microplastics

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Reduction in the Input of Microplastics into the Aquatic Environment via Wastewater Treatment Plants in Germany

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Abstract: Microplastic (MP) has emerged as a significant environmental challenge due to increased plastic production and its widespread presence in the environment. This study aimed to assess MP concentrations throughout the treatment process at nine wastewater treatment plants (WWTPs) in Germany, from influent to effluent. A customized sampling technique was employed, followed by field and laboratory preparation and the quantification of polymers (PE, PP, PS, PMMA, and PET) using TED-GCMS. MP concentrations decreased progressively in the WWTPs, with influent concentrations ranging from 2.5 to 13.6 mg/L. Effluent concentrations in the conventional WWTPs ranged from 0.001 to 0.051 mg/L, while advanced treatment via filtration yielded concentrations below the limit of quantification at 0.005 mg/L. All tested of the WWTPs demonstrated an over 99% removal efficiency for microplastics. Despite effective retention by the WWTPs, a critical evaluation of the results is necessary. There is a need to optimize existing technologies and enhance the standardization of sampling, processing, and measurement methods, as well as intensify efforts towards creating preventive measures to reduce plastic emissions.

Keywords: urban water management; rotating sieve filter; TED-GCMS

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1. Introduction

1.1. State of Knowledge and Motivation

Over the past century, the production and consumption of plastics have rapidly expanded due to their diverse properties and applications. The fact that most plastics are non-biodegradable, which is advantageous for many products, poses a significant problem when it comes to disposal [1]. Various degradation processes and pathways continue to contribute to the formation of microplastics (MP) [2]. "Microplastics" is a colloquial term referring to solid plastic emissions, encompassing a wide array (>200) of individual plastics with distinct material properties and chemical compositions. According to ISO/TR 21960:2020 (en) [3], microplastics are defined as solid, water-insoluble plastic particles ranging in size from 1 µm to 1000 µm (=1 mm).

Microplastics enter the environment through many different pathways and can be found in all environmental compartments. They occur in the atmosphere [4], soil [5], ocean [6], and even in freshwater [7]. Urban wastewater is considered to be a major contributor to the transport of microplastic emissions to the aquatic environment. Either directly via stormwater runoff, combined sewer overflows (CSO), or discharge via wastewater treatment plants (WWTPs). But WWTPs can also lead to microplastic loads being retained in the urban water flow between the point of origin or release and the receiving water

body. Nevertheless, so far, studies on the retention of microplastics in WWTPs have had limited comparability and reproducibility due to differences in the sampling and analysis methods used. However, studies which were based on particle numbers showed that deviating particle size clusters in the influent and effluent of WWTPs differ by several orders of magnitude [8–12]. According to different researches [8,9,12–17], between 95% and over 99% of MPs are removed from the influent in WWTPs. Indicating that microplastic particles in WWTPs are largely removed from the wastewater and are primarily transferred to the sludge.

Microplastic accumulation in sewage sludge poses a potential risk to the environment and human health if the sludge is utilized as fertilizer. Microplastic particles transported to fields can thus be leached into groundwater [18] or otherwise can be further transported by wind or fluvial erosion. Rolsky et al. (2020) published an evaluation of land application rates in various countries [19]. For instance, Norway (82%), Ireland (63%), the US (55%), China (45%), and Sweden (36%) predominantly utilize it for agricultural purposes, while in Finland (89%) and Scotland (40%), it is commonly used as soil compost. However, if this treated sludge is directed to landfills, the possibility of MP particles entering the environment via landfill leachate exists. Nonetheless, the variability in sampling, processing, and analysis methods currently hinders the ability to provide precise assessments regarding the quantities and types of MP particles. This inconsistency presents a significant challenge to achieving comparability across different study outcomes [20].

In addition to this significant research gap, there is currently only limited reliable knowledge concerning the extent, precise origins, and pathways of microplastic pollution entering into water bodies, as well as suitable measures for reducing these inputs.

But the latest revision of the European Urban Wastewater Treatment Directive (UWWTD) creates immediate and practical incentives to further investigate microplastic emissions in wastewater. In alignment with the emphasis on organic micropollutants, the new UWWTD expands its scope beyond mechanical-biological treatment to prioritize their elimination. The UWWTD currently demands advanced wastewater treatment for urban areas with more than 10,000 inhabitants in catchments with sensitive water bodies. In this context, filtration processes, which are often used to eliminate phosphorus and trace substances, can also contribute to a further reduction in the amount of microplastics discharged from WWTPs.

With reference to the current state of knowledge and new regulatory demands, the general objective of this study is to present a mass-based MP quantification for the retention of microplastic particles in WWTPs and the additional removal of advanced wastewater treatment stages such as cloth filtration, microsieving, and spatial filtration (sand filters) on a large scale. A total of nine WWTPs in Germany were monitored during different sampling campaigns over a period of four years. Samples were analyzed for microplastics in the influent and effluent, and in some cases at different process stages. Due to the very good solids separation available in Germany, a good retention performance is expected.

1.2. Challenges in MP Quantification

Due to the variety of particle characteristics in terms of density, size, and shape, microplastics present as a particulate mixture of floating, suspended and sedimentable substances and are heterogeneously distributed throughout the different environmental compartments (soil, water, air). In addition, different stages of aging and degradation of the microplastic particles and their agglomeration and coagulation with other particles, as well as the formation of biofilms on the surface, complicate sampling and identification [20]. This makes analysis difficult, and intensive sample preparation leads to losses [21].

The aim of every analysis should thus be the reliable identification and quantification of polymers despite the complex matrix. To date, various methods of MP analysis have been made available, including visual, spectroscopic, thermoanalytical, and chemical. So far, the spectroscopic and thermoanalytical methods, especially in combination, have provided the most promising results [22,23].

Fourier transform infrared spectrometry (FTIR) and Raman spectroscopy (RM) are the main spectroscopic methods used to identify MPs and nanoplastics (NPs) [23–25] and are regarded as one of the most popular methods [26,27]. The number, size, and morphology of microplastic particles can be determined, but their mass cannot be quantified. Extracting the particles also requires complex sample preparation. Mass quantification can be carried out using thermoanalytical methods, which are destructive analyses where the samples are pyrolysed, followed by gas chromatography (GC) and mass spectrometry (MS) [28,29]. The analysis is qualitative and quantitative, but does not provide information on the morphology, size, or number of particles.

The amount of microplastics in a given matrix can be measured by spectroscopic methods in different ways, such as particle number (MPP). The result is either given by area (e.g., MPP/m^2, MPP/km^2 for open waters) or by volume (MPP/m^3) and is primarily used for ecotoxicological assessment, for example [30]. Thermoanalytical methods lead to the quantification of MP as mass concentration with volume reference (e.g., mg/L, µg/L) [29,31–34]. A conversion between the two parameters, particle number and mass concentration, is not possible for environmental samples [35]. Both methods are justified and they can result in a more coherent understanding if they used in combination [22].

In the thermoanalytical method, consisting of thermoextraction and desorption followed by gas chromatography–mass spectroscopy (TED-GCMS), a relatively large amount of sample is pyrolyzed, without further extraction, and the degradation products are measured indirectly in the GCMS [29,30]. The pyrolysis of polymers produces specific markers or degradation products. The pyrolysis process takes place in a thermogravimetric analysis (TGA). The decomposition products of the sample and the polymers in the decomposition gases are passed over an adsorbent. In the decoupled GCMS the decomposition products are desorbed, chromatographically separated, and detected [33]. An advantage of TED-GCMS is the low effort required for sample preparation [36]. However, this also leads to the main disadvantage of this measurement technique: matrix effects occur, which cause overlaps in the chromatograms and some polymer markers cannot be clearly identified [37]. This particularly affects the evaluation of PE [38]. These overlaps can lead to over-quantification or underestimation.

The main challenges in the determination of MP in environmental samples are the lack of standardization and the high technical effort involved in the analysis. The literature presents a variety of methods for sample preparation, analysis, and evaluation [20,39]. However, a retrospective and comparative analysis of the literature is difficult due to the different methods used. In urban water management, mass concentrations or the resulting loads are commonly used, e.g., TOC, COD, or PAH. For this reason, a thermoanalytical method was chosen in this work to determine mass concentrations of microplastic in the urban water system in Germany. Due to the high sample throughput, a low amount of sample preparation was also considered. The TED-GCMS, was developed for this purpose and was, therefore, chosen as the analytical device [29,32].

2. Materials and Methods

2.1. Reference Material

In the present study, Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyethylene terephthalate (PET), Polymethyl methacrylate (PMMA) were investigated in the WWTP samples. The polymer standards were mainly provided as powder by Federal Institute for Materials Research and Testing (BAM) and from Polymer Standards Service (PSS-Polymer). The polymer standards had a particle size range with an upper separation limit of 1000 µm and a lower separation limit of 10 µm. These polymers were chosen because they are the most commonly produced ones and they can be quantified in the TED-GCMS [40,41]. For the purposes of the work in the present study, the individual polymers have been summarized as microplastics (MPs).

2.2. Operation Procedure

Due to the ubiquitous distribution of microplastics, there is a risk of contamination throughout the analytical chain. For this reason, it is important to ensure plastic-free or low-plastic working conditions, which is also important with regard to the abrasion of parts that do not come into contact with the medium. Silicone tubing, stainless steel or glass containers, stainless steel submersible pumps, and special peristaltic pumps were used. The work was carried out during the coronavirus period, but care was taken to work without FFP2 masks wherever possible. Lab coats and cotton clothing were worn in the laboratory, and all containers and syringes were made of glass or ceramic. Strict quality assurance, which includes the collection and evaluation of blank values during all analysis steps, is essential in this context and was also incorporated.

2.3. Investigated WWTPs

In Germany, 97% of the population is connected to the public sewerage system. The domestic wastewater of 83,073,000 people is treated in 8891 WWTPs [42]. Depending on the population equivalents (P.E.), WWTPs in Germany are divided into different size classes (size class—1: < 1000 I 2: 1001–5000 I 3: 5001–10,000 I 4: 10,001–100,000 I 5: > 100,000 I). The majority of the wastewater produced is treated in WWTPs in size classes 4 and 5. In 2019, the total volume of wastewater treated in Germany was 9.048 billion m^3, comprising 56.7% wastewater, 26% precipitation water, and 17.3% infiltration water [42].

Conventional wastewater treatment is based on mechanical wastewater treatment (screens and sieves, grit chamber, primary clarification) and biological treatment (usually in the form of natural wastewater treatment, trickling filters, or aeration tanks) with subsequent secondary settling, as shown in Figure 1. For the separation of solids, the screenings and grit chamber material, the light material/fat trap material, and the sewage sludge act as sinks.

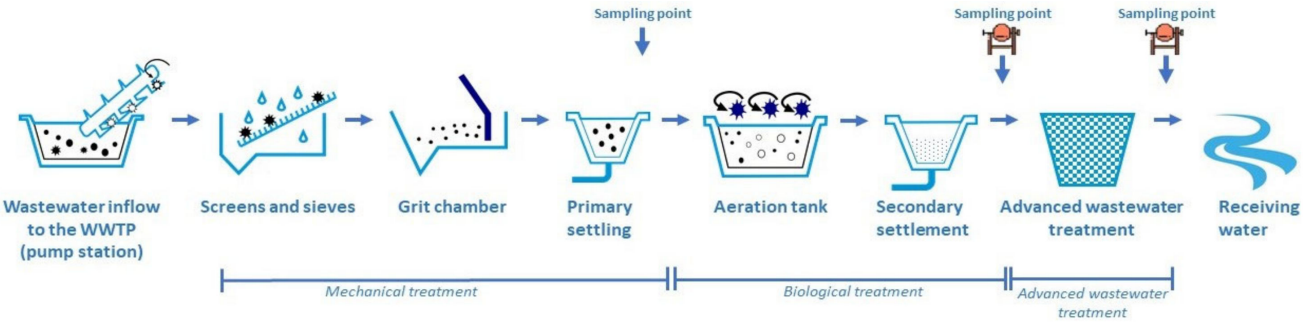

Figure 1. Wastewater flow diagram of a conventional wastewater treatment plant with additional wastewater treatment.

Table 1 provides an overview of the investigated WWTPs. The investigated WWTPs were selected according to their size class and the existence of advanced wastewater treatment. Some reference sites without advanced wastewater treatment were also included. A total of nine WWTPs in Germany were analyzed. These plants are located in both urban and rural areas and reflect typical wastewater conditions in Germany. Samples were typically collected in three measurement campaigns of 24 h each to smooth out fluctuations in the daily chart.

Table 1. List of sampled sites with size class, population equivalent (P.E.), annual effluent, and process structure of the WWTP, and dates of the sampling campaign.

Abb. of WWTPs	Size Class	Population Equivalent [P.E.]	Annual Discharge [m^3/y]	Process Structure	Sampling Period (24 h Composite Sample)
W1	5	428,000	19,185,643	Conv. mech.-biol. WWTP [1] with additional 2-stage filtration (1. fixed bed reactor with methanol dosing; 2. fine filtration with $FeClSO_4$ dosing)	06./07.08.2019 08./09.06.2021 09./10.06.2021
W2	5	400,000	15,977,064	Conv. mech.-biol. WWTP [1] with additional biological aerated filter	23./24.07.2019 01./02.06.2021 02./03.06.2021
W3	5	350,000	15,512,500	Conv. mech.-biol. WWTP [1] with additional pile cloth media filtration in pilot operation	30./31.10.2019 01.-04.11.2019 04./05.11.2019
W4	5	275,000	17,898,200	Conventional mechanical–biological wastewater treatment	16./17.06.2020 18./19.06.2020 27./28.10.2020 28./29.10.2020
W5	4	70,000	6,237,647	Conventional mechanical–biological wastewater treatment	18./19.05.2021 19./20.05.2021 20./21.05.2021
W6	4	93,000	1,788,410	Conventional mechanical–biological wastewater treatment with additional continuous sand filtration (grain size 1–2 mm)	30./31.07.2019 14./15.06.2021 16./17.06.2021
W7	4	20,000	557,972	Conventional mechanical–biological wastewater treatment with additional continuous sand filtration (grain size 1–2 mm)	13./14.08.2019 21./22.06.2021 22./23.06.2021
W8	4	100,000	1,012,199	Conventional mechanical–biological wastewater treatment with additional flock filtration by space-layer filter (0.7–8 mm grain size)	15./16.08.2019
W9	3	15,000	Not stated	Conventional mechanical–biological treatment in a Sequencing Batch Reactor (SBR)	17./18.08.2022 18./19.08.2022 23./24.08.2022

[1] Conv. mech.-biol. WWTP = conventional mechanical–biological wastewater treatment.

2.4. Sampling

There is a whole series of standards for the sampling of water in relation to different case scenarios, see, for example, ISO 5667 series [43]. According to current knowledge, sampling is determined more by its practicability than its representativity. Due to the different properties of the plastic particles mentioned above, it is practically impossible to represent all microplastics to the same extent in a single sample. When preparing a field sample, that means taking a partial sample from the total quantity; it is important to ensure that the sample is representative in terms of time and space [43]. For example, temporal fluctuations in the wastewater system should be compensated for by 24 h or better flow-oriented composite samples and spatial fluctuations in the water profile should be compensated for by multipoint sampling. Good mixing conditions for the entire quantity increases the probability of capturing the particles without selective exclusion. Therefore, sampling points with turbulent flow conditions were preferably selected (e.g., after a spill edge or points with increased flow velocity) [44].

The sampling volume depends primarily on the selected detection method and the associated limit of quantification as well as the particle size to be analysed. Depending on the solids content of the medium to be analysed, very large sample volumes (see WWTP effluent in Table 2) are sometimes necessary to generate sufficient analyte for MP detection.

Although the large sample volumes increase the representativeness of the sampling, they must be concentrated to a standard laboratory volume without contamination and losses.

Sampling of wastewater with high content of solids in the influent and effluent of the grit chamber as well as in the preliminary settling and aeration tank effluents was carried out with an automatic sampler (BasicEx 1 mobil, ORI Abwassertechnik GmbH, Hille, Germany). The sample volume was taken over 24 h (dosing 125 mL every 5 min), and collected in a stainless steel container. Larger sampling volumes are required for the effluent of the secondary clarification and for the effluent of the final filtration due to the very low solids concentration. Peristaltic or submersible pumps were installed at these points, which extract the wastewater continuously over 24 h. In order to avoid contamination of the sample, silicone hoses and stainless steel pumps were utilized for sampling. The usual sampling volumes are shown in Table 2:

Table 2. List of sample volumes depending on the solids content of the wastewater to be sampled.

Type of Wastewater	Sampling Technique	Sampling Volume [l]
Wastewater with high solids content	Peristaltic pump (automatic sampler)	1–25
Wastewater with low solid content	Peristaltic/submersible pump	800–5000

2.5. Sampling Preparation in the Field

In order to convert large sample volumes into a laboratory standard, the solids contained in the sample must be concentrated. A tried-and-tested principle for concentrating solids is separation by sieving. The problem with this method is the formation of a filter cake, which blocks the meshes of the sieve and reduces the flow rate. For this reason, an apparatus with a rotating and continuously rinsed sieve filter ("RoSi") was developed, see Figure 2. The apparatus essentially consists of an inclined, rotating sieve, which is continuously fed on the front side and rinsed back with filtrate from the underside. This prevents the build-up of a filter cake and a separation with a defined lower limit of 10 µm can be realized. Large-volume field samples (up to several m^3) can thus be concentrated to a volume of approx. 2 L. The feed can be applied manually or automatically by pumps. The volume flow can be adjusted using a slide valve, and peak flows of up to 2 L/s can be achieved. The apparatus is designed for mobile use and can be operated continuously over longer periods (>72 h). After the sieving process, the retained solids are rinsed back with a pressurized sprayer (6 bar), transferred to glass bottles via a stainless steel funnel, and collected as a laboratory sample (Figure 2).

Figure 2. Field sample preparation process using the rotating sieve filter (RoSi) to concentrate the solids (>10 µm) for large-volume sampling.

2.6. Sample Preparation in Lab

To determine the MP content in environmental samples, several steps are necessary, as shown in Figure 3. After sampling, the sample preparation and subsequent detection took place in the laboratory of the Department of Urban Water Management at the TU Berlin. The aim was to produce an analytical sample in the laboratory with as little contamination and loss as possible. This method is based on the separation of solid matter by freeze drying (GT) using Beta LSC+, Martin Christ. Therefore, the laboratory samples were first transferred into aluminium trays and dried for 52 h (0.370 mbar, 0 > 25 °C surface temperature). After determining the weight, the dry mass was homogenized for 5 min in a swing mill (MM 2000, Retsch Gmbh, Haan, Germany) at 80 rpm or, in the case of solids $\geq$ 5 g, in a planetary mill (Pulverisette 5, Fritsch GmbH, Idar-Oberstein, Germany). Before the sample was added to the crucible for TED-GCMS measurement, an internal standard (ISTD) was added as a relative reference. The analytical sample was then weighed to approximately 10 mg and measured in the TED-GCMS. To avoid contamination during sample preparation in the laboratory, the work was performed in flow boxes. Furthermore, only glass and ceramic containers were used. The TGA/DSC values obtained were processed to check homogenisation. The resulting GCMS chromatogram was analysed in the Agilent ChemStation with a detailed report of peak areas and other parameters as output. The MP content was determined using an external calibration with matrix inclusion and the response value of the report. The final MP concentration was calculated from the sample volume, dry residue, analytical sample weight, and MP content calculated from calibration.

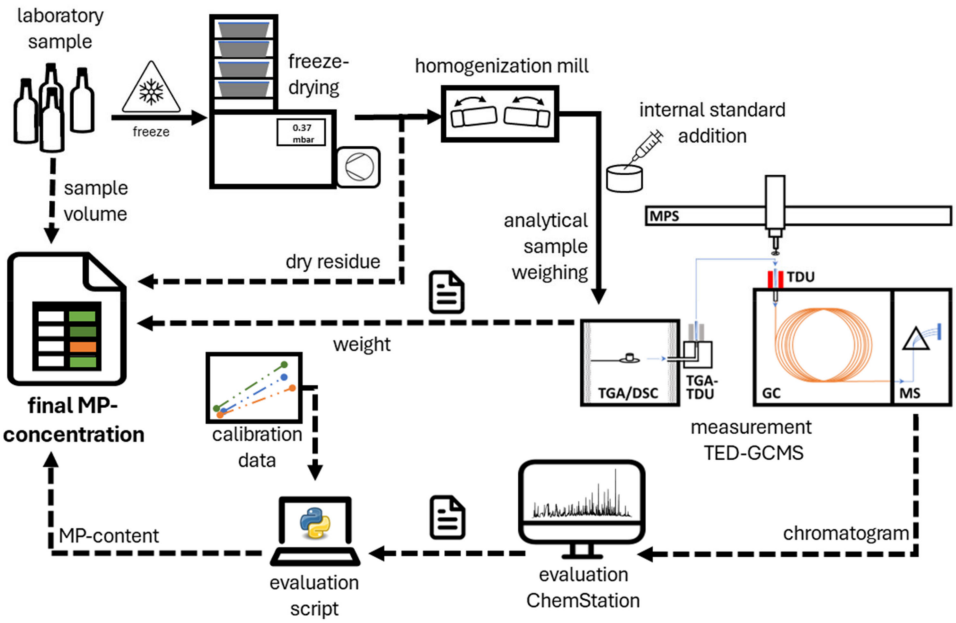

Figure 3. Rough work steps from sampling for determination of the MP content: solid line = sample path; dashed line = data path.

2.7. Detection

The measurement was performed using Thermal Extraction–Desorption Gas Chromatography Mass Spectrometry (TED-GCMS). The principle of this is based on detecting specific decomposition products of the polymers, that are formed during pyrolysis, in the GCMS. This involves coupling thermogravimetric analysis (TGA/DSC 3+, Mettler Toledo, Columbus, OH, USA) with GC and MS (GC 7890, MS 5977 Agilent, Agilent Technologies, Santa Clara, CA, USA). For the measurement, up to 10 mg of dried and ground sample was weighed. The crucible containing the sample was placed in the TGA oven at 25 °C and then heated to 600 °C with a heating rate of 10.5 °C min-1. During the measurement, the pyrolysis products were conducted with a purge gas (50 mL N 2/min) through a conditioned

thermal desorption tube filled with an adsorber material (Sorb-Stars Cat. No. 50 100, ENVEA GmbH, Poissy, France). After the TGA measurement, the tube containing the loaded SorbStar was removed and transferred to the thermal desorption unit (TDU) of the GC where thermal desorption was performed at 280 °C. The analytes were cryo-enriched at −100 °C before being injected into the GC. Cooling was performed with liquid nitrogen (N2). The analytes were then passed through the GC column with the helium carrier gas and chromatographically separated. A temperature gradient of 30–300 °C was used for accelerated separation and narrower peaks. In quadrupole MS, the analytes were ionized at 70 eV and measured in scan mode between MZ 35-350. The method was adopted and adapted from Dümichen et al. [29]; the exact method parameters can be found in the Appendix B Table A2. Triple measurements were always performed to better identify outliers and determine homogeneity using TGA data. Before each series of measurements, a blank crucible was measured without sample but with internal standard (ISTD). As ISTD, 4 µL of 8-deuterated styrene (PSS Polymers, Batch No: psd 83096, PDI = 1.03) dissolved in toluene was used as a relative reference value.

2.8. Evaluation

The MSD ChemStation software G1701AA from Agilent Technologies was used for data analysis. A quantization database was created using the markers of the polymers (Table A1, Appendix A). All markers of the respective polymer were included for quantification. The method includes other pyrolysis products, but they were not used for quantification. PE was quantified with *m/z* 81 and 55. Quantification of PS did not include styrene; this was used only for qualification. Values below the LOQ were automatically discarded. After calculating the MP content by external calibration with matrix inclusion, a statistical analysis was performed using a Grubbs outlier test with alpha = 0.5. The markers were not weighted, and the results were averaged.

2.9. Calibration

External calibration with matrix inclusion was used to calculate the results for each polymer mass content. For this matrix calibration, first polymers (5–150 µg) followed by the samples (10 mg) entered the TED-GCMS for measurement. The aim of this calibration method was to estimate the influence of matrix effects depending on the medium. Therefore, samples from different media were selected. The presence of sufficient solid matter and well-defined peaks, even without a spike, were necessary. Matrix samples included influent and effluent from the wastewater treatment plant, dewatered digested sludge, and river water. The environmental samples were also measured in triplicate without polymer spikes. The polymer peak areas of the sample measurements without spikes were averaged and subtracted from the results of the spiked measurements. The overall results were combined and analysed for all environmental media. The implementation corresponded to the standard addition combined with an external calibration.

The method's standard deviation, limit of detection (LOD), and limit of quantification (LOQ) were calculated following DIN 32645:2008-11 [45] (Table A1). Values less than the LOD were discarded and those less than the LOQ were not included in the final calculation.

3. Results

A quality control process was carried out in detail and will be published in a separate publication. The uncertainty of the measurements was estimated in accordance with ISO 11352:2012 [46] and was based on the recovery rates of each analysis step. Overall, the results of the quality control revealed a measurement uncertainty for the data sets collected in this study of 85%, composed of errors related to sampling (87%), sample preparation in the field (4%), sample preparation in the laboratory (31%), and the error of detection (20–41%).

In Figure 4, the MP measurements are plotted logarithmically as a bar chart. The bars are color-coded according to the proportion of each plastic type (PE, PS, PP). The

weighted average MP per treatment step is highlighted in a transparent color. It is based on the sample volume specified in µg/L. The MP concentrations in the WWTPs gradually decrease as treatment progresses. The mass concentrations ranged from 2.5 to 13.6 mg/L (weighted average 9.346 mg/L; n = 5) in the influent and from 0.5 to 11.0 mg/L (weighted average 3.035 mg/L; n = 25) in the effluent of the sand trap. In the effluent of conventional WWTPs, concentrations of 0.001–0.051 mg/L were measured (weighted average 0.0136 mg/L = 13.6 µg/L; n = 26) and in the effluent of the advanced wastewater treatment using filtration, concentrations of <0.0001 (limit of quantification)—0.005 mg/L (weighted average 0.001 mg/L = 1 µg/L) were measured. The microplastic eliminations show the same order of magnitude in each of the eight plants of different size classes and with comparable treatment technology. The microplastic removal efficiencies of all of the tested WWTPs were over 99%, indicating that the realized treatment technologies did not significantly differ in terms of their effects on the microplastic removal rate. Only advanced additional treatment could further remove MPs. Here, the slight differences in the effluent values are due to different operating modes, as the comparison of the effluent concentrations of the two identical sand filters demonstrates. The only increased discharge values were observed in WWTP W9, as anticipated, given that the discharge quality requirements applicable to WWTPs of smaller size classes are lower.

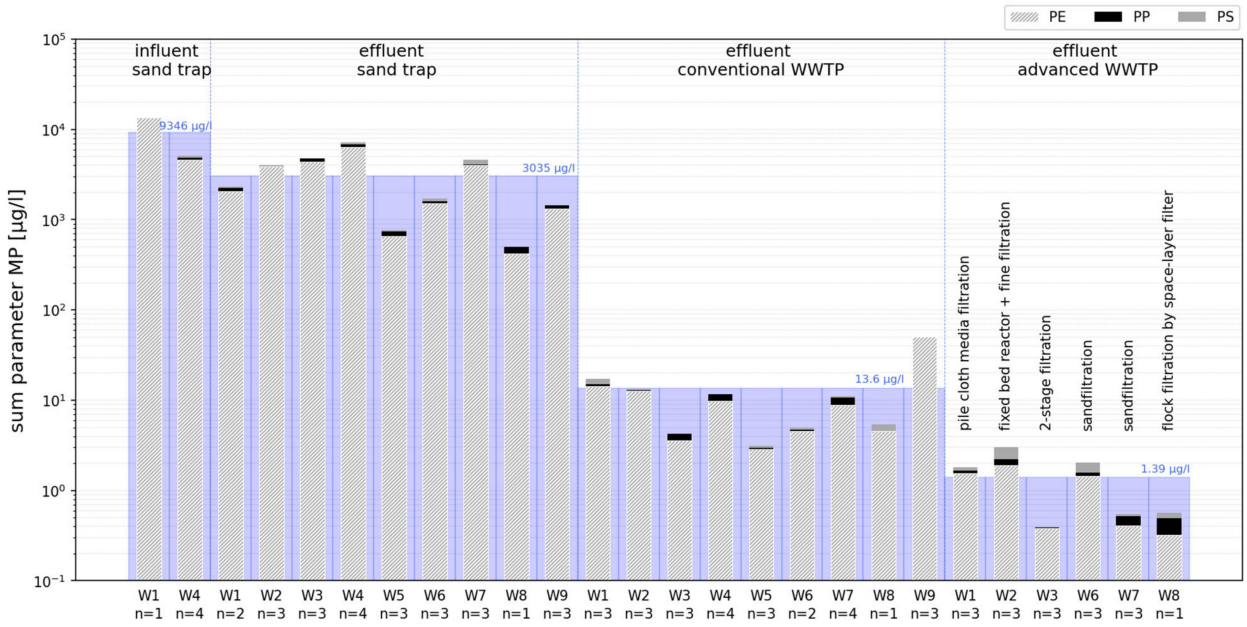

Figure 4. MP as a sum of the parameters of different WWTPs in µg/L with corresponding size classes. The course of the WWTPs is shown from right to left; the last stage shows the respective filtration of the advanced WWTPS.

In all of the WWTPs, PE was the predominant plastic type, followed by PP and PS. The plastic types PET and PMMA were not detected or were below the LoD. The average mass fractions were 91% PE, 6% PP, 3% PS in the influent and 89% PE, 7% PP, 5% PS in the effluent of conventional WWTPs and varied slightly in the effluent of advanced filtration by 75% PE, 13% PP, 13% PS.

In Figure 5, the MP concentrations of each process stage are graphically summarized as logarithmic boxplots. The distribution of the individual measurements can be seen as dots inside the boxplots. The concentrations of the MPs entering the screen or grit chambers are in the order of 10 mg/L in total. In the effluent of conventional wastewater treatment processes, values of 10^{-3}–10^{-1} mg/L are achieved. Downstream filtration processes result in values of 10^{-4}–10^{-3} mg/L and, when isolated, 10^{-2}—as a rule of thumb an order of magnitude of 1 µg/L could be assumed here.

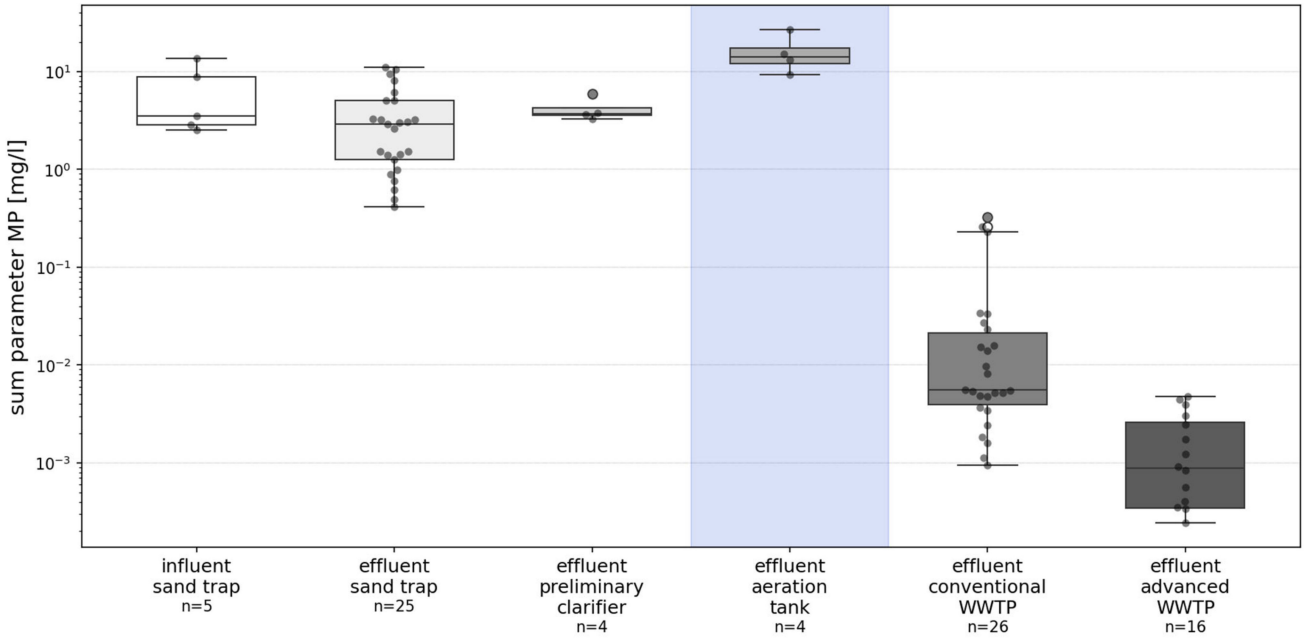

Figure 5. MP as a sum parameter in mg/L of different WWTP stages as boxplot. The box for the biological process in which the MP is accumulated is highlighted in blue in the centre.

The mean mass fraction of MPs in relation to the total solids in a wastewater sample is 1.8% in the influent and 2.4% in the effluent of sand traps and 3.1% after the preliminary treatment step. It decreases to 0.9% in the effluent of the biological treatment stage and remains at 1.1% in the effluent of the conventional and 1.0% after advanced wastewater treatment.

4. Discussion

4.1. Mass Concentration

The results are largely confirmed by thermoanalytical measurements by Spelthahn et al. (2019), Lee et al. (2023), and Altmann et al. (2023) [47–49]. Funck et al. (2021) measured PS concentrations in the same order of magnitude using pyr-GCMS [50]. Spelthahn et al. (2019) found an MP concentration of 10.4 mg/L in the influent and 0.0006 mg/L in the effluent of a WWTP [47]. Majewsky et al. (2016) found a concentration of PE of 0.081–0.257 mg/L in the effluent of WWTP using thermal analysis and differential scanning calorimetry (TGA-DSC) [51]. Xu et al. (2023), in contrast, determined the mass concentrations of total MP in the influent of two tested WWTP to be in the magnitude of 0.026 mg/L [52]. Lee et al. (2023) estimated the MP concentrations in the influent and effluent of WWTP using TED-GCMS with maximum values of 0.16 mg/L and 0.001 mg/L [48].

Considering the measurement inaccuracy, the results are within a tight range and fluctuate within an order of magnitude. During the treatment process in the WWTP, the MP concentration in the incoming wastewater is gradually reduced. A higher concentration of MP can be observed in the effluent of the biological treatment stage (see effluent aeration tank in Figure 5). The values indicate the incorporation of MP into the biomass and the discharge via the sludge path. With regard to the further environmental fate of MPs, it is important to distinguish between the various disposal options for MP-enriched sludge. In 2022, 80% (1.34 million tons) of sludge from municipal WWTPs in Germany was thermally recycled [53]. In this case, it can be assumed that the plastic particles are also incinerated and eliminated. As already mentioned, the load of microplastics in sewage sludge is of importance in the international environmental context when sewage sludge is used as a fertilizer. MP particles may affect processes in soil ecosystems [54] or be transferred to other environmental compartments [18]. There are only limited results on mass-related

MP concentrations in sludge. For example, Dierkes et al. (2019) describe concentrations of 3.7–3.9 mg MP/g dry matter in sewage sludge for the polymers PE, PP, and PS [38].

The investigation of mass concentration in the field of wastewater treatment can be used to extrapolate MP emissions within defined boundaries and for the estimation of mass balances. Here, the result of a mass balance is usually the difference between an input and an output, taking into account the associated uncertainties. Mass balances are only useful in practice if the input, output, and associated uncertainties can be accurately determined. The approximate balances are affected by large balance deficits, which result, among other reasons, from the lack of data from the operation of WWTPs. Based on our own measurements and the annual effluent discharges listed in Table 1, the estimated MP releases range from 0.0003 to 0.21 tons per year. Similar mass flows have been calculated in other studies, although the conditions of the investigations, the wastewater composition, and the treatment infrastructure vary significantly. Xu et al. (2023) estimated that about 0.321 and 0.052 tons of MPs and NPs are released from two tested WWTPs in China [52]. Hansen et al. (2017) estimated that the total Danish emission of microplastic to the aquatic environment is approx. 11 tons per year discharged with the treated wastewater [55]. And Funck et al. (2021) estimated normalized annual loads of PE based on population equivalents (P.E.) ranged from 2.8 to 8.4 mg per year and inhabitant [50]. Overall, it is evident that, due to effective solids removal, only a small fraction (3% or less) of the microplastics in WWTPs effluent are discharged to the aquatic environment. Based on measured influent concentrations, it becomes apparent that without the treatment of urban wastewater, a considerable quantity of microplastic particles would enter the aquatic environment. This is a particularly problematic given that Jones et al. (2021) estimate that 48% (171.3 billion m^3) of wastewater worldwide is not collected or treated annually [56].

4.2. Camparison to Particle Size

TED-GCMS is a destructive method, so there is a lack of information related to the particle size. With thermoanalytical determination methods, collecting information about particle size distribution is only possible with increased sampling and measurement effort, as can be seen in [49], where all of the samples were collected by fractional filtration over mesh sizes of 500, 100, 50, and in some cases 5 µm. Basically, we assume that a small number of large particles overwhelm many small particles in terms of the mass balance and, correspondingly, a few small particles only slightly contribute to the mass [57]. Although microplastics are typically defined as particles smaller than 5 mm, significantly more small particles are found than large particles. Lee et al. (2023) [48] found that the size of most microplastic particles (>80%) in both influent and effluent from WWTPs was below 300 µm, which is consistent with the results of previous studies ([30,50,58,59]). Plastic fractions with particle sizes above that of microplastics (>5 mm) are retained by around 100% [10]. Microplastics with particle sizes smaller than 0.5 mm were easily trapped during secondary treatment processes. Studies by Spelthahn et al. (2019) show a 45% proportion of particles sized 1–5 mm at the influent and a 10% of particles < 63 µm, but values of < 10% for particle sized > 1 mm and 40% for particles that were 20–63 µm in the effluent after sand filtration [47].

According to Xu et al. (2023) and Okaffo et al. (2024) the mass concentration of total nanoplastics (<1 µm) decreased from 9.1–27.7 µg/L in the influent to 0.71–1.75 µg/L in the effluent of WWTPs, indicating that the particle size range (<10 µm) not considered in this study is largely retained (with approximate removal rates of 91–96%) and has a negligible mass fraction with respect to our own measurements [52,60].

4.3. Distribution of Plastic Types

Various types of microplastics are known to flow into municipal wastewater. According to an review by Liu et al. (2021), twenty-nine plastic types were detected in the influent and the effluent of the WWTPs [61]. PE, PP, PA, PES, PS, and PET were the six most commonly detected microplastics in the wastewater, and their highest abundances

were 64%, 33%, 10%, 75%, 24%, and 29%, respectively [8,9,11,12]. While Franco et al. (2019) detected PVC (52%) [62], Lee et al. (2023) detected PTFE (57%) [48], Hansen et al. (2017) detected nylon (76.8%) [55], and Gündoğdu detected PEST (51%) [63] as the dominant plastic type in the influent of WWTPs. The differences in their results could be attributed to differences in the wastewater compositions in the catchment areas as well as in the analytical and pretreatment methods they used. Lee et al. (2023) pointed out that the analysis of the four components (PS, PE, PET, and PP) by both TED-GCMS and FT-IR gave contrasting results [48]. TED-GCMS detected PE as the most abundant compound, whereas FT-IR detected PP as the most abundant component. It should, therefore, be noted that the dominant plastic types analyzed with FT-IR (e.g., PTFE, nylon, PVC) are not among the plastic types detected with TED-GCMS.

4.4. Evaluation of the Measurement Technology

The analysis of MP is problematic due to uncertainties caused by matrix effects, especially for certain polymers such as PE. The presence of a high organic content can degrade peak identification, potentially leading to an overestimation of MP content and compromising the reliability of the chromatogram interpretation [31]. If the amount of organic matter is too high, sample preparation may be useful and the perceived advantage of TED-GCMS will be lost [64]. In some cases, such as for PVC, the quantification or qualification of polymers using the analytical method TED-GCMS is difficult or not possible [65]. With this background, the measurement results for the occurrence of microplastics should generally be critically questioned, especially those for PE.

The ability to analyze polymers using the TED-GCMS method is limited to instances where a suitable calibration method is available, which in turn takes a considerable amount of time. Standard addition, an established matrix-adapted calibration method, is too time consuming to perform to evaluate a high level of sample throughput and for continuous monitoring, making it difficult to enforce limits where automated evaluation would be beneficial. A promising solution for a less time-consuming matrix-adapted calibration could be the use of a matrix calibration, which has been applied in this work, but still requires detailed validation. So far, the initial approaches used by [65] have shown valid results.

4.5. Recommendations for Action and Regulation

From a regulatory perspective, the MP research carried out in recent years has sharpened the perception of microplastic pollution, moving away from the end-of-pipe focus. It has been made clear that the use of plastics on the scale observed currently potentially represents a serious global environmental problem that has both social and international origins and therefore also requires appropriate solution strategies.

Despite significant progress in the development of analytical methods, there is still a need for further harmonization of the methods in order to improve the comparability and reproducibility of the results. This is also an essential prerequisite for mentoring programs or regulatory approaches. However, the discrepancy between the research and routine operation is still too great. The analysis of microplastics requires a great deal of time and equipment compared to the measurement of standard parameters in wastewater technology. Microplastics will, therefore, not become a routinely determinable wastewater parameter for monitoring programs or the self-monitoring carried out by operators of WWTPs in the medium term. Appropriate technical and financial support is required for larger measurement campaigns. The measurements taken at WWTPs show that the amounts of MPs can be recorded and specified as part of the total suspended solids, which enables further approaches.

In view of the small proportion of microplastic emissions to the aquatic environment from wastewater treatment plants, a general regulation of microplastic emissions from WWTP effluents does not appear to make economic sense based on current knowledge due to the resources required. We would first have to examine whether the funds required for this could be used more efficiently for other input paths (e.g., combined sewer overflows,

precipitation water, industrial discharges, sludge utilization) in order to achieve comparable environmental relief potentials. Materials flow models may be helpful for this purpose.

5. Conclusions

The aim of this work was to evaluate the concentrations of MP at nine WWTPs in Germany, from influent to effluent. A customized sampling procedure was applied, followed by on-site and laboratory processing and the quantification of polymers (PE, PP, PS, PMMA and PET) using TED-GCMS. All wastewater treatment plants tested showed a removal efficiency over 99% for MP, indicating that MP particles are generally retained to a significant extent in conventional treatment processes. The measured concentrations of MP in the influents of the WWTPs show that large amounts of microplastics are transported in domestic wastewater. Without the treatment of urban wastewater, these large amounts of microplastics would enter the aquatic environment. Germany achieves a high international standard for the degree of connection between plants and the amount of solids separation in municipal wastewater treatment. Furthermore, a high rate of thermal utilization of sewage sludge is also achieved, thus eliminating the MPs contained in it. In the context of global microplastic emissions, sewage sludge utilization and the discharge of untreated wastewater must be considered and can represent a major leakage of MPs from urban areas into the environment. It is also necessary to implement appropriate retention systems as barriers to prevent untreated wastewater from entering environmental compartments.

In the field of urban water management, it is essential to critically examine the necessity of monitoring and optimizing existing end-of-pipe technologies. Looking ahead, research should prioritize minimizing microplastic introduction into water bodies by focusing on untreated discharges, such as stormwater discharges and CSOs. Identifying and implementing measures to reduce the potential cleaning required along these pathways can be particularly effective. To reduce microplastic emissions, further substantial technical and economic investments are required, complementing prevention strategies addressing the production and use of plastic products in accordance with the "polluter pays" principle.

However, there is currently only limited reliable knowledge concerning microplastic pollution into water bodies. It is therefore imperative to advance the harmonization of analytical methods for the parameters of MP. Despite the significant advancements that have been made in terms of analytical methods, further standardization is necessary to enhance the comparability and reproducibility of results.

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Appendix A

Table A1. Quantification database of the targeted polymers.

Polymer	Polymer Marker Abbr.	Substance	LoD	LoQ	Retention Time (min)	Quantifier (*m*/*z*)	Qualifier (*m*/*z*)
PE	PE1_55	1,11-dodecadiene	2.5	6.8	16	55	55, 95, 109
	PE2_55	1,12-tridecadiene	2.1	5.9	19	55	55, 67, 95
	PE3_55	1,13-tetradecadiene	1.4	3.9	21	55	55, 95, 109
	PE4_55	1,14-pentadecadiene	2.7	8.1	24	55	55, 95, 109
	PE5_55	1,15-hexadecadiene	0.1	0.2	26	55	55, 96, 110
	PE1_81	1,11-dodecadiene	2.0	5.5	16	81	81, 95, 109
	PE2_82	1,12-tridecadiene	0.4	1.3	19	81	81, 67, 95
	PE3_82	1,13-tetradecadiene	2.4	7.1	21	81	81, 95, 109
	PE4_82	1,14-pentadecadiene	1.8	5.2	24	81	81, 95, 109
	PE5_82	1,15-hexadecadiene	1.4	4.3	26	81	81, 96, 110
PMMA	PMMA1	methyl-methacrylate	0.6	1.7	4	100	69, 41, 39
PP	PP1	2,4-dimethylhept-1-ene	1.7	5.2	6	70	126, 83, 210
	PP2	2,4,6-trimethylnon-1-ene	6.3	15.9	13	111	69, 125, 210
	PP3	2,4,6-trimethylnon-1-ene	3.5	9.6	13	111	69, 125, 210
	PP4	2,4,6,8-tetramethylundec-1-ene	1.3	3.3	19.7	111	69, 125, 210
	PP5	2,4,6,8-tetramethylundec-1-ene	0.8	3.4	19.8	111	69, 125, 210
	PP6	2,4,6,8-tetramethylundec-1-ene	2.2	6.2	20.1	111	69, 125, 210
PS	PS1	styrene	0.9	5.6	8	104	78, 51
	PS2	2,4-diphenyl-1-butene	1.5	4.1	30	91	104, 208
	PS3	2,4,6-triphenyl-1-hexene	3.2	7.3	43	91	117, 207
PET	PET1	methylbenzoate	6.7	18.4	13	105	77, 136, 51
	PET2	vinylbenzoate	6.2	18.0	15	105	77, 51
	PET3	ethylbenzoate	5.2	15.3	16	105	77, 122, 150
	PET4	benzoic acid	8.5	25.4	18	105	122, 77, 51
	PET5	diethyl terephthalate	5.2	15.3	27	177	149, 105, 121
	PET6	divinyl terephthalate	8.5	25.4	26	175	104, 76
PA	PA1	ε-caprolactam	2.3	6.6	19	113	30, 84, 55
SBR	SBR1	4-phenylcyclohexene	1.4	3.7	20	158	104, 78, 117

Appendix B

Table A2. TGA/TED-GCMS parameters.

TGA	
Model	**METTLER TOLEDO**
Weigh-in weight (sample)	10 mg
Weighed sample (pure substances)	2–200 µg
Method gas flow	30 mL min
Shielding gas	20 mL min
Total gas flow	50 mL min
Heating rate	10.5 °C
Heating range	25–600 °C
Thermal desorption	
Parameter	Wert
Model	GERSTEL TDU 2
Mode	splitless
Gas flow	34 mL/min He
Transfer temperature	280 °C
Heating rate	40–200 °C
Cryotrapping and injection	
Type	GERSTEL CIS4
Operating mode	Solvent Vent
Split mode	Low split, 1:3
Heating range	−100–270 °C
Heat rate	12 °C/s

Table A2. *Cont.*

TGA	
Model	**METTLER TOLEDO**
Gas chromatography	
Model type	Agilent 7890B GC System
Column	Agilent HP-5MS
Pressure range	6.3 psi
Gas Flow	1 mL/min He
Heating range	30–300 °C
Heating rate	5 °C/min
Mass spectrometry	
Model name	Agilent 5977B GC/MSD
Interface Temperature	325 °C
Ion source temperature	230 °C
Quadrupole temperature	150 °C
Ionisation Mode	EI, 70 eV
Mode	Scan, 35–350 m/z

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