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How well is microlitter purified from wastewater? : A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant

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How well is microlitter purified from wastewater? – A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant

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Abstract

Wastewater treatment plants (WWTPs) can offer a solution to reduce the point source input of microlitter and microplastics into the environment. To evaluate the contributing processes for microlitter removal, the removal of microlitter from wastewater during different treatment steps of mechanical, chemical and biological treatment (activated sludge) and biologically active filter (BAF) in a large (population equivalent 800 000) advanced WWTP was examined. Most of the microlitter was removed already during the pre-treatment and activated sludge treatment further decreased the microlitter concentration. The overall retention capacity of studied WWTP was over 99% and was achieved after secondary treatment. However, despite of the high removal performance, even an advanced WWTP may constitute a considerable source of microlitter and microplastics into the aquatic environment given the large volumes of effluent discharged constantly. The microlitter content of excess sludge, dried sludge and reject water were also examined. According to the balance analyses, approximately 20% of the microlitter removed from the process is recycled back with the reject water, whereas 80% of the microlitter is contained in the dried sludge. The study also looked at easy microlitter sampling protocol with automated composite samplers for possible future monitoring purposes.

Key words: WWTP, microlitter, microplastics, wastewater, sludge, reject water, microlitter budget
1. Introduction

Litter has become a serious problem in aquatic environments worldwide. Litter includes both organic and inorganic materials like glass, metals, rubber, wood, paper, textiles and, for the most, plastics (OSPAR 2014). Microlitter comprises litter particles smaller than 5 millimetres. Microlitter, and particularly its plastic subtype, microplastics, has received considerable attention over the past decade (Thompson et al. 2004, Barnes et al. 2009, Ladewig et al. 2015). Microplastics are of concern because of their durability and potential to be transferred within food webs (Cole et al. 2013, Setälä et al. 2014). Microplastics may cause mechanical stress when ingested, but also expose marine organisms to various hazardous substances, such as plasticizers (Fries et al. 2013), toxic metals (Rochman et al. 2014) and persistent organic pollutants (POPs) (Rios et al. 2010, Chua et al. 2014). These micropollutants are either added to the plastics during production or adsorbed from the surrounding water (Teuten et al. 2009). In aquatic environments, microplastics can also function as artificial “microbial reefs” and transport non-indigenous and possibly harmful species (Zettler et al. 2013). In addition to microplastics, also non-synthetic textile fibers has been proposed to have potential to transport chemical pollutants throughout the aquatic environment (Ladewig et al. 2015).

Microlitter consists of primary and secondary particles. Primary particles are intentionally microscopic in, e.g microbeads in peeling lotions and textile fibers, while secondary microlitter is fragmented from larger particles (Barnes et al. 2009). Both aquatic and land-based sources have been identified contribute to the amount of litter in marine environments (Law et al. 2010). Land base sources include public littering, poorly managed landfills, riverine transport, stormwater and untreated municipal sewage.

Recently, wastewater treatment plants (WWTPs) have been suggested to act as one of the land base sources or entrance routes for microlitter to the aquatic environment (Magnusson & Norén 2014, Talvitie et al. 2015, Murphy et al. 2016). First studies have shown that microlitter can be efficiently (> 98 %) removed from the wastewater during the wastewater treatment (Magnusson & Norén...
2014, Carr et al. 2016, Murphy et al. 2016). However, treated effluents still contain microlitter particles like plastic microbeads from toothpaste and textile fibers (Browne et al. 2011, Talvitie et al. 2015, Carr et al. 2016).

As vast volumes of effluent waters are discharged continuously into aquatic environments globally and the amounts are expected to grow due the population growth and urbanization (UN Water 2015), the role of WWTPs as an entrance route of microlitter to aquatic environments may be significant. At the same time, WWTPs can offer solutions to reduce the input of microlitter into the environment. Despite of this potential, very little attention has yet been drawn to the actual removal of microlitter during different type of wastewater treatment processes. Here we report detailed data on the removal of microlitter during different treatment steps in a large (population equivalent 800 000) advanced WWTP. The balance of microlitter in WWTP were estimated to further evaluate the removal and distribution of microlitter during the treatment processes. Also, the effect of microlitter size and shape on their removal in different treatment steps were determined. The further objective of this study was to establish an easy-to-use protocol for monitoring of WWTPs. In the end, we report the evaluation of microlitter and microplastic load discharged into the marine environment with effluents.

2. Materials and Methods

2.1 Description of the selected WWTP

Selected WWTP (Viikinmäki, Helsinki Region Environmental Services Authority, HSY) is the largest wastewater treatment plant in Finland and the Nordic Countries, treating the wastewaters of ca. 800,000 inhabitants in the Helsinki metropolitan area. An average of 270 000 cubic meters of treated wastewaters are discharged from the WWTP into a Gulf of Finland, Baltic Sea every day. The treatment process in Viikinmäki WWTP is based on activated sludge method and has multiple treatment steps based on pre-, chemical- and biological treatment. The nitrogen removal has been
enhanced with a tertiary denitrifying biological filter. In 2015, 95% of organic material (BOD₇),
98% of suspended solids (SS), 95% of total phosphorus (P-tot) and 90% of total nitrogen (N-tot)
were removed during the treatment process of the selected WWTP.

Pre-treatment includes coarse screening (10 mm), grit removal, chemical treatment and primary
sedimentation. In order to remove phosphorus, ferrous sulphate is dosed in the sand removal prior
to secondary clarifier. In biological treatment biodegradable matter and nitrogen are removed from
the wastewater with activated sludge method. Activated sludge process includes aeration tanks and
secondary clarifiers. Hydraulic retention time in the process is approximately 25 hours and sludge
retention time varies between 6 – 12 days. Most of the activated sludge is recycled from secondary
clarifiers into the aeration tanks as return activated sludge but part of it is also continuously
removed from the process. This excess sludge is returned to primary sedimentation and sent to
sludge treatment together with raw sludge. The nitrogen removal is further improved in tertiary
treatment process with biologically active filter (BAF). During the BAF process, wastewater flows
through tightly packed polystyrene beads. The beads provide a surface for micro-organisms to
attach and grow. While growing, they consume organic material as well as phosphorus and convert
nitrates to nitrogen gas.

Viikinmäki WWTP has also a solids handling treatment. Organic matter in the sludge is
anaerobically digested to produce biogas, i.e. methane and consecutively used for the plant’s own
energy consumption. After the digestion, sludge is dewatered with centrifuges. For dewatering, the
sludge is conditioned with flocculation chemical polyacrylamide (PAM). PAM induces a release of
the water during dewatering by enhancing the aggregation of sludge particles into larger particle
groups called flocs. Dewatering generates reject water, which is conducted via a settling tank into
the beginning of the wastewater treatment process. The dried sludge is processed further in
composting fields and used in green construction. The plant produces annually around 60,000
tonnes of dried sludge which has a dry solids (TS) content of 29%.
2.2 Sampling methods

The samples were collected from the plant influent, after pre-treatment, after the activated sludge (AS) process, plant effluent, excess sludge, reject water and dried sludge (SD fig. S1). Sampling was carried out during a seven-day period 14.9 – 20.9.2015 with three different sampling methods; grab sampling (here meaning one sampling occasion at a certain time), 24-hour composite sampling and 24-hour sequential sampling (Table 1).

Table 1. Sampling methods (grab sampling, 24h composite sampling, 24h sequential sampling), sampling locations (wastewater, sludge) and sampling days.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grab sampling (wastewater)</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Grab sampling (sludge)</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grab sampling (reject water)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24h composite sampling (wastewater)</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>24h sequential sampling (wastewater)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>
2.2.1 Grab sampling of the wastewater and sludge

Grab samples from wastewater were collected from each sampling site in water process. Three replicates (n = 3) were taken from each sample types consecutively. Sampling was done by pumping water from the wastewater stream was (at depth ∼ 1 m) onto the designated filter with an electric pump (Biltema art.17-953). Filtering set up previously designed for microplastic sampling in wastewaters was used (Talvitie et al. 2015). The respective filter mesh sizes were 300, 100 and 20 µm, giving size fractions of > 300 µm, 100 – 300 µm and 20 – 100 µm (SD fig S2). The volume of each sample (Table 2.) was measured with a flow meter (Gardena Water Smart Flow Meter) attached to the pump. This volume of filtered water depended on the water quality and filter size. The volumes of replicate samples differed, since the water quality varied.

This sampling method is not applicable for influent water due to its high amount of organic material which rapidly clogs the filters allowing only small water volumes to pass. For the influent sampling a metallic beaker to collect water from the wastewater stream surface was used and the samples were later filtered in laboratory with the same filter set up.

Samples from the excess sludge and reject water were collected with the same method as influent samples, while dried sludge was collected by hands from the conveyor belt after dewatering process. All sludge and reject water samples were placed into pre-cleaned plastic containers and transported into the laboratory for filtering. The sludge and reject water samples were diluted before filtering by mixing subsamples of wet sludge (1 gram), reject water (10 gram) and dry sludge (0,2 gram) with 1 liter of tap water. Diluted sludge and reject water samples were then filtered with the filtering device as the wastewater samples. Details of different samples are presented in table 2. To prevent contamination during the sampling, all equipment was rinsed carefully with tap water prior to sampling.
Table 2. The sample volumes/weights with sampling locations and mesh sizes of the filters

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>sample volume/weight 300 µm filter</th>
<th>sample volume/weight 100 µm filter</th>
<th>sample volume/weight 20 µm filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>0.1 l</td>
<td>0.1 l</td>
<td>0.1 l</td>
</tr>
<tr>
<td>After pre-treatment</td>
<td>50 – 333 l</td>
<td>7 – 10 l</td>
<td>0.5 l</td>
</tr>
<tr>
<td>after AS</td>
<td>200 – 333 l</td>
<td>20 – 30 l</td>
<td>1 l</td>
</tr>
<tr>
<td>Effluent</td>
<td>1000 l</td>
<td>100 l</td>
<td>2 l</td>
</tr>
<tr>
<td>Excess sludge</td>
<td>1.2 ml = 1 g</td>
<td>1.2 ml = 1 g</td>
<td>1.2 ml = 1 g</td>
</tr>
<tr>
<td>Dry sludge</td>
<td>0.2 g</td>
<td>0.2 g</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Reject water</td>
<td>10 ml = 10 g</td>
<td>10 ml = 10 g</td>
<td>10 ml = 10 g</td>
</tr>
</tbody>
</table>

2.2.2 Composite sampling

24-hour composite samples were collected from all sites in water process (Table 3.). Composite samplers (ISCO 3700) in each sampling location took flow proportional, discrete samples at regular 15 min. intervals over 24-hour period of time. The samples were collected into plastic containers placed in refrigerators. Both, the containers and refrigerators were carefully cleaned prior to sampling to avoid contamination from room dust. From the containers, samples were poured into the filter device using a measuring glass. Sampling was performed three times during the week; Tuesday, Thursday and Sunday (Table 1.). To assess possible contamination, blank samples of tap water were used as controls following the same methodological procedure as the actual samples.
Table 3. The 24-hour composite sample volumes with sampling locations and mesh sizes of the filter.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>sample volume with 300 µm filter</th>
<th>sample volume with 100 µm filter</th>
<th>sample volume with 20 µm filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>0.1 l</td>
<td>0.1 l</td>
<td>0.1 l</td>
</tr>
<tr>
<td>After pre-treatment</td>
<td>13.2 – 14.5 l</td>
<td>8.5 – 10.5 l</td>
<td>0.5 l</td>
</tr>
<tr>
<td>After AS</td>
<td>11 – 14.5 l</td>
<td>11 – 14.5 l</td>
<td>1 l</td>
</tr>
<tr>
<td>Effluent</td>
<td>10.5 – 13.5 l</td>
<td>10.5 – 13.5 l</td>
<td>2 l</td>
</tr>
<tr>
<td>Control</td>
<td>14.5 l</td>
<td>14.5 l</td>
<td>2 l</td>
</tr>
</tbody>
</table>

2.2.3 Sequential sampling

Influent and effluent sampling were performed simultaneously with automated samplers (ISCO 3700). The samplers took 24 samples at 1-hour interval. After sampling, 3 samples (3 hours) were pooled together, resulting 8 samples per sampling. To avoid contamination, the bottles and the samplers were cleaned carefully before the sampling. The sampler device formed a closed system for entire sampling period. After the sampling, bottles were immediately closed until filtering.

Control samples prepared of tap water were preserved in pre-cleaned bottles in the sampler for 24-hours and treated the same way as the actual sequential samples.

2.3 Analyses of microlitter

2.3.1 Analyses with stereo microscope

All the filtered samples were stored in clean Petri dishes. Samples were visually examined using a stereomicroscope (Fiberoptic-Heim LQ 1100, magnification ×50), light projected from above to get good image of surface structure of microlitter particles. The particles were counted, divided into
fibers, fragments, flakes, films and spheres and their coloration documented. The morphological properties of the particles were inspected with micro tweezers to exclude soft, easily disintegrating organic materials. Organic litter like food scraps and paper (cellulose), were excluded from the examination. To detect possible contamination during transport and microscopic analyses, three control samples were carried along during the sampling in the WWTP.

2.3.2 Material identification of microlitter

The chemical composition of microlitter particles from effluent samples were analysed with imaging Fourier Transform infrared spectrometer (FTIRi) (Spectrum Spotlight 300, PerkinElmer, Waltham, MA, USA). All together three effluent samples, one replica from each day (Monday, Wednesday and Saturday) were chosen for analyses and all together 752 particles were included into the analyses. Particles were hand-sorted from the filters with fine tip tweezers under the stereomicroscope and carefully rinsed with distilled water to remove organic matter that was attached to them. Rinsed particles were placed onto ZnSe windows designed for FTIRi microscopy and let to dry for few hours. Each sample window was photographed with the FTIRi and particles identified from the picture. The particles were exposed one by one to infrared radiation in wave length region of 700 - 4000 cm$^{-1}$ using single point transmission mode. To analyse the spectra obtained with FTIRi, the Thermo Scientific™ Hummel Polymer and Additives FT-IR Spectral Library was used. The materials of textile fibers were analyzed with textile fiber library made ourselves from pure model fibers (purchased from Lahti University of Applied Sciences, Faculty of Technology) (SD fig. S3 – S10). The model fibers included cotton, wool, linen, silk, viscose, polyester, polyacryl, polyamide, and polypropene fibers.
2.3.3 The data analyses

The removal of microlitter during different treatment steps were statistically analyzed using analysis of variance (ANOVA).

For the microlitter balance analyses, the average microlitter flow was calculated by multiplying the average microlitter concentrations with the corresponding average flow along each wastewater treatment step. The equation can be expressed as:

\[ \text{ML} = Q \times C \]

ML (microlitter d\(^{-1}\)) is the flux of microlitter and Q (L d\(^{-1}\)) is wastewater, reject water or sludge flow. C (ML L\(^{-1}\)) is the average microlitter concentration measured in the wastewater, reject water or sludge.

The retention capacity of microlitter in WWTP was calculated as:

\[ \left( \frac{[\text{Influent}] - [\text{Effluent}]}{[\text{Influent}]} \right) \times 100 \]

3. Results and Discussion

3.1 Grab sampling of wastewater and sludge

Most of the microlitter particles (97.4% - 98.4%) were removed already during mechanical and chemical pre-treatment phase (table 4). During pre-treatment, microlitter concentrations decreased significantly in all three sampling occasions (Monday: \( F = 190.668 > 7.709; P < 0.05 \), Wednesday: \( F = 14.246 > 7.709; P < 0.05 \) and Saturday: \( F = 37.689 > 7.709; P < 0.05 \)). This finding is consistent with previous studies examining the removal of microlitter during wastewater treatment processes (Talvitie et al. 2015, Carr et al. 2016, Murphy et al. 2016). Pre-treatment in Viikinmäki WWTP includes screening, grit removal and chemically enhanced primary sedimentation. Purpose of the treatment is to remove grit, particulate materials as well as phosphates and colloidal matter from the
wastewater. According to our results, these techniques remove efficiently also microlitter. In influent, majority of microlitter particles are probably attached to grit and larger particles and removed from the wastewater along with them.

Concentration continued to decrease significantly also during AS process, except on Wednesday when the variation between the replicates were so high that although microlitter was clearly removed to a lower level, the result was insignificant with P-value 0.05 (Monday: $F = 7.966 > 7.709; P < 0.05$, Wednesday: $F = 7.472 > 7.709; P < 0.05$, Saturday: $F = 42.097 > 7.709; P < 0.05$).

Together AS process further decreased the microlitter concentration in range $[7\% - 20\%]$ (table 4).

During the treatment, microlitter particles are mixed with flocs and settled into the sludge during secondary sedimentation. Small part of the microlitter, however, escapes the treatment.

According to our results, the tertiary treatment, biologically active filter (BAF), didn’t decrease microlitter concentration (table 4). The main purpose of BAF in Viikinmäki WWTP is to remove nitrogen from the wastewater but according to the preliminary study (Talvitie et al. 2015) the filtering effect was expected to remove a proportion of the microlitter particles left in the secondary effluent. After the BAF, the discharged effluent contained 0.7 – 3.5 microlitter particle per liter of wastewater. This result differs from the study of Carr et al. (2016), where no microlitter after the tertiary treatment was detected. Differences in the sampling methods, especially volumes make this comparison difficult, but both works clearly underline the efficiency of the first steps of the processes in the purification efficiency. The two WTPs also differ in the techniques used for tertiary treatments, which may have caused differences in the removal result. Where BAF appears to be inefficient to remove microlitter, other techniques, like gravity filters, may have a better removal capacity.
Table 4. The average microlitter concentration, including all the fractions (> 300 µm, 100 – 300 µm and 20 – 100 µm), in influent, after pre-treatment, after AS and in effluent. Data is given in number of microlitter particles per L⁻¹ of wastewater. Figures represent mean values ±SE, n =3.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Monday</th>
<th>Wednesday</th>
<th>Saturday</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>636.7 (±38.8)</td>
<td>686.7 (±155.0)</td>
<td>380 (±52.2)</td>
</tr>
<tr>
<td>After pre-treatment</td>
<td>14.2 (±4.0)</td>
<td>10.9 (±2.9)</td>
<td>9.9 (±1.0)</td>
</tr>
<tr>
<td>After AS</td>
<td>1.0 (±0.6)</td>
<td>1.3 (±0.9)</td>
<td>2.0 (±0.2)</td>
</tr>
<tr>
<td>Effluent</td>
<td>3.2 (±0.7)</td>
<td>0.7 (±0.6)</td>
<td>3.5 (±1.3)</td>
</tr>
</tbody>
</table>

To evaluate the microlitter balance of the WWTP, excess sludge, dry sludge and reject water were also analyzed for one sampling day. The results are collected to table 5. The average wastewater flow during the sampling day (Wednesday) was 2.82 × 10⁸ L d⁻¹.

Table 5. The average microlitter concentrations and flow rates in excess + raw sludge mixture, dry sludge and reject water. Data is given in number of microliter particles per g⁻¹ or L⁻¹ of sludge. Concentrations are mean values ±SE, n=3 and flows day average.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Recess + raw sludge</th>
<th>Dry sludge</th>
<th>Reject water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microlitter per gram</td>
<td>76.3 (±4.3)</td>
<td>186.7 (±26.0)</td>
<td>12.9 (±0.3)</td>
</tr>
<tr>
<td>Microlitter per liter</td>
<td>63611.1 (±3543.7)</td>
<td>NA</td>
<td>12866.7 (±275.4)</td>
</tr>
<tr>
<td>Average flow (L d⁻¹)</td>
<td>2.92×10⁶</td>
<td>1.84×10⁵</td>
<td>2.74×10⁶</td>
</tr>
</tbody>
</table>

A microlitter balance over the treatment process is presented in Fig. 3. The overall balance and the balance of the pre-treatment are summing up to an error of approximately 20% of the influent load. This indicates that the microlitter sampling and analysing have been successful in different parts of the water and solid flows. When not removed from the WWTP with effluent or dried sludge,
microlitter particles are recycled inside the WWTP with the activated sludge and reject water. During the digestion organic matter is degraded, but non-biodegradable or slowly degradable particles like plastics are not affected by this sludge handling. In dewatering of raw and excess sludge, the reject water is separated and conducted into the beginning of the wastewater treatment process. Balance analysis indicates that reject water acts as considerable inner source of microlitter particles back into the process (fig 1.). Approximately 20% of the microlitter removed from the process is recycled back in the reject water whereas 80% of the microlitter is contained in the dried sludge.

Fig 1. Microlitter balance and distribution in the WWTP. White arrows represents wastewater and black-coloured represents sludge. Figures are microlitter flow per day (ML/d).

The dried sludge is transported to composting fields. After composting, the product is used in green construction. As Viikinmäki WWTP produces annually around 60,000 tonnes of dried sludge,
enormous amounts of microlitter are ending up to the environment with sludge.

**3.2 24-hour composite samples**

24-hour composite sampling was performed to study the average concentration and removal of microlitter during the wastewater treatment over one day period. Sampling was performed three times during the sampling week; Monday to Tuesday, Wednesday to Thursday and Saturday to Sunday (Table 6.). The method was also evaluated for possible microlitter monitoring purposes.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Tuesday</th>
<th>Thursday</th>
<th>Sunday</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>900.0</td>
<td>390.0</td>
<td>630.0</td>
</tr>
<tr>
<td>After pre-treatment</td>
<td>23.8</td>
<td>10.1</td>
<td>4.1</td>
</tr>
<tr>
<td>After AS</td>
<td>2.8</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Effluent</td>
<td>2.8</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Blank</td>
<td>0.4</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The trend of microlitter removal during different treatment steps determined with 24 – hour composite sampling was very well in line with grab sampling results. Also the microlitter content per liter was in the same range. Surprisingly the variation between sample days especially in influent wastewater was larger with 24h composite samples (390.0 – 900.0 particles per L⁻¹) than with grab samples (380±52.2 – 686.7±155.0).

Automated samplers provide an easy microlitter sampling protocol. This can be utilized in monitoring. However, if the microlitter concentration is very low, composite samples might give false zero results, as the sample volumes are so small (in our study, only 10-20 liters). In this case,
grab sampling with larger sample volumes might be required. Another clear disadvantage of composite sampling is the microlitter contamination. Microlitter type that easily contaminates the samples is textile fiber. As it is also one of the most common microlitter types in wastewater (Habib et al. 1996, Zubris et al. 2005, Talvitie et al. 2015), the contamination distorts the results and easily leads to overestimation of microlitter and microplastics in wastewater. During this study, a great care was taken to minimize contamination during the composite sampling. However, the efforts, contamination of microlitter particles was continuously detected, being between 0.4 – 0.8 microlitter per L$^{-1}$ of water, which accounts for over 30% of the estimated microlitter content in the effluent water. No contamination was detected due to the transportation and analyses.

24-hour sequential sampling

In-day variation in the microlitter concentration was detected in both influent and effluent samples (Fig 2). The night time (10 pm – 7 am) concentrations were generally lower, average concentrations in influent 476.7 and effluent 0.8 microlitter L$^{-1}$, compared to day time (7 am – 10 pm) concentrations of 584 in influent and 1.7 microlitter per L$^{-1}$ in effluent. No contamination was detected from blank sequential samples. The lowest microlitter concentration during day time was detected during 1 – 4 pm and microlitter concentration increases towards the early evening hours. This might have had an impact on our results from grab sampling, as the sampling was performed always in day time during low concentration hours.
Fig 2. 24-hour sequential samples. Microlitter concentrations in influent and effluent. Data is given in number of microlitter particles per L\(^{-1}\) of wastewater. One sample consist of three-hour period pooled together.

The variation trend in microlitter concentration is in line with day-time activities in households which influence the amount of microlitter coming to the WWTPs. The in-day variation in microlitter concentration has to be taken into account when evaluating the total amounts of microlitter entering and leaving the WWTP with discharged effluents. These results supports the use of composite sampling or e.g long-term large-scale sampling described by Carr et al. (2016) when evaluating the role of WWTPs as source of microlitter pollution.
3.3 Analyses of microlitter

3.3.1 Analyses with stereomicroscope

The proportion of the different microlitter size fractions differed between the wastewater treatment steps (Fig. 3). Pre-treatment had the greatest impact on microlitter size distribution, efficiently removing larger size fractions (≥ 300 and 100 – 300 μm), and particles in the smallest fraction (20-100μm) became most abundant. In effluent samples, the slight increase of particles of 100-300 μm in size was caused by the emergence of clear crystal fragments in this fraction. Origin of these fragments remained unknown.

![Size fractions diagram]

Figure 3. The proportion of the different size classes of microlitter during the wastewater treatment steps. The distribution is based on number of particles.

Also the proportion of particle types/shapes changed during the purification process (Fig. 4). In the influent the fibers made up around 70 % of the total microlitter particles, and in effluent only 30 %. Most of the fibers were removed already during pre-treatment. In influent, textile fibers probably
attach easily to grit and to other larger organic waste material and settle down to sludge efficiently during primary sedimentation. The proportion of fragments increased during the treatment. Majority of the fragments detected in effluent consisted of clear fragments. Relative proportion of flakes was approximately the same in all treatment phases.

Figure 4. The proportion of microlitter shape categories during the wastewater treatment phases. The distribution is based on number of particles.

3.3.2 Material identification

All together 752 microlitter particle were included in the material identification. However, the overall success rate for material identification was relatively low, only 18 % (table 8). Especially clear fragments remained unrecognized. Reasons for overall weak success rate were unrecognizable particles (e.g. inorganic minerals and metals), limits of the FTIR spectroscopy and weak quality infrared spectra. The cause for weak quality spectra can be e.g the biofilm contaminating the particles. The biofilm in our wastewater samples generally gave spectrum peaks at wavenumber of
1000 – 2500 cm\(^{-1}\). In those wavenumbers the biofilm was blocking the possible peaks from the actual material of the particle and hindered the analyses. Scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) could probably increase the percentages for successful analyses by e.g. confirming inorganic composition of the particles. Some chemical treatments have been tested for removal of biological matter from samples when analysing the microplastics from wastewater (Tagg et al. 2015). However, if natural materials e.g. cotton textile fibers are included into the examination, the chemical treatments can harm the materials and complicate the analyses.

Table 8. Microlitter types from effluent samples included into the material analyses, the success rate of the analyses and detected materials (PE=polyethylene, PS=polystyrene, PP= polypropylene PES=polyester, NA = not available).

<table>
<thead>
<tr>
<th>Particle types</th>
<th>Included</th>
<th>Successfully analyzed</th>
<th>%</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibers</td>
<td>108</td>
<td>108</td>
<td>100</td>
<td>See fig.7</td>
</tr>
<tr>
<td>Fragments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>26</td>
<td>3</td>
<td>12</td>
<td>PE x 2, PS</td>
</tr>
<tr>
<td>Black</td>
<td>18</td>
<td>3</td>
<td>17</td>
<td>PE x 2, PP</td>
</tr>
<tr>
<td>Red</td>
<td>4</td>
<td>1</td>
<td>25</td>
<td>PP</td>
</tr>
<tr>
<td>Yellow</td>
<td>3</td>
<td>3</td>
<td>100</td>
<td>PES</td>
</tr>
<tr>
<td>Green</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>Brown</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>White</td>
<td>4</td>
<td>1</td>
<td>25</td>
<td>PP</td>
</tr>
<tr>
<td>Clear</td>
<td>507</td>
<td>14</td>
<td>2.8</td>
<td>PE (minerals?)</td>
</tr>
<tr>
<td>Silver</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>NA (metals?)</td>
</tr>
<tr>
<td>All</td>
<td>571</td>
<td>25</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
All of the 108 fibers from effluent samples were successfully analysed with FTIRi. Textile fiber is easily identifiable litter type and this helps further material analyses. However, majority of the natural textile fibers gave relatively weak spectrums and it was hard to found a match for them in commercial polymer libraries. To solve this problem, the spectrums were analysed with textile fiber library made from model fibers. With the help of the library, materials of all textile fibers were ascertained.

The top two textile fibers were cotton (44%) and polyester (33%) (Fig 5.). In overall, 66% of the all textile fibers were natural fibers of cotton, linen or wool. Natural textile fibers have been more or
less excluded from the scientific microlitter studies and the focus has been more on synthetic fibers. This is probably due the general perception that because natural fibers degrade faster and are “organic” by nature, they do not pose harm to the environment. Opposite opinions state that natural fibers may actually act as carriers to harmful substances because textiles from organic fibres have often been treated with harmful chemicals, such as flame retardants. Also, like microplastics, natural fibers may also absorb pollutants from surrounding water and faster degradation compared to synthetic ones can lead to quicker release of chemicals into the surrounding environment (Ladewig et al. 2015). As the textile fiber, from washing of clothes (Browne et al. 2011), is one of the most common litter types in wastewater and both the natural and synthetic fibers can have negative impacts in environment, we recommend that when evaluating the role of WWTPs as point source of microlitter, natural textile fibers would be included into the examination.

Figure 5. Materials of fibers and their percentage in effluent samples.

Microlitter type observed frequently in our effluent samples was clear polyethylene fragment, the type found in some widely used cleansing scrubs (fig 6, SD fig S11). When a particle has a very distinct and recognizable profile (size, shape and color), it is possible to find its origin. For example
Carr et al. (2016) discovered that the most common particle found in their effluent samples, blue polyethylene fragments, resembled the ones found in toothpaste.

Figure 6. On the left: polyethylene fragments, covered with brownish biofilm, from effluent samples. On the right: polyethylene fragments from cleansing scrubs.

However, clear PE fragments consisted only a small part from all clear particles found from our effluent samples (Table 8). Most of the clear particles were hard crystals which remained uncharacterized. Wastewater contains a lot of microlitter and microplastic particles that are unrecognizable and it is difficult to estimate their possible material before material analyses. Particles are either secondary microparticles deriving from fragmentation of larger litter items or primary microparticles from unknown source. Analyzing these particles is particularly challenging when material is not suitable for FTIR spectroscopy and hence the spectra gained from the analyses are unclear.
3.4.3 The role of WWTPs as an entrance route for microlitter

The amount of microlitter entering the marine environment with the effluent varied between 2.0×10^8 to 7.9×10^8 particles per day and the ascertained average MP load varied between 1.7×10^6 to 1.4×10^8 particles per day (Table 9).

Table 9. Flow rates (m³/d), microlitter concentrations (MLs/m³) and microlitter load (ML/d), microplastic concentrations (MPs/m³) and microplastic load (MPs/h) from WWTP with effluent.

<table>
<thead>
<tr>
<th>Date</th>
<th>Monday 14.9</th>
<th>Wednesday 16.9</th>
<th>Saturday 19.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (m³/d)</td>
<td>219024</td>
<td>281750</td>
<td>224294</td>
</tr>
<tr>
<td>ML concentration (ML/m³)</td>
<td>3200</td>
<td>700</td>
<td>3500</td>
</tr>
<tr>
<td>ML outflow (ML/d)</td>
<td>~ 7.0×10^8</td>
<td>~ 2.0×10^8</td>
<td>~ 7.9×10^8</td>
</tr>
<tr>
<td>MP concentration (MP/m³)</td>
<td>651</td>
<td>6</td>
<td>161</td>
</tr>
<tr>
<td>MP outflow (MP/d)</td>
<td>~ 1.4×10^8</td>
<td>~ 1.7×10^6</td>
<td>~ 2.0×10^7</td>
</tr>
</tbody>
</table>

In their study Murphy et al. 2016 estimated the daily discharge of 6.5×10^7 MPs in large secondary WWTP (PE 650 000, treating 260 954 m³ of wastewater per day) and Carr et al. (2016) calculated a daily discharge of 0.93×10^6 MPs also in large (treating 1.06 million m³ of wastewater per day) secondary WWTP. Our results, together with these studies, indicate that secondary and even tertiary WWTPs may constitute a considerable source of microlitter and microplastics given the large volumes of effluent discharged to the aquatic environment constantly.

4. Conclusions

Our work provides a detailed information on the stepwise removal of microlitter in a tertiary level WWTP. Most of (97%) the microlitter in wastewater was removed during the pre-treatment and AS
treatment further decreased (7% - 20%) the microlitter concentration. Tertiary treatment BAF didn’t have any significant impact on microlitter concentration. Pre-treatment had the greatest effect also on microlitter size distribution, efficiently removing larger size classes of ≥ 300 and 100 – 300 µm. Of the different types of microlitter, fibers and films were most efficiently removed from the wastewater. The microlitter balance confirmed the applicability of our sampling and analysing methods and showed that 0.1% of the microlitter entering the plant ended up in the effluent and the rest was removed with the sludge. 20% of the microlitter in the removed sludge returned to the process with reject water.

Automated composite samplers can provide relatively easy microlitter sampling protocol. With grab sampling, larger sample volumes and hence statistically more representative results are gained. The method is neither so sensitive to contamination. However, the grab sampling method requires much more time and effort compared to composite sampling with automated equipment. The grab sampling also ignores the in-day variations in microlitter concentration. If microlitter is examined over longer period or regularly e.g. for monitoring purposes composite sampling with automated samplers can offer a practical sampling tool.

According to our results 2.0×10⁸ to 7.9×10⁸ microlitter per day and 1.7×10⁶ to 1.4×10⁸ microplastics per day was discharged into the Baltic Sea with effluent. Given the large volumes of effluent discharged to the aquatic environment constantly, even tertiary level WWTPs may constitute a considerable source of microlitter and microplastics.

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http://www.ospar.org/v_meetings/browse.asp?menu=00550520000000_000000_000000


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Highlights

- The microlitter retention capacity in investigated WWTP was over 99%.
- The size and shape of microlitter particles has impact on their removal in WWTP.
- Microlitter balance analysis for the wastewater treatment process for performed.
- Microlitter sampling protocol for monitoring purposes was investigated.
- WWTPs can constitute entrance route for microlitter into the aquatic environment.