November 2023

ADDRESSING MICROPLASTICS IN ALTERNATIVES ASSESSMENT

A White Paper by the Sustainable Chemistry Catalyst
of the Lowell Center for Sustainable Production at UMass Lowell

www.sustainablechemistrycatalyst.org

AUTHORS

Aude Bechu and Molly Jacobs

ACKNOWLEDGMENTS

The Sustainable Chemistry Catalyst is grateful to the following who provided review and comments on an early draft of this white paper:

- Saskia van Bergen, Marissa Smith, Rae Eaton and Sean Zigah, Washington State Department of Ecology
- Andres Baun, Technical University of Denmark
- Steffen Hansen, Technical University of Denmark
- Lauren Heine
- Colleen McLoughlin, Enhesa
- Treye Thomas, U.S. Consumer Products Safety Commission
- Margaret Whittaker, ToxServices

This work was funded in part by the United States Environmental Protection Agency under assistance agreement PC-01J95801 to the Washington State Department of Ecology. The contents of this report do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABOUT

The Sustainable Chemistry Catalyst is an independent research and strategy initiative, based at the Lowell Center for Sustainable Production within UMass Lowell, that is focused on accelerating the transition to safer, more sustainable chemistry through research and analysis and stakeholder engagement with scientists, policymakers, and commercial actors.

Sustainable Chemistry Catalyst
University of Massachusetts Lowell
Lowell Center for Sustainable Production
600 Suffolk Street, Lowell, MA 01854
(978) 934-2997
www.sustainablechemistrycatalyst.org | www.uml.edu

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List of Abbreviations

6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
ABS	Acrylonitrile Butadiene Styrene
DEHP	Di(2-ethylhexyl) phthalate
ECHA	European Chemical Agency, which administers REACH.
ENM	Engineered Nanomaterials which are "materials in any external dimension in the nanoscale or with an internal surface structure at the nanoscale, which is 1 to 100 nanometers" (ISO, 2008).
EPA	U.S. Environmental Protection Agency, which administers TSCA.
GHS	Globally Harmonized System for the Classification and Labeling of Chemicals
HPDE	High density polyethylene
IC2 Guide	Interstate Chemicals Clearinghouse's (IC2) Alternatives Assessment Guide (2017).
LCA	Life Cycle Assessment is "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle"(European Commission, 2021)
LDPE	Low density polyethylene
OECD	Organization for Economic Cooperation and Development.
PAH	Polycyclic aromatic hydrocarbons
PAN	Polyacrylonitrile
PBDEs	polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl chloride
QSAR	Quantitative Structure Activity Relationship.
REACH	Registration, Evaluation and Authorization of Chemicals legislation, which regulates substance (chemical and nanomaterial) manufacturing and use in the European Union.
UNEP	United Nations Environment Program

Introduction

Supporting the transition to safer and more sustainable chemicals and materials requires minimizing the chance of a regrettable substitution. Alternatives assessment is defined as a "process for identifying and comparing potential chemical and non-chemical alternatives [e.g., materials, products, technologies] that could replace chemicals of concern on the basis of their hazards, performance, and economic viability" (National Research Council, 2014).

An array of plastic products has been presented as potential alternatives to chemicals of concern in recent alternatives assessments. For example, Washington State Department of Ecology examined other plastics as alternatives to per and polyfluorinated alkyl substances (PFAS) coatings used in food packaging applications (Washington State Department of Ecology, 2022). The assessment noted the potential for polymeric materials to form microplastics when considering exposure pathways. This potential to form microplastics led assessors to conclude that not enough information was available to complete the exposure assessment and therefore the plastic alternatives were discounted from further consideration.

This Washington alternatives assessment identified a gap in the field—existing alternatives assessment frameworks and guidance documents have not outlined methods for addressing microplastic formation and associated contamination. Microplastics can either be intentionally added to products, or generated during manufacturing, use, or as plastic products degrade during end of life. *Intentionally added* microplastics, such as the use of microbeads in personal care products and cosmetics, have been banned or are expected to be banned in multiple jurisdictions, including in the United States (US) and the European Union (EU) (114th US Congress, 2015). Although there are additional industrial uses of intentionally added microbeads that remain unregulated, impacts associated with *unintentionally generated* microplastics are gaining recognition given the significant production and consumption of plastics globally (OECD, 2022).

The Sustainable Chemistry Catalyst at the University of Massachusetts Lowell was asked by the Washington State Department of Ecology to propose considerations for addressing unintentionally generated microplastics within alternatives assessments. To support these considerations, this white paper first provides a brief primer on microplastics. Next, the paper outlines specific considerations for a model alternatives assessment framework, the Interstate Chemicals Clearinghouse's (IC2) Alternatives Assessment Guide (IC2 Guide, 2017). Although this paper focuses on adaptations to the IC2 Alternatives Assessment Guide, suggested approaches for addressing microplastics formation are generalizable to all alternatives assessment frameworks. Recommended considerations focus on specific components within the alternatives assessment approach including: (a) identifying potential alternatives, (b) hazard assessment, and (c) comparative exposure assessment. These infuse lifecycle thinking within these assessment components versus relegating considerations for microplastics to a separate lifecycle considerations module, which is considered optional in several alternatives assessment frameworks, including the IC2 Alternatives Assessment Guide. Recommendations in this white paper were informed by a literature review on microplastics and consultation with alternatives assessment and microplastics experts. The literature review is presented in **Appendix A**; readers are encouraged to consult this Appendix for additional background information.

Background

The production and consumption of plastics have resulted in extensive pollution of the natural environment with plastic debris. Plastic pollution contributes to ‘novel entities pollution’, one of the nine planetary boundaries. Researchers recently concluded that this ‘novel entities pollution’ planetary boundary has been crossed, creating high risks for humans and ecosystems (Persson et al., 2022). Widespread concern over plastic and microplastics pollution has spurred international dialog to adopt mitigative measures to alleviate this global crisis (UNEP, 2022a).

Among this plastic debris are microplastics, which are either intentionally added to products, generated during product use, or generated after a products disposal into the environment. Microplastics are globally pervasive pollutants, having been found in nearly all environments investigated including terrestrial (Dissanayake et al., 2022), marine and freshwater ecosystems (Horton et al., 2017; Obbard, 2018) as well as drinking water (Koelmans et al., 2019; Pivokonsky et al., 2018), air (O'Brien et al., 2023) and food (Bouwmeester et al., 2015; Conti et al., 2020).

Plastics use doubled from 2000 to 2019 (234 Mt to 460 Mt), outpacing growth in steel, aluminum, and cement (OECD, 2022). Given the growing use of plastics, concentrations of microplastics in the environment are expected to increase as it is nearly impossible to remove these persistent pollutants once dispersed throughout ecosystems (Geyer et al., 2017; Jambeck et al., 2015).

There is no universally accepted definition of microplastics, but microplastics are generally defined as plastic particles <5mm (OECD, 2021). The European Commission and California have defined microplastics as solid particles (California State Water Resources Control Board, 2020; ECHA, 2020). Some definitions have established a minimum size of microplastics at 1nm, while other organizations do not place minimum sizes (California State Water Resources Control Board, 2020; ECHA, 2020). Nanoplastics also have no universally accepted definitions. For example, the upper limit of sizes of nanoplastics has been proposed at 1000 nm and 100 nm ((EC, 2023b).

Microplastics are derived from plastic materials, but like above, there is no universally accepted definition of plastic. According to the European Commission, “plastics are usually defined as polymeric materials to which additives may have been added” (EC, 2019). This definition does not include unmodified polymers that occur naturally in the environment, such as proteins (EC, 2019). Polymers are substances that are made up of repeating monomers with varying molecular weights (ECHA, 2023). These are complex materials composed of base polymers, additives, and potentially unreacted monomers. The majority of plastics production is centered on six polymers: polypropylene (PP), low-density polyethylene (LDPE), high density polyethylene (HDPE), polyvinylchloride (PVC), polystyrene (PS), polyethylene terephthalate (PET), polyurethane (PUR) and focused on various applications, such as packaging, construction materials and textiles (see Figure 1). A recent analysis of chemicals in plastics found over 13,000 chemicals associated with these materials, with over 3,000 of these chemicals being chemicals of potential concern (UNEP, 2023). For example

- Bisphenol A is commonly used as a plasticizer in plastics such as polycarbonates. It is endocrine active and associated with a range of adverse health outcomes, including carcinogenicity, metabolic syndromes, reproductive toxicity among others (Vom Saal & Vandenberg, 2021).

- Di(2-ethylhexyl) phthalate (DEHP) is commonly used as a plasticizer in poly(vinyl) chloride (PVC). It is known to cause reproductive toxicity (Shinohara & Uchino, 2020).
- N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) is used to protect rubber against ozone and oxygen. 6PPD transforms in the environment into a 6PPD-quinone, a compound that is acutely toxic to certain salmonoid species (Tian et al., 2021).

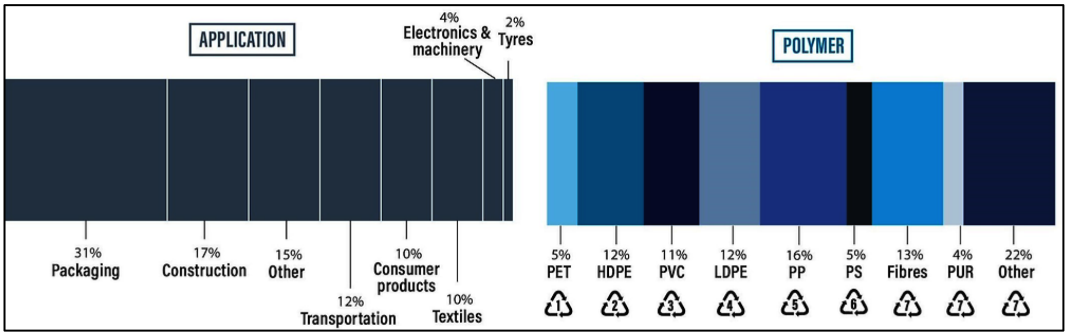

Figure 1: Percentages of application and plastic polymer globally, estimated by the OECD Global Plastics Outlook Database (2022, Figure 2.4 reproduced above).

Unintentionally generated microplastics (the focus of this white paper) originate from the degradation of larger plastic material, which primarily occurs during the end-of-life stage of plastic products but can also be associated with manufacturing and use stages. Physical, biological, and chemical degradation processes change the structural integrity of the plastic. Researchers have described three primary plastic degradation processes, including fragmentation, depolymerization and bioassimilation. of polymers (Colwell et al., 2023). For example, microplastics can be formed through fragmentation by physical abrasion, such as through continuous cutting on plastic culinary cutting boards, through the abrasion of synthetic textiles during laundering, or through the physical forces of waves, sand, and wind on a beach (Auta et al., 2017; Yadav et al., 2023). Exposure to ultraviolet radiation from sunlight promotes oxidation of the polymer matrix leading to a breakdown of the material (Andrady et al., 2022). The half-life of microplastics is expected to be up to 1000 years, depending on the plastic type (Koelmans et al., 2022).

Soluble products (such as monomers, dimers and oligomers) from the depolymerization process support bioassimilation – essential for plastics considered as biodegradable. According to the Group of Scientific Advisors to the European Commission, biodegradable plastics are defined as "the microbial conversion of all its organic constituents to carbon dioxide, new microbial biomass and mineral salts under oxic conditions [in the presence of oxygen] or to carbon dioxide, methane, new microbial biomass and mineral salts under anoxic conditions [in the absence of oxygen]"(European Commission, 2020). Biodegradation is dependent on a number of factors, such as relevant microbes being in close proximity to the soluble products so that they can be consumed and the presence of specific membrane carriers for cellular uptake. Solid polymers considered biodegradable will also degrade into microplastics. However, if the appropriate bioassimilation factors are present, the time in a microplastics stage is expected to be shortened as shown in Figure 2 when comparing lifetimes of polyethylene and polyhydroxyalkanoate, the latter of which is considered a biodegradable polymer (Colwell et al., 2023).

Transition States	Lifetime		
	Polyethylene (PE)	Polylactic Acid (PLA)	Polyhydroxyalkanoate (PHA)
Macro- and mesoplastic	Months to years	Months to years	Weeks to months * $r_D \approx r_B > r_F$
Micro- and nanoplastic	Hundreds of years * r_D *very slow*	Years * $r_F >> r_D$	Days to weeks
Soluble Products	Weeks to months	Weeks to months	Hours

*Figure 2: Plastic states and approximate lifetimes in natural environments for three plastic films; *Most persistent state. Figure reproduced directly from Colwell et al. 2023.*

Common sources of microplastics have been identified, including plastic packaging, synthetic textiles, cigarette filters, tires, agricultural plastic films (such as mulching films) and a variety of consumer products (Kershaw & Rochman, 2015; Li et al., 2022; Moran et al., 2021). More recently, paint was recognized as an important source of microplastics (Landrigan et al., 2023). Plastic recycling, even with appropriate technology controls, can also be a source of microplastics into waterways (Brown et al., 2023). Unintentionally generated microplastics from textiles, cosmetics and household products are often washed down the drain entering municipal waste water treatment systems where they currently evade filtration and treatment options, and subsequently contaminate freshwater as well as agricultural areas where sewage sludge is applied (Rolsky et al., 2020).

Human biomonitoring studies reveal concerns in humans, such as microplastics found in human blood (Leslie et al., 2022), lungs (Jenner et al., 2022) and placenta (Ragusa et al., 2021), demonstrating concerns for systemic exposure. Research characterizing the microplastics that were found in human placenta identified the sources such as pigments from stained polypropylene and other pigmented polymers used in paints, nail polish, cosmetics and personal care products (Ragusa et al., 2021). Microplastics also have been found in the feces of babies at roughly a magnitude higher than found in the feces of adults (J. Zhang et al., 2021). Researchers suggested that this finding may be associated with use of plastic products, such as bottles, teethers and toys by babies. Microplastics have also been detected in indoor and outdoor air (Zhang et al., 2020). Although research in this domain is currently relatively new, indoor microplastics are mostly to synthetic fibers from furniture and clothing in household environments (Vianello et al., 2019). Estimates of human inhalation of microplastics currently exceed estimates of ingested microplastics (Cox et al., 2019).

Based on a recent review of the literature by researchers at the California Department of Toxic Substances Control, **Appendix B** outlines a selection of hazard and exposure concerns associated with microplastics from a range of parent polymeric materials. Although an understanding of health effects in humans is an under-researched area, *in vivo* studies documented that some forms of microplastics can cause inflammatory responses (Li et al., 2020), reproductive toxicity (Amereh et al., 2020; Xie et al., 2020), organ toxicity (Y.-L. Wang et al., 2021) and can disrupt endocrine systems (Amereh et al., 2019; Hou et al., 2021). The bioaccumulation potential of microplastics, especially among marine organisms remains a topic under investigation (Miller et al., 2020). Existing studies also demonstrate that microplastics can cause developmental and reproductive toxicity in aquatic organisms, including reduced growth (Zimmermann et al., 2020), altered development (Gardon et al., 2020) as well as reduced reproduction (Cole et al., 2015). The ToMEX database is an ongoing effort to compile microplastics toxicity studies (Mehinto et al., 2022).

Chemical additives used in the original plastic as well as sorbed chemical contaminants can significantly influence toxicity concerns for microplastics. Due to their hydrophobic nature and large surface area, microplastics in both aquatic and terrestrial ecosystems easily sorb and therefore have the potential to transfer contaminants, including for example persistent organic populations, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxin-like chemicals, polybrominated diphenyl ethers (PBDEs), heavy metals, pharmaceuticals, pesticides, and herbicides (Martinho et al., 2022). The impact of these sorbed and inherent chemical additives on the toxicity of microplastics remains a debate in the field.

Although research on microplastics' widespread impacts is still in its infancy (especially regarding impacts on humans), there is clear evidence of uncontrolled exposures across ecosystems and emerging evidence of harm.

Addressing Unintentionally Generated Microplastics in Alternatives Assessment: Specific Considerations

This section outlines considerations for addressing microplastics in alternatives assessments based on the emerging knowledge regarding microplastic pollution as informed by a review of the literature in **Appendix A.** The literature to date establishes a foundational principle that guides provisions for alternatives assessment: *Unintentionally generated microplastics are unwanted pollutants where exposure can induce negative impacts, especially on marine and terrestrial organisms.*

Specific considerations below seek to improve existing practices in alternatives assessment using the IC2 Alternatives Assessment Guide (Version 1.1) as a model framework, but are also applicable to other guidance documents (IC2 Guide, 2017). Considerations outlined address concerns related to *unintentionally generated* microplastics during manufacturing, use, and the end of life of specific polymeric materials that are being evaluated as potential substitutes for a chemical of concern in specific applications/functions.

Recommendations below outline considerations for addressing microplastics in 3 alternatives assessment components: (A) identifying potential alternatives, (B) hazard assessment and (C) and comparative exposure assessment. Other components in alternatives assessment, such as life cycle considerations or materials management, could capture the question of microplastics generation potential as well. However, these modules are not routinely used and input from experts recommended that provisions for addressing microplastics generation should be captured within required/routinely used assessment modules.

Risk management practices, life cycle assessment methods, and policies focused on microplastics are only in their infancy (see **Appendix A**). As such, recommendations outlined in this white paper should be revisited and reassessed as progress is made in both research and policy to address and mitigate microplastics pollution.

A. Identification of Alternatives

With the chemical of concern and its application in mind, identifying functionally similar alternatives for consideration is one of the first steps in an alternatives assessment. Two considerations are recommended below for use during the scoping stage of identifying alternatives to reduce the potential of including options in the assessment that could be problematic from the standpoint of contributing to microplastics pollution.

1. *Is the alternative under consideration a chemical used in a polymer, an alternative polymer, or an alternative polymeric material? Is it possible to consider other non-polymeric alternatives?*

As demonstrated in Figure 3, it is important to consider the generation of microplastics when alternatives assessments focus on: (a) a chemical used in a polymer, (b) a polymer, and (c) alternative polymeric materials that contain additives (i.e., plastics). The first opportunity to minimize harms associated with microplastic generation associated with an alternative is to scope and identify alternatives that are non-polymeric focusing the function needed and the application/material/product delivering this function.

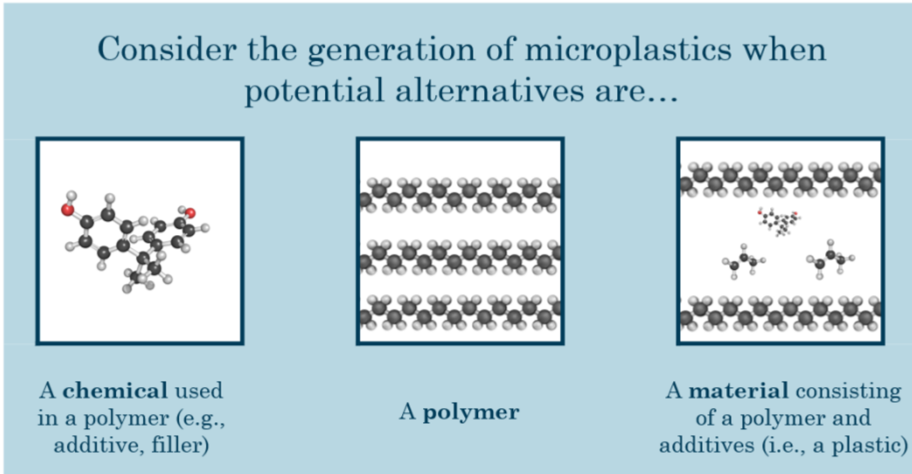

Figure 3: Scope of alternatives that should address generation of microplastics, which include (a) a chemical used in a polymer, (b) polymers, and (c) alternative polymeric materials that contain additives.

Alternatives assessments aim to identify safer alternatives for a particular chemical of concern for a *particular function*. To avoid regrettable substitutes that contribute to the microplastics pollution challenge, assessors should not just consider functional requirements when identifying alternatives for further evaluation, but also the application/material/product delivering such functionality. For example, when considering alternatives to phthalates in PVC for food wrap, assessors should broaden the scope of the potential alternatives to consider options that could replace the function while also decreasing the generation of microplastics. This could include analyzing food packaging materials with non-polymeric materials, such as paper. If an assessor only focuses on alternative additives/plasticizers, the microplastics concern is overlooked.

2. Is the function, application, or disposal of the alternative contributing to known or suspected sources of microplastics pollution? Are there alternatives that will lower or negate the potential for microplastic generation?

Based on evidence to date, all solid polymers have the potential to generate microplastics resulting from degradation (Colwell et al., 2023). Although specific physicochemical properties of the polymer as well as conditions of use and disposal can mitigate the generation and transport of microplastics and/or lessen the time spent in a microplastics phase (see Figure 2 above), it is important to consider life cycle scenarios when alternatives are first identified to avoid problematic substitutes.

Below is a list of sources of microplastic pollutants identified in the literature (Table 1). Such lists can be used to first question whether the function or application of a given polymeric alternative is of concern for microplastics generation. These functions/applications are prone to conditions that promote fragmentation. An understanding of sources of microplastics pollution is continuously evolving; literature reviews will be an important resource to identify whether the function/application that is the focus of the alternatives assessment is an important source of microplastics pollution.

Table 1: Examples of Sources of Microplastics (not comprehensive)	
Agricultural mulch films	Plastic beverage containers, including bottles
Cigarette filters	Plastic bags
Cosmetics	Plastic food prep surfaces (cutting boards)
Composite asphalt-plastic roads	Plastic tea bags
Footwear soles	Polymeric adhesives
Fishing nets	Plastic food packaging
Household product containers	Plastic lumber
Machine parts	Road markings
Marine coatings	Rubber turf
Paint (marine coatings, interior and exterior paints)	Rubber coatings
Packaging material	Synthetic textiles
Plastic pellets	Tires
Personal care products	Toys
Sources: (Boucher & Friot, 2017; Hernandez et al., 2019; Kershaw & Rochman, 2015; Kiruthika & Rajkumar, 2023; Landrigan et al., 2023; Magnusson et al., 2016; Moran et al., 2021; Osman et al., 2023)	

A pragmatic approach for identifying less problematic polymeric alternatives is to *deselect* options with:

1. A short use life.
2. Ability to generate microplastics given conditions of use (e.g., through washing, abrasion or constant exposure to environmental conditions).
3. A high potential for emissions into the environment due to waste management practices.

Examples of such considerations are outlined below (Table 2). Microplastics can be formed after plastics are exposed to one of many different environmental factors such as UV radiation, heat, chemicals, mechanical stress, and exposure to organisms (see **Appendix A** for more details).

Table 2: Use and end of life scenarios that impact microplastics generation and subsequent exposure.
Note: The examples used are for illustration purposes only and are only relevant to the specific scenario outlined.

Use or end of life condition	High potential scenario: microplastics generation	Lower potential scenario: microplastics generation
Function	Function includes abrasion and/or washing *EXAMPLE: Tires, carpets, synthetic clothing*	Function involves minimal movement of a plastic component *EXAMPLE: Plastics used in building insulation*
Product lifetime/lifespan	Single-use plastics or short-lived items *EXAMPLE: Single-use food/drink containers*	Durable plastics that are used for many years *EXAMPLE: Plastic used in automobile interiors*
Environmental conditions supportive of fragmentation during use	Exposure to UV radiation and environmental conditions such as freezing/ thawing that accelerate fragmentation *EXAMPLE: Agricultural mulch films, outdoor paints*	Limited to no exposure to UV radiation and other environmental factors that accelerate fragmentation during use *EXAMPLE: Plastic cover on television screens used indoors*
Expected end of life disposal treatment	Waste management practices, including composting practices, that do not effectively destruct polymeric materials *EXAMPLE: Disposal of biodegradable polymers in facilities not using appropriate industrial composting practices*	Waste management practices, including composting, that effectively destruct/degrade polymers *EXAMPLE: Disposal of biodegradable polymer using appropriate industrial composting practices*

If a polymeric material is a potential alternative, the assessor can pursue options with properties and environmental conditions that are supportive of biodegradation. Biodegradable polymers are more easily broken down into low molecular weight compounds such as water, methane, and carbon dioxide by microorganisms (Suzuki et al., 2021). *However, it is important to emphasize that suitable environmental conditions are a prerequisite for biodegradation of polymers to occur (e.g., both physical conditions such as heat, as well as the presence of appropriate microorganisms).* Without such conditions, biodegradable polymers are no different than conventional polymers regarding their ability to generate microplastics and to stay in this stage for long periods of time (C. Wang et al., 2021). As such, when identifying biodegradable alternatives, the assessor should note the environment in which biodegradation was tested (i.e., marine, freshwater, home compost, industrial compost, Figure 4) and the accompanying certification (EEA, 2023).

Environment	European Reference Standard	Certification and logos	Notes
Industrial composting	EN13432	OK compost INDUSTRIAL TÜV AUSTRIA; kompostierbar; CIC COMPOSTABILE; INDUSTRIAL COMPOSTABLE DIN Geprüft	EN 13432 refers to packaging. In addition, EN 14995 is a similar European standard for compostability of non-packaging products in industrial composting plants.
Well-managed home composting conditions	No European standard	HOME OK compost TÜV AUSTRIA HOME; HOME COMPOSTABLE DIN Geprüft	The OK compost home label builds on a certification scheme developed by TÜV Austria Belgium NV. The DIN-Geprüft Home Compostable label is based on French standard NF T51-800 and/or the Australian standard AS 5810. National standards also exist in Belgium and Italy. A draft European standard exists for plastic carrier bags suitable for treatment in well-managed home composting installations (prEN 17427:2020).
Soil	EN17033	BIODEGRADABLE IN SOIL DIN Geprüft	EN17033 applies to mulch films only.
		SOIL OK bio-degradable TÜV AUSTRIA SOIL	Based on a certification scheme developed by the label provider, but can be compliant with EN 17033 on request by adding two additional ecotoxicity tests.
Freshwater	No European standard	WATER OK bio-degradable TÜV AUSTRIA WATER	Based on a certification scheme developed by the label provider.
Marine water	No European standard	MARINE OK bio-degradable TÜV AUSTRIA MARINE	Based on a certification scheme developed by the label provider, using American standard ASTM D7081 (withdrawn) as a basis.

Figure 4: European standards for the degradability of plastics in different environments (reproduced directly from EEA, 2023)

Assessors are especially encouraged to explore non-polymeric alternatives during the identification of alternatives that negate the concern for microplastics formation. For example, when searching for a replacement of a hazardous flame retardant in plastic computer housing, the assessor is encouraged to explore not only alternative chemicals and plastics, but also alternatives that do not require polymer use, such as aluminum.

It is not advised to screen out alternatives that may contribute to the formation of microplastics at this stage. As alternatives assessment are used to transition towards safer alternatives, a microplastic-forming alternative may still be safer than the chemical of concern and other alternatives in the following hazard assessment, despite tradeoffs. When identifying alternatives, it is important to elevate consideration of non-polymer alternatives, biodegradable polymeric alternatives where conditions for biodegradation are easily achieved, and uses of polymeric materials that have a low potential for microplastics generation.

B. Hazard

The previous identification of alternatives section encourages assessors to select alternatives for consideration that are less likely to contribute to microplastics pollution. During the hazard assessment step, hazard traits, including potential for generating microplastics, are more comprehensively evaluated. The hazard assessment of alternatives is a required module in all alternatives assessment frameworks. The assessment compares a number of human and environmental hazard traits among the chemical of concern and alternatives in order to identify red flags and potential tradeoffs.

Below are two options for addressing microplastics generation in the hazard assessment. The first captures the issue of degradation, which is addressed through persistence and captured in existing hazard assessment methodologies. The second option includes microplastics generation as an additional, separate hazard endpoint which will be more resource-intensive to currently operationalize. This second option is included to support the evolution of hazard assessment methodologies to better address microplastics for the evaluation and selection of safer materials and products.

Option 1: *Adapt existing hazard assessment methodologies for persistence, by including a notation for microplastics formation in hazard classification scores as appropriate.*

Microplastics are generated from the fragmentation (a type of degradation) of plastics from environmental, biological, and physical/mechanical forces, eventually becoming the size considered to be that of a microplastic or nanoplastic. Currently, the rate of degradation (e.g., half-life of the chemical/material in various environmental media) is captured through the hazard trait of persistence. Thus, one option to elevate considerations of the generation of microplastics in an alternatives assessment is to better connect persistence with microplastics generation potential through use of a notation on the classification score, as shown in Figure 5.

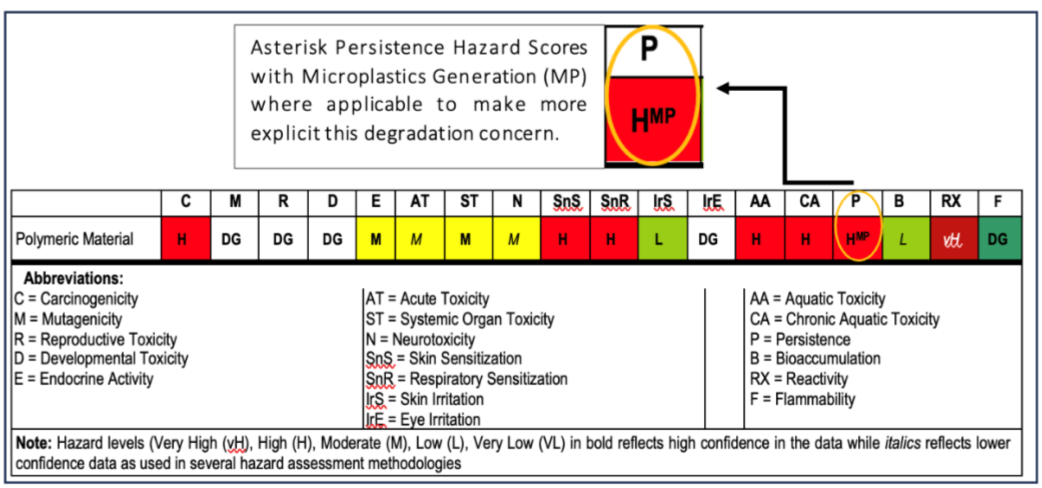

Figure 5: Using a MP asterisk associated with persistence score to make more explicit this additional hazard connected to environmental degradation and resulting microplastics generation.

The use of a MP asterisk on the persistence score is intended to make more explicit the inherent hazard concern related to microplastics generation as related to environmental degradation. This option leverages existing hazard traits that are associated with microplastics generation, but also makes explicit where such concern exists when using heat maps/stop light matrices to better support comparisons among alternatives and with the chemical of concern. Assessors who are using existing hazard assessment methods (such as GreenScreen, Cradle to Cradle, etc.) can simply add an MP asterisk to relevant polymeric alternatives as a flag and expand on any concern for microplastics generation in narrative form in the assessment write-up. This written assessment should further describe concerns related to microplastics generation, such as:

- Evidence of biodegradability and whether such conditions will be likely given the reasonably foreseeable conditions of use/disposal of the alternative.
- How concerns for microplastics generation may attenuate current scores/classifications for other key hazard traits, such as acute/chronic aquatic toxicity or bioaccumulation.

Undoubtedly there will be data gaps that limit use of existing toxicology data for specific polymeric alternatives in a microplastics form. The purpose should not be a detailed hazard assessment of the microplastic, but rather how knowledge of potential microplastic generation may modify understanding of the overall hazard summary of the alternative.

Issues of conditions of use and expected end of life treatment as outlined in Table 2 are addressed in the exposure assessment component of an alternatives assessment and should be further evaluated.

Option 2: ***Include a new hazard endpoint when evaluating polymeric materials – "microplastics generation".***

Generation of microplastics is an intrinsic hazard trait that could be captured as a new hazard endpoint (Figure 6). The purpose of this endpoint is to characterize the microplastics-related intrinsic hazard trait for polymeric alternatives under review.

	C	M	R	D	E	AT	ST	N	SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F	MP
Polymeric Material	H	DG	DG	DG	M	*M*	M	*M*	H	H	L	DG	H	H	M	*L*	*vH*	DG	*vH*

Abbreviations:

C = Carcinogenicity
M = Mutagenicity
R = Reproductive Toxicity
D = Developmental Toxicity
E = Endocrine Activity

AT = Acute Toxicity
ST = Systemic Organ Toxicity
N = Neurotoxicity
SnS = Skin Sensitization
SnR = Respiratory Sensitization
IrS = Skin Irritation
IrE = Eye Irritation

AA = Aquatic Toxicity
CA = Chronic Aquatic Toxicity
P = Persistence
B = Bioaccumulation
RX = Reactivity
F = Flammability

MP– Microplastics generation

Note: Hazard levels (Very High (vH), High (H), Moderate (M), Low (L), Very Low (VL) in bold reflects high confidence in the data while *italics* reflects lower confidence data as used in several hazard assessment methodologies

Figure 6: Additional hazard category to capture microplastics (MP, microplastics generation)

It is important that future work evolve hazard assessment methodologies to focus on the microplastics generation as a relevant hazard trait. Although there is ongoing research to understand the physicochemical characteristics, including the ability of these materials to adsorb environmental contaminants, that impart different toxic effects of a given microplastic, this is level of assessment is not needed for alternatives assessment. The question is not what toxicity endpoints are relevant to microplastics, but rather that microplastics in and of themselves are a specific hazard to be avoided in the evaluation and selection of safer alternatives to toxic chemicals. There is precedent to consider size alone as an intrinsic hazard. For example, air quality regulations in the U.S. and globally address particles under 2.5 μm as an inherent hazard and regulate them as such.

As captured in the literature review (**Appendix A**), there is a growth in methods that can be used to evolve hazard assessment methodologies to support ranking the level of concern regarding the generation and impact of microplastics for specific polymeric materials. Hazard assessment methods developers are encouraged to draw from approaches outlined in the existing literature such as those outlined by Boersma et al. (2023) and Yuan et al.(2022) to help rank the potential of biodegradable or nonbiodegradable alternatives to generate microplastics. Factors which can inform scoring methodologies (e.g., "high," "moderate," "low") include considering: (a) particle size (b) degradability and (c) inherent hazard of the polymer material (which includes considerations of the monomer and additives) as expanded upon below:

- **Can the alternative material form particles <5mm during use or end of life stages?** Size of microplastics is one factor that mediates transport in the environment and uptake by organisms. Because polymeric materials have the potential to degrade during different stages of the lifecycle it is crucial that the hazard assessment capture all stages, including disposal and the potential for the mismanagement of plastic waste (OECD, 2022).

- The shape of microplastics also mediates transport and degradation in the environment. At the time of writing, the shape of microplastics has not been conclusively linked to changes in hazard of microplastics. Therefore, assessors/hazard assessment methods developers are encouraged to explore the literature to determine whether microplastic shape can mediate hazard. In absence of data that demonstrate otherwise, a precautionary approach should be used that assumes the formation of microplastics for any polymeric materials classified as high/very high for persistence.

- **Will the alternative material degrade sufficiently in the environment in which it would most likely be found?** As described earlier in this white paper, effective biodegradation of polymeric materials is dependent on environmental conditions that support the necessary microbial activity to breakdown the structure of the polymer. Biodegradable plastic PLA has been found in oceans, albeit at low amounts (<1% of sample) compared to commodity plastics (e.g., polyethylene) (Peeken et al., 2018). Oxo-degradable plastics, which include additives to increase the fragmentation rates of plastics, only accelerate the formation of microplastics. It is unclear whether these plastics biodegrade or mineralize following fragmentation, and the EU plans to phase out such plastics (EU, 2019). The structure of the polymer is determined by the chemical bonds, crystallinity, additives, and surface-to-volume ratio. Yaun et al (2022) recently gathered biodegradability estimates for common plastic types.

- **Is there inherent concern for the hazard of the polymeric material, including parent monomers and additives?** Studies have observed that the toxicity of a given microplastic partially depends on the specific polymer type, which is inclusive of its parent monomers, residual catalysts, and additives (Appendix B). For example PVC or ABS are described as high concern in approaches used to rank polymers in hierarchies for microplastics because of the inherently hazardous (e.g., carcinogenic) monomers. Existing hazard assessment methods for polymeric materials such as those outlined by GreenScreen® also include evaluation of components in polymers if they are present at ≥ 1000 ppm (0.1%) (e.g., additives). In absence of data that show otherwise, the precautionary approach is to assume that the higher the toxicity of the polymer material considering all components, including additives, the higher the toxicity of the subsequently generated microplastics.

Table 3 provides a sample illustration of how the above questions can be used to support the development of a categorical scoring methodology that can be further refined based on data inputs and pilot testing for a new microplastics generation hazard endpoint.

Table 3. Preliminary Ideas for the Development of a Microplastics Generation Categorical Scoring Methodology, identifying low, medium, and high hazards. For Illustration Purposes Only

A. Can the alternative material form particles <5mm during use or end of life stages?	B. Will the alternative material degrade sufficiently in the environment in which it would most likely be found?	C. Is there inherent concern for the hazard of the polymeric material, including monomers or additives?
Available data demonstrates that the alternative polymeric material forms microplastics during use or end of life	Available data demonstrate persistence	Contains highly hazardous monomers or additives
The polymeric alternative is used outside where environmental conditions magnify fragmentation	No evidence of biodegradability based on reasonably foreseeable environmental conditions	
The function/use of the polymeric material is known to have problematic end of life waste management practices		
Polymeric material is used in a semi durable application in enclosed environments and there is moderate concern for problematic end of life waste management practices	Data demonstrates biodegradability but appropriate disposal treatment practices to support biodegradation cannot be assured	Contains moderately hazardous monomers or additives
Polymeric material is durable, not exposed to the environment, and used in a place/scenario with high plastic waste recovery rates	Data demonstrates biodegradability, including considering reasonably foreseeable disposal/compost treatment practices	Does not contain hazardous monomers or additives

Figure 7 below provides a schematic diagram that summarizes Option 1 (using current methods) and Option 2 (future directions for the field) to address microplastics in the hazard assessment component of an alternatives assessment.

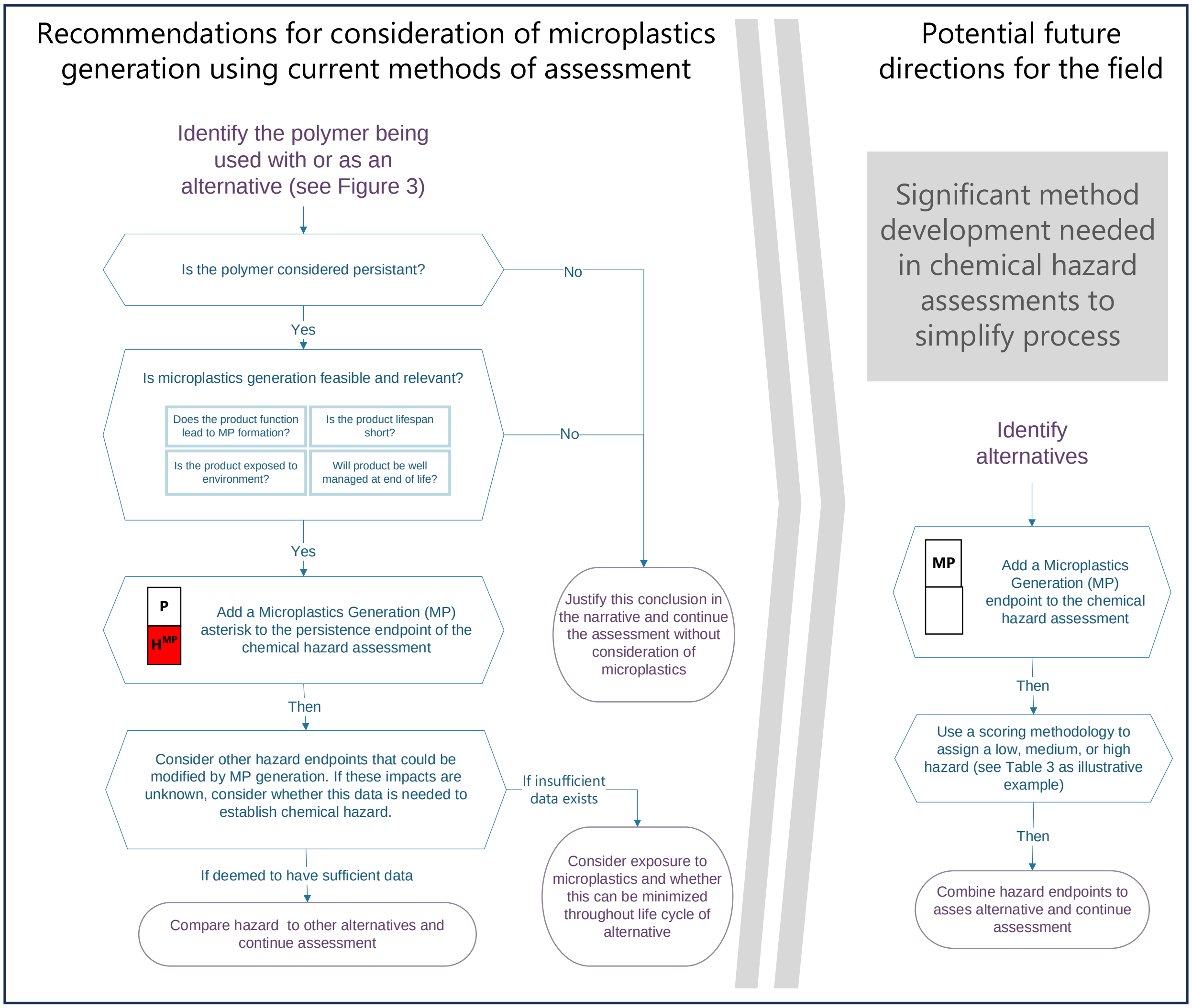

Figure 7: Method developments in chemical hazard assessments have the potential to simplify assessment of microplastics generation hazard. This is an illustrative example of assessment after advancement.

C. Exposure Assessment

The assessment of exposure is generally conducted after the hazard assessment to examine the intrinsic exposure potential of alternatives. An exposure assessment may be deemed unnecessary if an alternative is of low enough hazard such that if exposure were to occur, harm is unlikely. However, when alternatives have specific hazards, additional consideration of intrinsic exposure potential help to make final determinations as to whether an alternative is safer or not considering exposure scenarios, routes of exposure and physicochemical properties. The following two additional considerations for exposure to microplastics generated from alternatives are intended to supplement existing exposure assessment approaches for the evaluation of alternatives.

1. ***What are the relevant use conditions for the alternative? Do either use or disposal conditions lead to plastic fragmentation and release into the environment?***

Certain uses of alternatives are correlated with the generation of microplastics (Table 1). At times, the function of the alternative is linked to its potential to degrade during or after use, such as tire treads and agricultural mulch films. Considering exposure scenarios and conditions of use, the questions below derived from Table 2 can be used to explore whether the alternative polymeric material may have worse tradeoffs for human health and the environment than the current chemical of concern. These factors were considered during the alternative identification process. However, if polymeric alternatives were selected for assessment, these factors should be more fully explored in the exposure assessment component. Factors and associated questions relevant to the exposure potential include:

- What is the expected life span of the alternative (e.g., shorter lifespans, such as single use products, are more problematic for microplastics formation)?

- Given the function needed of the alternative, how likely is it that microplastics will be generated (e.g., if washing/abrasion is inherent to the function of a polymeric alternative, there could be a high concern for microplastics generation)?

- Given the environmental conditions where the alternative will be used, how likely is it that microplastics will be generated (e.g., applications that have reduce exposure to environmental conditions that promote fragmentation will lessen the concern for microplastics formation during the use phase)?

- Given the expected end of life treatment of the alternative and its location/geography, how likely is it that microplastics will be generated (e.g., open landfills, mismanagement of plastic waste and non-industrial composting practices (for biodegradable polymers) will enhance concern for microplastics formation during the disposal stage)?

These above questions arise from research findings regarding environmental conditions supporting microplastics generation during use or end of life. For example:

- Common misuses of plastic products, such as microwaving plastic cups to reheat liquids, have the potential to form microplastics (Hussain et al., 2023).
- Using hot water on plastic tea bags has been shown to support the generation of microplastics (Ali et al., 2023).
- The likely geography of disposal should be considered as certain countries are at higher risk regarding plastic waste mismanagement (UNEP, 2021).
- The availability of industrial composting may also be relevant for certain biodegradable plastics like PLA. This should be considered when examining the potential end-of-life scenarios for the plastic alternative.
- Microplastic release from recycling facilities has been detected, but not thoroughly mitigated through technology or policy (Brown et al., 2023).

Unless there are data to demonstrate otherwise, a precautionary approach calls for the assumption that microplastic release into the environment is likely regardless of the end-of-life scenario for polymeric materials that are considered persistent.

2. ***Acknowledging that it is difficult to link microplastics in the environment to specific plastic products, has the alternative's plastic polymer been found in bio- or environmental monitoring studies?***

In the research literature, microplastics found in the environment are categorized by size and (sometimes) polymer type. Microplastics are often heavily transformed by biofilms or other biological processes, which obscures chemical identification. Despite these challenges, plastic polymers have been identified in the environment, in terrestrial organisms and humans(Sun & Wang, 2023; Zolotova et al., 2022).

Assessors should link the properties and functions of microplastics found in monitoring studies to the properties/functions of the specific plastic alternative under assessment. For example, microplastics from a specific type of PET lining on single use packaging may not have been studied in the environment. However, PET from plastic packaging has been found in environmental samples (Ryan et al., 2021). Thus, the assessor can use this property (polymer backbone) and function (single use packaging) to assume that the alternative, PET lining, has a high probability of being detected in the environment. Assessors should consider whether existing study data are similar enough (or not) to the alternative under assessment as justified based on the grouping of physicochemical properties.

Conclusion

Microplastics present a pressing global concern for human health and the environment. The alternatives assessment community has a responsibility to ensure that substitutes for chemicals of concern do not add to this pollution burden. The goal of this white paper and recommendations contained is to spur continued dialog regarding needs and opportunities to address microplastics within alternatives assessments, including needs for future methods development work. Recommendations outlined in this white paper should be revisited and reassessed given the ongoing progress in both research and policy domains to address and mitigate microplastics pollution.

APPENDIX A: Literature review of microplastics to support considerations in alternatives assessments

A review of the literature was conducted to address how microplastics pollution could be associated with potential substitutes considered during an alternatives assessment. The literature review explored current knowledge, including methods and strategies to better identify and flag concerns related to the generation of microplastics that could be addressed by specific components of an alternatives assessment to rule out alternatives that have the potential to contribute to microplastics pollution.

This is not a comprehensive literature review on occurrence and hazards of microplastics,[1] but rather focuses on elements of the current literature that inform components of alternatives assessment including: (1) identifying potential alternatives for consideration, (2) hazard assessment, and (3) comparative exposure assessment considerations. These components are consistent with modules in the IC2 Alternatives Assessment Guidance and other alternatives assessment frameworks. This review will examine alternatives assessments of plastics that have the potential to form microplastics. In addition, the adjacent fields of life cycle assessment (LCA) and risk assessment of microplastics derived from plastic products will be reviewed to inform potential considerations for alternatives assessment.

Background and Identification of Microplastics

Although there is not a universal definition of microplastics, regulatory programs are beginning to outline definitions:

- The California State Water Resources Control Board: "Microplastics in Drinking Water' are defined as solid polymeric materials to which chemical additives or other substances may have been added, which are particles which have at least three dimensions that are greater than 1 nm and less than 5,000 micrometers. Polymers that are derived in nature that have not been chemically modified (other than by hydrolysis) are excluded" (California State Water Resources Control Board, 2020).
- The European Union uses the term "synthetic polymer microparticles" (EC, 2023a).
- The OECD and GESAMP acknowledge different definitions on microplastics, concluding that microplastics are "solid synthetic polymer particulates with a size < 5 mm". (OECD, 2021)

Microplastics fall into two categories:

1. Primary: Intentionally added microplastics, such as microbeads in personal care or industrial microbeads that are used as abrasives (OECD, 2022).
2. Secondary: Microplastics formed after the fragmentation of plastics.
    a. Unintentionally generated through the mechanical or environmental degradation of plastic products during use or at end of life and released as pollutants into the environment. The composition of microplastics is associated with parent polymeric

[1] Although there are numerous systematic reviews on microplastics, the Interstate Technology Regulatory Council (ITRC) recently issued a helpful "guidance" document on microplastics that provides readers with a strong state-of-the-science overview – see link here.

material. Examples include tire wear particles and particles released from synthetic textiles from washers and dryers. In 2019, 2.6Mt of unintentionally generated microplastics leaked into the environment (OECD, 2022).

b. Unintentionally generated microplastics, which are released into the environment as macroplastics (e.g., fishing nets) and then degraded into microplastics in the environment. In 2019, 19.4Mt of macroplastics were released into the environment (OECD, 2022).

Unintentionally generated microplastics are the focus of this review.

Microplastics are derived from their parent polymeric material. According to the European Commission, "plastics are usually defined as polymeric materials to which additives may have been added" (EC, 2019). This definition does not include unmodified natural polymers that occur naturally in the environment, such as proteins (EC, 2019).

Plastics can be derived from both fossil and biobased materials. The OECD estimates that over 90% of plastics in commerce are synthesized from virgin petroleum products, while 6% of plastics in commerce are from recycled sources (OECD, 2022). As a result, most of the microplastic pollution and related environmental and human health concerns due to the petroleum-based polymers.

Plastics that are synthesized from monomers of biobased origins and/or are biodegradable are generally referred to as bioplastics. Bioplastics are a relatively small portion of the plastics market (less than 1% in 2019), but their market share is growing (OECD, 2022). Bioplastics may or may not be biodegradable in the environment. Biodegradation is dependent on a number of factors, such as relevant microbes being in close proximity to the soluble products so that they can be consumed and the presence of specific membrane carriers for cellular uptake. Solid polymers considered biodegradable will also degrade into microplastics. However, if the appropriate bioassimilation factors are present, the time in a microplastics stage is expected (Colwell et al. 2023).

Biodegradable plastics are designed to be converted into CO_2 and water by the microorganisms in soil and water. Testing methods for biodegradability in different environments are outlined by the OECD, ISO, and European Committee for Standardization (CEN) (Filiciotto & Rothenberg, 2021). Conditions such as temperature, humidity, occurrence of microorganisms affect the rate of biodegradation. Biodegradable plastics have the have the potential to generate microplastics and to remain in such a stage if optimal environmental conditions are not available (C. Wang et al., 2021).

Formation of Microplastics: Many Sources Impacted by Different Degradation Processes

Unintentionally formed microplastics are commonly generated in two ways: (1) during the use of a plastic product and (2) after the improper disposal of a plastic product. However, microplastics can also be generated elsewhere in the plastics lifecycle.

Plastic products that create microplastics during their use phase may do so through abrasion or washing. For example, tires breaking on the road can lead to the formation of tire wear particles (a microplastic). The washing of synthetic textiles may lead to the formation of microfibers which are not adequately captured by wastewater treatment plants. (Auta et al., 2017; Yadav et al., 2023).

Plastic products, if released into the environment, may undergo hydrolysis, biodegradation, thermal degradation or photodegradation, leading to the formation of microplastics (UNEP, 2023). These physical, biological, and chemical degradation processes change the structural integrity of the plastic, resulting in continuous fragmentation. Other changes to the physiochemical properties of plastics, such as through biofouling, may be significant but currently underexplored in the scientific literature (Wayman & Niemann, 2021).

There is also the potential for plastics to be released into the environment during production, commonly through spills. Plastic pellets that are not yet molded into the final product are commonly called nurdles. Nurdles have been documented in the environment and after spills, but there are no estimates as to global amounts of nurdles present in the environment to date (Sewwandi et al., 2022; Tunnell et al., 2020).

The mechanisms by which plastics degrade to form microplastics varies depending on the environment and type of plastic. Common degradation mechanisms are listed in Table 1, but these mechanisms often occur in tandem.

Table 1: Degradation mechanisms of plastics, which may form microplastics (Liu et al., 2022; K. Zhang et al., 2021).

Degradation mechanism	Description
Mechanical degradation	The impact of many physical forces on plastics, such as sheer, abrasion, collision, abrasion, freezing, or thawing. This mechanism commonly fragments plastics rather than release small molecules such as mineralized products (CO_2, H_2O, etc.)
Biodegradation	Complete or partial conversion of plastics to carbon dioxide and water (aerobic conditions) or methane and carbon dioxide (anaerobic conditions) that is driven by microorganisms (bacteria, fungi, enzymes, algae or a combination).
Photodegradation	Light (mostly high energy ultraviolet radiation; UV) causes various chemical reactions such as chain-breaking or cross-linking of plastics. Depending on many conditions, photodegradation can lead to fragmentation of a plastic or its conversion to small molecules such as mineralized products (CO_2, H_2O, etc.).
Chemical degradation	Chemical degradation involves either water (hydrolysis) or oxygen (oxidative degradation). These processes can be relatively slow in the environment but have been accelerated in laboratory studies to break down microplastics.
Thermal degradation	Generally, not relevant in environmental conditions, thermal degradation refers to heat treatments used to either identify or break down polymer chains and release monomers. Extreme events such as explosions or wildfires may cause thermal degradation of plastics.

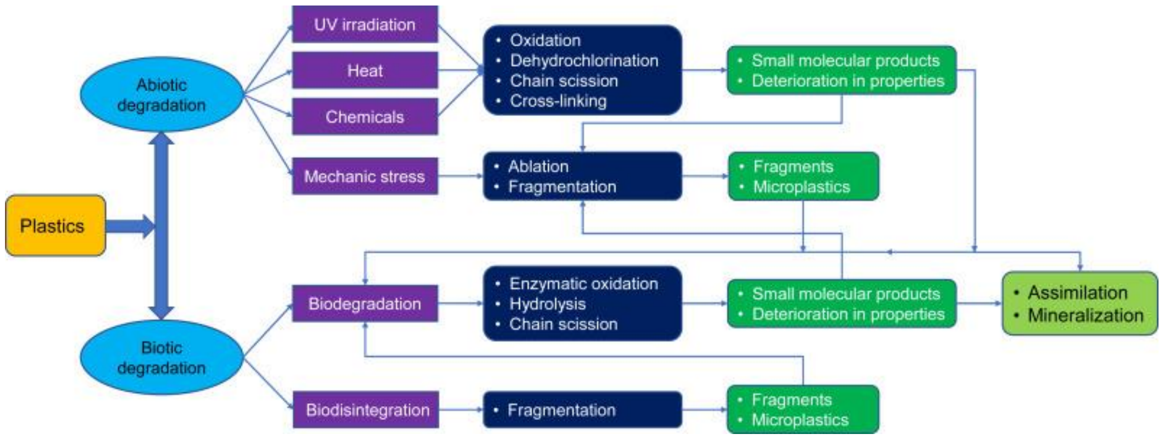

Figure 1: Degradation routes of plastics (K. Zhang et al., 2021).

Hazard assessment of unintentionally generated microplastics: Readiness of existing methods

Alternatives assessment relies on existing methods for hazard assessment of chemicals, such as the Globally Harmonized System ("Alternatives Assessment Guide Version 1.1," 2017). Due to the complexity of plastics as a material, the practice of a GreenScreen® assessment has been applied instead to plastic monomers and plastic additives (Rossi & Blake, 2014).

Chemical hazard assessments such as GreenScreen, Cradle to Cradle Certified, and ChemFORWARD, include persistence, which captures degradability and therefore relevant to the primary hazard trait of microplastics. However, To the best of the authors knowledge, hazard assessments of plastics have not yet captured microplastics as a degradation product. The half-life of microplastics is expected to be anywhere from 100-1000 years, depending on the plastic (Koelmans et al., 2022). Such persistence would translate into “very high” based on definitions of persistence established by EPA through its PBT profiler (persistence, bioaccumulation, and toxicity) and used by hazard assessment methods, such as GreenScreen (Clean Production Action, 2018). REACH (Annex XVIII) would classify this as “very persistent” (ECHA, 2017).

Microplastics have various physicochemical characteristics that are crucial to report to ensure the reproducibility of toxicological studies and the use of these studies in risk and alternatives assessments. Assessments of toxicological studies have identified eight key characteristics of microplastics that toxicological studies should report (see Table 2) (de Ruijter et al., 2020; Gouin et al., 2022).[2]

While the toxicity studies of microplastics are increasing in quantity and quality, alternatives assessors may have data gaps in their analysis of toxicological studies of unintentionally derived microplastics:

- The physicochemical properties of the microplastic generated from the alternative plastic product may be unknown.
- The microplastic generated from an alternative plastic product may not have been assessed in toxicity studies.

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[2] These studies also point out necessary experimental design components, but these are not included here.

- The microplastics generated from an alternative plastic product may be subject to further degradation (i.e., weathered) before encountering the receptor.

Table 2: Criteria used to evaluate the *in vitro and in vivo* impacts of microplastics (de Ruijter et al., 2020; Gouin et al., 2022).

Property	Description
Particle size	Size is a crucial factor explaining effects of microplastics and thus it should be reported. If a range of sizes is used; a full (i.e., ≥10 bins) size distribution is measured and reported. If a single size is used, that size is measured with an indication of measurement error and reported.
Particle shape	Shape is a crucial factor explaining effects of microplastics and thus it should be measured and reported. Shapes are measured with high resolution pictures and reported.
Polymer type	Polymer type can be a factor explaining effects of microplastics and thus should be reported. Polymer identity is confirmed with methods such as FTIR, Raman spectroscopy, or similar methods.
Polymer chemical components	To test particle toxicity, the toxicity of other chemicals in solution or mixture should be ruled out. This includes additives present in microplastics, chemicals associated with food particles and surfactants (e.g., Tween). Chemical effects other than from the polymer or solution/mixtures are ruled out.
Aging and biofouling of polymer	Aging and biofouling occurs in the environment and they could affect the uptake of microplastics; therefore, it is crucial to consider these factors for an ecological relevant experiment. Microplastics should have undergone process to make them more environmentally realistic, accounting for biofouling. Additionally, pictures of altered particles should be provided.
Source of microplastic	Specification on where microplastic stock or solution is purchased and/or how it is self-made maximizes the reproducibility and thus, it should be reported. The origin and/or production of microplastic in own laboratory should be reported in detail.
Polymer surface chemistry	Particle surface chemistry properties such as charge, hydrophobicity, etc. in the test medium should be reported.
Microbial contamination of microplastic	Presence of microbes, verified with the presence or absence of endotoxin, should be reported.

Hazard assessment of unintentionally generated microplastics: Adaptation of methods to account for physicochemical properties of microplastics.

The practice of hazard assessment for unintentionally generated microplastics can be informed by the actions of policymakers, life cycle assessment practitioners, and risk assessors.

In risk assessment, probability density functions (PDFs) have been proposed to address the wide array of microplastic properties (Koelmans et al., 2022). PDFs are mathematical functions that are fit to different parameters of microplastics and microplastic data from environmental samples with the aim of determining exposure and effect thresholds (Koelmans et al., 2022). These models remain under development and have not yet reached a consensus in the field. Similarly in life cycle assessment the determination of hazards of microplastics based on physicochemical properties have been explored quantitatively using effect factors.

In essence, these groups above have moved forward with grouping approaches to characterize the potential hazards of unintentionally generated microplastics. The inherent hazards of microplastics are currently derived from key physicochemical properties: (a) the parent polymeric material, including additives; (b) contaminants in environmental media that can adsorb onto the microplastic; (c) size and (d) shape.

Parent Polymeric Material and Additives

Microplastics are derived from numerous polymeric materials. Plastics such as PVC, ABS, PUR, and PAN have high inherent toxicity given the monomers used, many of which are carcinogenic and mutagenic (Lithner et al., 2011).

Chemicals present in plastics include oligomers, unreacted monomers, plasticizers, and other additives – the latter of which can account for a large proportion of the overall weight of the materials (e.g., phthalates in PVC) (UNEP, 2023). Additives too also can display a wide array of hazards. A recent analysis of chemicals in plastics found over 13,000 chemicals used as additives or monomers, with over 3,000 of these chemicals being chemicals of potential concern (UNEP, 2023). There is currently a debate in the field regarding how to measure the release of chemical additives from plastics into the environment, but there is emerging evidence that chemical additives are released from plastics during weathering (Rani et al., 2017).

Chemical changes of plastics as they degrade into microplastics are important for considering their impacts. These chemical changes can also be limited to surface impacts but still can have consequences for chemical pollutant uptake (Al Harraq et al., 2022).

The persistence of biodegradable plastics is a concern when biodegradation of the plastic cannot be achieved based on environmentally conditions needed (Ainali et al., 2022). For example, polylactic acid (PLA), which is compostable under industrial composting conditions, has been demonstrated to persist in the environment for years (Greene, 2012). The hazards of biodegradable plastics that are not biodegradable will be similar to those of non-biodegradable plastics. Plastics that are biodegradable under environmentally relevant conditions, such as poly(3-hydroxyalkanoate) (PHA), are hypothesized to be less persistent (Greene, 2012). ECHA, in the context of intentionally added microplastics, has recently proposed specific biodegradability tests that it considers as benchmarks for determining the persistence of microplastics in the environment (EC, 2023a).

Different polymers also have varying degradation rates in the same environment. However, there are only a few measurements of these degradations rates in the environment available to date (Chamas et al., 2020). For example, only one report of PVC degradation met the criteria of Chamas et al.(2020), which found no degradation of PVC after 32 years.

The polymer type and source of microplastic are both key components to proposed PDFs for risk assessment (Mehinto et al., 2022). These data are available due to the Toxicity of Microplastics Explorer (ToMEx) database, which has been built to gather high quality microplastics toxicity data (Mehinto et al., 2022). Although PDFs could theoretically cover the presence of chemical additives in polymers due to the methods using continuous dose response curves informed by polymer types (Koelmans et al., 2023), the connection of polymers to additives has not yet been explored.

The polymer type and additives have been considered in LCA methodologies when deemed relevant to the endpoint and when enough data is available (Lavoie et al., 2022). The exposure and effect factor (which considers the hazard assessment of microplastics) has been deemed generic for microplastics due to the lack of data and lack of significant differences between existing data based on polymer type, particle size, and shape (Corella-Puertas et al., 2023; Corella-Puertas et al., 2022; Lavoie et al., 2022) . These effect factors have been used for the life cycle assessment of specific microplastics, such as polystyrene microplastics, tire and road wear particles, and plastic food container litter emissions (Corella-Puertas et al., 2022).

Adsorption of contaminants in environmental media onto microplastics

The toxicity of microplastics in the environment may also come from the chemical contaminants that adsorb onto the plastic debris. Due to their hydrophobic nature, large surface area, and increased reactivity, microplastics in both aquatic and terrestrial ecosystems easily adsorb and transfer (act as a vector for) contaminants (Martinho et al., 2022). Researchers have determined parameters – such as molecular weight and hydrophobicity – can lead to chemical leaching with half-lives of years to decades (UNEP, 2023). Although microplastic-mediated exposure to hazardous chemicals is currently has not reached consensus among researchers, there is evidence that plastic debris in the environment causes chemical exposures to marine species (UNEP, 2023). Examples include the transfer of persistent organic populations, such as polychlorinated biphenols (PCBs), dioxin-like chemicals, polybrominated diphenyl ethers (PBDEs), heavy metals, as well as polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals, pesticides, and herbicides (Martinho et al., 2022).

The understudied nature of the sorption of contaminants to microplastics has let to limited incorporation into methods in risk and life cycle assessment. Although PDFs in risk assessment could theoretically cover the presence of chemical sorbed to microplastics because of the methods use of continuous dose response curves informed by polymer types and the source (Koelmans 2023), the specific connection to sorbed contaminants has not yet been explored.

Size

Microplastics are generally defined as any plastic particle <5mm in size in at least one dimension. In practice, this definition encompasses many different plastics; both drinking straws (less than 5mm diameter) and degraded plastic fragments that are only 10 nm wide are considered microplastics. Microplastics they can exist in a variety of sizes and size can influence their toxicity due to enhanced bioavailability. Experts have noted that the 5 mm upper limit for microplastics was originally proposed by the National Oceanic and Atmospheric Administration (NOAA) based on knowledge that particles of this size were considered more likely than not to be ingested compared to larger particles (Arthur et al., 2009).

As particle size decreases, surface/volume ratios increase which influences the uptake by organisms as well as cellular interactions (Jeong et al., 2016). In an analysis of 114 studies on the ecotoxicity of microplastics, et al. found that toxicity of microplastics may increase as microplastics size decreases (Beiras et al 2020). However, the heterogeneity of microplastics used in the study resulted in a low r^2 of 0.28 (Beiras et al 2020).

The further decrease of microplastic particle size leads to the generation of particles with dimensions are on the nanoscale (<100nm), which are commonly referred to as nanoplastics. The toxicity testing of nanoplastics is currently in its infancy, and this is a considered as serious data gap in the assessment of microplastics.

Risk assessment methodologies have identified mass of microplastics as a possible proxy to size since the densities of environmental microplastics are generally 1 g/mL (Kooi & Koelmans, 2019). Microplastic size, because of its inclusion in the ToMEx database, can also inform PDFs used for risk assessment. ToMEx excludes nanoplastics due to their smaller size and its current focus on microplastics (Koelmans et al., 2020).

Life cycle assessment practitioners have proposed to use the effect factor of microplastics for nanoplastics until there is data available for the toxicity of nanoplastics (Lavoie et al., 2022).

In the risk assessment of intentionally added microplastics, ECHA proposed a grouping of microplastics that have an upper size limit of 5 mm. This proposal stems from the science (as this size range is "readily ingested by organisms in the environment") as well as practical considerations (this size range is monitored by many marine litter programs). ECHA considered the use of minimum size limit for restriction regulations limiting intentionally added microplastics but concluded that such a value could lead to regrettable substitutions since nano plastics have not been proven safe (EC, 2023a).

Shape

Researchers have identified between 4 to 7 different types of microplastics defined by shape or morphology, which include fiber, fiber bundle, fragment, sphere (or bead), pellet, film, and foam (Rochman et al., 2019). These shapes are correlated to specific primary product sources. For example, fibers and fiber bundles tend to shed from clothing or carpet, and foam often comes from expanded polystyrene foam products such as insulation or food packaging (Rochman et al., 2019).

Although the toxicology of microplastics is only emerging, some studies are showing shape-dependent effects. Different shapes may have different impacts on different species, and consensus has not yet been reached. For example, a recent study found that chronic exposure to polystyrene microplastics to *Daphnia magna* revealed that spheres/beads where more toxic than other shapes of comparable sizes/diameters (Schwarzer et al., 2022). However, studies on daggerblade grass shrimp (Palaemonetes pugio) indicated significantly higher mortality from fibers compared to spheres and fragments of polypropylene (Gray & Weinstein, 2017). When testing zebrafish, Qiao et al. (2019) also found that fibers were more toxic than fragments and beads.

The shape of microplastics has also been shown to be linked to the persistence of the particles in the environment (Chamas et al., 2020). For example, fibers are expected to degrade faster than spheres (e.g., nurdles) due to their increased surface area.

Risk assessment PDFs have simplified shape considerations of environmental microplastics to aspect ratio and surface area (Koelmans). The inclusion of shape in the ToMEx database also lends itself to the inclusion of shape in risk assessment methods.

Precautionary approaches by governments on the grouping of microplastics mainly rely on size determinations, although shape was acknowledged early on as one of the key properties to determine toxicity (Kershaw & Rochman, 2015). When considering intentionally added microplastics, ECHA proposed the inclusion of fibers with an aspect ratio length/diameter >3. This proposal stemmed from WHO guidelines on asbestos, which were deemed similar enough to differentiate fiber-like particles (ECHA, 2020).

Other physicochemical properties

There are other physicochemical properties of microplastics that may influence the resulting toxicity of microplastics. Properties such as the presence of biofilms have been studied by certain groups, but consensus has not yet emerged in the field (Liu et al., 2020). In addition, surface chemistry changes because of environmental weathering are not yet standardized and commonly tested in toxicity tests (Alimi et al., 2022).

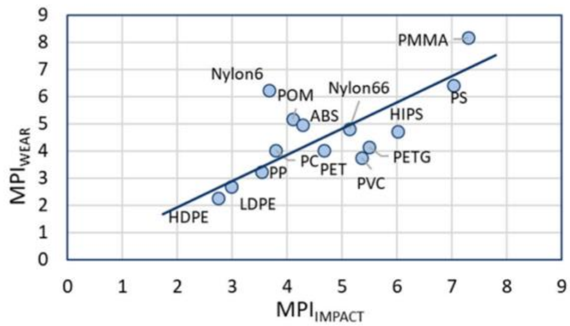
Due to the exponential rise in microplastics toxicity studies, these physicochemical properties, and others, may soon be linked to toxicity.

Use of properties to inform hazard bands

The use of physicochemical properties of microplastics to inform hazard bands is in its infancy. Physicochemical characteristics were considered for the restriction of intentionally added microplastics under REACH and included: polymer type, particle size, and biodegradability (ECHA, 2021). These few characteristics justified grouping due to the potential uptake of microplastics by animals due to their small size, microplastics' persistence, their further degradation into smaller particles, and the difficultly to remove microplastics from the environment.

Considering whether an alternative has the potential to form microplastics is highly dependent on the inherent physicochemical properties of parent polymeric material. There is growing array of methods being developed to predict the ability of a given plastic to form microplastics. Two such approaches are briefly reviewed below from Boersma et al. (2023) and Yuan et al. (2022). These approaches use different criteria and thus there are differences in how each of them ranks the potential of specific polymeric materials to form microplastics.

Boersma et al. (2023) proposed the use of a Microplastic Index (MPI) methodology to predict the generation of microplastics based on several mechanical and physical polymer properties such as the properties that impact the strength (determining crack growth) and wear resistance (relevant to abrasion). Critical dimensions of breaking polymers can be predicted through use of these parameters that are an indication for the size of the microplastics, which are formed by impact, friction etc., when external stressors are applied to the material, by wind, water or soil abrasion. A high MPI indicates a high tendency towards the formation of microplastics. As shown in Figure 2, PMMA demonstrates the greatest potential for microplastics formation while HDPE demonstrates the lowest potential.



Acronyms: ABS (acrylonitrile-butadiene-styrene terpolymer); HDPE (high density polyethylene); HIPS (high-impact polystyrene); LDPE (low density polyethylene); PET (polyethylene terephthalate); PETG (polyethylene terephthalate glycol); POM (Polyoxymethylene); PMMA (poly(methyl methacrylate); PP (polypropylene); PC (polycarbonate); PS (polystyrene)

Figure 2: Predictions from the Microplastic Index [reproduced from Boersma et al 2023]

Yuan et al. (2022) developed a semi-quantitative approach for ranking the intrinsic ability of various plastics to form microplastics in the marine environment – this tool is not supportive of formation of microplastics in terrestrial environments (Yuan et al., 2022). The approach uses a scoring algorithm based on: (a) global waste generation, (b) mean density, (c) degradability in marine environments, (d) particle size and (e) inherent hazard of the monomer (excluding specific additives which can compound hazards). Based on this approach, the investigators ranked 36 polymers. The top 10 plastics that are most likely and least likely to produce microplastics are noted in Table 3. The authors suggested that reducing microplastics in the marine environment requires greater use and development of biodegradable plastics (e.g., EPS, polylactic acid (PLA), and PVAc). There are several plastics such as PP, PC, PET, LDPE, and HDPE have a large production capacity and their risk values are low, but it will require strict management on their use and recovery to avoid contamination. Polymers such as ABS, SAN, TPU, and UP, are low in current production amounts, but have a high potential for creating microplastics and have high potential toxicity.

Table 3: Likelihood of microplastics formation in marine environments, top 10 most and least likely polymers to form microplastics in marine environments, based Yuan et al. 2022 methodology

Least likely to form microplastics in marine environments	*Most likely* to form microplastics in marine environments
Polymer	Polymer
PVDF [polyvinylidene fluoride]	PUR [polyurethane]
EVA [Ethylene-vinyl acetate]	PVC [polyvinyl chloride]
PA 11/12 [polyamide]	PAN [polyacrylonitrile]
PAA [polyacrylic acid]	ABS [acrylonitrile-butadiene-styrene terpolymer]
EPS [expanded polystyrene]	PMMA [poly(methyl methacrylate)]
PLA [polylactide]	SAN [styrene acrylonitrile copolymer]
PVAc [polyvinyl acetate]	TPU [Thermoplastic polyurethanes]
PPD-T [Poly(p-phenyleneterephthalamide)]	UP [unsaturated polyester]
UF [urea formaldehyde resin]	PET [polyethylene terephthalate]
PPS 1 [Polyphenylene sulphide]	PS [polystyrene]

Note: The full list of polymers can be found in Table 6 of the original article.

To the best of the authors' knowledge, no quantitative structure-activity relationships (QSAR) methodologies have been implemented with respect to unintentionally generated microplastics. When considering intentionally added microplastics (whose properties can be more easily obtained than microplastics in the environment), ECHA did not identify QSARs for biodegradation of microplastics. Read across from monomer biodegradation was also not deemed relevant (ECHA, 2020).

Exposure to unintentionally generated microplastics

In alternatives assessment, an exposure assessment is meant to qualitatively or quantitatively assess differences in exposures between alternatives across the life cycle. Degradation products, such as microplastics should therefore be considered in an alternatives assessment.

Because of the chemicals focus of alternatives assessment, few *materials*, such as plastics have been assessed with this method. Washington DOE stated that microplastics represent an additional exposure pathway in the alternatives assessment of PFAS in food packaging (Washington State Department of Ecology, 2022). The analysis of alternative plastic materials, LDPE and PP, did not reveal conclusive information regarding the size, shape, and environmental fate (including degradation) of potentially generated microplastics. This led to a significant data gap, which discounted LDPE and PP as alternatives for further assessment.

Exposure considerations in alternatives assessment are laid out as a series of questions in the IC2 Guide. These questions probe the potential exposure to hotspots of an alternative in its entire life cycle, by considering both the function of the alternative as well as the alternatives' physicochemical properties. In addition, these questions ask assessors to determine whether the alternative or its pollutants have been identified in biomonitoring studies.

It is with these questions in mind that human and environmental microplastics exposure was reviewed.

Exposure linked to physicochemical properties of plastics and microplastics.

The fate of microplastics in the environment has also been linked to physicochemical properties – both through experimental studies as well as modelling.

Experimentally, microplastics have been characterized by their shape, size, and polymer composition (Brander et al., 2021; Kershaw & Rochman, 2015). Methods in each of these domains continue to evolve in the scientific literature and in government policy (Wong & Coffin, 2021).

For example, in LCA models, the rates of degradation and sedimentation of microplastics has been proposed based on their size, shape, and polymer type (Corella-Puertas et al., 2023; Maga et al., 2022). These rates have influenced the fate of microplastics and their subsequent contributions to the impacts of the plastic product. For example, the characterization factors of microplastics, which quantitatively reflects a combination of hazard and exposure considerations in LCA, can vary by orders of magnitude depending on the polymer type, shape, and size (Corella-Puertas et al., 2023).

Microplastics' physicochemical properties also change throughout their lifetime. For example, human exposure to microplastics from plastic products be of concern because of exposure to mobile additives. However, after microplastics have aged in the environment, such mobile additives may be disassociated from plastics and therefore be of lesser concern to animals ingesting microplastics. Such hypotheses are the focus of scientific studies(Luo et al., 2020), but consensus and actionable guidelines for alternatives assessors are not yet available.

How exposure concerns impact microplastics risk assessment

Due to the ubiquitous nature of microplastics, many organizations have called for the precautionary approach to the risk management of plastics and microplastics:

- The UN Environment Programme, concludes that a precautionary approach to plastics and microplastics pollution is warranted (UNEP, 2021).
- The Group of Chief Scientific Advisors, gathered by the European Commission, acknowledged current data gaps in both the measurement of exposure and hazard of microplastics. They concluded that the currently-available evidence demonstrated there was no widespread risks to humans or wildlife, but that there are significant grounds for precautionary measures due to the high rate of accumulation of microplastics in the environment (European Commission, 2019).
- The State of California's microplastics strategy also calls for a precautionary approach to the risk assessment of microplastics due to their high persistence and increasing concentrations in the environment, and potential to lead to hazardous impacts (Brander et al., 2021).
- The Government of Canada also echoes the need for a precautionary approach to microplastics management (Government of Canada, 2020)
- The Risk Assessment Committee (EU) could not conclude that microplastics had a "safe threshold" of exposure based on existing data (ECHA, 2020). Current data prohibit reliably quantifying hazards to the environment using reported thresholds.
- A recent report by the Nordic Council of Ministers, written to support Global Plastics Treaty negotiations, also calls for a precautionary approach to microplastic pollution due to microplastics being considered non-threshold contaminants (Norwegian Institute for Water Research, 2022).

This has led to significant efforts to decrease the exposure of microplastics to both humans and animals. Unintentionally generated microplastics, the focus of this review, are not yet broadly regulated. The EU Commission is developing legislation to decrease releases of tire- and textile-derived microplastics. The ongoing negotiations surrounding the Global Plastics Treaty, with its intent to be legally binding, will also consider microplastics pollution. In conclusion, the mitigation of microplastic pollution is not yet implemented at scale (UNEP, 2022b).

APPENDIX B: Survey of Hazard Traits of Microplastics

Excerpted from: California Department of Toxic Substances and Control. (2021). Green Ribbon Science Panel Background Document: Microplastics. November.

The objective for this table for the purpose of the background document noted above, was to cast a broad net to determine the scope of hazard traits potentially associated with microplastics and to obtain summary information. Some caveats to consider regarding the information presented in this table include:

- The hazard traits summarized in this table should be reviewed in regard to the physical chemical properties (particle size and shape, polymer type, color, age, hydrophobicity, density, surface area, and crystallinity, among others), rather than the specific material-type (e.g., chemical composition) of the microplastic.
- Many hazard traits are not associated with a specific material type, and this topic warrants further research.
- Some of the studies cited in this table may not represent real-world exposure scenarios. This should also be more thoroughly reviewed to determine if the hazard traits listed are in fact a concern.
- Due to the fact that most of the research on the hazards associated with microplastic exposures has been conducted only within the last few years, there are lot of data gaps.
- Some of the hazard traits identified in this table are based on only a few studies, or even just a single study. New research should be monitored to determine the extent to which it supports these preliminary findings.
- When assessing hazard traits associated with microplastics, differentiating between plastics (bulk size) versus microplastics. As state of science evolves, particle size should be carefully reviewed when assessing hazard traits.

Hazard Trait Category	Hazard Trait	Brief Summary of Evidence	Type of Plastic	Reference
Toxicological	Immunotoxicity	Alters cellular metabolism, although long-term effects of these changes are not well understood: “Phagocytosis of MP [microplastics] by macrophages induced a metabolic shift toward glycolysis and a reduction in mitochondrial respiration that was associated with an increase of cell surface markers… and cytokine gene expression associated with glycolysis. The gastrointestinal consequences of this metabolic switch in the context of an immune response remain uncertain, but the global rise of plastic pollution and MP ingestion potentially poses an unappreciated health risk.” PVC may cause adverse impacts to immune system.	Polystyrene microplastic	(Teuten et al. 2009; Lambert et al. 2017; Alimi et al. 2018; Rochman et al. 2019; Merkley et al. 2021)
Toxicological	Nephrotoxicity	“Evaluated in human kidney proximal tubular epithelial cells…and male C57BL/6 mice.” The study found: Higher levels of reactive oxygen species and inflammation markers, and lesions, causing mitochondrial dysfunction.	Polystyrene microplastic	(Wang et al. 2021)
Toxicological	Neurotoxicity	Passing through blood brain barrier into brain, in some instances may cause behavioral disorders, other effects.	Various	(Mattsson et al. 2017; Prust 2020)
Toxicological	Respiratory Toxicity	Conducted in a human alveolar epithelial A549 cell line: affects cell viability, causes inflammation and other effects. PS nanoparticles with sizes 50 nm and smaller were shown to be a potential risk to human respiratory system. Occupational polypropylene flock exposure can cause impairment of pulmonary function due to inhalation of respirable-sized particles with aerodynamic diameters less than 10 microns.	Polystyrene nanoplastics	(Atis 2005; Xu et al. 2019)

Hazard Trait Category	Hazard Trait	Brief Summary of Evidence	Type of Plastic	Reference
Toxicological	Carcinogenicity	Polystyrene (PS) is considered hazardous because its monomer, styrene, is a suspected carcinogen. In an *in vitro* study, PS nanoparticles caused numerous toxicological effects in human lung cells, some of which are associated with cancer. Polyvinyl chloride (PVC) and polyurethane (PU) may be carcinogenic to organisms.	Polyvinyl chloride, polyurethane, polystyrene	(Teuten et al. 2009; Lambert et al. 2017; Alimi et al. 2018; Rochman et al. 2019; Xu et al. 2019)
Toxicological	Genotoxicity	In an *in vitro* study, polystyrene nanoparticles entered lung cells. Polystyrene nanoparticles were toxic to the cells and damaged genetic information, such as gene transcription.	Polystyrene	(Xu et al. 2019)
Toxicological	Endocrine Disruption	Polyvinyl chloride may cause endocrine disruption and adverse impacts on immunity. Polyethylene terephthalate, one of the most common environmentally detected plastics, is suspected to leach additives, many of which are endocrine-disrupting chemicals. Plastics leach chemicals that cause endocrine effects.	Polyvinyl chloride, polyethylene terephthalate, high-density and low-density polyethylene, polystyrene, polypropylene, polyethylene terephthalate, polyurethane, and polylactic acid	(Teuten et al. 2009; Lambert et al. 2017; Alimi et al. 2018; Rochman et al. 2019; Zimmermann et al. 2021)
Environmental	Eutrophication	"Eutrophication is aggravated by intensifying microplastic pollution and resuspension."	Various	(Zhang et al. 2020)
Environmental	Wildlife Reproductive Impairment	Adverse effects on reproduction in organisms. Decreases in fertility (mice). Long-term ingestion affects fish growth and reproduction (by 50% in one study).	Polyethylene, polyvinyl chloride with and without additives, polyurethane	(Ribeiro et al. 2019; Rochman et al. 2019; Cormier et al. 2021)

Hazard Trait Category	Hazard Trait	Brief Summary of Evidence	Type of Plastic	Reference
Environmental	Wildlife Survival Impairment	Reduction of feeding rate, reduction of predatory performance, physical damage, induction of oxidative stress, decreased neurofunctional activity, oxidative damage, development of pathologies, and mortality in marine organisms. Bioaccumulation of polybrominated diphenyl ethers (PBDEs) was observed in earthworm (*Eisenia fetida)* after 28 days' exposure to polyurethane foam, showing that PBDEs may accumulate in organisms ingesting soils containing microparticles. The earthworms were exposed to PBDE-containing polyurethane foam microparticles. Parent birds may expose their offspring to plastics during feeding. More plastic was found in the intestines of juvenile birds than in adults. The tendency of discolored (i.e., yellowed) microplastics to have larger amounts of PCBs is ecotoxicologically important, because certain species of birds and fish ingest colored plastics selectively. Depending on polymer type some microplastics may cause cancer, endocrine disruption, and adverse impacts to immune system.	polyurethane, polyurethane with PBDEs or PCBs, polyvinyl chloride, polyethylene, polystyrene, polypropylene, polyethylene terephthalate	(Endo et al. 2005; Teuten et al. 2009; Lambert et al. 2017; Alimi et al. 2018; Ribeiro et al. 2019; Rochman et al. 2019)
Environmental	Loss of Genetic Diversity, Including Biodiversity	Marine biodiversity may be impacted by organisms suffocating, ingesting, and becoming entangled in plastics.	Polyvinyl chloride, polyurethane	(International Union for Conservation of Nature (IUCN) 2020)

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