Sustainable Communities and Waste

National Environmental Science Program

Understanding Microplastics

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Understanding Microplastics

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The Sustainable Communities and Waste Hub acknowledges all Aboriginal and Torres Strait Islander Traditional Custodians of Country and recognises their continuing connection to land, sea, culture, and community. We pay our respects to Elders past, present, and emerging. We support Aboriginal and Torres Strait Islander peoples and their aspirations to maintain, protect and manage their culture, language, land and sea Country and heritage.

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Executive Summary

This document compiles the progress updates for IP2.02.01 project on Understanding Microplastics. The document is in completion of Grant Milestones RP2022 Milestone 4, RP2022 Milestone 6, RP2023 Milestone 5, RP2023 Milestone 6. The interplay of ideas between these milestones will be leveraged to generate valuable insights for IP2 and future knowledge products.

This document covers:

- **A literature review of current best practices for detecting and quantifying micro and nano plastics**
- **Identification of environmental matrices for further investigation in IP2**
- **Identification of sources (things that generate microplastics) and sinks (places where microplastics accumulate)**

Detection and Quantification of Micro- and Nanoplastics

- Up to 60% of all plastics ever manufactured is in landfill or the environment presently, > 350 Mt annually, and only 9% of that is recycled.
- Almost half of all plastics manufactured are for packaging and concentrated into < 10 polymer varieties, topped by PE, PP particles, and fibres of polyester and amide origin.
- 'Microplastics' (MPs) are a broad category of polymeric waste with no standard classification but are generally counted when < 5 mm in size.
- There is no global set of standards for microplastic detection and characterisation.
- Currently, most measurement is performed manually in the marine environment or coastal regions via nets and filters, which can omit results from smaller material fractions.
- Several *in-situ* techniques have been proposed for detecting microplastics by spectroscopic means. These include the utilisation of fluorescent probes, impedance spectroscopy, and visual diffractometry.
- Manual collection of MP particles is often simple but time-consuming and prone to contamination. Terrestrial microplastics must be collected either at their emission point or by hand.
- Analytical Techniques such as Fourier-Transform Infrared Spectroscopy (FTIR) and hyphenated systems (instruments conjoined in series for simultaneous analysis) incorporating pyrolysis and Gas Chromatography-Mass Spectroscopy (GC-MS) are the current industry best practices for rapid

microplastic identification. However, analysis can be expensive and time-consuming.

Sources and Sinks of Microplastics

- Microplastic pollution has been globally measured by composition, with particles and fibres made from polyester (56%), acrylic (23%), PP (7%), PE (6%) and polyamides (3%) as the most frequent.
- Fibres and textiles comprise 35% of the global microplastic stock, primarily through domestic washing operations, with every kilogram of clothes washed emitting an estimated 300 mg of particles and fibres <1 mm long.
- The other main contributors to global MP pollution are vehicle tyres (28%), city dust (24%), and road markings (7%)

Impacts of Microplastics on Environmental Matrices

- MPs have been detected in seafood, foods, beverages, and drinking water. In PET-bottled water, up to 4000 individual MP fragments have been measured per litre of fluid.
- Plastic fragments can be taken into the body by ingestion, inhalation and through the skin, but the long-term tracking and impacts on health have not been studied yet.
- MP particles may leach additives which can act as endocrine disruptors, into the body. They can also cause oxidative stress, tissue damage, and chronic inflammation without additive leaching.
- Plastic fragments have been detected in the digestive tracts of many animals, particularly in marine organisms. It is estimated that up to 60% of fish worldwide have come into contact with microplastics. Acute, deleterious impacts of microplastic uptake have been recorded in microalgae, plankton, mussels, and seabass.
- Though trophic transfer has been recorded between prey and predator, little evidence has been found to suggest the bioaccumulation of toxins.
- MPs have been found to disrupt interspecies lines of communication in plants, alter soil pH levels, and diminish chemo-physical soil stability in terrestrial environments.

Harmful Additives in Plastics

- Plastics contain ~7% additive content on average. Most of that content is comprised of (on average), plasticisers (34%), fillers (28%), and flame retardants (13%). Many additives, identified as toxic, have been found to leech out of plastics and into the environment.
- Numerous international bodies like the UN and the EU have developed lists of controlled plastic additives. Lists and databases are linked.

Identified Gaps in Microplastic Literature for Further Investigation

- Lack of standardised microplastic classification scheme and definitions.

- Inconsistent measurement parameters across various studies (particle sizes, masses, shape, and polymer variants).
- Minimal research on terrestrial MPs.
- Lack of corrective measures proposed for MP emitters.
- Long-term health impacts of microplastics.
- Relationship between additive content and breakdown pathways for plastics to microplastics.

Topics scheduled for Inclusion in this Report

- Breakdown pathways for common microplastics.
- Physico-chemical properties of MPs.
- The role of 'Bio-Plastics' and biodegradable plastics in MP pollution or its reduction.
- Technological solutions to the microplastic problem.
- Legislative responses to global microplastic pollution.
- More detail in the literature gaps chapter

Abbreviations

Abbreviation	Definition
ATH	Alumina Trihydrate
BPA	Bisphenol A
CCD	Charged-coupled device
CO_2	Carbon dioxide
CNT	Carbon nanotubes
DSC	Differential scanning calorimetry
EDS	Energy-dispersive X-ray spectroscopy
FTIR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
HDPE	High density polyethylene
ID	Identification
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
MP	Microplastic
MW	Molecular weight
NESP	National Environmental Science Program
PBAT	Poly(butylene adipate-co-terephthalate)
PCL	polycaprolactone
PE	Polyethylene
PET	Polyethylene terephthalate
PHA	Poly(hydroxly-alkanoate)
PLA	Polylactic acid
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PVC	Poly(vinyl Chloride)
PUR	Polyurethane
RP3	Research Plan 3
SCaW	Sustainable Communities and Waste
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SUP	Single-use plastic
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TSCA	Toxic Substances Control Act (USEPA)
TTP	Tritol phosphate
USEPA	United States Environmental Protection Agency
UV	Ultraviolet

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Introduction to Plastics

1. Introduction and Background to Plastics

Plastics are a broad category of synthetic polymer-based materials traditionally synthesised from fossil fuel sources, including crude oil and natural gas. Polymers consist of Repeating chains of covalently-linked monomers (single units), whose backbone typically consists of hydrocarbon units *polymerised* synthetically with adjacent functional groups or structural linkages, giving distinct material properties suited to almost any application.

Plastics were first synthesised in the late 19th century in nitrocellulose, and *Bakelite*, whose properties held similarities to natural polymers in their strength and ductility but could be moulded into any shape with heat or chemical treatment (Geyer, 2020). Plastics are categorised by their physical response to heat. *Thermoplastics* become ductile at elevated temperatures, while *thermosets* form three-dimensional networks at raised temperatures via irreversible reactions. There are over 300 types of plastics commercially available, and magnitudes more functional sub-variants when common additives such as flame retardants and plasticisers are considered (Chen et al., 2021; Geyer et al., 2017).

Since their widespread commercial adoption in the mid-20th century, plastics manufacturing has surpassed any other human-made material, with an annual global production yield growing from 2 Mt (megatons) in 1959 to 359 Mt in 2018 (C. Wang, Liu, et al., 2021). Of this mass, an estimated 60% remains in landfill or is otherwise incorrectly disposed of in the environment. Herein lies the downfall of the world's most suitable engineering materials, their relative chemical stability compared to many natural organics, metals, and ceramics, leading to synthetic materials remaining in the environment for hundreds of years.

The gradual breakdown of these materials can lead to the leaching of toxic additives and small fragments into soil, waterways and the digestive tracts of humans and animals, with sometimes deadly consequences(Chen et al., 2021; Graham, 1973). Up to 50% of all plastics are *Single-Use* (SUPs), whose production, use and degradation compound negative impacts on the environment due to their inability to biodegrade (Geyer et al., 2017a) and contribution to global greenhouse gas emissions at every step of their life cycle, reaching emission rates of 1.34 Gt (Gigatonnes) by 2030 and 2.8 Gt per year by 2050 (Shen et al., 2020). Currently, proven methods of plastic disposal (besides landfills) are limited to thermal recycling processes, including melt re-extrusion, incineration and pyrolysis - methods whose gaseous products have been found to make significant contributions to greenhouse gas emissions in their own right (Alston & Arnold, 2011; Cudjoe & Acquah, 2021; Mendes et al., 2004).

Apart from its physical impact on the environment, the photodegradation of SUPs into microplastics negatively affects marine ecosystems. These microplastics are physically ingested by organisms at all levels of the food chain, presenting dangerous physical and chemical hazards to marine biota and their dependent marine ecosystems (Cole et al., 2011; Shim & Thomposon, 2015). Current estimations found that at least 690 different marine organisms have encountered plastic debris, with 10% of them ingesting microplastics (Gall & Thompson, 2015). Of the estimated 6000 Mt of SUPs discarded to date, research has found that merely 9% were recycled and 12% incinerated (Geyer et al., 2017a). Recycling of solid plastic waste is divided into four categories, primary (re-extrusion), secondary (mechanical), tertiary (chemical), and quaternary (energy recovery), with cost, material and energy efficiency generally deteriorating with each progressive step (Al-Salem et al., 2009).

2. Common Plastics and Additives

Globally, plastic waste comprises approximately 93% polymer resin and 7% additive by mass, with the vast majority of the latter comprising plasticisers, flame retardants and fillers. Summarised breakdown of global plastic stock is given below(Geyer et al., 2017b).

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Table 1 Breakdown of global plastic stock by industry sector

Market Sector	LDPE, LLDPE	HDPE	PP	PS	PVC	PET	PUR	Other	Total
Transportation	0.1%	0.8%	2.6%	0.0%	0.3%	0.0%	1.6%	1.4%	6.7%
Packaging	13.5%	9.3%	8.2%	2.3%	0.9%	10.1%	0.2%	0.1%	44.8%
Building / Construction	1.1%	3.3%	1.2%	2.2%	8.1%	0.0%	2.4%	0.5%	18.8%
Electrical/Electronic	0.5%	0.2%	0.9%	0.6%	0.4%	0.0%	0.4%	1.0%	3.8%
Consumer & Institutional Products	2.9%	1.7%	3.8%	1.8%	0.6%	0.0%	1.0%	0.2%	11.9%
Industrial Machinery	0.2%	0.1%	0.2%	0.0%	0.0%	0.0%	0.3%	0.0%	0.8%
Other	1.7%	0.9%	4.2%	0.7%	1.4%	0.0%	2.5%	1.7%	13.2%
Total	20.0%	16.3%	21.0%	7.6%	11.8%	10.2%	8.2%	4.9%	100.0%

Table 2 Categorical breakdown of global additives by percentage

Additive Type	Percentage
Plasticisers	34%
Flame Retardants	13%
Heat Stabilisers	5%
Fillers	28%
Impact Modifiers	5%
Antioxidants	6%
Colorants	2%
Lubricants	2%
Light Stabilisers	1%
Other	4%

Table 3 A categorical summary of polymer and additive volumes by weight in 2015

Polymer Type/Additive	2015 Primary Production (Mt)	2015 Primary Waste Generation (Mt)
LD, LDPE	64	57
HDPE	52	40
PP	68	55
PS	25	17
PVC	38	15
PET	33	32
PUR	27	16
PP & A Fibers	59	42
Other	16	11
Additives	25	17
Total	407	302

3. Common Types of Microplastics and Their Structures

Based on the work by Browne *et al.* (Browne, 2015), the main contributors to global microplastic pollution are polyesters, acrylics, polypropylene, polyethylene and polyamides. The structure and breakdown pathways of these polymers will be discussed below. The list is organised in order of the categories stipulated in the international standard **ASTM D7611/D7611M-19: *Coding Plastic Manufactured Articles for Resin Identification1*** (*ASTM D7611/D7611M - Standard Practice for Coding Plastic Manufactured Articles for Resin Identification - Engineering Workbench*, n.d.)

3.1. Polyethylene (Resin ID 2-HDPE & 4-LDPE)

The term polyester describes several varying polymers containing ester groups in the backbone of the polymer material rather than in the side chains. These polymers are derived primarily from dicarboxylic acids and diols (*Polyesters and Polyamides - Google Books*, n.d.). Polyesters are widely used to produce synthetic textiles, filaments and fibres but also form the base material of many photographic films and tape-recorded media.

Polyesters are broadly classified as being thermoplastic or thermosetting, with the former further broken down into linear aromatics, elastomers, liquid crystalline, engineering plastics, aliphatics and poly(hydroxyl alkanoates). The most common polyester is poly(ethylene terephthalate) (PET), systematically, *poly(oxy-1, 2-ethanediyl-oxycarbonyl-1,4-phenylene dicarbonyl.* PET is typically white or translucent with high heat resistance and chemical stability (*Polyesters and Polyamides - Google Books*, n.d.) The material had a higher UV absorption cut-off (313 nm) than polycarbonate (290 nm) and displayed strong resistance against sunlight, making it a persistent pollutant in waterways. Polyester was found to contribute up to 56% of microplastic litter in a 2011 survey of aquatic environments (Browne et al., 2011).

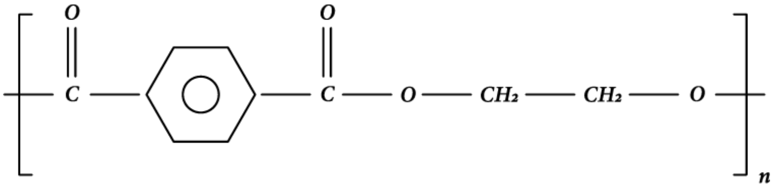
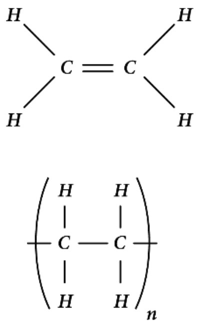


Figure 1 Structure of PET polyester

3.2. Polyethylene (Resin ID 2-HDPE & 4-LDPE)

Polyethylene is one of the most produced polymer materials on the planet due primarily to its structural simplicity, consisting of monomers of connected methylene groups derived from various petrochemical sources. The simplicity of its structure allows for polymers of varying densities to be produced for various applications, from plastic shopping bags in the case of LDPE to engineering plastics with HDPE. Low-density variants feature chain branching, preventing crystallisation from occurring, and resulting in an amorphous, flexible membrane, whereas HDPE features sections of ordered chains in compact configurations, producing a material with high impact strength and good mechanical properties (Paxton et al., 2019). Polyethylene is also highly resistant to chemical attack, only soluble in specific solvents such as xylene and toluene at specific raised temperatures. The chemical stability of PE is one of the main factors leading to its presence as a microplastic pollutant in marine environments, contributing to an estimated 6% of global stock (Browne et al., 2011). The main variations of PE are given below.



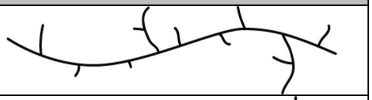
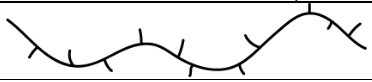
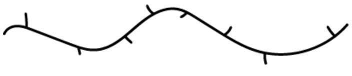
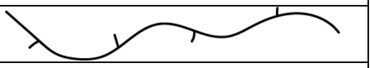
Category	Density	Typical Chain Branching
Low Density Polyethylene (LDPE)	0.910-0.925 g/cm^3	
Linear Low Density Polyethylene (LLDPE)	0.919-0.925 g/cm^3	
Medium Density Polyethylene (MDPE)	0.926-0.940 g/cm^3	
High Density Polyethylene (HDPE)	0.941-0.965 g/cm^3	
Ultra High Molecular Weight Polyethylene (UHMWPE)	> 0.966 g/cm^3	

Figure 2 Chemical and chain structures of polyethylene resins

3.3. Polypropylene (Resin ID 5-PP)

Polypropylene (PP) is a common thermoplastic polymer derived from petrochemicals. Structurally, PP resembles polyethylene, with a methyl side group arranged asymmetrically about the chain. The polymer is partially crystalline, with methyl groups systematically located around the polymer backbone, enabling close packing under the right conditions. It is widely used as an engineering thermoplastic because of its advantageous properties over polymers such as polyethylene, raw material cost, and ease of manufacturing [92].

Isotactic polypropylene is one of the main polymers in manufacturing-oriented film fibres and tapes. The material is commonly copolymerised with polyethylene for enhanced structural properties. Polypropylene represents roughly 7% of microplastics currently residing in the marine environment (Browne et al., 2011).

3.4. Acrylics (Resin ID 7- Other)

Poly(methyl methacrylate) (PMMA), also known as acrylic or acrylic glass, is a widely used engineering thermoplastic, useful for its optical qualities and is widely used as a substitute for glass due to its high impact strength, relatively lightweight and shatter resistance (Ali et al., 2015).

The PMMA monomer consists of a methyl ethylene backbone with a methoxycarbonyl functional group. The adjacent methyl group provides steric hindrance and prevents the material from crystallising, preserving its amorphous form and retaining a glassy structure. For this reason, acrylics are often used in applications previously occupied by glass.

Acrylics are thermally stable and resist UV light, making them a strong candidate for microplastic pollution, occupying 23% of estimated global quantities (Browne et al., 2011).

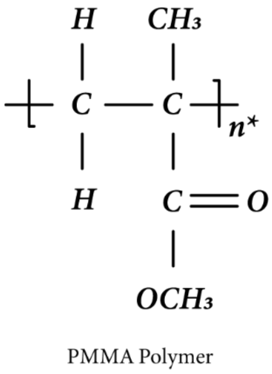
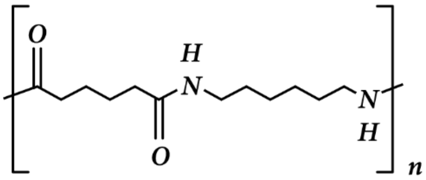
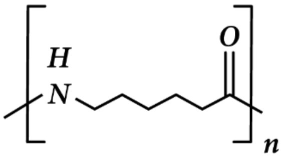
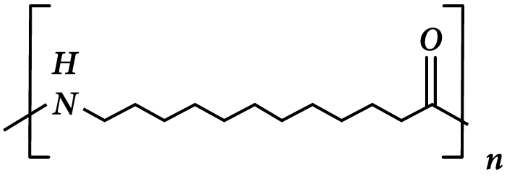


Figure 3 Chemical structure of PMMA (acrylic) resin

3.5. Polyamides (Resin ID 7-Other)

Polyamides are a group of fibrous thermoplastics most commonly known as Nylon. The material is widely applicable to the textiles industry and has been manufactured commercially for over 80 years at the time of writing (*Polyesters and Polyamides - Google Books*, n.d.). The main variants, Nylon 6 and 66, are the most common in commercial products worldwide. Nylon 6 is synthesised from diacid and diamine monomers, while Nylon 6 is produced from *caprolactam.* The number 6 in each variant's name refers to the number of carbon atoms in each monomer, with Nylon 66 being derived from two 6-carbon monomers initially (Shakiba et al., 2021). Extensively used for its mechanical properties, Nylon can be regularly found in clothes, moulded plastics, food packaging, and in many products in the biomedical industry due to its biocompatibility. The polymer is water absorbent, UV resistant and very chemically stable. For this reason, Nylon is frequently used in marine applications in nets and films and is regularly identified amongst mixed marine plastic litter, making up approximately 3% of the global microplastic volume (Browne et al., 2011). Depicted below are the structure of nylon 6 and 66.

Table 4 Chemical structure of Nylon 6, Nylon 66, and Nylon 12

Name	Chemical Structure
Nylon 66	
Nylon 6	
Nylon 12	

4. Plastic Additives

Almost all plastics for commercial use are treated with additives to enhance their properties; this is especially prevalent for enhancing thermo-physical characteristics. Polymeric substances suffer from low thermal resistance and tensile strength, properties helpful for forming but dangerous over extended periods in high-stress environments due to creep and fatigue. Plastic additives fall into several categories: plasticisers, impact modifiers, lubricants, stabilisers, thickeners, and flame retardants (Polymer Properties Database, 2019). Some common thermoplastic additives likely present in this study's materials is discussed below.

4.1. Plasticisers

Working with pure plastic resins can be difficult and prone to property degradation. This is often mitigated by either reducing molecular weight, blending with more workable polymers (Keitz et al., 1984; Zhou et al., 2007)or adding plasticisers. However, these methods often negatively affect plastic thermophysical properties, so a balance must be sought (Liang et al., 2011). Some common plasticisers variants include phthalic (Graham, 1973; Kozlov et al., 1962), benzoic (Gallez et al., 1976), trimellitic (Onu et al., 1976), and tritolyl phosphate (TTP) (Onu et al., 1976; Sundararajan et al., 2004).

4.2. Impact modifiers

Glassy plastics can suffer from physical ageing below their glass transition temperature (~150℃), leading to embrittlement of the product. This issue is mitigated by adding ductile and elastomeric materials to the matrix to increase ductility (T. W. Cheng et al., 1992). Some common impact modifiers include elastomers (Kanai et al., 1994; Li et al., 2016; Lin et al., 2019), block copolymers (C. Cheng et al., 1994), and core-shell rubbers (soft inside with a hard shell) (T. W. Cheng et al., 1992)

4.3. Lubricants

These additives (and plasticisers) improve the ease of plastic processing and reduce potential damage to equipment. External lubricants like fatty acids, paraffin, and polyethylene (low MW) reduce friction (Polymer Properties Database, 2019), whilst internal lubricants lower the bulk viscosity of the resin. Typical internal lubricants include oxidised polyethylene (Harding, 1996; Wolverton & Theberge, 2016), fatty acid esters and waxes (Štěpek & Daoust, 1983). Mould-releasing agents such as graphite/CNTs (carbon nanotubes) (Kausar et al., 2017; Richard Booser, 1993), silicone oils (Brown, 1993) and metallic oxides (Singh et al., 2020) may also be added to allow the formed plastic to slip free more easily from the mould.

4.4. Fillers

The bulk volume of plastics can be increased by adding inert mineral materials known as fillers. These additives usually take the form of inexpensive inorganic compounds, which contribute not only mass but also resistance to thermal expansion and increased heat deflection temperatures (Bose & Mahanwar, 2004; Demirer et al., 2018; Katz & Milewski, 2003; Polymer Properties Database, 2019; Stark & Berger, 1997). Joint fillers used in thermoplastics include calcium carbonate (Charde et al., 2018; Ghosh, 2022), kaolin (Jang, 2016), mica (Bose & Mahanwar, 2004; Pastorini & Nunes, 1999), silica (Kodali et al., 2021; Luyt et al., 2011), glass (Kuram, 2019), carbon black (Hilarius et al., 2013; Krueger & King, 2003), and alumina (Patel et al., 2013). Fillers can be mixed with colourants or selected based on the appearance of the extruded plastic product; TiO_2, for instance, is often added to give the surface of resins an enamel-like appearance (Yu et al., 2009).

4.5. Stabilisers

Additive compounds are often included in thermoplastics which slow down the process of material degradation by heat, oxidising agents and radiation. Antioxidant stabilisers can come in the form of free-radical scavengers such as sterically hindered phenols or peroxide scavengers, such as TTP (Wiles & Carlsson, 1980; Zweifel, 1998). Radiation damage can be mitigated by resin treatment with light stabilisers and UV light absorbers to prevent photocatalytic decomposition. Polycarbonate is moderately photostable and does not require extensive photo stabilisation in typical outdoor environments (Feldman, 2002).

4.6. Thickeners

The ideal rheological properties of plastic resins can be achieved by adding exogenous polymers containing salt-forming or hydrophilic (in aqueous solutions) functional groups that encourage crosslinking or networking, hindering intermolecular sliding mechanisms (Mussard, 2007; Polymer Properties Database, 2019). Alternatively, thickeners can create three-dimensional networks by interacting with hydrophobic functional groups (Aubry & Moan, 1997; Mussard, 2007). Volume-exclusion thickeners can also increase viscosity by swelling upon introducing a specific solvent (Zhu et al., 2018).

4.7. Flame Retardants

Flame retardancy, the tendency to reduce flammability, is typically increased by adding exogenous compounds to the polymer matrix. Retardants are classified as either organic or inorganic. Common organic flame retardants are usually composed of brominated or chlorinated compounds (Georlette et al., 2000; J. Green, 1994; Levchik & Weil, 2006), the efficacy of which increases with relative halogen content. Organophosphates and organophosphonates also regularly feature in flame retardant additives (J. Green, 1994; Levchik & Weil, 2005; Y. Z. Wang et al., 2003). Popular inorganic flame retardants include aluminium hydroxide (ATH) and magnesium hydroxides (which decompose into metal oxides and water endothermically) (J. Green, 1996; Rakotomalala et al., 2010; Stinson & Horn, 1995), zinc borate (J. Green, 1996; Yang et al., 2013), antimony oxides (Jadhav & Jhabarmal, 2018; Levchik & Weil, 2005; Morgan & Gilman, 2013), and hydromagnesite (Jadhav & Jhabarmal, 2018; Morgan & Gilman, 2013).

5. Banned and Tracked Additives Lists and Conventions

Source	**Name**	**Institution**	**Scope**	**Comment**
(*The Red List - International Living Future Institute*, n.d.)	ILFI- Red List & Watch List	International Living Future Institute	Global-NGO	List of most harmful materials in the building industry
(*Annex III Chemicals*, n.d.)	Rotterdam Convention	UN	Global	Treaty of banned substances for exporting and importing
(*Listing of POPs in the Stockholm Convention*, n.d.)	The Stockholm Convention	UN	Global	Treaty set to eliminate, restrict and reduce the presence of Persistent Organic Pollutants (POPs)
(*Plastic's Toxic Additives and the Circular Economy*, 2020)	IPEN List of Substances of Concern	IPEN, UNEP	Global	Guide to dangerous plastic additives
(*Plastic Additives Initiative Supplementary Information on Scope and Methods*, 2019)	European Chemical Agency Plastic Additive Initiative List	ECHA	Europe	List of hazardous plastic additives
(*How to Access the TSCA Inventory | US EPA*, n.d.)	USEPA TSCA Non-Confidential Chemical Inventory	USEPA	USA	List of deemed toxic substances by the USEPA
(*About Us – HBM4EU – Science and Policy for a Healthy Future*, n.d.)	EU Human Bio-Monitoring Agency List of Hazardous Substances	HBM4EU	Europe	List of candidates for potential substance bans in EU
(*Candidate List of Substances of Very High Concern for Authorisation - ECHA*, n.d.)	ECHA List of Substances for Very High Concern	ECHA	Europe	List of worst substances for tracking and potential banning in EU

Microplastics

6. Definitions and Categorisation

Microplastics (MPs) are now well established as a significant environmental pollutant most commonly observed in marine and coastal ecosystems. The term 'microplastic' has been broadly used to describe plastic particulates ranging from a few μm to 5mm in size (Cole et al., 2011; Shim & Thomposon, 2015; Thompson et al., 2019) resulting from inappropriate or negligent waste disposal and transport practices. Microplastics are often broken down by size class, as seen below in **Table 5.**

Table 5. Microplastic sub-classes (Andrady, 2017)

Class	Size ranges	Separation Technique
Macro	>25 mm	Visual Counting
Meso	1 - 5 mm	Neuston nets
Micro	1 – 1000 μm	Microfilters
Nano	<1 μm	Nano filters

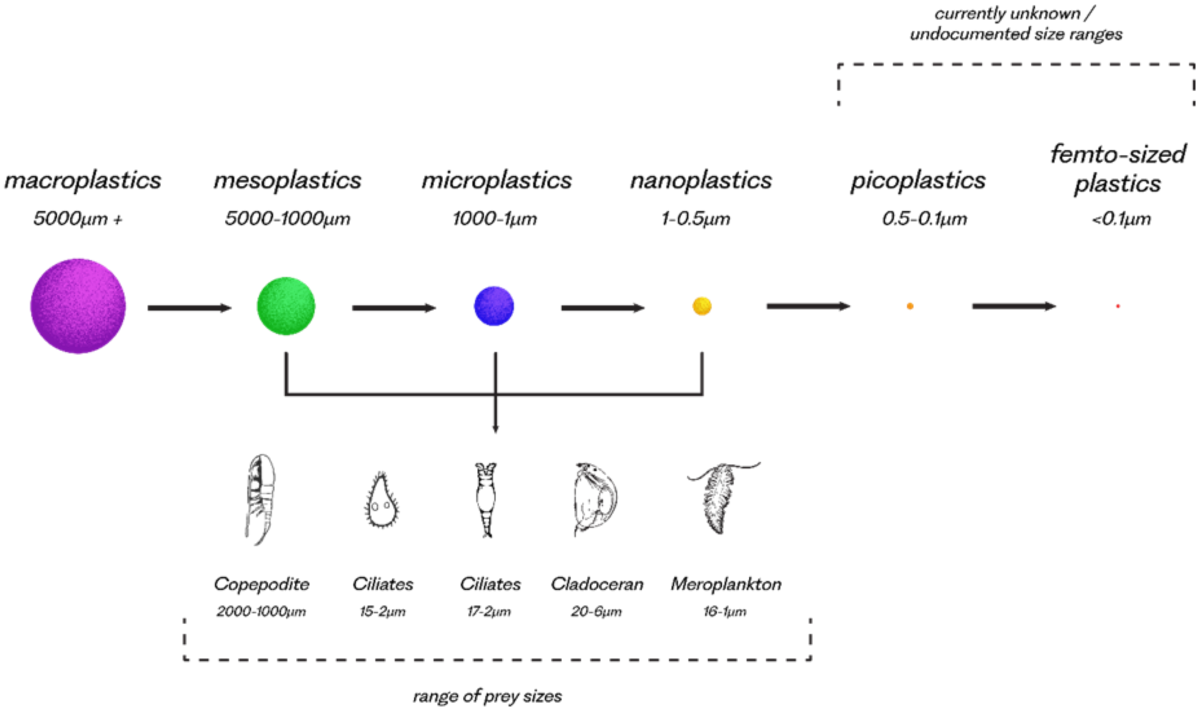


Figure 4 Microplastic size classification chart

For the present work, *microplastics* refer to those materials <5 mm.
MPs are also commonly categorised by their origins; *primary* MPs are industrially manufactured on a 'micro-scale' and enter the environment either post-consumer (such as exfoliants in personal care items or sand-blasting media (Kazour et al., 2019; Rochman et al., 2015) or accidentally via spills. The latter often comes in the form of 'nurdles', pelletised polymers transported for injection moulding and forming, which have been found ingested by marine organisms and colonised by harmful bacteria in some studies (Jiang et al., 2021; Rodrigues et al., 2019).The other, more numerous category is *secondary* microplastics, whose presence is derived from the

mechanical, chemical or photodegradation of more oversized plastic items to sub-micron sizes (Barnes et al., 2009). Both categories are problematic to various ecosystems, but the latter represents a severe challenge to tracking, cleaning and recycling efforts due to its largely unregulated and diverse sources.

7. Plastic Fragmentation and Breakdown Process

7.1. Mechanisms of Microplastic formation

The double-edged sword of plastics as a material class is their relative resistance to decomposition by various means. As has been widely understood, some polymeric materials can remain in environments and landfills for extremely long periods. Nonetheless, plastics are not infallible and will fragment by various means, described mainly as biotic and abiotic, the latter involving some biological process. The generally poor bioavailability of plastics typically means that the former category typically provides the initial means of fragmentation from macro to microplastic (<5 mm) sizes (Zhang et al., 2021).
Abiotic degradation pathways include changes in physical and chemical structures by mechanical means or environmental factors, including light, heat, and erosion by air and water. In the marine environment, where water and sunlight are particularly significant, photodegradation can occur by free-radical mediated reactions initiated by UV radiation. UV stabilisers, including phenols and antioxidants, can hinder these processes but leach additives into the environment (Zhang et al., 2021). This form of degradation of simple polymers like PE is far less than those with complex structures and active side groups like PVC, PS, and PET.

Biotic degradation of plastic occurs through interaction with living organisms in the environment. These processes typically occur either physically by biting or chewing or biochemically, as with some bacteria, insects, and fungi from Zhang *et al.* depicts the main degradation pathways from macro- to micro- plastic in the environment.

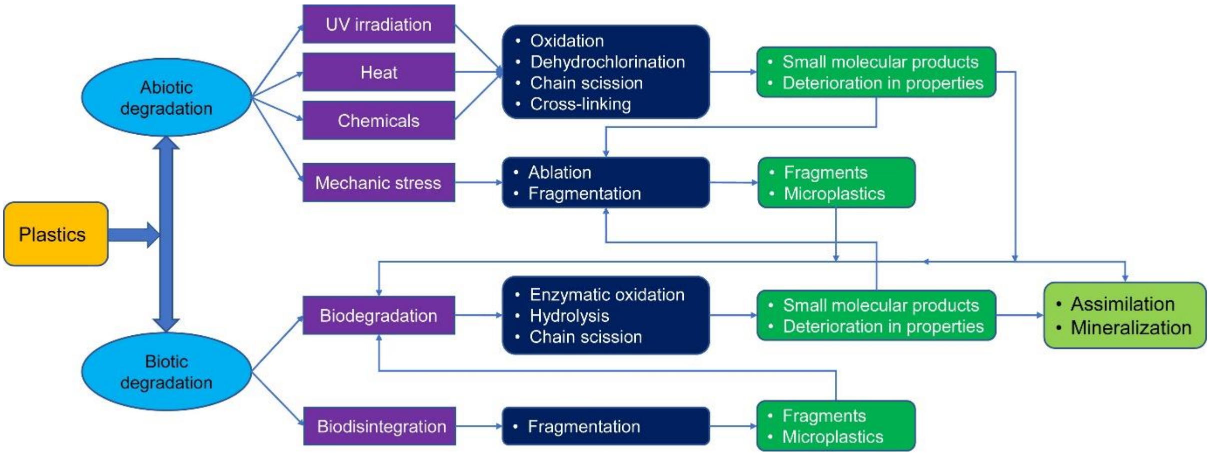


Figure 5 Pathways for degradation of plastics in the environment from Zhang et al.

The contribution of additives such as BPA, plasticisers and flame retardants to the degradation process in plastics is a significant gap in the literature, with some researchers observing that increased additive content relates to faster breakdown and leaching of additives due to interactions between UV radiation and the irregular surface morphologies of these materials (greater surface areas from light-absorbing imperfections facilitating more rapid reactions) (Sait et al., 2021). This relationship and the relationship between additive content at large is a relatively understudied theme of microplastic research.

7.2. 'Bioplastics' and their Breakdown

An increasingly popular range of alternatives to typical plastics like PE, PP, and PET are biodegradable or *bioplastics*. This class of materials is categorised less by common chemistry than as an umbrella term for the alternate range of these polymers. As such, there can be much confusion between bioplastics and bio-based plastics. The former is any polymer that can degrade biologically, resulting in theoretical CO_2 and H_2O endpoints.

Typical examples of biopolymers include polylactic acid (PLA) and poly(hydroxly-alkanoate) (PHA). Interestingly, the loose definition of biodegradable allows several petrochemical-based polymers to be included, such as polycaprolactone (PCL) and poly (butylene adipate-co-terephthalate) (PBAT) (Qin et al., 2021).

On the other hand, bio-based plastics are derived entirely from renewable origins; plants, animals, and microorganisms. They are most commonly derived from biofuel or bioethanol but are not necessarily biodegradable, as seen in examples like bio-PE and bio-PVC, which have the same properties as their synthetic counterparts (Qin et al., 2021). A graphical summary of the degradation steps of bioplastics is depicted below in **Figure 6** from the work of Qin *et al.* (Qin et al., 2021). As depicted, though the path of bioplastics may be more rapidly undertaken by organic means, the penultimate and most pertinent step to this report is the generation of microplastics, which inevitably find themselves alongside their synthetic counterparts in a myriad of environments.

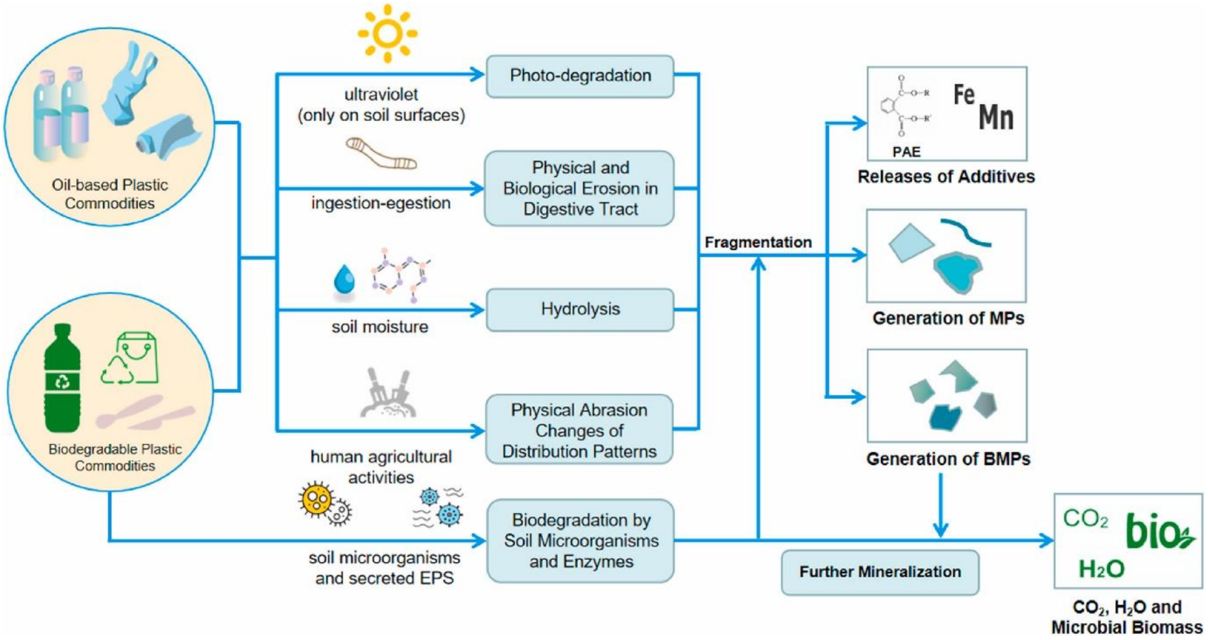


Figure 6 Comparative pathways for Oil-based and Biodegradable plastic commodities

8. Sources of Microplastics in the Environment

Microplastic wastes have accumulated in the environment through several pathways, which will be briefly summarised here. The first and most glaring source is the breakdown of larger plastic debris spilled into the marine environment via maritime activities or terrestrial effluent. The relative abundance of smaller particles in oceanic environments compared to coastal and intertidal regions suggests that fragmentation is a typical pathway for these materials (Browne, 2015) Crucial to this pathway is the density and hence relative buoyancy of plastic samples in the environment; the denser of the two is more prevalent on the sea floor. Hence monitoring must occur at various locations in the marine environment (Andrady, 2017). Fragmentation through mechanical means occurs distinctly from other, more subtle chemical means, including photolysis, hydrolysis and thermal oxidation (Andrady, 2015).

As mentioned above, cleaning products that use plastic abrasion as their primary exfoliation technique, be that cosmetic or industrial. Very little work has been done to quantify the extent of these plastics in the industry. However, some analyses on household cleaning products conducted by Fendall and Sewell (Fendall & Sewell, 2009) identified irregular particles ranging from 4-1200 μm, which certainly end up in marine environments via domestic drainage systems. Similar studies have yielded congruent results, identifying polyethylene and polystyrene microplastic particles, particularly as prevalent contributors to this source. That work found that the US could be emitting >250 t of micron-sized PE annually (Gouin et al., 2011; Zitko & Hanlon, 1991), though varied analysis still needs to be conducted on individual products to determine precise quantities of MP emissions from cleaning products (Browne, 2015).

A global survey completed by Browne *et al.* [17], of samples from sandy shores, sediment from sub-tidal zones, effluent from treatment plants and domestic washing machines revealed startling data concerning the prevalence of MPs in coastal environments. That study identified textiles as a significant contributor to global plastic waste and microplastics. Those experiments conducted on sandy shores globally identified primarily synthetic fibres of polyester (56%), acrylic (23%), PP (7%), PE (6%) and polyamides (3%) at numbers of up to 40 fragments per 250 mL of sediment in some locations. Analysis of former (pre-2000) sewerage treatment plants still contained more than twice the number of fibres than reference sites more than ten years on.

Alarmingly, experiments with washing machines identified that all garments (polyester shirts, blankets and fleeces were tested) washed released > 100 fibres per L of effluent, with fleeces releasing nearly 2000 per wash. Hence, domestic clothes washing may contribute to a large proportion of global microplastic pollution in marine environments. More recent studies have identified synthetic clothing as the number one contributor to microplastics worldwide (35%), followed by tyres and city dust, as seen below in **Table 6.** Adapted from Boucher and Friot (Boucher & Friot, n.d.).

Table 6 A categorical summary of global microplastic contributions

Source	Proportion (%)(Boucher & Friot, n.d.)
Synthetic textiles	35
Tyres	28
City dust	24
Road markings	7
Maritime coatings	3.7
Personal care products	2
Plastic pellets	0.3

Further recent data indicates that domestic clothes washing could contribute up to 308 mg of microplastics per kilogram of washed fabrics, most abundantly of 360-660 μm length, which can easily pass through typical wastewater treatment plants and into the marine environment (de Falco et al., 2019).

As mentioned above, rubber vehicle tyres have been estimated to contribute to over a quarter of the world's microplastic pollution. A recent study by Kole *et al.* (Jan Kole et al., 2017) found that per capita globally, the average person emits 0.81 kg of tyre waste into the environment annually. Car tyres were found to dwarf other sources of microplastics, including plane tyres, turf and road markings. The researchers also found up to 7% of particulate matter in the air comes from tyre wear and tear. Tyre wear and tear consists of mainly natural or synthetic vulcanised rubber (containing sulphur) with up to 40% carbon black or silica nanoparticles.

Microplastic particles from car tyres have been found to range from 10 nm-400 μm (Aatmeeyata et al., 2009; Dahl et al., 2006; Kreider et al., 2010), with the majority of those finding their way to waterways or into contact with living organisms where sub-micron particles, particularly, can pose respiratory and carcinogenic hazards (Jan Kole et al., 2017).

9. Impacts of Microplastics

9.1. Microplastic Toxicity

The wide varieties of fragmented plastic pose a nuanced yet widespread risk to lifeforms that come into contact with them. Organisms in aquatic, soil and airborne environments all have the potential for microplastic ingestion. The question then becomes, what are these interactions' outcomes and long-term effects? Toxicity should be investigated holistically, considering the direct impacts of both organic and inorganic emissions, including BPA, heavy metals, and plasticisers, as well as indirect emissions through the adsorption of secondary toxins onto their surfaces (C. Wang, Zhao, et al., 2021).

Several studies have already identified microplastic exposure in human subjects, particularly through oral ingestion of seafood (Dehaut et al., 2016) sugars (Liebezeit & Liebezeit, 2014), beer (Liebezeit & Liebezeit, 2013), and, most distressingly, in drinking water (Koelmans et al., 2019). Regarding ingestion, it has been estimated that through drinking water alone, the average person can ingest up to 9 particles per L of drinking water and 4000 individual MP fragments per L of PET-contained water, though the mass of the latter particles is considerably smaller (Eerkes-Medrano et al., 2019).

9.2. Impacts on Humans

The three main routes for the uptake of microplastics in the human body are skin contact, ingestion, and inhalation (Prata et al., 2020; Rahman et al., 2021). Dust and tyres contribute to most of the inhaled microplastics, while MPs accumulating in food and drinks lead to their ingestion and uptake in the digestive tract (Carbery et al., 2018). This pathway, however, is complex and interdependent on the network of environmental interactions that lead to this build-up. As such, few studies have successfully tracked the quantitative transfer of these materials from animals to humans. The human skin membrane is not porous enough for the transfer of micro/nano-sized particles to transfer through, but other orifices, including hair follicles, wounds, and sweat glands, may be sites for the dermal transfer of MPs (Schneider et al., 2009)

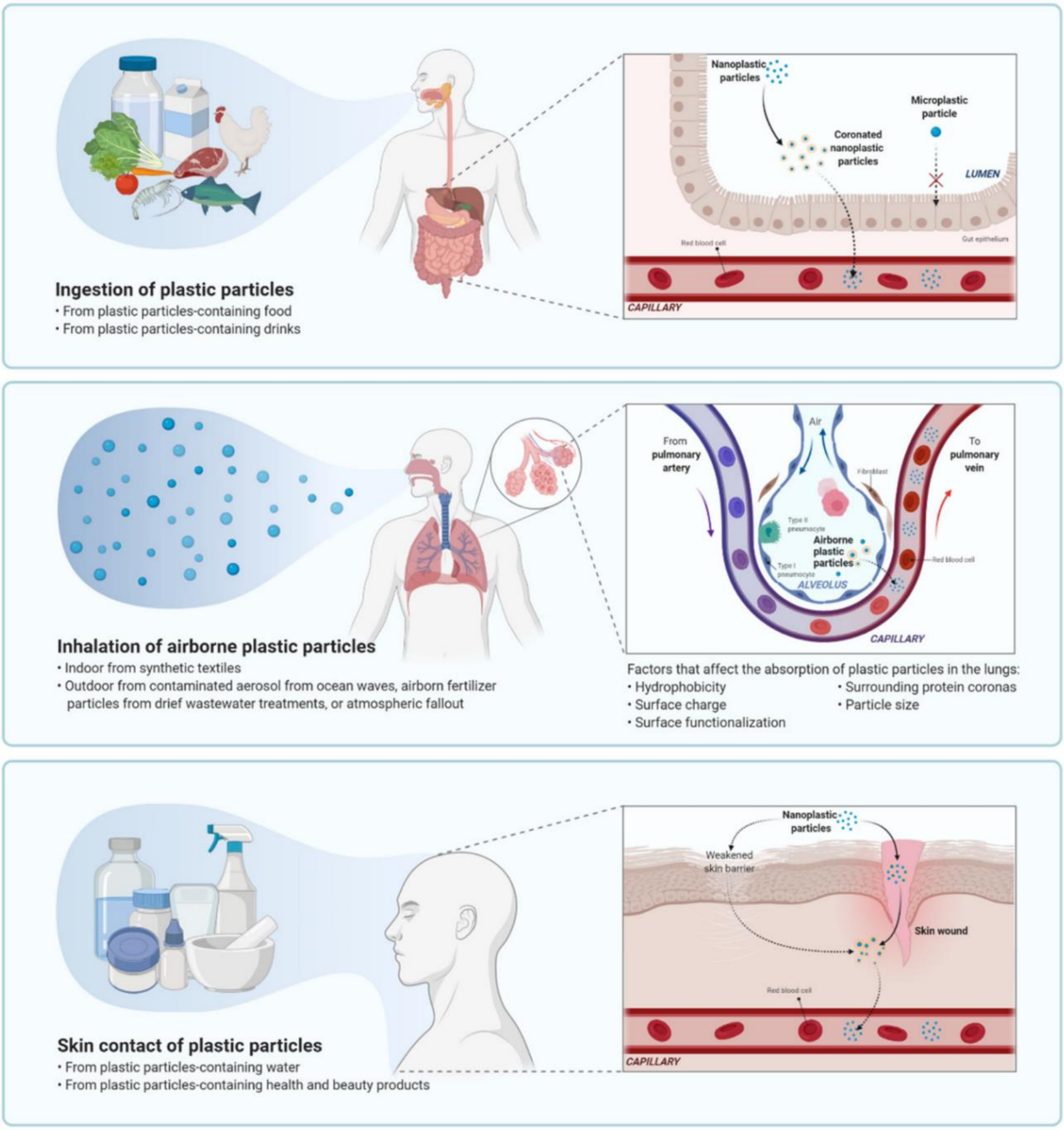


Figure 7 Pathways and sources of microplastics in the body (Swee-Li Yee et al., 2021)

MPs may be toxic even without leaching macromolecules into cells in the human body. The mere presence of these particles can cause oxidative stress, causing chronic inflammation and damage to sensitive tissues (Schirinzi et al., 2017) The size and shape alone of MPs may cause toxicity, with particles absorbed by the gastrointestinal tract (Doyle-McCullough et al., 2007), wherein they may translocate to other organs via the bloodstream, including the liver and spleen, when absorbed with particle sizes of up to 50 μm in some cases (Bellamkonda et al., 2021). Once they reach these target organs, they can cause tissue damage and severe inflammation (Schymanski et al., 2018; Wright & Kelly, 2017).

One significant hazard of plastic uptake into the human body is exposed to toxic additives, including bisphenol A (BPA), phthalates, and halogenated flame retardants. Leached BPA from plastics has been shown to influence the development of endocrine disorders (Koelmans et al., 2014; Rani et al., 2015). Furthermore, BPA has also impacted liver health, insulin resistance, and the fetus's health and development (Soriano et al., 2012). Such issues have been recorded at exposure concentrations as low as 0.2 ng mL^{-1} (Galloway, 2015)

9.3. Impacts on Animals

Numerous studies have detected microplastics in animals' digestive tracts, mainly fish and marine biotas. One study of fish and mussels caught off the coast of Chinese cities, Qingdao and Dongying, found plastic debris in upwards of 70% of sample organisms, with 1-4 fragments detected per animal on average (Ding et al., 2019). Another study estimated that up to 60% of fish worldwide contained microplastics internalised in their bodies at any time (Sequeira et al., 2020). Some collected impacts of microplastic exposure by marine organisms are summarised below in **Table 7,** adapted from work by Prata *et al*. (Prata et al., 2020).

Table 7 Impact of different microplastic exposure by marine organisms

Organism	**Plastic Species**	**Min. Effective Concentration (mg L^{-1})**	**Size (µm)**	**Impact**	**Source**
Chlorella Pyrenoidosa **(microalgae)**	PS	10	1-10	Reduced Photosynthetic activity	(Mao et al., 2018)
Daphnia Magna **(plankton)**	PE	12.5	1	Immobilisation	(Rehse et al., 2016)
	PS	0.01	2	Mortality	(Aljaibachi & Callaghan, 2018)
	Proprietary polymer	0.02	1-5	Reproduction impairment	(Pacheco et al., 2018)
	Proprietary polymer	0.1	1-5	Trans generationally reduced growth and reproduction	(Pacheco et al., 2018)
Mytilus **(mussels)**	HDPE	4.6 ×10^{5} fragments L^{-1}	1-50	Impacting homeostasis; increased energy expenditure	(Détrée & Gallardo-Escárate, 2018)
		0.8	0.5-316	Reduced attachment strength	(D. S. Green et al., 2019)
		1.5 ×10^{7} fragments L^{-1}	1-50	Impact on metabolic enzymes, induced antioxidant response	(Détrée & Gallardo-Escárate, 2018)
Dicentrarchus Labrax **(European seabass)**	Proprietary polymer	0.7	1-5	Neurotoxic, Cause oxidative stress, decrease swimming performance	(Barboza et al., 2018)

Besides these recorded impacts, however, little evidence has been found to describe bioaccumulation effects in these aquatic systems (Duis & Coors, 2016). Recently, some studies have identified instances of *trophic transfer* between prey and predator, namely in the cases of predatory fish (Welden et al., 2018), aquatic birds (Nelms et al., 2018), and captive seals (D'Souza et al., 2020), but with no evidence of accumulation.

The primary hazards of microplastics in biota are not due to their size. Instead, the surface characteristics of particles allow for the adsorption of pollutants or the release of dangerous monomers, including plasticisers, aromatic hydrocarbons, polychlorinated biphenyls, and cyclohexanes (Prata et al., 2021). These particles' high specific surface area allows an ideal environment for the growth of dangerous microorganisms, including some pathogenic species (Kirstein et al., 2016; Viršek et al., 2017). Furthermore, the adherence of organic particles to the surfaces of microplastic fragments can form biofilms, which, acting as an enhanced substrate, provide the foundations of a surface ecosystem (Michels et al., 2018; Zettler et al., 2013). This combination of microplastic and organic microbiota can lead to infections, changes to the host organism's gut microbiota, or potentially act as vectors for invasive species in new environments (Lu et al., 2019).

10. Managing Microplastic Pollution

10.1. In-Situ Sampling

Currently, best practices for analysing and managing are conducted manually and periodically through several sampling and filtration techniques suited to the analysis (Prata et al., 2019a). This literature survey has revealed a significant gap in continuous detection technology for MPs in aquatic and coastal environments (where they are most prolifically accumulated). Several recent works have used spectroscopic and other analytical techniques to identify MPs *in situ* or with minimal sample preparation.

Costa *et al.* (Costa et al., 2021) used particle fluorescence to detect microplastics on salt and sand particles. Using a spectrofluorometer and a pyrene probe, they observed linear increases in pyrene fluorescence as the non-polar particles migrated to like sites on polystyrene fragments, marking them. This technique detected MP quantities in concentrations of ~0.2 μg g^{-1} on sea salt particles. Another study by Erni-Cossola *et al.* (Erni-Cassola et al., 2017) using the same technique with fluorescent Nile Red dye, detected MPs (Nylon-6, PE, PP, PS) between 20-1000 μm in size in seawater and sediment samples.

One of the most significant challenges for rapidly detecting MPs is differentiation from organic and other inorganic particles. Colson and Michel (Colson & Michel, 2021) suggested a solution for this problem by conducting flow-through analysis using impedance spectroscopy. By comparing current signals through the spectrometer, the researchers could not only distinguish polymer (PE) beads from organisms and seeds of like scales (7 polymer samples, 6 organic, 2 seeds, from 200-1200 μm size) but also measure the size of the particles. Notably, this technique achieved a >90% particle recovery rate for microplastic flow and a 1% false positive rate for organic/plastic identification. This technique could prove to be an effective method for rapid microplastic analysis.

Another direct sensing method proposed by Asamoah *et al*. (Asamoah et al., 2019) used a portable optical sensor. By combining the specular reflection signal (from a photodiode) and interference patterns (from a CCD camera) of contaminated water, researchers could identify the species, size, and non-planarity of transparent PE and PET. Though simple and effective as a feasibility study, this technique was not validated for more complex suspensions of mixed MPs nor the differentiation of synthetic and organic materials. This technique only applies to transparent and translucent particles and has limited scope and applicability in the diverse macrocosm of microplastic pollution.

10.2. Sampling and Preparation for Further Analysis

There are various methods for taking environmental samples to assess the quantities and qualities of microplastic contamination. Understanding the extent of MP distribution (aside from being the focus of many studies) is critical for selecting techniques for taking samples. As succinctly summarised by Prata *et al.* (Prata et al., 2019a) in their widely cited critical review:

> *'Microplastic distribution is largely influenced by meteorological, temporal and geographical factors that may compromise the reproducibility of the results. On the other hand, methodology and quantity of sampled material may influence representativeness of results.'*

Hence, the sampling phase of any environmental analysis is critical to the experiment's outcomes. The researchers also highlighted the current inconsistency of data and information gaps regarding the lack of a standardised classification system and the inclusion of specific fibres or polymeric rubber, which are often excluded. Nonetheless, a summary of water and sediment sampling techniques is described in **Table 8**, adapted from Prata *et al.* (Prata et al., 2019a).

Table 8 Water and sediment sampling techniques for environmental analysis

Sample	Technique	Lower Detection Limit (μm)	Sample Size	Ease of Use	Cost	Equipment	Other Advantages/Disadvantages
Water	Neuston and Manta nets	333	Large	Easy	High	Boat Nets Tow Ropes	• The large yield of MPs
	Plankton Nets	100	Medium	Easy	High	Boat Nets	• Requires water flow • Cloggs / breaks easily
	Sieving	Custom	Medium	Easy to collect, laborious to sieve	Low	Sieves Buckets	• Time-consuming • Manual water transfer
	Pumps	Custom	Large	Effortless	High	Pumping equipment Constant energy	• It needs to be powered constantly • Apparatus contamination • Heavy equipment
	ex-situ filtration/sieving	Custom	Low	As tricky as *in situ* sieving with more transport	Medium	Filters/sieves Transport Sufficient containers for transport	• Time-consuming • Container/apparatus contamination
Sediment	Beach sediment collection	Nil	Large	Easy	Low	Tools to reach depth	• Density varies with depth
	Seabed collection	Nil	Medium	Easy	High	Boat Collection apparatus	• Variation with sample area and depth • Disturbs sediment surface

10.3. Managing Terrestrial Microplastics

One of the most significant literature gaps in MP research is their impact on terrestrial environments (de Souza Machado et al., 2018). This deficiency is a glaring issue considering that all measured marine microplastics were manufactured, used, and likely degraded somewhat on land. It is currently estimated that terrestrial MP contamination dwarfs that of marine by between 4 and 23 times in terms of volume (Horton et al., 2017). Some reasons for this inconsistency of research focus may be the ease of sampling in marine environments or observations that marine organisms may more likely come in contact with floating microplastics and ingest them than terrestrial ones. Regardless of the reason, terrestrial contamination has received far less research attention in this space.

Though many of the same management principles apply when discussing marine and terrestrial microplastics, their impacts differ considerably. Polymers have been found to interrupt the physico-chemistry of plant-soil networks due to the leaching of plastic additives, including endocrine disruptors such as phthalates and BPA (de Souza Machado et al., 2018). Smaller fragments with poor solubility can disrupt cell walls in organisms, affect membrane permeability, and induce oxidative stress. (Forte et al., 2016). Combined microplastic dispersion effects in soil could likely affect soil health and texture, an essential factor of the water cycling system and a fundamental building block of ecosystem health. (Bergmann et al., 2016). Many hydrophobic and amphophilic compounds facilitate a delicate interplay of communication and nutrient transport. The presence and structure of these organic compounds, often secreted by fungi, is crucial for soil stability and resistance to erosion (Rillig, 2005). It has been suggested that the interactions between hydrophobic microplastic surfaces and these compounds may alter soil structures effecting, environmental stability and organism health throughout the food chains (Hodson et al., 2017)

11. Analytical Techniques for Characterising Microplastics

As discussed above, there is no broad framework for the processing of potential microplastic samples. There is, however, a growing body of work dedicated to refining these processes, as seen in the graphic published in Prata *et al.'s* (Prata et al., 2019b) 2019 critical review of the subject. This work and other comparative and primary studies were used to inform the below assessment of best practices.

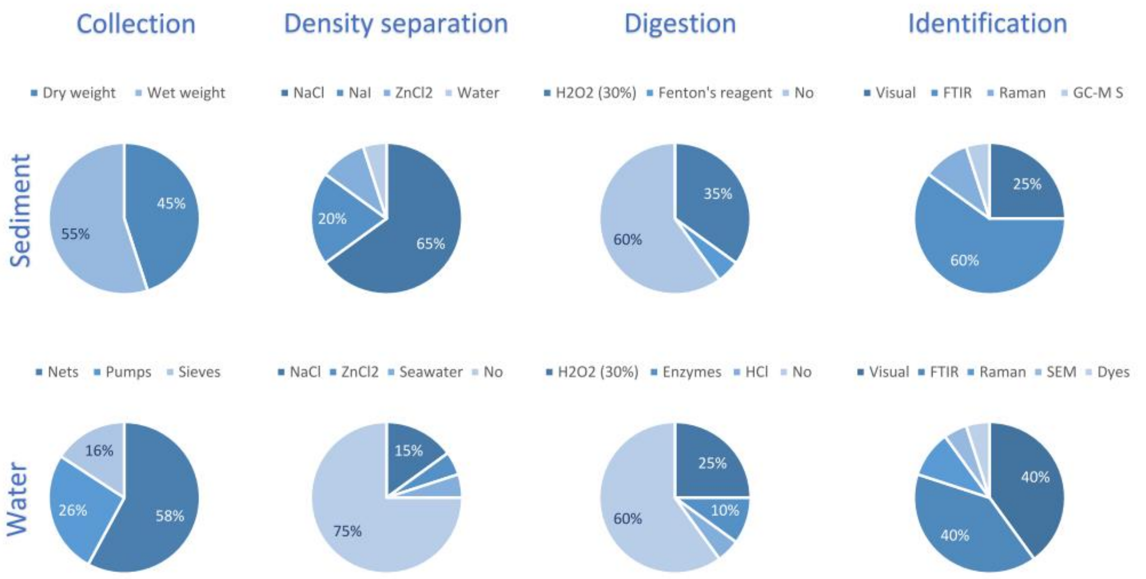
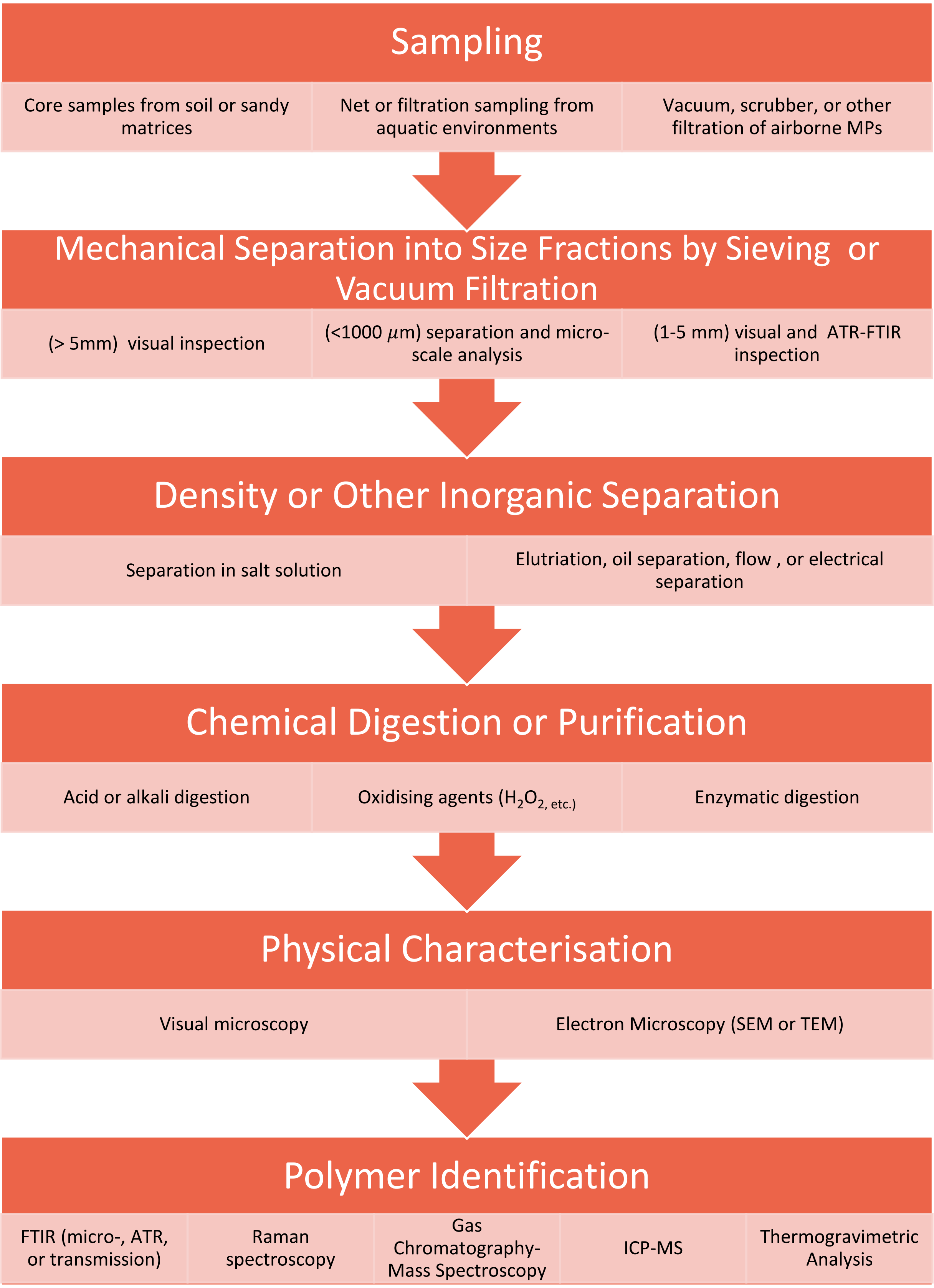


Fig. 1. Details from sampling methods reviewed from the literature for microplastics in sediment (top row, N = 20) and water (bottom row, N = 20) regarding collection, density separation, digestion, and identification.

First, we will discuss the various methods available for such characterisation work.

Much of the information in this section is collated from the below sources (Inc, n.d.-a, n.d.-b; Jung et al., 2021; Shim et al., 2017).

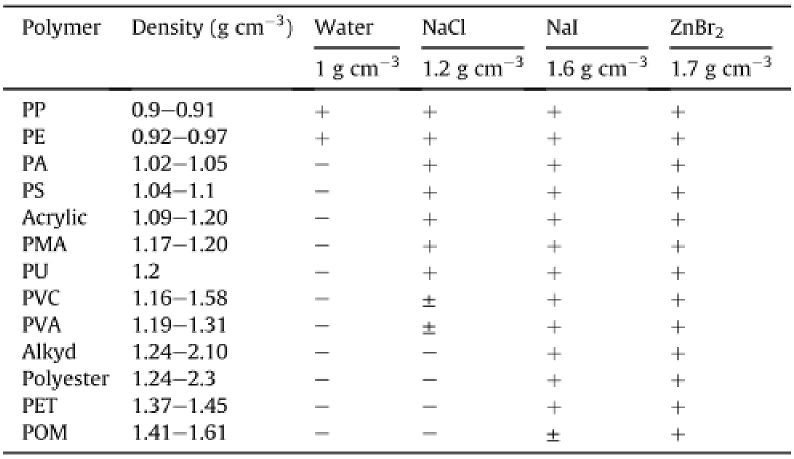
11.1. Typical Analytical Workflow for Microplastics



12. Detail of Microplastic Processing Techniques

12.1. Separation and Purification Techniques

Experiments undertaken by the authors have confirmed the need for further purification steps after mechanical separation techniques. First-hand work conducted using only sieving as a separation technique resulted in imprecise measurements of plastic components in FTIR analysis. For instance, a micro-FTIR analysis of 100 collected sediment particles may yield 1 PET particle, and some false negatives of organic polymers detected as synthetics. Removal of silt, and organic particles, increases the relative proportion of detectable polymers in any given sample of remaining particles. Prata *et al.* (Prata et al., 2019b) recommended the use of a dense salt solution by which to float out relatively light polymeric materials from the sampled matrix. The choice of such a salt for preparing this solution is crucial as not to sink relatively dense plastics such as PET. For this reason, salts such as NaI and ZnCl, are favoured over NaCl, though each comes with it, cost and hazard considerations, with these dense salts being highly toxic. The below table, taken from the review, (Prata et al., 2019b)provides a guideline for the applicability of some salts to separate target polymers. As such, sodium iodide salt is recommended for this application.



Polymer	Density (g cm^{-3})	Water	NaCl	NaI	$ZnBr_2$
		1 g cm^{-3}	1.2 g cm^{-3}	1.6 g cm^{-3}	1.7 g cm^{-3}
PP	0.9–0.91	+	+	+	+
PE	0.92–0.97	+	+	+	+
PA	1.02–1.05	−	+	+	+
PS	1.04–1.1	−	+	+	+
Acrylic	1.09–1.20	−	+	+	+
PMA	1.17–1.20	−	+	+	+
PU	1.2	−	+	+	+
PVC	1.16–1.58	−	±	+	+
PVA	1.19–1.31	−	±	+	+
Alkyd	1.24–2.10	−	−	+	+
Polyester	1.24–2.3	−	−	+	+
PET	1.37–1.45	−	−	+	+
POM	1.41–1.61	−	−	±	+

Organic components may then be selectively removed by acid, alkali, or enzymatic digestion, though this step may degrade target polymers depending on individual chemical interaction. Nitric and hydrochloric acids have been utilised to this affect but each have been recorded as impacting the final quality or population of original microplastics found in sample matrices (Prata et al., 2019b). Sequential acid and alkali (HCl and NaOH) treatment has been found to provide good material recovery rates and digestion of organic particles.
Alternatively, treatment of samples with H_2O_2 (up to 35%) has been found to efficiently remove organics from particle matrices, at better rates than acid and alkali digestion in some cases (Prata et al., 2019b).

12.2. Analytical Techniques

Visual Identification

Collection, sorting and identification of plastics are performed on beaches with a tray, forceps, and naked eyes.

Advantages

- Simple, fast, and easy
- Allows identification of colourful plastics from other materials and contaminants.

Limitations

- Sorting is limited to a sample size range of 1 – 5 mm
- Confusion when plastics' colours are similar to the interfering organic or inorganic particles
- High possibility of false identification
- High possibility of missing small and transparent plastic particle
- No polymer composition data
- No chemical confirmation
- Does not allow identification of the type of microplastic/polymer.

Optical Microscopy

Observation of magnified microplastic particles was performed using an optical microscope. The maximum magnification level of an optical microscope is 1000x.

Advantages

- This technique is ideal for microplastics whose size falls in the hundreds of micron range. This method provides detailed surface texture and structural information, especially for identifying ambiguous plastic-like structures.

Limitations

- Microplastic sizes < 100 microns with no colour and typical shape are still challenging to characterise with confidence as plastic
- Sediment particles not entirely removed by chemical digestion also make microscopic observation difficult
- No chemical confirmation
- High possibility of false identification (i.e., between coloured plastic and coloured cotton fibre)
- High possibility of missing small and transparent plastic particle
- No polymer composition data
- Do not allow identification of microplastic/ polymer type.

SEM+EDS

Very high-resolution (up to 10^6 magnification) images can be generated from the interactions between accelerated electrons and the target material's physical structure. EDS measurement analyses the resultant x-rays emitted from the material to determine its elemental makeup.

Advantages

- Provide higher magnification which allows further detailed surface texture and structural information
- Higher magnification facilitates the discrimination of microplastics from organic particles
- EDS provides the elemental composition of the same object and helps identify carbon-dominant plastic with inorganic particles.

Limitations

- SEM/ EDS is expensive
- The colours of plastic cannot be used as identifiers in SEM (The image in SEM is black and white)
- Only elemental data is generated by EDS (i.e., No detailed polymer composition data)
- Heterogenous materials often result in inaccurate data
- Nonconductive samples may need to be coated with a conductive film, usually resulting in the analysis being destructive
- The technique does not allow the identification of microplastic/polymer types.

TGA

Thermogravimetric analysis (TGA) monitors a material's thermal stability and the fraction of volatile compounds. It measures the mass change of samples as a function of thermolysis temperature to quantify the volatile compounds, and the derivative of the mass-change curve determines the mass-loss rate.

Advantages

- Allow identification of the plastic based on the different thermolytic profiles each plastic material exhibits.

Limitations

- The mass change curve and differential thermogram (DTG) curves of some plastics partially overlap between 300-500℃, which may result in a high possibility of errors in the identification
- Organic materials such as biological matter, plants, and soil components, which are volatilised at the plastic temperature range, may affect the results
- Analysis is destructive.

DSC

Differential Scanning Calorimetry measures the small thermodynamic changes occurring within a sample when heated in an inert environment. When a phase change occurs between a solid and a liquid, additional latent heat is required in the sample compared with the blank reference. The different heat requirements of the sample and reference holders during phase change provide information on the glass transition region, crystallisation, and melting temperatures of polymeric materials.

Plastics can be identified by comparing these thermolytic profiles to the established libraries. Different plastic materials exhibit specific thermolytic behaviours in a broad temperature range, allowing for the identification of specific types of plastics

Advantages

- Confirmation of plastic types
- Allows identification of the plastic based on the different thermolytic profiles each plastic material exhibits
- Highly sensitive to small particles.

Limitations

- Applicable to identify only a few types of plastics, mainly PE and PP. Other plastics (i.e., PET, PA, PES, PVC, PU) are hard to distinguish due to the overlapping thermolytic profiles of plastics
- High possibility of errors in the quantification of the plastic fraction in environmental samples
- Destructive analysis.

FTIR

FTIR uses infrared radiation to excite the vibrational modes of chemical bonds in a sample, producing an absorption spectrum that can identify the chemical bonds present and distinguish nano plastics from other particles.

A well-established polymer spectrum library enables not only the confirmation of plastics but also the identification of specific polymer types. FTIR spectroscopy provides information on the specific chemical bonds of particles. Carbon-based polymers are easily identified by this method, and different bond compositions produce unique spectra that discriminate plastics from other organic and inorganic particles.

Advantages

- Allow accurate identification of microplastic from organic and inorganic materials.
- Allow identification of polymer types based on the different unique spectra each different plastic/polymer produces.
- No possibility of false data by chemical confirmation of all the plastic-like particles
- Non-destructive analysis
- Detection of down to 10-micron plastic in size

Limitations

- Expensive instrument
- Laborious work and time consuming
- Aggregated plastic may be counted together (complex spectrum)
- Irregularly shaped plastics may produce refractive errors in the reflectance mode (complex/ false spectrum)
- Microplastic <100 microns may require more time for identification by ATR-FTIR
- An experienced operator is required to interpret the spectra accurately, especially with weathered plastic that may have low hitting potential in the FTIR library
- ATR-FTIR measurement is a form of surface contact analysis. The pressure produced by the ATR probe may damage highly-weathered microplastic. Sharp inorganic particles can also damage ATR probes

- Unable to identify micro and nano-plastic with a size of fewer than 10 microns
- It may require proper separation of plastics from environmental samples.

Raman Spectroscopy

This technique uses a laser beam contacting the particle surface, generating different frequencies of back-scattered light depending on the molecular structure and atoms present, which produce a unique spectrum for each polymer. Raman analysis not only identifies plastics but also provides profiles of the polymer composition of each sample similar to FTIR.

In terms of the combination of non-destructive chemical analysis with microscopy, Raman spectroscopy is comparable to the FTIR method, including the requirement for expensive instrumentation. The different responses and spectra between FTIR and Raman spectroscopy from a microplastic can compliment each other in complex microplastic identification. The smaller diameter of the laser beam in Raman spectroscopy relative to FTIR allows the identification of microplastics down to a few μm in size.

Advantages

- Unlikely false positive results by chemical confirmation of all the plastic-like particles
- Reduction of false negative data
- Non-destructive analysis
- Non-contact analysis
- Detection of down to 1-micron plastic in size.

Limitations

- Expensive instrument
- Laborious work and time-consuming for whole particle identification
- Interference by pigment
- Unable to identify micro and nano-plastic with a size of less than 1 micron
- The laser can burn sensitive samples.

Pyrolysis-Gas Chromatography-Mass Spectroscopy (GC-MS)

Pyro GCMS generates information on the chemical identity of polymers through characteristic degradation products using fingerprint chromatography. This technique breaks down heat-liberated off-gases from the thermally transforming material into fragments identified based on their mass/electrochemical charge ratios. This technique allows for the detection of plasticisers and other additives.

Advantages

- Able to identify and quantify the polymer types of microplastic accurately
- Able to analyse additive chemicals within microplastic
- Bulk samples can also be analysed, providing summed microplastic concentration data by weight
- Able to quantify microplastic polymers in complex environmental and biological samples, including soil, water and marine organisms
- Detection below 1-micron plastic, which include micro and nano plastics.

Limitations

- Expensive instrument

- Requires well-trained and experienced operators
- Laborious work and time-consuming for instrument runs and data processing compared with FTIR and Raman spectroscopy
- Complicated process
- Complex chromatogram profiles of environmental samples
- Lack of enough data library
- Destructive analysis.

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