



Small-sized microplastics and pigmented particles in bottled mineral water

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ABSTRACT

Up to now, only a few studies about microparticle contamination of bottled mineral water have been published. The smallest analysed particle size was 5 µm. However, due to toxicological reasons, especially microparticles smaller than 1.5 µm are critically discussed. Therefore, in the present study, 32 samples of bottled mineral water were investigated for contamination by microplastics, pigment and additive particles. Due to the application of aluminium coated polycarbonate membrane filters and micro-Raman spectroscopy, a lowest analysed particle size of 1 µm was achieved.

Microplastics were found in water from all bottle types: in single use and reusable bottles made of poly(ethylene terephthalate) (PET) as well as in glass bottles. The amount of microplastics in mineral water varied from 2649 ± 2857 per litre in single use PET bottles up to 6292 ± 10521 per litre in glass bottles. While in plastic bottles, the predominant polymer type was PET; in glass bottles various polymers such as polyethylene or styrene-butadiene-copolymer were found. Hence, besides the packaging itself, other contamination sources have to be considered.

Pigment particles were detected in high amounts in reusable, paper labelled bottles (195047 ± 330810 pigment particles per litre in glass and 23594 ± 25518 pigment particles per litre in reusable paper labelled PET bottles). Pigment types found in water samples were the same as used for label printing, indicating the bottle cleaning process as possible contamination route.

Furthermore, on average 708 ± 1024 particles per litre of the additive Tris(2,4-di-tert-butylphenyl) phosphite were found in reusable PET bottles. This additive might be leached out from the bottle material itself.

Over 90% of the detected microplastics and pigment particles were smaller than 5 µm and thus not covered by previous studies. In summary, this is the first study reporting about microplastics, pigment and additive particles found in bottled mineral water samples with a smallest analysed particle size of 1 µm.

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Abbreviations: CV, Coefficient of variation; µ-FTIR, micro-Fourier transform infrared spectroscopy; PET, Poly(ethylene terephthalate); EDTA, Ethylene diamine tetraacetic acid tetrasodium salt; SDS, Sodium dodecyl sulphate; PA, Polyamide (nylon-6); PE, Polyethylene; PP, Polypropylene; PS, Polystyrene; PC, Polycarbonate; PVC, Poly (vinyl chloride); CLS, Classical least squares; PB15, Pigment Blue 15; PV23, Pigment Violet 23; PY83, Pigment Yellow 83; PW6, Pigment White 6.

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1. Introduction

Since the first reports about small plastic pieces in oceans in the early 1970s (Carpenter et al., 1972; Carpenter and Smith, 1972), a lot of studies have been published investigating the abundance of so called microplastics in different environmental compartments (Auta et al., 2017; Eerkes-Medrano et al., 2015; Horton et al., 2017). Microplastics are small plastic pieces with a size below 5 mm. Besides these plastics, coloured polymer particles as well as pure pigment particles were also detected (Imhof et al., 2016; Lenz et al., 2015). It has been shown that various animals ingest plastics instead of or with their food (Ivar do Sul and Costa, 2014; Wright et al., 2013).

Hence, toxicological risks resulting from the intake of these particles are discussed covering three main topics: the particles themselves, polymer additives and adsorbed contaminants (Browne et al., 2008, 2013). Particles themselves may cause inner abrasions or blockage of the gastro-intestinal system of animals (Wright et al., 2013). Small particles might translocate into body tissues and cause harm (Browne et al., 2008), with the smallest size fraction (<1.5 µm) being more likely to penetrate deeply into organs (EFSA, 2016; Yoo et al., 2011). Furthermore, chemicals such as additives and contaminants, which adhere to particles, might be leached out after oral intake of the particles (Browne et al., 2013). Regarding pigments, primarily metals might leach out from the particles (Imhof et al., 2016).

Since the detection of microplastics in commercial seafood (Li et al., 2015; Van Cauwenberghe and Janssen, 2014), the issue of a potential contamination of foods with microplastics became increasingly important. Studies were performed about the occurrence of microplastics in German beer (Liebezeit and Liebezeit, 2013), honey and sugar (Liebezeit and Liebezeit, 2014), table salts (Karami et al., 2017; Yang et al., 2015), drinking and mineral water (Mintenig et al., 2014; Schymanski et al., 2018).

In all of the above named studies, separation of particles from food matrix was realised via filtration and particle analysis was performed on the filter surface. Depending on the food type, sample pre-treatment with nitric acid (Van Cauwenberghe and Janssen, 2014) or hydrogen peroxide (seafood, honey and partly table salts) (Li et al., 2015; Liebezeit and Liebezeit, 2013; Yang et al., 2015) was necessary to digest organic material. Particle identification was performed in various ways: visual identification with a microscope (partly after colouring) (Liebezeit and Liebezeit, 2013, 2014), micro-Fourier transform infrared spectroscopy (µ-FTIR) (Li et al., 2015; Mintenig et al., 2014; Yang et al., 2015) or micro-Raman spectroscopy (Karami et al., 2017; Schymanski et al., 2018). The spectroscopic methods were either used after visual pre-sorting of particles or spectra were generated for all detected particles.

The results of some of these studies were critically discussed due to the analytical methods applied. There was a lack in the prevention of blank values and the clear identification of the potential microplastics (EFSA, 2016; Lachenmeier et al., 2015). However, among the methods used in the above mentioned studies, µ-FTIR and micro-Raman spectroscopy showed to be adequate for conclusive polymer identification. Whereas µ-FTIR is usable to identify particles greater than 10 µm, micro-Raman spectroscopy enables analysis down to a particle size of 1 µm (Käppler et al., 2016). Wiesheu et al. (2016) and Schymanski et al. (2018) showed the applicability of micro-Raman spectroscopy to the analysis of beverages (beer and mineral water) for microplastics. While in the first paper, only one mineral water sample was analysed, the second one shows the results for 38 mineral water samples. The highest amount of microplastics (241 particles/l) was found in a reusable bottle made of poly(ethylene terephthalate) (PET).

However, microparticles smaller than 5 µm were not analysed. Regarding toxicological risks for humans after the oral intake of microplastics, especially small particles are of particular concern (EFSA, 2016).

The aim of the present study was to investigate mineral water samples for microparticle contamination, including the particle size larger than 1 µm. Therefore, micro-Raman spectroscopy was combined with special, newly developed aluminium coated polycarbonate membrane filters (Oßmann et al., 2017). Thus, even microparticles in a size of 1 µm could be visualized and clearly identified. 32 bottled mineral water samples from three different packaging types (single and reusable bottles made of PET and glass bottles) were analysed for microparticle contamination. In addition to microplastics, we extended our investigation to pigmented and additive particles.

2. Materials and methods

2.1. Precautions to avoid sample contamination

To avoid contamination by air, all steps of sample preparation were performed in a laminar flow box (clean room class ISO 5 after EN DIN ISO 14644–1, Spetec GmbH) and filter membranes were stored in closed glass petri dishes after sample preparation. All persons wore lab coats made of cotton. For analytical procedures, only ultrapure water (Veolia Water Solutions and Technologies, Purelab flex, 0.2 µm filtered) was used. All added solutions were filtered through a syringe membrane filter (Cellulose acetate, 0.2 µm, GE Healthcare Life Sciences Whatman™) prior to use. Hardware made of plastics was avoided to be used whenever possible. Glassware was treated for 15 min with sodium dodecyl sulphate solution (0.3 g/l prepared from SDS, AppliChem Panreac ITW Companies, > 99%, 0.2 µm filtered) in an ultrasonic bath. This detergent proved to be more suitable in removing microplastics from the glass surface than pure water. Afterwards, glassware was rinsed once with Ethanol 50% (v/v, ultrapure water/Ethanol absolute, Fisher Chemical, > 99.8%) and three times with ultrapure water in the laminar flow box.

2.2. Samples

32 samples from 21 different brands of mineral water were purchased in Bavarian food stores. Twelve samples were packaged in reusable bottles made of poly(ethylene terephthalate) (PET), ten samples in single use bottles made of PET and ten samples in glass bottles including one single use and nine reusable glass bottles. Among the reusable PET bottles, four pairs of a newish and a frequently reused bottle were analysed. The pairs were from the same batch each and belonged to three different brands. Newish bottles were differentiated from older ones based on the frequency of scratches on the outside of the bottles and the cloudiness of the bottle material, which both enhance during reutilisation. The characteristics of all samples such as the bottle type or volume are summed up in Table S1 in the Supplementary data.

2.3. Sample preparation

After removing the labels, all bottles were cleaned thoroughly with detergent and rinsed with deionized water to avoid sample contamination via the outside of the bottles. Before opening, bottles were allowed to dry in a laminar flow box. Each sample was mixed by inverting the bottle and then transferred into a pre-cleaned Erlenmeyer flask. Depending on the content of calcium and magnesium ions in the sample (as listed on the labelling of water samples), an equimolar amount of an ethylene diamine tetraacetic

acid tetrasodium salt (EDTA) solution (250 g/l, prepared from EDTA tetrahydrat, Fluka, > 99%, 0.2 µm filtered) was added and the sample was left to stay for 15 min. Particles consisting of calcium or magnesium carbonate got dissolved by complexing these cations with EDTA. Accordingly, the total particle number was reduced leading to decrease in the measurement time. Afterwards, 3 ml of a sodium dodecyl sulphate (SDS) solution (100 g/l, prepared from SDS, AppliChem Panreac ITW Companies, > 99%, 0.2 µm filtered) were added per litre sample. Prior tests showed that plastic particles could be suspended easier by adding this detergent, resulting in a higher sample homogeneity (Oßmann et al., 2017). To obtain analysable particle numbers on the filter surface, samples were mixed and an aliquot of 250 ml of the initial sample volume was filtered via vacuum through an aluminium coated polycarbonate membrane filter as described by Oßmann et al. (2017) (pore size 0.4 µm; filtration unit: msscientific, KG13B/500, filtration area ~113 mm²). The funnel of the filtration unit was first rinsed with ~5 ml Ethanol 50% to destroy foam (v/v, ultrapure water/Ethanol absolute, Fisher Chemical, > 99.8%) and then continuously with ultrapure water. Subsequently, filters were immobilized and flattened using two rings of metal und a microscope slide. In this way, the microscopic focus on the flat filter surface and particle locations remained constant (Oßmann et al., 2017). To avoid contamination, filters were stored in closed glass petri dishes.

Water samples were analysed in blocks. Within each block, one blank value was analysed to check for sample contamination. In total, seven blanks were evaluated. Blank values were prepared in a similar way like water samples: 0.5 l of ultrapure water was mixed with 2.5 ml of EDTA (250 g/l) solution. After a waiting time of 15 min, 1.5 ml SDS solution (100 g/l) were added. Due to the added chemicals and the absence of buffering capacity (unlike in mineral water), the pH-value of this solution is so basic that the aluminium layer of the membrane filter would be destroyed. To prevent this, the pH-value was adjusted to ~7 by adding hydrochloric acid (25%, Bernd Kraft, p. A., 0.2 µm filtered). 250 ml of the initial sample volume were filtered as described above.

2.4. Micro-Raman spectroscopy

2.4.1. Identification of microplastics

After the sample preparation, particles were analysed directly on the filter surface with micro-Raman spectroscopy using an XploRa Plus system, operated by LabSpec 6 software (Horiba Scientific). The Raman system was equipped with two lasers (532 nm and 785 nm) and a cooled charge-coupled device (CCD) detector. Gratings with 600 grooves/mm, 1200 grooves/mm or 1800 grooves/mm were used. The confocal hole width was set to 300 µm, the confocal slit width to 100 µm. System calibration was performed by zero-order correction of the grating and additionally on the 520.7 cm⁻¹ peak of a silicon wafer.

As the identification of all particles on the whole filter surface (113 mm²) would be extremely time consuming, referring to Imhof et al. (2016), five spots of 1 mm² were examined for each sample, resulting in an analysed sample area of 4.4%. On each site an image montage (1 mm × 1 mm) was recorded with a camera (Infinity 3, Lumenera) using a 50× objective (Olympus MPlanN 50×/0.75 BD) in dark field illumination (reflected light). An example of an image montage as well as the locations of the spots are displayed in Figs. S1 and S2 in the Supplementary data. On these image montages, all particles greater or equal than 1 µm were analysed with the Particle Finder Module of the software as shown in a previous publication (Oßmann et al., 2017). First, the size and coordinates were documented for each particle by image analysis. Second, Raman spectra were recorded for all particles with one laser (532 nm, 600 grooves/mm, and ~3.2 mW at the sample, 2 × 1 s).

Spectrum range was set from 150 cm⁻¹ to 3500 cm⁻¹. Intensity correction algorithm of LabSpec 6 was applied to get a better comparability of recorded spectra with a data base (BIORAD, KnowItAll® Informatics System Horiba Edition). For some samples, due to high particle numbers, the analysed areas of 1 mm² had to be divided into 3 or 4 smaller image montages. For the calculation, the results were summed up to each mm².

Most particles showed no straight spectral baseline (e.g. background caused by light fluorescence), which was corrected by subtracting a polynomial baseline. However, a few particles showed high fluorescence. For these particles, Raman spectra were recorded manually with a second laser (785 nm, ~5.3 mW at the sample, 600 grooves/mm or 1200 grooves/mm), resulting in evaluable spectra in most cases. The acquisition time and the number of accumulations were set individually for each measurement.

Spectra could not be compared automatically with a database. To simplify analysis, all spectra were screened for plastics using classical least squares algorithm (CLS), a mathematical process based on Beer's law (Workman and Howard, 2010) and a software option of LabSpec 6. The evaluation with CLS was supported by Microsoft Excel 2010. Spectra of different synthetic polymers (polyamide (nylon-6, PA), polyethylene (PE), polypropylene (PP), polystyrene (PS), polycarbonate (PC), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC)) were set as standard references. Furthermore, spectra of other materials present in the samples (e.g. colours) were used as reference, after confirming their identities with a database. Each measured spectrum was calculated as the sum of all references and the theoretical composition was displayed. In this way, spectra similar to a reference were highlighted. If a spectrum showed to be a mixture of two or more references, all of them were highlighted. In Fig. S3, an example for the analysis with CLS is shown. In order to avoid missing of unknown substances (which were not set as reference) and false positive effects, the results of CLS were checked manually. Again, unknown substances were identified by comparing with spectra from a database. Although a review of the results was necessary, CLS simplified data evaluation and decreased analytics time considerably.

Some spectra appeared to be polymeric, but were not clearly recognizable (e.g. due to low intensity, high noise or interference with non-polymeric spectra). For these particles, manual remeasurement with adjusted values for acquisition time and accumulation runs was performed. Partially, the application of a grating with a higher number of grooves/mm was necessary to achieve conclusive spectra.

Particles might also consist of several components, which adhere together. In such cases, Raman mapping of single particles was recorded using a step size of 1 µm, to check their position-dependent composition. The number of the identified particles was classified in four groups depending on their size: ≤1.5 µm, >1.5 µm to ≤5 µm, >5 µm to ≤10 µm and >10 µm.

2.4.2. Identification of colours on paper labels

Colours used for the printing of paper labels from four different brands of mineral water packed in glass bottles and from two different brands of reusable PET bottles were identified using micro-Raman spectroscopy. Labels were removed from the bottles and analysed directly with the Raman system described in section 2.4.1. Images were recorded in bright field illumination (reflected light) and Raman parameters were set individually for each measurement. Identification of the colour spectra was performed by comparing with spectra from a database. These findings were further confirmed by comparing with spectra of several pigments (Heubach GmbH, Germany): Pigment Blue 15 (PB15, HEUCO Blue 515400, HEUCO Blue 515303), Pigment Violet 23 (PV23, AQUIS

Violet 90230, HEUCOSPERSE I VS 1621 E) and Pigment Yellow 83 (PY83, MONOLITE Yellow 108304).

2.5. Calculation

As described in sections 2.3 and 2.4.1., for each sample a volume of 250 ml was filtered and five spots of 1 mm² were analysed for particles. To get better comparability with other studies, detected particle numbers were extrapolated to 1 L mineral water. Assuming an even particle distribution in the initial sample and over the filter surface, we multiplied the particle number detected on the analysed area of 5 mm² by 22.6 to calculate the total number of particles on the filter surface and again by 4 to calculate the number of particles in 1 L mineral water. The limitations caused by this extrapolation are discussed in section 4.4.1.

3. Results

3.1. Microplastics

The results for microplastics in mineral water samples (depending on the bottle type) are summed up in Figs. 1–3. Fig. 1 shows the mean number of microplastics projected to 1 L sample volume. Fig. 2 exhibits the particle size distribution in percent. In Fig. 3, the distribution of the polymer type is displayed. Detailed results for all samples are shown in Figs. S4A (blank samples), S5 (single use PET bottles), S6 (reusable PET bottles) and S7 (glass bottles) in the Supplementary data.

3.1.1. Blank samples

Although we took several precautions to avoid contamination of the samples with microplastics, we were not able to prevent contamination completely. On average, 384 ± 468 microplastics/l were found in blank samples (Fig. 1), consisting mainly of PP, some of PS, PE and PET (Fig. S4A). We did not find PC particles in the blank values. But as the filter membranes were made of PC and as only single particles of this material were detected in the water samples, we excluded PC from the results (Schymanski et al., 2018).

3.1.2. Mineral water

Microplastics were detected in almost all bottled water samples. They showed very different amounts of microplastics (Figs. S5–S7), resulting in a high uncertainty per bottle type. Water from single

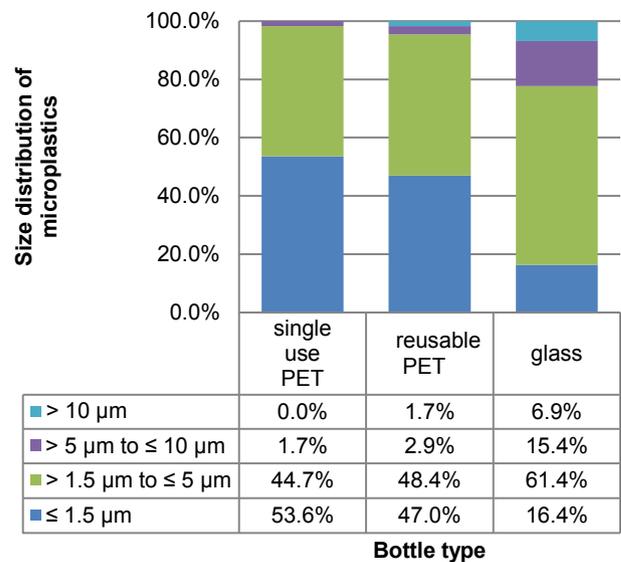


Fig. 2. Size distribution of the detected microplastics depending on the bottle type (material).

use PET bottles displayed the lowest amount with 2649 ± 2857 microplastics/l. Water from reusable PET bottles contained on average 4889 ± 5432 microplastics/l and water from glass bottles 6292 ± 10521 microplastics/l (Fig. 1). The highest amount of microplastics was detected in one of the glass bottles (35436 microplastics/l; sample g1 in Fig. S7). When removing this outlier, a mean value of 3074 ± 2531 microplastics/l for water from glass bottles was calculated, which is in the range of single use PET bottles. In the four newish, reusable PET bottles (sample r4n, r5n, r6n and r7n) similar amounts as in single use PET bottles (2689 ± 4371 microplastics/l) were detected; whereas obviously higher amounts (8339 ± 7043 microplastics/l) were measured in the corresponding older bottles (sample r4o, r5o, r6o and r7o). Regarding the material of the particles, solely the number of PET particles was increasing (see Fig. S6).

The size distribution of microplastics (Fig. 2) is very similar for single use and reusable PET bottles. Over 95% of the plastic particles were smaller than 5 μm and even about 50% were smaller than 1.5 μm. In glass bottles, larger particles (~15% were >5 μm and

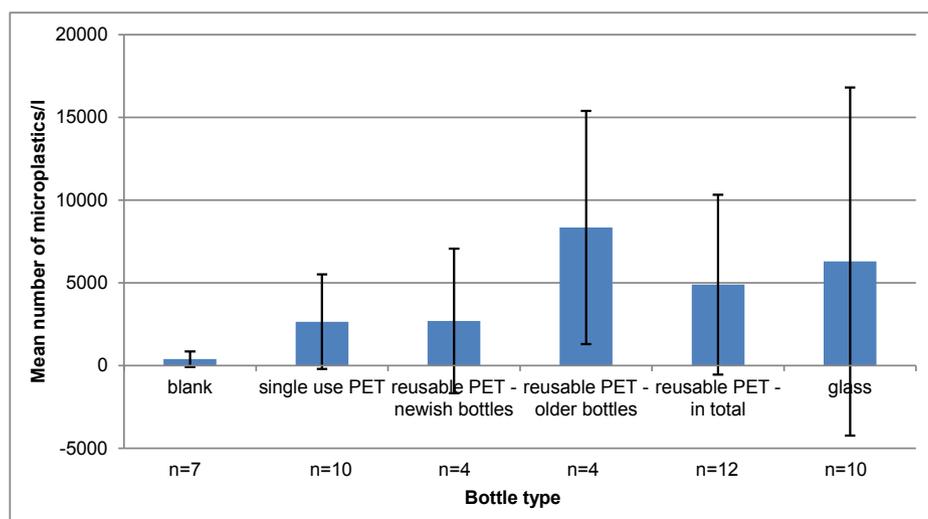


Fig. 1. Mean number of microplastics projected to 1 L sample volume function of the bottle type (material). Error bars indicate \pm standard deviation. n: number of samples.

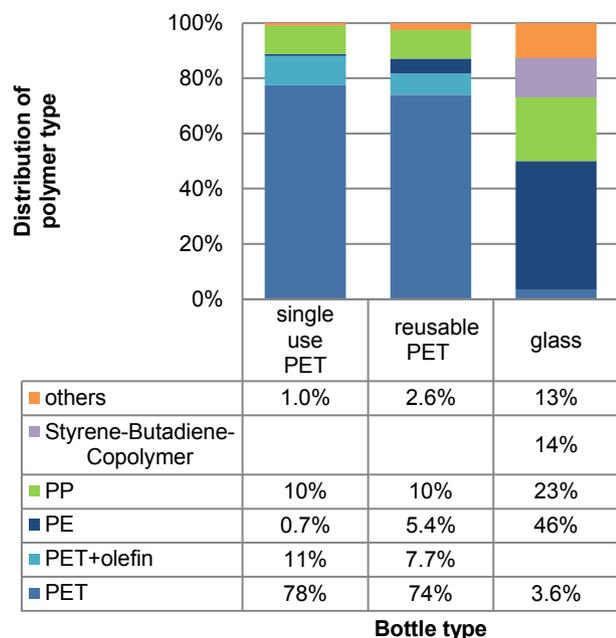


Fig. 3. Polymer type of the detected microplastics with respect to the bottle type (material). Others: sum of PS (+olefin), PP + pigment, PVC, PA, poly(p-phenyleneterephthalamide), polytetrafluorethylene. Detailed information for each sample can be found in Figs. S5, S6 and S7.

$\leq 10 \mu\text{m}$ and $\sim 7\% > 10 \mu\text{m}$) occurred more frequently.

In water from bottles made of PET (single use and reusable), most microplastics showed the spectrum of PET, partly interfered by an olefinic or a pigment spectrum. By contrast, in water from glass bottles PE (46%), PP (23%) and a styrene-butadiene-copolymer (14%) were the predominant polymer types (Fig. 3).

As already mentioned above, several PET particles also showed characteristic bands of pigments or olefinic bands. Some of these particles were investigated with Raman mapping to check their spatial composition. In Fig. 4, the results are shown for a particle consisting of PET and PB15. Characteristic spectral bands of PET were detected on every measuring point. PB 15 could only be verified at a part of the particle, indicating that two particles of different material were stacked together in this case. In samples with olefinic interference (e.g. sample s1), high numbers of particles with Raman spectra similar to erucamide were also found (data not shown). This olefinic interference might be caused by adherence of this substance to plastic particles.

3.2. Pigmented particles

The mean number of pigmented particles, their size distribution and the distribution of the pigment types are shown in Figs. 5–7, respectively. Figs. S4B (blank samples), S8 (single use PET bottles), S9 (reusable PET bottles) and S10 (glass bottles) exhibit further detailed results about detected pigmented particles for all samples. Samples showed very different amounts of pigmented particles (Figs. S8–S10), resulting in a high uncertainty per bottle type.

3.2.1. Blank samples

In blank samples we found 554 ± 477 pigmented particles/l. The most particles consisted of Pigment White 6 (PW6, titanium dioxide, anatase and rutile), but some also of PB15 and PV23.

3.2.2. Mineral water

In mineral water from single use PET bottles, mainly the same

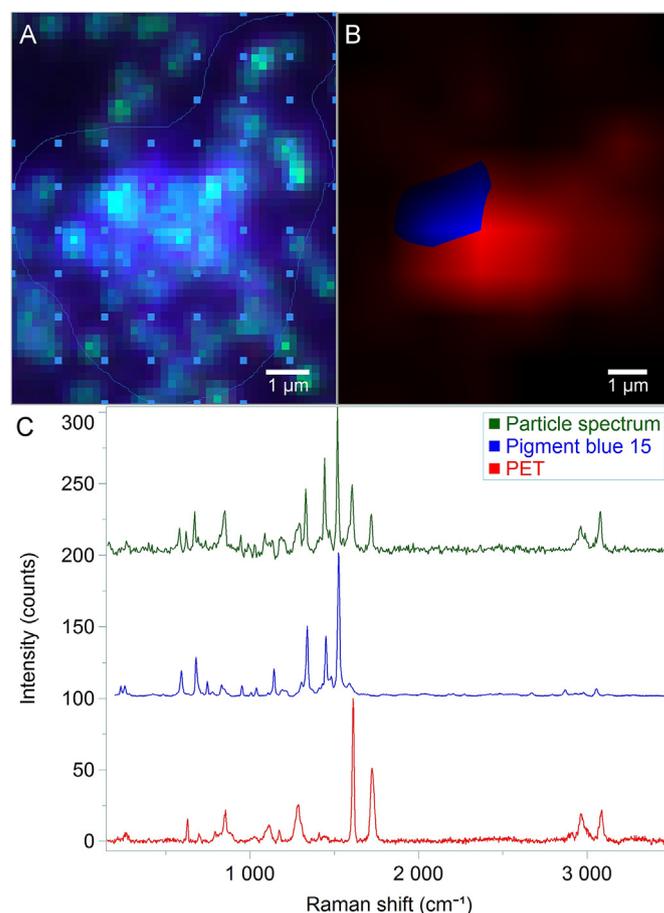


Fig. 4. A. Microscopic image of a particle consisting of PET and Pigment Blue 15 on the surface of an aluminium coated polycarbonate membrane filter and the raster for Raman mapping (magnification $50\times$, dark field illumination). B. Result of the Raman mapping over the particle surface using the Raman spectrum of PET (red) and Pigment Blue 15 (blue) as reference. The respective dominant spectrum is shown in the corresponding colour. C: Raman spectra of the particle and references for Pigment Blue 15 and PET (Measurement parameters: 532 nm, 600/1200/1200 grooves/mm, hole $300 \mu\text{m}$, slit $100 \mu\text{m}$, acquisition time $2 \times 5 \text{ s}/2 \times 2 \text{ s}/2 \times 2 \text{ s}$, objective $50\times$ laser power $\sim 3.2 \text{ mW}/1.2 \text{ mW}/3.2 \text{ mW}$ at the sample, intensity correction applied, baseline corrected, normalized by maximum). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

quantity of pigmented particles as in blank samples was found. Only two samples showed higher amounts of PW6, resulting in a mean value of 1175 ± 1179 pigmented particles/l (Fig. S8 and Fig. 5).

In contrast, we detected higher amounts of pigmented particles in water from reusable PET bottles (11074 ± 18967 pigmented particles/l) and even higher amounts in water from glass bottles (195047 ± 330810 pigmented particles/l). Among these two bottle types, all samples from reusable bottles labelled with printed paper showed significantly higher concentrations (>10000 pigmented particles/l) than bottles labelled with plastic or the single use glass bottle (cf. Table S1, Figs. S9 and S10). Moreover, we found higher contents in older reusable PET bottles than in the corresponding newish ones (sample r6n/o and r7n/o in Fig. S9).

In water from all bottle types, most of the pigmented particles were smaller than $5 \mu\text{m}$ (Fig. 6). In addition, $\sim 40\%$ of the pigmented particles in water from single use PET bottles to $\sim 53\%$ in water from glass bottles were smaller than $1.5 \mu\text{m}$.

Whereas in water from single use PET bottles PW6 was the predominant pigment type, in water from reusable PET bottles and glass bottles PV23, PB15 or a spectral mixture of two or more pigments were dominant (see Fig. 7).

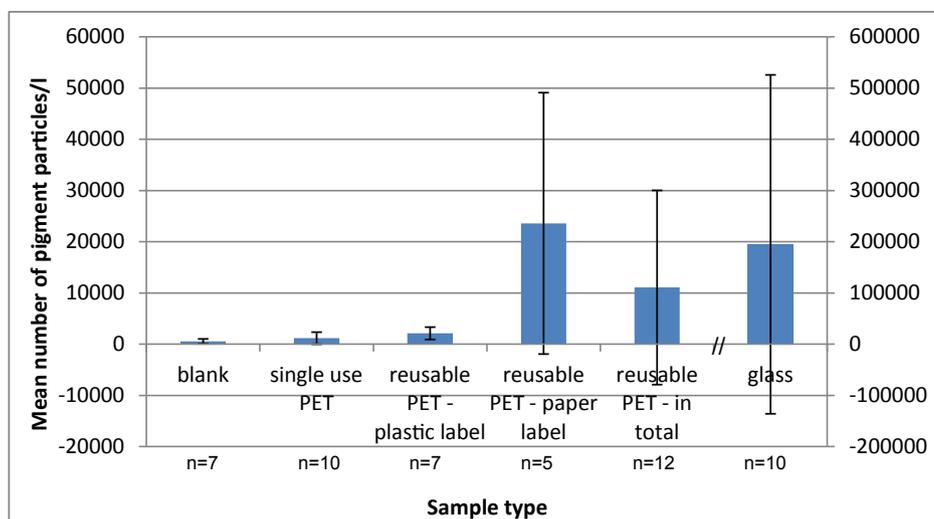


Fig. 5. Mean number of pigment particles projected to 1 L sample volume function of the bottle type (material). Error bars indicate \pm standard deviation.

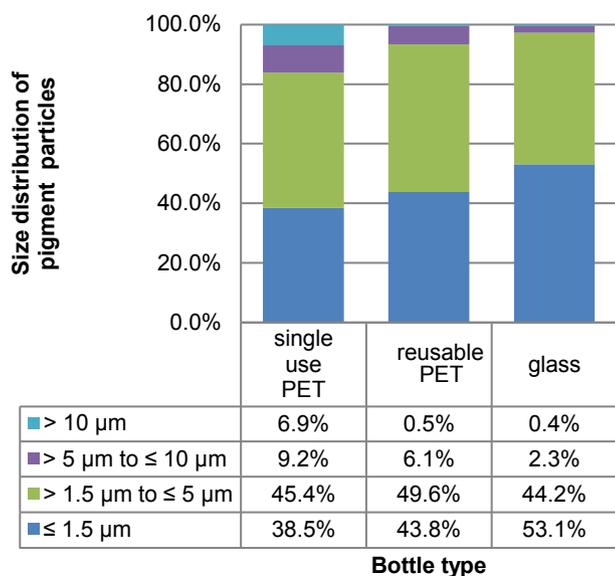


Fig. 6. Size distribution of the detected pigment particles depending on the bottle type (material).

3.2.3. Pigments on paper labels

The analysed mineral water samples were packaged in different bottle types being labelled with printed paper or plastic labels (see Table S1). As we found higher amounts of pigmented particles in reusable bottles labelled with paper, the pigments used for printing of the paper labels were also analysed. In Fig. S11 microscopic images of the surface of a paper label are displayed. The labels are printed with spots in mainly four to five colours: blue, red, yellow, white and green (which showed to be a mixture of blue and yellow). Based on their Raman spectra (see Fig. S12), the colours were identified as PB15, PV23, PY83 and PW6 (anatase and rutile). The pigment of the red spots could not be identified due to the lack of a matching reference spectrum. However, we did not detect this spectrum for any particle found in water samples. The pigment types found on paper labels of glass and PET bottles were the same. In Fig. S13 Raman spectra of PB15 measured on an isolated particle from a mineral water sample, a blue spot on a printed paper label and a reference powder (HEUCO Blue 515303) are compared. These spectra showed to be almost identical.

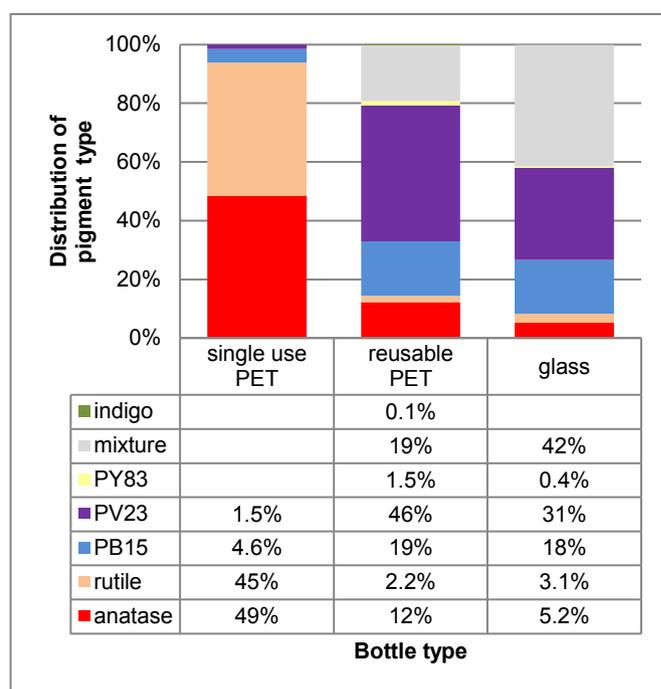


Fig. 7. Pigment type of the detected coloured particles with respect to the bottle type (material). PY83: Pigment Yellow 83, PV23: Pigment Violet 23, PB15: Pigment Blue 15. Detailed information for each sample can be found in Figs. S8, S9 and S10. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.3. Additives

Solely in water from reusable PET bottles, we identified 708 ± 1024 particles/l of the antioxidant Tris(2,4-di-tert-butylphenyl)phosphite (see Fig. S14). 11.7% of the particles were $< 1.5 \mu\text{m}$, 56.9% $> 1.5 \mu\text{m}$ and $\leq 5 \mu\text{m}$, 23.4% $> 5 \mu\text{m}$ and $\leq 10 \mu\text{m}$ and 5.3% $> 10 \mu\text{m}$. A second substance could not be identified due to a missing reference spectrum. Because it shows similar spectral elements to Tris(2,4-di-tert-butylphenyl)phosphite (see Fig. S15), we estimate it to be an antioxidant, too. But as this cannot be confirmed and as this substance was found in one single sample

only (542 particles/l, sample r4o in Fig. S14), we excluded it from the data.

To check the composition of some of these particles, a mapping over the particle surface was performed similar to the coloured PET particle above (section 3.1.2). In Fig. S16 the result is exemplarily displayed for one particle. All spectra were identified as Tris(2,4-di-tert-butylphenyl)phosphite and no underlying polymer was detected.

4. Discussion

Actually, only one peer reviewed study about the contamination of bottled water with microplastics (having analysed multiple samples) has been published. Schymanski et al. (2018) investigated bottled water from different packaging types via filtration (without former sample pre-treatment) and micro-Raman spectroscopy. They presented data about microplastics $>5\ \mu\text{m}$, sparsely addressed pigmented particles and did not mention additives. In the present study, we analysed 32 samples of mineral water packaged in different bottle types for contamination with microplastics, pigmented particles and additives. Using special filters and micro-Raman spectroscopy, we were able to investigate particles down to a size of $1\ \mu\text{m}$. By dissolving calcium or magnesium carbonate particles during sample pre-treatment, we decreased the total particle number and thus the measuring time considerably. In addition, we analysed the influence of the age of reusable PET bottles on the content of microplastics in bottled water and identified labelling with paper labels as potential source for contamination with pigmented particles.

4.1. Microplastics

4.1.1. Microplastics content

According to Schymanski et al. (2018), we detected microplastics in mineral water from all bottle types. The lowest contents were detected in single use PET bottles. In contrast, the highest microplastics content was found in a glass bottle (sample g1). Furthermore, the total number of microplastics was significantly higher in our study as seen in Table S2, where the results of both studies are compared. Since 98.3% (single use PET bottles), 95.4% (reusable PET bottles) and 77.7% (glass bottles) of the detected microplastics were $\leq 5\ \mu\text{m}$ in our study, these particles were not covered by Schymanski et al. (2018). Comparing the amount of microplastics with a diameter greater than $5\ \mu\text{m}$, numbers are in a similar range for single use and reusable PET bottles. In water from glass bottles we found about twenty times higher amounts of microplastics (see Table S2). Even when removing the outlier (sample g1), the mean number of microplastics (greater than $5\ \mu\text{m}$) was about ten times higher (673 ± 953 particles/l) than in the study of Schymanski et al. (2018). This discrepancy might be partly explainable due to different brands analysed in the two studies or the differences in methodology (see also section 4.4.1).

Schymanski et al. (2018) pointed out that the analysis of microplastics with micro-Raman spectroscopy is important since $\mu\text{-FTIR}$ spectroscopy is not suitable to identify particles $<20\ \mu\text{m}$. As over 90% of the determined microplastics were smaller than $5\ \mu\text{m}$, our results show that it is of great importance to analyse food for the smallest size of microplastics. Regarding potential health effects for humans due to the oral intake of microplastics, in particular the smallest microplastics ($<1.5\ \mu\text{m}$) are considered critically (EFSA, 2016; Yoo et al., 2011).

Among the twelve analysed reusable PET bottles, we analysed four pairs of one newish and one older bottle for three brands. On average 2689 ± 4371 microplastics/l were found in newish, 8339 ± 7043 microplastics/l in older bottles. For three pairs (Fig. S6,

r4n/o, r5n/o, r6n/o) microplastics content was clearly higher in water from the older bottle. Only for one pair the difference was small (Fig. S6 r7n/o). Regarding the polymer type of the detected particles, solely the amount of PET particles increased from newish to older bottles. This increase in microplastics consisting of the bottle material indicates a significant influence of the bottle age on contamination with microplastics (see also section 4.1.2 and 4.1.3.).

4.1.2. Distribution of polymers

Comparing the polymer distribution among the detected microplastics with the results of Schymanski et al. (2018), they are very similar for single use and reusable PET bottles. In water from both bottle types we found predominantly PET. Whereas Schymanski et al. declared 30% of microplastics in water from single use bottles as 'others' which could not be clearly identified because of an unavailable standard spectrum, we did not find particles with such a Raman spectrum.

In mineral water from glass bottles, we found only a small amount of PET particles (3.6%), whereas Schymanski et al. (2018) detected 41% PEST (used for the sum of PET and other polyesters) particles. Beside this variation, we only detected single particles of PA instead of 12% in the other study. By contrast, we found 46% PE (Schymanski et al.: 35%), 14% of a styrene-butadiene-copolymer and 6% PS (partly interfered by olefinic spectrum), while Schymanski et al. did not detect a relevant amount of PS.

These differences as well as the above mentioned unidentified polymer in the study of Schymanski et al., might be explainable by different mineral water brands analysed in the two studies.

4.1.3. Potential sources for contamination with microplastics

Concerning the potential sources for the contamination of bottled mineral water with microplastics, Schymanski et al. (2018) already suspected the packaging: bottle and cap. In bottles made of PET (single use as well as reusable), PET was the predominant polymer in both studies. Furthermore, reusable PET bottles showed a higher content of microplastics than single use bottles. We could also show that water from older, frequently used PET bottles had a higher content of PET particles than water from newish bottles. Newish bottles proved to have similar amounts of microplastics as single use bottles. Schymanski et al. (2018) presumed a 'stress' influence on the amount of delivered particles for reusable PET bottles. This assumption could explain the higher content of PET particles in older bottles, whose inner surface might be affected, e.g. during the washing process.

The contents of microplastics in glass bottles might be a result of an abrasion of the caps on the hard glass bottleneck (Schymanski et al., 2018). While this is a possible explanation for the polymers PE and PP, the packaging cannot be the source of contamination in glass bottles especially for polymers like PS, styrene-butadiene-copolymer or PET. Schymanski et al. (2018) 'recommended to take a closer look at the production, cleaning and refilling processes' of reusable bottles. Regarding our results for the content of pigment particles in mineral water (see sections 3.2.3 and 4.2.), we presume the machinery for bottle cleaning as a significant source for microplastics. The washing liquor might be contaminated with microplastics due to the abrasion of machine parts or contaminated returned empties. Contaminated washing liquor would lead to contamination of the bottles (inside and outside). However, we did not find PS or styrene-butadiene-copolymer in water from reusable PET bottles, which are of course machinery washed, too. Since PET is more sensitive, reusable PET bottles are washed in general at lower temperature and concentration of the washing liquor, compensated by a longer time for cleaning purposes. In contrast, glass bottles are washed intensively, which may also affect the material of the washing machinery more aggressively. This might

have an influence on contamination with microplastics, too.

To clarify this assumption, further experiments, like the investigation of cleaned, unfilled bottles or a successive analysis of mineral water beginning with samples at the bore head and during the filling process, have to be performed. Thereby, the conditions of sampling, especially the sampling container have to be critically reviewed to avoid contamination during the sample process.

Size distribution of microplastics in glass bottles is shifted to particles $>5\ \mu\text{m}$ compared to PET bottles. Almost all of the particles $>5\ \mu\text{m}$ in glass bottles consisted of PE or PP, which are probably caused by abrasion from the caps on the hard glass bottleneck (see above). As this contamination source is less relevant for PET bottles, this might be an explanation for the different size distribution.

4.2. Pigments

While investigating mineral water for microparticle contamination, we detected also partly high amounts of pigmented particles. The sample with the highest content (over 1.1 million pigmented particles/l) was water from a glass bottle. All water samples from glass bottles were contaminated, beside one sample from a single use glass bottle which contained only small amounts of PW6. In water from single use PET bottles and most reusable PET bottles, pigmented particles were only scarcely present (<4500 particles/l), whereas in three reusable PET bottles, higher amounts (~ 18000 particles/l to ~ 62000 particles/l) of pigmented particles were detected. Schymanski et al. (2018) found coloured particles in all samples from glass bottles (115 ± 102 particles/l) and in one type of returnable PET bottle (27 particles/l). These particles showed a similar spectrum as 'blue nitrile gloves' (worn during the experiment), 'heliogen blue' or the 'polypropylene blue bottle caps' (used during experiments). However, they were not able to identify the source of these particles. As with the contents of microplastics, we also detected higher amounts of pigmented particles. In total, 91.5% of the pigmented particles were $\leq 5\ \mu\text{m}$. These were not analysed by Schymanski et al. (2018).

Besides PW6 (titanium dioxide) and PB15, which were already observed by Schymanski et al. (2018), we also found other pigment types such as PV23, PY83 or spectral mixtures of two or more pigments. These spectral mixtures might be caused by conglutination of two or more particles (as mentioned in section 3.1.2) or by a real mixture of colours. These pigment types were also reported by Imhof et al. (2016) to be found in limnetic ecosystems. Even so, we rule out a transfer of pigmented particles from freshwater to mineral water sources. All samples that exhibited a higher content of pigmented particles were reusable bottles (PET or glass) and all of them were labelled with paper. The only single use glass bottle as well as the plastic labelled, reusable PET bottles displayed almost no or only small amounts of pigment particles.

Accordingly, we investigated the colours used for printing on the paper labels from several brands and found the same pigments as in mineral water samples. Paper labels, in contrast to plastic labels, are normally not removed from reusable bottles before the cleaning process. Thus, paper labels come into direct contact with the washing liquor so that pigment particles find their way into the washing liquor and from there into the bottles. The following rinsing steps with fresh water seem not to be efficient enough to remove this contamination of the inner surface of the bottles.

On average, water from glass bottles showed higher amounts of pigmented particles as water from paper labelled reusable PET bottles. As described in section 4.1.3., reusable PET bottles run through a more gently washing process. Colder, less concentrated washing liquor (as used for PET bottles) might remove fewer pigments from paper labels as that used for glass bottles. This would result in a lesser contamination of reusable PET bottles.

Among the water from reusable PET bottles which were contaminated with pigment particles, two were newish and two older from the same brand. In the newish ones, we found obviously smaller amounts of pigmented particles (1808 and 814 particles/l) than in the corresponding older bottles (35256 and 61652 particles/l). This leads us to the hypothesis, that pigment particles which were brought inside the bottles during the washing process, take hold on the potentially affected, rough inner surface of older reusable PET bottles and cannot be removed as easy as from newish bottles.

Nevertheless, further tests have to be performed to clearly demonstrate the washing liquor as the source for contamination of water samples with pigmented particles. For example, the investigation of cleaned, unfilled bottles or of the washing liquor itself might be useful.

PW6 (titanium dioxide) was not only detected in water from reusable bottles labelled with paper, but also in water from two single use PET bottles, the single use glass bottle and some reusable PET bottles with plastic labels. In these cases, the pigments used for label printing cannot be the source for the contamination with the pigmented particles. However, titanium dioxide is also used as material filler or UV-blocker (Lenz et al., 2015). Thus, it might be added to other materials used during the filling process of water, e.g. filter materials, which could lead to contamination. To achieve a definite cause for this observation, further tests are required.

4.3. Additives

Besides different microplastics, we also detected several particles of the antioxidant additive Tris(2,4-di-tert-butylphenyl)phosphite in water from eight of the twelve analysed reusable PET bottles. The remaining four samples were from one brand and filled in a different bottle type. In mineral water from single use PET or glass bottles, no additive particles were found. Tris(2,4-di-tert-butylphenyl)phosphite is used as hydro peroxide scavenger in the manufacturing process of plastics (Welle, 2007) and might be leached out from the bottle. We did not detect any polymeric spectrum when investigating these particles with Raman mapping. Nevertheless, we cannot exclude that they consisted of a mixture of the polymer and the above named additive (Lenz et al., 2015).

4.4. Method assessment

4.4.1. Partial analysis

In the present study, our aim was to investigate mineral water for microplastics down to a particle size of $1\ \mu\text{m}$ using micro-Raman spectroscopy. By the use of aluminium coated PC membrane filters (Oßmann et al., 2017), we were able to generate reliable Raman spectra of the smallest particles ($1\ \mu\text{m}$) without destruction. Using gold coated PC membrane filters as they were applied by Schymanski et al. (2018), non-destructive Raman measurement of particles less than $5\ \mu\text{m}$ was only possible by decreasing laser power to a minimum, combined with a prolonged measurement time (Oßmann et al., 2017). As total particle number in mineral water strongly increased with analysing smaller particle size, we had to reduce sample volume to 250 ml, to achieve analysable particle numbers. Additionally, the more particles are present on the filter surface, the more particles stack together and are recognized as one single particle. Furthermore, regarding the measurement time, all particles on $5\ \text{mm}^2$ from the total filtration area ($113\ \text{mm}^2$) were analysed. If we would have analysed all particles on the entire filter surface, only a maximum of two samples instead of 32 would have been investigated in the same time.

Schymanski et al. (2018) filtered the whole sample volume (0.7–1.5 l) through a $\sim 12.6\ \text{mm}^2$ filter and analysed particles greater

than 5 µm. As they had a maximum of 5000 particles analysable per sample, they also used extrapolation. In contrast, we analysed up to ~23000 particles per sample.

Every extrapolation causes additional uncertainty. Even so, to get a better comparability of our results with other studies, we decided to calculate particle numbers per litre sample volume. Assuming an even distribution of the particles in the initial sample volume and over the filter surface, multiplying the particle number detected on the analysed area by 22.6 resulted in the total particle number on the filter surface and multiplying again by 4 resulted in the number of particles in 1 L mineral water. Accordingly, an entire factor of 90.4 is used. One particle detected on the analysed area results in 90 particles/l, which might lead to an overestimation. During method validation, three aliquots of one sample were analysed in a similar way. The coefficient of variation (CV) of the microplastics content between the three aliquots was up to 50% with a mean value of only ~10 microplastic particles/5 mm² (resulting in ~900 particles/l). This CV includes the variation caused by the analysis of a partial volume as well as the variation caused by the analysis of a subarea. The analysis of microplastics is a kind of trace analysis, where a CV of 50% is not unlikely. In addition, a strong reliance was observed between the CV of the particle number among the five analysed spots and the particle number itself. This CV did not decrease with a higher number of analysed squares; even with 21 analysed spots the CV remained constant. As a consequence, particle numbers less than 10 particles/5 mm² (resulting in ~900 particles/l) might be considered with an uncertainty over 50%.

Summarized, partial analysis and extrapolation might lead to over- or to underestimation of contamination. Nevertheless, a complete analysis of all particles on the filter surface in a size class beginning with 1 µm is nearly unfeasible.

4.4.2. Interference of Raman spectra

As already mentioned above (section 4.4.1), particles might stick together and thus were recognized as one single particle. This was demonstrated exemplarily for one 'blue PET particle' in Fig. 4. In some samples, interference with an olefinic spectrum was also observed, which might be caused by adherence of highly detected erucamide to plastic particles. Furthermore, some particles might be a mixture of several components like a polymer and a pigment or an additive. Depending on the generated Raman spectra, such particles might be recognized as one of the components or as a mixture. Even though we tried to differentiate between plastic, additive and pigment spectra, we cannot ensure that some microplastics were missed as their spectra were totally covered by additive or pigment spectra. This already showed to be a problem in previous studies and might lead to underestimation of the microplastics content (Imhof et al., 2016; Lenz et al., 2015).

4.4.3. Blank values

Microplastics are ubiquitously present. Thus, when performing analytics of microplastics, it is important to follow several precautions to avoid sample contamination and to monitor it via blank samples. Nevertheless, it is difficult to completely avoid sample contamination (Schymanski et al., 2016, 2018). In the present study, small amounts of PP and PS and single particles of PE and PET were detected. We paid attention on avoiding plastic products during analytics whenever possible. However, e.g. the housing of the filter of the ultrapure water system and the syringe filter as well as the syringe itself (used for filtration of chemical solutions) were made of plastics (PC, PP) and might have led to sample contamination. Even so, as the unfiltered chemicals (EDTA, SDS) were highly contaminated with microplastics, blank values could be decreased considerably by using these filters.

5. Conclusions

In the present study, 32 samples of mineral water were investigated for microparticle contamination. In water from all bottle types, variable amounts of microplastics were detected. Mineral water from reusable bottles (PET as well as glass) showed higher amounts of microplastics than water from single use PET bottles. In water from PET bottles, the predominant polymer was PET, indicating a contamination via the bottle material. In water from glass bottles, various polymer types like PE, PP or a styrene-butadiene-copolymer were found. Possible contamination sources are the bottle cap, the washing machinery or other steps during filling process. Additionally, water from frequently reused PET bottles showed higher amounts of microplastics than water from newish PET bottles. This was possibly caused by aging of the bottle material. In reusable PET bottles, also few particles of an antioxidant additive were found. These might be leached out from the bottle material.

Apart from microplastics, partly high amounts of pigmented particles were detected in water from reusable bottles labelled with printed paper. The colours used for label printing were the same as those found in mineral water samples. The most possible way of contamination might be the washing liquor used in the cleaning process of the bottles, which comes into contact with the labels and also the inner surface of the bottles.

In total, about 90% of the detected microplastics and the pigmented particles were ≤5 µm and about 40% were even <1.5 µm. Considering toxicological aspects for humans via the oral intake of microplastics with food, analysis of the smallest microplastics is crucial. In the present study, a method is shown enabling analysis of particles down to a size of 1 µm. This important size class could only be achieved by using aluminium coated PC membrane filters and micro-Raman spectroscopy. Furthermore, data about microplastics, additive particles and pigmented particles in mineral water are presented.

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Conflicts of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.05.027>.

References

- Auta, H.S., Emenike, C.U., Fauziah, S.H., 2017. Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. *Environ. Int.* 102 (Suppl. C), 165–176. <https://doi.org/10.1016/j.envint.2017.02.013>.
- Browne, M.A., Dissanayake, A., Galloway, T.S., Lowe, D.M., Thompson, R.C., 2008. Ingested microscopic plastic translocates to the circulatory system of the mussel, *Mytilus edulis* (L.). *Environ. Sci. Technol.* 42 (13), 5026–5031. <https://doi.org/10.1021/es800249a>.
- Browne, M.A., Niven, S.J., Galloway, T.S., Rowland, S.J., Thompson, R.C., 2013. Microplastic moves pollutants and additives to worms, reducing functions linked to health and biodiversity. *Curr. Biol.* 23 (23), 2388–2392. <https://doi.org/10.1016/j.cub.2013.10.012>.
- Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., Peck, B.B., 1972. Polystyrene spherules in coastal waters. *Science* 178, 749–750.
- Carpenter, E.J., Smith, K.L., 1972. Plastics on the sargasso sea surface. *Science* 175 (4027), 1240.
- Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* 75 (0), 63–82. <https://doi.org/10.1016/j.watres.2015.02.012>.
- EFSA, 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. *EFSA J* 2016 14 (6). <https://doi.org/10.2903/j.efsa.2016.4501>.
- Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ.* 586 (Suppl. C), 127–141. <https://doi.org/10.1016/j.scitotenv.2017.01.190>.
- Imhof, H.K., Laforsch, C., Wiesheu, A.C., Schmid, J., Anger, P.M., Niessner, R., Ivleva, N.P., 2016. Pigments and plastic in limnetic ecosystems: a qualitative and quantitative study on microparticles of different size classes. *Water Res.* 98, 64–74. <https://doi.org/10.1016/j.watres.2016.03.015>.
- Ivar do Sul, J.A., Costa, M.F., 2014. The present and future of microplastic pollution in the marine environment. *Environ. Pollut.* 185, 352–364. <https://doi.org/10.1016/j.envpol.2013.10.036>.
- Käppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K.-J., Voit, B., 2016. Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both? *Anal. Bioanal. Chem.* 408 (29), 8377–8391. <https://doi.org/10.1007/s00216-016-9956-3>.
- Karami, A., Golieskardi, A., Keong Choo, C., Larat, V., Galloway, T.S., Salamatinia, B., 2017. The presence of microplastics in commercial salts from different countries. *Sci. Rep.* 7 (46173) <https://doi.org/10.1038/srep46173>.
- Lachenmeier, D.W., Kocareva, J., Noack, D., Kuballa, T., 2015. Microplastic identification in German beer - an artefact of laboratory contamination? *Deut. Lebensm.-Rundsch.* 111. Jahrgang 437–440.
- Lenz, R., Enders, K., Stedmon, C.A., Mackenzie, D.M., Nielsen, T.G., 2015. A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. *Mar. Pollut. Bull.* 100 (1), 82–91. <https://doi.org/10.1016/j.marpolbul.2015.09.026>.
- Li, J., Yang, D., Li, L., Jabeen, K., Shi, H., 2015. Microplastics in commercial bivalves from China. *Environ. Pollut.* 207, 190–195. <https://doi.org/10.1016/j.envpol.2015.09.018>.
- Liebezeit, G., Liebezeit, E., 2013. Non-pollen particulates in honey and sugar. *Food Addit. Contam.* 30 (12), 2136–2140. <https://doi.org/10.1080/19440049.2013.843025>.
- Liebezeit, G., Liebezeit, E., 2014. Synthetic particles as contaminants in German beers. *Food Addit. Contam.* 31 (9), 1574–1578. <https://doi.org/10.1080/19440049.2014.945099>.
- Mintenig, S., Löder, M., Gerdt, G., 2014. Mikroplastik in Trinkwasser, Untersuchung im Trinkwasserversorgungsgebiet des Oldenburgisch-Ostfriesischen Wasserverbandes (OOWV) in Niedersachsen, Probenanalyse mittels Mikro-FTIR Spektroskopie, Oldenburgisch-Ostfriesischer Wasserverband (OOWV). Alfred-Wegener-Institut, Helgoland.
- Oßmann, B.E., Sarau, G., Schmitt, S.W., Holtmannspötter, H., Christiansen, S.H., Dicke, W., 2017. Development of an optimal filter substrate for the identification of small microplastic particles in food by micro-Raman spectroscopy. *Anal. Bioanal. Chem.* 409 (16), 4099–4109. <https://doi.org/10.1007/s00216-017-0358-y>.
- Schymanski, D., Goldbeck, C., Humpf, H.-U., Fürst, P., 2018. Analysis of microplastics in water by micro-Raman spectroscopy: release of plastic particles from different packaging into mineral water. *Water Res.* 129, 154–162. <https://doi.org/10.1016/j.watres.2017.11.011>.
- Schymanski, D., Goldbeck, C., Humpf, H.-U., Fürst, P., 2016. Kunststoffpartikel sind überall - auch in Lebensmitteln? *Nachr. Chem.* 64 (9), 842–846. <https://doi.org/10.1002/nadc.20164052892>.
- Van Cauwenberghe, L., Janssen, C.R., 2014. Microplastics in bivalves cultured for human consumption. *Environ. Pollut.* 193, 65–70. <https://doi.org/10.1016/j.envpol.2014.06.010>.
- Welle, F., 2007. Alltäglich und doch unscheinbar - Lebensmittelverpackungen. *Chem. Unserer Zeit* 41, 96–106. <https://doi.org/10.1002/ciuz.200700401>.
- Wiesheu, A.C., Anger, P.M., Baumann, T., Niessner, R., Ivleva, N.P., 2016. Raman microspectroscopic analysis of fibers in beverages. *Anal. Methods* 8 (28), 5722–5725. <https://doi.org/10.1039/c6ay01184e>.
- Workman Jr., J., Howard, M., 2010. Classical Least Squares, Part I: Mathematical Theory, 2016/09/15. <http://www.spectroscopyonline.com/classical-least-squares-part-i-mathematical-theory>.
- Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine organisms: a review. *Environ. Pollut.* 178, 483–492. <https://doi.org/10.1016/j.envpol.2013.02.031>.
- Yang, D., Shi, H., Li, L., Li, J., Jabeen, K., Kollandhasamy, P., 2015. Microplastic pollution in table salts from China. *Environ. Sci. Technol.* 49 (22), 13622–13627. <https://doi.org/10.1021/acs.est.5b03163>.
- Yoo, J.-W., Doshi, N., Mitragotri, S., 2011. Adaptive micro and nanoparticles: temporal control over carrier properties to facilitate drug delivery. *Adv. Drug Deliv. Rev.* 63 (14–15), 1247–1256. <https://doi.org/10.1016/j.addr.2011.05.004>.