration profiles. In future, the maximum filterable volume of treated waste water could be increased by using a cascade of a minimum of two cartridge filters with different pore sizes.

3.2. Sample processing

The 7-day oxidative treatment of the samples produced very good results (Fig. 2). A shorter exposure period proved to be insufficient in preliminary trials. Reliable identification of the polymers is as complete a destruction of the organic polymers as possible.

3.3. Raman microspectroscopy

In the case of spectroscopic methods, there is a conflict of interests between a high signal-to-noise ratio and a short analysis time. Main factors affecting the analysis time are the step size, the exposure time and the repetition rate.

According to the manufacturer of the Raman spectrometer used in the present study, a good signal-to-noise ratio is normally achieved with a repetition rate of 8–16 (Thermo Scientific, 2016). In preliminary trials, the effect of different repetition rates (n = 10/20/

| Polymer | Trade name | Polymer | Trade name |
|---------|------------|---------|------------|
| Acrylonitrile butadiene styrene (ABS) | Polylac 756 | Polyethylene terephthalate (PET) | Eastar AN014 |
| ABS | Terluran H1 10 | Polyamide (PLA) | Ingeo 4043D |
| Ethylene vinyl acetate (EVA) | Escorene UL 00728 | PP | Novolen 1102 L |
| Polyamide 6 (PA6) | Durethan B305 | Polystyrene (PS) | Empera 251 L |
| PA6 | EHTlamid B natur 1000 | Polyurethane (PU) | Desmopan 1080A |
| PC | Wonderlite 122 | PU | Desmopan 359 |
| PC/ABS copolymer | Bayblend T 85 XF | Polystyrene chloride (PVC) | Doeflex DVF 409-230 |
| PE (HD) | Lupolen 5021 D | Styrene acrylonitrile (SAN) | Starflex HF-5661 H |
| PE (LD) | ExxonMobil LD 605BA | | |
3.4. Recovery rate

For particles 250–300 μm, a recovery rate of 90% was determined for the total filter area. The recovery rate for the total filter area extrapolated from the cross-shaped sub-area was 47%. For particles 90–106 μm, the recovery rate was 66% for the total filter area; the extrapolated recovery rate was 71%.

The recovery rates were determined using spherical PE particles of different size classes. Such primary MPPs are rarely observed in a natural waste water matrix (Mintenig et al., 2017; Murphy et al., 2016). Biofilms on the particles or aged particles may have an impact on the particle behavior (e.g. surface adsorption behavior). The use of such defined particles only allows an approximate estimate of the recovery rate.

The recovery rates determined show that extrapolation of the particle counts for the cross-shaped mapping area can lead to over- or understatements. Further research will be needed.

In preliminary trials, a recovery rate of 80% was found for particles 250–300 μm. The recovery rate for particles 90–106 μm was 83%. In these trials, the complete filter area was analyzed without extrapolation. Compared to the preliminary trials, minor modifications were made to the procedural steps in this study. For this reason, the recovery rates of 47% and 71% determined for particles 250–300 μm and particles 90–106 μm respectively were classified as single determinations. The great variations between the recovery rates determined in the preliminary trials and the present study are partly attributable to the extrapolation of the particle count for the non-representative cross-shaped measurement sub-area. Further recovery studies will be needed.

3.5. Blank

Extrapolated to the total filter area, three PET particles and seven PET fibers, six PP particles and 25 PTFE particles were identified. In addition, 16 cobalt blue and copper phthalocyanine color pigments were detected that could not be assigned to a polymer. For nine particles, no match was found in the reference spectral library.

The few PP and PET particles are likely to have been introduced via the indoor air or contaminated equipment. PET fibers can also enter the sample via these pathways. As polyester fibers widely used in textiles normally also consists of PET (Baur et al., 2013), sample contamination with airborne textile fibers is likely. Of particular note are the determined PTFE particles. Given its density of 2.1–2.2 g m⁻³ (Baur et al., 2013), PTFE should actually have been separated in the density separation step. PTFE is used as a material for chemical process equipment, for anti-stick surface finishes and other surface coatings (Woebcken et al., 1998). Introduction via the laboratory tools and equipment cannot be ruled out.

The low blank value testifies to good laboratories practices and confirms the precautions and measures taken to prevent plastic contamination of the laboratory materials and equipment. A minimum of three blanks have to be run to be able to make a statistical statement.

3.6. Chemical resistance of plastics

Raw material manufacturers have published laboratory test results on the chemical resistance of their products (Bürkle GmbH, 2017). These results can be used as a reference for the durability of polymer resins. The chemical resistance tests performed as part of this study complement the raw material manufacturers’ information. They provide a clearer picture of the resistance of the polymers studied under the conditions of the applied MP separation procedure.

The results from the chemical resistance test of the plastic granulates are summarized in Table 3. The chemical resistance is ranked as follows (adapted from Bürkle GmbH, 2017):

1 – highly resistant
2 – resistant
3 – conditionally resistant
4 – not resistant

The tests showed that EVA, PA6 (EHLamid B natur 1000) and PU exhibit poor resistance to the chemicals employed. These plastic granulates showed changes in shape, mass, the Raman spectrum and partly also in colour. The PS granulate was classified as conditionally resistant as it showed major changes in the surface structure after treatment. The PA6 (Durethan B30S) granulate is chemically resistant under the conditions of the test method. PLA, PET and PVC exhibited a minor change in the visual appearance of the surface texture, but did not show any fractionation so that they were classified as resistant. Fractionation was only observed with PA6 (EHLamid B natur 1000). Unlike the tested starting materials PC and ABS, the PC/ABS mixture exhibited a slightly changed surface texture after treatment. SAN, ABS, PC, LDPE, HDPE and PP showed no changes in the characteristics investigated and were classified as
MPF-length was 3600 μm. 58% of the MPFs had a single determination (see 2.5.1 and 2.5.2). The highest particle Blanks and recovery rates were not considered because of the maximum MPP size was 1000 μm. Table 4 highly resistant.

The PE, PET, PP and PVC polymers frequently encountered in waste water samples exhibit good to very good chemical resistance under the conditions of the analysis procedure applied. Of particular note is the difference in the chemical resistance between the two different PA6 granulates. According to Bürkle GmbH, 2017 PA is not resistant to the applied chemicals. Depending on the application, plastics are blended with co-polymers or additives (Domininghaus et al., 2012). Therefore a general statement on their resistance is not possible. Based on the observed poor chemical resistance observed with EVA, PA6 ad PU, these polymers cannot be determined with the analysis procedure applied in this study.

3.7. Microplastics in the WWTP effluent

The size distribution of the measured particles in all samples is summarized in Table 4. Approx. 95% of all particles were in the 10 ≤ dp < 30 μm and 30 ≤ dp < 100 μm size classes. Few particles had a dp ≥ 100 μm and only two particles from the samples had a dp > 500 μm. The minimum MPP size in all samples was 10 μm and the maximum MPP size was 1000 μm. The MP size classes in the dry and wet weather samples show a similar distribution. Particles tend to be larger in dry weather conditions and smaller in wet weather conditions. All MP count results are rounded to two significant digits due to the sampling procedure (grab sample) and the extrapolation from the measured sub-area to the total filter area.

The size distribution of the MPFs is presented in Table 5. More than 80% of the MPFs had a length of between 100 μm and 1000 μm. 58% of the MPFs had a fiber width of between 10 μm and 30 μm. The minimum MPF-length was 20 μm and -width 2 μm. The maximum MPF-length was 3600 μm and -width 180 μm.

Table 4 Size distribution of MPPs in all samples.

| Polymer    | Change in mass | Change in visual appearance | Change in spectral change | Resistance |
|------------|----------------|-----------------------------|---------------------------|------------|
| ABS        | none           | none                        | none                      | 1          |
| EVA        | major          | major                       | minor                     | 4          |
| PA6 (EHLamid) | major       | major                       | minor                     | 4          |
| PA6 (Durethan) | none        | minor                       | none                      | 2          |
| PC         | none           | none                        | none                      | 1          |
| PC/ABS     | none           | minor                       | none                      | 2          |
| PE (HD)    | none           | none                        | none                      | 1          |
| PE (LD)    | none           | none                        | none                      | 1          |
| PET        | none           | minor                       | none                      | 2          |
| PLA        | none           | minor                       | none                      | 2          |
| PP         | none           | none                        | none                      | 1          |
| PS         | none           | major                       | major                     | 3          |
| PU         | major          | major                       | major                     | 4          |
| PVC        | none           | minor                       | none                      | 2          |
| SAN        | none           | none                        | none                      | 1          |

were identified in each sample. PET accounted for the largest share in all samples. PVC was detected in three samples. Polymethyl methacrylate (PMMA) and phenoxy resin were only found in Sample 7. Polysulfone (PSU) only occurred in Sample 5. The mean value across all samples was 3500 MPPs m⁻³.

The MPF counts for the individual samples are compiled in Fig. 5. The highest MPF count at 2500 m⁻³ was found in Sample 5 (wet weather sample with the shortest retention time in the WWTP), the lowest MPF count at 300 m⁻³ in Sample 1. In Samples 2–7, the PET fiber fraction dominates. PE fibers were detected only in Sample 2. PSU fibers occurred only in Sample 1. The mean value across all samples was 1100 MPFs m⁻³.

Fig. 6 plots the MPP and MPF counts as a function of the retention time of the waste water in the WWTP. Dry weather samples (retention time > 40 h) tend to contain fewer fibers and particles than wet weather samples. On average, the wet weather samples contained 4500 MPPs m⁻³ and 1500 MPFs m⁻³. The average MPP and MPF counts in the dry weather samples were 2300 m⁻³ and 730 m⁻³ respectively.

The MPP and MPF size distributions and the different polymer types identified underline the diversity of the matrix examined. From a particle size of dp ≥ 100 μm, it can be assumed that smaller particles will be hidden by these larger particles. This particle size is present in minor proportions, obviating the need for additional sample fractionation. The result of Mintenig et al., 2017 that most of the MPPs in municipal WWTP effluents are sized <500 μm was confirmed by the present work. The small number of larger particles in the treated effluent suggests that these are separated with the excess sludge. Mintenig et al., 2017 reports that 59% of the detected particles range between 50 μm and 100 μm in size. In the present study, 60% of all the MPPs found in the dry weather samples can be assigned to a comparable size class (30 μm–100 μm) (Table 4).

Due to the small number of grab samples analyzed, a statistically significant correlation between the retention time and the MP count cannot be established. The samples analyzed are indicative of an elevated particle input during wet weather and at short retention times in the WWTP. For the results to be statistically
significant, the number of samples analyzed would have to be increased significantly. Alternatively, representative results could be obtained by qualified grab samples.

The elevated MP count in the WWTP effluent during precipitation events can be explained by the higher flow velocity and hence the poorer settlability of the particles. Moreover, MP can enter the water cycle via urban surface runoff (Andrady, 2011; Dris et al., 2015).

The total dry weather MP load determined is in good agreement with the loads reported by Mintenig et al., 2017 who analyzed exclusively dry-weather samples. With an average dry weather total load of 3000 MPPs m⁻³, the Rüsselsheim/Raunheim WWTP lies in the range of the Schillig (approx. 2·10⁴ MPPs + MPFs m⁻³) and Holdorf WWTPs (approx. 1.4·10⁴ MPPs + MPFs m⁻³) mentioned in Mintenig et al., 2017.

In the WWTP effluents examined by Mintenig et al., 2017, polyester fibers predominated. This is confirmed by the results of the present study. It is obvious that the polyester fibers originate from textiles and have entered the WWTP effluent via the residential waste water. Introduction via the washing of polyester fiber-containing clothes decreases with increasing number of washings, and the release of fibers during tumble drying is approx. 3.5 times higher than during washing (Pirc et al., 2016).

In a Danish study, Denmark’s ten largest WWTPs were sampled. Particle sizes between 20 and 500 μm were detected. During dry weather, 5800 MPPs L⁻¹ were found on average. PE, PA and PP were identified in the WWTP effluent, PA accounting for the largest share. Fibers were not considered in the study (Vollertsen et al., 2017). In a further study the above mentioned ten largest WWTPs in Denmark were examined as well (Simon et al., 2018). With an average number of 120 MPPs L⁻¹, the results indicate a significant lower count of microplastic particles than the previous study. Nevertheless, the results mentioned are high, compared to other studies. It remains to be clarified whether Danish WWTPs emit multiple times more MPPs than the WWTPs in Lower Saxony or the Rüsselsheim/Raunheim WWTP.

Based on the results of various studies, Miklos, et al., 2016 calculated the median of the MP count per m³ of water from various surface waters, arriving at 3.28 MPPs m⁻³. The quantity of MPPs emitted by WWTPs is multiple times higher. MP emissions can be further reduced by an additional treatment stage, especially by a membrane separation process or by adding activated carbon followed by cloth or sand filtration. Thus, Mintenig, et al., 2017 report that tertiary filtration (cloth-media disk filter) at the
4. Conclusion

With the determination of the MP emission from a WWTP by Raman microspectroscopy, this study makes a contribution to identifying pathways of MP emissions to the environment. The characterisation of the MP load is crucial to the assessment of potential environmental impacts. Visual detection methods do not allow a reliable identification of MPPs. Due to major variations in the analysis methods applied, results are hardly comparable across research groups. A standardization of the sample processing and analysis procedures is needed. Based on the long analysis time with Raman- and FTIR-measurements, currently many research groups are analyzing only a sub area of the MPS. Due to major variations in the identiﬁcation of MPPs. An automated analysis method is currently under development. The aim is to further reduce the overall analysis time by excluding filter areas without particles from the measurement. Analyzing MP in environmental samples is a critical component to estimate their abundance and identify emission pathways. In a next step, MP separation from waste water, e.g., by ﬂocculaton and subsequent sedimentation or ﬂotation, should be investigated. The long-term goal is to prevent MP releases to the environment. For MP emissions into aquatic systems via WWTP eﬄuents, this means the identiﬁcation of emission sources. Moreover, a comparative study of MP releases through surface runoff and residential waste water in the sewer system would be helpful. If the main sources of plastics in the WWTP inﬂuence are known, MP releases to aquatic environments can be mitigated through appropriate treatment systems and education of industrial dischargers and consumers.

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