Science of the Total Environment 648 (2019) 631–635

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Low numbers of microplastics detected in drinking water from ground water sources

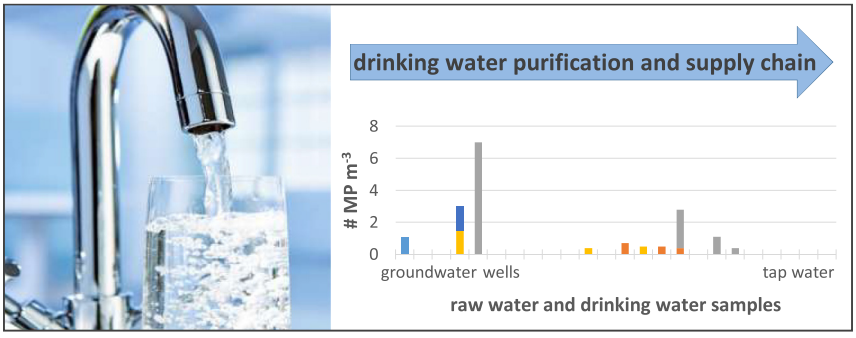
Mintenig S.M. *[,1], Löder M.G.J. [2], Primpke S., Gerdts G.

Alfred-Wegener-Institut, Helmholtz-Zentrum für Polar- und Meeresforschung, Biologische Anstalt Helgoland, P.O. Box 180, 27483 Helgoland, Germany

HIGHLIGHTS

- Identification of microplastics >20 μm using FTIR imaging.
- Examination of 40 m^3 ground water and drinking water for microplastics.
- Negligible microplastic contamination of drinking water (<1 particle m^{-3}).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 June 2018
Received in revised form 13 August 2018
Accepted 14 August 2018
Available online 16 August 2018

Editor: D. Barcelo

Keywords:
Ground water
Drinking water purification
FTIR imaging
Human health

ABSTRACT

Microplastic particles have been detected in various natural habitats and the digestive tracts of several species. These particles have also been reported in commercially available seafood, salt or bottled water starting discussions on potential implications for human health. To be able to assess the related risks, exposure concentrations and pathways need to be known. Here, we analysed ground water and drinking water for the presence of microplastics (>20 μm) using FTIR imaging. Samples were taken at different positions within the drinking water supply chain. Determined concentrations ranged from 0 to 7 microplastics m^{-3} raw water or drinking water with an overall mean of 0.7 microplastics m^{-3}. These particles were identified as polyethylene, polyamide, polyester, polyvinylchloride or epoxy resin and between 50 and 150 μm in size. Plastic is a resistant and durable material, still, the abrasion of plastic equipment used during water purification or transport is a likely explanation for the plastic particles detected in water samples.

1. Introduction

The contamination of natural habitats with plastic litter can be observed in many places and is considered a topic of emerging concern (Eerkes-Medrano et al., 2015). A lot of research has been conducted on microplastics, which are polymer particles or fibres smaller than 5 mm. These plastics have been detected in the marine (do Sul and Costa, 2014) and freshwater environment (Eerkes-Medrano et al., 2015; Jambeck et al., 2015; Mani et al., 2015), and in the digestive tracts of several species (Rummel et al., 2016; van Cauwenberghe and Janssen,

* Corresponding author at: Utrecht Univerity (S.M. Mintenig), P.O. Box 80115, 3508 TC Utrecht, The Netherlands.
E-mail address: s.m.mintenig@uu.nl (S.M. Mintenig).
[1] Present address: Copernicus Institute of Sustainable Development, Environmental Science Group, Utrecht University, P.O. Box 80115, 3508 TC Utrecht, The Netherlands.
[2] Present address: Animal Ecology I, University of Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany.

https://doi.org/10.1016/j.scitotenv.2018.08.178
0048-9697/

2014). So far, it is not yet completely known if and how ingested microplastic might harm organisms. Ingested microplastics might cause local inflammations in the gut, but a transport via membranes or into organs, as it might occur for nanoplastics (<100 nm), seems unlikely (Bouwmeester et al., 2015). In recent years microplastic particles and fibres have been reported in commercially available seafood (Tanaka and Takada, 2016; van Cauwenberghe and Janssen, 2014), salt (Iniguez et al., 2017; Yang et al., 2015), honey (Liebezeit and Liebezeit, 2015) as well as tap water (Kosuth et al., 2017). Though partly questioned and criticized for missing contamination controls or for omitting the identification of selected particles (Lachenmeier et al., 2015; Mühlschlegel et al., 2017; Rist et al., 2018), these studies started discussions on potential implications of these microplastics for human health. Schymanski et al. (2018) identified small plastic particles in bottled drinking water and concluded that packaging materials were responsible for the contamination (Schymanski et al., 2018).To be able to fully assess the risks microplastics could pose to human health, actual exposure and pathways need to be determined (Bouwmeester et al., 2015; Wright and Kelly, 2017). While it is necessary to examine food and beverages, we should not forget the impacts of packaging materials, or our general wide usage of plastic materials in daily life (Rist et al., 2018).

The purpose of this study was the identification of microplastics in large volumes of drinking water that derived from the purification of ground water. The samples were taken at different positions in the supply chain, ranging from groundwater wells to drinking water from conventional household taps to asses if and where a contamination with microplastics would occur. To identify potential microplastics, Fourier transform infrared (FTIR) microscopy coupled to a focal plane array (FPA) detector was applied which enabled the identification of microplastic particles down to a size of 20 μm (Löder et al., 2015; Mintenig et al., 2017).

2. Material and methods

2.1. Drinking water purification

The Oldenburg-East-Frisian water board (OOWV) supplies the drinking water for an area of 7500 km^2 in the north-western part of Germany. Per year, the OOWV provides 71 million cubic meters of drinking water. Exclusively groundwater (extracted from wells at least 30 m deep), hereafter referred to using the technical term 'raw water', is transported to fifteen drinking water treatment plants (DWTP) and purified by applying several filtration and aeration steps (Fig. 1). After purification, the drinking water is stored in tanks or directly fed into the distribution system and transported to the consumers. All pipes are made of high- density polyethylene (HDPE), polyvinylchloride (PVC) or cast iron. In the DWTP, all reaction and storage tanks have an inner layer of epoxy resin to avoid corrosion, and aeration tanks have built in rings of polypropylene (PP) to enlarge the surface area.

The responsibility for quality and transport of the drinking water ends for the water board at the water meter of each household, the water pipes within houses are handled by the individual consumers.

2.2. Sampling

The sampling took place between August 13th and 20th 2014. The DWTPs in (1) Nethen, (2) Holdorf, (3) Grossenkneten, (4) Sandelermoens and (5) Thuelsfelde were chosen, here the raw water at the DWTP inlet and the drinking water at the plant outlet were sampled. Additionally, one consumer household in the distribution system of each DWTP was selected where the drinking water was sampled at the water meter and at a conventional water tap. The distance between the DWTP and the household varied between 5 and 42 km. Additionally the ground water of three wells with an approximate depth of 30 m was sampled in the area of Holdorf. Thereby, the samples covered all steps of drinking water purification, transportation and supply (Fig. 1).

The raw water and drinking water samples were filtered through 3 μm stainless steel cartridge filters (4 7/8″, Wolftechnik, Germany) that were placed in filter housings (made of styrene acrylonitrile (SAN) and PP) with flexible PVC hoses attached. The inlet tube was attached directly to a water tap which was opened far enough to allow a water flow of approximately 10 L min^{-1}. The pressure at the DWTP inlet was generally lower and the raw water was filtered with a flow rate of about 5 L min^{-1}. A flowmeter (Gardena, Germany) was connected to the outlet tube of the filter housing to determine the volume of filtered water.

Before usage, the filter units (filter housing with stainless steel cartridge filter) were rinsed with analytical grade water (Milli-Q), closed and not opened outside the laboratory. At each sampling position the inlet tube was primed for five minutes and a new filter unit was used. The filtration of raw water was stopped earlier when iron oxide blocked the cartridge filters and led to a significant reduction of the water flow. Between 300 and 1000 L of raw water and 1200 to 2500 L of drinking water were filtered. After completion, the filter units were kept closed and stored refrigerated at 4 °C.

2.3. Sample treatment

In the laboratory, residual raw water and drinking water was removed from the filter units by using filtered (0.2 μm) compressed air. Then, the units were filled again with diluted hydrochloric acid (Carl Roth GmbH & Co. KG, Germany, 0.2 μm filtered, pH = 2) to dissolve calcium carbonate and iron precipitates. After 24 h the filter units were emptied, the cartridge filters removed from the units and rinsed with

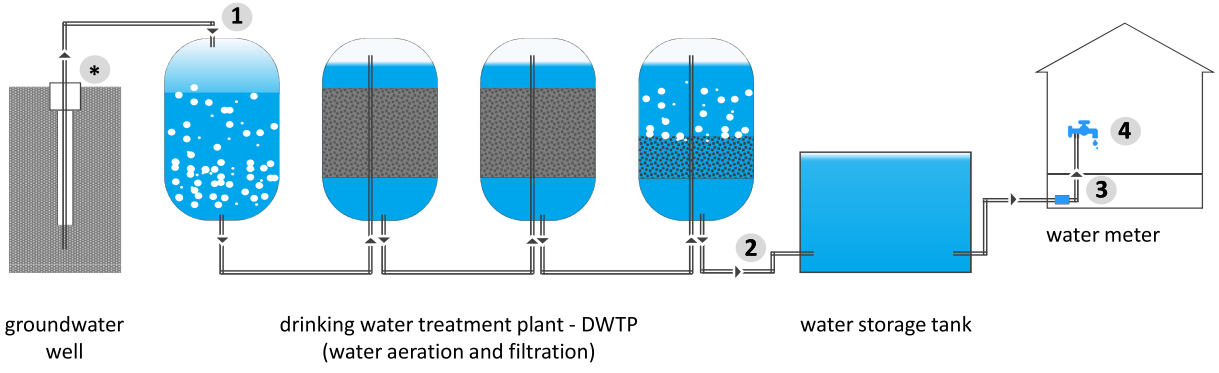


Fig. 1. Scheme of the drinking water purification and supply chain (OOWV), with locations marked where (1) the raw water, (2) the drinking water at plant outlet, the drinking water at the (3) water meter and (4) a conventional water tap in a selected household were sampled. This was repeated in five drinking water supply areas. Additionally, the ground water at three wells was sampled in one area (*).

Milli-Q and ethanol (30%, Carl Roth GmbH & Co. KG, Germany, filtered over 0.2 μm). The retentate was collected on 3 μm stainless steel filters (47 mm in diameter) that were subsequently transferred into glass bottles and covered with 30 mL hydrogen peroxide (35%, Carl Roth GmbH & Co. KG, Germany). The bottles were closed using aluminium foil and incubated for 24 h at 40 °C. Finally, each sample was enriched onto a 0.2 μm aluminium oxide filter (Anodisc 25 mm, Whatman, U.K.) by using an in-house fabricated filter-funnel with an inner diameter of 11 mm (Mintenig et al., 2017). The filters were dried at 40 °C in half closed glass petri dishes for subsequent analysis.

The raw water samples contained high amounts of iron oxide particles which were removed performing a density separation using a zinc chloride solution ($ZnCl_2$, Carl Roth GmbH & Co. KG, Germany, 1.6 g cm^{-3}). After a settling time of 24 h, the settled material was purged and the supernatant filtered on Anodisc filters as described above.

2.4. Contamination mitigation

It is of special importance to control and mitigate contamination when working with samples where microplastic concentrations are expected to be low. Therefore, we chose filter units that were kept closed outside the laboratory. In the laboratory only clothes made of natural fabric and clean cotton lab coats were worn. The lab surfaces were wiped with ethanol (30%), the equipment was rinsed with Milli-Q and ethanol before usage and covered with aluminium foil directly after. Also the samples were covered directly with aluminium foil when being placed open. Since we could not fully avoid the usage of plastic, four blank samples (150 L of pre- filtered drinking water, 3 μm) were treated and analysed in parallel to the water samples. Contaminating fibres were counted using a stereo light microscope (Olympus SZX16, Olympus K.K., Japan), the presence of particles was determined for two blank samples using FTIR imaging. All raw water and drinking water samples were corrected for the mean of the four blank samples.

2.5. Micro-FTIR analysis

FTIR analyses were performed with a Hyperion 3000 FTIR microscope with a 15× cassegrain objective, equipped with a 64 × 64 FPA detector and a Tensor 27 FTIR spectrometer (all Bruker Optik GmbH, Ettlingen, Germany).

The filters were placed on calcium fluoride windows for the measurements which were performed applying settings published by Löder et al. (2015) with a binning factor of 4 and a spectral resolution of 8 cm^{-1} with 6 co-added scans. By this, the whole filter surfaces were analysed. The data were analysed using the software OPUS 7.2 and followed the same steps as presented in an earlier study (Mintenig et al., 2017). In short, particles were identified via manual analysis of false colour images. These were produced using two polymer specific regions, firstly between 1480 and 1430 cm^{-1} (C—H bending, aromatic ring stretching) and secondly between 1790 and 1700 cm^{-1} (C═O stretching) (Löder et al., 2015). Thereby highlighted particles were approached manually, identified via a library search and recorded their colour and longest dimension.

3. Results

3.1. Contamination

The blank samples revealed that a contamination with microplastic particles and fibres occurred during sample handling. Varying numbers of fibres (45 ± 22, $N = 4$) of different colours, mostly black (18%) and transparent (78%), were detected in the blank samples. The contamination with particles consisted predominantly of blue fragments (average 81%, Fig. 2), from which some particles resulted in spectra with characteristic IR bands of PP and SAN. Thereby, the filter units were detected as the main source of contamination. Remaining polymers were detected in comparably low numbers (Table 1). The averaged fibre and polymer specific microplastic particle counts from the blank samples were subtracted from numbers detected in raw water and drinking water samples. Further, all blue SAN and PP particles were excluded from analysis since they could be clearly identified as coming from the lids of used filter units and they were detected in both, control and water samples (Fig. 2).

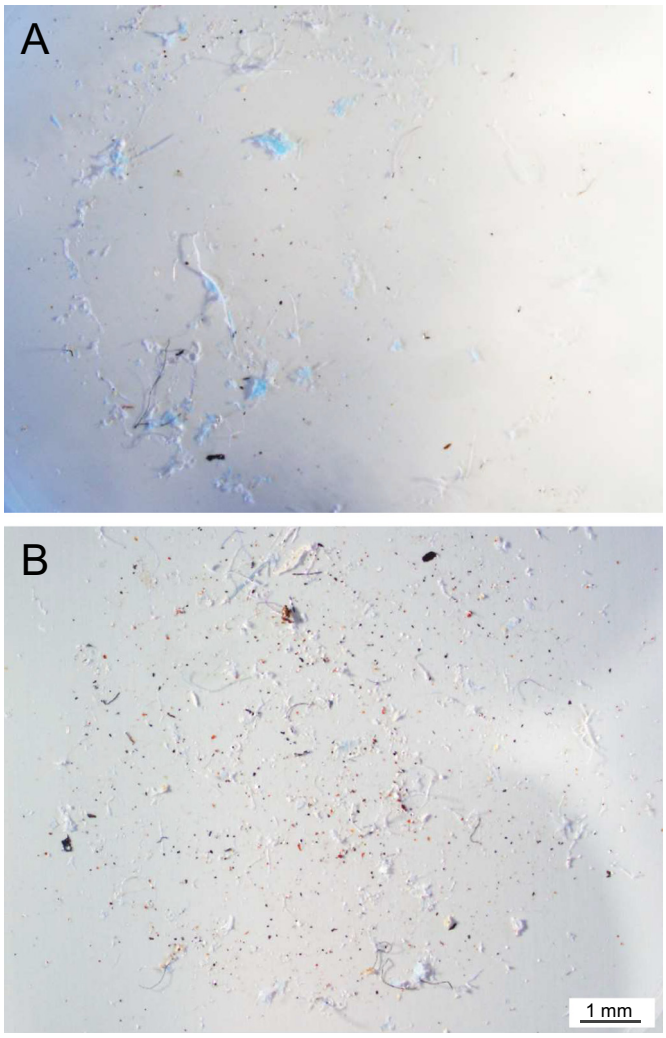


Fig. 2. Pictures of Anodisc filters containing a control sample (A) and a drinking water sample (B) taken with a stereo light microscope. The filter units caused a contamination with SAN and PP fragments coloured light blue to transparent.

3.2. Microplastics in raw water and drinking water

In 14 of the 24 water samples no microplastic particles were detected. Less than one microplastic particle per cubic meter was determined in five of the samples, another four samples contained between one to three microplastics per cubic meter, and one sample seven

Table 1
Determined plastic particles in the blank samples that were analysed using FTIR imaging.

	PP	SAN	PE	PEST
Control 1	97	27	5	11
Control 2	43	7	3	8
Mean	70	17	4	10

microplastic particles m^{-3} respectively. In total, five different polymer types were identified in raw water and drinking water samples (Fig. 3). The majority of particles (62%) was made of polyester (PEST), and detected mainly in two water samples. Occasionally, particles of PVC (14%), PA and epoxy resin (both 9%) as well as PE (6%) were detected at different positions in the purification and supply chain. All microplastic particles were in a size range of 50 to 150 μm.

Fibres were categorized by colour, counted and determined in all water samples. The material of the fibres was not identified further. Between 3 and 46 fibres m^{-3} were detected in the raw water and drinking water samples. Considering that the blank samples were contaminated with 27 to 76 (average 45) fibres, our results indicate that the drinking water was not contaminated with fibres, but that these were introduced during sample handling.

4. Discussion

4.1. Microplastics in raw water and drinking water

In total 24 samples of raw (9 samples, eight cubic meters) and drinking water (32 cubic meters) were examined for the presence of microplastics. Especially when expecting low numbers of microplastics, high sample volumes are required to generate representative results. This was achieved by using cartridge filters in closed filter units: Up to 1000 L of raw water and 2500 L of drinking water were filtered this way. Microplastic concentrations varied between 0 and 7 particles m^{-3}, whereby 14 samples contained no microplastics (Fig. 3). When adding individual samples, a total microplastic concentration of 0.7 particles per cubic meter water was determined which is low and in contrast to results presented earlier: Studying global drinking water Kosuth et al. (2017) determined between 0 and 57 (average 4.3) plastic particles L^{-1}. While the authors controlled for sample contamination, the results might be limited due to the small sample volumes (0.5 L) or the missing identification of particles.

The examined water samples were taken at different stages of the drinking water purification and supply chain to evaluate if and where contamination occurred (Fig. 1). However, no differences in detected microplastic concentrations between the treatment steps were found that allowed drawing such conclusions. All particles were characterized as small fragments of 50 to 150 μm and were made of five different polymer types, namely PEST, PVC, PE, PA and epoxy resin. Four of these polymer types can be explained by their wide usage in the purification and supply chain: the tanks in the DWTPs are coated with epoxy resin to avoid corrosion, pipes in DWTPs or households are frequently made of PVC or PE and fittings of PA. Although plastic is a resistant and durable material, abrasion can occur and is a likely explanation for the determined plastic particles in raw water and drinking water.

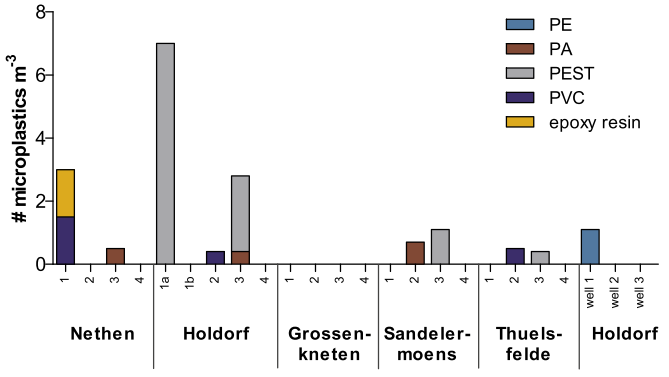


Fig. 3. Microplastic particles identified in (1) raw water, (2) drinking water at plant outlet, drinking water at the (3) water meter and (4) a conventional water tap in a selected household in five drinking water supply areas. Additionally, the ground water extracted from three wells (30 m depth) was tested in the area around Holdorf.

Next to plastic particles, dark and transparent fibres were encountered in all raw water and drinking water samples. However, the parallel treated blank samples revealed that these fibres were introduced during sample handling. An unidentified contamination might also be the explanation for strongly varying results and subsequent conclusions when analysing microplastics in honey (Liebezeit and Liebezeit, 2015; Mühlschlegel et al., 2017) or beer (Lachenmeier et al., 2015; Liebezeit and Liebezeit, 2014). While Liebezeit and Liebezeit (2014) determined up to 79 fibres and 109 plastic fragments per litre beer, Lachenmeier et al. (2015) followed the same approach and reported no pollution with microplastics after they found comparable microplastic numbers in blank (15 ± 9 fibres and 20 ± 13 fragments L^{-1}) and actual samples (16 ± 15 fibres and 21 ± 16 fragments L^{-1}). These contaminations are likely to derive from airborne contamination or the materials used during the production process (Bouwmeester et al., 2015; Lachenmeier et al., 2015; Wright and Kelly, 2017). Considering all research done on microplastics, the contamination with fibres is one of the most frequently discussed and inconsistently handled problems (Wesch et al., 2017; Woodall et al., 2015). It seems that clean air conditions might be required to ultimately prevent this type of airborne contamination (Hermsen et al., 2017; Schymanski et al., 2018; Woodall et al., 2015).

Being aware of this problem, closed filter units were used for sampling that avoided airborne sample contamination during sampling and sample transport. However, abrasives of the filtration unit led to the exclusion of all blue PP particles from analysis (Fig. 2).

4.2. Further research

Our results indicate a minor microplastics contamination of drinking water that is derived from the purification of ground water. Microplastics should further be examined in drinking water that originates from surface waters where the presence of microplastics is almost undoubted (Eerkes-Medrano et al., 2015) and by which a potential removal of microplastics during water purification can be studied. Plastics are durable, widely used and, by now, an almost indispensable material in our daily life. The sampled DWTPs used different plastic types for pipes, fittings or tanks. It is likely that the determined microplastic particles were introduced as a consequence of abrasion: if this happens for particles of 50 to 150 μm in size, this might happen more frequently for smaller particles. Using FTIR imaging we were able to identify particles down to a size of 20 μm. Schymanski et al. (2018) examined bottled drinking water with micro- Raman spectroscopy and found that 80% of detected microplastics were in a size range from 1 to 20 μm. Until now, the effects micro- (and nano-) plastics might have on the human health are not known. More studies are needed that determine particle toxicities and (dietary) exposure routes (Bouwmeester et al., 2015; Wright and Kelly, 2017) to assess related risks. However, we should always place results and report risks in the context of the general wide usage of plastics in our daily life (Koelmans et al., 2017; Rist et al., 2018). In fact, a possible contamination of food and beverages by plastic packaging materials is likely considering the contamination caused by the equipment used here.

5. Conclusions

In this study 40 cubic meters of raw water and drinking water, exclusively deriving from ground water, were examined resulting in concentrations of 0 to 7 microplastic particles m^{-3}. The overall mean of 0.7 microplastics m^{-3} indicates a low contamination of drinking water with microplastics (>20 μm) and a negligible human exposure via drinking water directly. The here detected microplastic particles were probably introduced as abrasives of plastic materials used during drinking water purification and transport. Considering this, plastic packed food and beverages should be studied further for the presence of microplastics and smaller nanoplastics.

Acknowledgements

This study was funded by the Oldenburg-East-Frisian waterboard (OOWV).

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