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Analysis of microplastics in water by micro-Raman spectroscopy: Release of plastic particles from different packaging into mineral water

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ABSTRACT

Microplastics are anthropogenic contaminants which have been found in oceans, lakes and rivers. Investigations focusing on drinking water are rare and studies have mainly been using micro-Fourier Transform Infrared Spectroscopy (μ-FT-IR). A major limitation of this technique is its inability to detect particles smaller than 20 μm. However, micro-Raman spectroscopy is capable of detecting even smaller particle sizes. Therefore, we show that this technique, which was used in this study, is particularly useful in detecting microplastics in drinking water where particle sizes are in the low micrometer range. In our study, we compared the results from drinking water distributed in plastic bottles, glass bottles and beverage cartons.

We tested the microplastic content of water from 22 different returnable and single-use plastic bottles, 3 beverage cartons and 9 glass bottles obtained from grocery stores in Germany. Small (−50-500 μm) and very small (1−50 μm) microplastic fragments were found in every type of water. Interestingly, almost 80% of all microplastic particles found had a particle size between 5 and 20 μm and were therefore not detectable by the analytical techniques used in previous studies. The average microplastics content was 118 ± 88 particles/l in returnable, but only 14 ± 14 particles/l in single-use plastic bottles. The microplastics content in the beverage cartons was only 11 ± 8 particles/l. Contrary to our assumptions we found high amounts of plastic particles in some of the glass bottled waters (range 0−253 particles/l, mean 50 ± 52 particles/l). A statistically significant difference from the blank value (14 ± 13) to the investigated packaging types could only be shown comparing to the returnable bottles ($p < 0.05$).

Most of the particles in water from returnable plastic bottles were identified as consisting of polyester (primary polyethylene terephthalate PET, 84%) and polypropylene (PP; 7%). This is not surprising since the bottles are made of PET and the caps are made of PP. In water from single-use plastic bottles only a few micro-PET-particles have been found. In the water from beverage cartons and also from glass bottles, microplastic particles other than PET were found, for example polyethylene or polyolefins. This can be explained by the fact that beverage cartons are coated with polyethylene foils and caps are treated with lubricants. Therefore, these findings indicate that the packaging itself may release microparticles. The main fraction of the microplastic particles identified are of very small size with dimensions less than 20 μm, which is not detectable with the μ-FT-IR technique used in previous studies.

1. Introduction

Microplastic contamination is receiving increased attention and the impact on the environment but also on food has become evident. In the early seventies the tiny plastic pieces were reported for the first time being present in the Atlantic (Carpenter et al., 1972; Carpenter and Smith, 1972; Colton et al., 1974). Since then, a constant increase of microplastic pollution in marine waters has been observed (Thompson et al., 2004). In recent years, an increasing number of studies revealing the presence of microplastic particles in fresh water from sources, such as lakes and rivers (Ivleva et al., 2017; McCormick et al., 2016; Sruthy and Ramasamy,

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2017), as well as in the atmosphere (Cai et al., 2017; Dris et al., 2016) were reported.

In addition to the marine microplastics input into our diet by consuming fish and seafood (Cole et al., 2013; Davison and Asch, 2011) that may be contaminated by leaking pollutants and additives in microplastic (Bakir et al., 2014; Mato et al., 2001), the direct exposure of microplastics by humans via other sources, especially such as drinkable water, needs to be considered. Currently, there is almost no published data on the microplastics content of drinking- or mineral water available.

A publication about synthetic particles in German beers (Liebezeit and Liebezeit, 2014) has been discussed (Lachenmeier et al., 2015; Wiesheu et al., 2016). In this context one type of beer and one sample of bottled mineral water was analyzed by means of μ-Raman spectroscopy. The authors found fibers in the blank and the beverage samples, but the results did not show statistically significant differences (Wiesheu et al., 2016). In the study, by Wiesheu et al. (2016), only one single PET fiber was found in one of the water samples but no statements about the total amount of other fibers or particles were made. The study also didn't reveal anything about the type of water or the type of packaging. The authors recommended further analysis of fiber content in different beverages and investigations of the sources of contamination, pointing out the importance of working under extremely clean conditions in order to reduce contamination of the samples.

The Helmholtz Center for Polar and Marine Research (Alfred-Wegener-Institute, Bremerhaven, Germany) investigated a total of 40.000 L raw- and tap water in Lower Saxony by means of μ-FT-IR (Mintenig et al., 2014). In four blind samples fiber concentrations comparable to the other raw- and drinking water samples were detected, implying a contamination through the exposure of the water sample (fiber input through laboratory air). In 10 out of 24 samples 0.4–7 microplastic particles per m^3 drinking water were found which the authors affiliated to the abrasion of pipes and fittings used in the drinking water system. The particles found had sizes between 50 and 150 μm.

Using μ-FT-IR-spectroscopy, particles can be detected down to a lower size limit of 20 μm. Due to the higher resolution of up to 1 μm, μ-Raman spectroscopy is able to visualize very small microplastic particles that were most likely overlooked up to now (Ivleva et al., 2017). Especially for the analysis of food, the detection of very small microplastic particles is important, because of the possible implication on human health. It is expected that smaller particles could possibly be better absorbed by the digestive system than larger ones (Hussain et al., 2001). As a result, an increased accumulation in humans could be the consequence.

2. Material and methods

2.1. Materials

Particle counting and identification was done with the Single Particle Explorer (SPE, rapID, Berlin), a μ-Raman spectroscope with a 10x, 20x and 50x objective (NA = 0.55) and a 532 nm (≤20 mW; grating of 1040 lines/mm) and a 785 nm (≤50 mW; grating of 1450 lines/mm) Raman laser with adjustable laser power. A maximum of 5000 particles/scanning counts per measurement can be analyzed with the SPE. The smallest particle size that can be analyzed is 1 μm.

A specially manufactured filtering apparatus was needed for filtration (filtr.AID, rapID, Berlin) with a filter funnel that had a highly polished bottom, ensuring tight closure with the filter membrane. The inner diameter of the funnel was 4 mm, top diameter 10 cm and the filtration volume was 100 ml.

Since gold hardly emits any Raman signals gold coated polycarbonate filter (filtr.AID membranes, rapID, Berlin, 3.0 μm pore size and inner diameter of 24 mm) were used. In order to obtain a smooth surface of the filter membrane a specific gold filter sample holder was supplied with the device. This sample holder consisted of a base and a clamp, in between the filter was clamped (see Supporting Information S1). The gold filter sample holder was designed to fit exactly into the sample tray of the Single Particle Explorer. This guaranteed the center of the filter to be always in the middle and the filter membranes to stay plane. These settings were essential for the subsequent automatic image analysis, particle counting and Raman analysis.

2.2. Types of water

Water samples (volume range 700 ml–1500 ml) from 12 different returnable and 10 single-use plastic bottles, 3 beverage cartons and 9 glass bottles were obtained from grocery stores in Germany. The water samples were classified into “still mineral water”, “medium sparkling” and “sparkling”, corresponding to its carbonic acid content. Four plastic bottled waters (one single-use and three returnable bottled waters) of same brand/manufacturer but with different batch numbers were purchased six weeks later to check the influence of production dates on microplastic content.

All analyses were performed in triplicate.

2.3. Procedures performed to prevent particle contamination

2.3.1. Air-borne and water-borne contamination

In order to avoid a particle contamination from indoor air, all steps of the filtration process were conducted using a laminar flow workbench (cleanroom class ISO 3, Envair eco air H, Envair Deutschland GmbH, Emmendingen). The bench was periodically checked for proper operation with a particulate measuring device (Trotec, PC200, Heinsberg, Germany).

In all filtration and handling steps, a laboratory coat made of 100% cotton, particle free nitrile gloves and arm sleeves were worn in the laboratory. Before every work step, gloved hands were washed with detergent and thoroughly rinsed with Milli-Q water.

In order to create a blank value with very low microplastic content, different water sources were analyzed and a following cleaning process (see 2.3.2) developed. The overall lowest particle contamination was achieved using an ultra-pure water system (Milli-Q-, Advantage A10, Merck Millipore), fed with deionized water. As endfilter a 0.22 μm membrane filter for particulate-free and bacteria-free water (Millipak Express 40 Filter, Merck Millipore) was used.

Before filtration, each filter was analyzed with the μ-Raman spectroscope and tested for polymer particles present (“pre-counted”). The number of plastic particles detected in this “pre-count” was subtracted from the number of the detected polymer particles after filtration of the samples or the blanks. In general, these “pre-counted” values were very small (mostly between 0 and 4, highest value observed was 33 plastic particles).

2.3.2. Cleaning process

A complex cleaning process was necessary to assure that the filtration setup and the glass vessels did not contribute to particle input. Even the smallest irregularities in the glass vessels could be a source of particle accumulation. Therefore, all vessels were checked for any cracks or scratches.

In a first step, glass funnel and vessels were intensively cleaned with deionized water, detergent and cleanroom wipes. Then, they were sonicated in Milli-Q water for 30 min and subsequently extensively rinsed with Milli-Q water. All vessels were setup immediately on the clean bench. In order to ensure that no new particles accumulated an imaging microscope at the clean bench