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Microplastics in German paper mills' wastewater and process water treatment plants: Investigation of sources, removal rates, and emissions

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ABSTRACT

Although the paper industry processes polymeric materials and discharges large amounts of wastewater, no research on microplastics in the wastewater from paper mills has been published to date. This study is the first to investigate this issue. The wastewater treatment plants of twelve representatively selected German paper mills were investigated using an analysis protocol based on μ-Raman spectroscopy. The results show that treated process water from surface waters is negligible as a source of microplastics (MPs) $\geq$ 20 μm. The microplastics concentrations in untreated wastewater range from 10^6 to 10^8 (MPs $\geq$ 20 μm)/m^3. Sources of microplastics in wastewater include recovered paper, functional polymers, and coating colors, among others. The most frequently detected polymers are polyethylene and polystyrene. In four cases, moving bed biofilm reactors were identified as a source of microplastics. The microplastics concentration in treated wastewater ranges from 10^2 to 10^4 (MPs $\geq$ 20 μm)/m^3. Hence, the removal rate of the wastewater treatment plants exceeds 99 %. Mechanical treatment and the activated sludge process have the highest removal rates of all treatment stages. The loads emitted into surface waters range from 10^6 to 10^8 (MPs $\geq$ 20 μm)/h, comparable to municipal wastewater treatment plants with a population equivalent of over 10,000 inhabitants. Compared with other wastewater-related emissions (the total emissions of municipal wastewater treatment plants, or combined sewer overflow), the contribution of paper mills to microplastics in the aquatic environment is low. The results of the removal efficiency can be transferred to other branches of industry and municipal wastewater treatment plants.

1. Introduction

Although a great deal of research has been conducted on microplastics in the last decade, there is a lack of knowledge regarding the contribution of industry to microplastics pollution of the aquatic environment. Research has focused on municipal wastewater treatment plants (WWTPs) (Bäuerlein et al., 2023; Horton et al., 2020; Mintenig et al., 2017; Roscher et al., 2022; Salmi et al., 2021; Vercauteren et al., 2023; Wolff et al., 2021; 2019, among others). Industrial plants such as plastics recycling facilities (Suzuki et al., 2022), plastics production plants (Barkmann et al., 2021; Bitter & Lackner, 2020; Weber et al., 2020; Wolff et al., 2021), and industrial parks (Barkmann-Metaj et al., 2023) have recently been investigated in several studies. To the authors' knowledge, there are no studies of high methodological quality investigating microplastics emissions from other branches of industry. This is unsatisfactory, because the characteristics of different branches of industry or even individual plants do not allow general conclusions to be drawn based on a few studies.

Wastewater discharge and the use or production of polymer-containing materials are important factors when prioritizing which

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Abbreviations: BAF, biological aerated filter; C, concentration; COD, chemical oxygen demand; DAF, dissolved air flotation; EPS, expanded polystyrene; EPT, effluent of the primary treatment; EST, effluent of the secondary treatment; ETT, effluent of the tertiary treatment; IAT, influent of the aeration tank; IWWTP, influent of the wastewater treatment plant; LOQ, limit of quantification; MBBR, moving bed biofilm reactor; MPF, microplastic fiber; MPP, microplastic particle; MPs, sum of MPP and MPF in a sample; MQ, mean annual discharge of rivers; n.d., not determined; PAP, recycling code of paper and cardboard; PE, polyethylene; PET, polyethylene terephthalate; PEq, population equivalent; PFA, perfluoro alkoxy alkane; PLA, polylactide; PP, polypropylene; PS, polystyrene; PU, polyurethane; PVC, polyvinyl chloride; Q, mean discharge of a WWTP; SD, standard deviation; TPCL, typical; TSS, total suspended solids; WTP, water treatment plant; WWTP, wastewater treatment plant; X, load; ΔC, change in concentration; Ρ, density.

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branches of industry should be investigated apart from the plastics industry. Both factors apply to the paper industry: in Germany, where this study was conducted, the average specific wastewater discharge of paper products is 8.7 m^3/Mg. However, this figure varies for different types of paper products and raw materials: 25 m^3/Mg for special and woodfree paper (made of virgin fibers), and < 4 m^3/Mg for packaging paper, 14 m^3/Mg for tissue paper, and 8 - 10 m^3/Mg for graphical paper made of recovered paper. In total, 149 German paper mills, which make up the largest paper industry in Europe (Fritsch et al., 2022), discharge 229 × 10^6 m^3 of wastewater per year. Of the paper mills, 55 % ($n = 82$), representing 71 % of total German paper production, discharge wastewater directly into surface waters (Weßel et al., 2022).

Although paper products primarily consist of cellulose fibers, polymeric materials are important during the production process or as additives to the paper: for instance, plastics enter the stock preparation in paper mills via recovered paper. In all, 83 % of all raw materials for paper production in Germany are recovered paper (Die Papierindustrie, 2024). Examples of plastics in recovered paper are foils, packaging materials, expanded polystyrene (EPS), composite packaging materials with polymeric coatings, adhesive tapes, graphical paper with coatings, packaging of advertising paper products, etc. Most of these plastics are separated from the pulp during stock preparation. This results in 800, 000 Mg/a of residue (Weßel et al. 2022), a significant proportion of which is plastic. Fragmentation of the plastics into microplastics is likely during collection, transportation, storage, and mechanical processing. It is unknown whether microplastics are released into the wastewater.

Apart from this, polymers are used for various purposes in paper production. There is variation in the composition of polymers, the retention and adhesion to the cellulose fibers, the proportion of polymers that enter the process water, and the amount of polymer in the paper product. Examples include the coating of paper with paints containing styrene-butadiene latices (graphical paper, packaging paper and cardboard, special paper), the use of styrene-butadiene copolymers in adhesives (cardboard), and the coating of paper with thermoplastics for food contact; these include polyethylene (PE), polyethylene vinyl acetate copolymer or polyethylene terephthalate (PET) as a barrier layer (4Evergreen Alliance, 2022). These polymers enter the production process through the reuse of broke and recovered paper. Middendorf (2023) assumes that the proportion of polymer-cellulose composites in the packaging industry will increase because these will be substituted for plastic packaging in future. Other possible sources of microplastics are plant components affected by abrasion, such as felts (mainly polyamides (PA)) and screens (mainly PET) in paper machines.

This study aims to close the knowledge gap regarding microplastics emissions from paper mill WWTPs. For this purpose, a representative selection of German paper mills with directly discharging WWTPs was chosen for a systematic investigation of microplastics emissions, sources of microplastics, and removal rates of the WWTPs. The emissions data make it possible to estimate the contribution of paper mills' WWTPs to overall microplastics emissions into European surface waters in comparison to municipal WWTPs. The results regarding the sources of microplastics will be of interest to the paper industry worldwide. The findings on the removal efficiency of WWTPs can be transferred to other branches of industry.

2. Materials and methods

2.1. Sampling sites

Twelve German paper mills were investigated. The plants were selected to give a representative picture of the German paper industry. The mills were selected based on their products, raw materials, and polymeric additives used. In 2023, the German paper industry produced 18.6 × 10^6 Mg of paper, cardboard and paperboard. Of this, approximately 83 % was made of recovered paper. Packaging materials account for 63 % of the products, graphical papers for 22 %, special papers for 8 % and tissue papers for 7 % (Die Papierindustrie 2024). The investigated paper mills were not selected in proportion to their frequency or the frequency of raw materials used, but rather to ensure that all types of mills represented in Germany were investigated. To this end, the assumption was made that results from mills that produce mass-quantity products (corrugated base paper, cardboard, tissue paper) can be transferred to comparable plants, as these plants use similar technologies for production and wastewater treatment. With increasing specialization of paper mills, the extrapolation of results from one paper mill to another is not possible. For this reason, special paper mills are disproportionately represented among the paper mills investigated in relation to their production volume and frequency in Germany.

The paper mills investigated produce several paper types, from cardboard and tissue paper to highly specialized products. For this purpose, different raw materials and polymeric paper additives such as coating colors and polymeric fibers are processed (see Section 1). For reasons of non-disclosure, only polymeric additives that were identified as a source of microplastics in wastewater are listed in Table 1.

For reasons of non-disclosure, it is not possible to give more information about the paper mills, production, wastewater treatment, or water treatment (see Sections 2.1.1 and 2.1.2).

2.1.1. Wastewater treatment plants

All paper mills investigated here operate directly discharging WWTPs which discharge the treated wastewater into surface waters. The wastewater consists of production wastewater from stock preparation (recovered paper processing, pulp production) and paper machines, sanitary wastewater, and stormwater from roads and recovered paper storage areas. The amount of sanitary wastewater is negligible compared to the total amount of wastewater. All WWTPs treat the wastewater with a mechanical (primary) treatment followed by a biological stage (secondary treatment). The specific type of treatment depends on the wastewater composition: due to a high chemical oxygen demand (COD) in the untreated wastewater, paper mills using recovered paper or with an integrated paper mill apply an anaerobic-aerobic biological treatment, while paper mills with a lower COD run an aerobic biological treatment. Except for paper mill F, all WWTPs use the activated sludge

Table 1
Paper mills' products, raw materials, and their use of coating colors and polymeric fibers or particles.

Paper mill	Product	Raw material	Application of coating colors	Addition of polymeric fibers or particles
A	Corrugated base paper	Recovered paper	No	No
B	Tissue paper	Recovered paper, virgin fiber	No	No
C	Cardboard	Mainly recovered paper	No	No
D	Tissue paper	Recovered paper, virgin fiber	No	No
E	Graphical paper	Recovered paper	Yes (minor part of the product)	No
F	Special paper	Virgin fiber	Yes (minor part of the product)	Yes (fibers and particles)
G	Special paper	Virgin fiber	Yes	No
H	Special paper	Virgin fiber	Yes	No
I	Cardboard	Virgin fiber	Yes	No
J	Graphical paper	Virgin fiber (integrated pulp mill)	Yes	No
K	Special paper	Virgin fiber	Yes	No
L	Tissue paper	Virgin fiber (integrated pulp mill)	No	No

process as the last stage of the secondary treatment. Five WWTPs have a tertiary treatment stage to reduce solids and phosphorus (see Table 2). These wastewater treatment processes are listed among the best available technologies by the European Commission's Joint Research Center (Suhr et al. 2015). It can be assumed that these processes are used in paper mill WWTPs throughout Europe. Most wastewater treatment processes in the paper mills investigated are standard processes that are operated in many municipal and industrial WWTPs worldwide (see Table S-4, Appendix E). Thus, the investigation of the microplastics removal rates of these processes and the evaluation of possible correlation between microplastics and other wastewater parameters are of high interest to other industrial branches and municipal WWTPs.

2.1.2. *Water treatment plants*

All paper mills investigated have a process water treatment plant (WTP). The effluents of five WTPs were sampled to serve as examples. Additionally, the influents of three of the five WTPs were sampled. All WTPs investigated have a filtration stage (see Table 3).

2.2. *Sampling*

The sampling was conducted from January 2022 to June 2024. The sampling points at each WWTP and WTP are listed in Tables 2 and 3.

Volume-reduced sampling was performed using the methods of Barkmann-Metaj et al. (2023) and Weber and Kerpen (2022) for WTP influents and effluents, tertiary treatment influents, and WWTP effluents (secondary clarifier, tertiary wastewater treatment, or maturation pond). The samples were taken periodically for 1 h - 2 h (discontinuous, 5–10 min intervals) (DIN EN ISO 5667-1, 2007). Cartridge filters with a stainless-steel membrane (pore width 10 µm, acura screen, Fuhr GmbH, Klein-Winterheim, Germany) were used. Instead of using a filter cascade, filters were replaced with a new filter when blockage occurred. A filter was considered as blocked when the sampling volume flow (max. 32 l/min without sampling line pressure) reached 10 l/min. Thus, one to four filters were used per sample. To reduce the risk of (cross-) contamination, the filters were positioned on the suction side of the pump (VGX 9/10, SPECK Pumpen Verkaufsgesellschaft GmbH, Germany). For purposes of redundancy, two filters were usually used in parallel. Depending on the accessibility of sampling points at each industrial site, samples were taken from stainless-steel sampling faucets, drain flumes, basins, or secondary clarifier effluents. Wherever possible, samples were taken from the center of flume streams with turbulent flow conditions. Sample volumes ranged from 0.061 to 0.888 m^3 for WWTP effluent samples, 0.070–0.192 m^3 for WTP influent samples, and 0.082–3.170 m^3 for WTP effluent samples, depending on the concentration of total suspended solids (TSS) and pressure loss due to an altitude difference between the pump and the water level.

Table 2
The paper mills' WWTP technologies, wastewater discharge, and sampling points (dot preceding text = sampled influent of a treatment stage; dot following text = sampled effluent of a treatment stage).

Paper mill	Primary treatment	Secondary treatment	Tertiary treatment	Mean discharge (Q) / m^3/h
A	• Dissolved air flotation (DAF)•	Anaerobic, activated sludge, sedimentation•	–	225
B	Sedimentation	Anaerobic, activated sludge, sedimentation•	DAF•	200
C	Coarse screen, sedimentation, fine screen•	Anaerobic, activated sludge, sedimentation	•DAF•	170
D	•Sedimentation	Anaerobic, activated sludge, sedimentation	DAF, maturation pond•	200
E	•Sedimentation	Moving bed biofilm reactor (MBBR), activated sludge, sedimentation•	–	300
F	•screen, sedimentation	Biological aerated filter (BAF) •	–	1000
G	Sedimentation	Trickling filter, activated sludge, sedimentation	UV disinfection, maturation pond•	225
H	•screen, sedimentation•	MBBR, activated sludge, sedimentation•	–	165
I	•Sedimentation	MBBR, activated sludge, sedimentation•	–	110
J	Sedimentation (partial flow)	Anaerobic (partial flow), •activated sludge, sedimentation•	–	960
K	Screen, sedimentation•	MBBR•, activated sludge, sedimentation•	Sand filter•	190
L	Screen, sedimentation (partial flow)	Anaerobic (partial flow), activated sludge, sedimentation•	–	1500

Table 3
WTP technology of the paper mills investigated, and sampling points (dot preceding text = sampled influent of a treatment stage; dot following text = sampled effluent of a treatment stage).

Paper mill	Water treatment technology
A	•Screen, sedimentation, sand filter•
B	Screen, ultrafiltration•
C	•Screen, sedimentation, gap-type filter (200 µm) • O_3
F	•Screen, precipitation + sedimentation, sand filter •, O_3 or Cl_2 (optional)
J	Sedimentation, sand filter•

Depending on the accessibility of the sampling points, samples from untreated or pretreated wastewater were taken as grab samples or as periodic (discontinuous, usually 5–10 min intervals) samples for 1–2 h (DIN EN ISO 5667-1, 2007). Where there was a high concentration of solids (generally TSS > 30 mg/l), samples were taken as liquid samples in glass bottles (1–15 l).

During volume-reduced sampling, the conductivity and temperature were measured using an inductive flowmeter (Picomag, Endress+Hauser AG, Reinach, Switzerland). Additionally, samples were taken for COD (LCK514, and LCK314, Hach Lange GmbH, Düsseldorf, Germany), pH, and TSS (DIN EN ISO 11923, 1997) analysis of the WWTP effluents.

Sampling was performed during production conditions which, according to the plant operators, were representative of the paper mill (in terms of raw materials, recovered paper grades, and products). If frequently occurring operating conditions existed, each condition was sampled. The last stoppage of production before sampling was at least two days previous.

Detailed information about each sample can be found in Appendix A.

2.3. *Sample preparation*

Sample preparation was performed using the methods of Wolff et al. (2019) (oxidative treatment) and Weber and Kerpen (2022) (density separation):

The organic matrix was digested in a two-stage oxidative process using hydrogen peroxide (H_2O_2, 50 %, technical, stabilized, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) for 24 h at 323.15 K followed by sodium hypochlorite (NaClO, 12 % Cl, stabilized, technical, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) for 6 d at room temperature. Because NaClO was more effective for the oxidation of pulp and cellulose fiber residues, the order of oxidative steps was switched for the treatment of untreated wastewater samples.

After oxidative treatment, inorganic matrix compounds were separated from the sample using density separation in sodium polytungstate (hydrate, ≥ 99.9 %, p.a., TC-Tungsten Compounds GmbH, Grub am Forst, Germany) with a density of 1700 kg/m^3. The density separation was intensified by centrifuging the sample for 5 min at 2400 rpm (Sigma 3–16 L, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany). After centrifugation, the suspensions were frozen for a minimum of 12 h at 243.15 K. Afterwards, the upper half of the centrifugation tube was thawed using ultra-pure water (MilliDI®, Merck KGaA, Darmstadt, Germany) (room temperature) from a squirt bottle (perfluoroalkoxy alkane (PFA), Brand GmbH + Co. KG, Wertheim, Germany) and transferred onto the analysis filter (silicon, 10 µm pore width, Smartmembranes GmbH, Halle, Germany) for µ-Raman spectroscopy.

The filter was evaluated using digital microscopy (VHX-7000, Keyence Corporation, Osaka, Japan) to check if µ-Raman spectroscopy analysis was possible. Where there were several layers of particles on the filter surface, agglomerates, or > 3500 particles (instrument limit for measurable particles), subsampling was performed using the methods of Wolff et al. (2021): the sample was re-suspended in 2-propanol (≥ 99.5 %, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and stirred in a beaker with flow breakers at 350 rpm with a 3-blade propeller stirrer. Aliquot subsamples were taken using volumetric pipettes or piston-operated pipettes and transferred onto an analysis filter. Generally, three subsamples were analyzed.

For sample transfer between the steps of sample preparation, stainless-steel mesh-filter membranes (pore width 10 µm, twilled weave, Spörl KG, Sigmaringendorf, Germany) were used for vacuum filtration. Ultra-pure water from a PFA squirt bottle and n-hexane (≥ 95 %, technical, VWR International GmbH, Darmstadt, Germany) from a glass syringe with stainless-steel needles and a Luer-Lock system were used.

2.4. *Mitigation of contamination, procedural blanks, statistical analysis, and recovery rates*

Measures of contamination mitigation were based on the study by Wolff et al. (2021). The sampling equipment and laboratory equipment with sample contact were made of glass, stainless steel, or polymers that were not included in the analysis: silicone hoses and gaskets made of nitrile rubber and polytetrafluoroethylene were used for sampling. Squirt bottles used for rinsing steps during sample preparation were made of PFA. The only exception was the use of polypropylene (PP) tips for the piston-operated pipettes. However, there were no signs of a significant PP contamination (see Table S-1, Appendix C).

Polycarbonate filter membranes (pore width 1.2 µm, Millipore Isopore RTTP04700, Merck KGaA, Darmstadt, Germany or pore width 5 µm, Cytiva Whatman™, Fisher Scientific GmbH, Hagen, Germany) were used for the filtration of chemicals (Kutralam-Muniasamy et al., 2023). All chemicals were filtered before use and stored in glass bottles.

Every step of sample preparation was conducted in a laminar flow box (MSC Advantage 12, Thermo Fisher Scientific Inc., Waltham, MA, USA). During storage or oxidative treatment, the samples were kept outside the laminar flow box, covered with aluminum foil or a custom-made silicone/stainless-steel filter membrane sealing.

During sample processing, the laboratory ventilation was running (air exchange rate 8 h^{-1}) (Noonan et al., 2023). The laboratory staff wore cotton lab coats and cleanroom-grade nitrile gloves (SimTec® NGB030, IAB Reinraumprodukte GmbH, Braunschweig, Germany) (Witzig et al., 2020).

Before use, all laboratory equipment was cleaned with a surfactant detergent (3 % polyethylene glycol lauryl ether (Brij® 35, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and 5 % sodium dodecylbenzene sulfonates (Carl Roth GmbH + Co. KG, Karlsruhe, Germany)) (Weber et al., 2021), tap water (microplastics ≥ 10 µm below the limit of quantification (LOQ) (Weber et al., 2021)) and ultra-pure water. Outside the laminar flow box, the equipment was covered with aluminum foil. After each sampling, the hoses were rinsed with 3 m^3 of tap water. Before sampling, the hoses were rinsed for 10 min with the water to be sampled.

Procedural blank samples were treated the same way as wastewater samples (without subsampling). During the sampling for this study, nine procedural blanks were analyzed. For the determination of the LOQ, the latest six procedural blanks in accordance with Barkmann-Metaj et al. (2023) were included in the calculation (preparation blank). For the evaluation of the blank value of the subsampling procedure, four procedural subsampling blanks were analyzed (subsample blank). The LOQs of the sample preparation and subsampling were calculated in accordance with DIN 32,645, 2008 for each polymer (independent of the size fraction) for the preparation blank and the subsampling blank (see Formula 1). If subsampling was necessary, the analytical result of each subsample was compared to the subsample LOQ. If the results were above subsample LOQ, the analytical result was extrapolated to the bulk sample. The bulk sample figure was compared to the preparation LOQ. If no subsampling was necessary, the results were only compared to the preparation LOQ. Only analytical results above preparation LOQ were extrapolated to microplastics concentrations (Barkmann-Metaj et al., 2023). Because the average blank was negligibly small compared to the analytical results above LOQ, it was not subtracted from the results.

$$LOQ = \bar{x}_{blank} + 10 * SD_{blank} \tag{1}$$

with

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

$$SD_{blank} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x}_{blank})}{(n-1)}})$$

: *standard deviation of the procedural blank values*

In cases where a polymer was detected in a sample rather than a blank, the LOQ was set to five items (microplastic particles (MPP) or microplastic fibers (MPF))/subsample and 20 items/bulk sample. These values were set according to the minimum LOQ of polymers detected in blank values. Blank values and LOQ can be found in Appendix C (see Tables S-1 and S-2).

Recovery rates of the analytical process including sampling, sample preparation, subsampling, and analysis using µ-Raman spectroscopy were determined in a prior study (Weber & Kerpen, 2022): PP-MPPs were recovered at a rate of 61 ± 10% (100–140 µm), 59 ± 18% (50–100 µm), and 9 ± 8% (20–50 µm), and polyvinyl chloride (PVC)-MPPs at a rate of 78 ± 14% (151 ± 37 µm). For reasons of comparability with other studies that do not include recovery rates, the results of this study were not offset against the recovery rates.

2.5. *µ-Raman spectroscopy*

Microplastics detection was conducted using a µ-Raman spectroscope (DXR2xi, Thermo Fisher Scientific Inc., Waltham, MA, USA) with a front-illuminated EMCCD detector. For measurements, the electron multiplier (EM) was turned off. All particles and fibers ≥ 20 µm were detected using the automatic particle recognition feature of the instrumental software OMNICxi (v.2.3, Thermo Fisher Scientific Inc., Waltham, MA, USA). Acquisition points were manually checked by a researcher. In cases where particles were not detected, acquisition points were set manually. If the software set two or more acquisition points for one item, the surplus acquisition points were deleted. Each particle and fiber detected were analyzed using a laser wavelength of 785 nm, a laser power of 8–10 mW, and a total exposure time of 6.75 s (three repetitions of 2.25 s each). The objective had a 20x magnification and a numerical aperture of 0.45. Spectra were recorded in the range of 50–3300 cm^{-1} and a resolution of 5 cm^{-1}.

For samples from the plants D - L, the recorded spectra were analyzed semi-automatically for the polymers PE, PET, PP, polystyrene (PS), and PVC using a machine-learning-based algorithm developed in a prior study (Weber et al., 2023): the machine-learning algorithm presorted the spectra according to the polymer classes and the probability of each. The presorted data were evaluated by one researcher.

Because the machine-learning method was not available for other polymers, all spectra from one subsample of each sample were compared to the reference library P/N L60001 (S.T. Japan Europe GmbH, Cologne, Germany) using OMNICxi and OMNIC (v 9.11.706, Thermo Fisher Scientific Inc., Waltham, MA, USA). Due to many false positive and false negative results, all spectra were manually checked by a researcher. If polymers of this type were detected in numbers > LOQ, all subsamples were evaluated for these polymers. This method was used for all spectra of samples from plants A - C.

The particle size was determined automatically by OMNICxi based on the largest particle diameter. Because the diameter was systematically exaggerated by 15 μm, the data were corrected by this figure.

3. Results and discussion

This section includes the main findings of the study. Further information, statistical analysis, and detailed analytical results can be found in Appendices A, B, C, D and E.

3.1. Microplastics emissions from wastewater treatment plants

3.1.1. Microplastics concentrations in treated wastewater

Except for the case of WWTP H, the average microplastics concentration in treated wastewater was < 100,000 MPs/m^3 (≥ 20 μm, sum of MPP and MPF) (see Fig. 1). In seven cases the concentration was > 1000 MPs/m^3. Only in four WWTP effluents was the concentration < 1000 MPs/m^3. In ten out of twelve effluents, only MPPs and no MPFs were detected. Only in one case the microplastics concentration can be attributed to the type of paper mill: The low concentration in the effluent of paper mill WWTP L (tissue paper, virgin fiber) are most likely caused by the fact that no polymeric additives are used at the paper mill which are likely to emit microplastics. The low concentration in the effluent of paper mill K can be attributed to the tertiary treatment stage (sand filtration). The influence of wastewater treatment on the microplastics concentrations is discussed in Sections 3.2–3.4. It is not possible to identify a single reason for the low discharge figures from plant J. Probably there are fewer emissions during production than at other plants that use coating colors, and the wastewater treatment works well. However, not enough data is available from plant J to draw final conclusions. The analysis result of each sample can be found in Appendix A. Estimations of the microplastic item loads of each WWTP and their influence on receiving waters are presented in Appendix D.

3.1.2. Comparison of paper mill WWTP emissions to WWTPs from other industries

Since MPFs were only detected in a few samples of paper mill wastewater (see Fig. 1), the comparison to other sectors of wastewater treatment was based on the MPP concentrations. For comparison, the microplastics item loads of the WWTPs were estimated (see Appendix D).

The emissions from a paper mill WWTP are comparable to emissions from industrial park WWTPs or municipal WWTPs with a population equivalent (PEq) of >10,000 inhabitants (see Fig. 2). In Germany, there are about 80 paper mills that are comparable to the paper mills investigated in this study (*n* = 12; 15 %). Especially for the paper mills processing recovered paper which produce cardboard, tissue paper, or corrugated base paper, the results of this study can be seen as representative, because these paper mills have similar raw materials, process technologies, and WWTPs. As the manufacturing processes, use of coating colors and polymeric fibers/particles, and WWTPs are different from paper mill to paper mill, the results of the paper mills producing special paper need to be interpreted more carefully. However, conclusions can be drawn regarding the influence of paper mill WWTPs on surface waters in comparison with municipal WWTPs: 92.6 % (*n* = 1799) of German municipal WWTPs have a PEq of over 10,000 inhabitants (DWA, 2023). Despite the insufficient availability of research data for most emission sources, according to the current state of knowledge, the microplastics emissions from these WWTPs play a minor

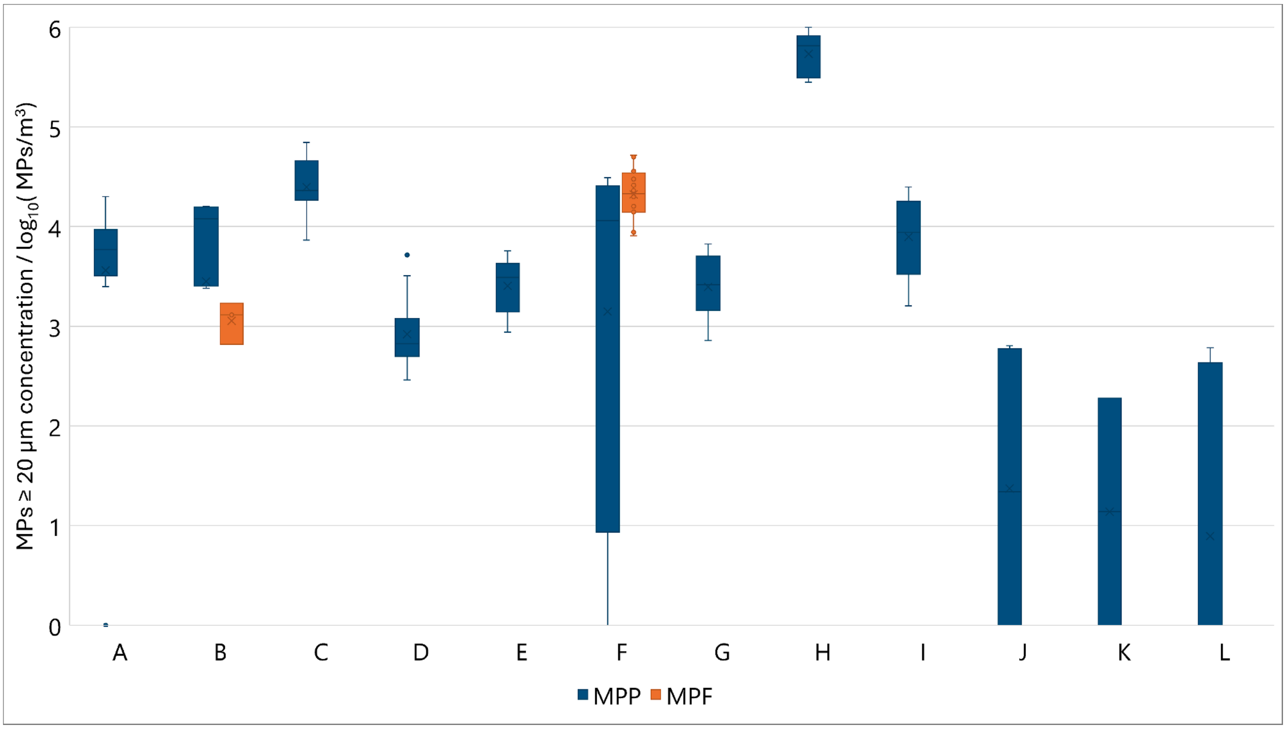


Fig. 1. Microplastics concentration in effluents of paper mill WWTPs.

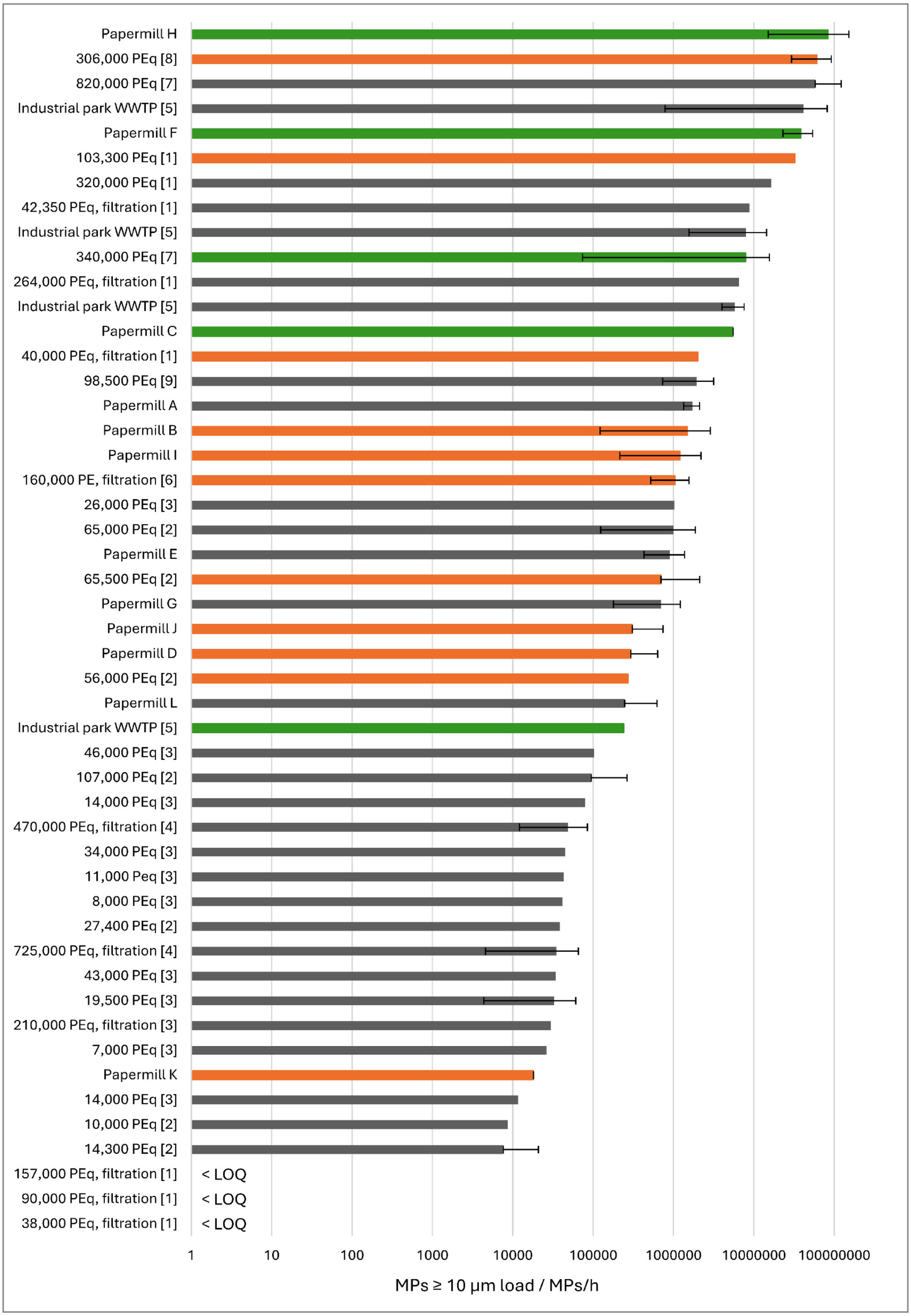


Fig. 2. Comparison of microplastics loads from municipal WWTPs (gray), industrial park WWTPs (green), and paper mill WWTPs (orange). The PEq of the municipal WWTPs is shown on the y-axis. In cases where the municipal WWTPs have a tertiary treatment stage with filtration, this is indicated by “filtration.” ([1] Horton et al., 2020; [2] Vercauteren et al., 2023; [3] Mintenig et al., 2017; [4] Wolff et al., 2021; [5] Barkmann-Metaj et al., 2023; [6] Salmi et al., 2021; [7] Roscher et al., 2022; [8] Bäuerlein et al., 2023; [9] Wolff et al., 2019).

role in microplastics emissions into the aquatic environment than combined sewer overflows or littering, e.g. (Hinzmann et al., 2022). Therefore, the overall proportion of microplastics emissions originating in paper mill WWTPs can be estimated as even smaller. However, on a local scale, paper mill emissions may have a negative influence on small aquatic environments (see Appendix D). In addition, microplastics are not biodegradable and accumulate in the environment.

The majority of MPPs in treated municipal wastewater consists of the polymers PE, PP, PS and PET. In Europe, where the comparatively evaluated studies were conducted, these plastics have a high production volume and a wide range of applications in consumer products (especially packaging). These plastics likely enter domestic and commercial wastewater. Production volumes are also high for PVC and polyurethane (PU), which are mainly used for construction and technical applications (PlasticsEurope 2020). It is plausible that they enter municipal wastewater too. The high standard deviation clearly shows that the polymeric distribution varies for different WWTPs. A reason for this could be differences in the analytical methods of the evaluated studies. Besides, the different catchments of the WWTPs can lead to differences in the polymeric distribution.

With a few exceptions, the same polymers were detected in the effluents of the industrial park WWTPs. The differences in the polymeric distribution can be explained by the products manufactured in the industrial parks (Barkmann-Metaj et al. 2023).

In treated wastewater from paper mills, polymers were found to be almost the same as in the other types of WWTPs. The main difference is an increased percentage of PS. In contrast to municipal and other industrial wastewater, PVC was not detected (see Fig. 3). Detailed information on the polymer distribution in paper mill wastewater can be found in Section 3.3. In Section 3.4 the sources of microplastics in paper mill wastewater are discussed.

Due to the different size fractioning in different studies, the size distribution of the MPPs is difficult to compare. The data in Fig. 4 show that the concentration of MPPs > 500 μm is almost negligible in treated wastewater from all types of WWTPs. The MPP size fraction < 100 μm is the most abundant in treated municipal and industrial wastewater.

With one exception, this also applies to paper mill WWTPs. The MPP size distribution in paper mill wastewater is discussed in detail in Sections 3.3 and 3.4.

3.2. *Microplastics removal in wastewater treatment plants*

The total removal rate was determined at seven out of twelve WWTPs (see Figs. 5, 6, Tables 4, 5). The removal rate is > 99.5 % in six cases (WWTPs A, C, D, E, F, and I). At WWTP H (removal rate: 92 %) microplastics were emitted into the wastewater during the wastewater treatment process (see Section 3.4). If MPPs emitted within the WWTP by the contact bed in the MBBR were not included in the calculation of the removal rate, the removal rate of WWTP H would amount to > 99 %. Total removal rates from 97 - 100 % have also been reported for other municipal (Horton et al., 2020; Salmi et al., 2021; Vercauteren et al., 2023) and industrial (Barkmann-Metaj et al., 2023) WWTPs.

High removal rates yielded by the activated sludge process (> 99 %; aerated tank in combination with sedimentation for sludge removal) indicate that the microplastics probably aggregate with activated sludge flocks and are removed from the wastewater with the excess sludge. Although no sludge samples were analyzed in this study to prove this assumption, there are no other plausible mechanisms that explain the microplastics removal during the activated sludge process. Other studies proved the accumulation of microplastics in sewage sludge (Horton et al. 2020; Franco et al. 2023). The excess sludge, along with the primary sludge and sludges from tertiary treatment in eleven out of twelve WWTPs, are utilized for energy by means of incineration. The sludges from WWTP A are fed into a material recovery process. No sludges are used as fertilizers in agriculture or for other soil-enriching purposes. Therefore, the sludges are a sink for microplastics.

The data from WWTP F show that high removal rates can also be achieved without the activated sludge process: it can be assumed that

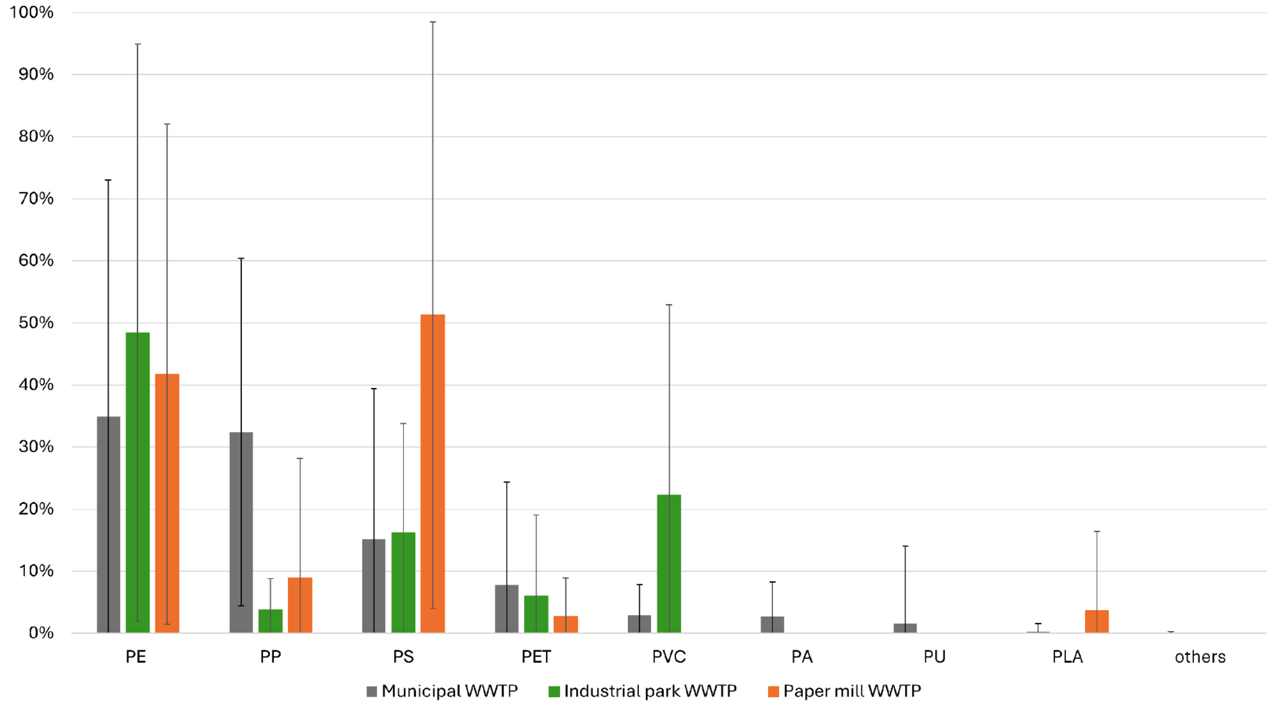
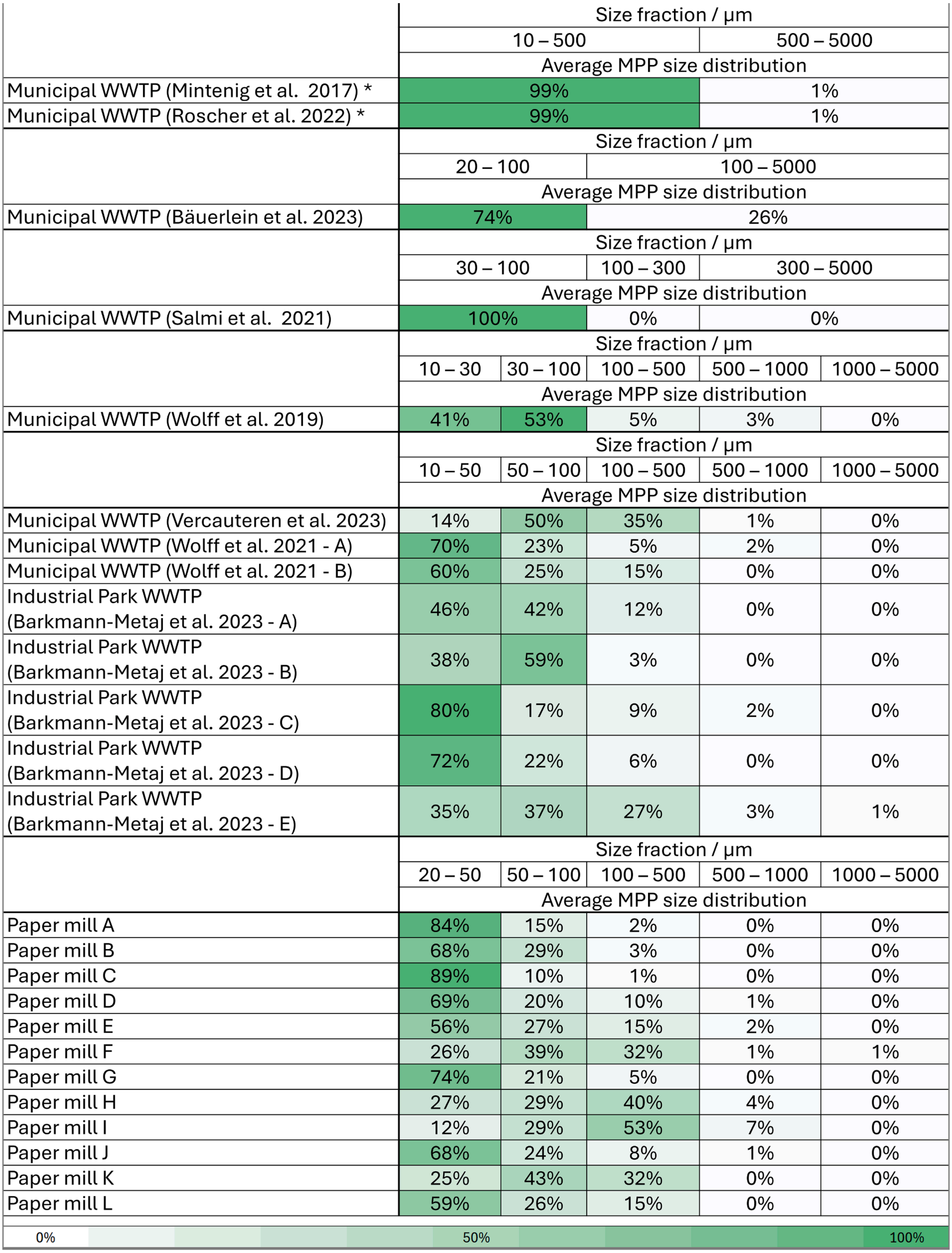


Fig. 3. Polymer distribution of MPPs in treated wastewater from municipal, industrial park, and paper mill WWTPs. (Horton et al., 2020; Vercauteren et al., 2023; Mintenig et al., 2017; Wolff et al., 2021; Barkmann-Metaj et al., 2023; Salmi et al., 2021; Roscher et al., 2022; Bäuerlein et al., 2023; Wolff et al., 2019). To ensure comparability of the data collected using μ-Raman spectroscopy, elastomeric microplastics were excluded from the data of Roscher et al. 2022 and Bäuerlein 2023 who used infrared spectroscopy.



	Size fraction / µm	
	10 – 500	500 – 5000
	Average MPP size distribution	
Municipal WWTP (Mintenig et al. 2017) *	99%	1%
Municipal WWTP (Roscher et al. 2022) *	99%	1%

	Size fraction / µm	
	20 – 100	100 – 5000
	Average MPP size distribution	
Municipal WWTP (Bäuerlein et al. 2023)	74%	26%

	Size fraction / µm		
	30 – 100	100 – 300	300 – 5000
	Average MPP size distribution		
Municipal WWTP (Salmi et al. 2021)	100%	0%	0%

	Size fraction / µm				
	10 – 30	30 – 100	100 – 500	500 – 1000	1000 – 5000
	Average MPP size distribution				
Municipal WWTP (Wolff et al. 2019)	41%	53%	5%	3%	0%

	Size fraction / µm				
	10 – 50	50 – 100	100 – 500	500 – 1000	1000 – 5000
	Average MPP size distribution				
Municipal WWTP (Vercauteren et al. 2023)	14%	50%	35%	1%	0%
Municipal WWTP (Wolff et al. 2021 - A)	70%	23%	5%	2%	0%
Municipal WWTP (Wolff et al. 2021 - B)	60%	25%	15%	0%	0%
Industrial Park WWTP (Barkmann-Metaj et al. 2023 - A)	46%	42%	12%	0%	0%
Industrial Park WWTP (Barkmann-Metaj et al. 2023 - B)	38%	59%	3%	0%	0%
Industrial Park WWTP (Barkmann-Metaj et al. 2023 - C)	80%	17%	9%	2%	0%
Industrial Park WWTP (Barkmann-Metaj et al. 2023 - D)	72%	22%	6%	0%	0%
Industrial Park WWTP (Barkmann-Metaj et al. 2023 - E)	35%	37%	27%	3%	1%

	Size fraction / µm				
	20 – 50	50 – 100	100 – 500	500 – 1000	1000 – 5000
	Average MPP size distribution				
Paper mill A	84%	15%	2%	0%	0%
Paper mill B	68%	29%	3%	0%	0%
Paper mill C	89%	10%	1%	0%	0%
Paper mill D	69%	20%	10%	1%	0%
Paper mill E	56%	27%	15%	2%	0%
Paper mill F	26%	39%	32%	1%	1%
Paper mill G	74%	21%	5%	0%	0%
Paper mill H	27%	29%	40%	4%	0%
Paper mill I	12%	29%	53%	7%	0%
Paper mill J	68%	24%	8%	1%	0%
Paper mill K	25%	43%	32%	0%	0%
Paper mill L	59%	26%	15%	0%	0%

Fig. 4. Size distribution of MPPs in effluents of municipal, industrial park and paper mill WWTPS.
* Mintenig et al. (2017) and Roscher et al. (2022) provide the mean value of analysis results from multiple WWTPs (Roscher et al. $n = 2$; Mintenig et al. $n = 12$).

the combination of mechanical treatment and a filtration effect of the BAF results in the > 99.8 % removal rate for MPPs and > 99.9 % for MPFs.

Two different technologies for primary treatment were investigated: at WWTP A, a DAF reduces the microplastics concentration by about 84 %. The analysis results of samples from the effluent of the primary sedimentation of WWTP I are < LOQ. Therefore, the removal rate can be considered as ≤ 100 %. The high removal rates of the primary treatment

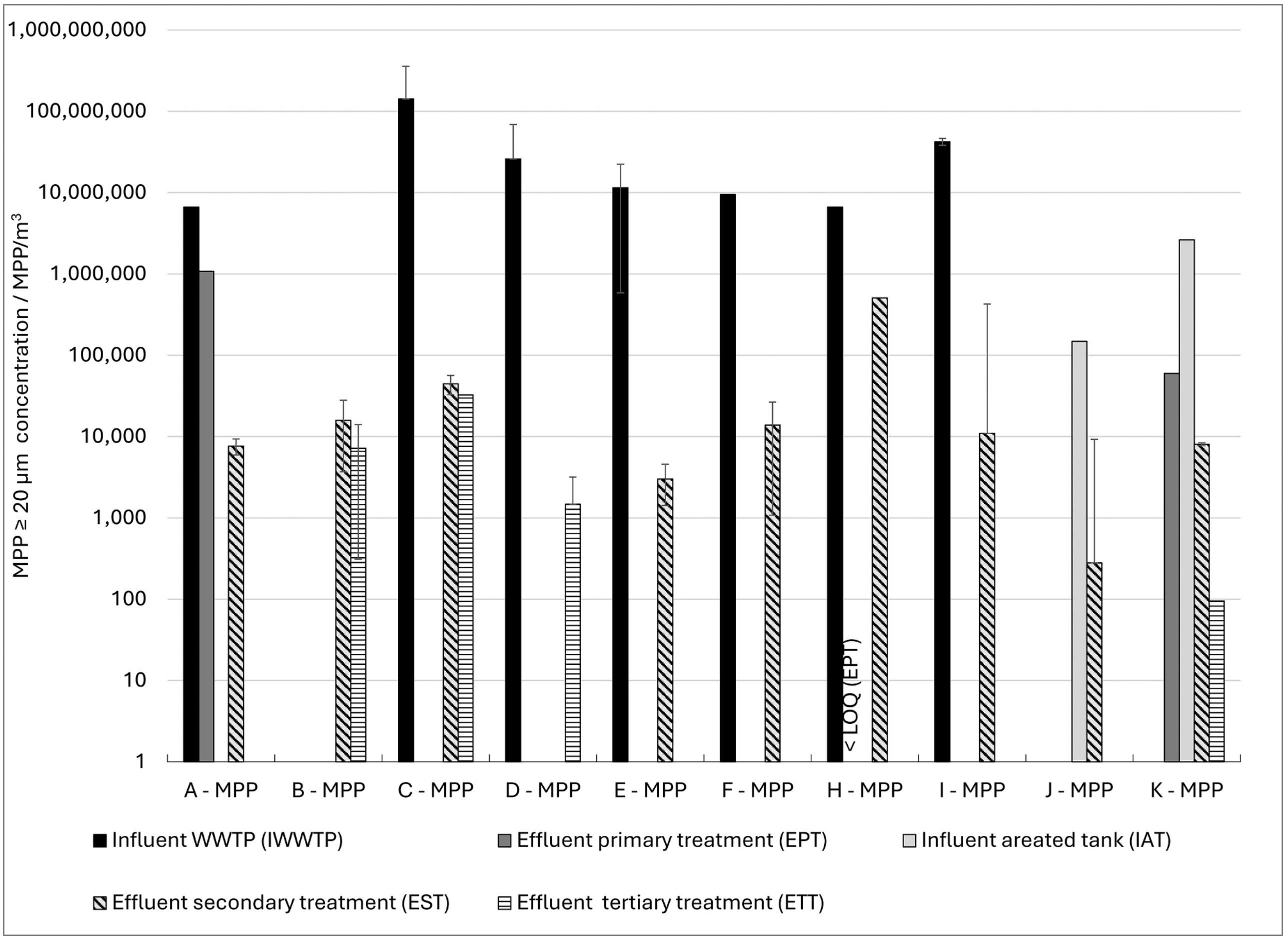


Fig. 5. MPP concentration at different treatment stages of the paper mill WWTPs.

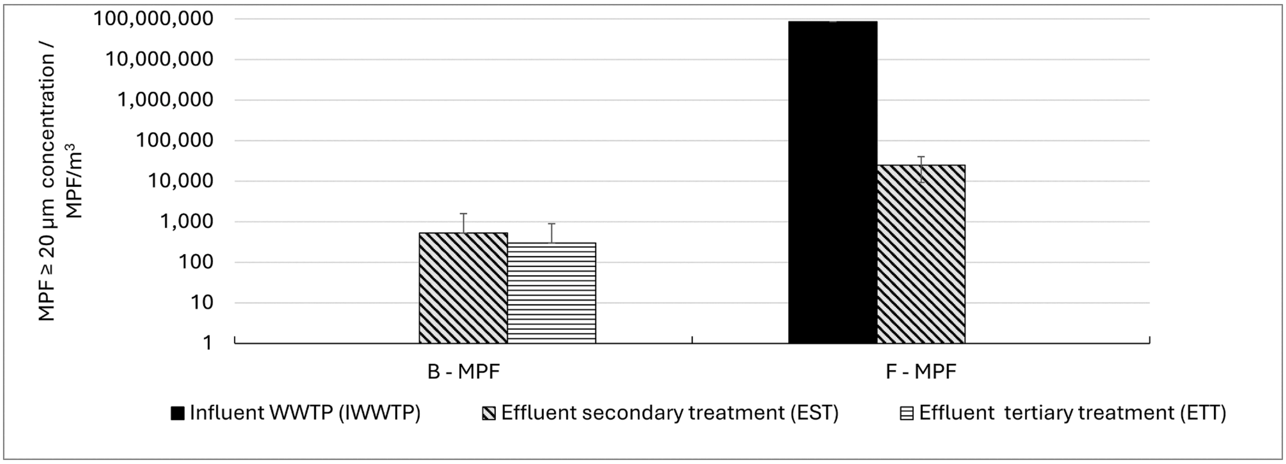


Fig. 6. MPF concentration at different treatment stages of the paper mill WWTPs.

Table 4
MPP removal rates of different stages of the paper mill WWTPs.

	A	B	C	D	E	F	H	I	J	K
	Removal rate / %									
Total WWTP	**99.9**	n.d.	**> 99.9**	**> 99.9**	**> 99.9**	**99.9**	**92.4**	**> 99.9**	n.d.	n.d.
Primary treatment	**83.8**	n.d.	n.d.	n.d.	n.d.	n.d.	**≤100**	n.d.	n.d.	n.d.
Activated sludge process	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**99.8**	**99.7**
Tertiary treatment (incl. malfunction)	n.d.	**54.7**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tertiary treatment (excl. malfunction)	n.d.	**92.3**	**27.2**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**98.8**

Table 5
MPF removal rates of different stages of the paper mill WWTPs.

	B	F
	Removal rate / %	
Total WWTP	n.d.	**> 99.9**
Tertiary treatment (incl. malfunction)	**42.9**	n.d.

stages are plausible, as the removal of solids is the main purpose of this treatment stage. Microplastics are part of the solid matter in wastewater.

Two types of tertiary treatment were investigated. Rapid sand filtration (downstream) at WWTP K removed 98.8 %. The high removal rate of sand filtration has also been reported in other studies (Al-Azzawi et al., 2022; Bitter et al., 2022; Wolff et al., 2021). A DAF is used for solids removal at WWTPs B, C, and D. In all cases, flocculation agents are dosed to improve the process. On two out of four sampling days at WWTP B, the flocculant dosing system had a malfunction. The microplastics removal rate of the DAF under standard operation is 92 %. The aerating system of the DAF at WWTP C malfunctioned on three sampling days and was out of order on the fourth. Under these conditions, the removal rate of the DAF was determined at 27 %. The removal rate of the DAF of WWTP D was not determined. However, the low effluent concentration at WWTP D indicates that the DAF has a positive effect.

The removal rates determined in this research correspond well with the data from other studies (see Table 6). Processes for the removal of solids are suitable for removing microplastics from wastewater. Filtration processes are only suitable for low solids concentrations. An increase of the removal rate in the mechanical and biological treatment stages can be achieved by optimizing the processes, for example by using precipitants and flocculants in primary and secondary clarifiers, avoiding denitrification in the secondary clarifier by adjusting the nitrogen dosage (common at paper mill WWTPs), or optimizing denitrification stages, improving sedimentation by abating the flow in primary and secondary clarifiers, etc. These changes also have a positive effect on other parameters (TSS, COD, and phosphorus, among others) (DWA, 2016). The development of stand-alone processes for microplastics removal as part of advanced wastewater treatment is not necessary. Processes for microplastics removal should be combined with other treatment objectives, particularly regarding costs, required space, energy, and the necessary chemicals. Suitable and established technologies are (sand) filtration combined with a dosage of powdered activated carbon, granulated activated carbon as a fixed bed filter, sand filtration combined with ozonation, and pile cloth filtration. These processes can be applied to combine microplastics removal with trace substance elimination, as well as phosphorus, TSS, and COD reduction.

Table 6
Removal rates (rounded) of microplastics from wastewater treated using different wastewater treatment technologies.

Stage	processes	Removal rate / %	Study
Total WWTP		92.4 - 99.99	This study
		99.6 ≤ 100	Horton et al., 2020
		98.9	Salmi et al., 2021
		92.6 - 99.4	Vercauteren et al., 2023
		92.7 - 99.6	Barkmann-Metaj et al., 2023
Primary treatment	DAF	83.8	This study
		90	Barkmann et al., 2021
	Chamber filter press	99	Barkmann et al., 2021
	Sedimentation	≤ 100	This study
		90	Hinzmann et al., 2022
		92	Salmi et al., 2021 (incl. screen and sand trap)
Secondary treatment	Anaerobic treatment	0	Barkmann-Metaj et al., 2023
	Activated sludge process (with sedimentation)	99 – 99.9	This study
		98	Barkmann-Metaj et al., 2023
Tertiary treatment	DAF	92.3	This study
	Sand filtration	98.8	This study
		99	Wolff et al., 2021
		72 - 91	Funck et al., 2021
		97	Bitter et al., 2022
	Pile cloth media filtration	99	Bitter et al., 2022
		98	Mintenig et al., 2017
	Microfiltration	99	Bitter et al., 2022
	Disc filter	94	Salmi et al., 2021
	Granulated activated charcoal (packed bed, downflow)	99	Bitter et al., 2022

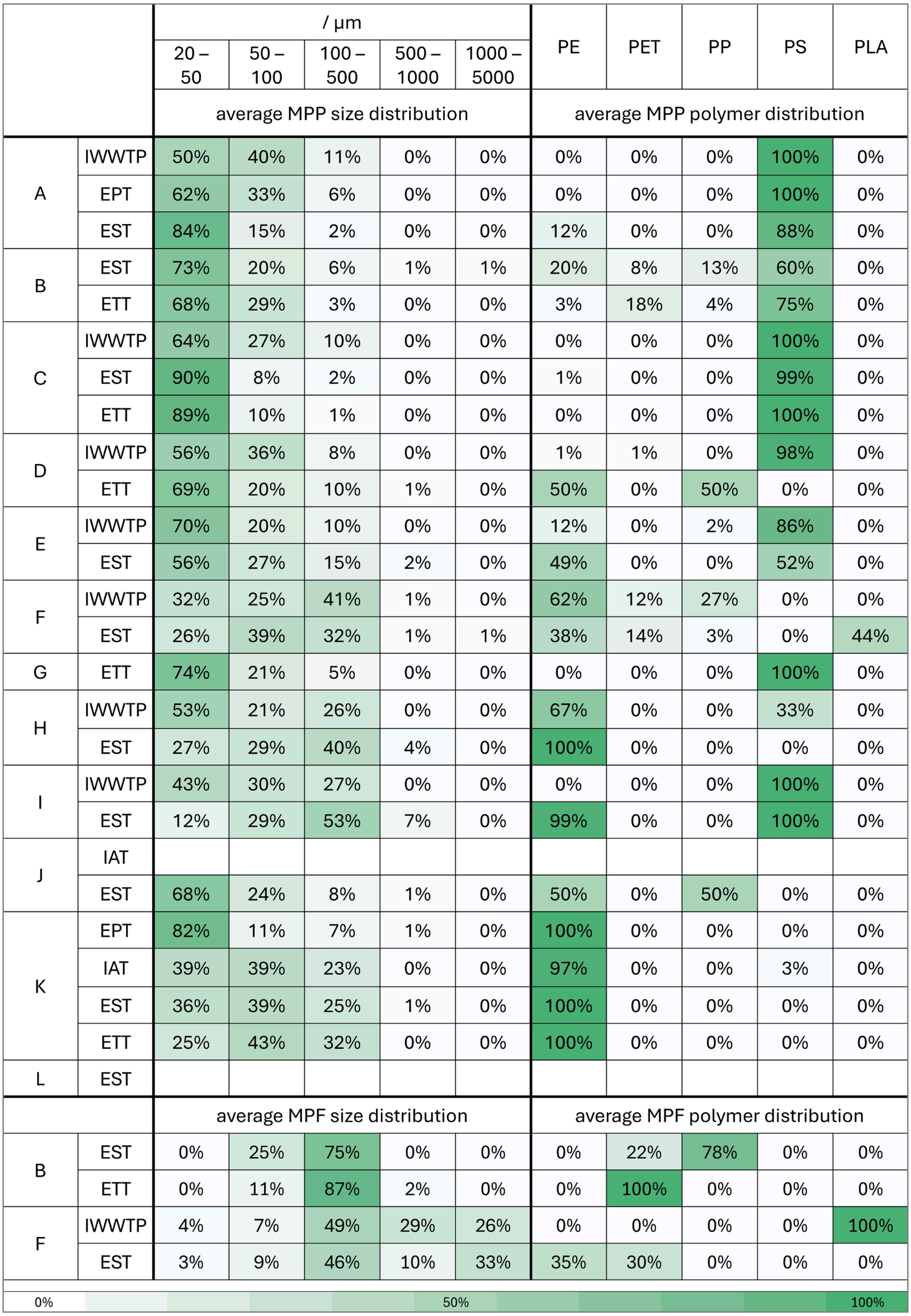
The influence of different treatment stages on the polymer and size distribution across the WWTPs is discussed in Sections 3.3 and 3.4.

3.3. *Microplastics size and polymer distribution*

Fig. 7 shows the polymer and size distribution of MPPs in wastewater at different process stages in the paper pill WWTPs. PS-MPPs are most abundant in the influent of WWTPs of recovered paper processing paper mills. In mills A - C PS is also the most frequently detected polymer in the effluent. The most probable source of PS is recovered paper (EPS in recovered packaging paper, especially in cardboard boxes). At WWTPs D and E, the percentage of PS decreases from the effluent to the influent. PE- and PP-MPPs are detected instead. At WWTP D, it is uncertain where these polymers originate from. In mill E the PE-MPPs probably originate from the MBBR (first stage of the two-stage biological treatment). In the other paper mills (H, I, and K) that operate MBBRs, the PE-MPPs in the effluent of the WWTP can be traced back to the MBBR with high certainty (see Section 3.4), while the MPPs in the influent originate from paper production (mainly coating colors containing PE- and PS-copolymers). The PS particles in the effluent from plant G also originate from the production of coated paper. At WWTP F, the MPPs and MPFs (PE, PET, PP, PLA) detected in the influent and effluent can be traced back to polymer particles and fibers added to the produced papers. As with mill D, the sources of PE and PP in the wastewater from mill J are presumably diffuse. They could originate from plant components in production or WWTPs (e.g. pipelines, machine parts).

In all paper mills, MPPs > 500 μm make up at most a single-digit percentage of the MPPs in untreated and treated wastewater. This MPP percentage is also rare in municipal and other industrial plants. This is plausible, because microplastics are generated by the continual fragmentation of macroplastics and large microplastics. This is particularly evident in the data from the mills processing wastepaper, where the plastics in the recovered paper are stressed mechanically and probably fragment extensively. In mills A to D, the proportion of the smallest particle size fraction increases from the influent to the effluent. This could indicate a further fragmentation of the MPPs within the WWTPs, or the fact that larger MPPs can be removed more effectively. A higher removal rate of larger particles is a plausible result, especially in mechanical treatment (sedimentation, screening, flotation), when the MPP are not yet aggregated with activated sludge. If the MPPs or MPFs are incorporated in activated sludge flocs, the sedimentation property of the sludge is decisive for the separation of the microplastics aggregated with it. An exception to this are the PE-MPPs ($\rho < 1000$ kg/m^3), which originate from the MBBRs. These MPPs tend to be larger than the MPPs from production-related sources. This is plausible, because they are first released in the WWTP and do not undergo much additional fragmentation there due to the short retention time and the moderate chemical-physical and mechanical stress. Due to their low surface-to-volume ratio, the biofilm that likely forms during the retention time in the aerated tank could not lead to sedimentation of these MPPs in the secondary clarifier. Because of their low density, they do not sediment in the secondary clarifier.

On average, the MPFs (only detected in plants B and F) are considerably larger than the MPPs. In the wastewater from factory B, MPFs were only detected in the influent and effluent of the DAF on one



		/ µm					PE	PET	PP	PS	PLA
		20 – 50	50 – 100	100 – 500	500 – 1000	1000 – 5000					
		average MPP size distribution					average MPP polymer distribution				
A	IWWTP	50%	40%	11%	0%	0%	0%	0%	0%	100%	0%
	EPT	62%	33%	6%	0%	0%	0%	0%	0%	100%	0%
	EST	84%	15%	2%	0%	0%	12%	0%	0%	88%	0%
B	EST	73%	20%	6%	1%	1%	20%	8%	13%	60%	0%
	ETT	68%	29%	3%	0%	0%	3%	18%	4%	75%	0%
C	IWWTP	64%	27%	10%	0%	0%	0%	0%	0%	100%	0%
	EST	90%	8%	2%	0%	0%	1%	0%	0%	99%	0%
	ETT	89%	10%	1%	0%	0%	0%	0%	0%	100%	0%
D	IWWTP	56%	36%	8%	0%	0%	1%	1%	0%	98%	0%
	ETT	69%	20%	10%	1%	0%	50%	0%	50%	0%	0%
E	IWWTP	70%	20%	10%	0%	0%	12%	0%	2%	86%	0%
	EST	56%	27%	15%	2%	0%	49%	0%	0%	52%	0%
F	IWWTP	32%	25%	41%	1%	0%	62%	12%	27%	0%	0%
	EST	26%	39%	32%	1%	1%	38%	14%	3%	0%	44%
G	ETT	74%	21%	5%	0%	0%	0%	0%	0%	100%	0%
H	IWWTP	53%	21%	26%	0%	0%	67%	0%	0%	33%	0%
	EST	27%	29%	40%	4%	0%	100%	0%	0%	0%	0%
I	IWWTP	43%	30%	27%	0%	0%	0%	0%	0%	100%	0%
	EST	12%	29%	53%	7%	0%	99%	0%	0%	100%	0%
J	IAT										
	EST	68%	24%	8%	1%	0%	50%	0%	50%	0%	0%
K	EPT	82%	11%	7%	1%	0%	100%	0%	0%	0%	0%
	IAT	39%	39%	23%	0%	0%	97%	0%	0%	3%	0%
	EST	36%	39%	25%	1%	0%	100%	0%	0%	0%	0%
	ETT	25%	43%	32%	0%	0%	100%	0%	0%	0%	0%
L	EST										
		average MPF size distribution					average MPF polymer distribution				
B	EST	0%	25%	75%	0%	0%	0%	22%	78%	0%	0%
	ETT	0%	11%	87%	2%	0%	0%	100%	0%	0%	0%
F	IWWTP	4%	7%	49%	29%	26%	0%	0%	0%	0%	100%
	EST	3%	9%	46%	10%	33%	35%	30%	0%	0%	0%

Fig. 7. MPP size and polymer distribution at the different treatment stages of the paper mill WWTPs.

sampling day. The source is unclear. In the size detected, the MPFs in the wastewater from mill F are used in the paper mill as an additive in special paper.

In Section 3.4, the sources of microplastics in wastewater from paper mills are discussed in detail.

3.4. *Sources of microplastics in wastewater treatment plants*

The size and polymer distributions (see Fig. 7) allow us to draw conclusions as to the origin of the microplastics.

Recovered paper: PS is the most abundant polymer of all microplastics in untreated and treated wastewater of the paper mills processing recovered paper, A - E (excepting D). There are two plausible sources of the PS-MPPs: one is coated paper in the recovered paper. Styrene-butadiene-latices are often used as ingredients in coating colors for graphical paper or packaging cardboards (4evergreen alliance, 2022). The coating is likely to fragment during stock preparation. Fragmentation of the coating of packaging into MPPs during disintegration was proven in laboratory-scale experiments as part of this research project. The other source for PS-MPPs is EPS. EPS is used for the direct packaging of goods inside packaging boxes and is a common contaminant in recovered paper. Macroscopic-scale EPS particles were observed in large quantities in untreated wastewater and rainwater at paper mills A and E, for example. Other polymers in the wastewater of the paper mills processing recovered paper are PE, PP, and PET. These polymers are frequently used for plastic packaging or plastic-paper-compound packaging and are visible in recovered paper on a macroscopic scale. PE copolymers are used for coatings as well (4evergreen alliance, 2022).

Polymeric fibers and particles: It was possible to trace the MPF and MPP polymers PE, PET, PP, and polylactide (PLA) in the untreated and treated wastewater of paper mill F back to the polymeric fibers that are added to the paper products in the paper mill.

Coating colors: The PS-MPPs in the treated wastewater of paper mill G (coating), the PE- and PS-MPPs in the untreated wastewater of paper mills H and K (coating, functional polymers), and the PS-MPPs in the untreated and treated wastewater of paper mill I (coating) can be traced back to the polymer containing coating colors used for paper functionalization or finishing. The polymeric component of the coating could enter the wastewater during preparation, application, or due to the use of coated broke in the stock preparation (up to $>$ 10 % of the stock).

MBBRs: The first stage of the biological treatment of the WWTPs of paper mills E, H, I, and K are MBBRs. In the MBBRs, PE carriers are used as a surface for a bacterial biofilm to grow. The MBBRs at paper mills E and I, as well as the ones at H and K, are each equipped with similar plastic carriers. The staff at paper mills E and I reported a fragmentation of the carriers. At WWTP I, macroscopic fragments of the carriers were observed in the aeration tank and secondary clarifier. Especially at WWTP H, it was possible to observe the abrasion of material from the carriers caused by contact with the concrete walls of the tank, and by pumping. The measurement of carriers from MBBR H showed a loss of material of about 1 mm in diameter. At the time of sampling, the MBBR at WWTP H had been in operation for several years, while the MBBR at plant K was a few months old. The analysis results from plants E, H, I, and K prove the emission of MPPs from the MBBRs with high certainty: at plant E the average percentage of PE increased from 12 % to 49 % in the WWTP influent compared to the effluent. The increase is most likely due to fragments from MBBR carriers. This effect was even more evident at plants H, I, and K. At plant H, no MP $>$ LOQ was detected in the effluent of the primary clarifier, while the concentration in the effluent of the WWTP was the highest effluent concentration in this study (100 % PE) (see Fig. 1). Furthermore, while only PS was present in the influent of WWTP I, the MPPs in the treated wastewater consisted of 99 % PE. At WWTP K, the microplastics concentration increased within the MBBR. In all three cases, there was no source for the PE-MPPs other than the carriers in the MBBRs. Another indication for the MBBRs as the source of microplastics was the MPP size distribution. After the MBBR, the MPPs are comparatively large. This may be a sign of less aged and fragmented MPPs compared to those that originate from stock preparation or paper production. While the problems of recovered paper and coating colors only apply to the paper industry, the release of MP from MBBRs is likely to be a problem in all WWTPs where MBBRs are operated.

Diffuse sources: While it was possible to trace the majority of microplastics back to their sources in the paper mill or WWTP, there were a few cases in which this was not possible. The sources of PE and PP in the effluent of WWTP D are unclear. As the majority of the PS-MPPs in the influent of WWTP D (98 %) were eliminated to $\leq$ 100 % in the WWTP, it is unlikely that the PE and PP in the influent would not have been eliminated at the same rate. The PE and PP probably entered the wastewater during wastewater treatment. WWTPs usually have several parts made of PE and PP (pipes, valves, etc.) Likewise, the sources of the MPP in the wastewater of paper mills J (PE, PP) and L (PS) are unknown. Besides the WWTP, the paper mill may also be a source of MP. During the industrial process of paper production, in many cases (waste)water is in contact with plastic materials. High temperatures, processing chemicals, age, and mechanical stress may increase the potential of microplastics being released from plastic materials.

3.5. *Correlation analysis of the microplastics concentration in treated wastewater with other wastewater parameters*

A correlation between the microplastics concentration in the treated wastewater and other water parameters was only observed in a few cases. The comparison of the correlation between the same parameters at different WWTPs yielded contradictory results.

While the MPP concentrations in the effluents of the secondary clarifier and the tertiary treatment at WWTP B (DAF) and WWTP K (sand filtration) correlate positively with the TSS, the TSS correlation is negative at WWTP C's secondary effluent clarifier. The positive correlation at plants B and K is plausible. The purpose of DAFs and sand filters is to reduce the TSS. The MPPs are likely aggregated with the TSS (mainly non-sedimented activated sludge flocks), because the concentration of MPPs in the effluent of the DAF increased parallel to the TSS during a malfunctioning of the DAF. The incorporation of microplastics into the activated sludge flocks is indicated by the fact that the activated sludge process shows high removal rates (see Section 3.2). Therefore, the TSS-MPP correlation would have been expected to be positive at WWTP C as well. The negative correlation could be a sign of differences in paper production between the sampling days. This theory is strengthened by the fact that the COD (dissolved) also showed a negative correlation with the MPP concentration. However, the risk of a spurious correlation is high due to the low number of samples ($n = 3$) (see Fig. 8).

The data situation is similarly inconclusive regarding the influence of precipitation. The precipitation data were obtained from the Climate Data Center of the German Meteorological Service (DWD, 2024). The MPP concentration correlates negatively with the precipitation in the 24 h before sampling at WWTP E. However, this is probably a spurious correlation: the MPP concentration was the same on sampling days one and two, and on three and four, respectively. There was no precipitation on sampling days one and two, while the amount of precipitation was similar on sampling days three and four. Therefore, the number of $n = 4$ samples is misleading, because the pair of variates that influence the correlation coefficient is effectively $n \approx 2$ (see Fig. 9).

At WWTP I, the effluent MPP concentration positively correlates with the amount of precipitation. This is plausible, because the retention time in the secondary clarifier decreases due to the stormwater discharge into the WWTP. The poorer sedimentation is also reflected in the TSS concentrations (see Fig. 10). However, there might be another reason for the high TSS and MPP concentrations on sampling day three: between sampling days two and three, there was a two-week operational shutdown. The WWTP operating staff reported that a shutdown of the production usually results in higher TSS values for a few weeks. Due to the reduced COD load during the shutdown, the activated sludge biocenosis changes, resulting in poorer sedimentation properties of the sludge.

Although a positive correlation between TSS and microplastics is plausible due to the aggregation of microplastics with the activated sludge flocks, no correlation between the TSS and MPP concentration was observed at the other WWTPs. The same applies to the other parameters (see Appendix A). This indicates that different factors influence the microplastics concentration (production, raw materials, precipitation, WWTP operation, etc.) Based on this data set, there is no general standard parameter that can be used as an indicator for the microplastics concentration in paper mill wastewater. However, the data from WWTP

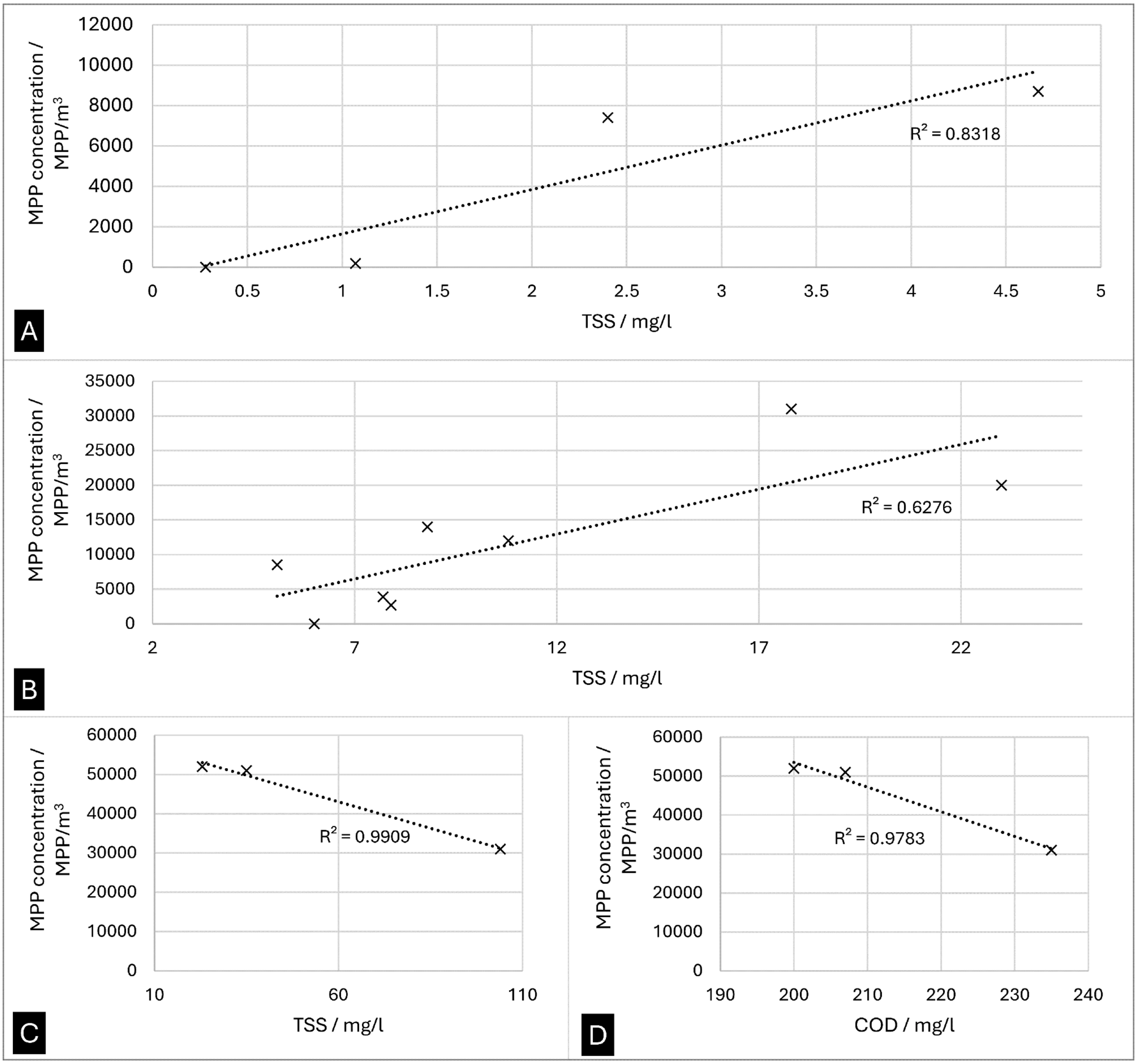


Fig. 8. Correlation analysis of the MPP concentration and the TSS in the secondary and tertiary treatment effluent of WWTP K (A) and B (B) and correlation analyses of the MPP concentration and the TSS (C) and COD (D) in the effluent of the secondary clarifier of WWTP C, respectively.

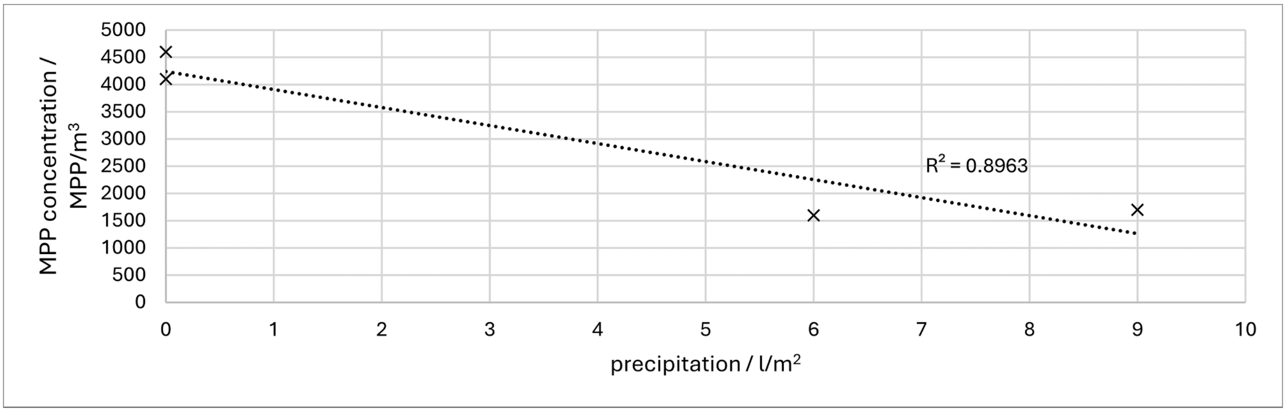


Fig. 9. Correlation analysis of the MPP concentration in the effluent of the secondary clarifier of WWTP E and precipitation in the 24 h before sampling.

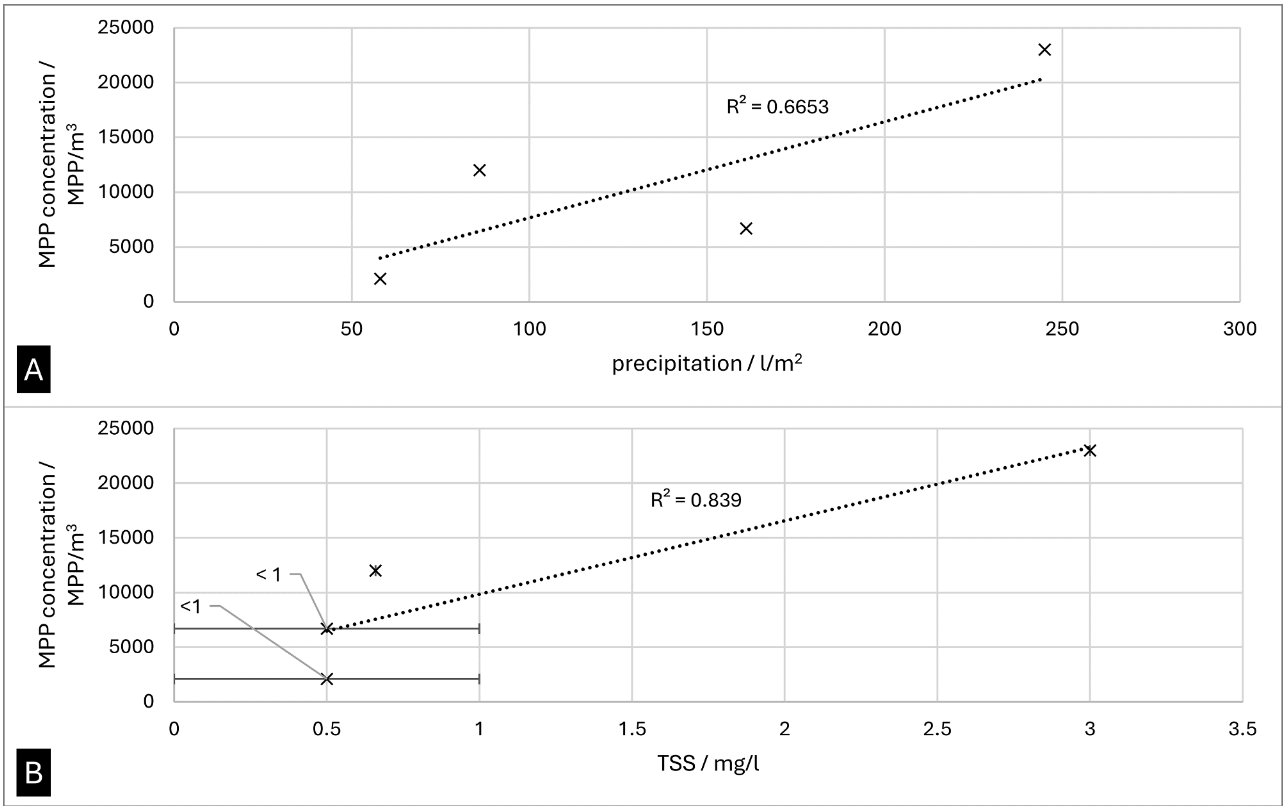


Fig. 10. Correlation analysis of the MPP concentration in the effluent of the secondary clarifier of WWTP I and precipitation in the 24 h before sampling (A) and the TSS (B), respectively.

B and K show that a correlation between microplastics and the TSS is possible. This has also been demonstrated for municipal WWTPs (Wolff et al. 2021). As there are several factors influencing the microplastics concentration in wastewater, it is important to note that no conclusions can be drawn from the correlation between microplastics and other parameters from one WWTP to another.

3.6. Microplastics in process water

No microplastics were detected in the process water of the paper mills A, B, C, F, and J (see Fig. 11). Therefore, process water originating from surface water sources can be neglected as a source of microplastics in paper mill wastewater. This also applies to other industries that use comparable technologies for process water treatment. The filtration stage at the WTPs is probably the most effective for microplastics removal. At WWTPs, filtration systems are reported to have high removal rates (see Section 3.2, Bitter et al. (2022))

The microplastics concentrations in surface waters that are used as a source of process water are similar to the microplastics concentration in treated wastewater. Therefore, reuse of (further) treated wastewater as an additional source of process water is not likely to lead to an increase in microplastics in process water.

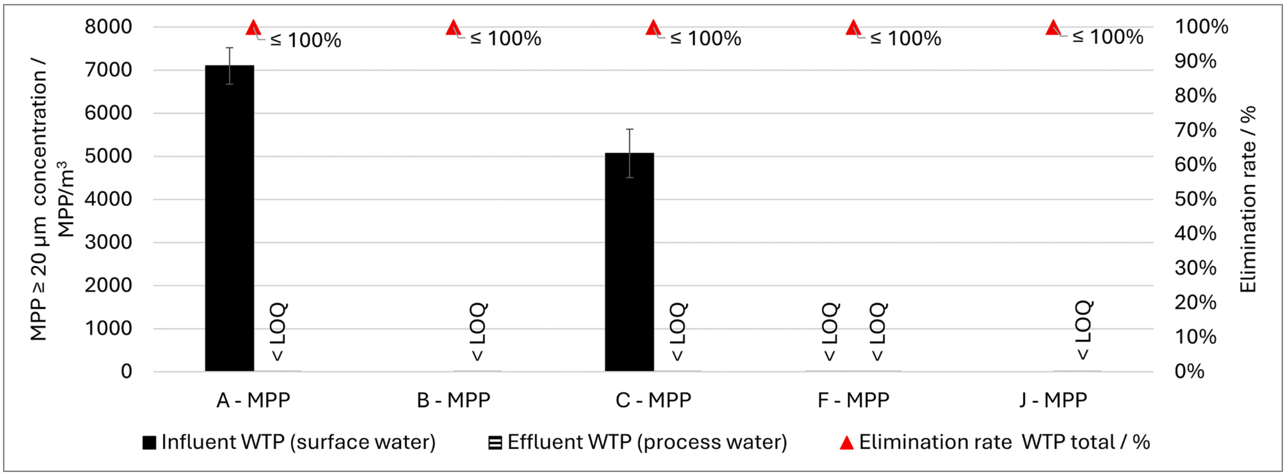


Fig. 11. MPP concentrations in the influents and effluents of the paper mill WTPs and MPP removal rates of the WTPs.

4. Implications for other industrial branches and municipal wastewater treatment

The water treatment processes analyzed in this study are operated in many industrial branches and municipal plants for process water treatment and wastewater treatment (see Table S-4, Appendix E). In general, it can be assumed that the microplastics removal rates of WWTPs and WTPs in paper mills can be transferred to other comparable plants in different industrial branches. However, industry-specific features in the operational mode need to be considered in individual cases, such as retention time in sedimentation tanks or dosage of flocculants. The fact that MBBRs release microplastics is relevant for all branches that operate these plants. Due to MBBRs, WWTPs operated in industries not processing plastics (e.g. the food industry) can emit microplastics. This should be considered when selecting WWTPs for further studies. Furthermore, the findings are particularly relevant for industries that are assumed to emit microplastics via wastewater (especially the chemical and textile industries).

5. Conclusions

The results of this research show that paper mill WWTPs are effective sinks for microplastics. >99 % of microplastics are removed during mechanical treatment and the activated sludge process. Microplastics primarily accumulate in the sewage sludge. However, the use of plastic materials in wastewater treatment can also be a source of microplastics (plastic carriers in MBBRs).

Filtration processes reduce microplastics concentrations in process water to concentrations below the limit of quantification.

These results are likely to apply to WWTPS and WTPs of other industrial branches and municipal facilities.

Compared to other sources (municipal WWTPs, combined sewer overflow, littering), the contribution of paper mills to overall microplastics emissions into surface waters is low.

Measures such as the reduction of plastic contaminants in recovered paper, the design of paper products for recycling (reduction of difficult-to-separate polymer-based composite packaging) and the improvement of material flow management for the reuse of broke have the best potential for reducing emissions from paper production. In addition to optimizing the operation of WWTPs, the use of available technologies for advanced wastewater treatment may further reduce microplastics emissions.

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CRediT authorship contribution statement

Felix Steinfeld: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Antje Kersten:** Writing – review & editing, Project administration, Funding acquisition. **Samuel Schabel:** Writing – review & editing, Funding acquisition. **Jutta Kerpen:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Felix Steinfeld reports financial support was provided by German Federal Ministry of Economic Affairs and Climate Action. Antje Kersten reports financial support was provided by German Federal Ministry of Economic Affairs and Climate Action. Samuel Schabel reports financial support was provided by German Federal Ministry of Economic Affairs and Climate Action. Jutta Kerpen reports financial support was provided by German Federal Ministry of Economic Affairs and Climate Action. Felix Steinfeld reports writing assistance was provided by AngloDoc. Felix Steinfeld reports administrative support was provided by Kuratorium für Forschung und Technik in der Papier- und Zellstoffindustrie im VDP e.V. Antje Kersten reports administrative support was provided by Kuratorium für Forschung und Technik in der Papier- und Zellstoffindustrie im VDP e.V. Samuel Schabel reports administrative support was provided by Kuratorium für Forschung und Technik in der Papier- und Zellstoffindustrie im VDP e.V. Jutta Kerpen reports administrative support was provided by Kuratorium für Forschung und Technik in der Papier- und Zellstoffindustrie im VDP e.V. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.123016.

Data availability

Data will be made available on request.

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