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Review

Microplastics as Source or Sink of Potentially Toxic Elements: Dynamics in The Soil-Plant System

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Abstract

Soil is among the environmental compartments increasingly affected by microplastics (MPs) contamination, mainly coming from industrial activities, agricultural practices, atmospheric or waterborne transport, and improper waste disposal. Despite the increasing attention to the fate of MPs in soil over the last years, research in this area is still limited compared to aquatic ecosystems. The introduction of MPs into the soil environment can modify both the soil properties and the interactions among soil components, plants and microorganisms, thus affecting also the mobility and availability of other contaminants, such as potentially toxic elements (PTEs). This review critically examines the complex dynamics between MPs and PTEs in the soil ecosystem, in particular in agricultural soils, and the conditions under which MPs can act as a source or a sink of PTEs. Indeed, microplastics can adsorb or complex PTEs on their surfaces, thus reducing their mobility and availability, or release/mobilize PTEs after their degradation or as micro/nano-vectors of PTEs. Understanding such mechanisms is relevant to evaluating the environmental risks associated with the co-presence of MPs and PTEs in soil, a situation very likely to occur in most contaminated sites as well as in soils strongly affected by anthropogenic activities.

Keywords: heavy metals; plastics; soil ecosystem; plants; microorganisms; soil properties; metal mobility; plastic degradation; potentially toxic metals; biodegradation

1. Introduction

The amount of plastic waste in the environment has gradually increased in recent decades with the increase in global plastic production (Brandon *et al*., 2019) and is estimated to continue growing in the future (Geyer *et al*., 2017). Plastic pollution nowadays affects different ecosystems and environmental compartments, from the hydrosphere to the lithosphere, atmosphere and biosphere (Pilapitiya and Ratnayake, 2024). The short life cycle of plastic products, together with the long-term persistence of plastic materials, contributes to their accumulation in the environment. In 2024, about 460 million tons of plastic were produced, of which 20 million tons of plastic litter ended in the environment (IUCN, 2024). Once reaching an environmental compartment, plastics may undergo physical crushing, chemical aging, and (bio)degradation, causing plastics fragmentation into progressively smaller particles. Fragments of different sizes may interact with the environment in a very different way compared to the original material. Microplastics (MPs, particles in the size range

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between 1 μm and 5 mm) and nanoplastics (NPs, <1 μm), generated from the degradation of pristine plastics, have a high mobility and can easily diffuse in all the environmental compartments, entering living organisms, where they may interfere with biochemical processes (i.e., endocrine interference) or be magnified along the food chain (Amereh et al., 2020; Habumugisha et al., 2024). Although approximately two-thirds of plastic waste is distributed over land (Elsner et al., 2025), the majority of the scientific production over the past two decades has mainly focused on MPs behaviour in aquatic environments, and this discrepancy has widened in the recent years (Figure 1), reaching a ratio of about 3:1 in 2025 in favour of publications dealing with MPs in aquatic environments.

It is a matter of fact that MPs can alter the physical, chemical and biological properties of soil (Bouaicha et al., 2022; Wang et al., 2022a). Nevertheless, the comprehensive understanding of MPs interactions with soil abiotic and biotic components remains elusive mainly due to the complexity and heterogeneity of soil ecosystems, as well as to the multitude of the pristine plastic polymers and their alteration products.

Among the many negative effects of MPs in the soil system, several works pointed out that MPs can influence the mobility and availability of plant nutrients (Wang et al., 2024) and potentially toxic elements (PTEs) (An et al., 2023; Wang et al., 2020; Yu et al., 2020; 2021). PTEs are elements that can be harmful to living organisms when present in elevated concentrations. While some of these metals are essential in trace amounts for biological functions, they become toxic when accumulate beyond safe thresholds.

Microplastics may either promote the retention or enhance the leaching of PTEs in soil. This dual behaviour depends on the nature, degree of alteration, shape, size and concentration of MPs, as well as on the properties of soil itself (Wang et al., 2022a). Plastics additives (filming agents, catalysts, colouring agents, etc.) can also play an important role in PTEs mobilization and/or fixation. Indeed, such additives may contain or can be PTEs themselves. In conclusion, the role of MPs in influencing the mobility and bioavailability of PTEs for plants and (micro)organisms in the soil system depends on several aspects, often very complex to investigate and predict.

The present review aims at critically examining the possible impacts of MPs in the soil environment, with a particular focus on their influence on the mobility and availability of PTEs. After reviewing the main types of MPs spread in soils and their possible source, the effects of MPs on the chemical and physical properties of soil are addressed, particularly considering those modifications that can trigger or reduce the mobility of PTEs. Then, the potential of MPs to act as a sink or a source of PTEs is discussed, considering the interactions of both pristine or aged MPs with the different abiotic (i.e., minerals, soil organic matter, soil liquid phase, etc.) and biotic (plants and microorganisms) soil components. Exploring these processes as a whole is useful for understanding the dynamics of PTEs in relation to the increasing diffusion of MPs pollution in terrestrial environments, both considering MPs as a source of PTEs pollution itself or as a new “artificial exogenous soil component” regulating PTEs sorption and desorption processes in soil.

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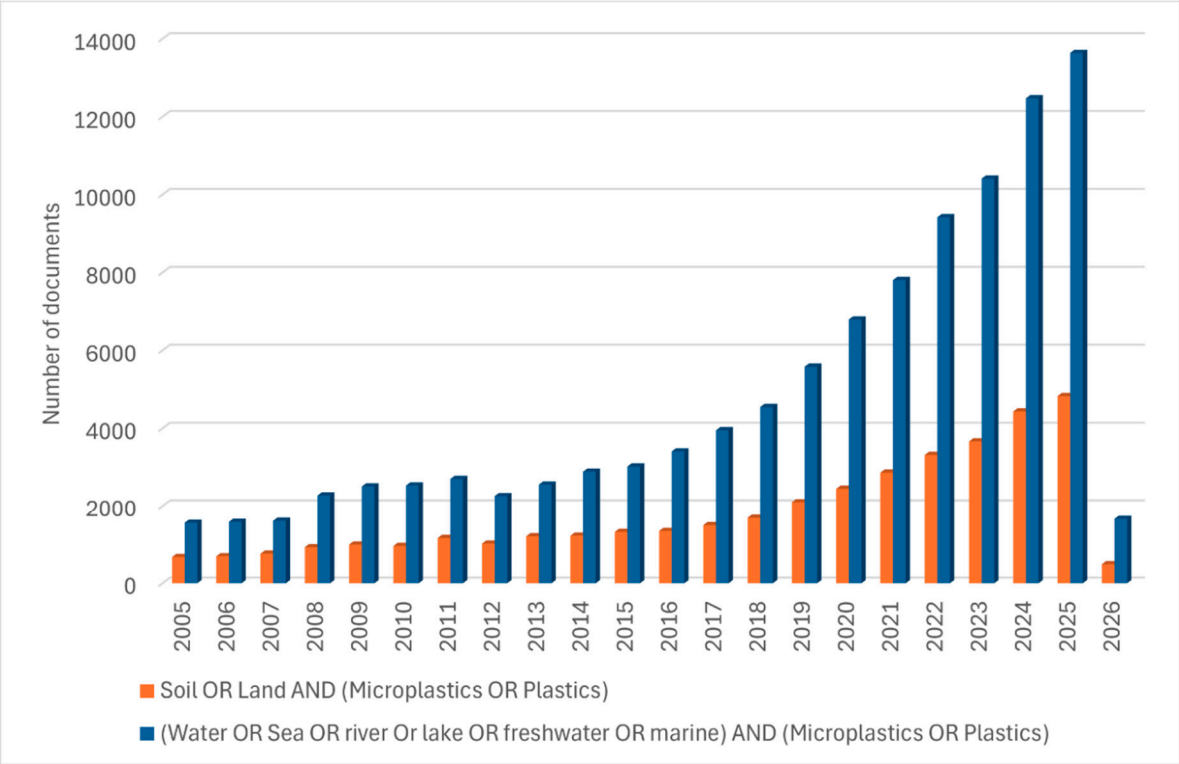

Figure 1. Number of documents (scientific articles, book chapters and proceedings) dealing with microplastics or plastics in water and land environments published from 2005 to early 2026. The data collection was performed on Scopus (scopus.com) using Boolean operators. For soil/land environment we used the following syntax: *"Soil OR Land AND (Microplastics OR Plastics)"*; for water environments we used the following syntax: *"Water OR Sea OR River OR Lake OR Freshwater OR Marine AND (Microplastics OR Plastics)"*.

2. Origin and Type of (Micro)Plastics in Soil

Soil is considered as a major sink for MPs. In a comprehensive study on 62 sites in 17 countries, MPs concentrations in soil have been found to be between 0 and 3,573 × 10^3 particles kg^{-1} of dry soil (En-Nejmy et al., 2024). Büks and Kaupenjohan (2020) have reviewed 23 studies on soil MPs contamination, for a total of 223 sampling sites, and reported common global MPs concentrations up to 13,000 items kg^{-1} of dry soil and 4.5 mg kg^{-1} of dry soil.

Microplastics in soil may originate from several sources. The origin of MPs is often site-specific and varies according to the type of soil (agricultural, industrial, mining soils or other types), climatic conditions, agricultural management, and waste management strategies (Sahai et al., 2025). For instance, in industrial soils MPs deriving from atmospheric deposition and plastic waste disposal may prevail over other inputs. Differently, in agricultural soils the primary source of MPs are plastic mulch films, followed by organic amendment with compost, biosolids or sewage sludge, and irrigation with contaminated waters (Fan et al., 2023; Sahai et al., 2025). Sources and types of MPs in agricultural soils are listed below in order of importance, from major sources to minor sources.

Mulch films, used worldwide to improve crop yields and water use efficiency, as well as to control weeds and pests (Sun et al., 2020a), are mainly made of polyethylene (PE) and, to a lesser extent, polyvinyl chloride (PVC) (Liu *et al*., 2021; Tian *et al*., 2022; Yang et al., 2022). PVC mulching films have been banned in several countries (Bläsing and Amelung, 2018), whereas the use of PVC is still allowed for greenhouse covering (Steinmetz et al., 2016). Removal of mulch films after their use is often labor-intensive and inefficient, leading to the accumulation of large amounts of plastic residues in the soil. Such residues become fragile by photodegradation under ultraviolet radiation, so they break down and shatter, releasing MPs (Huang *et al*., 2020; Yang *et al*., 2021).

Soil organic amendments produced from biowaste, municipal waste or sewage sludge are additional potential sources of MPs (Bläsing and Amelung, 2018; Zubris and Richards, 2005). During

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the composting process, for example, the elevated temperature and the increased microbial activity may speed up the fragmentation process, increasing the MPs content in compost and, consequently, in compost amended soils (Braun *et al*., 2021).

Irrigation with untreated or partially treated municipal wastewater can also contribute to soil MPs contamination. This practice is unfortunately increasing in several countries due to water deficit caused by climate change and population growth (UNESCO, 2020). MPs in wastewater may originate from the decomposition of synthetic textiles during washing, as well as from discharged cosmetics and personal care products. Their reduced size allows MPs to partially pass through treatment plants (De Falco *et al*., 2019). Agricultural fields irrigation with groundwater, river or lake water potentially contaminated with MPs and NPs can as well contribute, albeit to a lesser extent, to the plastic pollution of soils (Bläsing and Amelung, 2018).

Plastic waste is often deliberately disposed on agricultural soils, including packaging materials (containers for pesticides and fertilizers), plant pot trays, crops covering plastics, irrigation pipes, valves and fittings. Many plastic wastes are accumulated near the roads, and surface runoff or wind can transport (micro)plastics into the neighboring soils. Illegal landfills may also contain large amounts of plastics debris and MPs that end up in the soil. MPs may enter the soil also through the abrasion of agricultural machinery tires, construction materials and atmospheric depositions (Weber, 2022). Indeed, light MPs can be easily transported by the wind from landfills and roads (Sajjad *et al*., 2022; Tian *et al*., 2022).

The shape of the MPs recorded in soil ranges from fragments and fibers (the most common) to pellets, spherules, sheets, lines, and films (Xu et al., 2020; Yang *et al*., 2021). The most common types of polymers detected in soils are PE and polypropylene (PP), followed by polyamide (PA), polystyrene (PS), PVC, polyester (PES) and polyethylene terephtalate (PET) (Sahai et al., 2025; Yang *et al*., 2021). Bioplastics can be also found in soil due to their increasing production and use in agriculture. Polylactic acid (PLA) and polyhydroxyalkanoates (PHA) are the main bioplastics used in agriculture (European Bioplastics, 2024). Because of their easier degradability compared to conventional plastics, bioplastics may fragment more rapidly under environmental conditions, leading to the release of larger amounts of MPs and NPs into terrestrial ecosystems (Fei et al., 2024; Piyathilake et al., 2024).

Table 1 provides a detailed list of the main sources of (micro)plastic contamination in soil and, for each source, the type of polymers released and their potential PTE load is also reported.

Table 1. Main sources of (micro)plastic contamination of soils, related types of polymers released and potentially toxic elements (PTEs) content.

Source	Polymers	PTEs concentrations in (micro)plastics
Mulching films	• Main polymers: polyethylene (PE), namely high-density (HDPE), low-density (LDPE) and linear low-density PE, eventually copolymerized with ethylene vinyl acetate (EVA) or ethylene butyl acrylate (EBA) (Steinmetz et al., 2016) • Other polymers: polyvinyl chloride (PVC) (Wang et al., 2022b); polybutyrate adipate terephthalate (PBAT) and poly lactic acid (PLA) in biodegradable films (Reay et al., 2025; Yang et al., 2022)	Concentrations (μg m^{-2}) in mulching films: 490 ± 90 Zn (LDPE), 230 ± 140 Zn (PBA-PLA); < 50 Cd (PBA-PLA > LDPE); < 10 Cr (PBA-PLA > LDPE); < 10 Cu (PBA-PLA < LDPE); < 10 Pb (PBA-PLA = LDPE); < 1 As (PBA-PLA < LDPE) (Reay et al., 2025)
Greenhouse films	PVC (Steinmetz et al., 2016; Wang et al., 2022b); LDPE, EVA (FAO, 2021)	N/A

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Biosolids	• Main polymers: polyurethane (PU), alkyd resins, PA; other polymers: PE, PET, rubber, polyvinyl alcohol (PVA) (Adhikari et al., 2024) • Main polymers: PE, PP, PES; other polymers: acrylic, PS, PU, silicone and others (Crossman et al., 2020)	Concentrations (μg g^{-1}) in compost MPs (PE, PP, PS): 3017-5973 Zn; 504-1234 Cu; 765-916 Pb; 697-840 Cd (Surendran et al., 2024)
Sewage sludge	• PS, PE, PP, PET (Weber et al., 2022) • PET, PE, PP, nylon (Ziajahromi et al., 2021) • PES, PA, PE, PET, PP (Cydzik-Kwiatkowska et al., 2022)	Concentrations (μg g^{-1}) in sludge MPs: 200 – 2500 Cd (Li et al., 2019)
(Waste)waters used for irrigation	• Main polymers: polyethylene terephthalate (PET), PE, polypropylene (PP) (Ziajahromi et al., 2021) • Other polymers: polyester (PES), polyamide (PA), polystyrene (PS) (Magni et al., 2019; Wolff et al., 2019)	Concentrations (μg L^{-1}) in MPs of treated wastewaters: 439 Zn; 147 Cr; 51 Cu; 37 Ni; 35 Pb; 3.0 As; 2.5 Cd (Sarkar et al., 2021)
Tire wear	• Polybutadiene (PB) (Adhikari et al., 2024) • Polyisoprene (PI), PB (Johansson et al., 2024)	Concentrations (μg g^{-1}) in tire wear MPs: 4000 - 5000 Cu; 2000 – 4000 Zn; 3000 Co (Güney, 2024)
Atmospheric deposition	• PA, PU, PE (Adhikari et al., 2024) • Chlorinated polyethylene (CPE), polyimide (PI), PU, PVC, acrylate copolymer (ACR) (Yu et al., 2025)	4.9% Hg and trace concentrations of Pb in PE, PP, PS and PET airborne MPs (Kaydi et al., 2025)
Pipes and other equipment for irrigation	LDPE, HDPE, PVC, glass fibre reinforced plastic (GRP) (Scarascia-Mugnozza et al., 2011)	N/A
Pesticide containers and fertilizer bags	• LDPE, HDPE (Scarascia-Mugnozza et al., 2011) • PP, HDPE, PET (FAO, 2021)	N/A
Seedling plug trays, plant pots, twines, clips, tree guards, and other products	PP, PE, expanded polystyrene (EPS), PVC (FAO, 2021)	N/A
Polymer coated fertilizers	• PE, EVA, LDPE (FAO, 2021) • PE, PU (Katsumi et al., 2021) • PE – polyacrylic acid (PAA) copolymer, polyacrylamide (PAM), PAA (Isakov et al., 2025)	Maximum adsorption on coating MPs (mg g^{-1}): 22 Cd (PAM+PA+acrylates), 48 Cd (PE+PAA), 11 Pb (PAM+PA+acrylates), 25 Pb (PE+PAA) (Isakov et al., 2025).

3. Impact of MPs on Soil Properties Affecting PTEs Dynamics

Microplastics in soil can alter its physical, chemical, and microbiological properties. However, the impacts may differ depending on the polymer type and shape, and soil characteristics (Wang et al., 2022a). Such modifications can, in turn, affect the behavior of other chemicals already present in soil, including soil contaminants. Among contaminants, PTEs are present almost ubiquitously in soils all around the world, constituting one of the major threats to soil health. In addition, certain types of plastics may contain these elements in their structure, becoming a potential source of PTEs themselves (Table 1). A detailed discussion on MPs as PTEs sources as well as on their role in

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mobilizing/immobilizing PTEs will be provided in the following sections, this section covering only the impact of MPs on soil properties potentially affecting PTEs behavior.

As for soil physical properties, MPs can influence the soil structure by destroying stable soil aggregates. In fact, from a mechanical point of view, MPs act as discontinuity points allowing the fissuring and, consequently, the breaking of the aggregates (Zhang et al., 2019). This effect is particularly evident in the case of PA, PS and microfibers of PES and polyacrylic acid (PAA), while PE does not affect soil aggregation. The stability of the aggregates is also influenced by MPs shape. In fact, MPs in the form of films, fragments or fibers may trigger the destruction of soil aggregates, while foams can stabilize the aggregates (Lozano et al., 2021). The destruction of the aggregates causes an increase in the percentage of macropores (Zhang et al., 2019) with a consequent higher soil aeration (Lozano et al., 2021). An increased oxygenation can influence the redox conditions of the soil, changing the oxidation state of PTEs and speeding up the mineralization of organic matter, thus affecting PTEs mobility. The presence of MPs may also modify the soil water content. Since many MPs are characterized by hydrophobic surfaces, soil water availability, transport and holding capacity may be altered (de Souza Machado et al., 2019). Indeed, microplastic fibers may have an impact on water fluxes in soil and affect also soil microorganisms health and biodiversity (Lozano et al., 2021; Zhang and Liu, 2018).

As far as soil chemical properties are concerned, MPs can modify soil pH according to the type of polymer, dose, size and shape, incubation time, and soil type (Wang et al., 2022a). In particular, PE, PS and polytetrafluoroethylene (PTFE) can decrease soil pH, while PES and PLA have been reported to increase it (Feng et al., 2022; Lozano et al., 2021). A dose of 0.2-1% MPs particles does not produce a significant change in soil pH (Feng et al., 2022; Wang et al., 2020), while significant effects have been observed with 2% of MPs (Feng et al., 2022). Soil electrical conductivity (EC) may be also influenced by MPs (Hanif et al., 2024). For instance, Qi et al. (2020) observed a significant EC reduction with increasing MPs concentration. In general, MPs reduce soil cation exchange capacity (CEC) due to their hydrophobicity and lower content of active functional groups and negative surfaces, compared to soil colloids (Li et al., 2021; Wang et al., 2020; Wang et al., 2021). However, Wen et al. (2022) observed a CEC increase from 46 to 58 $cmol_{(+)}\ kg^{-1}$ after the addition of 0.5-4% of MPs, with higher CEC values reached with PA, polyurethane (PU), and low-density polyethylene (LDPE). This different behavior could be imputed to a pretreatment of the MPs with microwaves, which may have altered their surface properties.

Microplastics indirectly affect both the quality and quantity of soil organic matter (SOM) and dissolved organic matter (DOM), by enhancing the activity of peroxidase and fluorescein diacetate hydrolase enzymes, which decompose high-molecular-weight compounds into more easily dissolved low-molecular-weight compounds. This leads also to an increase in dispersed organic nitrogen and phosphorus (Liu et al., 2017). Microplastics affect soil respiration, interfering with carbon biogeochemical cycle, increasing the CO_2 emissions, and therefore contributing to global climate change (Wang et al., 2022a). This is mainly due to the increase in soil aeration caused by the destruction of soil aggregates, which promotes the metabolism of aerobic bacteria, and to the presence of biodegradable polymers which can be promptly decomposed by soil microorganisms.

MPs may also alter the biogeochemical cycle of sulfur, interfering with different enzymes such as sulfur dioxygenase, sulfur reductase and adenosine-5′-phosphosulfate reductase (Dong et al., 2024). All these changes in soil properties, besides endangering soil health and soil ecosystem services, can strongly affect PTEs availability, as discussed in the next Sections.

4. PTEs-Containing Plastics

Some MPs can modify soil properties also in terms of PTEs content because of their own PTEs native load up to concentrations of several thousands of $mg\ kg^{-1}$ (Table 1). Indeed, PTEs can enter in the composition of plastics through three main pathways: i) intentionally added within chemical compounds used as additives, ii) as catalyst residues or side reaction products, iii) arising from metal-containing recycled materials used to produce new plastics (Turner and Filella, 2021). Among these

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three routes of entry, the use of functional metal-based inorganic and organometallic additives has been historically the most relevant source of PTEs in plastic products (Murphy, 2001). Despite regulatory directives have been adopted in many countries in the last decades to forbid or restrict metal-based additives, as in the case of the Toy Safety European Directive 2009/48/EC (EU, 2009) and the Packaging and Packaging Waste Directive 94/62/EC (EU, 1994), plastics produced in the past and spread everywhere over the planet continue to exert their potential toxicity (Turner, 2016; Zhou et al., 2019).

Metal-based additives are (or were) used in plastic industry for multiple functions (e.g., fillers, stabilizers, flame-retardants, colorants, etc.), therefore different metal species can be found in plastic products depending on both the type of plastic and/or the function of the additive. Certain additives were used in almost all types of plastics, making metals (PTEs included) practically ubiquitous in plastics produced in the past. This is the case of metal pigments, which have been widely and extensively used as colorants for their excellent properties of thermal stability and chemical resistance. Along with non-hazardous metal-containing pigments, such as the white ZnS, ZnO and TiO_2 (the latter being the most used white pigment in plastic industry), many other compounds (mainly oxides and sulphides) may contain PTEs such as Cr(VI), Se, Cd, Hg and Pb. Such pigments are mostly insoluble and can reach concentration in plastic of 2.5% on a weight basis (Turner and Filella, 2021). Cadmium sulphide (CdS) and selenide (CdSe) are solid inorganic pigments used as yellow and red colorants, respectively. Among Cr(VI) compounds, lead chromate ($PbCrO_4$) is another well-known yellow pigment, while lead sulphate ($PbSO_4$), lead molybdate ($PbMoO_4$) and mercury sulphide (HgS) were used for red. Other metal-based additives can have more specific applications, sometimes being used for tailoring specific types of plastics for particular uses. For instance, the soluble organic compound Co(II) diacetate was employed mainly as catalyst but also as blue pigment, specifically for PET products. Cadmium, Pb and Sn inorganic and organometallic compounds have been instead extensively used as heat and light stabilizers in PVC industry, while the liquid As compound 10,10′-oxybisphenoxarsine ($C_{24}H_{16}As_2O_3$) and the tributyltin ($(C_4H_9)_3Sn$) were used in PVC and foamed PU with a biocide function (Turner and Filella, 2021).

PTEs may also occur in plastics as residues of catalysts employed in the productive process. For instance, Cr can derive from chromium(VI) trioxide (CrO_3) used for PE production, while organometallic forms of Hg (e.g., phenylmercury compounds) and Sn (e.g., dibutyltin dilaureate) are used as catalysts to produce PU.

Based on the data collected in previous review works (Hahladakis et al., 2018; Turner and Filella, 2021), it can be summarised that the uttermost and widespread contribution to PTEs content in plastics is ascribable to inorganic pigments, in a concentration range of 100-50,000 mg kg^{-1}, with Pb-Cr(VI)>Cd>Co>Hg. Additionally, the PTEs contribution arising from the use of stabilizers may range from 10 to 25,000 mg kg^{-1}, with minimal values for Sn compounds and maximum values for Pb-containing ones. As expected, the lowest contribution to PTEs content in plastics is that of catalysts residues, with a range of 5-3,000 mg kg^{-1} with Hg>Sn>>Cr(VI).

5. Microplastics as PTEs Sinks

Once in the soil, plastic fragments and particles can interact with soil components including free, adsorbed, complexed and fixed metals. According to their characteristics, plastics and in particular MPs and NPs can act as sorbents for both metal nutrients and PTEs. The type of interaction depends mainly on MPs characteristics (polymer type, specific surface area and ageing) as well as on PTEs and soil properties (soil physical and chemical conditions, metal species, biological activity, etc.), as graphically described in Figure 2.

Generally, pristine plastic polymers are considered hydrophobic materials, thus hindering metallic ions adsorption. However, the presence in the polymer structure of elements with high electronegativity (i.e., F, O, Cl, N, and Br) and polar functional groups (mainly amino, amide, carboxyl, carbonyl, alcoholic, phenolic groups) allows the formation of localised dipoles and charges (both positive and negative) along the polymer, making the plastic capable to interact with metal ions

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(McKeen, 2017). Polyamide can efficiently adsorb PTEs both in cationic and anionic form (Li et al., 2022; Tang et al., 2022; Zhou et al., 2020). In fact, Cr(VI) adsorption is higher on PA than PS and PE (Li et al., 2022). Similarly, Cd(II) was efficiently adsorbed onto PA, followed by PVC, PS, acrylonitrile butadiene styrene and PET (Zhou et al., 2020). Yang et al. (2019) have observed that, together with PA, also polymethylmetacrilate (PMMA) has a good adsorption capacity for Cu(II) in soils respect to PE, PS, PET and polyvinyl siloxane (PVS). PTEs in cationic form can be complexed by the amide group of PA, while anions are usually adsorbed by means of electrostatic interactions with the positive part of the formed dipole or, in acidic environment, by the protonated carbonyl group (Li et al., 2022; Tang et al., 2022).

Even if MPs preferentially sorb cations, PTEs anions can also be adsorbed by using different mechanisms: i) electrostatic interaction with other metal cations already bound to the polymer, ii) formation of innersphere complexes, and iii) formation of hydrogen bonds. Indeed, Li et al. (2022) observed that chromate adsorption onto PA increases with increasing Cu(II)/Cr(VI) ratio, demonstrating a positive correlation between the amount of the cation complexed by the polymer and the anion adsorption. Another anion, As(V) in the form of arsenate, can be chemically sorbed via the formation of an O-As bond on the surface of PE, the process also causing a partial reduction of As(V) to As(III) (Chen et al., 2023a). Differently, As(III) can be sorbed on PS only via electrostatic interactions (Dong et al., 2020). Finally, Dong et al. (2019) observed that arsenite is adsorbed onto PTFE by means of hydrogen bonds.

Arsenic adsorption on MPs can also led to a co-precipitation of As-sorbed MPs with soil Fe-Mn oxides, thus reducing its mobility (Yu et al., 2020; 2021). The presence of Cl in the polymer molecule improves the sorption properties of plastics towards PTEs. In fact, Lin et al. (2021) demonstrated that PVC can adsorb more Pb(II) than PE and PS. Zou et al. (2020) also found that chlorinated polyethylene (CPE) can adsorb more Pb(II), Cu(II) and Zn(II) than PVC, LDPE and high-density polyethylene (HDPE). Compared to PA, in these polymers, the PTEs sorption is mainly due to electrostatic interactions (van der Waals forces for PE, CPE, LDPE, HDPE, PVC, and cation-π interactions for PS) and not to complexation (Guo et al., 2021; Lin et al., 2021).

Polymers are characterized by different points of zero charge (PZC) or isoelectric points (IEP), and therefore the extent of the adsorption strongly depends on the soil pH. For instance, PVC and PE show an IEP of 6.59 and 6.44, respectively, while PA requires a pH of 3.6 to reach its IEP (Jang et al., 2022). This can explain why PA can complex cations also in acid soils, whereas PVC and PE adsorb PTEs only via electrostatic interactions at higher pHs.

Microplastics can indirectly adsorb PTEs via the interaction with soil humic substances (HS). The latter can form complexes with metal ions using different oxygenated and sulphur-containing functional groups. Then, on their turn, HS can be sorbed onto MPs, in particular onto the less crystalline portion of the polymer (Gao et al., 2021). The formation of MP-HS-metal complexes sensibly reduces the PTEs mobility in soil (Guo et al., 2021). The formation of a microbial layer around MPs (plastisphere) also facilitates PTEs adsorption due to several interactions of the functional groups of the biofilm molecules with PTEs (Li and Wang, 2023).

Degradation processes occurring in soil may change MPs chemical composition leading, for example, to the increase of oxygenated functional groups in the polymer structure (Singh and Sharma, 2008; Yang et al., 2023). The formation of these oxygenated groups shifts the PZC to lower pH values, allowing the adsorption and complexation of PTEs cations not only in mildly acidic, neutral and alkaline environments, but also under more acidic conditions (Gao et al., 2021). In fact, Li et al. (2022) demonstrated that aged PS and PE behave like pristine PA in the complexation of Cu(II) and subsequent adsorption of Cr(VI). Lang et al. (2020) observed that aged PS can adsorb more Cd(II) not only via physical but also via chemical adsorption due to the presence of C-OH, C=O, C-O-C and O-C=O groups. Yang et al. (2019) found that aged PMMA can adsorb more Cu(II) than pristine PMMA due to an increase in oxygenated groups. The opposite occurred in the case of PA, due to a reduction of the carbonylic and carboxylic groups after aging. Together with the increase of oxygenated functional groups, aged MPs show a higher specific surface area than pristine plastics,

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with a consequent higher availability of sorption sites (Duan et al., 2021; Gao et al., 2021; Li and Wang, 2023). The particles sorption area also increases because of a reduction in MPs size due to aging. An et al. (2023), after sequential extractions from soil, found that Pb in the less mobile oxidizable fraction was inversely correlated with MPs size. They also pointed out the direct correlation between MPs concentration and exposure time in soil, as well as the concentration of Pb and Cd in the oxidizable fraction, while the same parameters were inversely correlated to Cu, Pb and Cd concentrations in the more mobile fractions (i.e., acid soluble and reducible fractions). A change in PTEs partitioning in the different soil fractions was also observed by Yu et al. (2020). They found that MPs can reduce PTEs bioavailability by changing Cu, Cr and Ni speciation from the exchangeable, carbonate-bound and Fe-Mn oxides-bound fractions to the oxidisable organic matter-bound one. The same conclusions were achieved by Yu et al. (2021) studying the MPs effect on a soil subjected to multiple contamination (Cu, Cr, Ni, Cd, As and Zn). This reduction in bioavailability was observed in different aggregates (0.25-2.00 mm and 0.05-0.25 mm) and in non-aggregate silt and clay fractions.

However, the potential positive effects of MPs in reducing PTEs availability in soil by adsorption or complexation should be interpreted with caution. Indeed, if on the one hand MPs can immobilize PTEs, on the other hand they can facilitate the diffusion of PTEs both in the environment and in the biosphere acting as nano- or micrometric-sized vectors of PTEs (Abbasi et al. 2020). In terms of adsorption capacity, MPs can adsorb Cd at quite the same extent of soil colloidal particles: 0.2-0.7 mg g^{-1} onto MPs (Chen et al., 2024; Liao et al., 2025; Liu et al., 2025) with respect to 0.1-0.6 mg g^{-1} in the case of humic acids and clay minerals (Liu and Gonzalez, 1999; Shaker and Abishri, 2014; Vermeer et al., 1999). In the case of Cu, Zn and Pb, MPs show an adsorption capacity from half to one tenth that of other soil colloids. In particular, the adsorption capacity of MPs for these metals is in the range 0.4-1.4 mg g^{-1} for Cu, 0.4-1.3 mg g^{-1} for Zn and 1.5-1.8 mg g^{-1} for Pb (Chen et al., 2024; Liu et al., 2025). The complexity of the soil system, the interactions between soil components, and the interconnected influences of the different physical and chemical parameters on PTEs sorption processes make challenging the interpretation of the role of MPs as PTEs sorbents. This was pointed out by several authors who tried to model the effect of MPs on soil properties and PTEs mobility (An et al., 2023; Yu et al., 2020; 2021). The increase in soil pH and CEC promotes the adsorption of PTEs on MPs. On the contrary, PTEs adsorption is negatively correlated to DOM content, available phosphorous and some biochemical and microbiological parameters (easily oxidable carbon and microbial biomass carbon). However, as already discussed in Section 3, MPs can influence soil properties, and their presence can cause a decrease in soil pH and negatively affect carbon and nitrogen degrading enzymes. This, on turn, may affect amorphous Fe-(hydro)oxides, DOM and microbial biomass carbon, causing an increase in the mobility of PTEs (An et al., 2023; Yu et al., 2020; 2021). On the contrary, other studies have observed an increase in soil pH, after MPs addition and at increasing exposure times, favouring the sorption of PTEs (Qi et al., 2020; Wang et al., 2020; Zhao et al., 2021). These different results demonstrated that even if MPs can behave as potential metal sinks, their sorption capacity and their effect on PTEs mobility strongly depend on the type of soil in which they are dispersed. In addition, the presence of plants and the action of microorganisms, as well as the degree of alteration of the MPs (a characteristic rarely indicated in most of the studies) can further complicate the picture, as discussed in the next Sections.

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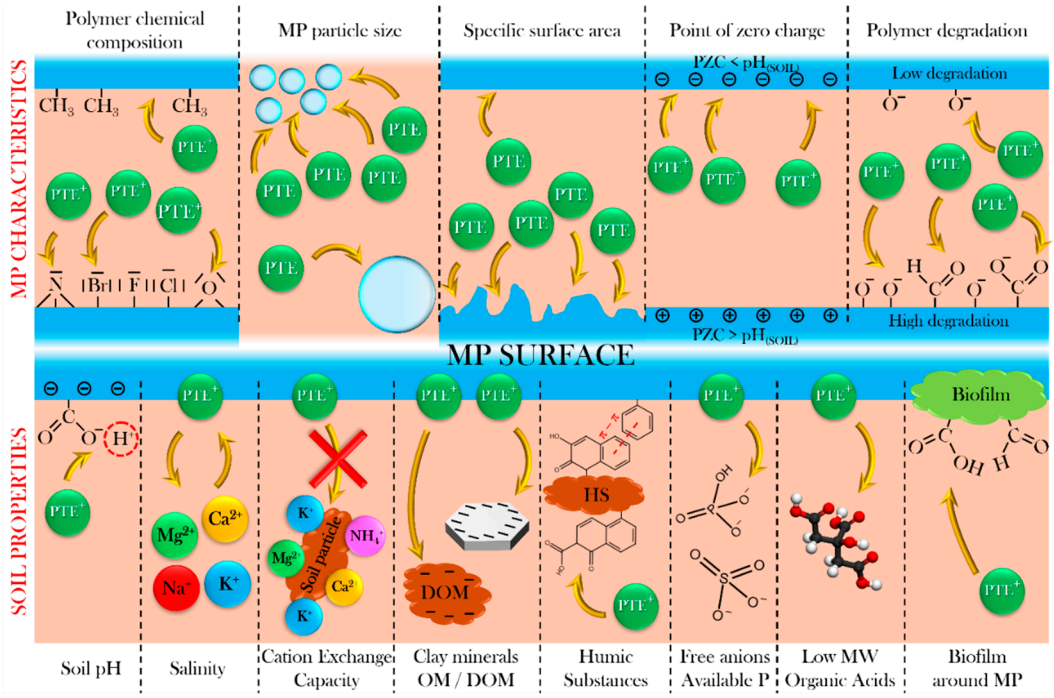

Figure 2. Representation of the dynamics of PTEs adsorption or desorption from MPs according to MP characteristics and soil physical-chemical properties.

6. Microplastics as PTEs Sources

As already described in Section 4, in certain types of plastics, metals and metal complexes are not chemically bound to the plastic polymer, but they are "encapsulated" in their structure (Hahladakis et al., 2018; Liu et al., 2020). Considering this aspect, the release of PTEs in the environment from MPs (in particular, from pristine plastics) is mainly due to the degradation process of the polymer respect to the alteration of the metal compound. These processes may lead to an increase in the availability of such MPs-trapped PTEs in soils. For example, Meng et al. (2021) found that the bioavailability of Cr, Cu, Mn, Ni, Pb and Zn increased after 60 days from the addition of metal-containing pristine PVC in soil. The release of these metals was favoured by the natural aging in the soil. Only Cd bioavailability decreased, which could be imputed to the capability of aged microplastics to adsorb this metal (Lang et al., 2020). Environmental conditions and polymer properties are the main factors influencing the release of PTEs in soil (Liu et al., 2020), as schematised in Figure 2. Although solar irradiation and temperature are usually considered the most important factors of polymer degradation, they do not play a key role in the soil environment. In fact, UV-light can only reach the soil surface, and only in absence of vegetation or litter. Therefore, photodegradation can influence solely the degradation of plastic coverings or mulching films, resulting in the subsequent release of their contained PTEs (Yang et al., 2023). In these cases, Pb is mainly released compared to other metals (Al-Malack, 2001). An important effect of temperature can be observed in the case of arson or controlled fire events which cause the release of metals from the plastics (Filella et al., 2020). In such cases, almost all the metals remain in the bottom ashes (hence, in the soil) except for Sb, which can volatilize in the atmosphere by 27 - 67% of its initial amount (Nakamura et al., 1996; Paoletti et al., 2001).

Soil pH has a strong effect on the weathering of plastics and mobilization of PTEs. Acid environments trigger the leaching of metals from the surface of MPs. The release of Ca, Ba, Pb, Cd and Zn from PVC increases moving from pH 9 to pH 5. In particular, the highest release of Sn, Cd and Ba has been observed moving from pH 6 to pH 5 (Al-Malack, 2001). Metal mobilization is rapid in the first 24 h as a consequence of the release from the surface of the MP, then slows down with exposure time (Turner and Filella, 2021). Such process is also influenced by the shape and weathering

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status of MPs. In fact, weathered MPs show more microcracks and surface irregularities than pristine MPs, resulting in an increased surface area, enhancing PTEs release (Turner and Filella, 2021). Biodegradation is another important path for the weathering of MPs and the release of PTEs in soils. Some organisms, such as earthworms, are able to degrade MPs after ingestion due to both the acidic environment of their digestive apparatus and the presence of microbial consortia in their gut (Duan et al., 2021).

Soil microorganisms also play an important role in degrading plastics in soil thus favouring the release of PTEs, as will be discussed in Section 7.2.

One of the main parameters influencing PTEs mobilization from MPs is the grade of weathering of the MPs. The higher the weathering, the lower the metal desorption (Liu et al., 2020). PTEs release from MPs is therefore initially faster, then becoming slower the longer MPs age in soil. Soil pH still plays a key role in the release of PTEs from weathered MPs, because under acidic conditions protons can displace the cations adsorbed on the sorbent surface. Soil salinity is another crucial factor affecting the release of metals from weathered MPs, again depending on the type of polymer. An increase of soil salinity, and therefore of EC, results in the release of higher amounts of PTEs in the soil. In fact, a high concentration of cations in soil competes with PTEs for the adsorption sites on the MPs surfaces (Gao et al., 2021). The effect of salinity on the desorption of Cu^{2+} from PA is less important than that from PMMA (Yang et al., 2019). The presence of free anions in the soil liquid phase, in particular Cl^-, HPO_4^{2-}, NO_3^- and SO_4^{2-}, enhances PTEs desorption from MPs surfaces (Al-Malack, 2001), posing problems in the case of fertigation with phosphates and nitrates in MPs-containing soils. The occurrence of low-molecular-weight organic acids (LMWOA) enhances the release of metals from the MPs surfaces. Citric, malic and ascorbic acids can easily complex Sb(III) (Filella et al., 2020); citric and oxalic acids trigger the release of Cu(II) from PA particles while, in the case of PMMA, only oxalic acid has an evident effect on Cu(II) desorption (Yang et al., 2019). Therefore, particular attention should be paid to plant roots exudation since exuded organic acids can promote PTEs release from MPs, as it happens for metals mobilization from soil particles (Terzano et al., 2015a). This peculiar aspect will be further discussed in Section 7.1. Soil organic matter and humic acids usually create co-polymers with MPs by forming π-π conjugation, thus increasing the sorption surface of the MPs and hindering the release of metals (Liu et al., 2020; Zhou et al., 2020). On the contrary, charged minerals like phyllosilicates may compete with PTEs for the adsorption sites on MPs (Liu et al., 2020). In particular, this can occur for the octahedral layer of phyllosilicates which can be positively charged and occupy the negatively-charged adsorption sites of MPs, reducing the adsorption of PTEs in cationic form and causing an increase of their mobility. Finally, microorganisms can have a double effect on the adsorption-desorption capability of MPs. The extrusion of organic acids can improve the desorption of PTEs while the formation of biofilms around the MP isolates the particles and limit the release of PTEs in the surrounding environment (Liu et al., 2020). The role of microorganisms in influencing MPs-PTEs interactions will be discussed in Section 7.2.

7. Rhizosphere Processes Affecting the Fate of PTEs Associated with Microplastics

When dealing with soils, and especially with cultivated soils, a special attention must be paid to the so called “rhizosphere”. This is the narrow region of soil that surrounds and is directly influenced by plant roots. It is a dynamic microenvironment where the chemical, physical and biological processes are expedited due to the action of plant roots and microorganisms. For the sake of clarity, these last two effects will be presented separately in the following Sections, but they cannot be considered in isolation, as they are part of the same interconnected system: the soil-plant system.

7.1. Plants

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Plants can modify the environmental fate of MPs and associated PTEs (encapsulated, adsorbed or simply coexisting) mainly through their root activity. They can i) modulate the rhizodeposition (Liu et al., 2025), ii) adsorb MPs and associated PTEs on the root surfaces (Yu et al., 2024), as well as iii) take up MPs and associated metals, and possibly translocate them to shoots (Li et al., 2020a; Xu et al., 2023) (Figure 3).

Some studies reveal that the root exudation pattern shifts toward the release of LMWOA when MPs are present in the rhizosphere. Liu et al. (2025) found that the combined exposure of lettuce (*Lactuca sativa* L.) to naturally aged MPs and PTEs (Cd and As) enhances the release of LMWOA, and these exudates in turn promote the mobilization of Cd and As in soil and their uptake by plants. Specifically, the exudation of oxalic, tartaric, citric, malic, and acetic acids appeared positively correlated with As accumulation, while that of malonic, succinic, and fumaric acids was positively correlated with Cd accumulation (Liu et al., 2025). Besides promoting the uptake of mineral nutrients by plants, root exudates can facilitate the desorption of PTEs retained on MPs surfaces and on other adsorption sites. Recently, Abbasi et al. (2020) demonstrated that a mixture of LMWOA (oxalic, citric, and malic acids) and sugars (maltose, sucrose, glucose, and fructose), simulating the composition of wheat root exudates, can desorb up to 34% Pb, 23% Cd and 15% Zn from PET MPs. It is well established that the cocktail of organic acids exuded by roots mobilizes metals in the rhizosphere by metal complexation, reduction and soil acidification (Schwab et al., 2008; Terzano et al., 2015b).

Nevertheless, a potential role of root exudates in increasing PTEs immobilization by adsorption on MPs surfaces should be also considered. Indeed, similarly to what observed for the natural organic matter, root exudates may be sorbed on MPs surfaces and then promote the co-adsorption of metals (Cao et al., 2021). In some cases, root exudates may promote the aggregation of MPs in the rhizosphere and, consequently, hinder the uptake by roots of MPs and their associated metals. Sun et al. (2020b) observed a more intense alteration of rhizodeposition of *Arabidopsis thaliana* in the presence of positively charged MPs, in particular a 2.6-fold increase of oxalate exudation was measured when plants were exposed to positively charged PS microparticles. This was explained as a plant defence response, since oxalate promotes the aggregation of positively charged MPs and hinders their entry into plant cells (Schwab et al., 2020; Sun et al., 2020b).

The surface charge of MPs also influences their adsorption on root surfaces, with consequences on metal uptake by plants. Both root exudates and cell walls possess an overall negative charge. As a result, positively charged MPs can be electrostatically attracted by root exudates and form a hydrophobic film adhering to the rhizodermis, which hampers the root absorption of water, nutrients and PTEs (Chen et al., 2023b; Schwab et al., 2020; Sun et al., 2020b). On the opposite, the negatively charged MPs escape the attraction exerted by root exudates and rhizodermis cell wall and, if smaller than 2 μm, they might move through the apoplast to the stele, otherwise they are simply repelled by roots (Schwab et al., 2020; Sun et al., 2020b).

Microplastics can enhance the absorption of PTEs by plants and, in some cases, their translocation to leaves. Xu et al. (2023) observed that PS MPs and NPs increased the accumulation of Pb, Cd, Cu and Zn in lettuce roots, as well as the translocation of Pb and Cd to leaves. Wang et al. (2021) found that increasing the concentration of PE MPs from 0.1 to 10%, Cd accumulation in lettuce roots and leaves also increased by up to 60%. Increments of Cd and As concentrations up to 80% were measured in shoots of lettuce when plants were co-exposed to naturally aged PE MPs at concentrations of 0.5 and 1% (Liu et al., 2025).

Several mechanisms may explain the enhanced accumulation of PTEs in plants exposed to MPs. Plastic particles smaller than 2 μm can enter the roots through the so-called "crack-entry mode", which is commonly used by several pathogens as a route of infection (Li et al., 2020a). Microplastics can pass through the epidermal cracks located at the emergence sites of the lateral roots, which correspond to discontinuity points of the Casparian band, and reach the xylem vessels via the apoplastic pathway, until they are translocated to shoots (Li et al., 2020a). Endocytosis and stomatal entry are additional mechanisms of MPs uptake by plants (Sun et al., 2021a; Yu et al., 2024). If MPs act as carriers of PTEs (i.e., by entrapment or adsorption of metals), their uptake will also facilitate

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the absorption and translocation of PTEs by plants. Xu et al. (2023) observed that MPs may damage the cell structures and facilitate the passive transport of metals through the cell membranes. Additionally, MPs may favour the active uptake of metals by promoting the biosynthesis of PTEs transporters, modulating the plant hormonal pool and the signal transduction system (Xu et al., 2023).

Sometimes MPs do not affect or may even reduce the uptake of PTEs by plants. For instance, PS MPs decreased the accumulation of Pb in roots of mung bean (*Vigna radiata* L.) (Chen et al., 2023b), and naturally aged PE MPs at 0.1% reduced or did not affect the accumulation of total As in roots and shoots of lettuce (Liu et al., 2024a; Liu et al., 2025). The variety of responses observed depends on the interaction between several factors, such as the type, concentration, and size of MPs, the type of metal and its concentration, as well as the soil properties and plant species.

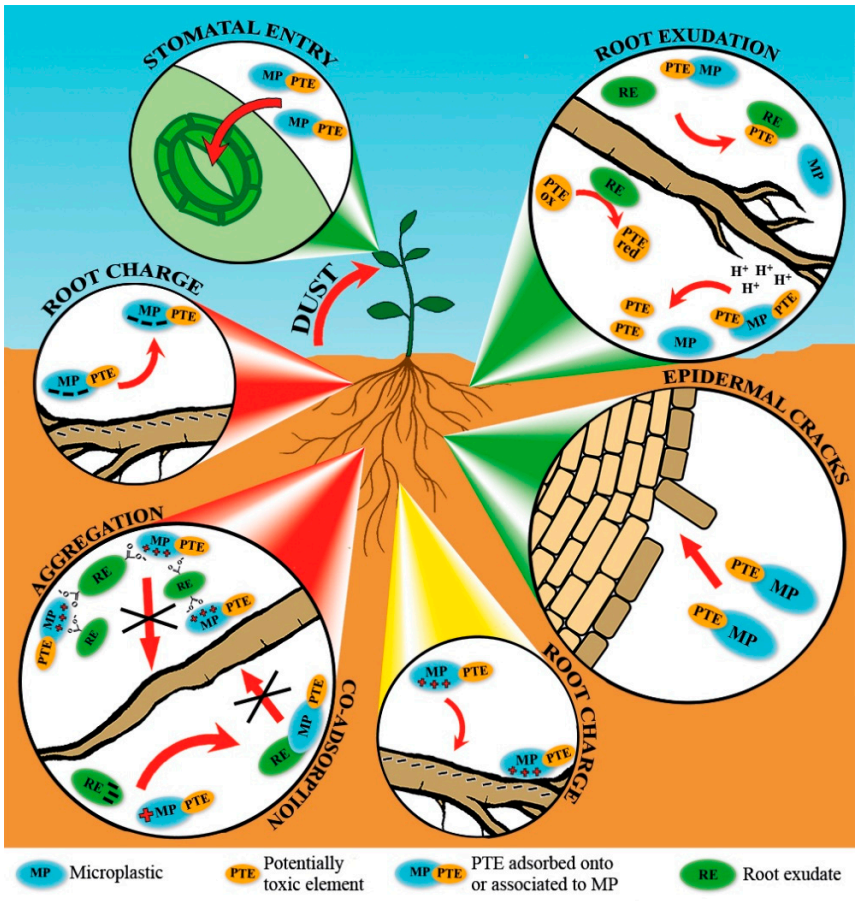

Figure 3. Representation of the main interactions between plant, soil, MPs and PTEs. The processes which trigger the entrance of MPs and PTEs in plants (marked with green cones) are the intake by stomatal entry, the action of root exudation (acidification, complexation and reduction of the metals) and the entrance via epidermal cracks. The process favoring the adsorption of MPs and their associated PTEs on roots (marked with a yellow cone) is the electrostatic interaction between negatively charged root surface and positively charged MPs. The processes which hinder the uptake of MPs associated with PTEs (marked with red cones) are the co-adsorption of PTEs by both root exudates and MPs, the aggregation of MPs and the electrostatic interaction between negatively charged MPs-bearing PTEs and the negatively charged surface of the plant root.

7.2. Microorganisms

The rhizosphere, beside the intense root activity, is also enriched with distinct microbial communities that actively interact with both the roots and soil particles (Shi et al., 2024), including MPs. These microbes include bacteria, fungi, archaea, and various protists that thrive in the nutrient-rich environment generated by plant root exudates. Indeed, root exudates organic compounds such as sugars, amino acids, and phenolic compounds serve as substrates for microbial growth and activity

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(Yaghoubi Khanghahi et al., 2024). In this complex "cocktail" of organic molecules, certain substrates can be selected by specific microbial populations capable of degrading MPs, which can then proliferate in this microenvironment (Thapliyal et al., 2024). The interactions occurring in soil are complex and multifaceted, influencing both MPs degradation and the release and bioavailability of PTEs (Feng et al., 2022), as discussed in the following sections.

7.2.1. Synergistic Interactions in Soil: The Role of Microbes in MP Biodegradation

Various microorganisms have established specialized mechanisms to transform complex synthetic materials into less harmful substances (Li et al., 2023; Zhang et al., 2021) (Figure 4). The biodegradation process is mainly divided into two pathways: aerobic and anaerobic biodegradation. Under aerobic conditions, enzymatic depolymerization followed by microbial assimilation may lead to partial or complete mineralization to CO_2 and H_2O, whereas anaerobic degradation in oxygen-limited microsites results in the production of methane (CH_4), ammonia (NH_3), organic acids, and reduced organic intermediates (Gewert et al., 2015; Gu, 2003). These processes are initiated by biodeterioration, in which extracellular enzymes (e.g., ureases and lipases) weaken the polymer integrity, followed by biofragmentation through hydrolytic and oxidative reactions that introduce functional groups and free radicals into polymer chains (Ali et al., 2021; Thakur et al., 2023). Other key enzymes involved in these processes include proteases, hydrolases, esterases, laccases, peroxidases, and other types of oxidoreductases, which collectively depolymerize MPs into oligomers and monomers that can be assimilated as carbon and energy sources (Thakur et al. 2023; Thapliyal et al., 2024; Yuan et al., 2020). Progressive fragmentation increases MP surface area and reactivity, enhancing microbial colonization and accelerating degradation, while simultaneously increasing the density of sorption sites for PTEs ions (Hahladakis et al., 2018; Liu et al., 2024b). Additionally, microorganisms can assimilate MP monomers as carbon sources for energy production through mineralization processes (Kjeldsen et al., 2018).

Moreover, biofilm formation on MP surfaces represents a critical amplification mechanism for these synergistic interactions. Biofilms create structured microhabitats that aggregate diverse microbial taxa, protect cells from environmental stress, and retain nutrients and PTEs within the extracellular polymeric substance (EPS) matrix (Briassoulis, 2023; Flemming et al., 2016; Han et al., 2020). Within these biofilm-associated microenvironments, microbial metabolism generates organic acids (e.g., citric, oxalic, and malic acids) that locally reduce pH and chelate metal ions, thereby increasing metal solubility and bioavailability (Chen et al., 2019; Mahto et al., 2022; Terzano et al., 2021). Such localized geochemical shifts can promote desorption of PTEs from both soil minerals and MP surfaces, enhancing their mobility and ecological exposure (An et al., 2023; Liu et al., 2024b).

Importantly, these synergistic microbe-MP-PTEs interactions are particularly relevant in soil and rhizosphere environments, where heterogeneous redox conditions and high microbial diversity prevail. Biofilm-mediated MP degradation can thus act as a dynamic interface linking polymer transformation with PTE redistribution, potentially increasing plant and microbial uptake of metals even when total soil metal concentrations remain unchanged (Rilling et al., 2019; Wu et al., 2024). This highlights the need to consider microbial cooperation, enzymatic diversity, and biofilm-driven microenvironments when assessing the environmental risks of MP biodegradation and its implications for PTE contamination in soils.

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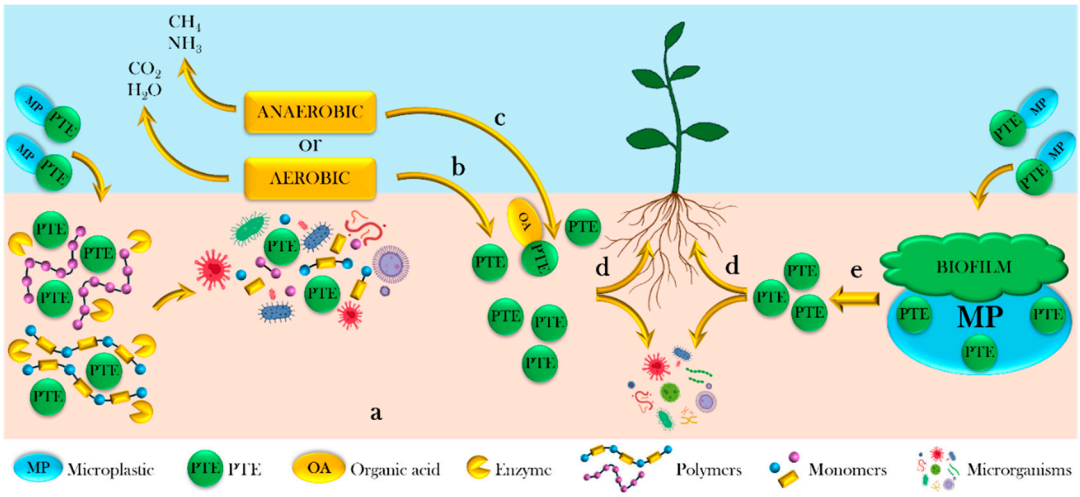

Figure 4. Schematic illustration of the biodegradation process of MPs via microbial action. After the dispersion of PTEs containing MPs (on the left), soil extracellular enzymes can drive the biofragmentation of the polymer which can cause the release of some PTEs (a). The resulting oligomers, dimers and monomers, formed after biofragmentation can still contain some PTEs. These products can be biodegraded by microorganisms which use them for their metabolism. The mineralization of these residues (b) can cause the release of PTEs. In anaerobic conditions (c), PTEs can also be released in association with organic acids. In all these cases, PTEs become more mobile and bioavailable, and they can be taken up by plant or assimilated by microorganisms (d). A further process is the formation of a microbial biofilm on plastic surface which enhances the plastic biodegradation and the release of PTEs (e), which can be then taken up by both plants and microorganisms (d).

7.2.2. Bacteria and Fungi in MPs Decomposition

The mobilization of PTEs associated to MPs in soil is strongly related to MPs biodegradation and, therefore, to the action of soil microorganisms, especially bacteria and fungi, capable of breaking the MPs polymers.

Among the microbial agents involved in MPs degradation, bacteria play a pivotal role due to their resilience and ability to metabolize various substrates. Within the Firmicutes phylum, species such as *Bacillus cereus*, *Alcaligenes faecalis*, *Bacillus sonorensis*, *Staphylococcus epidermidis*, *Burkholderia vietnamensis*, *Rhodococcus ruber*, and *Bacillus flexus* have been shown to effectively degrade PET and PS. In a study conducted by Auta et al. (2022), these bacteria caused a 18% reduction in MP weight, indicating active biodegradation. Additionally, the reported reduction in SOM during decomposition underscores the consumption of organic matter by microbial communities, as observed in various studies (Li et al., 2020b). Moreover, the decrease in pH during the biodegradation is primarily attributed to the accumulation of organic acids resulting from microbial metabolism (Esmaeili et al., 2013). This further promotes the oxidative or hydrolytic breakdown of ester or amide bonds in plastics (Auta et al., 2022), indirectly enhancing PTE mobility through pH-dependent desorption mechanisms (Alloway, 2013). Furthermore, members of the Proteobacteria phylum, particularly *Klebsiella sp.*, have shown remarkable efficacy in degrading PVC. Zhang et al. (2022) highlighted that *Klebsiella sp.* can survive and proliferate on PVC surfaces as a sole carbon source over 90 days, including the upregulation of esterase, lipase, and monooxygenase enzymes. Additionally, enhanced gene expression related to nutrient transport and oxidative stress response mechanisms suggests the adaptability of bacteria to utilize synthetic polymers for growth and survival (Zhang et al., 2022).

Fungi also play a key role in the biodegradation of MPs. Within the Ascomycota phylum, fungi such as *Aspergillus niger* and *Aspergillus fumigatus* have demonstrated significant potential for MP degradation, as indicated by Williams and Osahon (2021), who observed that the weight reductions in PP particles were considerable, surpassing 50%. It is established that fungal hyphae secrete extracellular enzymes that hydrolyse polymers, facilitating the degradation and assimilation of plastic materials (Okal et al., 2023). Furthermore, these fungi synthesize lignocellulosic enzymes such

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as laccases, peroxidases, and esterases, making them promising candidates for bioremediation (Sánchez, 2009). Earlier research by Osman et al. (2017) showed that *Aspergillus sp.*, belonging to the Ascomycota phylum, improved PU degradation efficiency by 20%, thanks to esterase enzyme activity that facilitated the hydrolysis of PU, as evidenced by the formation of a calcium complex during the process.

Several other species within the Ascomycota phylum, including *Fusarium oxysporum*, *Fusarium falciforme*, and *Purpureocillium lilacinum*, have been studied for their effects on PE, showing significant morphological changes on the PE surface, such as bumps, pits, furrows, swellings, and partial exfoliations, indicating oxidative processes targeting the methyl terminal groups of PE, facilitating biodegradation (Spina et al., 2021).

In soil systems, mycorrhizal fungi play a critical role in the rhizosphere by restructuring soil architecture, enhancing water retention, and increasing microbial diversity (Chang et al., 2024; Leifheit et al., 2021). Their extensive hyphal networks expand reactive surfaces for MP–soil interactions and can influence the redistribution and uptake of PTEs released during MP biodegradation, potentially increasing plant and microbial exposure to PTEs (AbdElgawad et al., 2024; Wu et al., 2024). This association benefits plants by improving the uptake of essential nutrients; however, it may also facilitate the release and uptake of PTEs from degraded MPs, which is detrimental to both plants and fungi (Leifheit et al., 2021).

7.2.3. The Dark Side of Biodegradation: Assessing Risks of PTEs Contamination in Soil

Incomplete biodegradation of MPs, including materials labeled as biodegradable, has important implications for the accumulation, mobility, and bioavailability of PTEs in soil systems. During partial degradation, MPs often undergo fragmentation, surface oxidation, and structural reorganization, leading to increased surface area, altered surface charge, and the formation of new functional groups (Qin et al. 2021). These changes can enhance the capacity of MPs to adsorb metal ions such as Pb, Cd, As, Cr, and Zn, effectively concentrating them at the plastic-soil interface (Chah et al., 2022; Liu et al., 2024b; Qin et al., 2021). As a result, MPs may function not only as passive contaminants but also as dynamic vectors that redistribute metals between solid phases and the soil solution, potentially increasing the fraction of metals that is environmentally mobile or biologically accessible.

Biodegradable MPs appear to pose distinct risks in this context. Several studies indicate that polymers such as PBAT and PLA exhibit stronger and more variable metal sorption–desorption behavior during degradation compared with conventional, non-degradable plastics (Li et al., 2020b; Qin et al., 2021). Incompletely degraded bioplastics can temporarily sequester PTEs on newly generated heterogeneous surfaces, followed by their gradual release as degradation proceeds or environmental conditions change. This pulsed retention-release behavior may increase PTEs bioavailability without changing total soil metal concentrations, thereby elevating ecological and toxicological risks, particularly for plants and soil biota (An et al., 2023; 2024). Evidence further suggests that aged or weathered biodegradable MPs can enhance the migration and transformation of elements, such as As, by modifying PTEs speciation and partitioning within soil matrices (Wu et al., 2025).

In parallel, incomplete MP biodegradation can indirectly influence metal behavior through its effects on soil microbial communities and microenvironments. MPs provide novel colonization surfaces for microorganisms, promoting biofilm formation and localized changes in pH, redox conditions, and ligand production, all of which can affect PTEs cycling and stabilization pathways (Sun et al., 2021b; Li et al., 2023; Jia et al., 2024). Such microbially mediated processes may further increase the mobility or bioavailability of PTEs, reinforcing the coupling between MP degradation dynamics and PTEs contamination. Collectively, current evidence indicates that incomplete MP biodegradation, particularly of biodegradable plastics, can exacerbate PTEs contamination by enhancing metal accumulation on plastic surfaces and facilitating subsequent remobilization. This underscores the need for risk assessments that move beyond total PTEs concentrations and explicitly

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consider PTEs speciation, bioavailable fractions, and time-dependent interactions between MPs, soil chemistry, and microbial processes (Kyrikou and Briassoulis, 2007; Liu et al., 2024b; Qin et al., 2021).

8. Conclusions and Future Perspectives

The presence of MPs in soil can affect the mobility and availability of PTEs. Indeed, MPs can influence soil physicochemical properties, plant physiological processes, and microbial activity thus affecting PTEs dynamics in soil. Moreover, once reaching the soil, MPs characteristics can be altered due to physical, chemical and biological degradation, modifying their interaction with PTEs. The complexity and heterogeneity of the soil environment make the identification and definition of all the variables influencing MPs-PTEs interactions very challenging. There is not a sole answer to the question if MPs are a source or a sink for PTEs in the soil system. They can act either as sinks or sources of PTEs depending on the type, size and characteristics of MPs (whether containing or adsorbing PTEs), and soil conditions (including plants and microorganisms), with a behaviour similar to that of SOM and DOM. They can adsorb PTEs on their surfaces (also forming complexes together with SOM, root exudates and biofilms), thus reducing their availability and mobility, or they can function as PTEs shuttles (especially smaller MPs or NPs), thus favouring their movement in the soil environment. Degradation and mineralization processes, either biotic or abiotic, can over time release PTEs encapsulated in or adsorbed on MPs. MPs toxicity to plants could facilitate PTEs uptake and translocation if they are both present in soil, as it might happen in many contaminated sites.

Future studies should unravel several key aspects that have been scarcely considered to date. Among them, the influence of the alteration status of MPs on the mobility of PTEs in soils. Another open question is the role of plants in plastic degradation in the rhizosphere, and the metabolic pathways of MPs and associated PTEs once taken up by plants. As for microorganisms, understanding the interactions between MPs biodegradation, microbial ecology, and PTEs bioavailability will be the key to developing effective strategies and policies for mitigating plastic and PTEs pollution in terrestrial ecosystems. Moreover, future studies should consider real-world conditions to investigate the long-term ecological impacts of MPs degradation and the resulting byproducts, including released PTEs. The univariate approach should be abandoned in favour of a multivariate one which consents to investigate the phenomenon considering correlations among different variables instead of single-factor effects. Special attention should be paid to the environmental implications of MPs originating from bioplastics, which often show more chemically altered surfaces compared to fossil fuel-based MPs, and therefore may interact more easily with PTEs. Additionally, once adsorbed and accumulated, PTEs can be more easily and rapidly released due to the faster (bio)degradation of biopolymers in soil. Finally, despite the large amount of experimental data available in the literature, there is a lack of models on MPs diffusion, degradation and interaction with PTEs in soil. All the experimental data acquired can be the basis for the development of predictive models in order to define the environmental potential risks connected to MPs presence in PTEs-contaminated soils, and to assess the role of MPs as a PTEs sink or source in specific soil conditions.

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