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Solutions to microplastic pollution - removal of microplastics from wastewater effluent with advanced wastewater treatment technologies

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Discfilter Rapid sandfilter Dissolved air flotation Membrane bioreactor

0.5 – 2.0 MP/L (secondary effluent)
0.7 MP/L (secondary effluent)
2.0 MP/L (secondary effluent)
6.9 MP/L (primary effluent)

0.03 – 0.3 MP/L (final effluent)
0.02 MP/L (final effluent)
0.1 MP/L (final effluent)
0.005 MP/L (final effluent)
Solutions to microplastic pollution - removal of microplastics from wastewater effluent with advanced wastewater treatment technologies

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Abstract

Conventional wastewater treatment with primary and secondary treatment processes efficiently remove microplastics (MPs) from the wastewater. Despite the efficient removal, final effluents can act as entrance route of MPs, given the large volumes constantly discharged into the aquatic environments. This study investigated the removal of MPs from effluent in four different municipal wastewater treatment plants utilizing different advanced final-stage treatment technologies. The study included membrane bioreactor treating primary effluent and different tertiary treatment technologies (discfilter, rapid sand filtration and dissolved air flotation) treating secondary effluent. The MBR removed 99.9% of MPs during the treatment (from 6.9 to 0.005 MP L⁻¹), rapid sand filter 97% (from 0.7 to 0.02 MP L⁻¹), dissolved air flotation 95% (from 2.0 to 0.1 MP L⁻¹) and discfilter 40 – 98.5 % (from 0.5 – 2.0 to 0.03 – 0.3 MP L⁻¹) of the MPs during the treatment. Our study shows that with advanced final-stage wastewater treatment technologies WWTPs can substantially reduce the MP pollution discharged from wastewater treatment plants into the aquatic environments.

Key words: microplastics, wastewater effluent, tertiary treatments, MBR
Introduction

Microplastics (MPs) are defined as plastic particles < 5 mm. Primary MPs are intentionally manufactured in small sizes like virgin resin pellets, microbeads in personal care products, industrial scrubbers used in abrasive cleaning agents and plastic powders used for moulding, while secondary microplastics result from the fragmentation of larger plastic particles. Fragmentation can occur during the use of materials like textiles, paint and tyres, or once the plastics have been released into the environment. Both primary and secondary MPs are found from environmental samples (GESAMP 2015). MPs have the potential to adsorb persistent organic pollutants (Rios et al. 2010, Chua et al. 2014) and heavy metals (Rochman et al. 2014) from the surrounding water environment. Further, variety of plastic additives, like flame retardants and plasticizers, are included in the plastics during manufacturing. It has been proposed that if MPs with their micropollutants enter food webs through digestion by biota, this may lead to ecosystem and human health impacts (Browne et al. 2013, Rochman et al. 2015, Miranda and de Carvalho-Souza 2016).

Wastewater treatment plants (WWTPs) can act as a barrier but also as entrance routes for microplastics to aquatic environment. Conventional wastewater treatment with primary and secondary treatment processes can remove MPs from the wastewater up to 99 % and most of the MPs are removed already during pre-treatment phases (Carr et al. 2016, Murphy et al. 2016, Talvitie et al. 2017). Despite of the high reduction ability, conventional WWTPs may actually be a significant source of MPs given the large volumes of effluents that are discharged (Mason et al. 2016, Murphy et al. 2016, Mintenig et al. 2017, Talvitie et al. 2017).

During the last decades wastewater treatment has continuously been required to increase the quality of the final effluents. However, the technologies to improve the quality of the final effluent are not specifically designed to remove microplastics and do not necessarily remove MPs from the effluent (Mason et al. 2016, Talvitie et al. 2017). Few studies suggest, however, that with some advanced
final-stage wastewater treatment technologies the removal of the MPs from effluents can be further improved (Carr et al. 2016, Mintenig et al. 2017, Ziajahromi et al. 2017).

The aim of this study was to examine the efficiency of different advanced final-stage treatment technologies to remove microplastics from effluent. This study includes tertiary treatments; discfilter (DF), rapid sand filtration (RSF) and dissolved air flotation (DAF) and membrane bioreactor (MBR). In addition, we examined which MP types (size and shape) were removed and which were left in the final effluent after the treatments. The study was repeated with 24-hour automated composite samplers to include in-day variation to examination of MP removal and concentration. We performed comprehensive FTIR analyses to all and whole samples included in the study. In the end, we estimated the proportion of primary and secondary MPs in final effluents.

2. Materials and Methods

2.1. Description of the selected WWTPs and advanced wastewater treatment technologies

The most commonly used advanced final treatment stage technologies were selected for our study. The tertiary treatments included different filtering (sand and cloth) and flotation techniques. Also, membrane bioreactor was selected.

Micro-screen filtration with discfilters (DF) was examined in Viikinmäki WWTP located at Helsinki, a metropolitan area of Finland. Viikinmäki WWTP process is based on primary clarification, conventional activated sludge (CAS) process and a tertiary denitrifying biological filter (BAF). More detailed characteristics of each WWTPs included in this study is given in supplementary data (SD. Table. S1). The pilot-scale discfilter (Hydrotech HSF 1702 -1F) consists of two discs composing each of 24 filter panels. The pilot unit was so-called inside-out system where the influent water is introduced inside the filter panels. The particle removal is based on physical retention in filters and sludge cake formation inside the filter panels. The sludge cake
formation decelerates the filtering, causing water level rise inside the cylinder. When water meets the level sensor, backwash is initiated. Backwash is performed with high pressure (in this case 8 bars) to rinse off the sludge cake. The particle and nutrient removal can further be enhanced with coagulants. In this study iron based coagulant and cationic polymer were used with dosages of 2 mg/L and 1 mg/L, respectively. Hydraulic retention time (HRT) in the pilot was 4 minutes and flow ~ 20 m$^3$/h. The overall filtration area was 5.76 m$^2$ and pore size of the filters was either 10 or 20 µm (Rossi 2014).

Rapid (gravity) sand filters (RSF) as full-scale tertiary treatment was examined in Kakolanmäki WWTP (Turku Region Waste Water Treatment Plant), city of Turku, Southern Finland. In RSF, the wastewater is filtered through a layer of sand. The sand filter composed of 1 meter of gravel with gain size of 3-5 mm and 0.5 meter of quartz with grain size 0.1 – 0.5 mm. Apart from physical separation removing suspended solids, adhesion by microbes removes nutrients and microbes. Before the sand filter the process is based on CAS method.

Dissolved Air Flotation (DAF) as full-scale tertiary treatment was examined at Paroinen WWTP (Hämeenlinna Region Water Supply and Sewerage Ltd) located in city of Hämeenlinna, Southern Finland. In DAF, water is saturated with air at high pressure and then pumped to a flotation tank at 1 atm, forming dispersed water. The released air bubbles in dispersed water adhere to the suspended solids causing them to float to the surface, from where it is removed by skimming. Before the flotation, flocculation chemical Polyaluminium Chloride (PAX) is added to the wastewater with dosage of 40 mg/L to enhance flocculation. Before the DAF, the process is based on CAS process.

Membrane bioreactor (MBR) pilot unit was examined at Kenkäveronniemi WWTP, located in city of Mikkeli, South-East of Finland. Kenkäveronniemi WWTP is generally based on primary clarification, CAS process and secondary clarifier effluent on hygienization using peracetic acid solution. The MBR pilot included Submerged Membrane Unit (SMU) and ultrafiltration (UF)
The membrane system consisted of 20 flat-sheet membrane cartridges installed inside the filtration tank. During the filtration, the water is forced through membranes under negative pressure created by pumps and collected to the separate tank. MBRs are the combination of membrane filtrations processes with suspended growth biological reactors. This combination treats primary effluent containing suspended solids as well as dissolved organic matter and nutrients. Hence the MBR technology replaces secondary clarifiers in CAS systems. In the MBR pilot unit the effective membrane area was 8 m$^2$ and the nominal pore size of the membranes 0.4 µm. HRT values varied from 20 to 100 h and the flow between 40 to 90 l/h (Gurung 2014).

### 2.2 Sample collection

Sampling at the four different WWTPs took place between April 2014 and August 2015. The actual sampling dates and times are given in supplementary data (SD. Table S2.). Samples with three replicates were collected before and after the treatments. The replicates consisted of three independent water samples. A custom made filtering device with in-situ fractionation was used (Talvitie et al. 2015). The mesh-sizes of the filters were 300, 100 and 20 µm, giving particle size fractions of > 300 µm, 100 – 300 µm and 20 – 100 µm. Sampling full-scale treatments (RSF, DAF) was performed by pumping water (depth ≈ 1 m) from the wastewater stream into the filtering device with an electric pump (Biltema art.17-953). In pilot-scale treatments (discfilters, MBR), the samples were collected from the taps designed for sampling, into the filter device. In addition, samples after the CAS in Kenkäveronniemi WWTP were collected to see the possible improved removal capacity provided by MBR method compared to CAS. Water sample volumes were measured with a flow meter (Gardena Water Smart Flow Meter) and varied with the wastewater quality and filter size (Table 1.). The sampling was stopped before the filters were clogged with organic matter. After the sampling, the filters were collected to petri dishes and stored in room temperature.
Table 1. Sample volumes (L = liters) before and after the treatments for each filter size. DF 10 = discfilter with pore size 10 µm, DF 20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

<table>
<thead>
<tr>
<th></th>
<th>DF 10</th>
<th></th>
<th>RSF</th>
<th></th>
<th>DAF</th>
<th></th>
<th>MBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>6 L</td>
<td>Before</td>
<td>50 L</td>
<td>After</td>
<td>50 L</td>
<td>After</td>
<td>1000 L</td>
</tr>
<tr>
<td>After</td>
<td>50 L</td>
<td>After</td>
<td>1000 L</td>
<td>Before</td>
<td>333 L</td>
<td>After</td>
<td>1000 L</td>
</tr>
<tr>
<td>CAS</td>
<td>500 L</td>
<td>CAS</td>
<td>140 L</td>
<td>CAS</td>
<td>140 L</td>
<td>CAS</td>
<td>50 L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>DF 20</th>
<th></th>
<th>RSF</th>
<th></th>
<th>DAF</th>
<th></th>
<th>MBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>50 L</td>
<td>Before</td>
<td>50 L</td>
<td>After</td>
<td>4 L</td>
<td>After</td>
<td>140 L</td>
</tr>
<tr>
<td>After</td>
<td>4 L</td>
<td>After</td>
<td>140 L</td>
<td>Before</td>
<td>50 L</td>
<td>After</td>
<td>50 L</td>
</tr>
<tr>
<td>CAS</td>
<td>140 L</td>
<td>CAS</td>
<td>50 L</td>
<td>CAS</td>
<td>140 L</td>
<td>CAS</td>
<td>140 L</td>
</tr>
</tbody>
</table>

Additional sampling was carried out with automated 24-hour composite samplers. Composite samplers in each WWTPs took a sample proportionally and discretely at an interval of 15 min. over a 24-hour period before and after the treatment unit (Table 2.). The samplers collected wastewater into plastic containers located in closed refrigerators. The discfilter was not included in the composite sampling as the WWTP was not able to provide the equipment.

Table 2. The 24-h composite sample volumes (L = liters) before and after the treatments for each filter size. RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

<table>
<thead>
<tr>
<th></th>
<th>RSF</th>
<th></th>
<th>DAF</th>
<th></th>
<th>MBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>25.5 L</td>
<td>Before</td>
<td>16.1 L</td>
<td>After</td>
<td>6.1 L</td>
</tr>
<tr>
<td>After</td>
<td>27.4 L</td>
<td>After</td>
<td>5.8 L</td>
<td>After</td>
<td>6.1 L</td>
</tr>
<tr>
<td>300 µm</td>
<td>4.0 L</td>
<td>100 µm</td>
<td>25.5 L</td>
<td>20 µm</td>
<td>4.0 L</td>
</tr>
</tbody>
</table>

2.3 Wastewater characteristics of the selected WWTPs

The main wastewater characteristics of the MP sampling sites are summarized in Table 3. The results were obtained from the analysis of 24-hour composite samples collected for the weekly
monitoring programs of plants. The samples were taken around the same time as those for the MP study.

Table 3. Average wastewater characteristics before and after the treatments. DF 10 = discfilter with pore size 10 µm, DF 20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DF 10 Before</th>
<th>DF 10 After</th>
<th>DF 20 Before</th>
<th>DF 20 After</th>
<th>RSF Before</th>
<th>RSF After</th>
<th>DAF Before</th>
<th>DAF After</th>
<th>MBR Before</th>
<th>MBR After</th>
<th>CAS Before</th>
<th>CAS After</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS [mg/L]</td>
<td>4.3</td>
<td>3.6</td>
<td>11</td>
<td>4</td>
<td>5.8</td>
<td>1.7</td>
<td>15</td>
<td>5</td>
<td>40</td>
<td>&lt; 1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>BOD [mg/L]</td>
<td>5.3</td>
<td>3.8</td>
<td>6.3</td>
<td>3.6</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.6</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>COD [mg/L]</td>
<td>40</td>
<td>3.6</td>
<td>50</td>
<td>43</td>
<td>43</td>
<td>37</td>
<td>NA</td>
<td>33.1</td>
<td>300</td>
<td>31</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Ntot [mg/L]</td>
<td>5.5</td>
<td>5.2</td>
<td>7.8</td>
<td>8</td>
<td>11</td>
<td>13</td>
<td>NA</td>
<td>21.7</td>
<td>69</td>
<td>43</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Ptot [mg/L]</td>
<td>0.2</td>
<td>0.08</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>6.4</td>
<td>1.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Flow [m³/d]</td>
<td>480</td>
<td>480</td>
<td>63170</td>
<td>16855</td>
<td>2.2</td>
<td>8904</td>
<td>2.2</td>
<td>8904</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4 Characterization of microparticles

All samples were visually examined using a stereo microscope (model EZ4 HD; Leica Microsystems GmbH, Wetzlar, Germany), with an integrated HD camera. All textile fibers and particles suspected as plastics were counted and the particles further classified as fragments, flakes, films and spheres, and their coloration documented. Particles with cellular structures and soft, easily disintegrating (organic) materials were excluded from the further examination. Chemical composition of the pre-selected particles were analyzed with imaging FTIR spectroscopy (Spectrum Spotlight 300, PerkinElmer, Waltham, MA, USA). The particles were individually picked from the samples, rinsed with distilled water and placed onto ZnSe windows and let to dry for approximately one hour, after which each window was photographed and analyzed with the FTIR. The FTIR spectra were recorded in transmittance mode, in wavelength region of 700 – 4000 cm⁻¹ at 4 cm⁻¹.
resolution and with 15 scans. To analyze the spectra, the Thermo Scientific™ Hummel Polymer and Additives FT-IR Spectral Library was used. Fibers were analyzed with textile fiber library previously described in Talvitie et al. (2017). The characterization technique allowed to include all particles size > 20 µm.

2.5 Contamination Mitigation.

To minimize contamination, all equipment included in the sampling protocol were rinsed thoroughly with tap water right before the use. Filters were checked with microscope to ensure sufficient rinsing. After sampling the filters were placed in petri dishes. Avoiding MP contamination is challenging and therefore three independent controls were made by filtering 100 L of tap water. The tap water was filtered straight from the tap into the filter device and filters treated as actual samples. The pump was not included in the controls. For the 24-hour composite sampling, the controls samples were made by collecting tap water to plastic containers and containers were left inside the sampler (closed refrigerator) for 24-hour period. After the 24-hour period, the water was filtered and treated as actual composite samples (Talvitie et al. 2017).

3. Results and Discussion

3.1 Removal of MPs from effluent with advanced technologies

All advanced final treatment stage technologies; discfilters (DF), rapid sand filters (RSF), dissolved air flotation (DAF) and membrane bioreactor (MBR) removed > 95 % of microplastics (> 20 µm) from effluent (Table 4).

Table 4. The average microplastic concentrations before and after the treatments. DF 10 = discfilter with pore size 10 µm, DF 20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor. Data is given in number of microplastics per liter of effluent. Figures represent mean values ± SE, n = 3.
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Effluent type</th>
<th>Before (MP/L⁻¹)</th>
<th>After (MP/L⁻¹)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF 1</td>
<td>Secondary</td>
<td>0.5 (± 0.2)</td>
<td>0.3 (± 0.1)</td>
<td>40.0</td>
</tr>
<tr>
<td>DF 2</td>
<td>Secondary</td>
<td>2.0 (± 1.3)</td>
<td>0.03 (± 0.01)</td>
<td>98.5</td>
</tr>
<tr>
<td>RSF</td>
<td>Secondary</td>
<td>0.7 (± 0.1)</td>
<td>0.02 (± 0.007)</td>
<td>97.1</td>
</tr>
<tr>
<td>DAF</td>
<td>Secondary</td>
<td>2.0 (± 0.07)</td>
<td>0.1 (± 0.04)</td>
<td>95.0</td>
</tr>
<tr>
<td>MBR</td>
<td>Primary</td>
<td>6.9 (± 1.0)</td>
<td>0.005 (± 0.004)</td>
<td>99.9</td>
</tr>
</tbody>
</table>

With the MBR technology, MP concentration decreased from 6.9 (± 1.0) to 0.005 (± 0.004) MP L⁻¹. The MBR treats primary clarified wastewater with much higher MP concentration compared to secondary effluent, giving higher removal percentage than tertiary treatments (table 4). However, MBR gave also the lowest MP concentration of the final effluent, which indicates, that MBR is the most efficient technology in this study to remove MPs from wastewater. The result is expected as the MBR filters had the smallest pore size (0.4 µm) of for all the studied filters.

The detection of only two MPs (both synthetic textile fibers) after the MBR could derive from occasional breakthroughs of filters, from small leaks between seals in the unit, or from airborne contamination in open tanks. Without the pilot-scale MBR, the MP concentration in secondary effluent in Kenkäveronniemi WWTP was 0.2 (± 0.06) MP L⁻¹. Hence, the advanced MBR technology releases ~2.5 % of the MPs compared to CAS.

With RSF, MP concentration decreased from 0.7 (± 0.1) to 0.02 (± 0.007) MP L⁻¹. During RSF, MPs are caught between the sand grains or adhered to the surface of the sand grains. The adhesion could be possibly further improved with coagulant, however, in Kakolanmäki WWTP no coagulant additions were used. The MP concentration also decreased clearly in DAF treatment from 2.0 (± 0.07) to 0.1 (± 0.04) MP L⁻¹. During the flotation, microplastics are transported to the surface of the flocs due to their buoyancy. The floating matter is then removed by skimming device. As flotation
is particularly designed to remove low-density particles, it can be expected to efficiently remove plastics, at least those that have lower density than water.

The DF also decreased the MP concentration from 0.5 (± 0.2) to 0.3 (± 0.1) with 10 µm and from 2.0 (± 1.3) to 0.03 (± 0.01) with 20 µm filter pore size. However, the variation between the replicates were so high in both cases, that the results should be handled with care. Additionally, pore size 10 µm gave much smaller MP removal capacity compared to 20 µm, although smaller pore size was expected to remove MPs more efficiently. Due to the disturbances in the earlier treatment processes in the WWTP, the quality of the plant effluent (pilot influent) varied during the sampling period. During the DF 10 µm sampling, the varying quality of the pilot influent led to excessive polymer additions, which in turn caused the volume differences between the replicates after the treatment (Table 1.), as sticky polymer flocs blocked the filters quickly. The excessive polymer addition also resulted in membrane fouling in the discfilter pilot, which led to accelerated backwash frequency. During the high-pressure backwash, part of the MPs probably passed the filter cloth to the final effluent, lowering the removal efficiency. During the DF 20 µm sampling, probably the high SS concentration (Table 3.) led to volume differences between the replicates before the treatment (Table 1.).

The controls with tap water revealed no MP contamination of the samples. However, the control samples were processed without pumping, as they were filtered straight from the tap. Pumping can possibly give slight background level to those samples where pump was used (Mintenig et al. 2017).

Our finding supports previous studies on the efficient removal of MPs in tertiary phases. Carr et al. (2016) reported MP (> 45 µm) free effluent after tertiary gravity filters. Mintenig et al. (2017) reported the tertiary post-filtration unit (pile cloth media filtration, MECANA) to remove MPs > 500 µm completely and 95% of the MPs 20 – 500 µm (concentration decreased from 0.2 to 0.01 MP L⁻¹). Additionally, Ziajahromi et al. (2017) found 0.28 MP L⁻¹ after tertiary ultrafiltration and 10
0.21 MP L\(^{-1}\) after reverse osmosis. However, as mentioned in the introduction, wastewater treatment technologies are not specifically designed to remove microplastics, and not all of them necessarily remove MPs. This can be seen our previous study (Talvitie et al. 2017), where the tertiary treatment, biologically active filter (BAF), didn't decrease MP concentration and in Mason et al. (2016) where clear correlation between tertiary filtration and reduced microparticle discharges could not be detected.

Also according to our 24-hour composite sampling RSF, DAF and MBR removed MPs > 20 µm from wastewater (Table 5.). However, the actual MP concentrations and therefore the removal capacities differ from results gained with large-volume grab sampling. The reasons for differences are probably low sample volumes, low MP concentrations and airborne contamination. When the MP concentration is very low, composite samples might give false zero results, as the sample volumes are so small (in this study varying from 4.2 – 27.4 L). This can be seen from RSF results where no MPs after the treatment were detected (Table 5.).

Table 5. The average microplastic concentrations before and after the treatments according to 24-hour composite samples including rapid sand filters (RSF), dissolved air flotation (DAF) and membrane bioreactor (MBR). Data is given in number of MPs per liter of effluent.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Effluent type</th>
<th>Before (MP/L(^{-1}))</th>
<th>After (MP/L(^{-1}))</th>
<th>Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSF</td>
<td>Secondary</td>
<td>0.4</td>
<td>&lt; 0.04</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>DAF</td>
<td>Secondary</td>
<td>2.3</td>
<td>1.2</td>
<td>48</td>
</tr>
<tr>
<td>MBR</td>
<td>Primary</td>
<td>3.2</td>
<td>0.2 (After CAS 0.5)</td>
<td>94</td>
</tr>
</tbody>
</table>

In our previous study (Talvitie et al. 2017), the background level (contamination) in composite samples comprised over 30% of the actual microlitter results, meaning that the method is sensitive to contamination. In this study, the WWTP personnel were asked to take 24-h composite samples with their own monitoring equipment. The personnel were instructed to thoroughly rinse equipment
with tap water and keep them covered in all times. Despite the effort, the contamination probably explains the higher MP concentration values after the DAF and MBR treatments with composite samples (Table 5.) compared to large-volume grab samples (Table 4.).

Many WWTPs include automated composite samplers for monitoring different parameters from wastewater. Automated samplers provide an easy and fast MP sampling protocol. Composite samples also include in-day variation, which is important when evaluating the total number of MPs in effluents discharged to the environment (Talvitie et al. 2017). However, according to our results, the low sample volumes together with low MP concentration and sensitivity to contamination leads easily to false estimation of MP concentrations in effluents. Recent studies emphasize the necessity of standardized and harmonized methods when evaluating the amount of MPs discharged from WWTPs (Murphy et al. 2016, Mintenig et al. 2017, Ziajahromi et al. 2017). Our study suggested using in-situ pumping and filtering device with large volume sampling when examining the MPs in secondary and tertiary effluent.

3.2 The effect of size and shape of the MPs on their removal in different treatment technologies

The RSF, DAF and MBR removed all size fractions. The DF also removed all size fractions, but due the variation between the replicates, the results should be handled with care. Before the treatments, in primary or secondary effluents, the smallest size fraction (20-100µm) was the most abundant in three out of four WWTPs (Fig 1.). This finding supports our previous study where pre-treatment efficiently removed larger size fractions (>300 µm, 100 – 300 µm) and the smallest size fraction (20 – 100 µm) became most abundant (Talvitie et al. 2017). The results highlight the need for final treatment stage technologies to remove particularly the small-size (< 100 µm) MPs from wastewater. According to the results, we also suggest including small size fractions (< 100 µm) into the examination when evaluating the role of WWTPs as a point source of MPs into the
environment, as particularly smaller MPs are left in effluents after the conventional treatment processes.

Figure 1. Concentration of MPs in each size fraction (20 -100µm, 100 – 300µm, >300µm) before and after the treatments. DF10 = discfilter with pore size 10 µm, DF20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

All shapes of MPs were removed efficiently during treatments (Fig 2.). Fibers comprised the majority of MPs detected in our samples, and contributed to 39 - 81% before and 29-100% after the treatments of total MPs (Fig 2.). Most of the fibers entering the WWTPs are removed already during pre-treatment phases (Talvitie et al. 2015 and 2017), however, a proportion of them also passes through the process entering the effluent. Hence, the final-stage treatment technologies have to be able to remove particularly fibers to efficiently increase the removal capacity of MPs from wastewater.
Figure 2. Concentration of MPs in the different MP shape categories before and after the treatments.

DF10 = discfilter with pore size 10 µm, DF20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

3.3 FTIR analysis

Altogether 13 polymers were identified: polyester (PES), polyethylene (PE), polypropylene (PP), polystyrene (PS), polyurethane (PU), polyvinylchloride (PVC), polyamide (PA), acrylamide, polycrylate, alkyd resin, polyphenylene oxides (PPO) and ethylene vinyl acetates (EVA). PES dominated the samples (av. 60%), followed by PE (av. 14%), polyacrylates (av. 7%), PVC (av. 5%), PS (av. 4%) and PP (av. 3%). Most of the PES comprised of textile fibers and most of the PE of microbeads that are, based on their particular shape and size, most likely from personal care products (Fendall and Sewell 2009, Schneiderman, 2015, Talvitie et al. 2017). The Discfilter and MBR decreased the number of polymers during the treatment. In their study, Mintenig et al. (2017) also detected clear decrease in the amount of polymers (from 6 to 3) during the postfiltration. In this study, with RSF and DAF, more polymers were detected after the treatment (Table. 6.). Largest
sample volumes (1000 L) was sampled after the DAF and RSF and it is possible that with the larger volumes more rare polymers was detected, increasing the amount of detected polymers. The same polymer were probably present but not detected with lowers samples volumes before the treatment.

Table 6. The amount of different polymers and their percentages before and after the advanced wastewater treatments. DF 10 = discfilter with pore size 10 µm, DF 20 = discfilter with pore size 20 µm, RSF = rapid sand filters, DAF = dissolved air flotation and MBR = membrane bioreactor.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>DF10 Before</th>
<th>DF10 After</th>
<th>DF20 Before</th>
<th>DF20 After</th>
<th>RSF Before</th>
<th>RSF After</th>
<th>DAF Before</th>
<th>DAF After</th>
<th>MBR Before</th>
<th>MBR After</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES (%)</td>
<td>75.36</td>
<td>66.67</td>
<td>45.89</td>
<td>100</td>
<td>18.16</td>
<td>28.38</td>
<td>24.10</td>
<td>82.24</td>
<td>70.08</td>
<td>100</td>
</tr>
<tr>
<td>PE (%)</td>
<td>14.49</td>
<td>33.33</td>
<td>0.66</td>
<td>4.11</td>
<td>30.99</td>
<td>1.86</td>
<td>47.08</td>
<td>12.01</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>PP (%)</td>
<td>2.9</td>
<td>16.45</td>
<td>32.89</td>
<td>16.35</td>
<td>1.71</td>
<td>1.86</td>
<td>8.82</td>
<td>0.88</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>PS (%)</td>
<td>4.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU (%)</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.7</td>
<td></td>
<td>0.88</td>
<td></td>
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<tr>
<td>PVC (%)</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td></td>
<td>1.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA (%)</td>
<td>4.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td></td>
<td>1.36</td>
<td></td>
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<tr>
<td>Polyamide (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.45</td>
<td></td>
<td>0.88</td>
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<tr>
<td>Acrylamide (%)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>1.45</td>
<td></td>
<td>2.76</td>
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<tr>
<td>Polyacrylates (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>32.07</td>
<td></td>
<td>9.71</td>
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<tr>
<td>Alkyd resin (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.86</td>
<td></td>
<td>0.88</td>
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<tr>
<td>PPO (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.14</td>
<td></td>
<td>0.04</td>
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<tr>
<td>EVA (%)</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total amount</td>
<td>6</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>7</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

Some of the previous studies have relied on visual identification of MPs (Dris et al. 2015, Talvitie et al. 2015, Mason et al. 2016). The MP analysis based on visual identification contains the risk of MP over/underestimation due the misidentification of particles. However, sample preparation (e.g digestion, staining and extraction) can reduce the risk of misidentification (Mason et al. 2016).

Most of the studies perform FTIR analysis to confirm the materials of MPs, but include visual pre-
selection of the particles prior to analysis (Carr et al. 2016, Murphy et al. 2016, Talvitie et al. 2017, Ziajahromi et al. 2017, this study) and therefore contain a risk of underestimation.

The FPA-based micro-FT-IR have been recently suggested for unbiased MP analysis method for environmental as well as wastewater samples (Tagg et al. 2015, Löder et al. 2015, Mintenig et al. 2017). In the method, the whole filters (pre-treated samples) are analyzed automatically and no visual pre-selection is needed. This gives clear advantage compared to methods based on visual pre-selection. However, the whole-filter analysis appear to be time consuming, especially when analyzing wastewater samples containing high number of particles. This may further lead to compromises like performing partial analysis of the samples in order to process the analysis in reasonable time (Mintenig et al. 2017). Further development of MP analysis is needed, particularly for challenging matrixes like wastewaters, for better estimations of quantities and qualities of MPs in wastewaters.

The proportion of primary and secondary MPs in final effluents were estimated. In secondary effluent, after the CAS process, the primary MPs comprised 19% and secondary MPs 81% of total amount of MPs. After the advanced final-stage treatments, in final effluent, the corresponding figures were 9% and 91%, respectively. The primary MPs comprised mainly of microbeads from personal care products and secondary MPs of synthetic textile fibers and fragmented pieces of plastics (Fig. 3.). The percentage of secondary MPs increased slightly with purification level. The reason for this is probably the escape of synthetic fibres from the treatments, due to their small size and morphology, which allow them to pass through small pore sizes.

The proportion of primary and secondary MPs in effluent samples were also estimated (the DF10 results are excluded from the examination). After the CAS process, in secondary effluent, the primary MPs comprised 19% and secondary MPs 81% of total amount of MPs. After the advanced final-stage treatments, in final effluent, the corresponding figures were 9% and 91%, respectively. The primary MPs comprised mainly of microbeads from personal care products and secondary MPs
of synthetic textile fibers and fragmented pieces of plastics (Fig. 3.). The proportion of secondary MPs increased slightly with purification level as the proportion of textile fibers increased. Due to their small size and morphology, fibers probably pass through the final-stage treatments more easily, compared to microbeads from cosmetics.

Figure. 3. A and B: primary MPs. Microbeads derived from personal care products. C and D: Secondary MPs. Fragments from break-down of larger plastics and synthetic textile fibers.

Dividing MPs into primary and secondary particles is a useful distinction as it can help to find their sources and identify solutions to reduce their input to the environment (GESAMP 2015). When MPs have a distinct shape and color, it may be possible to recognize them during visual inspection and hence estimate their source, like in a case of textile fibers and microbeads from cosmetics. The knowledge of the source gives the possibility to control the MP contamination before they enter
WWTPs and in environment. For example, companies and governments had started to regulate and ban the use of microbeads in personal care products (Microbead-Free Waters Act 2015). Also, filters for removing textile fibers from washing machine wastewater has been developed (Life + Mermaid 2017). However, even if part of the MPs entering WWTPs could be removed with source-based solutions, there will be still a significant proportion of unrecognizable primary and secondary MPs, which will remain the concern of WWTPs in a future.

Conclusions

All advanced final-stage wastewater treatment technologies included in our study removed microplastics (> 20 µm). The MBR decreased 99.9% of the MPs from primary effluent and gave also the lowest MP concentration in the final effluent. The RSF removed 97%, DAF 95% and DF 40 – 98.5% of the MPs from secondary effluent during the treatments. Given the large volumes of effluents constantly discharged into the aquatic environments, microplastic pollution should be taken into consideration, when designing advanced final-stage wastewater treatment technologies and applying them into WWTPs. The treatments also removed all size fractions and shapes of MPs. The smallest size fraction (20-100µm) and textile fibers were the most common MP types before and after the final treatment stages. This highlights the need for final-stage technologies to remove particularly small size and fiber-like MPs from effluents.

Our study included comprehensive FTIR analysis. MPs were made of 13 different polymers, with the majority determined as PES and PE. The proportion of secondary MPs increased slightly with purification level. The primary MPs comprised mainly of microbeads from personal care products and secondary MPs of synthetic textile fibers and fragmented pieces of plastics. The knowledge of the sources gives the possibility to source control of the MP pollution before they enter WWTPs.
Acknowledgments

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Highlights

- The detected microplastics were made of 13 different polymers, with the majority determined as polyester and polyethylene.

- Advanced wastewater treatment removed MPs efficiently from secondary effluents.

- The highest microplastics removal (99.9%) was achieved with membrane bioreactor (MBR).

- The smallest size fraction (20-100µm) and textile fibers were the most common microplastic types before and after the treatment.

- The proportion of primary and secondary MPs in effluent samples were estimated