

Formation, behavior, properties and impact of micro- and nanoplastics on agricultural soil ecosystems (A Review)

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ABSTRACT

Micro and nanoplastics (MPs and NPs, respectively) in agricultural soil ecosystems represent a pervasive global environmental concern, posing risks to soil biota, hence soil health and food security. This review provides a comprehensive and current summary of the literature on sources and properties of MNPs in agricultural ecosystems, methodology for the isolation and characterization of MNPs recovered from soil, MNP surrogate materials that mimic the size and properties of soil-borne MNPs, and transport of MNPs through the soil matrix. Furthermore, this review elucidates the impacts and risks of agricultural MNPs on crops and soil microorganisms and fauna. A significant source of MPs in soil is plasticulture, involving the use of mulch films and other plastic-based implements to provide several agronomic benefits for specialty crop production, while other sources of MPs include irrigation water and fertilizer. Long-term studies are needed to address current knowledge gaps of formation, soil surface and subsurface transport, and environmental impacts of MNPs, including for MNPs derived from biodegradable mulch films, which, although ultimately undergoing complete mineralization, will reside in soil for several months. Because of the complexity and variability of agricultural soil ecosystems and the difficulty in recovering MNPs from soil, a deeper understanding is needed for the fundamental relationships between MPs, NPs, soil biota and microbiota, including ecotoxicological effects of MNPs on earthworms, soil-dwelling invertebrates, and beneficial soil microorganisms, and soil geochemical attributes. In addition, the geometry, size distribution, fundamental and chemical properties, and concentration of MNPs contained in soils are required to develop surrogate MNP reference materials that can be used across laboratories for conducting fundamental laboratory studies.

List of symbols

AFM	atomic force microscopy
BDM(s)	biodegradable plastic mulch(es)
cryo	cryogenic
DLS	dynamic light scattering
d_p	average particle size of MNPs
FTIR	Fourier transform infrared spectroscopy
GC-MS	gas chromatography-mass spectroscopy
HDPE	high-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MPs	microplastics
MNPs	micro and nanoplastics

Micro-FTIR or μ -FTIR	Fourier-transform infrared spectroscopy-microscopy
NanoSIMS	nanoscale secondary ion mass spectrometry
NMR	nuclear magnetic resonance
NPs	nanoplastics
PBAT	polybutylene adipate terephthalate
PBS	polybutylene succinate
PE	polyethylene
PET	polyethylene terephthalate
PEVA	polyethylene-co-vinyl acetate
PEBV	polyethylene-co-vinyl butyral
PHA	polyhydroxyalkanoate
PLA	polylactic acid
PNEC	predicted no-effect concentration

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PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
pyro	pyrolysis
QA	quality assurance
QC	quality control
RCR	risk characterization ratio
SEM	scanning electron microscopy
SOC	soil organic carbon
SOM	soil organic matter
TED-	thermal desorption
TEM	transmission electron microscopy
UV	ultraviolet-visible spectral energy

1. Introduction

The rapid increase in plastic environmental pollution caused by growing plastic consumption poses a severe threat to terrestrial and aquatic ecosystems entailing significant impacts on flora and fauna (Malafaia et al., 2020; Ansari et al., 2022; Li et al., 2022; Sajjad et al., 2022; Xiang et al., 2022; Das et al., 2023). Synthetic plastics are frequently used for various industries such as agriculture, electronics, packaging, and building construction based on desired physical, chemical, and mechanical properties, including low weight, durability, and low production cost. The lack of recycling strategies and options results in frequent improper environmental disposal. The growing demand in these industries resulted in worldwide plastic production of 359 million metric tons in 2018 (PlasticsEurope, 2019; Napper and Thompson, 2020; Leal Filho et al., 2021; Um et al., 2023) and is projected to increase to 1200 million metric tons by 2050 (Dai et al., 2022). However, only 6 to 26% of generated plastics are currently being recycled (Alimi et al., 2018), and 25–28% are mishandled regarding their end-of-life, suggesting that a large portion of plastics accumulates either in the aquatic or terrestrial environment (MacArthur et al., 2016; Nizzetto et al., 2016a; O'Connor et al., 2016; Wright and Kelly, 2017; Alimi et al., 2018). Larger fragments exposed to environmental weathering conditions, such as ultraviolet (UV) light, wind, and hydrolysis, break down progressively into smaller fragments and particles (Kasmuri et al., 2022; Sun et al., 2022; Yang et al., 2022b) and form micro- and nanoplastics, (MPs and NPs), respectively.

MPs are defined as plastic particles of average size (nominal diameter; d_p) between 5 mm and 1 μm , whereas NPs have been defined as

“particles within a size ranging from 1 to 1000 nm resulting from the degradation of industrial plastic objects and can exhibit a colloidal behavior” (Gigault et al., 2018) (Fig. 1). However, the upper size limit of NPs is in several publications listed as 100 nm (Gigault et al., 2018). Generally, MPs and NPs (MNPs) are categorized as primary or secondary. Primary MNPs enter the environment in their size-reduced form from industrial manufacturing activities. Examples include microbeads, microspheres, and microfibers from textiles (Van Cauwenberghe et al., 2015), cosmetics, and manufacturing products (de Souza Machado et al., 2018a). Secondary MNPs are derived from larger plastic materials, including plastic debris and fragments, through breakdown and decomposition (Thompson et al., 2004; Silva et al., 2018). Due to their ecotoxicity to aquatic flora and fauna, MNPs have been mainly studied in or near bodies of water such as streams, lakes, and oceans. Approximately 5.25 trillion plastic particles reside in the oceans, most of which are MNPs (Mattsson et al., 2015). MNPs are known to cause harm to marine organisms, including fish and crustaceans, leading to reduced reproduction, growth, and fitness (Bouwmeester et al., 2015; Mattsson et al., 2015; Horton et al., 2017; Alimi et al., 2018; Lu et al., 2018; Schwabl et al., 2018). There are also reports of effects on related microbial communities, such as ecotoxicity and the lowering of community diversity (McCormick et al., 2014).

MNPs in agricultural ecosystems can potentially serve as a global threat to soil health and food production systems. MNPs, particularly in soil, originate mainly from agricultural plastic materials, most commonly mulch film, but also through irrigation water, street runoff, flooding, sewage sludge, agricultural compost, and air (Fig. 2) (de Souza Machado et al., 2018b; Pérez-Reverón et al., 2022b; Rolf et al., 2022; Schell et al., 2022; Salehi et al., 2023). Plastic films and materials are integral for contemporary agricultural practices, particularly for production of specialty crops such as vegetables and small fruit, and are associated with improved crop productivity, quality, and sustainable agricultural production (Hussain and Hamid, 2003; Scarascia-Mugnozza et al., 2011; Steinmetz et al., 2016). However, in recent years, “plasticulture” has led to concerns regarding plastic fragments’ production, dispersion, and retention in agricultural ecosystems, particularly of MNPs. Terrestrial MNPs have received relatively less attention than water-borne MNPs until the last few years, despite occurring at 4 to 23-fold higher amounts than in aquatic ecosystems (Nizzetto et al., 2016b; Horton et al., 2017; Alimi et al., 2018; Bläsing and Ameling, 2018). Another significant source of MPs in soil is deposition of airborne MPs near roadsides, originating from tire wear generated by friction

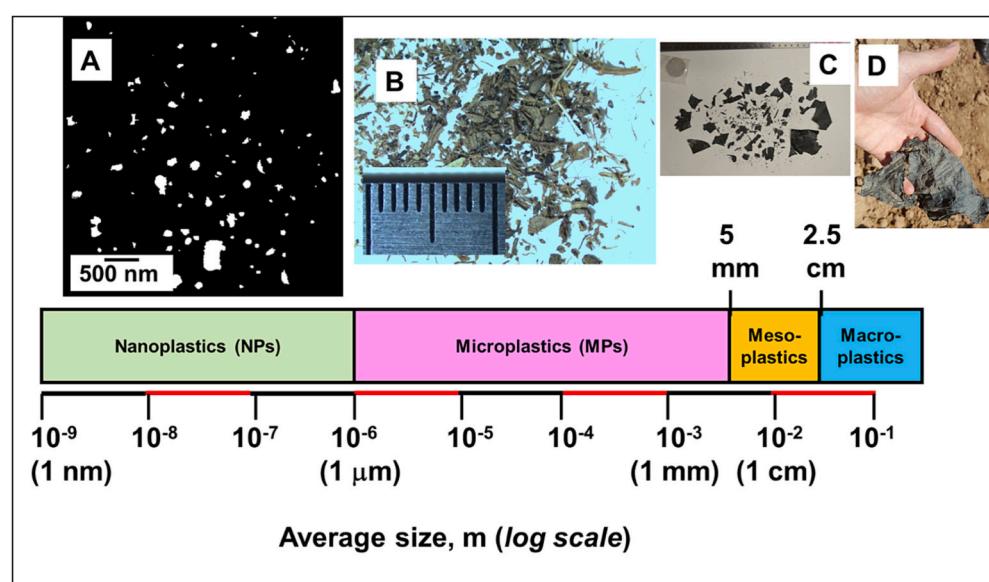


Fig. 1. Depiction of the length scale of plastic fragments, including MNPs and NPs, and images representing each subpopulation derived from biodegradable plastic mulch films (BDMs). **A** an atomic force microscopic image of NPs prepared from BDMs using a wet grinding technique; **B** MPs retrieved from soil employed for vegetable production using BDMs (ruler 1 cm in length); **C** mesoplastics retrieved from soil (a dime is shown in the upper left-hand corner: 1.8 cm in diameter); **D** macroplastics.

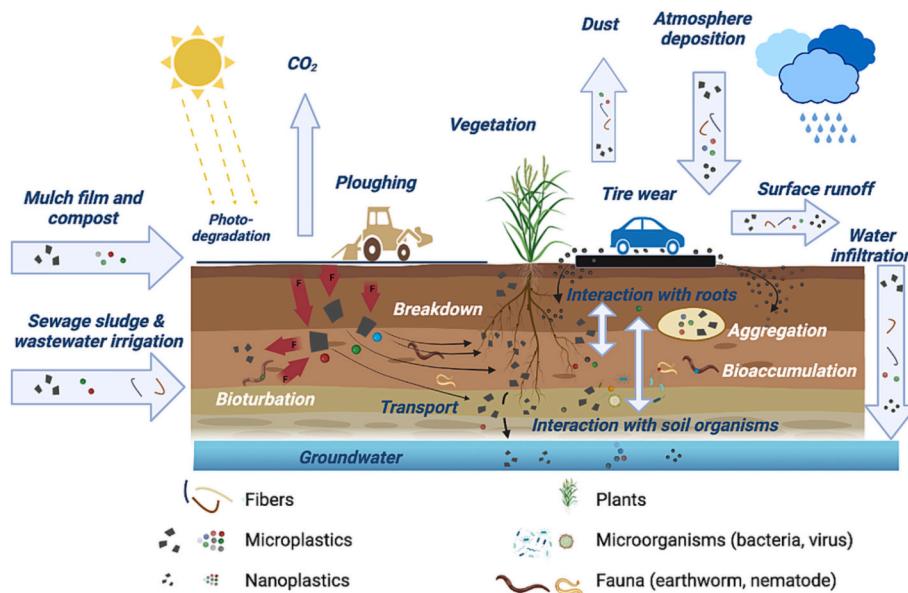


Fig. 2. Life cycle and dynamics of plastics and impact on agricultural soil ecosystems: sources, effects, and the fate of MPs in agricultural soil systems. Figure adapted from Tian et al. (2022) *Current Opinion in Environmental Science & Health*, Vol. 25, 100,311, Copyright 2022, with permission from Elsevier.

between the road and rubber (Kole et al., 2017). Tire rubber particles can negatively affect plant growth and alter the soil's biogeochemical properties resulting in reduced shoot and root growth and elevated soil pH levels (Leifheit et al., 2022).

MNPs residing in agricultural soils can affect terrestrial geochemistry, groundwater quality, and soil biota, including plants, earthworms, and microorganisms (de Souza Machado et al., 2018a; Zhang et al., 2018; Ren et al., 2021b; Wahl et al., 2021; Aransiola et al., 2023; Maddela et al., 2023) (Fig. 3). The formation of MNPs may lead to the release of poorly biodegradable and possibly ecotoxic compounds such as plasticizers (Sintim et al., 2020; Yu and Flury, 2021a). Moreover, their ability to serve as vehicles for transporting pesticides has been reported (Peña et al., 2023). Replacing conventional and poorly biodegradable plastics such as polyethylene (PE) with biodegradable polymeric mulch film components results in MPs and likely NPs that may reside in soil for several months.

Although several review papers have been published recently (Table S1), our review represents a more comprehensive and contemporary summary of the occurrence and impacts of MPs and NPs characterized by conventional and biodegradable agricultural plastics (Chae and An, 2018; Ng et al., 2018; Li et al., 2020a; Qi et al., 2020; Jin et al., 2022; Madrid et al., 2022; Wang et al., 2022a; Iqbal et al., 2023; Okeke et al., 2023).

Herein, we summarize the current understanding of the formation, degradation, transport, and physicochemical properties of MNPs

residing in agricultural soils, mainly derived from conventional and biodegradable plastic mulch films, and the potential impacts of MNPs on crops, fauna, and soil geochemistry. The advantages of different sampling, identification, and characterization methods frequently employed to extract MNPs from agricultural soils are reviewed. In addition, we highlight new research approaches to preparing MNPs that mimic those found in agricultural ecosystems, which can be used in fundamental studies. The methodology and literature review results are further described in the Supporting Information.

2. Sources of plastics and MNPs in agricultural soils

Human activities have released plastics into agricultural soils, including several primary and secondary sources (Fig. 2) (Weithmann et al., 2018; Corradini et al., 2019). The major source of secondary MPs is agricultural plastic materials (Qi et al., 2020; Serrano-Ruiz et al., 2021). Modern agroecosystems frequently employ plastics for crop cultivation, including as covers for high and low tunnels, silage films, bale wraps, drip tapes, irrigation pipes, and packaging for fertilizers and other agrochemical inputs (Table 1). Globally, agricultural plastic films accounted for a value of \$11.5 billion in 2021 and are estimated to reach \$15.7 billion in 2026, with a compound annual growth rate of 5.6% (von Moos et al., 2012; MarketsandMarkets, 2021). In this context, plastic mulching was frequently among the most significant contributors to plastic pollution in agricultural soil (Khalid et al., 2022; Khan et al.,

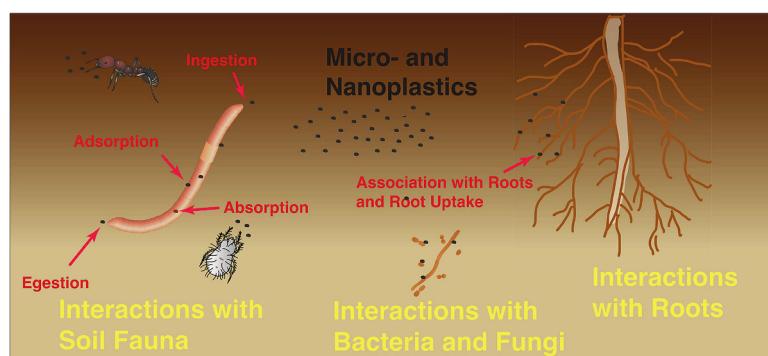


Fig. 3. Depiction of the interaction of MNPs in soil with soil organisms.

Table 1

Characteristics of conventional plastic materials employed for agricultural applications. Adapted from (Briassoulis et al., 2013; Zhu et al., 2018c) ^a.

Product	Composition	Additives	Service life, yr	Contamination, wt% ^b
Mulching films	LDPE, LLDPE, PEVA	Colorants ^c , UV stabilizers	0.5 ^d	60–80
Low tunnel films	LLDPE, LDPE	UV stabilizers, IR absorbers, anti-fog agents	0.5 ^d	60–65
High tunnel films	LDPE, LLDPE, PEVA/PEBV	Colorants ^c , UV stabilizers, silica filler, anti-dripping, –dust, and -fog agents, IR absorbers, stabilizers for resistance to agrochemicals	1–2.5	15–20
Silage films	LLDPE, PEVA PP, LLDPE	Colorants ^c , UV stabilizers	1	NA
Bale wrap and shrink films	LLDPE, PP, HDPE, PVC	Colorants ^c , UV stabilizers	1	NA
Agrochemical containers	PET, LDPE–HDPE,	Colorants, UV stabilizers, Thermal resistant additives	1	NA
Irrigation pipes	LDPE, HDPE	Colorants ^c	10–20	NA
Drip tape	LLDPE, HDPE LLDPE	Colorants ^c , UV stabilizers	1	NA
Fertilizer sacks	PE, PP	UV-stabilizers, ^c colorants	1	NA

^a Abbreviations: HDPE: high-density polyethylene, IR: infrared, LDPE: low-density polyethylene, LLDPE: linear low-density polyethylene, NA: data not available, PE: polyethylene, PET: polyethylene terephthalate; PEVA: polyethylene-co-vinyl acetate, PEVB: polyethylene-co-vinyl butyral, PP: polypropylene; PVC: polyvinylchloride, UV: ultraviolet.

^b refers to the weight of primarily adhering soil (contamination) on the film surface relative to the film dry weight after one growing season; common contaminants include soil and organic matter (e.g., residues of herbaceous plants, straw, and hay).

^c e.g., carbon black or TiO₂.

^d single cropping season.

2023; Zhou et al., 2023). Thin plastic mulch films with dimensions of ~20–100 µm thickness and ~1.2 m width are applied to the soil surface before adding seeds or seedlings (through holes placed in the film), resulting in a favorable microclimate underneath the films. Plastic mulches fulfill several roles in maximizing productivity for vegetables, small fruit, and other specialty crops, such as reducing weeds, controlling soil temperature (with their color playing a key role), minimizing evaporative water loss (thereby facilitating drip irrigation), and preventing soil erosion (Kasirajan and Ngouadio, 2012; Steinmetz et al., 2016; Hayes et al., 2019; Serrano-Ruiz et al., 2021). Recent findings state that plastic mulches have produced terrestrial PE concentrations of 60–300 kg ha⁻¹ and as high as 500 kg ha⁻¹ in China, likely associated with incomplete and improper retrieval and disposal (Liu et al., 2014; Bloomberg News, 2017; Tremblay, 2018). Environmental degradation of plastics occurs during their service life through factors such as UV radiation, rain, wind, and soil microbes that contribute to embrittlement and other forms of degradation, leading to the formation of MNPs (Fig. 2), as discussed in Section 4.1. MPs dispersed in soil from these sources may represent various biodegradable and non-degradable polymers with different shapes, including uniform-shaped spheres, beads, pellets, fibers, films, foams, and fragments (Xu et al., 2020; Chia et al., 2021).

The most common (poorly biodegradable) material for mulching and other applications of “plasticulture” is low-density-PE (LDPE), or linear

LDPE (LLDPE), where the latter possesses lower levels of branching in the molecular structure compared to the former (Table 1) (Hussain and Hamid, 2003; Scarascia-Mugnozza et al., 2011; Kasirajan and Ngouadio, 2012). LDPE possesses excellent mechanical properties for plasticulture, e.g., high tensile and tear strength, elongation, and low gas permeability (Table 2). Given that the molecular structure of PE is essentially a long-chain alkane (Fig. S1), LDPE is hydrophobic, which enhances its durability but also leads to poor biodegradability. Microorganisms may degrade conventional PE plastic, but degradation is slow, incomplete, and often not observed in environmentally relevant conditions (Montazer et al., 2020). Because of the latter attribute, LDPE films should be collected and recycled to fulfill sustainable agriculture best practices. However, retrieval and transport of PE films are laborious and expensive, and collection sites for recycled agricultural films are sparse, especially in North America (Steinmetz et al., 2016; Hayes et al., 2019; Serrano-Ruiz et al., 2021). Recycling and repurposing are further hindered by high contamination levels on the retrieved plastics (Table 1). As a result, used LDPE films have been mishandled by illegal burning, which leads to air pollution, by on-farm stockpiling, which leads to degradation and fragmentation of the films, or by burial in soil, which can produce MNPs (Kasirajan and Ngouadio, 2012; Hayes, 2021; Huerta Lwanga et al., 2023). Other traditional plastics used for agricultural applications include high-density PE (HDPE), polypropylene (PP), and polyethylene-co-vinyl acetate (PEVA) (Table 1).

To address the problems associated with the poor sustainability of LDPE and other traditional plastics, biodegradable plastics for agricultural applications were developed and introduced to the market, particularly for mulch films (i.e., biodegradable mulches, or BDMs; Table 2). BDMs ideally undergo complete biodegradation in the soil after being incorporated via plowing after crop harvest, but they can also be collected upon completion of their service life and composted (Steinmetz et al., 2016; Hayes et al., 2019; Serrano-Ruiz et al., 2021). Plowing BDMs into the soil saves on labor costs associated with mulch retrieval, as would be needed for PE mulches or composting at the end-of-life for BDMs (Velandia et al., 2019).

The most frequently employed polymer for BDMs is the co-polyester, butylene adipate-co-terephthalate (PBAT), composed of aliphatic units of adipic acid and butanediol and aromatic units composed of terephthalic acid (Fig. S1 and Table 2). When present at >35% mol, the terephthalate monomer provides excellent thermal stability, improves

Table 2

Properties of commonly used polymers in agriculture, as well as emerging biodegradable polymers ^{a, b}.

Polymer	Properties	T _g , °C	T _m , °C
<i>Conventional polymers; low biodegradability</i>			
LDPE	Hydrophobic, good vapor barrier, high tensile and tear strength	–78	105–115
PET	Strong and light-weight, low gas permeability, recyclable	67–81	250–260
PEVA	Semi-crystalline polymer useful for shape-forming applications, such as cabling and flexible packaging	(–30)– (–23)	45–100
<i>Biodegradable polymers</i>			
PBAT	Good thermal stability and mechanical properties; brittle	–30	120
PLA	High modulus and tensile strength, low elongation break, brittle, high T _g	60–65	150–160
PBS	Good thermal and chemical resistance	–28.5	116.4
PHA	good UV resistance, poor mechanical properties, poor resistance to acids and bases	2–8	160–175

^a Abbreviations for polymers is given in Table 1 and Fig. S1; T_m and T_g refer to the melting and glass transition temperatures, respectively, with the latter referring to the temperature at which the polymeric material changes morphology from a hard/glassy state of an amorphous polymer to a soft state.

^b data from (Bugnicourt et al., 2014; Wang and Deng, 2019).

mechanical properties, and contributes to plastic flexibility and biodegradability. However, a high terephthalate concentration (>55%) greatly diminishes the biodegradation rate (Witt et al., 1997; Witt et al., 2001). Polybutylene succinate (PBS; cr. Fig. S1) and polybutylene succinate-co-adipate are related polymers employed for the same applications.

Several other applications listed in Table 1 can potentially employ compostable plastics that can be retrieved and mineralized through composting for their end-of-life. For example, polylactic acid (PLA), the least expensive and most readily available among the biodegradable polymers, has excellent properties as a replacement material for LDPE in films, particularly with high tensile strength (Table 2) and is readily biodegradable under composting conditions (Sin and Tueen, 2019). PLA is prepared from lactic acid, a common metabolite produced from the fermentation of maize or other plant sources, or lactides, cyclic diesters formed by two hydroxy acids (Fig. S1). However, PLA biodegrades slowly under ambient soil conditions due to its high glass transition temperature (~55 °C), making it highly crystalline in morphology at ambient temperature (Sin and Tueen, 2019; Anunciado et al., 2021a). In addition, pure PBAT, PBS, and PLA are brittle, hindering film performance. This deficiency is addressed by blending the biopolymers with additional polymers, plasticizers, or processing aids. For example, Mater-Bi® (Novamont, Novara, Italy) and ecovio® (BASF, Ludwigshafen, Germany) are blends of PBAT with thermoplastic starch and PLA, respectively. Another commonly used biopolymer class for blending is polyhydroxyalkanoate (PHA), a copolyester comprised of different hydroxy fatty acid units, such as 3-hydroxybutyrate (Fig. S1). Commonly used plasticizers for agricultural plastics include glycerol and triethyl citrate, which possess a much more favorable environmental profile than traditional phthalate plasticizers (Serrano-Ruiz et al., 2021).

Interestingly, PLA and PHA are mainly biobased, i.e., are derived from renewable resources, meaning that their life cycles, from cradle to gate, produce a lower amount of atmospheric carbon dioxide than polymer precursors primarily derived from fossil sources, hence resulting in a smaller carbon footprint and impact on climate change. In contrast, traditional polymers such as LDPE and PP are derived from fossil fuels, and therefore their life cycles contribute more to greenhouse gas production. PBAT and PBS traditionally have been derived from petroleum; however, recent efforts have been made to increase their biobased content, such as the production of 1,4-butanediol from fermentation and the partial substitution of adipic acid by azelaic acid, which is derived from vegetable oils such as safflower oil via ozonolysis (Encinar et al., 2022).

In addition to agricultural plastics, indirect secondary sources contribute to the accumulation of plastic fragments and MNPs in agricultural soils, such as compost and biosolids applications, atmospheric precipitation, irrigation water, and adjacent streams and ponds that carry MNPs originating from wastewater treatment facilities, leachates from landfills, sewage sludge, and floodplain deposition (Ryan et al., 2009; Zhao et al., 2015; Dris et al., 2016; Bläsing and Amelung, 2018; Scheurer and Bigalke, 2018; Gao et al., 2020; Gui et al., 2021; Yu and Flury, 2021a; Pérez-Reverón et al., 2022b; Tian et al., 2022). Among the sources listed, compost and biosolids are the greatest contributors to MNPs in agricultural soil and their possible lateral and vertical transport into nearby waterways need to be taken into account (O'Connor et al., 2022; Porterfield et al., 2022). Although compost addition enhances soil fertility, the relatively high concentrations (1.20 g kg⁻¹) of MPs in compost suggest that this fertilization practice can contribute to MNPs' addition to agricultural land (Braun et al., 2021). Besides, additional agricultural practices, such as the input of polymer-encapsulated fertilizers, may be an additional source of MP contamination in soil (Katsumi et al., 2021).

Recent reports have found that atmospheric deposition is a major source of primary and secondary MPs in the terrestrial environment (Roblin et al., 2020; Wright et al., 2020). A modeling study identified tire wear and packaging as the primary contributors for MPs and

macroplastics in the terrestrial environment, respectively (Schwarz et al., 2022). The same study estimated that 0.8 million tons of MPs and 8.7 million tons of macroplastics entered the terrestrial environment in 2017. However, the study found that most terrestrial plastics resided along roadsides. A limitation of the study was that the degradation and transport of terrestrial MPs were not considered. A second study found that tire wear served as the major source of airborne MPs (Panko et al., 2013), and that natural soils received lower levels of tire MPs than roadsides and surface water (Kim et al., 2022).

3. Physicochemical analyses of MNPs retrieved from soil

3.1. Sampling of MNPs from soil and sample preparation for further analysis

Sampling MPs in the soil is commonly done by randomly taking soil cores or larger soil volumes from the field with replicates (Piehl et al., 2018; Scheurer and Bigalke, 2018; Corradini et al., 2019; Crossman et al., 2020). An appropriate sampling design must be developed based on the site, research questions being addressed, and other concerns in the same way designs are necessary for investigating other environmental contaminants (Möller et al., 2020). To accurately quantify MPs in soil, it is necessary to take samples representing the number of MPs in the field (Lang et al., 2022; Wang et al., 2022b; Li et al., 2023).

A unique aspect of MPs residing in the soil is that the concentration of MPs is not continuous but a discrete spatial variable. This inconsistency makes sampling with small cores, as often done in soil science, unreliable because the size of the cores may not be sufficient to obtain a reliable sample (Webster and Oliver, 2007). For accurate sampling, the total volume of the soil samples taken should reach the representative elementary volume (Webster and Oliver, 2007), which depends, in the case of MPs, on the concentration and spatial distribution (Yu and Flury, 2021b). The representative elementary volume decreases hyperbolically with increasing MP concentration and increases substantially when spatial dependence exists between MNPs. Given that MP concentrations and their distributions are not known *a priori*, it is advisable to maximize sample volume as much as possible, for instance, by taking a soil sample from a surface area of 1 m² (Yu and Flury, 2021b). As this constitutes a large amount of soil, the quartering method can reduce the soil sample (ASTM-C702/C702M, 2018). In addition, collecting replicates is recommended to assess the sampling variability.

After sampling soil from the field, soil samples are brought to the laboratory for plastic extraction and identification. Most methods of MP extraction from a soil matrix consist of steps to separate plastic from soil organic matter (SOM) and to isolate MPs from minerals, soil particles, or both (Nguyen et al., 2019; Schwaferts et al., 2019). In addition, when NPs are of interest, samples may require a concentration step before analysis (Schwaferts et al., 2019). Extracting MPs from the mineral soil matrix often relies on separations based on density, hydrophobicity, size, or some combination. Standard techniques are reviewed in Möller et al. (2020). The most documented approach separates low-density polymers from mineral soil in a saturated sodium chloride solution (Li et al., 2020a).

In contrast, denser polymers may require more expensive or hazardous salt solutions such as zinc chloride or zinc iodide. For example, English (2019) used a saturated silica solution with a density of 1.4 g cm⁻³ to isolate MPs from PE mulches and BDMs composed of PLA, PBAT, and PE. Grause et al. (2022) successfully separated MPs from the soil by employing Fenton's digestion method in combination with a centrifugation technique. Radford et al. (2021) found that separation in canola oil led to similar extraction efficiencies as zinc chloride for soils with less than 20% organic matter content. However, extraction efficiency with canola oil declined as the SOM concentration increased, unlike zinc chloride and sodium chloride extractions, which were not correlated with organic matter concentration. Furthermore, the efficacy varied with polymer type and particle size when using canola oil, zinc

chloride, and sodium chloride as extractant (Radford et al., 2021). Canola oil-based extractions are an attractive option because the extractant is less expensive and toxic than zinc chloride.

The density separation of NPs is less feasible than for MPs because buoyancy decreases with decreasing size (Wang et al., 2018; Nguyen et al., 2019). Because of this difficulty, size-depending filtration has become a desirable method for separating NPs (Hernandez et al., 2019; Materić et al., 2020). In addition, sequential filtrations can reduce damage to filters and allow the isolation of smaller particles (Hernandez et al., 2017). Other size-based techniques of potential use for NPs include gel electrophoresis and size exclusion chromatography, which could be adapted for use on much lower environmental concentrations of NPs (Nguyen et al., 2019).

SOM can be removed with acidic or alkaline solutions, oxidizers like hydrogen peroxide, Fenton's reagent (hydrogen peroxide and divalent iron), or enzymes such as proteases to aid in recovering MNPs from soil (Möller et al., 2020). Acid, alkali, or hydrogen peroxide may damage plastic particles while destroying organic matter, while Fenton's reagent and enzymatic digestions are often less damaging (Cole et al., 2014; Tagg and Labrenz, 2018). The relative efficacies of digestion strategies on seven common plastics are reviewed in Hurley et al. (2018). Biodegradable polymers like PLA and PBAT pose a unique challenge for recovery because they possess labile chemical bonds that are more susceptible to damage from these digestions than common synthetic plastics (Song et al., 2009). Digestion with Fenton's reagent has been shown to reduce the size of PLA and PBAT MPs and deposit iron-containing residue, interfering with subsequent spectroscopic analysis (Pfohl et al., 2021). Method verification should be performed to demonstrate that digestion to remove organic-rich substrates does not damage biodegradable MPs (Edo et al., 2022). Therefore, a knowledge gap exists in applying a proper method for efficiently removing organic matter from MPs.

3.2. Identification and quantification of MNPs

Many soil MP identification techniques are borrowed or modified from aquatic methods and thoroughly reviewed elsewhere (Miller et al., 2017; Hermen et al., 2018; Mai et al., 2018). As multiple methods of sampling, preparing, and identifying MPs from environmental specimens emerge, standardization efforts are necessary so that results are reproducible and comparable (Hermen et al., 2018; Cowger et al., 2020). Visual identification of MPs is the most commonly reported strategy to analyze environmental samples, with 79% of studies using either visual identification alone or combined with another analytical technique (Nguyen et al., 2019). However, visual identification may have a concerningly high error rate (Hidalgo-Ruz et al., 2012; Silva et al., 2018) and may not be consistent from person to person (Dekiff et al., 2014). For this reason, standards for the visual identification of MPs exist (MSFD Technical Subgroup on Marine Litter, 2013), and visual analyses should only be used with particles $>500\text{ }\mu\text{m}$ in size (Löder and Gerdts, 2015). Scanning electron, transmission electron, or atomic force microscopies (SEM, TEM, and AFM, respectively) can identify much smaller MNPs, although the tools are more costly in money and time. TEM offers a better resolution of $\sim 0.2\text{ nm}$ over SEM and can measure samples from $\sim 1\text{--}100\text{ nm}$, whereas the resolution for SEM is $\sim 1\text{ nm}$ and is capable of measuring samples $\sim 50\text{--}500\text{ nm}$ (Pérez-Reverón et al., 2022a; Zhao and Liu, 2022). SEM application is discussed in (Silva et al., 2018). Electron microscopy and dynamic light scattering (DLS) can also be adapted to target NPs (Schwaferts et al., 2019). Because visual and electron microscopic analyses cannot be used to identify the polymer type of MPs, they are often paired with spectroscopic analysis to identify MPs' molecular structure. Vibrational spectroscopy, such as attenuated total reflection FTIR (transmission), micro-FTIR, or micro-Raman spectroscopy, are three of the most common chemical identification methods (Käppler et al., 2016; Silva et al., 2018) (Fig. 4). The latter two entail the combination of vibrational spectroscopy with microscopy.

However, the latter two cannot identify particles smaller than $1\text{--}10\text{ }\mu\text{m}$ (Ivleva et al., 2017). Commercial and open-access spectral libraries help FTIR and Raman spectroscopy users identify the molecular nature of many MPs (Munno et al., 2020; De Frond et al., 2021), including rubber tire particles in sediments and soils (Mengistu et al., 2019). Spectra generally differ between pristine and environmentally weathered materials. Libraries of MP samples belonging to different polymers, sizes, and histories of particles can help improve plastic identification (Primpke et al., 2017; Munno et al., 2020; De Frond et al., 2021) (Fig. 5).

Furthermore, chemical identification of common MP polymers can be obtained by gas chromatography-mass spectroscopy (GC-MS) coupled with thermal desorption (TED-) or pyrolysis (pyro-) (Nguyen et al., 2019; Jung et al., 2021). These MS techniques destroy samples and cannot collect information about the size and shape of plastic particles (Du et al., 2020). Still, they can give quantitative information about the total plastic amount (Nguyen et al., 2019). GC-MS can identify the polymer type and concentration of NPs, but sample preconcentration is necessary (Schwaferts et al., 2019; Li et al., 2020b). In addition, nano-scale secondary ion mass spectrometry (NanoSIMS) has been used to quantify stable isotopes in various samples under high spatial resolution. For instance, Zumstein et al. (2018) traced the degradation of biodegradable polymers in soil using ^{13}C labeled PBAT, with $^{13}\text{CO}_2$ being measured, providing mass balances for the PBAT carbon polyester components by the derived ^{13}C , and which portion remained in the soil after incubation.

Nuclear magnetic resonance (NMR) spectroscopy may emerge as another chem technique to identify microplastic samples chemically. $^1\text{H-NMR}$ was used by Peez et al. (2019) to quantitatively identify PE, polyethylene terephthalate (PET), and polystyrene (PS) MPs (Peez et al., 2019). Nelson et al. (2020) used solvent extraction to remove PBAT polymers from soil and quantitatively identified them with $^1\text{H-NMR}$ (Fig. 6).

NMR may be sensitive to interference by solvent-soluble organic matter in the soil (Peez et al., 2019). However, the group found their technique allowed PBAT quantification in soils with up to 2% SOM. Quantitative analysis was impossible with a 41% organic matter peat soil (Nelson et al., 2020). Adequate sensitivity requires liquid-phase NMR, meaning further development is needed to identify solvents that can extract MPs out of the soil without analytes that would interfere with the NMR spectral quantification of other polymeric materials. NMR is not destructive to the dissolved polymer sample, but dissolution does remove information about particle size and shape, similar to GC-MS (Peez et al., 2019).

Laboratory studies can make use of other techniques like fluorescent markers such as Nile Red (Shim et al., 2016), isotopic labeling (Taipale et al., 2019; Tian et al., 2019), or analyzing for characteristic metals present in the plastics, such as the titanium in the white colorant titanium dioxide (Yu et al., 2022) to track MPs and learn about their transport through soil systems. Fluorescence staining can help identify MNPs with high recovery rates. Fluorescence staining techniques are widely used to quantify MPs, their distribution, movement, and concentration in various environmental matrices such as soil, water, sediments, and organisms (Duan et al., 2021; Wang et al., 2021; Liu et al., 2022b). Fluorescence staining of MPs is inexpensive and allows the detection of bulk environmental and laboratory samples. However, the limitations of this method are that not all plastics can be stained [e.g., polyvinylchloride (PVC), and polyamides] due to their low hydrophobicity (Shim et al., 2016) and that chemical composition determination requires additional spectroscopic techniques such as Raman spectroscopy and FTIR spectroscopy.

Additionally, current dyes can yield many false positives by binding to SOM present in the sample (Liu et al., 2022b). The results of fluorescence-based studies may be of limited relevance as they require higher MNP concentrations than those that typically occur in most agricultural ecosystem samples (Du et al., 2020). Another emerging quantification method is hyperspectral imaging to identify MPs *in-situ* in

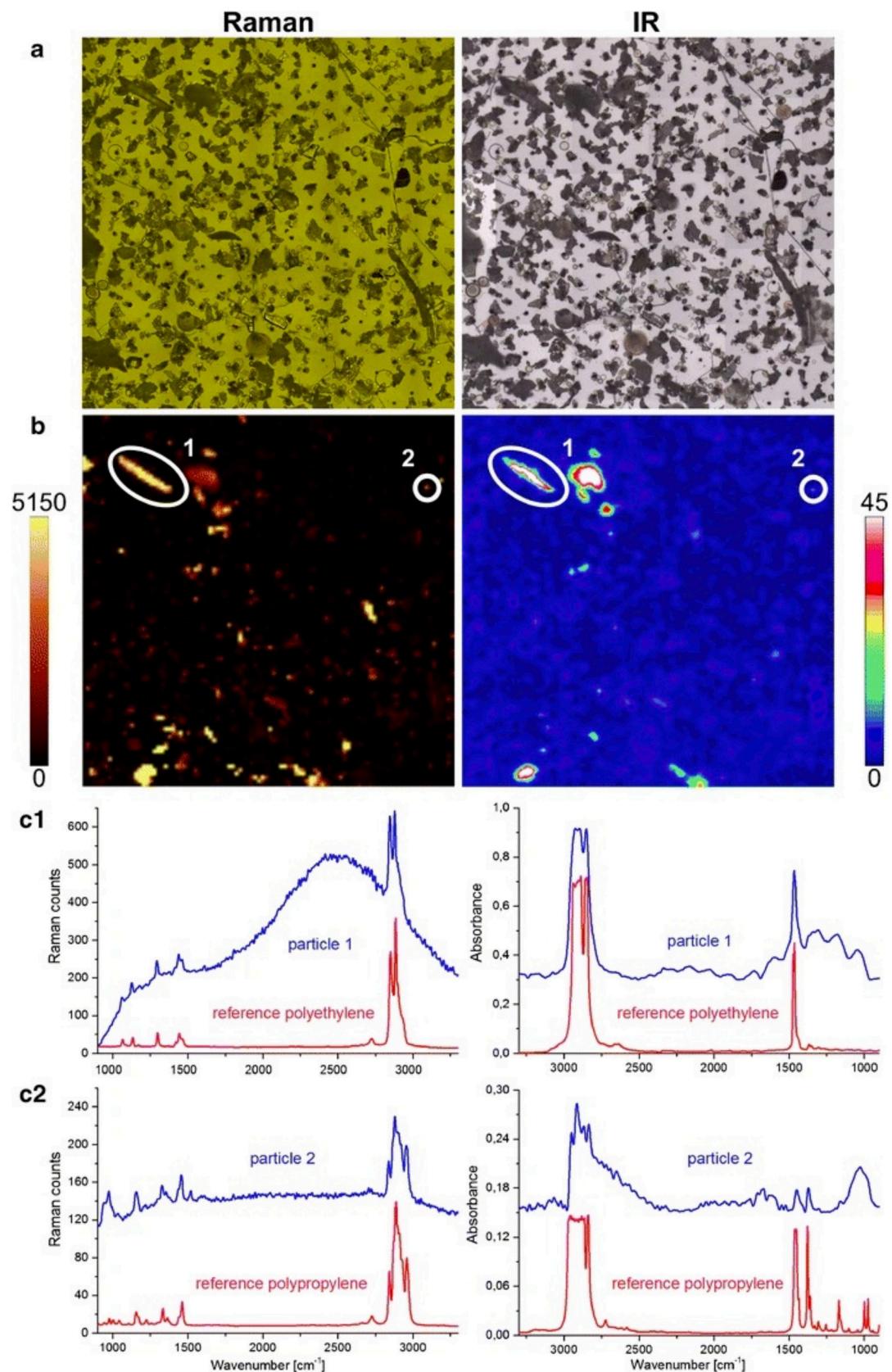


Fig. 4. Vibrational spectroscopic analysis of MPs. **a)** Raman image (left) and IR image (right) with false-coloring denoting the spectral intensity in the 2780–2980 cm^{-1} range. **b)** Raman spectrum (left) and IR transmission spectrum (right) of particle 2 in comparison with a reference of polypropylene. (figure adapted from *Analytical and Bioanalytical Chemistry*, Vol. 408, Käppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K.-J., Voit, B., Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both?, Pages 8377–8391, Copyright 2016, with permission from Springer Nature.

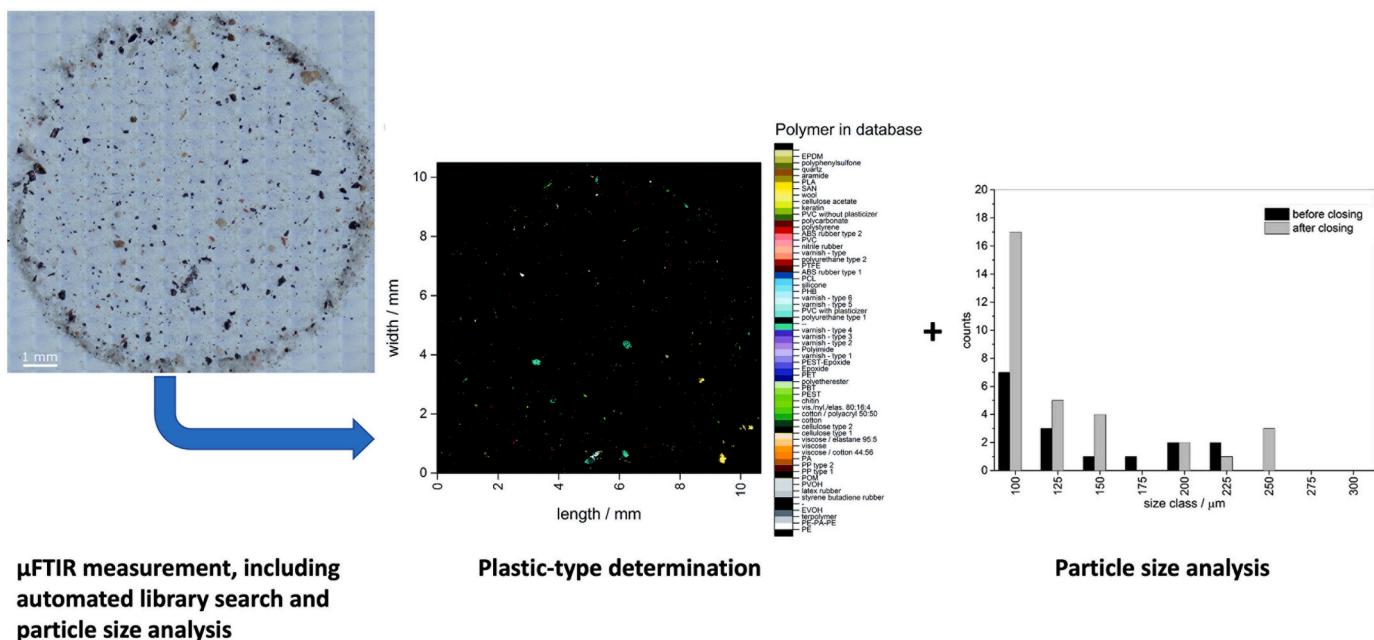


Fig. 5. Analysis of microscopical image of MPs determining the plastic type and particle size with polymer sample libraries. Figure compiled using Figures 1, 3a, and 5b from *Analytical Methods*, Vol. 9, Primpke, S., Lorenz, C., Rascher-Friesenhausen, R., Gerdts, G., An automated approach for microplastics analysis using focal plane array FTIR microscopy and image analysis. Pages 1499–1511, Copyright 2017, with permission from the Royal Society of Chemistry.

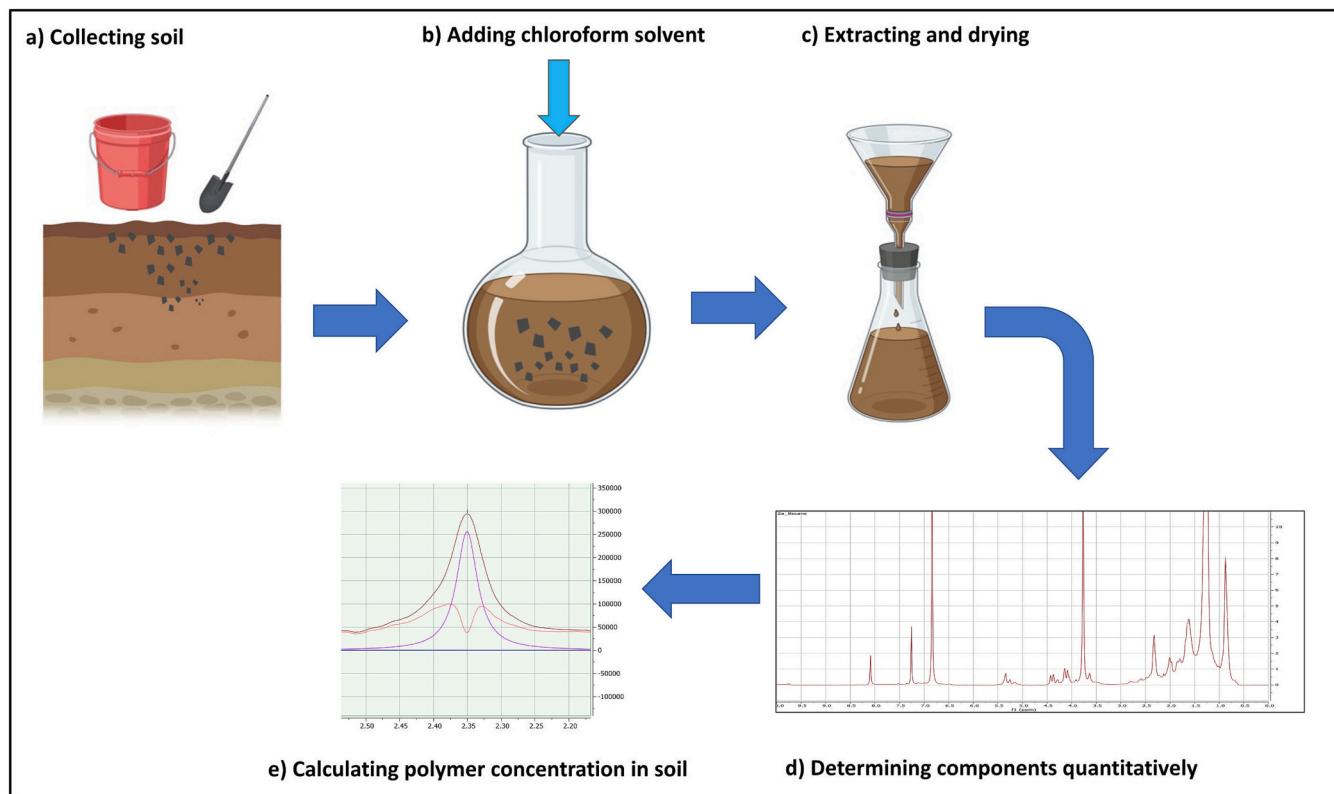


Fig. 6. Method to determine the MNP concentration in soil via solvent extraction and characterization through NMR. Figure adapted from *Environmental Science and Technology*, Volume 54, Nelson, T.F., Remke, S.C., Kohler, H.P.E., McNeill, K., Sander, M., Quantification of synthetic polyesters from biodegradable mulch films in soils. Pages 266–275, Copyright 2020, with permission from the American Chemical Society.

farmland soil (Ai et al., 2022).

3.3. Detection method harmonization and quality assurance

Standardization and harmonization efforts are necessary as methods for sampling, preparing, and identifying MPs from environmental

samples emerge to ensure that the results are reproducible and comparable between researchers (Hermsen et al., 2018; Cowger et al., 2020). Furthermore, researchers need to explore different techniques for quantification because of the diversity in geometry and chemistry of MNPs and sample matrices. As opposed to standardization, harmonization is the process of reporting methods and outputs so results can be compared across different labs using different techniques (Provencher et al., 2020). MNP preparation and quantification methods can present opportunities for sample contamination, so quality control (QC) and quality assurance (QA) measures are essential to maintain the validity of results. While standard procedures have not yet been widely adopted, a recent review of MPs in water and sediment found that QA/QC measures have increased extensively from 2016 to 2021 (Lu et al., 2021). Ziajahromi and Leusch (2022) list crucial QA/QC measures for MP sample preparation and quantification developed based on QA/QC procedures for other analytical protocols. Essential practices include using negative and positive controls, rinsing equipment and cleaning the work area, air filtration, and eliminating plastic tools and equipment. While these QA/QC procedures can seem like common sense, there is not much data to support which practices are necessary. For example, in an interlaboratory study where 98 labs participated in quantifying samples of PET in water, no analytical technology (pyrolysis GC-MS, FTIR, micro-FTIR, micro-Raman) or sample preparation method (including laminar flow hoods, non-polymer labware, laboratory blanks, use of gloves and others) was correlated with more accurate or consistent results than any other choice of techniques (Belz et al., 2021). Another interlaboratory study with 26 participating labs found no correlation between methods and accurate identification or quantification of MPs in samples (Van Mourik et al., 2021).

3.4. Preparation of surrogate MNPs for environmental studies

Fundamental environmental studies investigating risk assessment, toxicity, transportation, biodegradation, and fate, require representative surrogate model MNPs gained through environmental extraction (MPs) or artificial mechanical formation of MNPs. Isolation of environmental plastic fragments from the marine, air, and terrestrial environment requires multi-step protocols involving collection (as described in Section 3.1), sieving, cleaning, and sorting according to shape and size. Environmental retrieval of MPs from the soil is one viable approach to attain model plastic fragments and particles used for environmental studies. However, this approach generally results in relatively large-sized particles (~) at low concentrations, lacking the representation of small MPs (< 100 µm) or NPs occurring in the environment (Wagner et al., 2017). In addition, environmentally collected MPs represent significant variations in size and shape distributions and adhering organic and inorganic contaminants. Post-processing to remove impurities, as described in Section 3.1, may alter the particle surface properties, such as roughness and surface charge. Moreover, property changes in environmentally collected MPs post-treatment may bias the outcome of follow-up environmental studies (Wagner et al., 2017; Li et al., 2019).

As an alternative, a top-down method consisting of ambient or cryogenic (cryo-) milling and sonication using untreated bulk plastics has been employed to mimic environmental MP formation and biodegradation (Lagarde et al., 2016; Eitzen et al., 2019; von der Esch et al., 2020; Anderson and Shenkar, 2021; Kefer et al., 2022).

Furthermore, Naik et al. (2020) used photochemical degradation by UV irradiation to mimic the photo-chemical plastic degradation process. However, MNPs treated with a single-step approach do not reflect the multi-step degradation processes occurring in the environment involving the material's mechanical, thermal, photo-chemical, and biological changes. Procedures involving all significant degradation steps, such as those listed above, are still lacking, even when some protocols consider at least one primary "degradation" mechanism (Hebner and Maurer-Jones, 2020; Uheida et al., 2021). Higher control over MNPs size and polymeric composition can be achieved through

bottom-up formation approaches involving a chemical synthesis of µm-sized plastic beads or rods as a model for environmental MNPs (Rubin et al., 2021). For example, seeding polymerization synthesis resulted in a monodisperse particle population of MNPs and NPs (Cole, 2016). In the cited study, micro-scale rods (diameter = 10 µm and length = 40 µm) of uniform polymer type (PET or PP), shape, and size were generated that mimicked fibers found in nature (Besley et al., 2017; Coppock et al., 2017).

Bottom-up synthesis approaches allow for the generation of homogeneous, uniform model-MNPs, frequently used in environmental studies dealing with MP risk assessment (Rubin et al., 2021). In general, bottom-up approaches yield MNPs with a reasonable size control and homogeneity; however, they poorly represent MNPs isolated from environmental samples, including surface properties such as roughness and functionalization, similar to commercially manufactured spherical microbeads (Rubin et al., 2021).

Overall, the poor representation of structural and compositional characteristics of real MNPs by most surrogate MNPs results in limited data for certifying the validity of particle models employed for environmental studies such as fate and transport (Ateia et al., 2020; Liu et al., 2021). Ideally, model MNPs should mimic real MNPs' size (geometry), hydrophilicity, morphology, and surface functionality, as dictated by weathering forces (from sunlight) and thermal, photochemical, and mechanical degradation forces by employing lab-scale equipment (Rubin et al., 2021). However, the literature involving NP surrogate formation is much smaller than for MP surrogates due to the challenges of retrieving, identifying, and characterizing NPs residing in soil and replicating geometric and chemical properties of NPs in the laboratory. Several studies have been performed on NP formation through cryogenic milling, grinding, or both. For example, El Hadri et al. (2020) obtained polydisperse PS NP surrogate through ball milling using water dispersion (via surfactants and preservatives) and subsequent filtering, producing NPs with regular shapes that differ from MNPs encountered in agricultural soils. Caldwell et al. (2021) used mechanical milling to produce PET NPs. However, limitations of milling to prepare NPs are low yields and extended processing times (Ji et al., 2020). Mechanical treatment for a longer duration leads to friction-induced polymer overheating followed by thermal degradation or polymer agglomeration (Astner et al., 2019; Caldwell et al., 2021). Alternatively, Astner et al. (2019), Astner et al. (2022), Astner et al. (2023) applied wet grinding to form NPs from aqueous slurries of MPs derived from PE and BDMs via milling (46–840 µm), resulting in NPs of sizes of 50–800 nm. Wet grinding of aqueous slurries will not introduce artifacts resulting from overheating.

4. In situ formation and degradation of MNPs in agricultural soils

4.1. Impact of environmental factors above soil on degradation of plastics

Environmental formation and breakdown of MP into smaller sizes, and ultimately into NPs, occur in several steps involving thermal, mechano-chemical (e.g., ozone-induced or photooxidative) processes and biological disruption mechanisms (Singh and Sharma, 2008; Lambert and Wagner, 2016) (Fig. 7). Weathering processes on plastic mulches increase the surface area and the level of oxygen-containing functional groups, promoting film fragmentation into smaller particles and eventually into MNPs (Duan et al., 2021). The first stage entails the degradation of plastics during their service life due to agricultural weathering. Agricultural plastics are exposed to UV radiation from sunlight and undergo breakdown involving oxidation and molecular chain scission (Miles et al., 2017; Song et al., 2017; Zhang et al., 2021b; Yang et al., 2022b). In particular, molecular chain scissions following the Norrish type I and II degradation reactions lead to the photochemical cleavage of C-C and C-H molecular bonds and cross-linkage, leading to embrittlement (Ammala et al., 2011), which results in MP formation

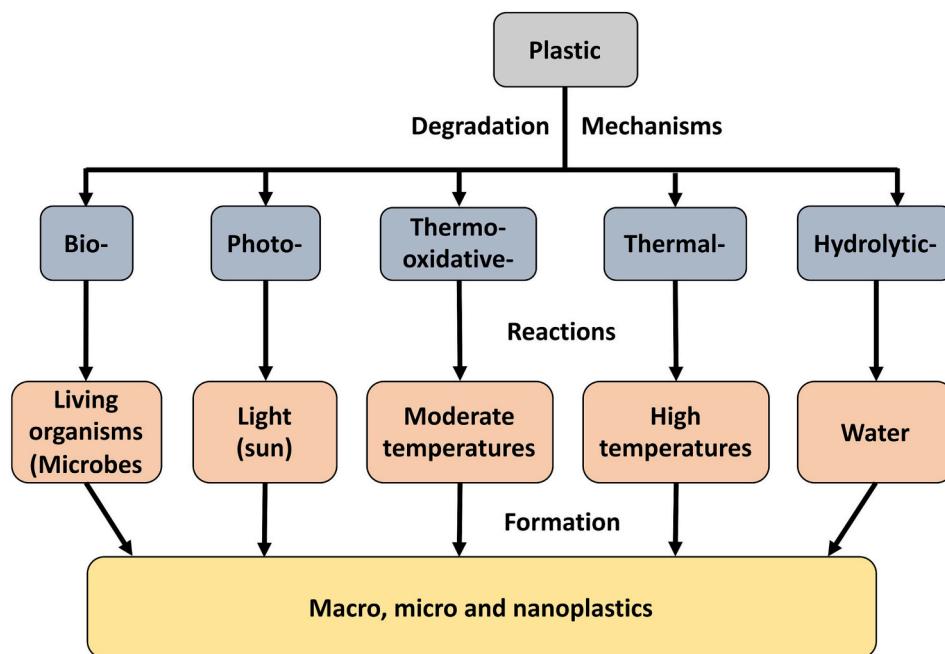


Fig. 7. Environmental factors impacting biodegradation of plastics. From (Sharma and Chatterjee, 2017). Reprinted from *Environmental Science and Pollution Research*, Vol. 24, Sharma, S., Chatterjee, S., Microplastic pollution, a threat to marine ecosystem and human health: a short review, Pages 21530–21547, Copyright 2017, with permission from Springer Nature.

(Julienne et al., 2019; Qi et al., 2020; Anunciado et al., 2021b). Embrittlement of plastics contributes to MNP formation due to the breakdown of macroplastics with an average particle size (d_p) of >25 mm and mesoplastics ($d_p = 5\text{--}25$ mm) (Gigault et al., 2018; Hartmann et al., 2019). The surface temperature of black-colored mulch films can reach $80\text{ }^{\circ}\text{C}$ (Ham et al., 1993), accelerating the photochemical reactions. Water can leach away minor components from the plastics, particularly after exposure to sunlight, such as plasticizers, colorants, or filler, or can induce hydrolysis, which can accelerate degradation and hence the formation of MPs (Astner et al., 2019; Serrano-Ruiz et al., 2020). Macro- and meso-plastics dispersed in water are subject to similar photodegradation reactions (Arthur et al., 2009; Rillig, 2012), relevant to MNPs near soil-water interfaces. Plastic films and MNPs deposited onto the soil surface may also contain adsorbed microbial communities that will affect the size reduction process of terrestrial MPs (Bandopadhyay et al., 2020) (Fig. 3). Furthermore, biofilm formation on MPs promotes the adsorption of inorganic and organic pollutants. Therefore, MPs can function as vectors for contaminant transport, impacting soil and aquatic (fresh and marine water) environments (Sooriyakumar et al., 2022).

“Oxodegradable” mulch films, composed of PE and catalysts that are triggered by photo- or oxo-reactions during their service life, will disintegrate macroscopically, thereby appearing to mimic the mineralization of BDMs. However, the degradation produces MPs that are recalcitrant to microbial assimilation or further breakdown. Therefore, many corporations and non-government organizations worldwide encourage the ban of “oxodegradables” from the marketplace (New Plastics Economy, 2019).

4.2. Size reduction of MNPs in agricultural soils

MPs undergo progressive aging in soil and other ecosystems, constantly changing their physiochemical characteristics, resulting in different environmental behaviors (Liu et al., 2021; Ren et al., 2021a; Zha et al., 2022). Environmental factors that impact MPs result in gradual size reduction, forming NPs of <1000 nm in at least two dimensions (Koelmans et al., 2015; Alimi et al., 2022). Generally, MP

fragments will break off from the surface of macroplastics. Terrestrial MPs will slowly and gradually undergo a size reduction to the nanoscale due to collisions with soil particles, bioturbation, and other events. Astner et al. (2019) simulated this process using wet grinding and found that MPs of $\sim 100\text{ }\mu\text{m}$ in size readily form large NPs of $100\text{--}500$ nm possessing a bi- or trimodal size distribution. Continual implementation of wet grinding passes produced NPs at $30\text{--}70$ nm (Astner et al., 2023). Overall, the size reduction process of MNPs in the soil is poorly understood.

4.3. Size reduction of biodegradable MNPs during microbial assimilation in soil

Size reduction will also occur during microbial assimilation of soil-incorporated biodegradable plastics, such as BDMs, resulting in MP formation (Anunciado et al., 2021a). MPs undergo a further size reduction to the nanoscale and ultimately undergo complete aerobic mineralization as the NPs become sufficiently small to pass through microbial membranes and metabolize within the cell (Zumstein et al., 2018). Factors that control biodegradation include BDMs’ film thickness, polymeric composition and molecular architecture (Villena et al., 2022), molecular-level changes of polymers due to agricultural weathering (Section 4.1) (Anunciado et al., 2021a), and contact with soil (Lucas et al., 2008; Kalka et al., 2014). Factors affecting biodegradation include environmental conditions such as moisture, temperature, and pH, and polymeric characteristics such as size, shape, molecular weight, and additives (e.g., surfactants) (Ahmed et al., 2018; Al Hosni et al., 2019). A minimum level of soil moisture is essential because it facilitates microbial metabolic reactions; but, excess soil moisture limits oxygen availability. Through the employment of a standardized laboratory test, PBS MPs of $d_p = 50\text{--}75\text{ }\mu\text{m}$ were found to readily undergo biodegradation for a compost-enriched soil tested, with the biodegradation rate increasing with a decrease of the initial diameter of the MPs fed to the bioreactor (Chinaglia et al., 2018). A subsequent paper predicted, based on kinetic modeling of the biodegradation data, that NPs of 100 nm size would fully biodegrade within three weeks (Tosin et al., 2019). However, the results have not been extended to other soils and polymeric

sources, nor has the latter prediction been verified experimentally.

When employing MNP surrogate materials derived from films composed of Mater-Bi®, Astner et al. (2023) found that MPs were more readily biodegradable than NPs, which contradicts the assumption that a larger surface/volume ratio for NPs would have increased exposure to microorganisms. This result is likely attributable to the observed loss of Mater-Bi®'s starch component when preparing NP surrogates from MPs via wet grinding. Moreover, the NPs' lower content of starch, the preferred carbon source for microorganisms, will result in them undergoing a slower biodegradation rate. This finding suggests that biodegradation may not necessarily increase for NPs when biodegradable plastics undergo size reduction. In addition, NPs are sufficiently small to be transported via groundwater as a suspension, allowing them to be leached away from the soil. However, such behavior is likely impacted by local environmental conditions in the soil, such as the degree of water saturation, biofilm formation on the plastic surface, the extent of humic acid and SOM present, and the inherent properties of the polymeric material. These factors will affect the surface chemistry of MNPs, including polarity and degree of surface roughness. Leaching associated with MPs can involve chemicals incorporated in the plastics during manufacturing or absorbed contaminants (Sridharan et al., 2022). Although MNPs formed from biodegradable agricultural plastics will ultimately undergo full mineralization, they may reside in the soil for weeks or months.

For example, Lang et al. (2020) determined that incorporation of BDMs in topsoils produced plastic debris at 170 kg ha^{-1} , which although being lower than plastic debris concentrations in fields treated with conventional PE mulches (259 kg ha^{-1}), is significantly high. Likewise, Sintim et al. (2020) demonstrated that the degradation of BDMs in field soils may take several years. It is also well known that the biodegradation rate of BDMs plowed into soils can be much slower and more variable than in standardized lab tests due in part to smaller surface area exposure of the tilled-in plastic and variability in soil quality, moisture, microbial communities, exposure time, and soil management practices (Li et al., 2014; Sintim et al., 2020). For instance, Griffin-LaHue et al. (2022) estimated, using field data and a zeroth-order degradation model, that it would take 21 to 58 months to reach 90% degradation of a BDM in a cool Mediterranean climate. Therefore, biodegradable plastic MNPs are likely to form in soil and reside there for several months before they are microbially assimilated, a duration in which they can impact soil ecosystems.

5. Mass transport of MNPs in agricultural soils

5.1. Overall trends for mass transport of MNPs in soils

For agricultural production, the biophysical properties of soil structure strongly influence erosion, nutrient cycling, water dynamics, soil fertility, and air permeability (Uteau et al., 2013). The soil structure is associated with aggregate stability, soil-water movement and retention, erosion, crusting, nutrient cycling, root penetration, and crop yield. Most MPs reside in the top (30 cm) soil layer (Zhang et al., 2021a), which can be impacted by farming practices such as tillage and harvesting. The presence of MPs in soil affects soil aggregate stability depending on MPs' hydrophobic or hydrophilic property (Bronick and Lal, 2005; de Souza Machado et al., 2019). Also, significant impacts of MPs on plant biomass, soil microbial communities, and plant tissues and roots were observed (de Souza Machado et al., 2018b) (Sections 6 and 7).

Furthermore, environmental factors can influence MPs' transport rates. For instance, multiple wetting and drying cycles accelerated the downward migration of MPs (O'Connor et al., 2019). Rillig et al. (2017b) described how the transport of MPs depends on environmental factors, such as rain and runoff, and found that the particle size (d_p of 21–535 μm) and polymer composition of MPs influenced the transport in a column experiment employing PE and PP pristine pellets in

combination with wetting and drying cycles, with the smallest PE-MPs showed the highest mobility.

The diffusivity of MNPs depends on the soil type, colloidal and surface properties, and the soil moisture level, all of which can be highly variable. Luo et al. (2020) and Wu et al. (2020) found that soil organic carbon (SOC), Fe_2O_3 clay, and pH influence the level of adsorption and transport of PS MPs. In addition, Wu et al. (2020) found that factors such as soil texture, saturation, porosity, and ion strength primarily dictate the migration of MPs in soils based on the coupled effects on surface charges causing electrostatic interactions between soils and MPs. In particular, the pore size of soil and MPs' texture impact the diffusion of MPs in soils (Lamy et al., 2013). Furthermore, two reports described that the soil particle size (especially when $<1 \text{ mm}$) and MP size influenced MP transport (O'Connor et al., 2019; Johnson, 2020). Hence, soil can act like a sink of larger retained MPs and a source to leach MNPs into the surrounding environment. The current research on MNPs' exchange between terrestrial and aquatic compartments is based on conceptual transport models (Horton and Dixon, 2018).

The properties of MPs, such as composition, particle size, shape, surface area, and density, influence behavior and potentially impact the soil environment. For example, the transport of smaller MPs into the soil and waterways occurs more likely, whereas irregularly shaped particles can entangle within the soil matrix. In agreement, the mechanical impact of agricultural activities, such as tillage, accelerates the breakdown of MPs fragments, resulting in the movement of MPs into deeper soil layers (Luo et al., 2020; Zhang et al., 2020). MNPs in the soil undergo further transformation by changing physical- and electrochemical particle characteristics such as size, density, shape, and surface charge, determining the fate, distribution, aggregation, and transport in terrestrial environments (Galloway et al., 2017; Lozano et al., 2021). Studies involving small-angle neutron scattering and neutron contrast matching techniques have found that larger-sized NPs formed from BDMs readily agglomerate with soil particles and can self-agglomerate. In contrast, smaller NPs are relatively inert, which will significantly increase the latter's transport through soil (Astner et al., 2020). In soil, NPs will likely be associated with an eco-corona formed by extracellular substances present in the soil solution. The formation of such eco-coronas can increase the colloidal stability of NPs and thus can promote mobility (Yu et al., 2023a).

Similarly, Yan et al. (2020a) showed that MPs undergo hetero-aggregation behavior with soil minerals and organic matter, which promoted the downward transport of MPs during simulated rainfall events and even for MPs with a lower density than water. A relatively smooth particle shape (most commonly spherical and granular) was essential for easier migration into deeper soil layers (Kurlanda-Witek et al., 2015; Rillig et al., 2017a). Rillig et al. (2019) found that microfibers showed slower vertical transport rates than microspheres. The fibrous or film-shaped particles hindered MPs migration in soil based on agglomeration and interaction with the soil (Rillig et al., 2017b; Tourinho et al., 2019) and entanglement with soil granules (O'Connor et al., 2019; Zhang et al., 2019). The surface chemistry of MNPs is also essential. Weathered MPs will more likely undergo greater diffusion than unweathered MPs, likely due to increased negative surface charge (Lang et al., 2020).

Furthermore, the density of MPs is variable and depends on plastic-type and additives, which can affect their behavior in soil and potential to migrate into waterways. Horton and Dixon (2018) described the importance of particle density and shape of MPs in context with vertical transport and retention in sediments. Furthermore, soil pore size directly influences the migration of MPs (Lamy et al., 2013). MPs, and more prominently NPs, present a significantly large surface area per volume, allowing for the adsorption of microorganisms (i.e., biofilm formation) and other soil components, such as SOM, leading to further property changes.

5.2. Horizontal transport of MPs to streams, bodies of water, and air

A major environmental concern is the horizontal transport of MPs caused by water runoff from the terrestrial environment into waterways such as streams (Bigalke et al., 2022). Transfer of MPs from terrestrial to aquatic systems can occur by either erosion, runoff, or drainage water from drained soils (Horton et al., 2017; Tagg and Labrenz, 2018). For example, Bigalke et al. (2022) found exponentially increasing numbers of polyamide and PE MPs as particle size decreased in water drainage samples from agricultural land. Furthermore, Rehm et al. (2021) described how soil erosion contributes to horizontal MPs transport during heavy rainfall events and indicated that arable land susceptible to soil erosion could be a substantial MP source for aquatic ecosystems. Also, Han et al. (2022) simulated rain-induced runoff using MPs with d_p s ranging between 0.25 and 50 mm and found that the pre-existing vegetation significantly enhanced the retention of MPs by 20%. In addition, higher mobility was observed for MPs < 1 mm compared to larger particles, and the rainfall amount was more critical than the rainfall frequency for horizontal transport. Rehm et al. (2021) investigated possible movement pathways of two HDPE MPs categories with d_p 's 53–100 μm and 250–300 μm caused by long-term rainfall events (1.5 years) and found that MP-soil interaction and the MP concentrations are crucial factors for lateral particle transport. The final MP distribution indicated that coarser particles were horizontally transported while finer particles were redistributed below the plow layer (0–10 cm). Rezaei et al. (2022) and Abbasi et al. (2023) investigated transport by wind erosion of MPs films, spheres, and fibers on agricultural land and found high mobility of terrestrial MPs and fibers, suggesting that soils act as a temporary sink and dynamic secondary source of atmospheric MPs transport.

5.3. Vertical transport via infiltrating water flow and bioturbation

There is the potential for MNPs to migrate vertically through the soil profile carried by water flow. While soils are likely to retain particles larger than 10 μm by filtration, smaller MNPs can be transported through the soil, governed by the factors controlling colloid transport in porous media, including the MNP size and surface properties, soil texture, moisture, and physiochemical properties (Yu and Flury, 2021a). Vertical transport of MPs may also be facilitated by the pre-establishment of crops (Horton and Dixon, 2018), as root growth can promote the formation of preferential flow pathways. Furthermore, the transport of MPs in soils can be influenced by soil biota movement (Rillig et al., 2017b). Zoo-biological factors such as bioturbation by soil fauna (e.g., larvae, earthworms, vertebrates) promote MNP transport by attachment, ingestion, and excretion, as discussed in Section 7 (Gabet et al., 2003; Cai et al., 2018; Zhang et al., 2018; Yan et al., 2020a) (Fig. 3).

5.4. Colloidal stability of MPs

The transport of MNPs in soil and from soil into water is directly related to their colloidal stability. Colloidal stability refers to the homoaggregation of MNPs and heteroaggregation between MNPs and soil or other particles via van der Waals and electrostatic forces, as described by the Derjaguin–Landau–Verwey–Overbeek theory (DLVO) (Hogg et al., 1966; Gregory, 1981). In the soil environment, MNPs are more likely to undergo heteroaggregation with various particles, such as oxides, biochar, and clay minerals (Cai et al., 2018; Wang et al., 2021). Wu et al. (2020) confirmed decreased mobility of PS NPs at higher Fe/Al content levels in three natural soils, which correlated with the heteroaggregation of PS NPs with Fe/Al oxides. Furthermore, the presence of SOM can lead to increased repulsive forces between MNPs and porous media, represented by a higher surface electronegativity for MNPs, promoting their transport through soil (de Souza Machado et al., 2019). Similarly, the presence of extracellular substances, such as proteins, can

lead to the formation of eco-coronas around NPs and lead to stabilization of NPs suspensions (Yu et al., 2023a).

In addition, the soil pH directly influences the surface charge of MNPs. An increased soil pH from 4.97 to 9.75 resulted in a higher negative zeta potential for PS (Wu et al., 2020). The shape and composition of MNPs significantly affect the surface charge and hydrophobicity and influence the steric hindrance and aggregation between MNPs in soil (de Souza Machado et al., 2018a). The colloidal stability of NPs was determined as the primary determinant of environmental fate and transport (Filella, 2007; Brahney et al., 2021; Pradel et al., 2023).

5.5. MNPs can facilitate the transport of heavy metals and pesticides

The broad dispersion of MNPs in agricultural soils enables interaction with pesticides and the ability to carry the latter through agricultural soils to plant roots and soil biota and into aquifers, potentially posing a risk to crop production and drinking water supplies (Wanner, 2021). Jiang et al. (2020) determined that fungicide was more strongly adsorbed by biodegradable PBS MPs compared to PE and PVC MPs, independent of environmental factors such as pH or salinity. This result likely reflects the increased adsorption by PBS MPs because of their relatively higher hydrophilicity. The formation of pesticide-laden MNPs can also occur via size reduction of macroplastics. Ramos et al. (2015) identified migration of pesticides into macroplastic fragments that can undergo size reduction into MNPs. MPs can also serve as vectors for microorganisms (Belo et al., 2022).

Similarly, MPs can also serve as vectors for minor components of concern from the agricultural plastic source, such as phthalate-based plasticizers or heavy metals (Serrano-Ruiz et al., 2021). MNPs can also deter the widespread transport of pesticides throughout agricultural ecosystems. Moreover, adsorption of pesticide-laden MNPs to soil can lead to the occlusion of pesticides from soil mineral matrices. Chi et al. (2021) showed that PS NP-glyphosate complexes were occluded in calcite and iron hydroxide particles, reducing the possible pesticide migration. Adsorption of pesticides or heavy metals can alter MNPs' adsorption behavior and surface properties (Barboza et al., 2018; Huang et al., 2019; Zhou et al., 2020) and sorption behavior.

Even though MPs can concentrate organic pollutants, adverse effects on ocean organisms or ecosystems appear to be minimal. MPs do transport adsorbed organic pollutants to new environments, and organisms do readily ingest MPs, but the transport of pollutants by MPs is dwarfed by transport through water, air, or environmental organic matter – which also sorbs hydrophobic pollutants (Koelmans et al., 2016; Rodrigues et al., 2019).

In some cases, sorption by MPs has been shown to make harmful pollutants less bioavailable, reducing their negative impact (Rodrigues et al., 2019). In contrast, some studies found adverse interaction effects on organism health when MPs and organic pollutants were applied as combined treatments in soil, as described in Section 7. Furthermore, MPs can impact soil microbial functions, confirmed by the observation that adsorbed organic matter enhanced MPs' metal retention capabilities (Wijesekara et al., 2018).

There are limitations in translating the studies described above, primarily based on lab-scale experiments, into field effects. The studies may use concentrations of plastic or organic contaminant that are rare or unseen in the environment. The constraints of the test system may remove environmental protective factors like contaminant avoidance or adaptation that mitigate negative effects. The observed toxicity endpoints may not translate to reduced individual or population health. For these reasons, more studies investigating the environmental behavior of MPs to sorb, release, or otherwise interact with organic contaminants are needed, as well as careful analysis of the results to extrapolate to relevant environments. Biodegradable plastic fragments can behave differently than other MPs in adsorption because of their different properties, including lesser hydrophobicity, as described above.

6. Potential impacts on crops

6.1. Impact on plant biomass and growth

MNPs can impact crops directly through interactions with roots and indirectly through modification of soil properties. Plastic in the soil has been reported to affect plant germination rate, shoot height, and biomass (Boots et al., 2019; Dong et al., 2020). For example, Serrano-Ruiz et al. (2023) found that BDM fragments and their released compounds altered tomato and lettuce plants' development and growth behavior. Boots et al. (2019) added HDPE and PLA plastic to a sandy clay loam at a 0.1% wt and clothing fibers at a 0.001% wt and found that HDPE, PLA, and clothing fibers reduced seed germination of ryegrass *Lolium perenne*, and PLA further reduced the growth of *L. perenne*, while HDPE increased root biomass. Meng et al. (2021) found that adding LDPE MPs (0.5 to 2.5% wt) into a sandy soil did not affect the shoot, root, or bean biomass of common bean (*Phaseolus vulgaris* L.) while adding PBAT (>2% wt) strongly reduced shoot, root, and bean biomass. On the other hand, Tong et al. (2023) found that PE and PVC (0.01 and 1% wt) increased the above-ground biomass while decreasing the below-ground rice biomass in paddy soil.

Different types of plastics, soils, and plant species can explain these somewhat inconsistent results. MNPs can alter soil properties, such as water holding capacity, nutrient availability, and microbial activity and composition, and thus affect plant performance (de Souza Machado et al., 2019; Ingraffia et al., 2022; Lian et al., 2022; Yu et al., 2023b). For example, de Souza Machado et al. (2019) found that among different types of MPs, polyester fibers, due to their linear shape, and flexibility, decreased soil bulk density while increased soil aggregation, water holding capacity, and microbial activity, and as a result significantly increased root and bulb biomass of onion (*Allium fistulosum*). Likewise, Lozano et al. (2021) found that adding different-shaped MPs, including fibers, films, foams, and fragments, increased water holding capacity and decreased bulk density while increasing soil aeration, microporosity, and water holding capacity, led to an increase in shoot biomass of *Daucus carota*. Nonetheless, significant effects of MNPs on soil physical properties are only expected at relatively high plastic concentrations (>0.5% w/w for fibers and > 2% w/w for granules), concentrations that are seldom observed in the environment (Yu et al., 2023b).

Ingraffia et al. (2022) reported that incorporating polyester microfibers (0.5% wt) into soil decreased soil bulk density while increasing N leaching, limited N uptake, and biomass accumulation in the shoot and root of maize. Liu et al. (2022a) found that adding PBAT MPs into soil enriched the abundance of *Bradyrhizobium*, *Hydrogenophaga*, and *Arthrobacter* bacteria in the bulk soil and rhizosphere soil and inhibited the growth of *Arabidopsis*. Thus, MNPs can positively and negatively affect plant biomass and growth, depending on whether the plastics can improve or deteriorate soil's physical, chemical, and biological properties.

6.2. Physiological impacts on plants

MNPs can cause several physiological responses in plants. For example, PS and polytetrafluoroethylene MPs caused oxidative bursts and cell damage in rice roots (Dong et al., 2020) and increased reactive oxygen species in *Arabidopsis* (Sun et al., 2020) when grown in hydroponic cultures. Similarly, an increase in reactive oxygen species and oxidative stress response was observed in *Lepidium sativum* when exposed to different types of MPs (Pignattelli et al., 2020). Dong et al. (2021) reported that PS MPs destroyed the tertiary structure of pectin methyl esterase of carrots and induced oxidative bursts in carrot tissue in hydroponic cultures. Colzi et al. (2022) found reduced photosynthetic efficiency and chlorophyll content of *Cucurbita pepo* L. when grown in soils spiked with PP, PE, PVC, and PET MPs. Lian et al. (2022) found that the presence of PBAT MPs at 2.5 g kg⁻¹ in soil severely disrupted the photosynthetic system of *Arabidopsis* and the degradation products of

PBAT (i.e., adipic acid, phthalic acid, and butanediol) affected the xenobiotic transport in *Arabidopsis*, leading to an inhibited growth of *Arabidopsis*. Zhao et al. (2023) found that PS and PP MPs enhanced the absorption of Cd of maize root into the rhizosphere amino acids and soil meltabilities synthesis and secretion.

These results suggest that MNPs not only affect plant physiology directly by themselves but also indirectly through releasing toxic degradation products and additives and changing contaminants' bioavailability.

6.3. Mechanisms for plant uptake

Roots can take up nanoparticles through several mechanisms: (1) via transport through the intra-cellular pore space (apoplastic pathway), (2) via transport through plasmodesmata into cells (symplastic pathway), (3) via incorporation into cells by membrane deformation (endocytosis pathway), and (4) via cracks in cell structures where lateral roots emerge (crack-entry pathway) (Craddock and Yang, 2012; Tripathi et al., 2017; Wiedner and Polifka, 2020). While these mechanisms allow entry of particles into roots and potential further transport into the xylem and shoot tissue, it is generally considered that only particles in the nanometer size range (< 100 nm in diameter) can be taken up by roots, i.e., there is a size-exclusion effect that prevents the uptake of particles in the micrometer size range (Pérez-de-Luque, 2017). Nonetheless, it was reported that plants could take up even particles of 200 nm and 2 µm: PS and polymethylmethacrylate NPs of 200 nm and PS MPs of 2 µm diameter were reported to be in the xylem of wheat and lettuce (Lang et al., 2020). In addition, Sun et al. (2020) reported that *Arabidopsis thaliana* could take up PS NPs (200 nm). Lian et al. (2022) found that 80 nm and 1 µm PS MNPs could be taken up by rice. Tang et al. (2023) reported the detection of 100 nm PS NPs in the roots and shoots of Chinese Flowering Cabbage. Song et al. (2023) reported that 80 nm PS NPs could enter the roots of dandelions.

Under what conditions NPs can be taken up by plants is still under debate. While it has been reported that plant roots can take up MNPs, the studies have only found an association of plastic particles with root cap cells, without intake into the interior of the root observed (Lang et al., 2020; Sun et al., 2020; Taylor et al., 2020; Tang et al., 2023). Rather than being taken up, NPs (40 nm and one PS bead) were pushed along the exterior of the roots as the roots were growing in the agar medium (Taylor et al., 2020). The difference between these findings on root uptake may be related to the different experimental systems used in these studies: Sun et al. (2020), Lang et al. (2020), Lian et al. (2022), Song et al. (2023), and Tang et al. (2023) grew plants in hydroponic solutions, whereas Taylor et al. (2020) grew plants in an agar medium, where mobility of plastic particles is significantly reduced compared to hydroponic solutions. Further studies are needed to clarify whether these findings are because of different experimental systems and whether plastic uptake by roots would happen in soil.

While the evidence is mounting that spherical microbeads can be taken up by plants grown in hydroponic solutions, there is no evidence until now that MNPs will be taken up when plants are grown in the soil and when MNPs are not model PS MNPs. These mechanisms can be explained by conditions for plant uptake in natural soil are very different from a hydroponic system, and plastic uptake is much less favorable.

7. Response of soil fauna to MNPs

7.1. Impact on microorganisms

Soil microorganisms (bacteria, archaea, fungi) comprise the bulk of soil living biomass and play critical roles in decomposition, nutrient cycling, SOM stabilization, soil aggregation, pollutant degradation, and many other functions integral to healthy soils. Evidence is building that these soil microbes can be affected by MP pollution. Bacteria colonize MPs in soils, with plastics selecting for distinct bacterial communities

compared to plant litter (Zhang et al., 2019) and bulk soil (Huang et al., 2019; Bandopadhyay et al., 2020; Wiedner and Polifka, 2020). Studies examining soil with added MPs have reported mixed effects of microbial community diversity and composition in the soil. For example, no changes to bacterial community structures were detectable upon the addition of 1% of $<100\text{ }\mu\text{m}$ MPs of PP, LDPE, and PS (Wiedner and Polifka, 2020), nor 0.1% and 1.0% of $<0.9\text{ mm}$ PVC MPs (Yan et al., 2020b). In contrast, adding 1% and 5% $\sim 678\text{ }\mu\text{m}$ PE and $\sim 18\text{ }\mu\text{m}$ PVC MPs resulted in altered enzyme activities and lower diversity of the bacterial communities (Fei et al., 2020). MP addition to soil microcosms has also decreased general microbial activity, as measured by fluorescein diacetate hydrolysis activity (Liu et al., 2017; Fei et al., 2020), which may ultimately change the character of dissolved organic matter in soils.

At the organismal level, the effects of MPs have been documented for soil fungi. For example, polyacrylic microfiber additions to soil microcosms resulted in mixed effects on different fungal strains and their contribution to aggregate formation: *Mucor fragilis* activity and aggregation were increased in the presence of microfibers. At the same time, *Chaetomium angustispirale* and *Gibberella tricincta* exhibited decreased activity and aggregation (Liang et al., 2019). There is less research examining individual soil bacterial strains and their interactions with MPs, but there are studies of bacteria from other environments. For example, PS MPs induced toxicity responses in the marine bacterium *Halomonas alkaliphila*, including increased extracellular polysaccharides (Sun et al., 2018).

Knowing that extracellular polysaccharides and other extracellular polymeric substances (e.g., proteins and lipids) from soil organisms are among the 'glues' used to cement soil aggregates and build SOM invokes questions about how meso- and microplastics might influence biologically mediated aggregation and organic matter formation in soils as significant drivers for building healthy soils.

7.2. Impact on soil mesofauna

Soil microfauna is essential to the soil food web, contributing to decomposition, nutrient cycling, and biodiversity. However, reports show that soil microfauna is interacting and affected by plastic fragments and MPs in the soil (Chae and An, 2018). For example, MP exposure can adversely affect motility, growth, metabolism, reproduction, mortality, and gut microbiome (Buks et al., 2020; Yang et al., 2022a; Wan et al., 2023). In addition, *microarthropods*, namely springtails (*Collembola*) and mites, can move MPs around the soil environment through their locomotion (Maaß et al., 2017; Luo et al., 2023), and predator-prey interactions promote this movement (Zhu et al., 2018a).

MPs filling pore spaces immobilized springtails (Su et al., 2019), and ingestion significantly altered the springtail microbiome and inhibited growth and reproduction (Zhu et al., 2018b). In addition, MP additions can significantly reduce the diversity of soil nematode communities (Yang et al., 2022a). Meta-analyses of current studies show that small particle sizes of MPs at high concentrations may most significantly contribute to toxicological effects across a range of soil microfauna, with reproduction and survival decreasing with increasing concentrations of MPs (Buks et al., 2020; Liu et al., 2023; Wan et al., 2023). While many of these experiments are conducted in controlled laboratory settings with sometimes artificially high concentrations of MPs, a recent probabilistic risk exposure assessment concluded that soil microfauna is exposed to MPs at concentrations that would cause adverse effects (Jacques and Prosser, 2021).

MP effects on the model nematode *Caenorhabditis elegans* provide insight into organismal interactions with MPs. *C. elegans* can take up MPs of varying compositions and sizes: when exposed to a suspension containing PS spheres of different sizes and surface properties, *C. elegans* selectively ingested PS spheres of size between 0.5 and 3 μm , and carboxylate-modified spheres were preferred over sulfate- or amino-modified spheres (Kiyama et al., 2012). A severe impact by MPs

ingestion at different sizes (0.1, 1.0, and 5 μm) and types by *C. elegans* resulted in decreased survival rates, body length, and reproduction, with evidence of increased intestinal damage and oxidative stress (Lei et al., 2018). Furthermore, this study found the highest lethal and damage rates caused at 1.0 μm MPs independent of composition, concluding that MPs' toxicity depends rather on size than composition (Lei et al., 2018).

7.3. Impact on soil macrofauna - earthworms

As with other biotas, there is growing evidence that MPs can harm soil macrofauna (Sanchez-Hernandez et al., 2020). The most studied macrofaunal group is the annelids (worms). Worms can actively take up MPs as they forage for food. Experiments in soil mesocosms showed that the anecic earthworm *Lumbricus terrestris* could move plastics around, ingest MPs, and transport plastics to deeper soil layers (Huerta Lwanga et al., 2016; Hodson et al., 2017; Huerta Lwanga et al., 2017; Rillig et al., 2017b) (Fig. 3). MPs can be ingested and then incorporated into the cast of earthworms (Huerta Lwanga et al., 2016; Adhikari et al., 2023).

Even macroscopic plastic pieces can be ingested if brittle by *L. terrestris* (Zhang et al., 2018). *L. terrestris* has also been observed to pull large, macroscopic plastic pieces into their burrows, thereby translocating macroplastics from the soil surface into the soil profile (Zhang et al., 2018).

In addition to the translocation of plastics by the movement of worms through the soil, studies have documented the detrimental effects of plastics on organisms. Decreased growth rates and increased mortality were observed after 60 days of exposure of *L. terrestris* to PS MPs in the litter at concentrations of 28, 45, and 60% dry wt. However, no effects were observed at 7% wt of plastic in the litter (Huerta Lwanga et al., 2016). No increased mortality was observed when *L. terrestris* was exposed to microfibers of 0.1 and 1% wt in soil for 35 days; however, increased cast production and stress (measured with genetic stress biomarkers) were observed in the 1% wt plastic treatment (Prendergast-Miller et al., 2019). No impairment of earthworm activity and weight was observed when MPs were applied to the soil surface, and earthworms were allowed to freely forage for food on the soil surface (Adhikari et al., 2023). Boots et al. (2019) exposed endogeic earthworms *Aporrectodea rosea* to 0.1% wt HDPE, 0.1% wt PLA, and 0.001% wt synthetic fibers mixed into sandy clay loam soil. After 30 days, no mortality was observed, but the earthworms exposed to plastics lost weight compared to earthworms in plastic-free control soil (Boots et al., 2019). Compost earthworms, *Eisenia* spp., exhibited oxidative stress responses and immune reactions after PE MPs (250 to 1000 μm) ingestions at concentrations of 0.006, 0.0125, 0.025, 0.5, and 0.1% wt in soil for 28 days, particularly at the three highest concentrations, but no effects on mortality or weight changes were observed (Rodríguez-Seijo et al., 2017; Rodríguez-Seijo et al., 2018). However, no oxidative stress responses were observed when *E. fetida* was exposed to PE ($<300\text{ }\mu\text{m}$) and PS MPs ($<250\text{ }\mu\text{m}$) at concentrations of up to 10% wt for 14 days (Wang et al., 2019). The shorter exposure duration may explain the different findings between these two studies. Whether toxic effects on earthworms are manifested depends on the concentration of the MPs and their chemical composition, surface properties, and shape. For example, exposure of *E. andrei* to 6-month soil-weathered Mater-Bi® (PBAT and starch-based) MP powder at concentrations of 1.25% wt soil did not show toxic effects in mortality and reproduction standard bioassay test for 28 and 56 days (Sforzini et al., 2016). On the other hand, exposure of *L. terrestris* to PET fibers (634 $\mu\text{m} \times 30\text{ }\mu\text{m}$) at concentrations of 0.05% wt soil for 14 days led to a decrease in cast egestion (Lahive et al., 2022). When soil organisms ingest contaminated plastics, contaminants adsorbed on the plastic surfaces can be transferred into soil organisms but do not necessarily cause harmful effects. For example, when *L. terrestris* was exposed for 28 days to Zn-contaminated PE MPs (1.32 mm \times 0.71 mm) in the soil at an MP concentration of 0.35% wt, MPs were ingested by the earthworms; however, effects on survival or weight change of the earthworms were observed (Hodson et al., 2017).

Furthermore, in an experiment where *E. fetida* was exposed to chlorpyrifos-contaminated MPs, the earthworms avoided ingesting the contaminated plastics. Thus, there was no evidence that the MPs would facilitate the transfer of chlorpyrifos into the earthworms (Rodríguez-Seijo et al., 2019). Similarly, PE and PS MPs did not enhance the uptake of polycyclic aromatic hydrocarbons and perchlorinated biphenyls by *E. fetida* in contaminated soil (Wang et al., 2019).

Whether MPs may or may not serve as vectors for enhanced uptake of contaminants depends on the type of plastic and contaminant and their concentrations. Sobhani et al. (2021) found that PET MPs enhanced the bioaccumulation of perfluoro octane sulfonate and perfluorooctanoic acid in *E. fetida* when exposed to PET in the soil at concentrations of 0.05 and 0.1% wt. However, no effects were observed at concentrations of <0.01% wt. PS MPs (10 and 100 μm) at soil concentrations of 0.01% wt enhanced the bioaccumulation of phenanthrene in *E. fetida* when exposed for seven days. Similarly, Huang et al. (2023) reported that PE MPs (<300 μm) enhanced the uptake of Cd in *E. fetida* at plastic concentrations of 7% to 30% wt. Exposure of *E. fetida* to MPs and the insecticide imidacloprid caused ecotoxicological effects, with the effects being more pronounced when both MPs and the insecticide were present simultaneously (Fu et al., 2023).

These contradictory results regarding the effects of MPs and contaminants suggest that MPs can enhance the contaminant bioaccumulation in earthworms, however, only when exposed to high plastic concentrations (Fig. 2). In addition, a recent report demonstrated that NPs released via partial abiotic degradation of polyhydroxy butyrate MPs were ecotoxic to microorganisms and *Daphnia magna* (González-Pleiter et al., 2019).

8. Risk assessment of MPs in agricultural soils

Soil biospheres fulfill a variety of essential ecosystem services in agriculture, e.g., decomposition and cycling of organic matter, food production, suppression of pests, gas exchange, and carbon sequestration. Previous sections described potential threats of MNPs in soil ecosystems, including to soil fauna and plants, and the possibility of entrance into the food web. MPs and particularly NPs can impact human health through various exposure pathways, such as ingestion of contaminated crops, meats, dairy products, and water or dust inhalation. The release of plastic pollution to soils is estimated to be several-fold higher than release to nearby bodies of waters and primary release routes are from tire rubber wear, littering, construction, and agricultural practices (Horton et al., 2017; Kole et al., 2017; Kawecki and Nowack, 2019). Therefore, risk assessment of MNPs in agricultural soil ecosystems is an important pursuit.

One of the first studies was by Jacques and Prosser (2021), who characterized the probabilistic risk potential posed by MPs to agricultural and urban soil ecosystems collectively through calculating thresholds for MPs that may adversely affect soil biota and deriving a conceptual model of the pathways of MP exposure to soil biota. The study utilized the scientific literature that provided MP concentrations in soils in units of items per kg of soil where either no adverse effect was reported or the lowest concentration that produced adverse effects, resulting in distribution functions (percent of species affected vs MP concentration). From the distributions, the 5th percentile was determined and used as a threshold value for risk. A wide range of threshold risk values was determined, from 0.01 items kg^{-1} to more than 10,000 items kg^{-1} , with the majority falling within the range 50–5000 items kg^{-1} . The highest threshold value, 18,760 items kg^{-1} , was likely attributable to the application of sewage sludge in soil (Zhang and Liu, 2018). Their study found that approximately 8150 items kg^{-1} served as the threshold MP concentration for risk, indicating that at 5% frequency, up to 28% of the biota species examined in the literature may be at risk from MPs (Jacques and Prosser, 2021).

Tunali et al. (2023) explored possible risks of MPs to soil organisms [plants, invertebrates (earthworms, springtails, and mites), and

microorganisms (bacteria, protozoa, and fungi)] using a probabilistic species sensitivity distribution model by evaluating the data available in the peer-reviewed literature up to August 2021. (Data for NPs were excluded from the analysis.) The approach involved all ecological levels and exposure pathways to stressors considered for a terrestrial environment (ECHA, 2017). Crucial endpoints, such as growth, reproduction, and survival, were considered for soil plants and animals. Unlike the study of Jacques and Prosser (2021), threshold values for MPs expressed in both number concentrations and weight percent per mass of soil were considered (Tunali et al., 2023). Risk characterization ratios (RCRs) were derived based on measured environmental concentration distributions for different land uses [urban and industrial, agricultural, and natural (undisturbed by human activity, such as forest or floodplain)] and geographical regions (Tunali et al., 2023). RCRs were calculated as the ratio of distributions for measured MP thresholds from the literature and the predicted no-effect concentration (PNEC). An RCR value >1.0 would indicate an environmental risk.

From evaluation of the literature, Tunali et al. (2023) found the global average MP concentration in agricultural soils (4400 items kg^{-1}) to be higher than in natural soils (1400 items kg^{-1}), but lower than in industrial and urban soils (28,000 items kg^{-1}) (Tunali et al., 2023). The mean PNEC for MPs in soil was determined to be 82,000 items kg^{-1} (0.08 wt%), which is 86-fold higher than for fresh water and 22-fold larger than for the marine environment. Approximately 4.8% of all soil-related reports in the literature for all exhibited RCR values ≥ 1 , representing values 40 times greater risk than for freshwater and 240,000 times greater risk than for marine habitats (Tunali et al., 2023). The percentage of reports with RCR ≥ 1 for agricultural soils was 2.8%, which is 58%-higher than for natural soils (1.8%) but well below the level for urban and industrial soils (13%). Environmental risks for MPs were found to be seven-fold higher in Asia than in Europe, with insufficient data available for the Americas to conduct a robust statistical analysis. The study found MPs derived from textiles, polyesters and polyamides, to have a slightly higher impact on toxicity in soil than other polymeric materials and for microfibers to exhibit slightly higher toxicity compared to spheres, fragments, and other MP geometries. MP size was determined to have an insignificant effect on risk assessment, in contrast to the hypothesis that a smaller size would lead to a greater impact. Tunali et al. (2023) identified several deficiencies in the current body of literature on environmental risks of MPs, which affected the reliability of their findings, such as non-representative data across geographical regions and land uses and the absence of MP size distribution and impact of environmental weathering. The same study also emphasized how the absence of standardized approaches for measuring MP concentrations in soils increased the uncertainty of the risk assessment.

To address research gaps for environmental risk assessment, strategies to improve procedures involve harmonization by employing environmentally realistic MP mixtures, soil information such as soil type, land usage, and sampling depth, enhancing the data's comparability and quality (Schnepf, 2023). Furthermore, a prospective risk assessment framework for MNPs should include exposure and fate pathways (degradation, aggregation, and chemisorption of pesticides and other toxicants), characterization of the physicochemical properties (size, shape, density, composition, and surface properties), and standardization of effect studies (relevant endpoints, sensitive species) at realistic environmental concentrations (Koelmans et al., 2022; Masseroni et al., 2022). Due to the lack of available data resulting from gaps in identifying and characterizing NPs in soil biota, the risks and hazards of NPs to soil fauna and plants remain largely unknown. For NPs, research on environmental concentrations, dissolution, aggregation, fragmentation, and degradation processes is still at an early stage. Thus, the field of nanotoxicology, particularly for NPs in terrestrial environments, is still evolving.

9. Conclusions

This review discusses the life stages of MNPs in agricultural soils, including sources, formation, transport, and potential impacts on crops, soil fauna, and contamination of groundwater and nearby streams and lakes. The current state-of-the-art for sampling MNPs from soil and characterizing their size, geometry, and chemical properties was reviewed, as well as approaches to prepare MNP surrogate materials that mimic terrestrial MNPs and can be used in fundamental studies. In addition to MNPs formed from conventional agricultural plastics such as PE, MNPs derived from biodegradable plastics, particularly mulch film, are described. Although the latter will ultimately undergo full mineralization, biodegradable MNPs will reside in soils for several months.

Several gaps in knowledge were identified. For instance, the transformation dynamics from MPs into NPs are poorly understood. The fast fragmentation of biodegradable plastics in soil compared to conventional plastics, coupled with the slow rate of mineralization, raises the question if a higher amount of MNPs could be released into soils compared to MPs derived from conventional plastics, which would result in a higher level of environmental plastic pollution. In addition, MNPs in soils may release polymeric degradation byproducts such as monomers and other decomposed chemicals, posing severe impacts on soil fauna and crops.

The current body of research on MNPs' effects on soil biota lags behind the literature on their impacts on marine organisms, raising concerns for soil health, soil biodiversity, and the safety of food production systems. In addition, soil ecosystems are more complex than aquatic ecosystems and thus present a more challenging system for sample collection and mimicking in laboratory experiments. MPs were first noted in soils in the 1970s but were not identified as an issue of concern until 2012 (Rillig, 2012). Most research on MNPs and soil biota has been published in the last three years (Helberger et al., 2020), utilizing oversimplified single-organism systems. As a result, we know much less about population- and community-level responses. In addition to understanding how soil organisms interact with and transport plastics, there should also be a continued focus on organismal health effects and essential components of soil health. The rising evidence from soil and aquatic ecosystems and work on model organisms such as *C. elegans* and *L. terrestris* shows that MPs can influence soil organisms and terrestrial food web dynamics.

Declaration of generative AI in scientific writing

Nothing to declare.

Submission declaration and verification

This paper has not been published previously, is not under consideration for publication elsewhere, and is approved by all authors and by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or any other language, including electronically without the written consent of the copyright holder.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.impact.2023.100474>.

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