

Review of Microplastic Pollution in the Environment and Emerging Recycling Solutions

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Abstract: Microplastic pollution represents a side-effect stemming from a global plastic waste mismanagement problem and includes degraded particles or mass produced plastic particles less than 5 mm in largest dimension. The small nature of microplastics gives this area of pollution different environmental concerns than general plastic waste in the environment. The biological toxicity of particles, their internal components, and their surface level changes all present opportunities for these particles to adversely affect the environment around them. Thus, it is necessary to review the current literature surrounding this topic and identify areas where the study of microplastic can be pushed forward. Here we present current methods in studying microplastics, some of the ways by which microplastics affect the environment and attempt to shed light on how this research can continue. In addition, we review current recycling methods developing for the processing of mixed-plastic waste. These methods, including hydrothermal processing and solvent extraction, provide a unique opportunity to separate plastic waste and improve the viability of the plastics recycling industry.

Keywords: Microplastic pollution; additive toxicology; marine plastic pollution; plastic recycling; sustainability

1 Introduction of Microplastics

1.1 Paper Overview

Understanding of current literature in microplastic pollution (MP) requires a knowledge of the background of microplastic particles, how the research is conducted with microplastic particles, what differentiates microplastics from other forms of pollution, and how scientists can deal with this problem. To provide this understanding, we first describe the nature of the microplastic particle: its formation and source. We define the most common methods for sampling of MP and separation of microplastic particles. This provides a background to explain the complex composition of MP and to reveal what differentiates MP from other plastic pollution. After organizing these main points of significance for MP, suitable methods for the recycling of mixed plastic products and microplastic particles, particularly those found in the aqueous environment, are recommended. Finally, potential areas for new research (e.g., novel methods for sampling MP to enhance the selectivity and improving accuracy from current methods) are suggested. This structure aims to synthesize research in several background areas of microplastic, such as toxicity, environmental pervasiveness, and chemical transport phenomena, and to provide useful commentary on how to proceed with research in this field.

1.2 Definition and Scope

Improper plastic waste management has become a rising problem facing humanity as oceans, waterways, and terrestrial areas all become choked with plastic waste products. As these products break

down, the small particles of leftover plastic, collectively referred to as microplastics, form a complex chemical and physical aggregate whose effects are currently being researched [1].

These effects face a common problem: they are easy to observe yet hard to quantify because of the widespread nature of plastic pollution and the existence of other stressors (e.g., climate change, toxic waste pollution). With other forms of pollution already affecting the environment, the effects specific to microplastic pollution can be precluded by pre-existing pollutants. However, the effects of plastic micro- and nanoparticles have been shown to disrupt biological functions in organizational levels as low as the cellular level [1]. Given these reasons, it is worth organizing current research on the topic and identify areas of continuing research.

The prevalence of microplastics is difficult to exaggerate. MP has been found in samples varying from 1000 to more than 5000 meters deep in the ocean [2], as well as in the Laurentian Great Lakes of the US [3], freshwater lakes in Mongolia [4], and sediment samples from the river Rhine in Germany [5]. They thus can be found in both the aqueous and sedimentary environments in a broad geographic section of the world. In addition, microplastics are theorized to collect in river waterways on their pathway towards entering the ocean -- thus transferring inland consumer products into the ocean as microplastic particles [5-8]. Researchers in China attempted to define the extent to which particle concentration differs from inland water sources to the ocean and concluded that inland freshwater sources displayed higher particle concentrations than oceanic or estuarine test sites [9]. On top of that, one recent study has reported that microplastic particles were found in human fecal materials [10].

Another noteworthy point is that MP has been found at the bottom of the ocean, even when most plastic found in MP samples floats in water [2].

2 Sampling of Microplastic Pollution

Fig. 1 shows the currently available methods for microplastic sampling. Basically, passive filtration, coring, and geographical water sampling are the traditional methods of microplastic collection. A promising new method for microplastic collection in the aqueous environment is magnetic extraction which has been recently used to selectively sample microplastic (Fig. 3) [11]. Further research would be recommended to gauge its relative effectiveness in collecting microplastic pollution in the environment.

Sampling of microplastics can be divided into two distinct sections: collection of samples and microplastic separation. Collection refers to the removal of a large quantity of either aqueous or sedimentary samples from the environment while separation is the process of selectively removing individual microplastic particles from the sample mass for further testing and characterization. To sample microplastics, many studies use visual identification by researchers to manually isolate or sort out possible microplastic particles (typically after density based separation and before characterization) [2,12].

Collection methods for microplastic are divided into aqueous and sedimentary. For aqueous samples, the floating nature of the plastic allows researchers to utilize neuston nets that are towed behind boats to catch plastic floating at various depths from the surface. This method functions under the assumption that most plastic is less dense than water and therefore will float to the top [13].

For sedimentary sampling, the wide variety of sediment present in the environment makes the process more complicated. Coring and sediment grabs are generally used to determine accumulation levels of sunk microplastic, or particles whose densities have been influenced by surface level changes and thus sink to the bottom. Generally, dug tests are conducted to the "lowest flotsam line" or the depth at which no more non-natural contaminants are present to the naked eye [14]. These sedimentary testing techniques are used in ocean, lake, and riverbed sampling. By utilizing distributed digging patterns, sedimentary microplastic testing techniques can allow researchers to determine accumulation zones for small plastic and their relative distribution levels in the environment [13].

Aqueous vs. Sedimentary Sampling Methods

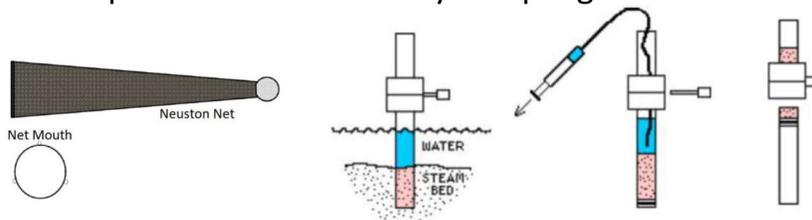


Figure 1: Example sampling diagram of a neuston net and a coring process [15,16]

For all collection methods of microplastic particles, error due to cross contamination with other polymeric products is highly likely given the prevalence of polymers in many products. Thus, positive and negative control samples should always be analyzed to account for possible contamination. In the authors’ experience, negative controls, which are defined as a sedimentary or aqueous sample that is known to contain no microplastics, can be used to determine any possible contamination during the testing procedure. In contrast, positive controls, which contain a designated amount of plastic particles, can be used to determine if a method is suitable to analyze microplastics. In particular, limit of detection and sensitivity of an analytical method is especially important for analyzing microplastic particles, which are present in a very low concentration in the environment [17-19]. For instance, a recent publication has found only 165 particles per kg of sediment sampled in urban river environments in UK [17].

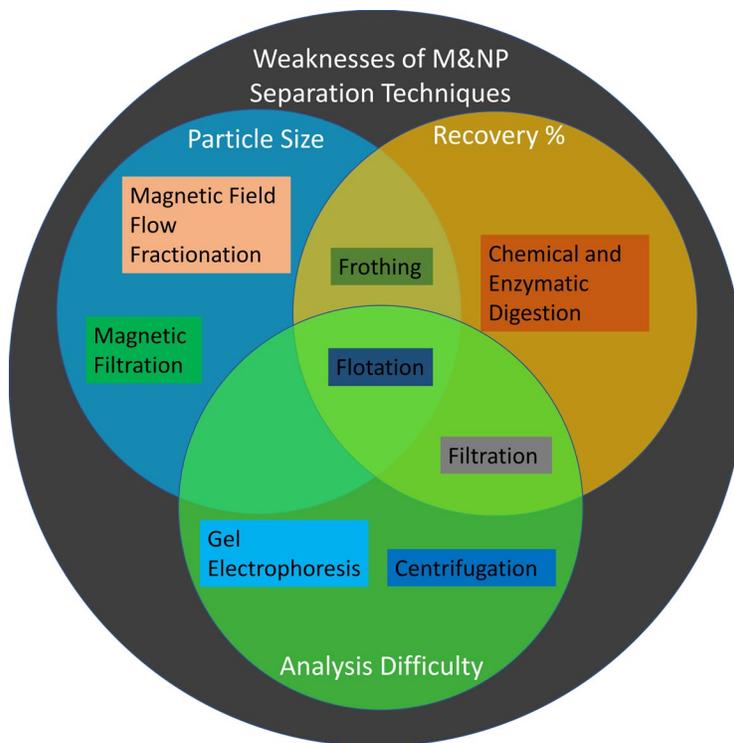


Figure 2: Venn diagram of weaknesses in current methods of microplastic separation from the environment. For example, frothing is located in the area covered by both Particle Size and Recovery % because it faces limitations in both areas. Background information was used from Nguyen et al. 2019 [19]

Given the prevalence of plastic in every-day items, negative controls can be very important. In addition, positive controls, which we define as pristine sedimentary and aqueous samples that have been spiked with a known amount of microplastic particles, prove very useful in developing new protocols for sampling of

microplastics. In the larger particle size range from 100 μm to 5 mm range, for instance, positive control samples can help to train researchers to search for microplastic in their samples more efficiently and establish better sampling practices. Thus, both forms of control sampling are very important for accurate results.

Once samples are collected, separation of the plastic fraction from the non-plastic fraction is needed. These methods use the differences between plastics and materials common in the environment to separate microplastic from aqueous, sedimentary, or mixed samples [19-22].

As stated in a recent review publication by Nguyen et al. (2019), plastics tend to be less dense than their surroundings and are more hydrophobic [19]. Capitalizing on this observation, however, is not as simple as naming the differences between synthetic plastics and water/sediment. Chemical and enzymatic digestion methods, various density separation methods, and various size-based particle filtering methods all have weaknesses which disrupt research findings by failing to measure particles of certain sizes, materials, and chemical histories accurately [19]. Thus, presented below is a diagram of the weakness shown by each microplastic separation method (Fig. 2). By showing the weaknesses of each method, researchers hope to give direction to how these individual methods can be coupled together with each other to make more comprehensive microplastic testing protocols.

Magnetic extraction, a recently proposed process for separation of microplastics, utilizes electrical interactions on the surface of microplastic particles to adhere to the surface of silanized iron nanoparticles which can then be easily extracted with a magnet (Fig. 3). The two largest advantages of this process are the speed at which separation can be conducted in aqueous and mixed sediment-water solutions and the high level of selectivity provided by this testing. Preliminary testing of this technique on laboratory prepared samples of microplastic achieved recovery rates of 84% and 78% in representative freshwater and sediment samples in a controlled environment, respectively [11].

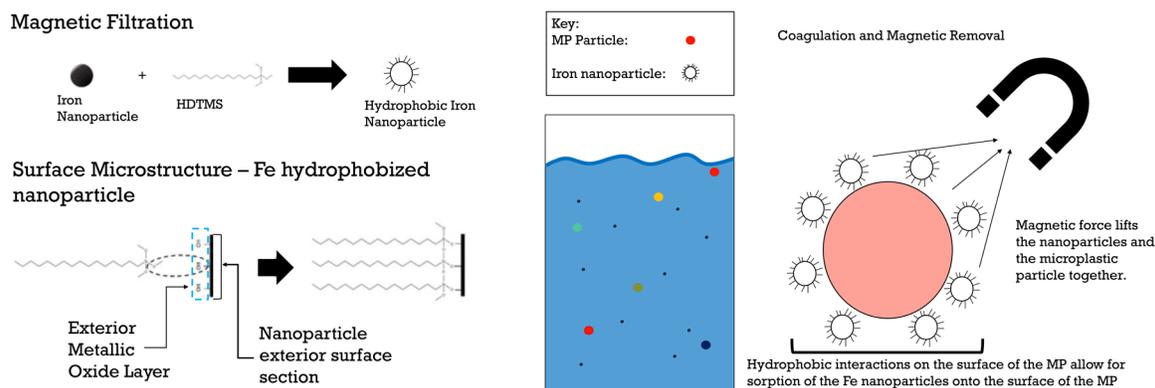


Figure 3: Reaction mechanism for silanization of iron nanoparticle for use in magnetic extraction [11]

This relatively high recovery rate is intriguing because it opens up the doorway for automatic retrieval of microplastic particles in a method similar to magnetic retrieval of microalgae for biofuel production [23]. This could be especially useful for recovery of microplastics in wastewater treatment plants, where high concentrations of MP per liter influent fluid have been observed [24].

Chemical and enzymatic digestion encompass the broad array of chemicals that researchers have used to separate microplastic particles. Common compounds used include hydrogen peroxides, hydrogen peroxides mixed with sulfuric acid, and Fenton reactants [14]. However, these methods could result in some loss of microplastic in the sample and therefore may have a bias towards certain polymers or particle sizes. Thus a new approach, to increase the selectivity of this process, was proposed by Löder et al. Their process, called Basic Enzymatic Purification Protocol (BEPP) utilizes a multistep, multi-compound chemical and enzymatic digestion process that raised the selectivity of the process to $84.5 \pm 3.3\%$ [25].

Centrifugation has the potential to increase the selectivity of other density-based separation techniques when screening for microplastics. However, the long sampling time required as part of running the centrifuge can be impractical from an experimental design perspective.

Gel electrophoresis depends on the size and charge of the particle and thus may not be microplastic-specific [19].

While magnetic field flow fractionation (MFFF) could be useful for removing particles magnetized by using silanized iron nanoparticles, it may not be practical for certain particle sizes [19]. For nanoplastics, developing an iron nanoparticle small enough to effectively bind to the surface of the plastic could prove challenging [19].

Frothing and flotation both face difficulties in capturing smaller particles because the effects on buoyancy of surface level changes are more significant at smaller sizes.

3 Composition and Characterization Methods

Chemical analysis of microplastic particles is very similar to that of feedstock polymers and thus is available in broad areas of literature. Tab. 1 represents a quick synopsis of the most widely used methods in the area of microplastic pollution research.

Table 1: Characterization methods for analyzing microplastic particles [26-32]

Characterization Method	Information provided	Feature
FTIR	Functional Groups	Successfully detect polymer types above 10 μm
Raman Spectroscopy	Functional Groups, molecular symmetry	High identification rate for fibers and particles
Chromatography with mass spectrometry	Mass to charge ratio which gives elemental/chemical compositions	Available to identify polymer/monomer compositions and organic plastic additives
Thermal analysis	Thermal performance of mixture samples	Indirect evidence for polymer types and possible quantification of polymer blends

In the field of microplastics, characterization is often used as a tool for verifying the polymeric nature of a suspected microplastic particle.

Characterization methods for microplastic particles include mass spectroscopic systems as well as other characterization methods like Fourier-Transform Infrared Spectroscopy (FTIR), Raman spectroscopy and MS-coupling processes [26-28]. These characterization methods have primarily been used to determine the monomer of the polymer matrix in the microplastic particles. Branching, polydispersity and other properties of polymeric materials have been largely ignored in microplastic-themed publications. Notably, few publications in this area claim the existence of polymer blends or copolymers as part of the composition of microplastics. The most commonly used method for microplastic particles specifically is FTIR spectroscopy because it is a high throughput screening method. In particular, FTIR can scan samples much faster (in a couple seconds) than other methods and is comparatively economical. FTIR gives information on the functional groups of the material and can be used to identify a likely monomer. However, FTIR presents limitations on analyzing MPs with particle size less than 10 μm . Diversity and relatively low concentration of components cause difficulty in identification and analysis, and some types of polymers are easily neglected when matching to the library standards [29].

Another alternative method, Raman spectroscopy, can also identify functional groups [30]. Compared to FTIR, Raman spectroscopy has a relatively high identification rate but specific procedures are typically

required to be set by researchers [31]. These two methods of characterization (FTIR and Raman spectroscopies) are likely popular because of their speed and ease of use. The ubiquity of microplastics makes fast sampling methods all the more important. Furthermore, micro-FTIR, micro-Raman (i.e., coupling a microscope with an FTIR/Raman) can be used on small sample masses and isolate a single particle for characterization with the assistance of visual images [14,25,30,32].

Gas and liquid chromatography (GC and LC, respectively), in addition, can be used to broadly identify polymers and additives present in MP. Coupled with mass spectrometry (MS) systems, they can also quantify organic and inorganic fractions in the plastic mixture. Samples tested using gas or liquid chromatography, however, cannot be analyzed further. For that reason, along with the difficulty of operating and analyzing the data produced by these properties, GC- and LC-MS are used less than FTIR.

However, in order to reduce the cost and increase the speed of the sampling, new research for microplastics testing is needed. For instance, one potential new area identified is the use of UV-light microscopy to quickly identify polymeric particles by fluorescent emissions. This has been used in the sampling of microplastics as a fast method of determining concentration in organisms [33] and could be adapted for effluent from waste treatment plants.

4 Composition

Micro and nanoplastic particles are complex mixtures of production-related chemicals and compounds sourced from the environment. These chemical components can be separated into four distinct categories: polymeric base substances, production byproducts, chemical additives, and leached environmental contamination (Fig. 4) [34].

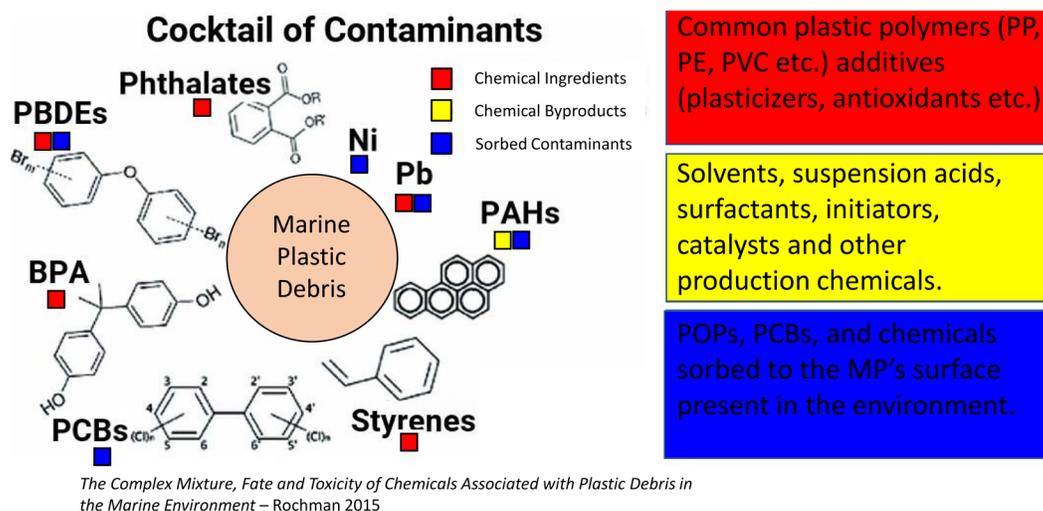


Figure 4: The “cocktail of contaminants” is a strong concept for visualizing the areas of risk associated with microplastics. It shows that while plastic is often organized by its polymeric content, additives, adsorbed chemical pollutants, and manufacturing byproducts are all present in the polymer matrix and thus need to be accounted for in terms of their effect on the environment (adapted from [34])

4.1 Polymeric Base Substances

Polymeric base substances refer to the plastic used in the production of the product, like polyethylene (PE), polycarbonate (PC), or polyvinyl chloride (PVC). While many plastic polymers are non-toxic, some monomers, such as vinylchloride (the monomer of PVC) is known to be mutagenic and carcinogenic [34]. Over time, chemically broken polymer chains within the plastic particles can enter the external environment where they continue to act as pollutants [34].

In an effort to better understand the composition of plastics found in one of the hypothesized-to-be most affected areas of marine plastic pollution, a research project [12] collected surface water MP samples from sampling sites around the Central-Western Mediterranean Sea. Through FITR analysis, they were able to characterize the polymer composition of each plastic particle.

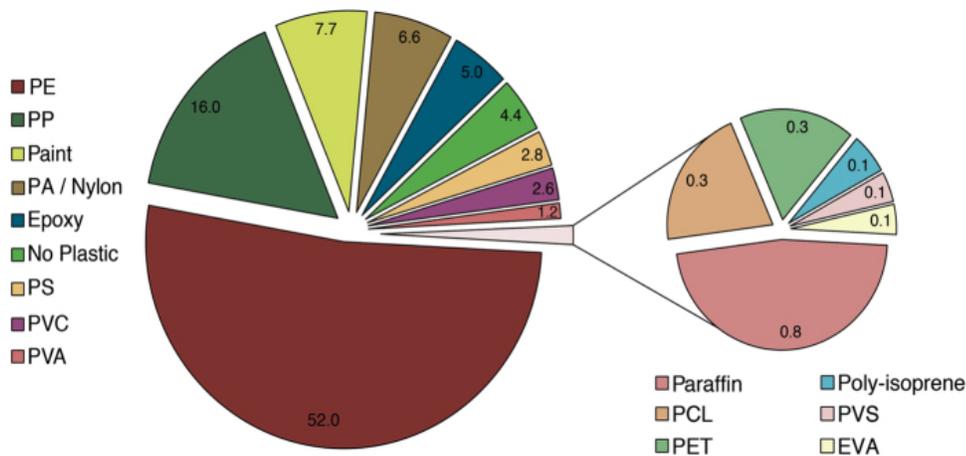


Figure 5: Mediterranean Microplastic pollution follows the given composition in microplastic particles. Likely due to the packaging industry in Europe, much of the plastic sampled contained polyethylene and polypropylene [12]

The distribution of plastic followed the trends in Fig. 5. The largest percentages were fragments and small films of old polyethylene and polypropylene substances that were likely used in single-use packaging material. In this case, the corresponding plastic substances used in the remaining polymeric combinations constitute plastics like paraffin wax which is linked to ship-based pollution in the Adriatic sea, polycaprolactone (PCL) which is used by hobbyists and by the biomedical industry, and other synthetic plastics like PVC and polyvinyl alcohol (PVA or PVOH).

These findings also suggest much higher concentrations of plastic pollutants than other similar studies conducted in the region. This could be resulting from their acceptance of particles up to 700 micrometers in size as a microplastic particle. However, with respect to the density of plastic pollution as distributed per volumetric unit of water, the results of this group's study are very similar to those previously considered in the region [12].

These findings exhibit a larger trend in microplastics research: materials most commonly used in single-use packaging make up the largest section of microplastic particles [12].

4.2 Production Byproducts

Production byproducts contain a wide variety of chemicals used in the production of plastic but are not necessarily intended components of the final plastic product. They can include organic solvents, suspension acids, surfactants, initiators, catalysts, and other byproducts [34].

4.3 Chemical Additives

Plastic additives, chemicals used to enrich the production quality of a certain polymer for manufacturing, represent the most complex subset toxicity-wise for plastic pollutants [34-36]. These include many persistent organic pollutants (POPs), halogenated and brominated flame retardants, and filler molecules with well-documented negative side-effects. They also include a broad range of newly developed and less well understood chemicals that have the potential to leach from the plastic.

One of the important effects of additives in plastic pollution is their ability to leach from the inner matrix of polymers in the plastic and end up in the environment [34]. Thus, studying the effect of leached chemicals in accumulation zones of plastic (such as landfilling sites, wastewater treatment plants, and

agricultural areas) is likely a useful and productive next step for microplastic research. Several studies have also advocated further research regarding the transport and fate of MPs in land [8,37].

4.4 Chemical Movement Phenomena

The surface area to volume ratio of plastic increases as the average particle size decreases. At this small size, the probability of an additive chemical leaching from the plastic increases [34]. Solar radiation, acidity and oxidants present in the environment can chemically degrade the plastic substance. The average length of the polymer molecules in the substance shows an inverse relationship to the ability of intermolecular forces to hold non-bonded, sorbed molecules of additive within the polymeric matrix [38].

For instance, the shorter the length of the polymer molecules, the better ability of intermolecular forces to hold potential pollutants. Thereby, (partially) degraded plastics could be more hazardous than non-degraded plastics.

However, pollutants already present in the environment also face an increased ability to stick to the surface of the plastic-especially as the size of the particle decreases. Small surface differences on the particles and aberrations from an originally smooth surface provide homes for bacterial colonies present in the ocean environment to grow and secrete biofilms, or layers of proteins and other biological macromolecules onto the surface of the plastic. The phenomenon of bacterial biofilm introduction on the surface of a microplastic particle is *ecocorona*, which can strongly affect a particle's ability to hold onto contaminants present in the environment. Plastic, originally hydrophobic and thus a difficult place for contaminants to become sorbed, could then be treated similarly to a biota-based molecule because of the biological and hydrophilic macromolecules that have been secreted on its surface [39].

Finally, if a large enough ecocorona is present on the plastic, the bacteria can accelerate the degradation of the particle, and make physical changes to the properties of the plastic by changing its apparent density (i.e., bulk density) and flow properties. This would make the conventional methods used for sorting the plastic for post-production processing ineffective [39].

5 Ecological Effects of Microplastic

The ecological effects of the microplastic particles are an ongoing area of research. Much of research seeks to understand the pervasiveness of the particles in the environment, especially giving context to how they can be affecting humans. Major concerns in the field of microplastics are summarized in Tab. 2.

Particles ingested by organisms in the environment can affect the overall ecology of the food chain. For example, zooplankton who eat too much plastic, represent a wasted opportunity for energy production in that trophic level of the food web. Thus, for lower trophic level organisms, a reduction in total energy can reduce the populations of all other organisms involved in the food web. This effect was shown to strongly affect populations of zooplankton due to loss of trophic energy from ingestion of plastic [39]. Finally, the effect of the ecocorona formed on plastic gives profound changes to how plastic pollution interacts with the environment. Ecocorona give plastic particles the ability to become transport vessels for pollutants and homes for bacteria present in the aqueous environment. Plastic materials, at small particle sizes, can accumulate pollutants from the environment by absorbing them onto biofilms that bacteria in the environment secrete onto the surface of the microplastic. Most common chemical risks are persistent organic pollutants (POPs)-chemicals set aside by the Stockholm convention to be either phased out or regulated because of their inherent and potential hazard to public health [41]. Other accumulates include halogenated flame retardants, pesticides, and nonylphenol [34]. The distribution of each of these chemicals varies geographically and thus plastic pollution can also be used as a method of sampling for research regarding global chemical contamination.

Table 2: Major concerns in the field of microplastics. Three respective categories to represent unique problems posed by microplastics

Properties of Microplastic Particles in the Environment		
Additive Leaching	Biological Disruption	Exterior Sorption
<p>1. Polymer Fragmentation and Degradation: Innocuous polymers can fragment into monomers with significant toxicological effects [34].</p> <p>2. Plasticizer Toxicity: Plasticizers, including BPA and phthalates, can make up a large portion by mass of a plastic material and can leach from the plastic [34], [40].</p> <p>3. Filler Toxicity: Filler chemicals, added to enhance the properties of plastic or make the production of plastic cheaper, can also present unique toxicological effects by leaching out of the polymer matrix [34], [40].</p>	<p>1. Physical Damage: Microplastics have been shown to cause inflammation and damage to biological levels of organization as low as cellular.</p> <p>2. Trophic Energy Decrease: For small organisms which make up the lower levels of biological trophic energy organization, such as zooplankton, a substitution of microplastics in place of normal feed for the organisms can lower the trophic energy passed on by the whole population [39].</p> <p>3. Changes in Bioturbation and Marine Snow: Microplastics can act like sediment inputs in each of these processes and change the amount and quality of sediment in the environment [39].</p>	<p>1. Bio-membranes and Ecocorona: These two layers of biological macromolecules that can accumulate via bacterial colonies on the surface of plastic can provide an outer layer to the plastic that is more susceptible to sorption by other chemicals present in the environment.</p> <p>2. Surface Coagulation: Once bio-membranes have formed on the surface of MP, coagulation of contaminants already present in the environment can form on the plastic.</p> <p>3. Geochemical Transport: Coagulation of contaminants on the surface of MP increases the impact of MP by allowing them to act as a transport vector for pollution already present in the environment [39].</p>

Accumulation also varies by type of plastic because of differences in diffusivity and crystallinity. In general, capacity for absorption and transport of POPs are positively correlated with both hydrophobicity and molecular weight of the polymer matrix [34]. Compound-specific interactions can also occur because of the chemistry between the polymer and specific compounds. Finally, the ratio of surface area to diffusion length is a strong determinant in affinity for accumulates and thus smaller particles are much better at absorbing chemical contaminants [42].

The fate of these chemicals can be a difficult question to measure because of the large scale of marine plastic pollution. Plastics are generally considered to be a new medium of transport for accumulates and pollutants used in the production of plastic products because more accumulation occurs on plastics than on other mediums. However, bonded or sorbed accumulates actually travel slower geographically than accumulates that are part of a water system [43].

Contaminants are also known to be able to transfer to organisms who ingest the particles which can disrupt physiological processes such as cell division, immunity, and secretion of hormones. Leaching occurs on a large scale basis because polymerization is rarely fully completed in the production process and thus monomers of the plastic are free to leave the substance. Additives are sometimes not chemically bonded to the plastic product and thus have a large ability to leach out of the plastic [34].

Previous studies regarding human exposure to microplastics have generally used non-human analog sources to measure the amount of plastic likely to be within the human food chain or the likelihood of humans eating these things and ingesting plastic. These studies, while giving more credence to the hypothesis that microplastic contaminants are widespread throughout human food consumption, had yet to directly quantify microplastic exposure in humans. A recent study identified MP in human stool samples and represents a first step at quantification of MP in the human body. While the study was conducted within research institutions of the European Union (EU), individuals tested came from countries both inside and outside the EU such as Germany and France but also Russia and Japan. Researchers interviewed stressed that more research was needed to provide more conclusive results [44].

6 Toxicological Analysis of Plastic Waste by Size

6.1 Link Between Microplastic and Nanoplastic Toxicity

Toxicology of MPs has been investigated to understand its hazardous impact on wildlife and underlying risks for human health. As plastics break down into MP, the large surface area of microplastic particles enables them to interact with phytoplankton, industrial debris and clays. This allows the formation of microplastic particles of a higher density which tend to be present in subsurface water [45,46]. These microplastic particles cause direct physical damage to feeding and digestive systems in organisms by internal abrasion, penetration and blocking [47-49]. Furthermore, the stability of digestive enzyme systems has been found to be vulnerable to microplastic particles taken up into the body tissues of invertebrates [50]. Seabirds may die from starvation as microplastic particles prohibit intake of nutritional food [51]. On the other hand, plasticizers, flame retardants and other harmful additives (Fig. 4) are commonly used during manufacturing of plastic resins. Removal of these chemicals is difficult which allows them to stay in the environment as hazardous pollutants. Microplastic particles also serve as a vector of persistent organic pollutants and toxic metals [52]. Transfer and release of toxins to the body may cause more severe indirect chemical injuries to aquatic animals including carcinogenic and endocrine-disrupting effects [53].

Microplastics' toxicity is also linked with the potential toxicity of its next form: nanoplastics. A potential concern raised by microplastics is that if they further break down to the nanoplastic level, the toxicity of microplastics can be significantly amplified. Nanoplastics can enter the gut or the respiratory tract and aggregate in the systemic circulations and tissues. Studies have shown that once the aggregates of nanoplastics in tissues surpass a threshold concentration, they can lead to inflammation [54]. For instance, evidence shows that polystyrene nanoparticles with the size of 64 nm lead to inflammation in rat lung tissue [55]. Polystyrene nanoplastics have also been shown to hinder algal photosynthesis, possibly due to reduction of air flow and light intensity [56]. Furthermore, a study suggests that nanoplastics ingested by adult Japanese rice fish (*Oryzias latipes*) can be accumulated in the gills, intestines, testis, liver, blood, and the brain, indicating that nanoplastics are able to pass through blood-brain barrier [57]. Additionally, studies have also shown that nanoplastics can penetrate cells as well. Rossi et al. (2014) used molecular simulations to show that nanoplastics can permeate easily into lipid membranes, which enables them to further permeate through cells and interact with biological macromolecules found within cells, such as lipids and proteins, and DNA [58]. Current evidence of a direct mechanism for microplastic contribution to toxic effects in the human body is limited because of difficulty in isolating microplastics as the only environmental stressor affecting a population. Even so, toxicological effects of methyl mercury transported to fish via microplastic have been documented [59].

In recent years, the Bisphenol A (BPA) plasticizer has been of high interest to consumers worried about the toxicological effects of the additive on their bodies. Horan et al, one of the original groups studying the toxicity of BPA, found that BPA-substitute additives like Bisphenol F and Bisphenol S have the potential to induce similar effects as those of BPA in mice populations [60]. This is a prime example of how chemical additives can have unintended consequences when leaching from microplastics into the human body or human food sources.

6.2 Potential Public Health and Sanitation Issues from Microplastics

The toxicological effects of microplastics present potential issues with public health and sanitation. Particularly regarding drinking water, microplastics' ability to cause inflammation of internal organs could cause health risks in the future if this is not mitigated. Microplastic, which has not been shown to produce inflammation of internal organs, could thus be considered safer than nanoplastics to the environment, but the potential for these particles to continue degrading to the nanoparticle size range represents a larger hazard than the original microplastic particle itself.

There is an increasing concern that MPs possess non-negligible risks for human health. The abundance of microplastic particles in shrimps, fishes and ducks across the ocean around the world has been reported recently [4,61,62]. As a result, daily interaction with microplastic particles in food webs was proposed through different ways such as oral, dermal and inhalational exposure [29]. Researchers hypothesize that this daily interaction could be a contributor to toxicological effects on humans. However, a mechanism for this toxicity has yet to be verified in recent publications.

7 Emerging Solutions for Microplastic Pollution

Literature indicates that microplastics are mainly derived from packaging materials (food and other types, more details are also available in Section 4 and Fig. 5). Given that microplastics are usually heterogenous in composition (e.g., pollutants sorbed on microplastics and additive content present in the plastics) and may be partially degraded from transportation process, recycling methods for microplastics therefore needs to be modified accordingly. The following discussion presents some possible options to recycle microplastics based on this consideration.

7.1 Solvent Extraction

One of the emerging solutions for recycling microplastic is use of solvent extraction (or dissolution-reprecipitation) technique. This is when a polymer is dissolved in a certain solvent and heated to a designated temperature where it is then cooled and put into a new non-solvent. This mixture (the polymer in the new non-solvent, or anti-solvent) can be finished by reprecipitating the original polymer so that it can be treated for analysis. In one article by Achilias et al. (2009), solvents were used to chemically recycle the polymers from plastic packaging and the results were summarized in Fig. 6 [63]. As Fig. 6 depicts, xylene appeared to be a good solvent for majority of the polymers with high yields in recovery. Different dissolution temperatures were also found to impact the yields. For instance, a higher temperature could increase the yield in recovering PS from about 88% to 94% using toluene as the dissolution solvent and n-Hexane as the non-solvent.

In another article by the same group, published in the Journal of Hazardous Materials in 2007, the dissolution-reprecipitation technique was also examined alongside the method of catalytic pyrolysis [63]. In the dissolution-reprecipitation method, two solvent/non-solvent systems, three dissolution temperatures and four initial polymer concentrations were investigated. Fig. 7 summarizes the percent recovery of polyolefins by dissolution-reprecipitation. As Fig. 7 shows, an increase in temperature resulted in increasing polymer recovery yields. However, increasing polymer concentration in the solvent shows decreased recovery values. This was found to be due to difficulties in stirring caused by the increased viscosity.

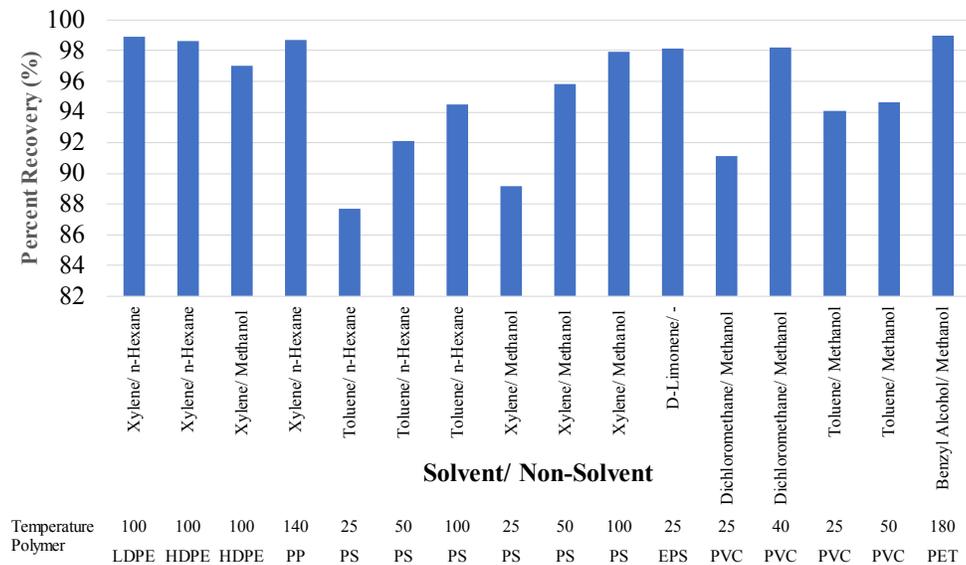


Figure 6: Using different solvents and non-solvents to dissolve and precipitate polymers from plastic packaging (adapted from [63])

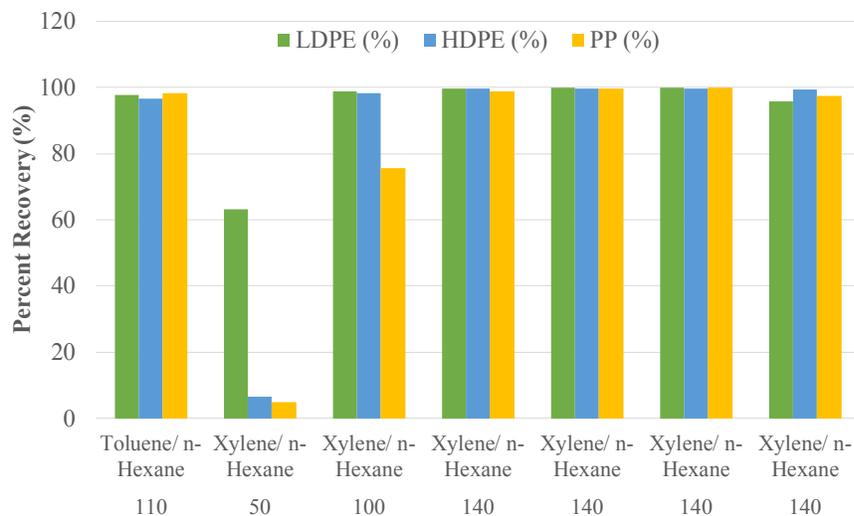


Figure 7: Using different solvents and non-solvents to dissolve and precipitate polyolefins (adapted from [63])

Recently, a spinout from the Proctor and Gamble Company was granted a patent that expanded on the solvent extraction technique to recycle polymers (particularly for polyolefins). The reason that they needed to invent this technology was that their current ways for recycling plastics are primarily mechanical. These are not efficient methods because they do not produce the virgin-like polymers therefore yielding cross contamination and co-dissolution of the products. There is a need for an improved solvent-based method to purify the contaminated polymers that is readily available and economically advantageous while also yielding a clear product to be used in pristine form [64].

In this specific patent, there were four methods for reclaiming polymers using supercritical fluids/solvents. Because the methods are complicated, figures are provided to help visualize the method (Fig. 8). One method was extraction, which is when the polymer is dissolved in a solvent through a range of temperatures and pressures and the contaminated fluid is then extracted while the polymer remains as a

product (Fig. 8(a)). Another method is dissolution, which is at least partial incorporation of a solute (polymeric or non-polymeric) in a solvent at the molecular level (Fig. 8(b)). Purification was another method which is separating a dissolved polymer solution from undissolved contamination at a temperature and pressure wherein the polymer remains in the fluid solvent (Fig. 8(c)). The final method was separation, which is separating the purer polymer from the fluid solvent at a temperature and pressure so the polymer precipitates in one layer (Fig. 8(d)). The four methods were examined at 180-220°C and 1,000-20,000 psi. Notably, extremely high pressures were needed, probably for maintaining propane and butane (solvents used in this patent) at their supercritical conditions.

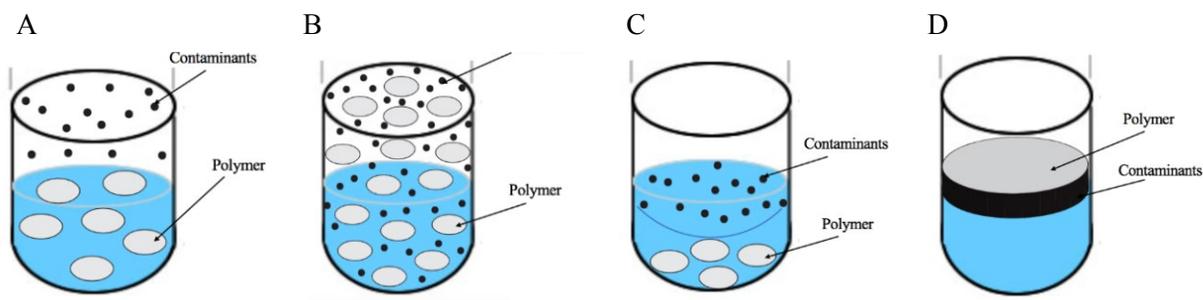


Figure 8: Four processes developed using supercritical propane and butane: (a) Extraction; (b) dissolution, (c) purification, and (d) separation (adapted from [64])

7.2 Hydrothermal Processes

Once sampling and separation are accomplished successfully, microplastic can be subject to industry-used recycling process in a large volume. Particularly, tertiary recycling has been brought into focus in this case. The summary of different techniques is shown in Tab. 3. An emerging tertiary recycling technology, hydrothermal processing (HTP) uses sub or supercritical fluids to depolymerize synthetic polymers. This new technology, with demonstrated research in its effectiveness for polyolefins, could be highly efficient in recycling of microplastics which are largely made up of polyolefins. The utility of HTP using supercritical water is its use of water as a non-toxic, eco-friendly solvent can reduce secondary pollution in post-processing of waste plastic through other chemical recycling methods. Li et al. [65] proposed a decomposition mechanism of brominated epoxy resin in supercritical water. Hydrogen bromide was formed via chain scission of epoxy polymer coupled with further free radical reactions and resulted in hydrobromic acid in the liquid products of the HTP reaction. Supercritical water HTL with added alkaline metals can also prevent the formation of corrosive gases due to release of halogen species by neutralizing acids formed in situ, which inhibits the generation of hazardous organohalogen compounds [66].

The critical state of water ($T \geq 380^\circ\text{C}$ with $P \geq 22.1 \text{ MPa}$) gives water specific properties such as dielectric constant, ionic strength and heat/mass transport coefficient, which correlates with high molecular diffusivity and low viscosity, allowing sub- or super-critical water to be a suitable chemical medium for complex reactions [69,70]. Meanwhile, possible reactions including hydrolysis, cracking, free radical reactions and cyclization indicate the feasibility for feedstock recycling and value-added chemical (e.g., aromatics) synthesis [71]. As a result, water in sub- or super-critical condition acts as a reaction medium, catalyst, reactant or product depending on the reaction pathways and reaction conditions [65].

However, heterogeneity in microplastics caused by compositions, particle sizes and absorbed chemicals from the environment complicates the selection and implementation of recycling process. Impurities in microplastics mean that particles must go through separation and sorting, repetitive washing and drying steps for mechanical recycling. Moreover, microplastics are susceptible to degradation during transportation and reprocessing, which limits the quality of products and application of mechanical recovery [67]. Conventional pyrolysis, as a thermochemical technique, can destroy polymer structures and convert them into oil products under higher temperatures. However, product distribution is complicated without further upgrading or separation. Catalytical pyrolysis attempts to promote reaction selectivity, but

sometimes lowers the oil yields, and therefore needs more investigation on catalyst selection and process optimization [69]. Most importantly, microplastic sampled from the aqueous environment may contain high moisture content that needs additional drying process before entering pyrolysis.

In short, compared to mechanical recycling and pyrolysis, HTP can be adapted to unsorted and contaminated plastics, which eases pretreatment and improves conversion efficiency.

Table 3: Summary of currently available recycling processes for microplastic

Methods	Mechanical Recycling [67]	Solvent Extraction [68]	Pyrolysis [69]	Hydrothermal Processes [70]
Description	Secondary recycling via-remanufacturing (e.g., melting)	Dissolution and extraction of the target polymer	Depolymerization via heat	Depolymerization via sub-/super-critical fluids with higher selectivity
Products	Recycled plastic or downcycled products (e.g., converting PET bottles into carpet)	Pristine-like recycled polymers	Oil Monomers	Oil Naphtha Wax Monomers Aromatics
Working Conditions	Manufacturing standards for different recycled polymers	25-150°C Ambient Pressure Solvents	400-800°C No solvents/water	350-600°C 5-35 MPa Water/co-solvents

8 Challenges and Bottlenecks

In literature and in practice, the largest issue of sampling microplastics is separating the plastic from large environmental sample mixtures. Separation techniques used for microplastics processing are generally inaccurate, time-consuming and specific to certain particle sizes. Recent research into this area has attempted to develop a standardized method of collecting small plastic particles using magnetic iron nanoparticles bonded to a hydrophobic silane tail that allows the hydrophobic interactions between the tail and the plastic polymer to sorb the particles to each other and be removed together with a magnet [19]. In addition, coupling current sorting methods used in nanomanufacturing, like magnetic field flow fractionation or gel electrophoresis with traditional microplastic separation methods could produce much more efficient sampling processes.

In addition, the transport and degradation mechanisms of plastic in the environment on the macro scale are poorly understood. The majority of plastics use occurs on land, yet much of plastic is assumed and observed to be in the ocean. Understanding how the plastic is broken down to the micro size and transported to the ocean could help to identify accumulation zones which present more efficient areas for plastic pollution cleanup.

Microplastics represent the tail-end of a larger recycling problem around the world. By waiting until the plastic has reached the microparticle size, society fails to take advantage of the residual value of the plastic material after a product has been discarded both in economic and environmental terms. Making full use of our currently available resources is top priority in promoting a healthier environment. In addition, the authors see some potential risks in public opinion towards recycling. Focus has recently been put on cities with “zero-sort” recycling because it saves the consumer from having to sort their waste. However, well-sorted recycling is one of the easiest ways to increase the amount of plastic that ends up being recycled each year, and thus represents another missed opportunity to reduce microplastic formation by closing the loop of recycling earlier on in the process.

9 Summary

- Microplastics are a ubiquitous pollutant formed from disposed plastic waste that results from mismanaged plastic waste.
- Sampling of microplastics from the environment is currently a time-consuming and imprecise process. Use of new sampling methods such as UV-vis microscopy and Magnetic Filtration of microplastics could vitalize this area of research to provide more data.
- Microplastics have a complex toxicological effect on the world around them. They can cause direct physical harm to organisms that ingest them, by harming organs in their digestive tracts and other areas. They also contain complex toxic chemical additives and sorbed organic and inorganic pollutants from the environment that give MP a large and unexpected set of toxicological effects.
- Microplastics also exhibit complex effects on their ecological environment. MP can disrupt biological cycles like bioturbation and marine snow because of their small size. They can also interrupt trophic energy transfer by taking the place of genuine nutrition in the food chain.
- Recent innovations in recycling methods that represent promising new paths forward to closing the loop for plastics product usage were also discussed. Hydrothermal liquefaction and solvent extraction are two processes that can be used for recycling of mixed plastic resins while also providing value-added material to the economy. Other, similar processes, such as pyrolysis, to hydrothermal liquefaction were also compared. It is expected that HTL has a great potential to use a benign compound, supercritical water, to depolymerize plastic waste and form useful chemical products such as fuels and naphtha.

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