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Distribution, Avoidance, Usage

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Preface

The rafting trip that Thomas Kipp (1st Chairman of the Rafting Association Schiltach) undertook with his self-built raft together with me and my son Enzo, Juri Jander (Master's thesis in the course SBE = Sustainable Bioprocess Engineering), Michael Kipp (son of Thomas) and Martina Baumgartner (Press Offenburger Tageblatt) on Saturday, April 29, 2017, from Biberach (Schwaibacher Bridge) to Gengenbach (Rafting Museum) in glorious sunshine, was a premiere and an unforgettable event of the most beautiful kind for everyone, except for the gentlemen Kipp (Rafting Association Schiltach) (Fig. 1). All participants could only understand the enthusiasm of Mark Twain from 1878, which is associated with the incomparable nature experience during a rafting trip (Twain 2014), even if there are many other more comfortable travel alternatives today, with one single restriction, which I will go into in more detail later.

The limitation is based on the spread of plastic waste along the river, which disrupts the superficial idyll as soon as the focus of the journey can only be directed towards it. The bushes, shrubs, and trees lining the riverbank reveal the plastic yield of a flood through their artificial adornment. As in a rake of a sewage treatment plant everything that the river carries with it gets stuck in the branches. When the water level drops again, the catch becomes visible to everyone, in stark contrast to the green nature.» What is frightening is not just the quantity, as every bush was successful with its filter arms, but the fact that the riverside vegetation only filters the river's edge currents and the main bulk of the plastic load, no longer visible, was transported with the faster flowing midstream into the Rhine and into the sea. This means, the visible plastic waste is only the tip of the iceberg and it is already unmistakable (Fig. 2).

The disposal of plastic waste in the river and its surroundings by some irresponsible and uninformed citizens was, viewed from the middle of the river, shockingly apparent, and it became clear that the growing massive plastic islands in the world's oceans are not exaggerations. Neither the young Dutchman Bojan Slat with his kilometers-long floating tube barriers nor a plastic-eating caterpillar will absolve us of the responsibility for our waters, because only proper disposal of our plastic waste can significantly reduce further increase. Also not visible is the microplastic load, which the water carries with it. A close look at the "plastic harvest" immediately shows what happens sooner or later with the plastic waste. It slowly disintegrates into ever smaller particles and seems to dissolve (Fig. 3).

Fig. 1 Rafting trip of the garbage collection action

Fig. 2 Plastic waste in the branches of the Kinzig

However, the problem is not solved, because what is missing from the plastic film has not dissolved at all, but is found as microplastic in our waters, where it can become a serious threat to marine habitats, but also to humans.

Fig. 3 Torn plastic bag

When I swam the Rhine in the record time of 28 days from source to mouth in the summer of 2014, I analyzed the 1231 kilometers of the river under various scientific questions together with a team of students and staff from different institutes. For the first time, as part of the science project "Rheines Wasser" (www.rheines-wasser.eu), the river was also examined for microplastic pollution along its entire length. From the Swiss Alps to the North Sea, the HFU research team filtered every 100 kilometers 1000 liters of the near-surface river water through an extremely fine metal sieve of a specially made portable filter pump for the project, and the filter residues obtained were meticulously evaluated with the support of the Alfred Wegener Institute on Helgoland. The results are presented and discussed in this book.

Even the Source of the Rhine is Polluted

In total, about eight tons of microplastic particles are carried by the surface water of the Rhine into the North Sea each year. This is only the proverbial tip of the iceberg. The actual burden of the Rhine with microplastics is likely to be many times higher. After all, we have only filtered the water to a depth of 15 centimeters. The majority of the microplastics, however, sink and are located in the lower layers of the river water or in the sediment, which has not yet been investigated.

In total, ten different types of plastic are found in the surface water of the Rhine. Particularly high were the proportions of polypropylene (PP), which is used, for example, for the production of cups, buckets and their plastic lids, and of Polyethylene (PE), from which plastic bags, tubes and other Packaging are produced. Together, these two types of plastic make up around 90% of the particles that the team has filtered out from the near-surface water. This is due to the fact that 15 centimeters below the water surface, one primarily finds those plastic particles that float on the water surface due to their low density—and PP and PE having lower density than water. In deeper water layers, you will probably increasingly find plastics with a higher density such as polyvinyl chloride or polyurethane.

The contamination of the Rhine water with tiny pieces of plastic begins already in Lake Toma at 2345 meters altitude in the Grisons Alps, which is commonly regarded as the source of the Rhine. This result initially surprised me, as sources of contamination, in this more or less untouched alpine landscape, were not immediately apparent.

The alarming results of the plastic pollution in the Rhine, about which I have reported in many lectures and presentations within the project "Rheines Wasser", have inspired me to write this book.

Consistently Too Low Pollutant Measurements?

The potential danger of water pollution by microplastics is primarily determined by certain properties of the small plastic particles that have adverse effects on humans and the environment. Foremost among these is the ability to attract organic pollutants—such as the highly toxic perfluorinated surfactants (PFT)—like a magnet. Microplastics can bind other pollutants, and transport them further in a more concentrated manner. However, since microplastics are usually filtered out of water samples to prevent sensitive analytical equipment from clogging, some of the pollutants are not detected by the standard water tests currently in use, such as those at the Rhine monitoring stations. Therefore, I assume that the contamination of waters with PFT and other organic pollutants, which are not completely eliminated in sewage treatment plants, is higher than the usual measurements revealed to us. Unless additional solid-phase extractions are performed, we get a false picture of the actual quality of our waters. The discrepancies can be quite significant depending on the type, quantity, and surface structure of the microplastic load and depending on the distribution equilibrium.

The fact that plastic particles act as carriers of pollutants, such as PFT, is particularly concerning because organisms living in the waters, as several studies have now shown, ingest microplastics. There, it not only enters the digestive organs, but it can also penetrate into the tissue and body cells—including the adsorbed pollutants. Another risk also comes from the additives such as plasticizers, flame retardants or dyes, which were originally intended to improve the properties of the plastic, but which, in the course of decomposition in water, separate from the plastic and are released into the environment. There is a possibility that these concerning ingredients can also be released from the plastic matrix by the gastric secretions during digestion in fish and also stored in the tissue. Section 2.6 is specifically dedicated to these additives.

Solutions must Address the Root Causes

To minimize the dangers posed by the contamination of waters with microplastics, it is necessary to address the causes of this contamination. A significant source of contamination are so-called Microbeads. These are plastic bodies in the micrometer range, which are mainly produced as additives for almost all types of personal care products—from exfoliants to sunscreens to toothpastes. There are now alternative solids that cosmetic manufacturers are increasingly switching their products to under appropriate pressure from environmental organizations like BUND (www.bund.net/mikroplastik). Here, both the consumer behavior and the willingness of the cosmetics industry to truly sustainable action are crucial to achieve improvements.

This also applies to the handling of plastic waste. Because microplastics also originate from the decay of macroplastics, that is, when larger plastic parts such as discarded PET beverage bottles or plastic bags are broken down into ever smaller components by physical, chemical, or biological means. I experienced firsthand that the Rhine is a huge plastic mill during my swimming marathon. Gravel, sand, and rocks carried by the Rhine are harder than plastics and grind down sunken plastic. Thus, a lot of microplastics are created by purely mechanical abrasion from macroplastics.

The incomplete or improper burning of plastics, the washing of synthetic textiles, sludge contaminated with plastic, sewage sludge or organic waste are further examples that favor microplastic contamination of waters. Often it is short-sighted action that causes us problems—for example, when recycling strategies are not thought through to the end. In the fermentation of expired fruit and vegetable products from supermarkets, for example, the products are often not carefully enough or not at all freed from their plastic packaging before they are shredded. This results in the packaging materials also being shredded and contaminating the fertilizer that is spread on the fields. These shredded plastic residues then end up in the groundwater with the next rainfall or in our rivers and lakes during heavy rain via the sewer system.

The main concern of this book is to create an awareness of the impact of microplastics on humans and nature. It explains the causal relationships between plastic waste, microplastics, and environmental chemicals. In addition, it provides the reader with a working guide to be able to examine microplastic particles and their ingredients themselves. An introduction to the laser diffraction spectroscopy and the infrared spectroscopy, enriched by experiences and practical examples from the industry in the field of plastic analytics, are part of the necessary tools. Sources and dangers of microplastics are presented and results are shown using the example of the most important inland water in Europe, the Rhine. The book is not only about exposing and denouncing grievances, but as a “hydrophilic” teacher, I see myself obliged to continue pointing out the “creeping danger”, to continue investigating it intensively scientifically and on the other hand to recognize opportunities on the research side. Chap. 4 shows the reader a perspective on how the special properties of microplastics could be used for water purification.

In honorable duty, I would like to thank everyone who supported the "Rheines Wasser" and "TenneSwim" projects, especially the master's students Jonas Loritz, Juri Jander, and Darius Hummel, as well as Dr. Thorsten Hüffer (University of Vienna) and Dr. Habil, Nikolaus Nestle (BASF), who provided me with some as yet unpublished data. Special thanks also go to the master's student Philipp Walter Neek for drawing the structural formulas. Many thanks to Ms. Birte Bayer from the Biological Institute Helgoland of the AWI, who, under the direction of Dr. Gunnar Gerdts, together with Jonas Loritz, analyzed the Rhine samples for microplastics. In addition, I would like to thank my assistants Ms. Dipl. Ing. Helga Weinschrott and Lars Kaiser, who supervise the physical-chemical and analytical internship with me, from which some results have found their way into this book.

Dear readers, last but not least, I wish you an inspiring and exciting read. You can get additional information at www.rheines-wasser.eu, www.facebook.com/RheinesWasser and www.tenneswim.org.

Heidelberg on the Neckar
In May 2018

Most sincerely
Prof. Dr. Andreas Fath

Reference

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Contents

Introduction: Microplastics—a Growing Threat to Humans and the Environment

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The topic of "environmental pollution by humans", whether through CO_2 emissions or radioactive nuclear waste, and how to counteract it, is becoming increasingly important. In this context, the entry of plastics into the environment plays a very special role (Cressey 2016). Plastics can be found almost everywhere in the environment, even far away from human civilization, and they do not degrade within a human lifetime. Thus, we ourselves feel the consequences of this type of environmental pollution on our own bodies and the action motto of many citizens: "Out of sight, out of mind" literally falls at our feet on the beaches (Cressey 2016) or via the sea salt into our food (Jander 2017).

1.1 How Much and Where are Micro-, Meso- and Macroplastics Found?

Since 1976, plastic has been the most used material in the world (ifw-Hamburg 2017). Since its boom in the 1960s, an estimated 8.3 billion tons of plastic have been produced worldwide (Garms 2017). According to a study in the journal *Science*, up to 12.7 million tons of plastic entered the world's oceans in 2015. Due to the further increasing production of plastic, without an immediate drastic change in our consumption behavior and intelligent disposal or reuse, the peak of annual pollution has not yet been reached even in this century. Current forecasts

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predict that annual pollution will increase tenfold by 2025 (Hoornweg et al. 2013). It is irrelevant whether the plastic waste is introduced into nature as so-called macro- (>25 mm), mesoplastic—(5–25 mm) or microplastic (particles from 100 nm–5 mm) (Napper et al. 2015).

Microplastic, plastic in the micrometer range, is a threat to the entire food chain in inland waters and oceans (Eerkes-Medrano et al. 2015; Desforges et al. 2015; Güven et al. 2017) that can also reach humans. Microplastics can harm organisms either through toxic plastic ingredients like DEHP or Bisphenol A or due to their large surface act as a "magnet" for toxins and pollutants in the water, for example pharmaceutical residues, and thus smuggle these substances into the microplastic-absorbing organism as a Trojan horse. Polymer particles in the form of nano- and microplastics thus act as vectors for pollutants (Anderson et al. 2016; Fröhlich and Roblegg 2012; Li et al. 2016; Ziccardi et al. 2016).

Animals are harmed both by the consumption of macroplastic in the form of, for example, plastic bags, which disrupts body functions due to its indigestibility, and by the fact that microplastics can be deposited in the tissue of plants and animals (EFSA) 2016; Avio et al. 2015; Taylor et al. 2016). The occurrence of microplastics in the environment is increasing, as is the release of the chemicals contained in the plastics (Teuten et al. 2009). So far, the focus of research has been on the investigation of waters (Lassen et al. 2015; Anderson et al. 2016; Li et al. 2016; Deng et al. 2017). However, as soon as microplastics are deposited in animal tissue, humans are also affected by microplastics through food intake (Rochman et al. 2015).

Primary microplastics are mainly found in cosmetic products, in the size range defined for microplastics. Secondary microplastics are formed by erosion of meso- and macroplastic under thermal, mechanical and photochemical influences.

While the American Congress under the Obama administration passed the "Microbead-Free Waters Act 2015" (https://www.congress.gov/bill/114th-congress/house-bill/1321/text), a law prohibiting the use of microplastics in cosmetic products from July 2017 in the USA, in Germany we rely on the insight of the producers. With recipe changes, they react on the one hand to the requirements of environmentally conscious customers, on the other hand, they want to shed the negative image that comes from a company presence on the BUND list as quickly as possible.

But even if we, legally forced or voluntarily, completely refrain from using microplastics in cosmetic products, the microplastic pollution of our waters will hardly change due to irresponsible disposal, because according to the results of the International Union for Conservation of Nature (IUCN), less than 2% of the microplastic amount in cosmetic products is responsible (Boucher and Friot 2017).

Rather, it can be assumed that the pollution of the oceans by plastic waste will continue to increase. According to a study by the Ellen MacArthur Foundation, by 2050 there will be more plastic by weight than fish in our oceans (World Economic Forum 2016). Despite improved waste management, the amount of plastic waste that is washed into the sea from the mainland each year is estimated to be 4.8–12.7 million tons (Jambeck et al. 2015). For the estimate, global data on waste quantity, population density, and economic status of 192 coastal countries were used. The respective infrastructure of waste management was also taken into account. The authors of the cited publication see their forecast of the continuously increasing amount of plastic waste in our oceans confirmed and state that without drastic improvements in waste disposal, this trend will continue.

Due to the resilience of plastic waste, the cumulative amount increases annually, even if the plastic waste slowly breaks down into smaller pieces and eventually into microplastics (if their diameter is less than 5 mm) (secondary microplastics), it still remains present, with all the negative aspects of the microscopic synthetic material mentioned in Chap. 2. The total plastic waste load that is introduced into the world's oceans already has a share of 15–31% microplastics (primary microplastics) (Boucher and Friot 2017). The main source for this is not cosmetic products, which as already mentioned only make up a share of 2%, but mainly car tires and synthetic clothing (Boucher and Friot 2017). Microplastic particles rub off on car tires made of vulcanized synthetic rubber, e.g. from NBR (acrylonitrile butadiene rubber), continuously while driving (Fig. 1.1). Each car driver can measure how much plastic is released into the environment each year by the decreasing tread depth of his tires per year. Tire wear therefore accounts for 28% of the total microplastic waste amount (Fig. 1.1) (Boucher and Friot 2017). The problem is not only the "rubber particles", but also their ingredients.

Fig. 1.1 Abrasion of a car tire with a sandpaper

In addition to the PAH-containing plasticizer oils, the plastic tire blackened with soot also contains carcinogenic polycyclic aromatic hydrocarbons (PAHs) (Federal Environment Agency 2016). The properties, detection and further occurrences of PAH are informed in Chap. 2.

The problem of the spread of tiny tire particles and their ingredients arises not only from abrasion, but also during the recycling of old tires, which are used, among other things, as shredded granulate as filling materials, e.g. on artificial turf sports fields (Fig. 1.2). On the plastic turf fields filled with rubber granulate, the granulate between the polyethylene artificial fibers ensures that the fibers are aligned accordingly and the low-maintenance field receives sufficient injury-preventing cushioning. This plastic is even less firmly attached to its place of use than the car tire and is exposed to all weather conditions. As a result, the granulate, which by definition also belongs to microplastics, is found in cleated shoes, jerseys, washing machines, households, parking lots, sewer channels and in the passing river (Fig. 1.2).

Carried by different paths of wind, rainwater, sewage or rivers, all microplastics end up in the sea as a collection basin, including the plastic granulate, which is spread as litter in animal stables together with or instead of straw (Environment Agency Austria n.d.). When the animal excrement is recycled in the biogas plant and the fermentation residues, which still contain the plastic granulate, are spread as fertilizer on the fields, the journey of the microplastics begins from there towards the sea.

Another source of contamination of rivers and seas with tiny plastic particles are synthetic fibers, which are released from the clothing during washing and enter bodies of water with the wastewater. These fibers account for about one third (35%) of the amount of microplastics in the world's oceans (Boucher and Friot

Fig. 1.2 Distribution of plastic granulate on an artificial turf football field

2017). No small problem, as these fibers add up to the equivalent of 15,000 plastic bags per 100,000 inhabitants, as researchers at the University of California in Santa Barbara have calculated (Hartline et al. 2016). But there is now a solution for this too: "Guppyfriend" (http://guppyfriend.com), a fabric bag for the washing machine, in which you put the clothing made of synthetic material before the washing process. This laundry bag made of a high-tech material acts like a filter and retains 99% of the broken fibers. The fact that a lot of fibers come together in one wash cycle is shown in Fig. 1.3. Here, only the swab of the sieve of a clothes dryer is visible. In the actual washing cycle before, an even larger amount of synthetic fibers is released and not retained by a sieve. In the washing drum, the aim during spinning is to separate the water from the clothing as quickly as possible, which would be prevented by a fine sieve. When washing a single fleece jacket, 1.7 grams of microfibers are released (Hartline et al. 2016; Fig. 1.3). In order to reduce the amount of synthetic fibers released into bodies of water, in addition to the laundry bag as an "intrinsic filter", we also have the option of replacing our synthetic clothing with textiles made from natural fibers such as cotton, jute, hemp, linen and silk.

Most polymers are rather non-polar, causing non-polar organic substances in water to accumulate on the surface through adsorption, and depending on the properties of the polymer, within the polymers through absorption. Due to the increased surface area relative to the mass and volume of the particle, microplastics can sorb larger amounts of pollutants than meso- and macroplastics. The uptake of polymer particles by animals and humans occurs rather arbitrarily with decreasing size, as the plastic particles can hardly or not at all be perceived

Fig. 1.3 Synthetic textile fibers. (Swab from the clothes dryer sieve)

(Fröhlich and Roblegg 2012). Due to physiological conditions, such as altered pH value and, for example, existing bile juices or similar in organisms, the desorption of organic substances from the polymer particles is favored. This establishes the bioavailability of the sorbed substances. Depending on the type and amount of substances, these can demonstrably negatively affect organisms (Bakir et al. 2014; Sleight et al. 2017).

The calculated amount of 4.8 to 12.7 million tons of plastic waste, which is transported annually from the coastal states into the sea (Jambeck et al. 2015), is contrasted by an amount of 236,000 tons of microplastic particles, which were determined in 2015 with the ejection of 11,854 nets. In this "combing" of the sea surface, only the Arctic Sea was excluded (van Sebille 2015). So the question arises, where the rest has remained, especially since the amount of plastic washed into the sea in previous years and that which is disposed of directly at sea, was not taken into account at all. Large amounts of plastic waste are collected in the great Pacific and other garbage vortices of the world's oceans (Moore et al. 2001). These amounts are also known. Millions of tons of so-called "Missing Plastic" are elsewhere: Part of it is certainly in the deep sea on the ocean floor, where plastics with a higher density than salt water sink or are pulled down by the attachment of marine organisms to the plastic particles floating on the surface (Woodall et al. 2014). While a portion of the plastic waste is washed back to our coasts, a considerable amount of microplastic accumulates in Arctic ice, which is orders of magnitude higher than in heavily contaminated surface water (Obbard et al. 2014). There are many indications of further microplastic sinks, such as a progressive fragmentation to nanoplastics, which is difficult to investigate and quantify. A difficult-to-estimate proportion of the plastic waste input into the oceans is absorbed by all possible marine habitats, starting with the smallest form of marine life, the plankton (Cole et al. 2013).

1.2 How Dangerous is Microplastic Really?

Many studies on the toxicity of microplastics for different species are based on too high concentrations, which have not yet been reached in waters. The direct influence of microplastics on the fertility was observed in 2016 in Pacific oysters, whose eggs and sperm showed poorer quality and consequently 41% fewer larvae could be produced than in the control group, which was in clean water without microplastic particles. The microplastic concentration to which the oysters were exposed corresponded to that in the sediment of their natural habitat (Sussarellu et al. 2016). A study in the same year showed that perch larvae preferred microplastics of comparable concentration to their natural food occurring in the aquatic environment, thereby significantly worsening their growth and chances of survival (Lönnstedt and Eklöv 2016).

1.3 The Microplastic Problem Starts at our Doorstep and Returns to the House

Not only the coastal states bear responsibility for the pollution of the oceans with plastic waste. Inland waters such as the Rhine also transport plastic waste and microplastics from riparian states into the sea (Fath 2016). Even the Black Forest contributes to the annual load into the Atlantic basin via the Kinzig, a tributary of the Rhine (Jander 2017).

In one cubic meter of Kinzig water, there are about 800 microplastic particles in the size range of 25 µm to 500 µm. Microplastic particles were also found in the stomach of a fish examined from the Kinzig, mainly polyethylene and polypropylene (Fig. 1.4), which it cannot distinguish from a natural food supply.

Compared to the number of microplastic particles in the Rhine (on average about 200/m^3) or the Yangtze (9000/m^3) (Wang et al. 2017), the 800 particles per cubic meter seem very high. However, the total load is crucial for the increasing pollution of the world's oceans with plastic waste. With a volume flow of the Kinzig of 5–10 m^3/s, 15–30 kg of microplastic particles between 10 µm and 500

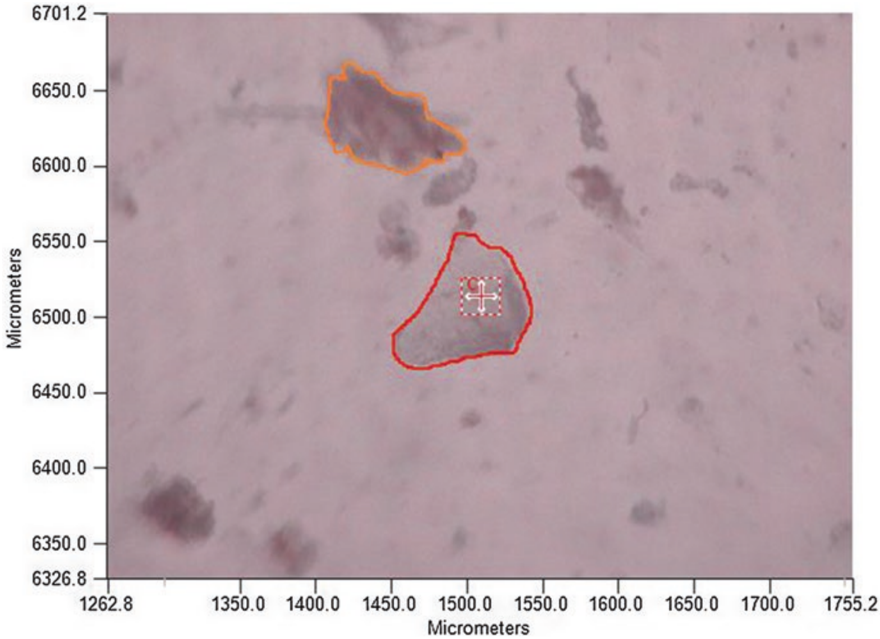

Fig. 1.4 Microplastics under the IR microscope. Polypropylene (PP, red) and polyethylene (PE, orange) from the stomach of the Kinzig fish

μm in diameter flow into the Rhine each year. In comparison, the Rhine transports about 8 tons of microplastics into the North Sea with an average volume flow of 2500 m^3. However, this is only the tip of the iceberg, as only the plastic particles near the surface are included in the calculation. So far, neither a depth profile has been created, nor do we know the sediment concentrations.

Due to the shallower depth and some rapids, plastics with a higher density than water, such as polyvinyl chloride, are measured in the Kinzig, which were detected in significantly lower proportions in the Rhine measurement, as they settle in the deeper river bed. Table 1.1 shows the percentage distribution of the different types of microplastics in 1 m^3 of Kinzig water in April 2017.

Studies on table salt, which is obtained in salt pans, show that some of our plastic waste finds its way back to us in the kitchen and our digestive tract as microplastics. We are essentially eating our own plastic waste. While no microplastics were detectable in rock salt from the mine, up to 18,400 particles per kilogram are found in Mediterranean salt (Jander 2017). Compared to the recently published values of only about 10 particles/m^3 in various commercially available salt products (Karami et al. 2017), the particle count in Mediterranean salt is very high. However, the values are not comparable. In the commercial salt products, only microplastic particles with a diameter larger than 145 μm were quantified. The particles that we (Jander 2017) measured had a diameter of 25–500 μm. This means that the number of smaller microplastic particles is orders of magnitude higher than that of larger particles.

In all samples, mainly polypropylene and polyethylene were found, which due to their lower density float on the water surface and thus predominantly ended up in the examined salt samples, which are obtained in salt pans (Jander 2017).

The detection of plastic particles in a salt sample over 30 years old (Fig. 1.5) from a salt pan in Formentera that was shut down in the 1980s shows that the problem of "microplastics in waters" did not just arise in recent years, but is probably as old as plastic production itself. Only the amount of microplastics has increased with rising production numbers. While the salt of the old sample contained about 6000 microplastic particles per kilogram, the number has tripled in a current salt sample from the same region (Jander 2017).

Table 1.1 Types of microplastics in Kinzig water. (Jander 2017)

PE (Polyethylene)	38.44%
PF (Phenoplasts)	23.12%
PP (Polypropylene)	7.66%
PS (Polystyrene)	15.45%
PSU (Polysulfone)	7.66%
PVC (Polyvinyl chloride)	7.66%

Fig. 1.5 Salt block

1.4 Countermeasures or Fight Against Plastic in the Water

Unfortunately, we can't do anything about the microplastics already distributed in our waters. It will gradually sink to the bottom of the oceans and embed itself in the sediment. However, we can already influence the thickness of this layer, which will be a testament to the plastic generation in a few centuries, by firstly no longer using primary microplastics in cosmetics and hygiene products and secondly reconsidering our plastic waste management and our plastic consumption by strictly following the three "r's": *reduce, reuse, recycle*. The photographed shopping cart in Fig. 1.6 with 51 plastic bags provides enough potential for this (Further tips for plastic reduction are listed in Chap. 4).

The consequences of a change in the composition of plastic waste entering the waters are visible in a short time even far from the entry point. Fulmars are effective biological indicators for these changes. A reduction of plastic granules in plastic waste since the 1980s led to a 75% reduction in fulmars as well as a 75% reduction in the subtropical North Atlantic plastic garbage vortex, while no trend was evident for consumer plastic products (van Franeker and Law 2015). Conversely, the example shows that improved global plastic waste disposal can lead to visible and tangible changes in the environment in a manageable period of time, even before our oil resources will be exhausted. But what to do about the gigantic amounts of macroplastic waste in the large ocean vortices? Boyan Slat, a young ambitious Dutchman, is cleaning up the oceans with kilometers-long U-shaped anchored floating barriers. They are not firmly anchored, but drift slightly slower than the ocean currents with them. In the process, the surface-near

Fig. 1.6 Shopping with 51 plastic bags

floating plastic waste collects in the nets attached under the barriers (The Ocean Cleanup 2018). Even though biologists are skeptical of this project, fearing that fish populations and plankton may be harmed, and even though engineers question the resilience of the barriers against the rough sea, this is so far the only approach to clean up before the plastic waste is no longer reachable. This approach must be supported. The barriers are not trawl nets and therefore no danger to healthy organisms, and the question of functionality under changing weather conditions will be answered in practice.

A completely different question arises in relation to the sorption properties of microplastics. Said properties are already being used in the form of passive samplers in analytics (Sect. 3.1; Müller 2017), in which special polymers are capable of binding pollutants in detectable concentrations and releasing them to a corresponding solvent. Could we not use these sorption properties to clean bodies of water, almost like a filter material? The fact that the sorption of pollutants to polymers is potentially possible has already been demonstrated (Muhandiki et al. 2008; Matsuzawa et al. 2010). If finely ground plastic waste could also be used for this purpose, after appropriate pretreatment for cleaning and roughening the surface, before it is burned anyway, it would become a valuable material again, in the sense of upcycling. The plastic waste would no longer be waste and would not be thoughtlessly discarded in the environment everywhere. This sounds like a utopian idea. Into which Sect. 3.2 provides an outlook (preliminary). On microplastic powder, which was produced from plastic waste using a cryogenic mill, as well as on commercially available plastic powder (sintering material for 3-D printers), the sorption of hormones, depending on the type of plastic and the surface, is investigated and quantified (Hummel 2017). It is determined by using different techniques whether the specific hormone is adsorbed or absorbed by plastic particles (Hummel 2017). This is a crucial question for the further development of microplastic as an effective water filter, to quantitatively remove hormones from wastewater and possibly even recover them through desorption with a suitable solvent and regenerate the filter material.

For the sorption experiments, the hormones 17α-ethinylestradiol (EE2), norethisterone (Nor) and estrone (E1) were used. They are also like DEHP, atrazine, imidacloprid and thiacloprid, to name just a few more representatives of this substance class, among the endocrine disruptors that occur in our wastewater. In sewage treatment plants, these trace substances are not completely degraded and therefore also found in rivers. Even in very low concentrations, hormones are capable of influencing the metabolism and reproduction of aquatic organisms (Manickum and John 2014).

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Microplastics

2

Contents

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2.1 Definition, Origin, and Use

Plastics, colloquially also referred to as plastic (not to be confused with a sculpture or sculpture of a sculptor), are used extensively due to their durability. This results in problems with environmentally friendly disposal, with microplastics playing a particularly important role.

The prefix "micro" comes from the Greek *mikros,* which means "small". Today, we use "micro" to denote the one-millionth part of, for example, a meter. This puts us in the order of magnitude of µm. Microplastics are therefore small plastic particles or fibers.

Plastics, on the other hand, are semi- or fully synthetic macromolecular materials. For the production of semi-synthetic materials, natural polymers, so-called biopolymers, such as cellulose, are used, which are further processed into artificial silk by esterification. The fully synthetic and non-degradable plastics with a decomposition time of several thousand years are synthesized from so-called petrochemically produced monomers. Depending on the functionality of the monomers, the individual building blocks are either linked together by a radical polymerization, polycondensation or polyaddition to form linear or branched high-molecular chains with $n > 1000$ chain links. During polymerization, different monomers can also be used in a chain propagation reaction, resulting in a multitude of possible polymers. As a result, there is now a wide range of plastics with different properties for a variety of applications. Plastics are extremely durable, flexible, and easily moldable, they impress with easy processing and are above all a cheap starting material. For a variety of applications, plastics are indispensable today. They are used in the automotive industry, in medical technology, in electrical engineering, in building services, in the construction industry, in games and sports, and much more.

The largest share of produced plastics is used for packaging. About 39% of the plastics produced in Europe are used for packaging purposes (PlasticsEurope 2013). The demand is increasing: Thus, the global plastic production increased from half a million tons in 1950 to 288 million tons in 2012. In 2012 alone, global plastic production increased by 2.8% compared to the previous year. However, at the same time, there was a decrease in production in Europe by 3%, which still represents an enormous amount with 57 million tons per year (PlasticsEurope 2013). In a study by the Wuppertal Institute (special issue 12. Vol. 46 of the plastic newspaper *Blessing or Curse*), the use of plastics is predicted to increase by a further 28% by 2030 if no recyclate initiative is undertaken. With increasing demand, the resulting waste volume also increases. No longer used plastic products end up in waste dumps, are burned or recycled, or to a large extent improperly disposed of, leading to headlines like "Garbage vortex burdens North Pacific—millions of tons of plastic end up in the sea every year". The accumulation of plastics in the Atlantic is also unmistakable (Fig. 2.1). This accumulating mountain of plastic waste

Fig. 2.1 Yield after a flood phase in a 10 m wide bay on the Cantabrian Atlantic coast near Comillias. Macroplastic on the way to microplastic. The plastic yield after the subsequent flood was comparable. The abrasion of the plastic articles over the rock chunks during the wave movements leads to mechanical crushing

obviously cannot be completely disposed of. Recycling often yields too little profit, and so it is inevitable that a large part enters our environment through various channels and can cause devastating damage with as yet unforeseeable consequences for our environment. Once plastics are exposed to the external influences of nature, the plastic breaks down into ever smaller particles—we speak of microplastics, an invisible threat to our wastewater.

The problem of the accumulation of plastics as macro or microplastics in our environment has been partially recognized, so that developments for products made from compostable plastics or degradable plastics such as the lactic acid-based Polylacticacid (PLA) have started. The advantage lies in the renewable raw material and the recyclable polymer (https://www.thyssenkrupp.com/de/produkte/polylactide.html).

Researchers do not agree on the exact definition of microplastics. There is not yet a unified definition for this form of plastic. Thus, Moore et al. (2011) refer to plastic particles larger than 5 mm as macroplastics, and those smaller than 5 mm as microplastics. In the publication by Browne et al. (2010), plastic fragments smaller than 1 mm are referred to as microplastics. The term "mesoplastics" is used by Andrady (2011) to distinguish between plastic that is visible to the human eye and that which is only perceptible under a microscope.

Plastic particles are now defined by their size (diameter) (Table 2.1).

Primary and Secondary Microplastics

Microplastics are further divided into primary and secondary microplastics. Primary microplastics include the smallest plastic particles in the micrometer range, so-called "Microbeads". These plastic shapes are produced by the industry for further processing (Liebezeit and Dubaish 2012). The smallest plastic particles are used in the cosmetics industry. In care products such as shower gel, washing peels, make-up or even toothpaste, plastic is added. Many toothpaste manufacturers have now refrained from using microplastics in their products due to the "invisible danger". This partial success is certainly also due to the Federation for Environment and Nature in Germany (BUND), which lists companies and their products containing microplastics on its website (www.bund.net/mikroplastik) and thus exposes them as "environmental sinners". The product range is several pages long and includes face care, body care, foot care and hand care products as well as shampoos, shower gels, powders, makeup, concealers, blush, eyeshadow, mascara, eyeliner, eyebrow pencils, lipsticks, lip gloss, lip liners, sun creams, shaving foam

Table 2.1 Size classification of "plastic". (Andrady 2011; Cole et al. 2011; Ryan et al. 2009)

Particle size	Designation
>25 mm	Macroplastics
5–25 mm	Mesoplastics
1–5 mm	L-MPP (Large Microplastic Particle)
<1 mm	S-MPP (Small Microplastic Particle)