

Determination of particles produced during boiling in different plastic and glass kettles via comparative dynamic image analysis using FlowCam®

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Abstract

In many everyday products containing plastics, tiny plastic particles are generated by mechanical, thermal or other influences and are released into the environment by various transport routes. These particles not only have a long lifecycle, but can also only be degraded very slowly in the ecosystem. Damage to humans and animals is possible if, for example, particles are ingested through food. The number of particles produced was determined on the basis of water investigations before and after boiling in plastic-based kettles compared to a glass kettle. The results are discussed in this paper.

1 Introduction

Many everyday objects consist at least partially of plastics [38]. In 2015, the private and commercial end use of plastics as a "pure" plastic product (e.g. packaging) or as a subcomponent of a system (e.g. automobile) in Germany was still around 12.06 million t, by 2017 the value had already risen to around 14.3 million t [6]. Similar increases in the production and processing of plastics have been recorded worldwide (Figure 1).

The most frequently produced and processed plastic, apart from polypropylene, is polyethylene which is, for example, contained in plastic bags or refuse bins [31]. Plastics are created by special chemical processes. One of the most important raw materials is crude oil. Depending on the ingredients and the circumstances surrounding these chemical processes, the plastic may have various properties at the end,

ranging from elastic, heat-resistant to break-resistant [31]. Degradation reactions of plastics result in microplastics (particles smaller than 5 mm), which, in addition to general plastic waste, are currently one of the biggest and most discussed environmental problems [24]. Since the start of mass production of plastic in the 1950s, it is hard to imagine everyday life without it [15,31]. Looking at the degradation process of plastics, several degradation paths can be observed [2,22,40]. The degradation of polymers can be induced by heat (thermal degradation), oxygen (oxidative and thermal-oxidative degradation), light (photo degradation), weathering (generally UV/ozone degradation). All polymers will undergo some degradation during service life. The result will be a steady decline in their (mechanical) properties caused by changes to the molecular weight and molecular weight distribution and composition of the polymer. Other possible changes include chain hardening, chain scission, color changes,

cracking and weight loss. The plastic fragments smaller than 5 mm are defined as microplastics [9,11].

Microplastics enter the human organism via the food chain (incl. drinking water) or through contamination of the air we breathe [28,32,34,39]. The persistence of microplastics in combination with increasing plastic and microplastic inputs into the environment as well as the constant fragmentation of plastic already introduced into the environment, lead to an ever increasing burden on the environment and thus also on humans [13,39]. Various studies have already proven numerous harmful effects of microplastics on the human organism [27,32,34,39].

So far, there has been a lack of well-founded statements about the minimum intake that poses a health risk to humans. In addition to the different sizes of the polymer particles, their chemical composition and their behavior in the body/organism must also be considered. Microplastics have already been

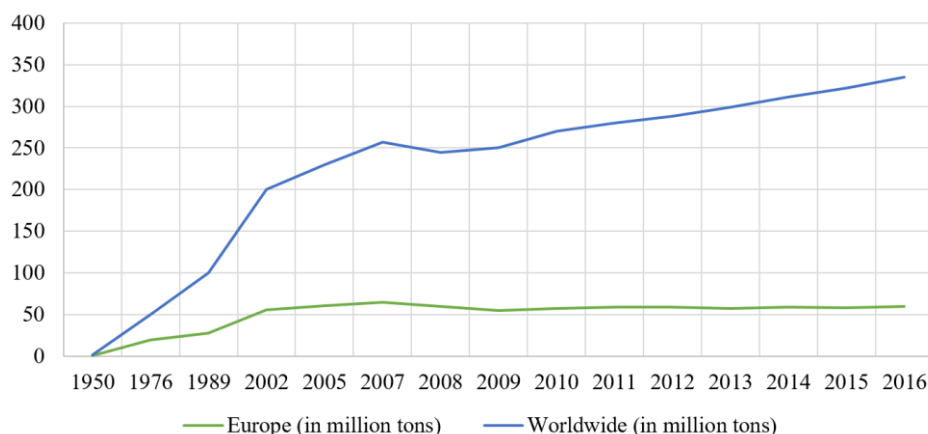


Fig. 1: Worldwide and European production volume of plastics in recent years from 1950 to 2016 in million tons [5,36]

detected in numerous foods such as sea salt, honey, sugar or beer. Investigations of tap water showed a low contamination of a few particles per cubic meter (variance between 0.4 to 7 particles/m³) [21,25,26,30]. Drinking water stored in plastic bottles showed with an average of 325 particles/m³ and a maximum of over 10000 particles/m³ a significant higher contamination [29]. How the particle formation and pollution in everyday objects is represented was experimentally worked out using water boiling in kettles made of plastic and glass and subsequently evaluated.

2 Material and Methods

Four plastic kettles from four different manufacturers were tested for the investigations. Table 1 shows an overview of the tested appliances.

Tab. 1: Overview of tested plastic kettles

Manufacturer	Model	Capacity
Emerio	WK-108992	1 liter
Philips	HD4646	1.5 liters
Braun	Multiquick 3	1.7 liters
OK.	OWK 103-W	1.7 liters

Tab. 1: Overview of tested glass kettle

Manufacturer	Model	Capacity
CIATRONIC	WKS 3641	1.5 liters

For all measurements particle-free water was used, which was demineralized according to the manufacturer specifications in accordance with VDE 0510. In addition, the water was pre-filtered with a Millipak 100 (Millipore) filter with a pore size of 0.22 µm before use.

2.1 Description of the initial setup of the kettle according to the respective operating instructions

Before carrying out the measurements, all kettles were pre-treated and cleaned according to the instructions in the respective operating instructions. The

Tab. 3: Description of the procedure for the first use of the kettle according to the operating instructions

Manufacture	Cleaning process / commissioning of the kettles
Emerio	The kettle was filled to the specified maximum with particle-free water. Three boiling processes were carried out without changing the water in between. The water was then disposed of.
Philips	The kettle was filled to the maximum with particle-free water. A boiling process was carried out. The water was then disposed of.
Braun	The kettle was filled to the maximum with particle-free water. Two boiling processes were carried out with. Between the two boiling processes, the water was exchanged and then disposed of.
OK.	The kettle was filled to the maximum with particle-free water. Three boiling processes were carried out without changing the water in between. The water was then disposed of.
CIATRONIC	The kettle was filled to the maximum with particle-free water. Three boiling processes were carried out with. Between the three boiling processes, the water was exchanged and then disposed of.

following steps were carried out for each kettle (Table 3).

2.2 Description of experiment

After cleaning the kettles in accordance with the instructions, each kettle was filled with particle-free water to approximately 70% of the maximum fill level (OK, Braun, Philips, CIATRONIC ca. 1.25 l, Emerio: ca. 0.75 l) in order to prepare the test (in vitro) samples.

Prior to each filling (referred to the amount of each fill level of the used kettles), 100 ml of water were taken of the kettle to get a blank sample.

The water was boiled in a kettle and after a short cooling time another 100 ml were taken from the water as a sample. The remaining water in the kettle was discarded. This procedure was repeated three times for each kettle so that a total of 6 samples were obtained for each kettle (3x blank, 3x sample). Thus, a total of 30 samples were measured.

2.3 Analytical determination of particle concentration by dynamic image analysis

A dynamic image analysis system of the type FlowCam 8400 from Fluid Imaging Technologies was used to determine the

particle numbers in the individual samples. This system is a combination of an optical microscope and a flow cytometer. An optical system coupled to a digital camera detects all particles in a defined sample volume that pass through a glass flow cell within a defined period of time (Figure 2).

Up to 10,000 images per minute can be captured by the system, resulting in digital images of each detected particle and over more than 30 different parameters describing particle size and morphology. Furthermore, a statistical evaluation of the particle size distribution and the particle concentration per milliliter is obtained (see Figure 3). The FlowCam 8400 can be equipped with four different objectives, allowing the analysis of particles in a size range between 1 and 1000 µm.

A 10x lens and a flow cell with a defined width of 80 µm were used for the experiments. A sample volume of 1 ml of each sample was analyzed at a flow rate of 0.2 ml/minute, resulting in a measurement time of 5 minutes for each measurement. The flow cell was flushed with 2 ml particle-free water and 2 ml sample before each measurement. After the measurements, the samples were

hermetically sealed and stored in a dark and refrigerated place.

3 Results and Discussion

The plastic-based kettle from OK. shows an increasing tendency towards particle emission with the number of cooking cycles. The other plastic-based kettles show fluctuating values. The measured data is summarized in Table 4 (annex).

It is striking that the majority of the particles (P) are in the size range < 10 μm .

The Emerio kettle has the lowest particle release among the plastic kettles with measured values between 3779 and 10433 particles (P)/ml. The Braun kettle, which delivers between 12294 and 16396 P/ml, achieves significantly higher values, followed by the Phillips kettle with 14610 - 20936 P/ml.

The OK. kettle emitted only 5297 P/ml in the first run, but increased the output to the maximum value of 29194 P/ml in the following runs. With a total sample volume of 0.75-1.25 l, the total number of particles is alarmingly high. A minimum of 5 million particles in the Emerio kettle in the first boiling cycle and a maximum of 33 million particles in the OK. kettle in the third boiling cycle was observed. In comparison, the CIATRONIC water kettle made of glass and metal contains significantly lower particle numbers of 578 - 1351 P/ml. Additionally no change in the particle output over time could be observed. The differences between the glass kettle and the plastic kettles are shown in Figure 4.

The measured blanks contain a maximum particle number of 304 P/ml, which shows a low level of external contamination of the samples. The purely optical particle detection does not allow the unambiguous identification of plastics or polymers. However, since the water in the plastic-based water kettles came into contact exclusively with the kettle's plastic, other plastic sources can be excluded and there is a high probability that these are plastic particles which are emitted by

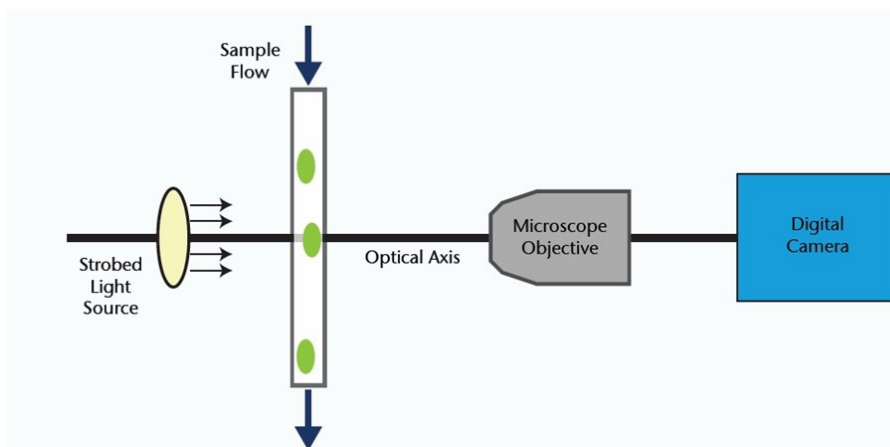


Fig. 2: Setup of the measuring apparatus for dynamic image analysis (Source: Fluid Imaging Technologies)

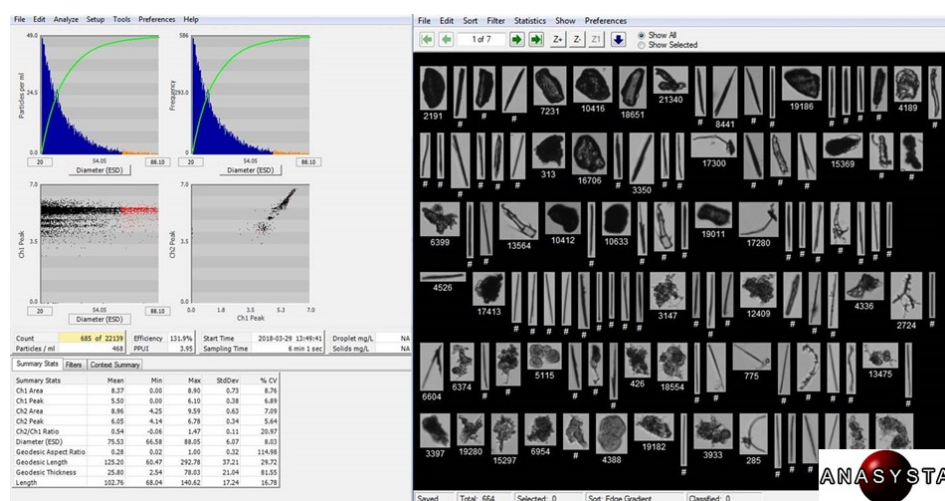


Fig. 3: Illustration of measurement results with Visual Spreadsheet®. Only the largest particles were selected in the histogram on the left (marked in red). On the right side the images of these marked particles are displayed. (Source: Anasysta e.K.)

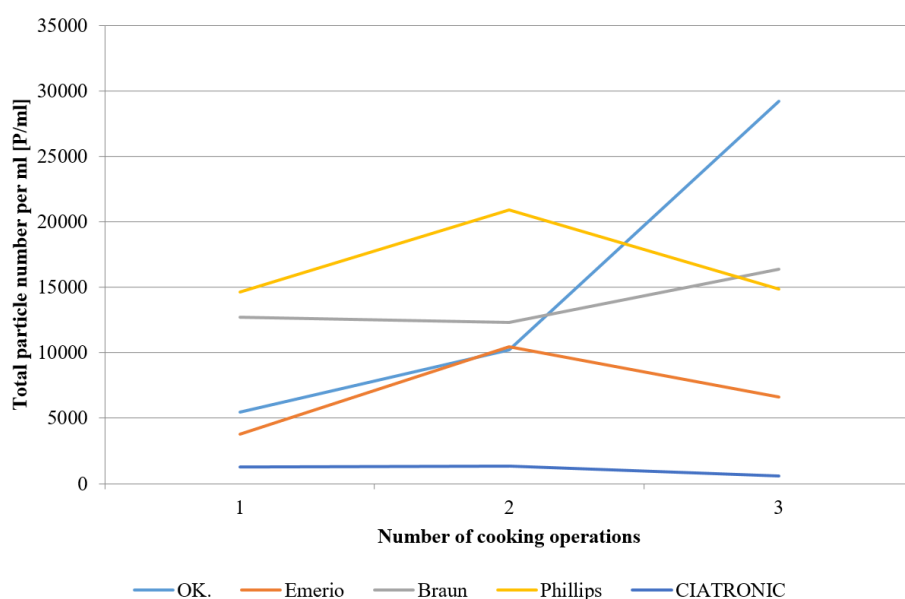


Fig. 4: Number of particles emitted by the kettles in each cooking cycle.

the water kettles due to the thermal load.

The results of the kettle test show a significantly higher particle generation rate after boiling the water in plastic-based kettles compared to the glass kettle.

In general, the resistance to degradation will depend on the chemical composition of the polymer. For example, polymers such as polyethylene (PE) and polypropylene (PP), such as used in the tested water heaters, are very susceptible to thermal degradation, even at room temperature, and can only withstand degradation when formulated with UV stabilizers and antioxidants [4,14,16,23]. The general mechanism of thermal-oxidative degradation of polymers is known, and based on a typical three step radical reaction (Figure 5).

4 Conclusion

Based on the test (in vitro) results and the scientific findings on polymers and their behavior in contact with heat or under UV influence, as well as the knowledge that an estimated 90% of the microplastics ingested are excreted, the particle numbers can be used to estimate the effects on humans and the environment [10,13,28,34].

The decisive factor for the transport in the mammal is the size of the particle. Microplastic particles $< 150 \mu\text{m}$ can potentially be absorbed via the intestinal mucosa and enter the lymphatic system, particles $< 110 \mu\text{m}$ can already enter the bloodstream via the portal vein and particles $< 20 \mu\text{m}$ are distributed via the bloodstream and can reach the internal organs from there [28]. Particles $< 100 \text{ nm}$ can even be transported into the brain, the reproductive organs and via the placental barrier into a fetus. In general, the smaller the particles, the higher the probability that they will be absorbed into the organism [39]. The absorption probability is additionally determined by the hydrophobicity as well as the charge and functionalization of the particle surface. Low hydrophobicity and negative surface charge lead to a higher

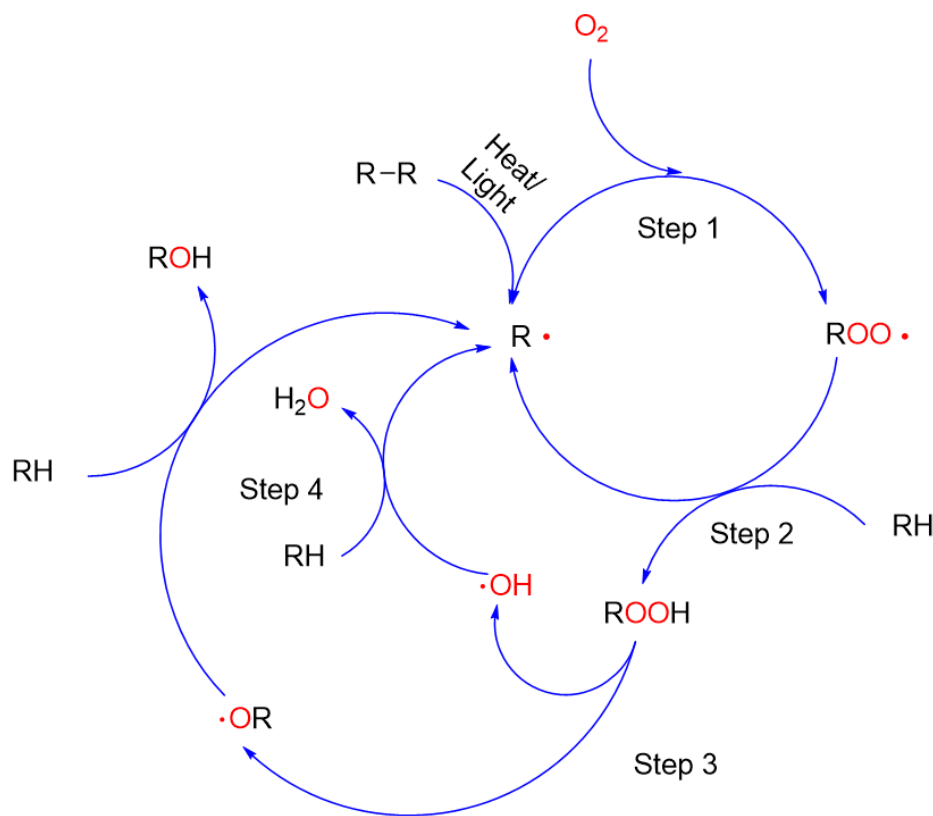


Fig. 5: Illustration of the mechanism of the degradation reaction by thermal decomposition or UV influence of polymer compounds (e.g. PE or PP) [8].

uptake. Furthermore, it is assumed that the deposition of biomolecules on the particle surface leads to the formation of a protein corona, which also strongly influences the uptake and transport behavior in the body [13,21,39].

In addition to the effects of absorption into the organism, it is important to assess the effect of microplastics that can bind, transport and release harmful substances such as DDT, dioxin or heavy metals into the body [1,35]. Also, most polymer blends contain harmful ingredients such as plasticizers or monomers, which have a direct effect on the organism, as these substances are usually classified as potentially dangerous and/or carcinogenic [3,27]. When these substances are embedded in the tissue, their release into the surrounding tissue can lead to a locally increased concentration and punctual damage [32]. The dangers of microplastics as foreign bodies in tissue include the formation of lesions and inflammations. Oxidative stress, necrosis and DNA damage can also be

triggered [28]. In addition, neurological behavior disorders are possible [33].

In order to mitigate the formation and effects of microplastics on humans and the environment, a recycling concept developed at all levels (political, economic, scientific) and, above all, applicable to all humans, as well as an efficient removal strategy for water-bearing systems and processes, in addition to a global avoidance strategy for disposable plastic products and the substitution of plastic articles in the area of daily use, are part of the current solution approaches [12,18,19].

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Annex

Table 4: Data collection of particle count and distribution per pass (number 1 – 3)

Number of passes	+50micron [ESD] P/ml	+25micron [ESD] P/ml	+10micron [ESD] P/ml	+5micron [ESD] P/ml	+2micron [ESD] P/ml	+1micron [ESD] P/ml	P/ml
OK.							
1	4	16	116	420	2665	2214	5435
2	0	1	34	153	4746	5262	10196
3	7	9	115	379	13588	15096	29194
OK. Blanks							
1	0	1	13	15	75	150	254
2	0	0	1	18	94	145	258
3	1	1	18	13	114	170	318
Emerio							
1	1	1	34	106	1180	2456	3779
2	0	0	23	73	4416	5920	10433
3	1	10	45	122	2770	3658	6607
Emerio Blanks							
1	0	0	6	15	104	110	235
2	0	0	4	12	65	113	194
3	0	0	0	4	85	214	304
Braun							
1	0	9	46	167	4890	7599	12711
2	0	9	51	178	3768	8288	12294
3	1	1	43	217	6320	9812	16396
Braun Blanks							
1	0	0	6	13	79	156	254
2	0	0	0	7	56	101	164
3	0	1	0	10	56	136	204
Philips							
1	0	1	54	376	6665	7514	14610
2	3	9	68	348	7827	12682	20936
3	1	4	38	242	5031	9570	14888
Philips Blanks							
1	0	1	6	10	79	126	223
2	0	0	1	12	65	97	175
3	1	1	4	4	75	175	261
CIATRONIC							
1	0	3	16	78	552	683	1281
2	0	1	16	97	490	747	1351
3	0	1	16	34	245	282	578
CIATRONIC Blanks							
5	0	0	3	6	126	139	274
6	0	1	6	9	97	128	241
7	0	0	4	12	63	85	164

References

- [1]Bakir A, Rowland SJ, Thompson RC (2014) *Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. Environmental pollution.* (Barking, Essex : 1987) 185:16–23.
- [2]Barnes, D. K. A., Galgani F, Thompson RC, Barlaz M (2009) *Accumulation and fragmentation of plastic debris in global environments.* Philosophical Transactions of the Royal Society B: Biological Sciences 364(1526):1985–1998.
- [3]Bergmann M, Gutow L, Klages M (2015) *Marine Anthropogenic Litter.*
- [4]Beyler CL, Hirschler MM (2002) *Thermal Decomposition of Polymers.* SFPE Handbook of Fire Protection Engineering 2 (Section 1, Chapter 7): 111–131
- [5]CHEManager (2018) *Kunststoff-Stoffströme in Deutschland.* Accessed 26 Nov 2018
- [6]Consultic, IK, PlasticsEurope, BVSE, VDMA, BKV (2016) *Produktion, Verarbeitung und Verwertung von Kunststoffen in Deutschland 2015 - Kurzfassung.* Accessed 05 Jun 2018
- [7]Conversio Market & Strategy GmbH (2018) *Stoffstrombild Kunststoffe in Deutschland 2017.* Accessed 26.22.2018
- [8]CROW polymerdatabase.com (2015) *Thermal-Oxidative Degradation of Polymers.* Accessed 26 Nov 2018
- [9]Eerkes-Medrano D, Thompson RC, Aldridge DC (2015) *Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs.* Water Research 75:63–82.
- [10]EFSA CONTAM Panel (2016) *Presence of microplastics and nanoplastics in food, with particular focus on seafood.* EFS2 14(6):30 pp.
- [11]Eriksen M, Lebreton LCM, Carson HS, Thiel M, Moore CJ, Borror JC, Galgani F, Ryan PG, Reisser J (2014) *Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea.* PLoS one 9(12):e111913.
- [12]European Commission (2018) *A European Strategy for Plastics in a Circular Economy.* COM(2018) 28 final, Brussels
- [13]Galloway TS, Cole M, Lewis C (2017) *Interactions of microplastic debris throughout the marine ecosystem.* Nature ecology & evolution 1(5):116.
- [14]Gardette M, Perthue A, Gardette J-L, Janecska T, Földes E, Pukánszky B, Therias S (2013) *Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content.* Polymer Degradation and Stability 98(11): 2383–2390.
- [15]Geyer R, Jambeck JR, Law KL (2017) *Production, use, and fate of all plastics ever made.* Sci. Adv. 3(7):e1700782.
- [16]Hakkarainen M, Albertsson A-C (2004) *Environmental Degradation of Polyethylene.* In: Albertsson A-C (ed) Long Term Properties of Polyolefins, vol 169. Springer Berlin Heidelberg, Berlin, Heidelberg, pp 177–200
- [17]Herbort AF, Schuhen K (2016) *A concept for the removal of microplastics from the marine environment with innovative host-guest relationships.* Environmental Science and Pollution Research (24(12)):1–5.
- [18]Herbort AF, Sturm MT, Fiedler S, Abkai G, Schuhen K (2018a) *Alkoxy-silyl Induced Agglomeration: A New Approach for the Sustainable Removal of Microplastic from Aquatic Systems.* J Polym Environ 62(8):1–13.
- [19]Herbort AF, Sturm MT, Schuhen K (2018b) *A new approach for the agglomeration and subsequent removal of polyethylene, polypropylene, and mixtures of both from freshwater systems - a case study.* Environmental science and pollution research international (25(15)):15226–15234.
- [20]Hüthig GmbH (2017) *Plasticseurope: Kunststoff weithin beliebt.* Accessed 26 Nov 2018
- [21]Iñiguez ME, Conesa JA, Fullana A (2017) *Microplastics in Spanish Table Salt.* Scientific reports 7(1):8620.
- [22]Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL (2015) *Marine pollution. Plastic waste inputs from land into the ocean.* Science (New York, N.Y.) 347(6223):768–771.
- [23]Kuroki T, Sawaguchi T, Niikuni S, Ikemura T (1982) *Mechanism for long-chain branching in the thermal degradation of linear high-density polyethylene.* Macromolecules 15(6): 1460–1464.
- [24]Law KL, Thompson RC (2014) *Oceans. Microplastics in the seas.* Science (New York, N.Y.) 345(6193):144–145.
- [25]Liebezeit G, Liebezeit E (2013) *Non-pollen particulates in honey and sugar. Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment* 30(12):2136–2140.
- [26]Liebezeit G, Liebezeit E (2014) *Synthetic particles as contaminants in German beers. Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment* 31(9):1574–1578
- [27]Lithner D, Larsson A, Dave G (2011) *Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition.* The Science of the total environment 409(18):3309–3324.
- [28]Lusher A, Hollman PCH, Mendoza-Hill J (2017) *Microplastics in fisheries and aquaculture. Status of knowledge on their occurrence and implications for aquatic organisms and food safety.* FAO Fisheries and Aquaculture Technical Paper, vol 615. Food and Agriculture Organization of the United Nations, Rome

- [29]Mason SA, Welch VG, Neratko J (2018) *Synthetic Polymer Contamination in Bottled Water*. *Frontiers in chemistry* 6:407.
- [30]Mintenig S, Gerdts G Dr., Löder M Dr. (2014) Abschlussbericht Mikroplastik in Trinkwasser. *Untersuchung im Trinkwasserversorgungsgebiet des Oldenburgisch-Ostfriesischen Wasserverbandes (OOWV) in Niedersachsen*. Probenanalyse mittels Mikro-FTIR Spektroskopie (Accessed 22.01.2019)
- [31]PlasticsEurope (2016) *Plastics – the Facts 2015*. An analysis of European plastics production, demand and waste data, Brussels, Belgium: Association of Plastics Manufacturers (Accessed 22.01.2019)
- [32]Prata JC (2018) *Airborne microplastics: Consequences to human health?* *Environmental pollution* (Barking, Essex : 1987) 234:115–126.
- [33]Rafiee M, Dargahi L, Eslami A, Beirami E, Jahangiri-Rad M, Sabour S, Amereh F (2018) *Neurobehavioral assessment of rats exposed to pristine polystyrene nanoplastics upon oral exposure*. *Chemosphere* 193:745–753.
- [34]Revel M, Châtel A, Mouneyrac C (2018) *Micro(nano)plastics. A threat to human health?* *Current Opinion in Environmental Science & Health* 1:17–23.
- [35]Rochman CM, Hentschel BT, Teh SJ (2014) *Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments*. *PloS one* 9(1):e85433.
- [36]Statista (2018) *Global plastic production from 1950 to 2016*. Accessed 25 Nov 2018
- [37]Sturm MT, Wilde A, Kluczka S, Schuhen K (2018) *Detektion von Mikroplastik im (Ab-)Wasser – Die Suche nach der Nadel im Heuhaufen?* *Analytik-News – Das Online-Labormagazin*(6):1–6
- [38]Umweltbundesamt (2017) *Kunststoffabfälle*. Accessed 26 Nov 2018
- [39]Wright SL, Kelly FJ (2017) *Plastic and Human Health: A Micro Issue?* *Environmental science & technology* 51(12):6634–6647.
- [40]Wright SL, Thompson RC, Galloway TS (2013) *The physical impacts of microplastics on marine organisms: A review*. *Environmental Pollution* 178:483–492.