Identification and Quantification of Microplastic in Sewage Systems by TED-GC-MS

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Abstract

The number of publications reporting the amount of microplastic (MP) all over the world increased rapidly. Methods used so far are very time consuming and not able to provide information on total contents. As harmonised sampling, sample preparation and analysis strategies are missing different studies can hardly be compared and quantitative data, including identification and mass contents of the polymers found, are missing. This leads to a lack of comprehensive understanding of MP occurrence, source and entry pathways into the environment.

We developed a method, Thermal Extraction/Desorption-Gaschromatography-Massspectrometry, as a fast screening method for MP analysis. Solid residues of water samples are heated up to 600 C under a N_2 atmosphere without any sample preparation. The collected decomposition gases are separated in a gas chromatography system and detected in a mass spectrometer. Mass contents of the identified polymers can be calculated.

In this presentation we will show first results from the influent of the wastewater treatment plant Kaiserslautern (Germany) and its combined sewage system as possibly entry pathway. In order to determine the relevance of wastewater split streams analysis of grey water will be conducted. Samples are fractionally filtered by a sieve cascade with mesh sizes of 500, 100, 50 µm.

Keywords: microplastic, TED-GC-MS, analysis, grey water, waste watertreatment plant

1. Introduction

Finds of microplastics particles (MP, particle size 1-1000 µm) in the environment are omnipresent nowadays, but little is known about the real extent in environment. Plenty of researchers discuss the same less articles of extrapolations of MP particles [Jambeck J.R. et al.], which were done just to get an idea of MP particle dimensions worldwide. A huge problem is that the extrapolations are based on a very low amount of measured data sets and are therefore very unreliable.

It is generally accepted that MP particles can be found all over the world. But it is totally unclear what are the entry pathways, where are the hotspots and what are the mass contents of microplastic pollution.

In recent years, we developed a fast screening method for determination of MP mass contents in water samples with very simple sample preparation (only hygienisation, drying and homogenization). This Thermal Extraction/Desorption-Gaschromatography-Massspectrometry (TED-GC-MS) [Duemichen E. et al,Eisentraut P. et al] allows us to analyse solid samples within 2 hours 30 minutes and, hence, getting the chance to measure a high number of samples for scientifically well-founded findings. This is of great importance for systems with high temporal and specific variations, like wastewater systems, as single results can mislead mass balances totally.

The following article is about the operating principle of the TED-GC-MS and shows first results of possibly MP entry pathways at the wastewater treatment plant Kaiserslautern, Germany.

2. TED-GC-MS as a fast screening method for microplastic analysis

At the fully automatized TED-GC-MS measurement, the solid sample is first heated under N_2 atmosphere up to 600 °C, the decomposition gases were than collected on a solid phase adsorber and afterwards gently removed from the adsorber for injection into the GC-MS system. Finally, a chromatogram, including mass spectra, is generated.

These chromatograms were screened after specific polymer marker molecules for identification of MP. For routine analysis it is screened for the most common polymers in nature, polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylenetherephthalte (PET), polyamide (PA), polymethylmethacrylate (PMMA) and styrene-butadiene-rubber (SBR) as tire component. The corresponding marker molecules and their limits of detection were presented in Figure 1.

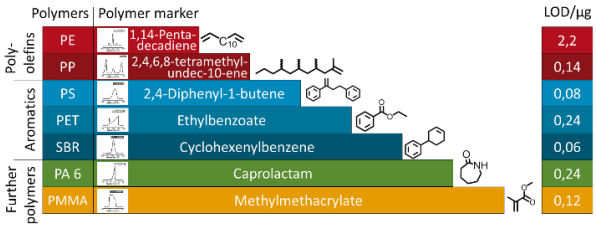

Figure 1. Polymer markers used for MP identification in TED-GC-MS and their corresponding limits of detection (LOD), determined without the matrix

3. Microplastic mass contents in different sewage system devices of urban water management

In the following, the first results of the MP analysis in various areas of an urban sewage system are presented (Figure 2). Within the Kaiserslautern catchment, samples were collected in the influent of the WWTP and the effluent of a stormwater retention tank (both untreated wastewater under dry-weather conditions)) and at the Reinighof, a farm with source separation on household level so that grey water (shower washing machine and kitchen wastewater) is available. Volumes of around 20 L where sampled. Subsequently a fractionated filtration was carried out with mesh sizes of 500, 100 and 50 µm (stainless steel mesh) [Bannick C.G. et al].

PP was found in all samples with nearly similar mass contents of 0.5 to 2.2 µg/mg dry mass, while PS had mass contents between 0.01 and 0.09 µg/mg with a more random distribution. The appearance of SBR is in line with expectations. SBR was found in high contents from 0.09 to 0.3 µg/mg in the influent of the wastewater treatment plant. No SBR was found in grey water. We found only traces of SBR in the stormwater retention tank. However, the amount is below the detection limit. Further measurement campaigns are needed for more resilient results of various water sources.

When looking at the results, it is apparent that the most commonly used polymer PE was not found. The TED-GC-MS is not very sensitive to PE (see Figure 1), so we assume that due to low sample volumes the detection limit for PE has not been reached and therefore we cannot measure a clear signal for PE.

4. Conclusion and Outlook

TED-GC-MS is proven to be a fast suitable screening method for MP analysis for water from the urban sewage systems. PP and PS could be found in all samples, whereas SBR is only detected in the influent of the WWTP of Kaiserslautern.
Our task for the near future is to take more samples, to repeat the measurements at various weather conditions, sampling at WWTP effluent and thus generate more real data to obtain representative data on the MP content of the urban wastewater system.

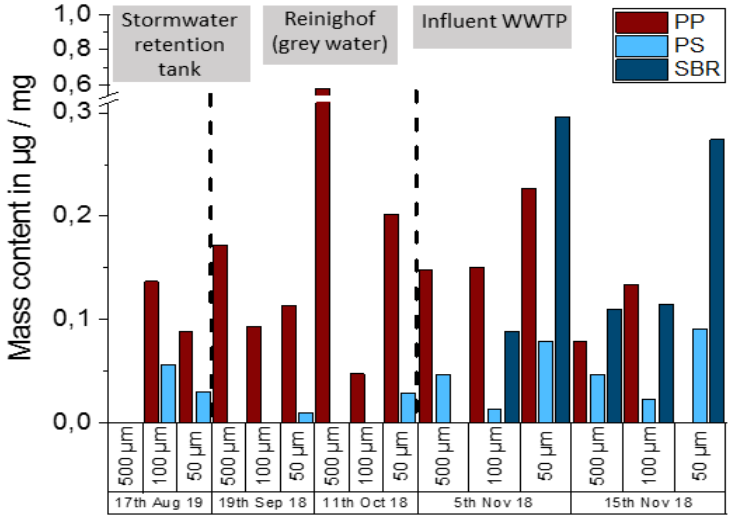

Figure 2. Mass contents of a stormwater retention tank (one day), Reinighof for grey water (2 days) and influent of WWTP (2 days)

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