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Synthetic particles as contaminants in German beers

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A total of 24 German beer brands was analysed for the contents of microplastic fibres, fragments and granular material. In all cases contamination was found. Counts ranged from 2 to 79 fibres L⁻¹, from 12 to 109 fragments L⁻¹ and from 2 to 66 granules L⁻¹. The results show a high variability between individual samples and samples from different production dates. Possible sources of this contamination with foreign materials are discussed.

Keywords: beer; contamination; synthetic fibre

Introduction

Increasing awareness of the occurrence of plastic contamination in the global environment has lead to increased observation and monitoring (Andrady 2003). Over the last decade the long-term fate of this environmental burden has also received attention, indicating that degradation of larger plastic may lead to the formation of micro-scaled plastic (Thompson et al. 2004). In the ensuing discussion other sources were also identified such as garments (Browne et al. 2011), cosmetics such as peelings or tooth pastes, or abrasives used in air blasting. Besides ending up in the waste water stream and via incomplete retention in sewage treatment plants in the natural aquatic environment (Browne et al. 2011; Dubaish & Liebezeit 2013) microplastic fibres may also become airborne from direct input from clothes put out to dry. Also, sewage sludge employed as fertiliser may contain microplastic (Habib et al. 1998; Zubris & Richards 2005). These may be transferred to the atmosphere by the wind after extended dry periods. Furthermore, agricultural polyethylene foils may become a source of microplastic fragments as these are tailored to disintegrate though the catalytic action of cobalt or other metal salts after a specified exposure time in the environment (Kasirajan & Ngouajo 2012).

Microplastic is defined as fibres, films, fragments or granular particles smaller than 5 mm in size and made of synthetic polymers. A lower limit has so far not been internationally agreed upon, although a large number of studies use 1 μm (cf. Hidalgo-Ruz et al. 2012).

There is presently only limited evidence that microplastic has negative effects on aquatic organisms, either directly by affecting the growth of the first filial generation of a marine zooplankter (Lee et al. 2013) or indirectly by transferring previously absorbed contaminants to fish (Browne et al. 2013; Rochman et al. 2013). Effects of microplastics ingested or inhaled by human consumers have until now not been investigated.

Particles of synthetic polymers have so far been described to be present in beer only by Hartmann (2006) who noted the presence of polyvinyl polypyrrolidone (PVPP) particles besides glass shards and label residues as well as aluminium particles which were also noted by Steiner et al. (2010). PVPP is used in granular form to clarify and fine beer prior to filtration. This suggests that small particles up to 55 μm in diameter, as found by Hartmann (2006), can pass the units used in beer filtration.

We have recently shown that microplastic contamination can be found in honeys (Liebezeit & Liebezeit 2013) and suggested possible pathways by which this contamination may reach the product including atmospheric transport. During this investigation it was found that regular tap water may also contain microparticles. Thus, external sources may contribute to particle loads. In the present communication we examine beer and show the presence of foreign particles in this product.

Material and methods

A total of 24 beer German brands was obtained from local supermarkets, among them the 10 most popular brands in Germany (data for 2012; see http://www.inside-getraenke.de). Twelve of these were of the regular Pilsener type, five were wheat beers and seven were alcohol-free Pilsener. Volumes filtered were 0.33 and 0.5 L with results calculated on a per litre basis. With the exception of the wheat beers, all samples were filtered over a 0.8 μm grey, gridded cellulose filter immediately after opening the bottles. The wheat beers could not be treated this way as the filters became clogged after about 200 ml had passed through. These samples were initially passed through a
40 μm stainless steel sieve. The material retained was then filtered as described above.

After extensive rinsing with 0.8 μm filtered deionised water the wet filter was covered with 6 ml Rose Bengal (4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein, 200 mg l⁻¹; Williams & Williams 1974; Lusher et al. 2013) to stain natural organic particles. After a reaction time of 5 min the dye was filtered off and the stained material washed dye-free with filtered deionised water. The non-stained material will be referred to as microplastic in the following, although it is recognised that only spectroscopic analysis (FT-IR or Raman spectroscopy) can provide unambiguous proof of the synthetic nature of the non-stained particles. After drying at ambient temperature the sample was analysed under a dissecting microscope at up to 80× magnification. No attempts were made to determine fibre lengths or polymer types.

Three Pilsener samples were analysed in duplicate and one alcohol-free brand was analysed in triplicate. In each case, different production dates (lot numbers) were used. One Pilsener of the same production date was analysed in triplicate.

To avoid airborne contamination (Liebezeit & Liebezeit 2013), the filtration unit and all other glassware used were covered during the whole workup procedure. Furthermore, the filters used were copiously rinsed with filtered water and inspected microscopically for particle contamination prior to use. Blank filters carried through the complete scheme gave a maximum of 2 fibres/filter. Laboratory air sucked through a previously rinsed filter for 1 h at 50 L min⁻¹ had two fibres, zero fragments and three granular particles. As the filters were exposed to the atmosphere for a maximum of 15 min during filtration and microscopic counting, contamination from this source can be neglected.

### Results and discussion

In all 24 beer samples microplastic was found (Table 1). In most cases individual particles were found, although entangled fibres were observed also in a few cases (Figure 1). Fragments were the most abundant foreign items while fibres and granular material had comparatively low numbers (Figure 2). Pilsener sample number 10 and one wheat beer brand (number 14) had the highest fibre numbers, while the second sample of number 10 had a low fibre content. This difference is also present for granular particles, while fragments had comparable values for the duplicates (Figure 2). One alcohol-free sample (number 21) had the highest fragment count. Again, the other two samples of this brand had lower numbers.

Most fibres were transparent, but blue, black or green ones were also present. Fragments and granular particles were whitish or transparent with the occasional occurrence of green and yellow ones. Kieselgur particles as described by Hartmann (2006) were not encountered. This indicates that filtration with this material is no longer in use, at least not with the brands analysed.

A clear overall dominance of one microplastic fraction could not be established. The relative contributions ranged from 5% to 71% for granular material, from 14% to 87% for fragments and from 3% to 57% for fibres (Table 1). A high variability was noted between different brands, but also between replicates (Figure 2 and Table 1) with RSDs of 130% (fibres), 205% (fragments) and 103% (granules). On the other hand, the sample of the same production date showed good agreement between replicates with RSDs of 24% (fibres) and 13% (fragments and granules). This high variability between samples from different production

### Table 1. Mean contents of microplastic contaminants in 24 German beer brands.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Fibres (n l⁻¹)</th>
<th>Fragments (n l⁻¹)</th>
<th>Granules (n l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilsener</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>25</td>
<td>33</td>
<td>17</td>
</tr>
<tr>
<td>standard deviation</td>
<td>21</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>maximum</td>
<td>79</td>
<td>88</td>
<td>61</td>
</tr>
<tr>
<td>minimum</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>n</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Wheat</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>26</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>standard deviation</td>
<td>25</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>maximum</td>
<td>70</td>
<td>50</td>
<td>66</td>
</tr>
<tr>
<td>minimum</td>
<td>8</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>n</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Alcohol-free</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>17</td>
<td>47</td>
<td>22</td>
</tr>
<tr>
<td>standard deviation</td>
<td>13</td>
<td>30</td>
<td>173</td>
</tr>
<tr>
<td>maximum</td>
<td>39</td>
<td>109</td>
<td>45</td>
</tr>
<tr>
<td>minimum</td>
<td>3</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>n</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 1. Examples of microplastic contaminations in German beers. White arrows indicate non-stained synthetic material.
dates suggests that the foreign particle load of the finished product depends on the actual conditions during production (see below).

While in the case of fibres and fragments the synthetic nature of the contaminating particles could be established by staining with Rose Bengal, in the case of granular material this is not as evident. In water samples from both Black Forest and Allgäu Alps springs, sand grains were found (authors’ unpublished data). As some of the breweries claim to use spring water for their beers, a sand contribution appears possible, as suggested by the morphological characteristics and the non-stainability. Although SiO$_2$ can be removed by treatment with hydrofluoric acid, this also holds for some synthetic polymers such as polystyrene or polyamide (Liebezeit et al. Forthcoming). Thus, the presence of sand grains can be unambiguously established only by spectroscopic analysis. However, these particles were relatively rare and most granules were whitish in appearance. Nevertheless, the numbers given represent an overestimation, to a certain extent.

In one beer sample an almost complete insect belonging to the Order Thysanoptera was found (Figure 3). Insect remains, commonly known as a part of filth, have also been reported in a.o. dog food (Brazis et al. 2008), grain (Neethirajan et al. 2007) or Italian honeys (Canale et al. 2014). Furthermore, in three samples glass shards of up to about 600 $\mu$m size were identified by their characteristic morphology, as also reported by Steiner et al. (2010). Filth of these types is considered to be a sign of inadequate product handling and storage (Gorham 1989; Zimmerman et al. 2002). The origin of the synthetic material found in the beers investigated is variable. One source may be atmospheric. Here, emission, i.e. the transport of particles into indoor air from various sources including machinery, room occupants and infiltration of contaminated outdoor air, track-in and spillage referring to the transport of particles and dirt into the system directly to surfaces and penetration, the transport of outdoor particles in air infiltrating into the indoor air, have to be considered (Schneider 2008).

Workers in breweries loose, as any other people, the outer part of their epidermis. Healthy skin typically sheds one cell layer per day, with the complete outer skin layer being shed within 1–2 days. This process can result in the release of several million skin scales per minute. A significant fraction can penetrate clothing and become airborne. Exfoliated skin cells are typically shed as individual hexagonal plates, 25 $\mu$m on a side and 0.1–0.5 $\mu$m thick. The median aerodynamic diameter of human skin cells is approximately 14 $\mu$m, although both smaller and larger sizes can be observed. Skin scales can be differentiated from fragments of synthetic materials as they can be dyed by Rose Bengal.

Clothing when worn may be an active source of both natural and synthetic fibres (Yoon & Brimblecombe...
Furthermore, washed clothing put out to dry in the open will also release large quantities of fibres. Synthetic mineral (e.g. rockwool or glass wool) fibres used in insulation may also become airborne. These are not stained by Rose Bengal but give characteristic microscopic images. These fibres were not encountered in the beers analysed.

Shearer (2003) found polyester fibres and glass particles in pharmaceutical products without discussing the possible origin of these particles. Similarly, Jack et al. (2010) reported on the presence of unwanted particle contamination in infusion solutions. It may be assumed that this contamination of medical products is derived from input via atmospheric sources. From this it is clear that there is also a large potential of airborne atmospheric particles from a variety of sources to contribute to foreign matter found in beers and other beverages.

The second potential source of particle input to beer can be sought in the materials used in the production process. A total of 66 accessory agents are permitted to be used in beer brewing in Germany (Metzger 2010), nine of these being used in the filtration step (activated charcoal, asbestos, bentonite, cellulose, cotton, isinglass, kieselgur, perlite and wood chippings). Filters used apparently allow particles larger than their nominal pore size to penetrate, as shown by the presence of PVPP or kieselgur particles in beer (Hartmann 2006). Glenister (1975) already reported on the presence of asbestos fibres in beer. Filter breakthroughs, cracking of filter media or separation from the container walls may also lead to an unwanted presence of particles in the finished product.

On the other hand, the bottles used may also become contaminated as unwanted impurities are not removed during cleaning or the cleaning process itself may introduce foreign particles. Steiner et al. (2010) related their particle findings in bottled beer to a malfunctioning bottle washing machine.

To what extent particles already present in the basic components used such as barley or hop are carried through the whole process is unknown. A large number of fragments and fibres that could not be stained with Rose Bengal were found in wheat and rye grain samples.

The small numbers of microplastic items in beer in themselves may not be alarming, but their occurrence in a beverage as common as beer indicates that the human environment is contaminated by micro-sized synthetic polymers to a far-reaching extent. This may be, at least in part, overcome by applying principles of hygienic industrial design (see http://www.ehedg.org).

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