

Whitepaper

Microplastic in Water Occurrence, Risks and Removal

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1. Microplastics – what's the problem?

Social and industrial progresses continuously improve our everyday life by yielding new materials, which fit our needs and stand out by their specially designed material properties. Hardly any other material has affected world's mass consumption and industry as plastics. These polymers feature plastic or elastic properties, thermal and biological stability and are cheap to manufacture.

However, these materials reach the environment with momentarily incalculable risks for human health and ecosystems. The pathways of plastics into the environment are manifold, but always strictly related to anthropogenic activities and influence. The first plastic polymers have already been designed in the end of the 19th century based on rubber and their production has been exponentially growing ever since. The first report on microplastics (MP) in surface water dates back to the 1970ies (Carpenter et al., 1972). Concerns about environmental and human impact only recently gained momentum, when Thompson et al. (2004) asked in the renown scientific journal *Science*: “*Lost at Sea: Where Is All the Plastic?*”. Following that, environmental research started focusing these small fractions of plastic litter regarding their occurrence, uptake by organisms, mobility, analysis, and control.

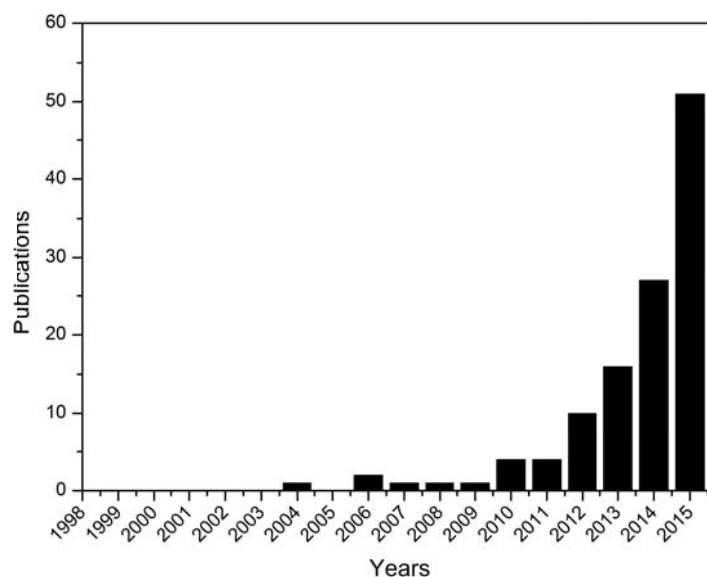


Figure 1. Publications dealing with microplastics in the environment over time; search performed with Web of ScienceTM; search term: ‘Environmental Microplastic’.

Microplastics are mostly defined as microplastic particles smaller than 1 - 5 mm. Their origin is basically divided into two classes: a) *primary microplastics* which are produced in this particle size for applications in cosmetics or for industrial purposes such as pellets or microbeads and b) *secondary microplastics* that are released from plastic litter by debris, decomposition and alteration processes. The latter class also encompasses fibers, which were found to be released from cloths during washing and mostly consist of polyester and similar polymers.

All of these polymers exhibit high recalcitrance to biological degradation resulting in half-lives in the range of months to centuries. Consequently, microplastics are accumulating in different environmental compartments and are hardly removable once having reached the environment. At the moment, different units are used to report microplastic concentrations. Most often items per volume are reported, but also items per surface area or weight per volume, which can make it difficult to directly compare between values reported in different studies.

2. Occurrence and Pathways

Microplastics can be considered as omnipresent in both marine and freshwater water systems worldwide. Since a high number of microplastic is expected to be released from mass consumption products such as tooth paste, peeling products or cloths, wastewater treatment plants are suggested to be major point sources of microplastics. The available data is not yet clear regarding the question if this is relevant to the overall microplastics occurrence via diffuse emissions (see 3.4.).

2.1 Wastewater Treatment Plant (WWTP) effluents

Microplastic particles (MP) also are ubiquitous in municipal wastewater. In Germany, microplastic concentrations between 80 and 9'000 MP/m³ were found in WWTP effluents (Minteig et al., 2014). The occurring microplastics can consist of more than 10 - 15 different polymer types. Generally, polyethylene, polypropylene, polyester, and polyamide are among the most abundant polymers found in water. The most abundant particle size is between 50 µm and 250 µm.

Microplastics can be present as particles, but also in the shape of fibers. Fibres are occurring in similar amounts as microplastic particles in the range of 30 – 10'000 fibers/m³ (Minteig et al., 2014) and can have lengths between 130 µm and 20 mm. Fibres can consist of polyester and polyamide as typical textile materials, but also of natural matter. As an orientation value, the yearly microplastic particle effluent load of a WWTP including fibers was estimated between 90 million to 10 billion MP/a.

2.2. Activated Sludge

Microplastics sorb onto activated sludge flocs or is easily incorporated in the latter. Amounts of 1'000 to 24'000 MP/kg dry mass were found in activated sludge from municipal WWTPs. It suggests that removal by activated sludge adsorption can be a major elimination pathway. Of the sludge of the WWTPs, around 75% is used for thermal energy production. However, disposal or agricultural use of activated sludge may also release microplastic to the aquatic environment.

2.3. Sediments

Sediments can represent a sink for microplastic with higher density than sea water or surface water. Further, biomass or agglomeration can additionally cause accumulation of microplastic particles in sediments. Sandy beaches are one of the hot spots for microplastic sedimentary accumulation. Higher accumulation can be expected here in areas with low flow velocities such as lagoons or shallow waters. Microplastic can make up a considerable amount of up to 3% of the beach sediment dry weight (Carson et al. 2011). The most abundant polymers are usually polyethylene, polypropylene and polystyrene. Generally, marine

microplastics do not differ significantly from freshwater microplastics in terms of particles size, color, shape, and polymer composition.

Almost no data is available for river and lake sediments. Microplastic has been found wherever studies have been conducted. One example is the St. Lawrence River, where the microplastic particles were suggested to stem from local WWTP and industrial emissions (Castaneda et al. 2014).

However, microplastics also are present in river shore sediments in proximity to industrial and densely populated urban areas, up to 1 g/kg and 4'000 particles/kg. The actual emissions of microplastic via industrial wastewater effluents are determined in the joint research project EmiStop (www.emistop.de)

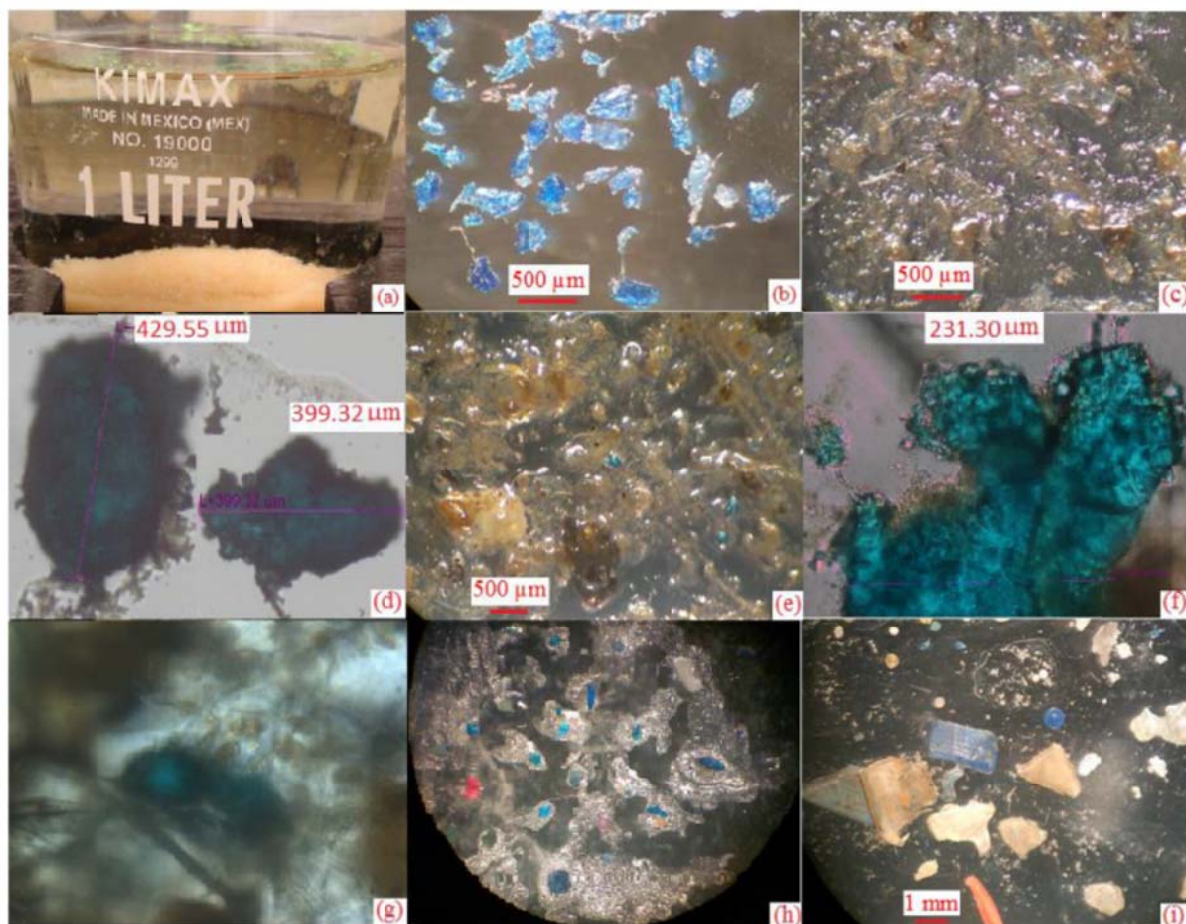


Figure 1. (a) Microbeads in mixed liquor; (b) microplastics in toothpaste; (c) biomass from a 180 µm sieve without microplastics; (d) microplastic in a sample from skimming; (e) biomass and blue microplastics; (f) blue microplastics extracted from final effluent; (g) blue microplastics covered with biofilm; (h) microplastics in a primary skimming sample; (i) microplastics in centrate of a WWTP. [Source: Carr et al. 2016].

2.4. Atmospheric Deposition

Apart from direct input via erosion of plastic litter and mass consumer products, microplastic can enter aquatic systems also via atmospheric deposition. This applies particularly to fibers. In urban and sub-urban areas, deposition between 2 and 400 particles/m²d were measured.

Roughly estimated, between 3 and 10 tons are deposited every year in the agglomeration of Paris (Dris et al. 2016). Hence, atmospheric deposition can be a pathway into the environment. Its relevance compared to the other sources is not clear so far.

2.5. Drinking Water

To date no microplastics have been found in groundwater, which is due to natural soil and aquifer filtration. Positive detections in drinking water can originate from the water pipeline network, e.g. from the abrasion of seals.

3. Sources & Products

3.1. Personal Care Products

Many personal care products contain microplastic such as shower gels, peelings, toothpaste and make-up products to improve their abrasive, adsorptive or opaque properties. The most frequently used polymers are here polyethylene (PE), polypropylene (PP) and polyamide (PA). The mass fraction of microplastic on the total weight of the according product can vary from a few up to 90%. The German Federal Environmental Agency (UBA) estimates an average use of 6 g microplastic per person and year via personal care products.

Plastic microparticles are also used in medicinal applications as a vector for active agents in humans. This application might increase in the future. In comparison to other emissions to the environment, the amounts used here are rather low.

Table 1. Sources of microplastics and their estimated yearly quantities in Germany (Source: modified from UBA 2015).

Sources	Quantity
	[t MP/a]
Primary Microplastics	
Cosmetic products	500
Detergents, cleaning agents in commerce and industry	<100
Blasting material for abrasive applications	<100
Micronized plastic waxes in technical applications	100'000
Secondary Microplastics	
Debris of plastic litter	unknown
Synthetic fibers from textiles	80 to 400
Loss of pellets during production and processing of plastics	21'000-210'000
Tire abrasion	60'000 to 111'000

3.2. Technical Applications and Industry

No reliable data is currently available about the use of microplastics in detergents in households, commerce or industry. Polyamide and polycarbonate is used in deburring agents in metal and polymer production.

Microplastic can also be a component of so-called plastic waxes. These waxes are used in a variety of technical applications such as pigments, paint, food packaging, adhesives and car products for leather, furniture or cars. These waxes are often produced from PE and are available as powder and granules. Microbeads and pellets lost or disposed during industrial production processes should be considered in particular since these can be quantitatively important (Table 1).

3.3. Microplastic from Plastic Waste

Microplastics can also be released from plastic waste and consequently reach the environment by diffuse input. Relevant plastic products often illegally disposed in the environment include for instance plastic bags and bottles, textiles but also tire abrasion. A large proportion of plastic is recycled, legally disposed on landfills or used for energy generation (Figure 2). Europe and in particular Germany belong to the biggest locations of plastic production worldwide.

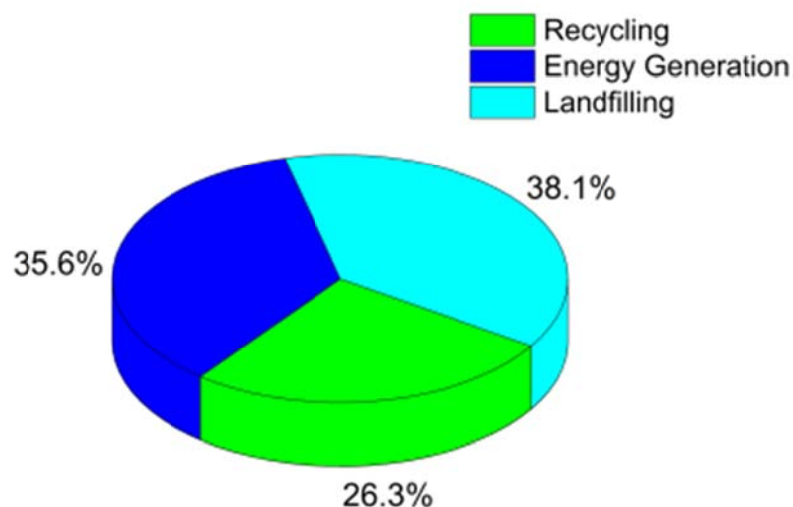


Figure 2. Treatment of Plastic Waste in Europe in 2012 [modified from UBA 2015]

For the time being, there is not enough data to benchmark the contribution of both legally and illegally disposed plastics to the overall microplastic contamination in the oceans. It is estimated that roughly 6 - 10% of the worldwide plastic production, which equaled 6 - 10% Mio t in 1990, sooner or later reaches the oceans. The largest proportion originates from ship waste dumping. Plastic pollution can be expected to continue and potentially increase considering the ever increasing production of plastics.

Another source for secondary microplastics are textiles. These are mostly manufactured using polyester, polyethylene, polyamide or elastan. They are not only used for cloths, but also for technical textiles e.g. in the automobile industry. The market share of synthetic fibers adds up to around two thirds of the total fibers. No estimations are available for the release of

fibers from technical textiles. For cloths, it was estimated that 80 to 400 t/a of microfibers are released during washing in Germany (UBA 2015).

Tire abrasion accumulates to approximately 60'000 to 111'000 t/a and originates from general traffic. Tires are made from rubber and polymers containing elastomers and comply with the definition of microplastic. A not negligible source is the loss of pellets and granules during industrial production processes.

3.4. Diffuse vs. Point Sources

A variety of studies demonstrated that MP are discharged in WWTP effluents. The lack of data and the uncertainty of upscaling calculations make it difficult to assess the impact of microplastics in WWTP effluents.

The German Environmental Agency investigated the relevance of microplastic sources with regard to marine pollution. The authors conclude that secondary microplastics play the greater role compared to primary microplastics from cosmetic products. For the moment, no correlation can be found between population density and the mass or number of particles in rivers. Also, no increased concentrations of microplastics have been found nearby WWTP effluents. In contrast, large scale estimations show a strong relationship between population density and sediment microplastic contamination at sandy beaches (Browne et al 2011), probably due to the larger impact of diffuse sources. The variability of microplastic contamination is expected to be much higher on a small scale given the river hydrodynamics and varying relative contribution of diffuse/point sources in different catchments.

4. Analysis

4.1. Sampling and Extraction

In natural water bodies either water samples or sediment samples can be analyzed for microplastics. Due to the light weight and small particle size, large water volumes must be sampled to obtain a measurable amount. The advantage of bulk water sampling is that in this step no particle size fraction is lost. However, the handling of large sample volumes such as 50 - 100 litres and more is cumbersome and therefore, sampling is often carried out with nets installed in the river or trawls to reach lower water depths. These nets usually have net mesh sizes of around 300 μm which means that smaller fractions are lost during sampling. On the other side, much larger water volumes can be sampled. Bulk water samples are further processed in the laboratory, usually by use of filtration cascades down to the lower μm range. This step can be very time-intensive regarding the large volumes. Sediment samples from shallow rivers are taken as the superficial layers by grab sampling. Another method is to put a pipe vertical on the river bed and homogenize water and sediment by stirring within the pipe. The sample is then taken from the suspension and extracted in the lab. Sediment samples from greater water depths can only be obtained by a sediment gripper. Sediment from the river shore can be taken at low water levels.

Filtration and sieving extracts not only microplastics, but all particles present in the sample. Therefore, state-of-the-art approaches use density floatation to separate the light polymers from heavier particles. Some plastic polymers exhibit a higher density than water and consequently settle in water. However, the density range is usually between 0.8 and 1.4 g cm^{-3} . For this reason, density separation is most commonly carried out in a salt solution with high den-

sity so that all plastic polymers float on the surface. Best results have been achieved with zinc chloride (ZnCl_2) solution, while some approaches used sodium chloride (NaCl). Due to its lower density, not all polymers can be separated with NaCl and the amount of microplastics might be underestimated. The issue linked to ZnCl_2 is that it is corrosive and classified as hazardous to the environment. It must consequently be disposed as hazardous material.

Sediments, sieving or filtration extracts are mixed with the salt solution by shaking. After settling, the microplastic floats on the surface and the supernatant is withdrawn for further processing. Density separated particles do not only necessarily consist of microplastics, but can contain other particles with similar densities. Most often organic matter is co-extracted with the microplastics. Visual inspection can help separating the particles, but identification is difficult, in particular for very small particles. In order to remove this organic matter, a digestion step with different oxidizing agents is possible. As agents, acids (i.e. hydrochloric acid, nitric acid, sulfuric acid) and bases (i.e. caustic soda) can be applied. Further, hydrogen peroxide has been proven to reliably remove organic matter from the extracts within 24 hours. Other approaches try to catalyze the breakdown of organic matter by the addition of enzymes. These reactions can last for several days. Momentarily, there still is a lack of standardized protocols and operating procedures for microplastic extraction from different matrices.

4.2. Characterization and Chemical Identification of Microplastics

The extracted microplastic is most commonly either weighted and given in weight per volume and/or the visible plastic particles are counted by visual inspection or using a microscope. Attention must be paid since chemical identification showed that a relatively large proportion of previously assumed microplastic particles were none. Further characterization can be carried out by analyzing their particle-size distribution. If there is a large amount of microplastic, this can be achieved by a sieving cascade. For smaller amounts that would not be retrievable from the single sieves, a particle size distribution analyzer is more suited. Other morphological characteristics are shape and color.

To identify the polymeric composition of the microplastics both Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy are used. Spectroscopy is often linked to a microscope to target the particle. The investigation of microplastic particles to obtain a representative composition of sample can be very labor-intensive. For qualitative identification, the obtained IR spectra of the unknown particle are matched with previously obtained spectra of pure polymers or available databases. The use of spectroscopy is well established in material and polymer sciences and is currently the most applied and reproducible method for microplastic identification. Other less often applied approaches are differential scanning calorimetry (DSC), sometimes coupled to thermogravimetry (TGA) or gas-chromatography and mass spectrometry.

The joint research project EmiStop uses both DSC and Raman spectroscopy to analyze the same water samples for their microplastic content. This allows a comparison of both analytical methods and enhances the reliability of the results (www.emistop.de).

Microscopic methods include scanning electron microscopy (SEM) for imaging and environmental scanning electron microscopy – energy dispersive X-ray spectroscopy (ESEM-EDS) to gain information about the elemental composition and surface morphology. Generally, the

ultimate identification can be challenging: A recent study showed that only 47% of visually identified microplastic could be assigned to a common polymer type (Dekiff et al. 2014).

5. Effects on Organisms and Ecosystems

Microplastics of small particle size are uptaken by aquatic (micro) organism or accumulated via the food chain. The ecotoxicological effects on individual organisms and how this affects ecosystem communities are not clear to date. The potential hazard is threefold: a) direct physical impact of particles in the organisms, b) the transport of organic contaminants adsorbed on microplastic and c) the leaching of polymers and plasticizers from plastic. Microplastics are of same particle size as sediments and plankton and therefore bioavailable to numerous aquatic species.

A number of species have been found to ingest microplastics of small particle sizes as well as fibers. Relevant particle sizes range from the mm range down to nm. For instance, microplastics between 20 and 1000 nm have been observed to be retained and accumulated in freshwater water flea (Rosenkranz et al., 2009). Other studies found disturbance of the digestive system and inflammatory response in tissues. Apart from that it has been observed that microplastics stick to microalgae altering their sinking behavior (Long et al., 2015). Rochman et al. (2013) found bioaccumulation of contaminants sorbed on microplastics in fish and consequent liver toxicity. Also, the transfer of microplastics and correlation with persistent organic contaminants have been found in sea birds, amphibians and reptiles also suggesting an accumulation in terrestrial species via the food chain. To date there is no clear statement about the toxicity and impact of microplastics on aquatic organisms in real ecosystems. Uncontroversial is that that microplastics of different particle size are uptaken by numerous organisms.

6. Microplastics in Policy and Regulation

Due to the recognition of plastic debris as an environmental challenge and the current media presence, several initiatives develop strategies to deal with plastic waste in particular with regard to marine systems such as the US Interagency Marine Debris Coordinating Committee (IMDCC) or the European Commission's Marine Strategy Framework Directive (MSFD). Less initiatives exist for freshwater systems and currently microplastics are no subject to any regulation.

Recent phase-outs of plastics in cosmetic by self-commitments of the industry as well as from several political initiatives indicate that a first steps are being taken to reduce the emissions of microplastics into the environment. For instance, the Netherlands, Belgium, Austria and Sweden advocated in an official joint statement to the EU in 2014 a ban of microplastics in cosmetics to protect their marine ecosystems. Regulations regarding the elimination of microplastic from waste water of the respective industries are also possible.

7. Removal in WWTPs

Currently, there is only scarce data available about the removal efficiencies of WWTPs. The available studies reveal that the removal of microplastic particles at all particle size fractions is > 90% (Table 1). The importance compared to the input of diffuse sources and relative to marine plastic pollutions is addressed in 3.4.

Major removal takes place during solid skimming and sludge settling indicating existing treatment processes are sufficiently efficient for the removal of the abundance of microplastics in wastewater (Carr et al., 2016). To remove remaining microplastic particles in the final effluent, cloth filters are suited and have been successfully applied to reduce the effluent microplastic load by 97%. Due to the particle nature of microplastics, filtration by membranes is the most promising removal treatment. First companies offer membranes to specifically remove (microplastic) particles from wastewater effluent. Another positive side-effect can be the increased removal of residual bacteria in the effluent.

Table 2. WWTP Removal efficiencies of microplastics reported in different studies.

Removal [%]	Country	Type	Reference
99.9	USA	Conventional WWTP	Carr et al. (2016)
99	Sweden	Conventional WWTP	Magnusson & Norén (2004)
97 of MPs in effluent	Germany	Filtration of effluent using a cloth filter	Mintenig et al. (2014)

Currently, no valid data on the removal efficiency of different waste water treatment processes is available. The few existing studies evaluated mainly on the concentration of microplastic in the influent and effluent of existing WWTP's. Efforts to enhance the microplastic removal are limited to filtration techniques.

The joint research project EmiStop pioneers in systematically evaluating the removal efficiency of wastewater treatment technologies for microplastics (www.emistop.de)

8. Alternatives

The public debate and potential adverse effects led to several self-commitments of global cosmetic producers. Several companies started to gradually phase-out microplastics in their personal care products. Current substitutes in use are i.e. microparticles produced from marine sand or particles made from polylactic acid. A Swiss supplier offers peeling particles from hardened palm oil. Generally, the requirement for microplastic replacements are biodegradable properties. Several initiatives try to achieve this either by the synthesis of biodegradable polymers or the use of natural products such as waxes or fruit seeds.

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