



Innovations in analytical methods to assess the occurrence of microplastics in soil

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ABSTRACT

The occurrence of microplastics (MPs, particles <5 mm) in the environment has raised concerns globally due to their extensive use, slow degradation, low recycling rates, and potential risks to the ecosystem and human health. In the last decade, research on MPs in soil ecosystems has increased but is relatively limited compared to studies on MPs in aquatic environments. The soil matrix complexity and the ubiquitous presence of MPs in the environment make the analytical method development, validation, and Quality Assurance/ Quality Control (QA/QC) procedures challenging to analyze MPs in soil. This review paper comprehensively summarizes the emerging techniques and state-of-the-art methods for extracting, analyzing, and characterizing MPs in soil. The choice in analytical technique ultimately relies on the research objectives, whether polymer type, morphological information, quantity, or the presence of MPs in soil is of interest. Among the reviewed studies, globally, a broad range of concentrations (up to 6.9×10^5 particles/kg) of MPs was observed. However, the data was mainly limited to China. Lastly, the validation of analytical methods, QA/QC procedures, and recommendations for future research are addressed. There are no standardized methods to analyze MPs in soil and validate analytical processes, making it difficult to compare methods and results among studies, resulting in large differences in reported results between laboratories participating in interlaboratory studies. This indicates a need to improve and further develop more robust and efficient analytical techniques for analyzing MPs in soil, conduct more interlaboratory studies, manufacture and use certified reference materials, and promote large-scale monitoring research globally.

1. Introduction

Globally, plastics (synthetic polymers) are used widely in daily human activities in various sectors. The estimated global production of plastics was 359 and 368 million tons in 2018 and 2019, respectively [1], and by 2050 the accumulative production is expected to have tripled [2]. The extensive use of plastics, the production rates, low remaining recycling rates, and slow plastic degradation contribute to an alarming accumulation rate of plastics in the environment [3,4]. Once in the environment, exposure to ultraviolet (UV) radiation and other physical and chemical wear may progressively fragment plastic into smaller plastic particles, including microplastics (MPs) [5–7]. MPs were initially categorized as plastic particles smaller than 5 mm in size [8]. The definition also included particles in the nano-size range [9].

However, the lower size limit is still under scientific debate [10]. A more comprehensive definition is particles size ranging from 1 μm to 5 mm [11]. MPs can be divided into primary MPs which are micro-sized fabricated, and secondary MPs that originate from the fragmentation of larger plastics [7,12]. MPs are present in different morphologies (e.g., fragments, filaments, and fibers) and are constructed from different polymer type (e.g., polyethylene (PE), polypropylene (PP), and polystyrene (PS) [3]. Large amounts of MPs can enter the soil via multiple sources, including soil amendments (e.g., compost and sewage sludge) [13–16], landfills [17,18], atmospheric deposition [19], irrigation with untreated waste and surface water [20], flooding, littering and road runoff [21]. In recent decades, many studies have focused on the source, occurrence, and fate of MPs in aquatic ecosystems [22–24], and the accumulation of MPs in marine or freshwater organisms [25,26].

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highlight and summarize the more frequently reviewed articles for the analysis of MPs in soil ($n = 8$, years 2016–2018); (4) evaluate the state-of-the-art methods compared to the emerging techniques to identify knowledge gaps; (5) collate the occurrence, abundance, characterization (polymer type, size, shape) of MPs in soil globally; (6) discuss challenges related to contamination, method validation, and QA/QC along with suggestions for future research.

The implemented method for retrieving literature by database searches, applying the PRISMA methodology and IRAMUTEQ analysis, is described in the [Supporting Information \(SI\)](#). In short, publications were retrieved by literature databases combined with cross-references, the papers were selected and analyzed based on the PRISMA methodology [37] and classified by the text mining software IRAMUTEQ [38]. [Fig. 1](#) presents the IRAMUTEQ results, showing classes dealing with contextual research about MP and soils ($n = 4$) and the analysis of MPs in soil and characterization ($n = 5$). The four contextual classes are related to (1) soil MPs and impacts on terrestrial fauna, flora, and micro-organisms (dark blue), (2) terrestrial and marine MPs, transfers in the human food chain (light blue), (3) MP sources (purple), (4) soil MP abundance in diverse agroecosystems (red). The five classes on soil MP characterization and analysis are related to (1) chromatography, polymer desorption analysis (pink), (2) analytical techniques such as visual detection and hyperspectral analysis (yellow-green), (3) spectroscopy and spectral transformation (orange), (4) organic matter removal, density separation (turquoise), (5) filtration, drying and sieving (green). This paper comprehensively analyzes these five classes and the one on soil MP abundance. The state-of-the-art methods are topics with high frequency, are non-discriminant and appear in the center of factorial correspondence analysis (FCA) axes. The emerging techniques are most discriminant, with low frequency, shown at the extremes of the axes ([Fig. 1](#)).

2. State-of-the-art methods of MPs in soil

2.1. Soil sample collection

Soil sample collection is the first step of the MP analysis in soil. The sampling material, area, depths, and points at each site are crucial for developing the sampling method for specific research questions [10]. The soil is a three-dimensional medium which makes soil sampling at different depths important. The reviewed studies analyzed various land uses, e.g., soils of agricultural lands, natural and urban lands (e.g., roadsides, dumping sites). MPs are heterogeneously distributed in the soil and can be obstructed by soil amendments and farming. To account for this heterogeneity, the composite sampling method is most commonly used in agricultural lands ([Table S2](#)). Samples from various discrete sites of the same size from a sampling area are combined and homogenized into one representative sample [10]. Other sampling methods included quadrat sampling [39,40] and grid and belt sampling [41], which provides a systematic approach, ensuring uniform coverage forming a pattern of sampling points. Random sampling provides an equal opportunity for each site to be sampled [16,42–44]. The drilling down boreholes to different depths [45] allows sampling different soil layers. Additionally, sampling from different measuring sampling plots ranging from 0.01 m^2 [46] to 300 m^2 [20] was applied. Among the studies, multiple sampling locations (excluding samples and replicates) ranged from 3 to 100 sites ([Table S2 and S5](#)). Various types of sampling equipment were reported for soil collection ([Table S2 and S5](#)), mainly of stainless steel material, such as shovels, and spades for surface samples, while corer and augers were used for deeper soil samples. Surface soil collection may be sufficient for MPs analysis in unused land. However, the soil depth must be considered to analyze the vertical distribution of MPs after ploughing [10]. The soil sampling depths among the studies ranged from 0 to 40 cm, sampling a single layer or multiple layers of soil in the top 20 cm from the surface ([Table S2](#)). The sampling amounts collected by combining subsamples of each sampling site to produce a

single composite sample varied between 1 and 3 kg [47–50] ([Table S2](#)).

2.2. Separation and extraction methods for MPs in soil

When analyzing soil, the type, profile, and constituents (i.e., soil organic matter (SOM), soil solutes, clay minerals, and silicates) must be taken into consideration [51]. The complex composition and heterogeneous soil sample make separating MPs from the soil challenging. In addition, plastic particles in soils are associated with soil aggregates, which can interfere with the analysis [21,52]. It is thus essential to analyze the soil characteristics, such as texture, pH or ionic strength, cation exchange capacity, aggregate stability, bulk density, SOM or organic and inorganic contents, to minimize the potential influence on separation and subsequent quantitative analysis of MPs [51]. After field sampling, the MPs are extracted from the soil for further analysis. Generally, the extraction methods for MPs in soil include drying and sieving, density separation, organic matter (OM) digestion, and filtration.

2.2.1. Drying and sieving

The collected soil samples are typically stored at 4°C in the laboratory and naturally air-dried before analysis to minimize the effect of soil humidity on the analysis. However, several studies ($n = 7$) oven-dried the samples at a temperature ranging from 30° to 75°C . The thermal deformation temperature of the common plastics is higher than 70°C , except for particles composed of poly(methyl methacrylate) (PMMA) [53]. Therefore, using a lower temperature may minimize the effect of melting, degradation, or glass transition of the MPs [51].

Sieving the soil MPs sorts the particles by specific size classes. The selected sieve mesh size determines the quantitative size range of the MPs. Mesh sizes between 1 mm [54] and 5 mm [20,55,56] are commonly applied. The remaining residues and large particles ($>5 \text{ mm}$) are visually classified and removed. Although the 5 mm mesh sieves fit the MP definition the most, 2 mm sieves are also applied to sieve soil MPs [15,57,58], typically for soil samples containing large amounts of plant roots and impurities [59]. Some studies sieved through 25-, 35-, or $50\text{-}\mu\text{m}$ [47,60,61], while others utilized multiples sieves [62] or 0.9–0.15 mm range of sieves [46] ([Table S5](#)). The utilization of the different sieves is, in the end, dependent on the research objective, which complicates the comparability of the results.

2.2.2. Density separation

Density separation is a common technique to extract and pre-concentrate MPs from the soil. In density separation, the MPs float in salt solutions with a higher density than the plastics [51]. The floatation technique applies solutions with different densities to target specific MPs. The densities of common MPs and floatation solutions are listed in [Table S3 and S4](#), respectively. Water and saturated sodium chloride (NaCl) are inexpensive and non-toxic but are limited to extracting low-density microplastics (LDMP) [63,64]. Other salt solutions, such as sodium iodide (NaI), zinc chloride (ZnCl_2), and calcium chloride (CaCl_2), are applied for the extraction of high-density microplastics (HDMP). The majority of the studies ($n = 25$) implemented a one-step or two separation technique and one study [15] used a multi-step technique with water, NaCl, and ZnCl_2 ([Table S5](#)). NaI and ZnCl_2 provide sufficient recovery of MPs. However, they are relatively expensive and hazardous which complicates the handling and disposal [65,66]. CaCl_2 is cheaper and not harmful for the environment or human health. However, it may also extract the SOM by potentially bridging the negative charge of the organic molecules to Ca^{2+} and its low density does not allow the separation of all MPs [67]. This demonstrates that the commonly used density separation solutions have limitations [64]. The extraction efficiency of the floatation technique relies on sample mass, sample to volume (floatation solution) ratio, and the mixing method used [65]. The floatation salt solution may also influence the size and shape of the extracted MPs from soil [55]. Because MPs can be

incorporated into soil aggregate fractions [21,52], the reviewed studies included, centrifugation, ultrasonic treatments, or utilized a continuous flow-air floating device to improve the separation efficiency by breaking down the aggregates [52,65,68].

2.2.3. Organic matter removal

Some components (e.g., SOM and organic fibers) in soils and MPs have similar densities and interfere with the MPs' visual and spectral analysis [21,64]. These components can also be extracted by density separation [67], making separating MPs from soils with high SOM content difficult [69]. As a result, the SOM and other organic materials that may interfere with the analysis are removed by digesting the soil samples [53]. Oxidative digestion with hydrogen peroxide (H_2O_2 , 30%), strong acid, alkali, and enzymatic digestion are common SOM digestion methods (Table S5). The frequently utilized Fenton's reagent (30% H_2O_2 and iron (II) sulfate (FeSO_4) catalyst), provides a rapid, low-cost, and effective method for the removal of SOM, but the digestion efficiency depends on the reaction temperature ($<40^\circ\text{C}$) and optimum pH (at 3.0) [53]. Although H_2O_2 and Fenton's reagent remove similar amounts ($>70\%$) of SOM from soils with low organic content, H_2O_2 may be more suitable for soils with high organic content [70]. The reaction does not require additional temperature monitoring and control, which minimizes the risk of damaging the plastic polymer. It also requires fewer reagents, reducing the costs per analysis [70]. Other chemical mixtures applied included 30% potassium hydroxide (KOH): sodium hypochlorite (NaClO) [71] and a combination of 0.5 M FeSO_4 , sulfuric acid (H_2SO_4), and 30% H_2O_2 [40]. In addition, one study applied enzymatic digestion with pancreatic enzymes to remove SOM [54]. To effectively digest SOM without damaging the MPs, the digestion method, reagent, temperature, concentration, and pH must be considered.

2.2.4. Filtration

Filtration is a solid-liquid separation technique that allows the separation of MPs from the supernatant floating solution [35]. This step is performed mainly before visual sorting and MPs identification. Filter size selection is essential to retain the preferred MPs on the filter surface. Filters with a porosity size between 10 and 20 μm are advised. However, small porosity may hinder the filtration process by slowing it down by clogging the pores [72]. Several filter materials were applied in the reviewed studies, such as cellulose acetate, glass (micro-) fiber, nylon, organic filter membranes, stainless steel sieves, and vacuum filters (Table S5). Along with the filter type, porosity sizes range between 1000-, 300-, and 100- μm mesh sizes [54] or 1 μm filtered with a vacuum pump [56] (Table S5).

2.2.5. Pressurized extraction methods

The pressurized fluid extraction (PFE) method applies solvents at subcritical temperature and pressure, to recover organic pollutants from solid materials [73]. The method was optimized to extract MPs from soil and waste materials with methanol at 100°C as an initial extraction step to reduce matrix interferences and followed by an extraction with dichloromethane (DCM) at 180°C and 100 bar. The extraction method demonstrated to be simple, fast, and cheap with the potential to be fully automated [73]. However, PFE followed by measuring solid residues with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) allows only mass-quantitative analysis and was not suitable for quantifying small MP concentrations [73]. The PFE followed by FTIR method was unable to determine the number and size of MPs in soil samples, as the results were presented as concentrations [73]. More recently, pressurized liquid extraction (PLE) was performed with tetrahydrofuran (THF) at 185°C as a pre-extraction step prior to pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) to reduce matrix interferences. THF is a less toxic and more volatile solvent than DCM and also reduces possible clogging of the tubing system [74].

2.3. Identification of MPs in soil

After extracting MPs from the soil samples, several analytical techniques are applied to determine MPs particle size and morphology, polymer type (chemical composition), and identify and quantify the polymers, as listed in Table S5. Generally, the MPs are identified and quantified by visual sorting and spectroscopic techniques.

2.3.1. Visual identification

To determine the size and quantity of MPs after extraction and distinguish MPs from other impurities, they are visually sorted by the naked eye or microscopic techniques [69]. This method is used to identify MP particles of 1–5 mm size [75] since it is challenging to observe MPs with a diameter $<1\text{ mm}$ [31]. The most commonly applied ($n = 18$) stereomicroscope determines the morphological characteristics (shape, surface texture, and color) of particle size $>500\ \mu\text{m}$ (Table S5). Although visual sorting is simple, inexpensive, and non-destructive, sufficient removal of organic impurities is essential to prevent false positives and misinterpretations [21,31]. In addition, it is difficult to distinguish between natural particles (such as aluminum silicate, quartz, stearic acid, and castor oil) and MPs [3]. The use of the hot needle test can confirm the distinction between natural and plastic particles using the synthetic particles' thermoplastic properties. The plastic particles melt while non-plastic material is burned into ashes [47]. Combining sample heating, microscopy with imaging software allows to visually identify the particle amounts, shape, and size distribution. After heating, the MPs increase in circularity, transparency, and shininess due to melting. The identification of the MPs particles from impurities is confirmed by comparing the two microscopic images (pre- and post-heating) [16,69,76]. Scanning electron microscopy (SEM) can be applied to further examine the MPs' surface morphologies (Table S5). While SEM provides high magnification images of the sample and information on the MPs degradation process, it is more costly and laborious (sample preparation and coating) [77].

2.3.2. Vibrational spectroscopy

Spectroscopic techniques such as FTIR and Raman (micro)spectroscopy are commonly applied methods for identifying and quantifying MPs in soil; 20 reviewed studies applied FTIR and 4 applied Raman (Table S5). The polymers are determined based on the light or energy absorption of characteristic functional groups [78]. FTIR and its optimization technologies, such as ATR-FTIR, micro-FTIR ($\mu\text{-FTIR}$), or FTIR coupled to a microscope, allows for MPs to be observed having size limits down to 10 μm for the latter two and $>500\ \mu\text{m}$ for ATR-FTIR [4, 59], while Raman spectroscopy can visualize size limits of MPs down to $>1\ \mu\text{m}$ and can reach $<1\ \mu\text{m}$ when coupled to a microscope [4]. FTIR and Raman (micro)spectroscopy enable simultaneous, non-destructive, and accurate analysis of MPs chemical and morphological properties such as polymer types, particle numbers, shapes, and sizes [4,10]. However, the accuracy of the identification of MPs depends largely on sufficient removal of interferences, such as SOM that causes background fluorescence. In addition, FTIR and Raman are sensitive to spectral interferences such as water and atmospheric CO_2 [10,21,79]. While both techniques are still widely applied and crucial for determining MPs morphologies, they are expensive, time-consuming, and cannot detect MPs' mass or concentration in the samples [51,77].

3. Emerging techniques for MPs in soil

3.1. Emerging separation and extraction methods

Different approaches for extracting soil MPs include the use of sodium bromide (NaBr) solution circulation [66], castor oil [80], olive oil [81], canola oil [70] for density separation, and enzymatic-oxidative digestion for SOM removal [82]. These emerging separation and extraction methods are summarized in Table 1. An automatic cycling

Table 1

Summary of alternative solution for density separation, oil extraction methods, and enzymatic digestion technique for the analysis of MPs in soil (using spiked samples in soil).

Soil information	Spiking	Separation and extraction method	Identification and quantification method	Results	Ref.
Soil samples from the suburb of Shanghai, China, and control soil.	PA, PP, PE, PET, POM, PVC, PC, ABS, PMMA, and PS. Size-classes 100–500, 500–1000, and 1000–3000 μm . Shapes, particle, fiber, or film shape.	An automatic cycling device using NaBr as circulation solution. Testing saturated solutions of NaBr, NaCl, and CaCl_2 .	μ -FTIR	<ul style="list-style-type: none"> Recovery rates for the different polymers: NaCl > 90% but cannot extract three types of high-density MPs. NaBr and CaCl_2 95–100%, in comparison, the NaBr filtration is fluent and delivers a significantly higher recovery rate of POM than CaCl_2 solution. Recovery rates for the sizes, specifically 100–500 μm PE MP: mean 75.0–96.7% for CaCl_2 solution and 96.7% for NaBr. Recovery rates for three shape-different PE MP: NaBr 85–98.3%. However, among the solutions, there were no significant differences. Application on real soil: floodplain soil 256.7 ± 62.2, paddy soil 190 ± 31.2, yellow-brown soil 155 ± 95.2, and farmland soil 136 ± 41.7 item kg^{-1}. MP size ranged from 0.03 to 4.76 mm. MP shapes included particle, fiber, and film. 	[66]
Agricultural soil, Münchenstein, canton of Basel Country, Switzerland	PP, PS, PMMA, and PET, fragmented and sieved into 0.3–0.5 mm and 0.5–1 mm fractions.	Oil separation method using castor oil added to soil with distilled water; Shake for 1 min; Settle for 15 min; Filter oil phase with cotton/ cellulose filter 25 μm .	Stereomicroscope and ATR-FTIR.	<ul style="list-style-type: none"> Valuable alternative for density separation, but additional cleanup can be beneficial depending on the environmental matrix. Straightforward and efficient protocol. Spike recovery rate: $99 \pm 3\%$ (mean \pm SD, dw). Average matrix reduction of $95 \pm 4\%$. Agricultural (real) soil matrix reduction $98 \pm 1\%$. 	[80]
Soil samples (1–5 cm) from two oat fields in Hollola, Finland: Simola and Mäkelä.	Self-made micro-polymers (0.2–2 mm): PE, PU, PS, PC, PVC, and PET 10 pieces in 25 g.	Oil extraction method , water, olive oil, settling 2 h, frozen at -40°C , ice removed from samples and filtered; Oxidation of OM , 30% H_2O_2 , 2 mmol/L $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, 2 mmol/L protocatechuic acid, and H_2O .	ATR-FTIR, range 4000–650 cm^{-1} , RS of 4 cm^{-1} with 32 scans; Microscope FTIR , spatial RS 4 cm^{-1} , 128 scans, 128×128 pixels, each pixel $5.5 \times 5.5 \mu\text{m}$ dimension	<ul style="list-style-type: none"> Easy and inexpensive extraction method. Excellent alternative method for the density separation method. No hazardous salt solutions needed. Applicable for the isolation of various polymers. The mean recovery rate of: <ul style="list-style-type: none"> Low density polymers PE and PU, $90\% \pm 2\%$. Medium density polymers PS and PC, $97\% \pm 5\%$ High density polymers PVC and PET, $95\% \pm 4\%$. It can be applied to MPs of size 0.2–5 mm using benchtop FTIR and down to 5 μm using microscope-FTIR. 	[81]
Soil types formed with clay material and fine sand (OM content $73 \pm (0.6\text{SE})$ and $12 \pm (0.9\text{SE})$).	Spiked polymers (PET, HDPE, PVC, LDPE, PP and PS) were created with 0.25–0.5 mm and 0.5–1 mm fractions.	OM removal , testing Fenton's reagent, 30% H_2O_2 and 10% KOH; Density separation , testing ZnCl_2 1.7 g cm^{-3} , NaCl solution 1.2 g cm^{-3} and canola oil; Vacuum filtered ; Ultrasonic treatment .	ATR-FTIR, range 4000–600 cm^{-1} , spectral RS 4 cm^{-1} .	<ul style="list-style-type: none"> KOH is unsuitable for OM removal from soils. Both H_2O_2 and Fenton's reagent resulted in similar > 70% OM digestion. H_2O_2 is preferred; it removes more OM from high organic content soils, is a simpler method, uses fewer reagents and is less costly. 	[70]

(continued on next page)

Table 1 (continued)

Soil information	Spiking	Separation and extraction method	Identification and quantification method	Results	Ref.
Silt-loam soil 0–10 cm from Agricultural field, Stuttgart, southwest Germany.	Spiked MP particles range 100–400 µm of PA, PE, PET, PVC, and PLA.	Density separation for particle < 500 µm, ZnCl ₂ solution ($\rho = 1.8 \text{ g cm}^{-3}$ in separation funnel); Enzymatic-oxidative digestion , duration (8d), included: a) 10% SDS, incubated for 48 h at 50 °C; b) Fenton's reagent, 1 h at 40 °C; c) Tris HCl 0.1 M buffer, pH9, protease, 12 h at 50 °C; d) NaAc 0.1 M buffer, pH5, pectinase, 48 h at 50 °C; e) NaAc 0.1 M buffer, pH5, viscozyme L, 48 h at 50 °C; f) NaAc 0.1 M buffer, pH5, cellulase, 24 h at 40 °C; g) Fenton's reagent, 1 h at 40 °C; Second density separation.	Stereomicroscope, ATR-FTIR and µ-FTIR; GPC, and DSC analyses.	<ul style="list-style-type: none"> The density separation methods using NaCl resulted in the lowest extraction rates. ZnCl₂ and canola oil showed similar overall recoveries. In soil with high OM content (>30%), ZnCl₂ obtained sufficient extraction efficiency. The use of canola oil minimizes environmental risk and is not hazardous. Demonstrates a reliable and robust method. Allows purification of ~250 g dry weight soil samples for spectroscopic analysis. Purification efficiency of spiked samples resulted in removing mineral matter > 99.9% dry weight and OM 77.2 ± 6.6%. The approach did not affect PA, PE, PET, PVC (100–400 µm). However, biodegradable PLA showed signs of degradation. A drawback: the need to regularly filter the samples over a vacuum filtration unit can be time-consuming and labor-intensive. Results from one agricultural soil sample: 85% fragments, 15% fibers, PP (32.5%), PS (27.5%), PE (22.5%), PET (10%), PBT (5%), and PAN (2.5%). Of the identified particles, 85% were < 201 µm: 10–100 µm (40%), 101–200 µm (45%), 201–300 µm (10%), 301–400 µm (2.5%), 401–500 µm (2.5%) 	[82]

ATR-FTIR, attenuated total reflection-Fourier Transform Infrared spectroscopy; DSC, differential scanning calorimetry; dw, dry weight; IPS, (expanded) polystyrene; GPC, Attenuated total reflection; HDPE, high-density PE; LDPE, light-density PE; µ-FTIR, micro-FTIR; MPs, microplastics; OM, organic matter; PA, polyamide; PAN, polyacrylonitrile; PBT, polybutylene terephthalate; PC, Polycarbonate; PE, polyethylene; PET, polyethylene terephthalate; PLA, polylactic acid; PMMA, poly(methyl methacrylate); PP, polypropylene; PVC, polyvinyl-chloride; PU, polyurethane; RS, resolution; RSD, relative standard deviation; SD, standard deviation; SDS, sodium dodecyl sulfate; SOM, soil organic matter.

device consisting of a separation system, vacuum filtration system, and solution circulation system was developed with an environmentally friendly salt, NaBr, for extracting MP from soil samples [66]. In combination with a vacuum pumping system, the separation system for soil MPs can operate automatically and continuously. The separation system increases the extraction efficiency and reduces the amount of separation liquid used and the operation time [66]. NaBr demonstrated high recoveries in comparison with NaCl and CaCl₂ for MP different in type, size, or shape [66]. The oil-based extraction methods are straightforward and efficient with regard to time, cost and health or environmental risk since no hazardous salt solutions are needed [70,80,81]. The oil-based extraction mechanism relies on the oleophilic properties of plastics, suggesting that the interaction between the long-chain fatty acids of the oil and the polymer backbone is strong enough to extract dense polymers to the oil layer [81]. The castor oil separation is non-toxic, demonstrates high MP recoveries, and the enclosed separation system minimizes sample contamination risk. However, depending on the soil type, additional purification using, e.g., H₂O₂, can be valuable [80]. The olive oil methodology demonstrates good recoveries and may have a higher affinity for PS than castor oil since 76% of PS MPs were not retained in the castor oil layer in non-spiked fluvial suspended solid samples [80,81]. Density separation using canola oil or ZnCl₂ resulted in similar overall MPs recoveries, and higher recoveries than NaCl. However, the extraction efficiencies of the canola oil method

decreased in soils with higher SOM content (>30%), suggesting that only then ZnCl₂ may be required [70]. Most recently, an extraction protocol for MPs from large (250 g) soil samples for spectroscopic analysis was developed with density separation followed by enzymatic-oxidative digestion [82]. The extraction protocol effectively removed stabilized SOM, had a high extraction efficiency (>99.9% for mineral matter and 77.2 ± 6.6% for OM removal), can extract large sample amounts, and can identify a wide range of polymers with particle sizes down to 10 µm [82]. Overall, high-density solutions (e.g., salt solutions, reagents, and oil) are considered the best options to achieve the highest MP recovery from soil samples.

3.2. Thermal analysis

The use of thermal analysis such as Py-GC-MS [74,83], thermogravimetric analysis-mass spectrometry (TGA-MS) [84], and thermal extraction and -desorption-GC-MS (TED-GC-MS) [78,85,86] determines mass fractions of the polymers and their additives by the detection of degradation products of heated samples. Their efficiency in identifying and enabling semi-quantitative to quantitative analysis of MPs in soil has been demonstrated, regardless of the inability to obtain particle number, morphological information, and destructiveness [78,85–87] (Table 2). Py-GC-MS thermally decomposes polymers under elevated temperatures (in the range of 500–1400 °C) in an inert atmosphere [3].

Table 2

Summary of emerging techniques and comparison of methods for the analysis of MPs in soil (using spiked standard loamy soil and environmental soil samples).

Spiked soil samples				
Soil information	Spiked MPs type	Analytical methods	Objective/Findings	Ref.
Surface layer of soil in Berlin; sandy substrate under oak trees; large amount of OM.	LDPE particles to soil, total 4.00 ± 0.04 mg.	TGA-SPE , under N ₂ at 25–600 °C, heating rate of 10 °C min ⁻¹ ; gas flow of 90 mL min ⁻¹ ; (solid-phase thermal extraction twisters , 10 mm × 0.5 and 1.0 mm. TDS-GC-MS : TDS, 25–200 °C, hold 5 min in splitless mode; GC , HP-1MS column (30 m × 0.25 mm i.d. × 0.25 µm df), program, 30–300 °C, rate of 5 °C, min ⁻¹ ; MSD , EI, 70 eV, in scan mode 35–350 <i>m/z</i>).	<ul style="list-style-type: none"> Quantification of PE-spiked environmental samples in a single step with TED-GC-MS. No interference of characteristic decomposition products. Higher (200x) sample masses in TGA than in Py-GC-MS. A pre-concentration would be necessary for real environmental (soil) samples. 	[78]
Standard loamy sand soil type 2.3 (LUFA Speyer, Germany).	Industrial pellets (1–3 mm) of PE, PP, PS, PET; 1 mass-% of each was weighted to the soil.	TGA-SPE , 20 mg sample, 600 °C, 10 K min ⁻¹ under N ₂ , flow 90 mL min ⁻¹ , solid phase absorber. Extraction for LC , THF or HFIP added to soil at 45 °C for 24 h. Raman , equipped with double diode laser, spectrometer and thermoelectrically cooled CCD camera, laser power 2.05 mW, integration time of 15 s, 10 accumulations, image scans 150, 170 µm. FTIR microscopy , transmission mode, range 3850–900 cm ⁻¹ , spectral RS 16 cm ⁻¹ . TDS-GC-MS : TDS, 25–200 °C, hold 5 min at 40 K min ⁻¹ ; GC , HP-1MS, 30.0 m × 250 µm × 0.25 µm; MSD , EI 70 eV in scan mode 35–350 <i>m/z</i> . LC : SEC , HFIP eluent at 0.5 mL min ⁻¹ ; RP-LC column PFG gel 7 µm, 25 × 0.46 cm, HFIP eluent 0.1 mL min ⁻¹ , column PL-RPS 5 µm, 25 × 0.46 cm, THF eluent 0.1 mL min ⁻¹ , UV detection.	<ul style="list-style-type: none"> Comparison of Raman, FTIR, TED-GC-MS and SEC-LC-UV. Analyzable sample amounts: TED-GC-MS (20 mg -up to 100 mg); SEC (500 mg); FTIR (1 mg); Py-GC-MS (1 mg); Raman (1 µg). Time efficiency: Raman (~40 min); LC (2 h); TED-GC-MS (3 h); FTIR (3–6 h). Identification: Raman, FTIR, and TED-GC-MS (PE, PP, PS, PET); LC (only PS and PET). Quantification, TED-GC-MS (possibly) and LC. Particle size distribution/ Visual image, Raman and FTIR. The appropriate method is dependent on the scientific question. 	[85]
Top 5 cm soil, Liabin bay district Panjin, China.	PE size 1–5 mm and 0.5–1 mm, 10 pieces of each material used per sample.	Traditional way : Density separation using NaCl solution, Microscopy, and Raman spectroscopy; Hyperspectral imaging system : used CCD camera combined with the digital controlled Pan-tilt for image acquisition, light source of 250 W tungsten-halogen, spectra data collected with 329 bands of λ range 400–1000 nm, 30 s image scanning time, 38 ms exposure time, and 39 ms frame period; PCA , SVM , MD , and ML .	<ul style="list-style-type: none"> The SVM algorithm resulted as the most applicable method for detecting white and black PE in soil, with less background noise than MD and ML algorithms. Shadows in the hyperspectral images affected black PE MPs classification results. Detection precision ranged from 58% to 84% depending on size and color. Limited to MPs size (0.5–5 mm). It can only be applied to surface soil. 	[92]
Standard loamy sand soil type 2.2 (LUFA Speyer, Germany) with 1.61 ± 0.15% organic C content.	Without IS: 0.284–2.015 mg PET spiked in 42.982–50.792 mg soil. With IS, cysteine: 0.107–2.238 mg PET spiked in 44.182–46.828 mg soil.	TGA-MS : TGA, 5 K min ⁻¹ pyrolysis ramp of 40–1000 °C under a 20 mL min ⁻¹ Ar 5.0 gas flow; MS , EI quadrupole, <i>m/z</i> ratios 12–154, mass RS of 40/41 was < 50 ppm.	<ul style="list-style-type: none"> Cysteine as IS improved signal sensitivity and linearity of quantitative analysis of PET. Real soil samples or soil with high SOM polluted with PET needs to be analyzed (would probably require simple sample preparation or chemically assisted pyrolysis). TGA-MS may require minimal sample preparation and is generally cheaper than TED-GC-MS, Py-GC-MS, or LC-MS. TGA-MS can analyze sample amounts up to 1 g and use various heating rates. LOD/LOQ PET, 0.06/1.72 wt%. 	[84]
Standard loamy sand type 2.2 (LUFA, Speyer RP, Germany) with 1.61 ± 0.15% organic C content.	0.5–5 wt% (PET, PVC, PE, PS) in soil.	TGA : 0.5- and 1-g soil, airstream 200 mL min ⁻¹ , 5 °C min ⁻¹ was applied from RT ~25–950 °C. TML in 10 °C intervals. SUMM (in the absence of blank soil): TML obtained by extracted from a	<ul style="list-style-type: none"> TGA compared to microscopy, analyzes the bulk soil and MPs likely covered by SOM, coated by biofilms, or incorporated in soil aggregates. TGA benefits, low costs, simplicity, time (~3 h), no sample preparation or blank needed. LOD/ LOQ PET, PS and PVC 0.33/1.15; 0.91/3.08 and 2.22/- wt%, respectively. SUMM failed to determine PE, probably due to PE and SOM degradation similar temperature ranges. 	[87]

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Table 2 (continued)

Spiked soil samples				
Soil information	Spiked MPs type	Analytical methods	Objective/Findings	Ref.
Standard soil type 2.3 (eutric fluvisol, organic carbon content 0.67mass %, LUFA Speyer, Speyer, Germany).	PE, PP, PS and PET cryo-milled polymers range 0.5–5mass%, size < 125 µm.	sample, calculate LMTL, subtract calculated LMTL from measured LMTL. sPCA : discriminate and quantify the MPs from each other. Real-world samples analyzed by TED-GC-MS , 60 mg soils 25 °C for 5 min, heated to 600 °C under N ₂ at 30 mL min ⁻¹ , switched to synthetic air up to 900 °C, further details described in[98]. NIR spectroscopy , spectral range 12,000–4000 cm ⁻¹ , RS of 8 cm ⁻¹ , zero- fill of 2 and transformed into absorbance values. Chemometrics , SVR and PLS-DA.	<ul style="list-style-type: none"> The robustness of the method against high SOM needs to be tested. Produces reliable results predicting MPs and polymer type, considered a complementary technique. After minimal conditioning (sieving and drying), MPs (PE, PP, PS, PET and PVC) can be detected at ~1 mass% in soils. For the detection and classification of MP, the SVR and PLS-DA model: sensitivity of 92% and 83%, and specificity of 100% and 90%, respectively. It took 5 min to measure homogenized samples. Quantitative information was unsuccessful so far with the NIR-chemometrics approach. 	[94]
Loess topsoil (0–30 cm) collected in Limburg, The Netherlands was used (50% of sand, 50% of silt and clay, and 3% of OM).	Laboratory made polluted soil samples, fraction size 1–0.5 mm for LDPE, PET and PVC, conc. range 0–100 g MPs kg ⁻¹	Vis-NIR spectroscopy , with a working range of 350–2500 nm, spectral RS of 3 nm for the 350–1000 nm region and 10 nm for the 1000–2500 nm region, recording the spectrum with a 1 nm interval; Multilinear model .	<ul style="list-style-type: none"> Suitable to identify and quantify LDPE, PET and PVC in soil samples at hotspots. Detection limit: ~15 g kg⁻¹; and accuracy: 10 g kg⁻¹. Vis-NIR results in fast, no extraction and direct quantification of MPs in a sample. However, vis-NIR spectra vary for different soil and there is a need for a spectral library to apply to multiple scenarios. The method repeatability for LDPE, PET, and PVC was 0.2–8.4, 0.1–5.1, and 0.1–9.0 g kg⁻¹, respectively. 	[93]
Standard soil samples (excl. MPs) from Zhejiang Academy of Agricultural Sciences. Surface soil of Farmland in Jingdezhen, China	Polymer standards: PE, PET, PP, PS, PA, and PVC.	Soil samples vacuum dried overnight in chamber at 50 °C to remove moisture; TGA-FTIR , transfer line at 270 °C, samples transferred into a ceramic crucible and heated from 30° to 650° C in a N ₂ atmosphere, FTIR at resolution of 8 cm ⁻¹ from 450 to 4000 cm ⁻¹ .	<ul style="list-style-type: none"> Measures the mass loss with temperature and the IR signal of pyrolytic substances in real time. Complex pretreatment is not needed, only pre-concentration. Pyrolysis products of PVC, PA, and PS are distinguishable but not of PE, PP, and PET. The recovery rate of spiked PS and PVC in soil ranged from 97.0% to 108.0%. No characteristic absorption peaks of PVC and PS were observed in surface soil, only strong bands of alkanes and olefins. 	[91]
Soil information Soil samples were collected across New South Wales, Australia, clay content 7.7–62%.	MPs spiking Soils spiked with PET and LDPE, conc. of 0–1000 mg MPs per 20 g of dry soil (0–5% by mass, 0–50 g kg ⁻¹).	Analytical methods Air-drying and sieving soil samples; vis-NIR spectroscopy , spectral range 350–2500 nm with 1 nm sampling interval and RS of 3 nm (at 700 nm) to 10 nm (at 1400 nm); CNN model , with convolution layer containing 32 layers, kernel size of 20.	Objective/Findings <ul style="list-style-type: none"> A promising method for screening MPs contamination in soil based on concentrations. A rapid approach for detecting type of MPs and quantity of contamination. Distinguishes between non-, low-, medium- and high- contaminated samples, but the degree of contamination in intermediate cases could not be differentiated accurately. Prediction accuracy of 69.3%. To improve future work: increase in sample size, including training model for MPs type prediction and expansion of the spectra library. 	Ref. [95]
Topsoil (~20% OM, bulk ρ = 1.33 g cm ⁻³) and sandy soil (>90% sand content, bulk ρ = 2.56 g cm ⁻³); Collected in Northern Ireland.	Contaminated soil with nylon powder, particle size range 50 µm–0.5 mm.	Resonance Microwave Spectroscopy with mathematical model . Samples complex permittivity measured in frequency of 5.0–6.0 GHz.	<ul style="list-style-type: none"> A promising tool to detect and quantify MPs in soil at ppt concentration levels. Sample preparation not required. Microwave spectroscopy can offer: Low cost; Real-time in-situ operation; and MPs detection in diverse environmental conditions outside of the laboratory. 	[96]
Agricultural soil samples (3.6% organic content), origin Baden-Wuerttemberg Germany.	Reference soil samples spiked with PET particles.	Sample extraction for LC-UV , depolymerize PET in its monomer terephthalic acid adapted and simplified from [99], followed by SPE to remove organic matrix interferences. LC-UV , equipped with binary pump, RP column (100 mm × 2.1 mm, 2.6 µm), mobile phase (ultrapure water with acetic acid and 1/1 v/v methanol/acetonitrile) with gradient, DAD at 240 nm. TED-GC-MS , based on[98, 100], 20 mg sample mass, ethyl benzoate used as a specific marker for PET (<i>m/z</i> value of 105).	<ul style="list-style-type: none"> The LC-UV method: Fast (30 min) analysis; Easily to automate; Simple data evaluation; No use of poisonous chemicals; The system that is available in routine labs; PET detection in any solid environmental matrix. Result agricultural soil samples: PET mass contents were 3.85 and 3.99 mg kg⁻¹, this is below the LOQ (6.05 mg kg⁻¹). The recovery of spiked samples using different PET sorts and soil types ranged from 94.8% to 101.9%. In other environmental samples (e.g., dust), LC-UV and TED-GC-MS result verified each other's results. 	[86]
			<ul style="list-style-type: none"> The frequency band 0.6–1.8Thz showed low signal-to-noise. 	[97]

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Table 2 (continued)

Spiked soil samples									
Soil information	Spiked MPs type	Analytical methods	Objective/Findings						Ref.
Topsoils 0–20 cm, collected in 9 suburbs of China, OM 0.1591–2.4539%.	LDPE and PVC, 0.3 g, 1 mm thickness, 13 mm diameter and used for 9 different soil and 13 different concentrations.	THz spectrometer , spectral range 0.1–4 THz, for analysis frequency band 0.6–1.8 THz, dynamic range 70Db in transmission mode, the time domain signal length 53 ps and time-domain signal scanning minimum accuracy 2 μm ; LS-SVM model .	<ul style="list-style-type: none"> The spectral data were used to build a local model for the MPs content in soil, and the LS-SVM local model to predict of MPs concentration in soil. Can predict the degree of MPs pollution in the soil of the corresponding region only. Predicted results: RMSE > 0.9400 and the R < 0.0500. 						
Three soils from Germany: RefeSol 06-A, LUFA 2.2, and WR with OM content 2.5%, 1.73%, and 5.16%, respectively.	PE, PP, PS (0.2 and 1.0 mg) spiked in 4 g soil, i.e., 50 and 250 $\mu\text{g g}^{-1}$.	Polymers were dissolved in TCB; The removal of OM, testing methanol, flocculation with $\text{KAl}(\text{SO}_4)_2$, or Fenton's digestion; Py-GC-MS: Pyrolyzer interface held at 300 $^\circ\text{C}$ for 3 min, flushed with 20 mL min^{-1} He, flash pyrolyzed 10 K ms^{-1} at 750 $^\circ\text{C}$ for 15 s; GC , transfer line 350 $^\circ\text{C}$, split/ splitless injector at 300 $^\circ\text{C}$ with 1:10 split ratio, ZB-5MS 30 m x 0.25 mm x 0.25 μm capillary column connected to a fused silica guard column, 1.3 mL min^{-1} He flow rate, oven program 40–300 $^\circ\text{C}$ at 8 K min^{-1} , transfer line 280 $^\circ\text{C}$; MS , 70 eV EI using total ion current < 10 ⁸	<ul style="list-style-type: none"> TCB extractions at 250 $\mu\text{g g}^{-1}$ spiking level from soils with less than 2.5% OM content (without any pretreatment performed) demonstrated the best recovery (70–128%). $\text{KAl}(\text{SO}_4)_2$ effectively removed interfering matrix constituents, but PE and PP recoveries were reduced. Methanol clean-up resulted in low recoveries and Fenton's digestion led to elevated recoveries. The calibration curve had a LOD of 1–86 $\mu\text{g g}^{-1}$ and repeatability was 3.2–7.2% RSD. The method is limited to soils with OM content < 2.5%. Thus, the method needs to be developed further to reduce matrix interferences. 						[83]
Real environmental soil samples									
Soil source/ Soil type	Location	Sampling (Depth; material; n. study sites)	Extraction method	Identification and quantification method	Abundance	MP particle type	MP particle size	MP particle shape	Ref.
Roadsides and potting	Cologne, Germany	/; Stainless steel spade; /	Pre-extraction using MeOH; PLE using THF	Py-GC-MS , GC Column 30 m x 0.25 mm id, 0.25 μm film thickness, MS in SIM mode	0.03–3.3 mg/g	PE, PP, and PS	< 1 mm	/	[74]
Farmland; forest land; factory; residential area; Industrial Park	Baoding City, Hebei Province, northern China	0–10 cm; stainless steel sampling shovel; 12 areas	Sieving , 35 μm ; OM removal with 30% H_2O_2 at 60 $^\circ\text{C}$ for 6 h; stand for 24 h	TOF-SIMS , spectra and images acquired using 30 keV Bi^{3++} (0.8pA, <1 ns pulse width, bunched beam) LMIG, 200- μs cycle time, mass range: 0–2933 u, positive and negative ion mode, mass RS > 6000	/	PP, 23.3%; PVC, 16.3%; PET and PA6, 30.2%	0–35 μm : 0–10 μm , 26.4%; 10–15 μm , 23.3%; > 25 μm , 9.3%	/	[60]
Farmland	Southeastern of Hebei Province, China	/; /; 3 sites + 1 buffer zone	Sieving , 25 μm stainless steel; OM removal with 30% H_2O_2 at 60 $^\circ\text{C}$ for 6 h; ultrapure water added; stand for 24 h	TOF-SIMS , spectra and images acquired using 60 keV Bi^{3++} (0.8pA, <1 ns pulse width, bunched beam) LMIG, 200- μs cycle time, mass range: 0–3000 amu, positive ion spectra and mass RS > 6000	/	PP, 34.38%; PA6, 28.13%; PET, 25%; and PVC, 12.5%	0–25 μm ; 10–15 μm , 34.38%; 20–25 μm , 25%; 15–20 μm , 15.63%; 5–10 μm and < 5 μm , 12.5%	/	[61]

CNN, convolutional neural network; dw, dry weight; FTIR, Fourier Transform Infrared spectroscopy; GC-MS, gas chromatography-mass spectrometry; HDPE, high-density PE; HFIP, hexafluoro isopropanol; LC-UV, liquid chromatography with UV detection; LC-MS/MS, liquid chromatography tandem mass spectrometry; LDPE,

low-density PE; LOD, limit of detection; LOQ, limit of quantification; LS-SVM, Least Squares Support Vector Machine; LTML, larger thermal mass loss; MD, mahalanobis distance; ML, maximum likelihood; MPs, microplastics; MS, mass spectrometry; μ -FTIR, micro-FTIR; NIRS, near-infrared spectroscopy; OM, organic matter; PA, polyamide; PC, Polycarbonate; PE, polyethylene; PET, polyethylene terephthalate; PLS-DA, partial least squares discriminant analysis; PP, polypropylene; PVC, polyvinyl-chloride; RS, resolution; Py-GC-MS, pyrolysis GC-MS; RS, resolution; SEC, size exclusion chromatography; sPCA, Sparse principal component analysis; SOM, soil organic matter; SPE, solid phase extraction; SUMM, soil universal model method; SVM, support vector machine; SVR, support vector machine regression; TCB, 1,2,4-trichlorobenzene; TDS, thermal desorption system; TED-GC-MS, thermal extraction-desorption-GC-MS; TGA, thermo-gravimetric; THF, tetrahydrofuran; THz, terahertz TML, thermal mass loss; vis-NIR, visible-near infrared.

The formed polymer-specific decomposition products are separated and analyzed using GC-MS and the generated mass spectra or respective pyrograms are identified by comparison with the available polymers databases [74,83]. Recently, PE, PP, and PS have been analyzed with Py-GC-MS [74,83], quantifying low concentrations in soils with high SOM [74]. Py-GC-MS allows for simple sample preparation and direct quantification of liquid sample aliquots but can only analyze small sample masses (<0.5 mg), which poses challenges to the sampling in case of inhomogeneity of the sample [78,83]. This makes it unsuitable for analysis of large amounts of sample or samples of organic-rich soils [83]. Since the method is unable to determine particle number and size, it is suitable as a fast screening method, complementary to microscopy and spectroscopic techniques [74]. Since environmental samples usually contain a mixture of polymers, the interactions between polymers and their pyrolytic products during thermal degradation can lead to secondary reactions, altering the pyrolytic yields and quantitation [88]. Further research is needed with regard to extraction methods prior to pyrolysis to reduce matrix interferences from specific soil constituents, expanding the applicability to a wider range of polymer types, assessing alternative solvent mixtures, identifying the interaction mechanisms between two polymers or their pyrolysis products, and in addition the use of reference material that could accurately mimic the co-pyrolyzed synthetic polymers [83,88].

TED-GC-MS analysis is a two-step method that combines thermogravimetric analyzer (TGA) with thermal desorption-GC-MS (TDS-GC-MS) [78,89,90]. First, the sample is thermally decomposed in a TGA at high temperatures (up to 1000 °C), trapping the gaseous decomposition products onto a solid phase adsorber, and finally, the solid phase adsorber is analyzed with TDS-GC-MS [90]. TED-GC-MS is a fast identification method that can analyze larger sample amounts (up to 100 mg) [78,90]. It was demonstrated that the TED-GC-MS can also be fully automated for comprehensive polymer analysis, enabling rapid and reproducible automated fractionated collection of thermal and thermo-oxidative decomposition products [90]. As MPs in soil samples may require laborious sample pretreatment, a TGA-MS with no sample pretreatment step was developed for PET in soil with $1.61 \pm 0.15\%$ OM content [84]. A TGA coupled to a soil universal model method (SUMM) to identify and quantify PET, PS, and PVC in similar loamy sand soil was also developed. Although it required no sample pretreatment or other detection technique, the SUMM failed to determine PE, potentially due to similarity in degradation temperature between PE and SOM [87]. Additionally, the robustness of the TGA-MS and TGA-SUMM method when applied to samples with high SOM needs to be evaluated and may require minimal sample preparation for soils with high SOM [84,87]. A TGA combined with FTIR was developed. The TGA pyrolyzes the samples and the FTIR analyzes the pyrolysis gas products. To quantify individual polymers, standards are used and calibrated on characteristic IR peaks at a specific decomposition temperature. The TGA-FTIR method demonstrated that it could measure the total mass of PVC, PS, and PA, identify and quantify PVC and PS, and its operation is simple and cost-effective. However, preconcentration of the soil samples is needed to reach the detection limit, and it cannot determine the particle size and shape [91].

3.3. Liquid chromatography

Liquid chromatography (LC) systems are used to analyze MPs in soil. Such a method included soil sample extraction with size-exclusion

chromatography (SEC) followed by FTIR for the identification and reversed-phase LC with UV detection (RP-LC-UV) for the quantification of PS and PET in soil samples [85]. THF and hexafluoroisopropanol (HFIP) were added to the soil reference material to extract PS and PET, respectively. The soil extracts were analyzed by RP-LC with recoveries of > 99% and about 80% for PS and PET, respectively. Another method to analyze PET in soil was the use of alkaline extraction, followed by determining terephthalic acid (monomer of PET) using LC-UV [86] (Table 2). The method required minimal sample preparation and achieved a LOD of 1.55 mg kg^{-1} and a LOQ of 6.05 mg kg^{-1} , based on a calibration of spiked PET in a reference soil matrix [86]. Applying fast separation and quantification methods such as SEC and LC-UV to analyze MPs in soil allows the use of calibration curves to quantify polymers and assess the amount of MPs in tested samples based on mass content [85,86]. The practicality of LC-UV is that it is often available in routine laboratories, it is a fast and simple method, easy to automate, has a relatively low detection limit, and the data evaluation does not require high user knowledge [86].

3.4. Additional innovations

In recent years, several analytical methods have been developed by combining techniques to provide fast analysis of MPs in soil samples. Such methods include hyperspectral imaging technology combined with chemometrics [92], visible-near infrared (vis-NIR) spectroscopy with a multilinear model [93], NIR spectroscopy (NIRS) combined with chemometrics [94], vis-NIR spectroscopy with a convolutional neural network (CNN) model [95], resonance microwave spectroscopy with a mathematical model [96], and terahertz (THz) spectroscopy with a Least Squares-Support Vector Machine (LS-SVM) model [97] (Table 2). Three studies combined NIR spectroscopy with a chemometric approach for MPs analysis in soil to detect the presence of MPs rapidly, in-situ [93–95]. Using NIRS with a partial least squares discriminant (PLS-DA) approach, several polymers (PE, PP, PS, PVC, and PET) were detected at levels above 0.5–1.0 mass% [94]. The vis-NIR spectroscopy with a CNN model method presented a rapid screening method to determine the level of MPs (PET and LDPE) contamination in soil with an accuracy of 69.3% [95]. In contrast, the Vis-NIR spectroscopy method with a trained multilinear model was able to identify and quantify various MP polymers (PET, LDPE, and PVC) in soil samples at hotspots [93]. These methods are limited to the current spectral library, reducing the model's accuracy, and the vis-NIR spectra vary with different soils. Another in-situ method included hyperspectral imaging technology combined with chemometrics to identify and determine MPs (0.5–5 mm) on the soil surface. The support vector machine (SVM) algorithm achieved the best results for detecting and correctly classifying black and white PE MPs with different sizes [92]. Recently, a different in-situ method was examined to detect and quantify MPs (50 μm –0.5 mm) in soil using resonance microwave spectroscopy. It is based on the permittivity contrast between uncontaminated soil and the MP particles. The mathematical model expresses the MPs concentration in the soil as a linear function of the measured S_{11} resonance frequency shift and relative permittivity. The best achievable level of contaminant resolution, lower than 100 ppm, is dependent on the sensitivity of the microwave receiver and the sensor probe Q-factor [96]. A method using THz spectroscopy with a LS-SVM local model was developed to rapidly predict MPs (LDPE and PVC) concentrations in soil. The local model is limited to predicting the degree of MPs pollution in the corresponding

region and is not yet universally stable. For quantifying MPs in different soils over a large area, the LS-SVM multivariate fusion model based on THz spectral data is efficient, providing high prediction accuracy and universal [97]. Additionally, time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been applied to determine MPs (<35- and <25 μm) rapidly in environmental soil while simultaneously obtaining MS and imaging information [60,61] (Table 2). TOF-SIMS analyzes sample surfaces and can provide high molecular specificity and imaging capability. However, these TOF-SIMS methods are qualitative, providing only the polymer type and size [60,61]. Ultimately, many innovations are in some stage of development, opening up this field of research and to advance the characterization and quantification of polymers in soil, each method with its own advantages and disadvantages.

3.5. Comparison of state-of-the-art methods to emerging techniques

State-of-the-art MPs detection methods, mainly visual sorting, microscopy assisted, SEM, FTIR, and Raman (micro)spectroscopy, provide reliable detection and identification, applicable with high accuracy in environmental samples [85]. These techniques, for which only small sample amounts are required (up to 1–2 mg), provide information on size, number, and degree of aging, and are non-destructive. However, they require extensive sample pretreatment to remove environmental matrix interferences. The aging conditions can impact MPs polymer analysis [85,101]. These complex methods are not (yet) suitable for large-scale sample analyses [97]. After sample pretreatment, the visual counting with an optical microscope allows quantification of MP particle numbers, reporting in units of, e.g., particles/kg [101]. FTIR or Raman combined with optical microscopy (micro-FTIR or -Raman) provides detailed visual microscopic information for quantification and chemical identification [101]. Thermal analysis techniques, mainly Py-GC-MS [74,83], TGA-MS [84], TGA-SUMM [87], TED-GC-MS [78,85,86,94], and TGA-FTIR [91] require simple or no sample pretreatment, provide simple, fast, and easy analysis, are independent on MPs size and shape and can be a fully automated system [78,84,90,102]. However, the methods are destructive, quantify based on the mass fractions of the polymers per sample and cannot provide direct information on the number of particles and particle morphology [85]. Similar to thermal analysis techniques, most of the emerging techniques do not allow the identification of MPs particle size or shape except imaging techniques, i.e., TOF-SIMS [60,61] and hyperspectral imaging technology combined with chemometrics [92]. TOF-SIMS can rapidly provide information on the size distribution and chemical identification of MPs [60,61] and the hyperspectral imaging method can directly determine and visualize MPs with particle sizes (0.5–5 mm) in soil [92]. However, they are less suited to quantify the amount of MPs particles in the soil. To obtain information on particle size, samples can be pre-sieved or pre-filtered [85]. Other emerging techniques providing quantification based on mass are LC-UV (mg/kg) [86], Vis-NIR spectroscopy combined with a multilinear model (g/kg) [93], and resonance microwave spectroscopy combined with a mathematical model (ppm) [96]. From the emerging techniques, two methods can detect and quantify MPs in soil but not identify the MPs polymer types, i.e., resonance microwave spectroscopy and THz spectroscopy combined with an LS-SVM model method [97]. The (Vis)-NIR spectroscopy-chemometric methods, hyperspectral imaging, resonance microwave spectroscopy and THz spectroscopy provided rapid and in-situ identification or detection of MPs in soil, required no sample preparation, and are non-destructive methods. The state-of-the-art methods are still widely used to analyze MPs in environmental soil (Table S5). As the emerging techniques are still in development, spiked standard loamy soil or environmental soil were commonly applied (Table 2). In Table 3, the state-of-the-art methods and characteristics of the emerging techniques are classified based on their ability to quantify MPs particles (1) and in which unit (2), identify MPs polymers (3), identify in-situ (4), the necessity of sample preparation and the related difficulty (5), analyze MPs particle sizes (6) or shapes (7), and whether

the method is destructive or applied on real environmental soil. The results of methods determining particle numbers or providing a detailed description of MPs (particle size and shape, state of degradation) are not comparable with the simple, rapid methods determining mass content [86]. For extensive detection and quantification of MPs in soil, one method only may not be sufficient to provide a comprehensive data set [85]. In the end, to successfully analyze MPs in soil, the choice of various technologies relies on the different research objectives and may need to apply multiple technologies to provide a complete detection of MPs [35, 85]. The identification and quantification of MPs in soil samples remains challenging. Thus, improving and further developing more robust and efficient analytical techniques focused on the rapid analysis of MPs in complex and organic-rich matrices such as soils is strongly recommended.

4. Method validation, quality assurance, and quality control

For sampling, processing, and analyzing MPs, QA/QC procedures are required (e.g., procedure blanks, dust-free laboratory, avoiding the use of plastic materials and synthetic clothes) to monitor and minimize contamination risks and ensure accurate study results [34]. Most studies used glass or metal materials for sampling, processing, and analysis [46, 103]. The materials were rinsed before use, with Milli-Q-, distilled-, deionized- or ultrapure water [42,44,50,104]. Reagents were often filtered through membranes, and samples and materials were covered by aluminum foil or glass lids to avoid airborne contamination [57,105]. Cotton coats (100%) and nitrile gloves (e.g., with a distinct color) were worn in the laboratory to prevent contamination or recognize potential contamination [54,55]. The background concentrations may also limit the quantification regarding the sensitivity of the detection system [74]. Therefore, procedural blank samples (without soil and absence of MPs, mainly solvents, and materials) are performed parallel to the analysis as negative controls [47,71]. When significant, the results are corrected by subtracting the background values. To test the reagent quality and airborne contamination in the laboratory, reagent blank filters were saved in a Petri dish and inspected at the end of the analysis [49]. In addition, positive controls (spiked matrix samples) were performed using relatively clean soils [43,54,62,103,105]. For instance, a study used six soil samples, spiked each with 15 particles (fragment, foams, fiber, five each) sized 1–5 mm, and achieved average recoveries ranging from 85% to 95% [56]. Another study conducted a recovery test for five polymers (PE, PVC, PP, PS, and PA), sizes 500 μm –2 mm, by spiking 30 particles of each into relatively clean soil, after MPs extraction and counting by stereomicroscope, the average recovery ranged from 76% to 112% [20]. In contrast, recoveries as low as 49% for acrylic were observed and above 77% for PA, PVC, PES, and LDPE (about 98%) [15]. The recovery experiments and values varied among the reviewed studies. Table S7 summarizes the recovery tests and the QA/QC procedures applied. While several studies mentioned QA/QC measurements, there is no uniform protocol or unique standard for contamination prevention on MP analysis. It would be beneficial to compare validation studies and QA/QC protocol to improve the MP analysis [101,106]. Besides sample contamination reduction and monitoring actions, other QA/QC requirements for analyzing MPs in soil research are lacking, such as the limited availability of certified reference materials and labeled standards. In order to obtain reliable results, comprehensive procedural validations and interlaboratory studies for sampling, sample treatment, and analysis need to be implemented [10, 23]. For the validation processes, a standard procedure is necessary for spiking small MP particles including MPs with different polymer types, sizes, forms, and different weathering stages (e.g., old or in perfect condition). Extra precautions must be taken spiking using small MPs since they tend to adhere to surfaces of materials used to collect and process samples [23]. In addition, there is a high need of labeled standards of different polymer types and chemical groups (with and without absorbed and additive chemicals) that come available as certified

Table 3
Comparison of state-of-the-art methods to emerging techniques for the analysis of MPs in soil.

	(1) Quantification	(2) Quantification unit	(3) Identification	(4) In-situ identification	(5) Sample pretreatment	(6) Analyzable particle size	(7) Analyzable particle shape	(8) Destructiveness	(9) Applicability on soil
	+ : Quantifies MPs particles in soil.-: Cannot quantify MPs particles in soil.	x: MPs count (e.g., particles per kg).* : Based on mass (e.g., g/kg, ppm, or wt%). NA: not applicable.	+ : Detects and identifies particle polymer type.-: Cannot identify the particle polymer type, only detect MPs.	+ : In-situ applicable.-: Not in-situ applicable.	-: Does not require sample pretreatment.+ : Requires simple sample pretreatment.+ +: Requires laborious sample pretreatment.	+ : Can identify MPs particle size.-: Cannot identify MPs particle size.	+ : Can identify MPs particle shape.-: Cannot identify MPs particle shape.	+ : Method is nondestructive.-: Method is destructive.	+ : Applied on real environmental soil sample.-: Applied on standard soil type.
State-of-the-art-techniques									
Microscope-assisted	+	x	-	-	++	+	+	+	+
FTIR	+	x	+	-	++	-	-	+	+
FTIR microspectroscopy	+	x	+	-	++	+	+	+	+
Raman	+	x	+	-	++	-	-	+	+
Raman microspectroscopy	+	x	+	-	++	+	+	+	+
Emerging techniques									
Py-GC-MS	+	*	+	-	+	-	-	-	+
TED-GC-MS	+	*	+	-	-	-	-	-	+
TGA-MS	+	*	+	-	+	-	-	-	-
TGA-SUMM	+	*	+	-	-	-	-	-	-
TGA-FTIR	+	*	+	-	+	-	-	-	+
LC-UV	+	*	+	-	+	-	-	+	+
TOF-SIMS	-	NA	+	-	-	+	-	-	+
Hyperspectral imaging technology	-	NA	+	+	-	+	-	+	+
-chemometrics									
NIRS - chemometrics	-	NA	+	+	-	-	-	+	-
Vis-NIR spectroscopy-Multilinear model	+	*	+	+	-	-	-	+	+
Vis-NIR spectroscopy-CNN model	-	NA	+	+	-	-	-	+	+
Resonance microwave spectroscopy-mathematical model	+	*	-	+	-	-	-	+	+
THz spectroscopy- LS-SVM model	-	NA	-	+	-	-	-	+	+

reference materials. These certified reference materials with known concentrations of target MPs are needed to improve the accuracy and validity of the analytical data [107]. Due to the lack of optimized and validated analytical methods for quantification of MPs in soil, there is an increased risk of contamination, underestimation, and overestimation of MP concentration, while the combination of validation studies (including procedural and spiked blank samples) are essential for assessing the method's reliability and validity [101,107]. To date, interlaboratory comparison studies focused mainly on other matrices than soil. A study conducted with 12 participating laboratories using seawater samples ($n = 2$) with added polymers in the size ranges of 400–1000 μm , determined only the particles number only without polymer identification [108]. MPs numbers varied among size classes with a standard deviation (SD) of $\pm 50\%$ [108]. Another study with 17 participating laboratories using ultrapure water samples ($n = 2$) with added polymers limited to size ranges of 8–140 μm observed large variances [109]. In both studies, a discrepancy in results was observed among the laboratories. Recently, a global interlaboratory study on MPs was conducted with 34 participating laboratories using 'standard' like test materials (pellets and tablets, $n = 12$) with added polymer particles in the size ranges of 150–300 μm and 2000–4000 μm [110]. Among the majority of the laboratories (53–100%), the polymer types were correctly identified, the reported weight had a relative standard deviation (RSD) ranging from 7% to 33%, and the reported particle quantity varied greatly (29–91%) among the laboratories [110]. The large differences observed between the laboratories results and those that

applied the same method highlight the complexity of analyzing small MPs, indicating an urgent need for comparability among reporting results, analytical methods, and validation of analytical processes. There is also an urgent need to continue with interlaboratory studies on MPs in soil materials.

5. Characterization and occurrence of MPs in soil

5.1. Polymer type

Identification of the polymer types is crucial to identify the source of MP pollution. The most common polymers reported (Table S5) of MPs in soil samples were PE, PP, PET, PS, PVC, and PA (Fig. 2). Three polymer types (PE, PP, and PET) were most common in the soils and compost, as they are often used in packaging materials, plastic mulching, and textiles [45,58,69,111]. Studies of soil samples of continuous mulching indicated that PE MPs were oxidized and degraded over time as the years increased [46]. PES/PET is widely used in plastic bottles. It was present in high abundance (57%) in the control soil and also in soils fertilized with pig manure (39%) [43]. Polymers linked to synthetic fibers (PA) and films from agricultural sources (PVC) dominated a considerable proportion in soils, 28–33% for PA [42,60,61], and 40% for PVC [16], and 80% for PVC [73]. Other less common polymers found included PS, PMMA or acrylic, Rayon, and synthetic rubbers [20,40,43,62,67].

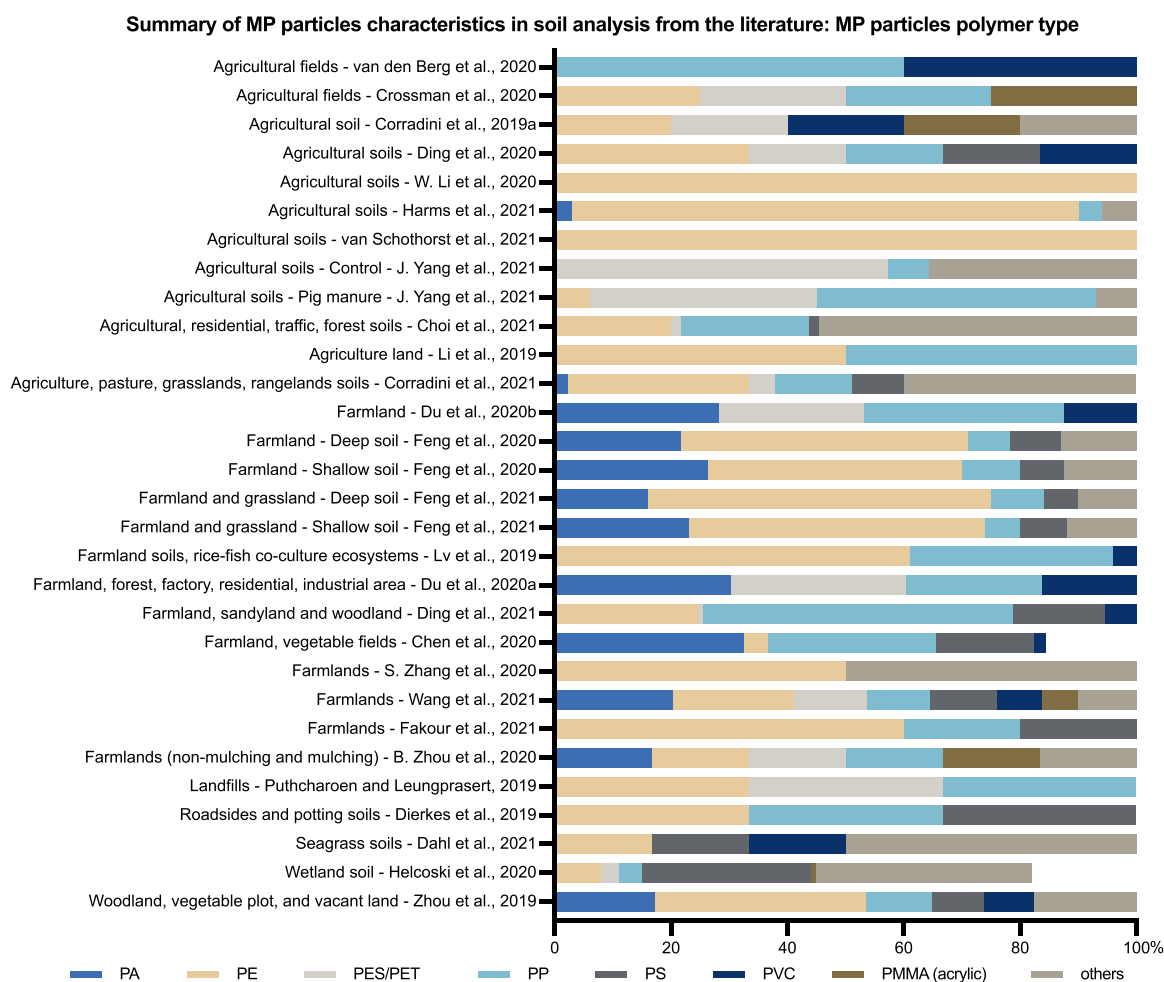


Fig. 2. Summary of MP polymer type particles (PA, PE, PES/PET, PP, PS, PVC, PMMA, and others) in soil from the literature (Table S5) corresponding to their soil source(s)/type(s) (y-axis).

5.2. Size

Generally, the MPs size is defined as plastic particles smaller than 5 mm [11]. However, the minimum particle size is determined by the sieve mesh size used after sampling, during sample pretreatment, and the membrane pore size of the filters used (Table S5). Thus, the reported size fractions varied widely across studies (Fig. 3). The majority of the studies observed small particle sizes (smaller than 1 mm) in soil environments with minimal detected MPs size of $< 5 \mu\text{m}$ [60,61]. One study reported the MPs particle size as particle area of $0.076 \pm 0.292 \text{ mm}^2$ and observed MPs fibers as small as $300 \mu\text{m}$ [49]. No difference in the size distribution of MP particles in soils between suburban roads and residential areas was observed, indicating that the locations of sampling sites is less relevant [42]. In contrast, one study observed a correlation between land use and MPs size, but the correlation decreased with decreasing particle size and the smaller size fractions of MPs in soil could be related to human and environmental factors [47]. Small-sized MPs have a larger surface area for the adsorption of chemicals and are more likely to be eaten or transported through an organism's body, making them more harmful [112,113].

5.3. Shape

The shape of MPs in soil was reported in 24 studies (Table S5). The most common shapes observed are fibers, fragments, films, and foams (Fig. 4). Fibers and fragments were the dominant shapes, followed by films. Fibers were dominantly ($>90\%$) found in agricultural and farm

soils and were related to the application of sewage sludge on the land or irrigation with wastewater [15,52], while in another sewage sludge application study, the majority ($>80\%$) of the MPs present were fragments [16]. Fragments were also mainly concentrated in mulch and farmland soils, tracing them back to plastic waste decomposition by UV radiation and weathering, agrochemical-containing bottles, and plastic package bags [20,48,71]. Films present in soil have been linked to plastic mulching and plastic packaging, where the film was dominant in greenhouse and mulching film lands [44,57,111].

5.4. Abundance

In general, the abundance of MPs in soils varied significantly between different land uses, soil types, and locations, with sources consisting of inputs of anthropological activities, littering, atmospheric deposition, plastic mulching, compost, sewage sludge, irrigation, and street runoff [21,106]. The occurrence of MPs in soils reported in studies published from 2016 to 2018 and 2019–2021 are summarized in Tables S5 and S6, respectively. The most frequently used abundance units were items per kg ($n = 14$), particles per kg ($n = 6$), MPs per kg ($n = 5$), and pieces per kg ($n = 5$). However, this review assumes they are the same unit (MPs per kg) and are therefore comparable (Fig. 5). Other abundance units were particles per gram, particles concentration per kg, items/ m^2 , mg/kg, and mg/g (Fig. 6). A wide range of MP concentrations, five orders of magnitude, has been reported, and no correlation was found with the different soil sources or soil types. Most MPs studies focus on China as China leads the world in plastic production,

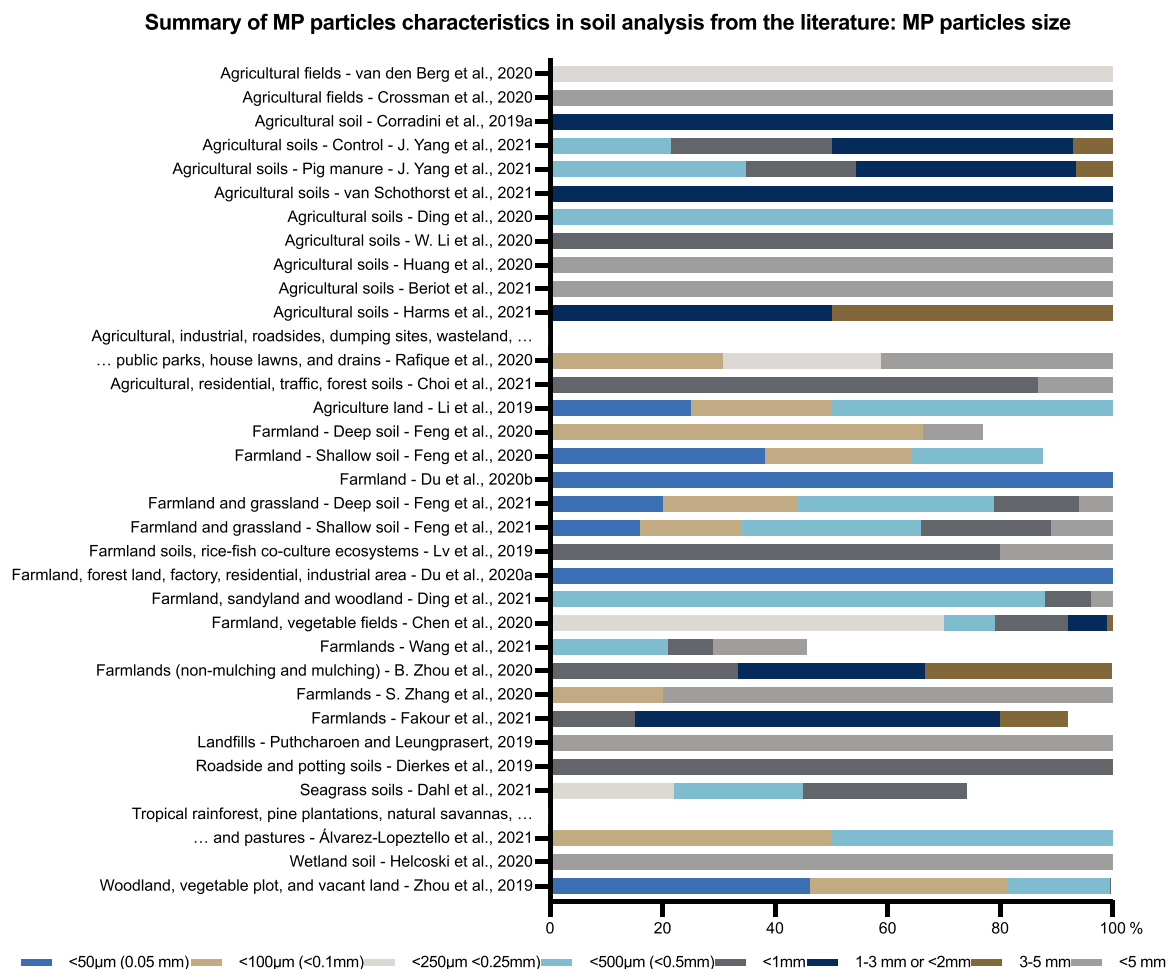


Fig. 3. Summary of MP particles size (<0.05 -, <0.1 -, <0.25 -, <0.5 -, <1 -, 1-3- or <2 -, 3-5-, and <5 -mm) in soil from the literature (Table S5) corresponding to their soil source(s)/type(s) (y-axis).

Summary of MP particles characteristics in soil analysis from the literature: MP particles shape

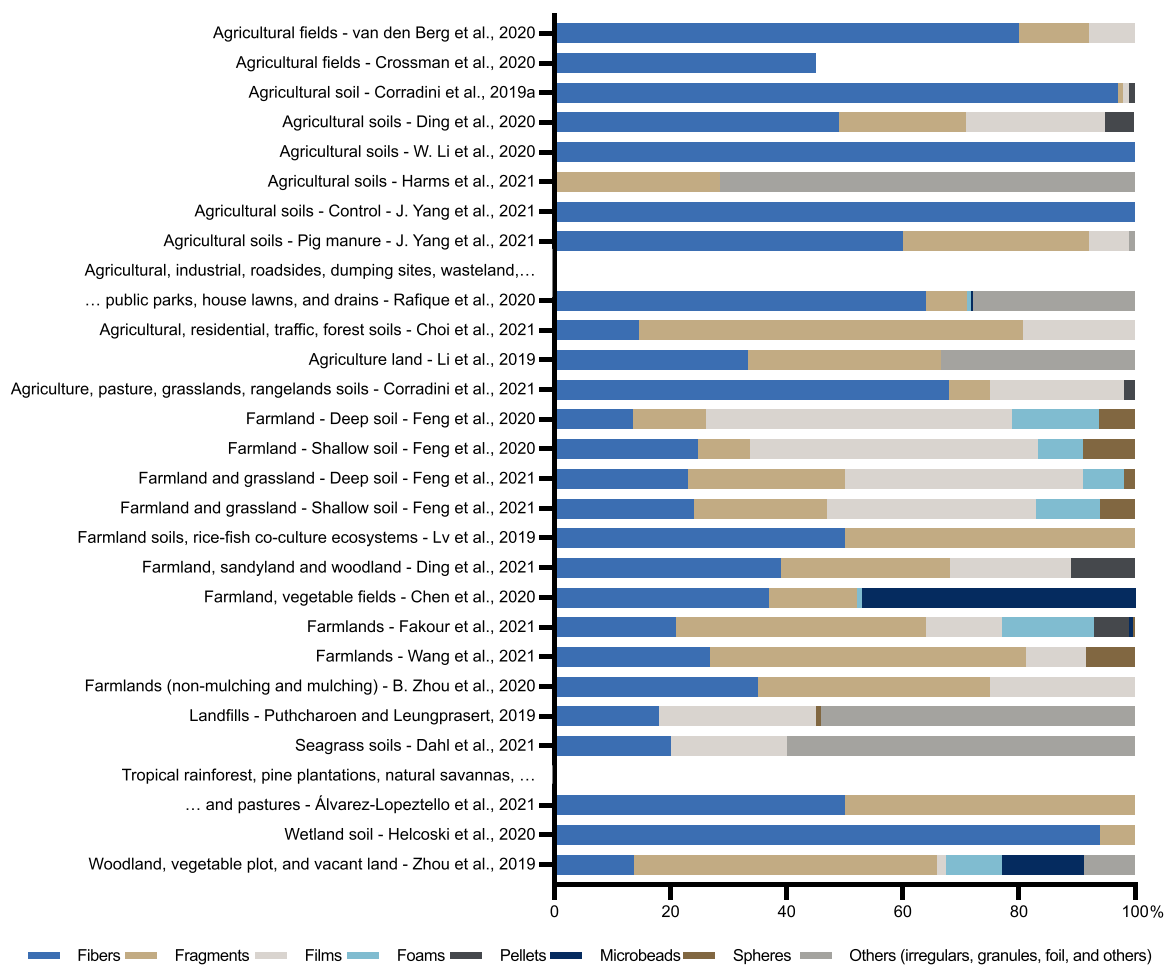


Fig. 4. Summary of MP particles shape (fibers, fragments, films, foams, pellets, microbeads, spheres, and others) in soil from the literature (Table S5) corresponding to their soil source(s)/type(s) (y-axis).

accounting for 31% of the total plastic production [1]. The abundance of MPs in different soils across China varied between 10.3 and 6.9×10^5 MPs per kg (Fig. S1). The abundance of MPs in woodland, vegetable plots, and vacant land in central China ranged from 2.2×10^4 to 6.9×10^5 particles per kg. It also showed that MP particles in soils contained different levels of heavy metals, and the heavy metal content in MP particles may be related to the MP abundance [71]. Several studies demonstrated that MPs in shallow soils of farmlands and grassland had a higher abundance than deep soils [44,57,114]. Mulching cropped soils contained higher MPs than non-mulching cropped soils, yet several other sources also contribute to the abundance of MPs in these soils [20]. Another study demonstrated that the abundance of MPs increased over time (5, 15, and 24 years) in hotspots where plastic mulching was continuously utilized [103]. Long-term application of pig manure to fertilize agricultural soils also contributed to MPs accumulation, with an average estimated concentration of 1.25 ± 0.61 particles kg^{-1} annually [43]. Apart from China, MPs in soil have been seldom reported in other countries and regions (Figs. 5 and 6). However, it still demonstrates the global pollution of MPs in soil and indicates a need for more comprehensive data on soil MPs.

6. Conclusions and future perspectives

The research on MPs in soil is still in its initial stage, lacking a standardized method for sampling, contamination prevention, validation, and reproducible analytical methods for analyzing MPs in

environmental soil. It is predicted that MPs distribution in the soil will grow due to the extensive use of plastic and increases global use with the lack of proper waste control. Therefore, being well informed on current methods, occurrence data, and interlaboratory studies is beneficial to predict and accurately evaluate the impact of MPs on the environment and human health in future research. This review article comprehensively summarizes the emerging techniques and state-of-the-art methods for extracting and analyzing MPs in soil (Tables 1, 2, S5, and S6), and presents the developments and differences. It presents differentiation between these methods (Table 3). An overview on the global occurrence, abundance, and characterization of MPs in environmental soil is shown (Table S5 and S6 and Figs. 2–6, S1). Among the reviewed studies, a wide range of MP concentrations (up to 6.9×10^5 MPs per kg) was reported. The polymer types (PE, PP, and PET), particle sizes (<1 mm), and shapes (fibers and fragments) were reported as most dominantly present in soil of different land uses. The available global monitoring data and knowledge on MPs in soil is still limited, and mainly data for China are available. Overall, the choice of analytical technique depends on the research objectives which implies that multiple techniques might be necessary to achieve a comprehensive set of data for MPs in soil [85]. If polymer type is of interest, a spectroscopic, a mass spectrometric method, a chromatographic (e.g., LC-UV), or a thermal technique is suggested, as microscopy or SEM cannot identify the particle polymer type. Microscopy is suitable for visually counting MP particles [109]. Mass-based analytical methods (e.g., Py-GC-MS, TED-GC-MS, TGA-MS) are time efficient, provide fast identification and quantification of MPs

Summary of MP particles occurrence in soil analysis from the literature: MP particles abundance

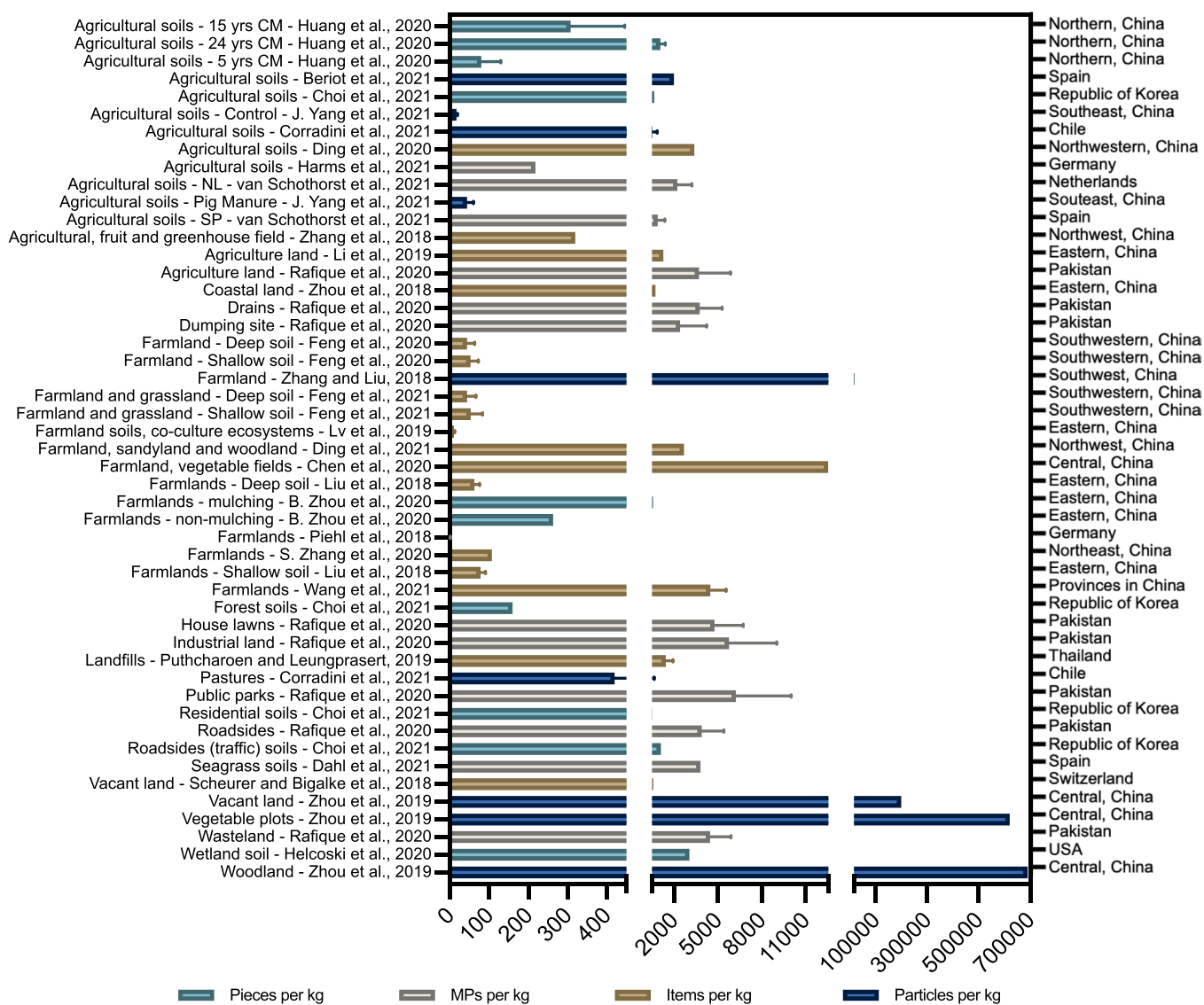


Fig. 5. Summary of MP particles abundance (given in particle per kg, items per kg, MPs per kg, and pieces per kg) in soil from the literature (Tables S5 and S6), corresponding to their soil source(s)/type(s) (left y-axis) or location (right y-axis).

in soil samples, but cannot provide particle numbers or information on particle morphology [101]. Spectroscopic methods (e.g., FTIR and Raman) provide detailed analysis of individual particles (i.e., MPs size, shape, degree of aging), requiring more time per measurement and requiring extensive sample pretreatment [85,109]. In the last years, the density separation and OM digestion methods have been improved. However, further developments are necessary to achieve high extraction and separation efficiency without affecting the MPs and throughput. Developing techniques (e.g., hyperspectral imaging, (vis-)NIR spectroscopy, resonance microwave spectroscopy, and THz spectroscopy) have the potential to rapidly (in-situ) detect, identify or quantify MPs in soil samples and can be applied in the future for MPs analysis [92–97]. The identified knowledge gaps are related to method validation using certified reference materials, QA/QC procedures, and comparability in applying analytical methods and reporting the results.

For a better understanding of the occurrence, analysis, distribution, and impacts of MPs in soils, more research is needed and should focus on: (1) establishment of a standardized method for sampling, validation, QA/QC procedures, extracting, identifying, and quantifying MPs in soil,

and reporting of results to improve the comparability of data; (2) establishment of certified reference materials for MPs in soil, certified MP particles standards (with different polymer types, sizes, shape, degree of aging), and labeled polymer standards with and without chemicals (e.g., absorbed and additive chemicals) to improve the accuracy and validity of MPs analytical data; (3) establishment of database libraries of spectral and mass information for the different polymers for instance made with certified standards; (4) organize more and improved interlaboratory studies to indicate variations in measurements reported in the current scientific literature and improve the reproducibility and robustness of the methods; (5) facilitate interstudy comparison by including extensive descriptions of sampling sites, soil properties, and QA/QC procedures; (6) organize large-scale monitoring studies to evaluate the global distribution of MPs in environmental soil; (7) further development of reliable and accurate in-situ techniques for rapid detection of MPs in soil; and (8) develop automated purification protocols to reduce intensive labor, background contamination, and potential errors, and advance to process samples simultaneously.

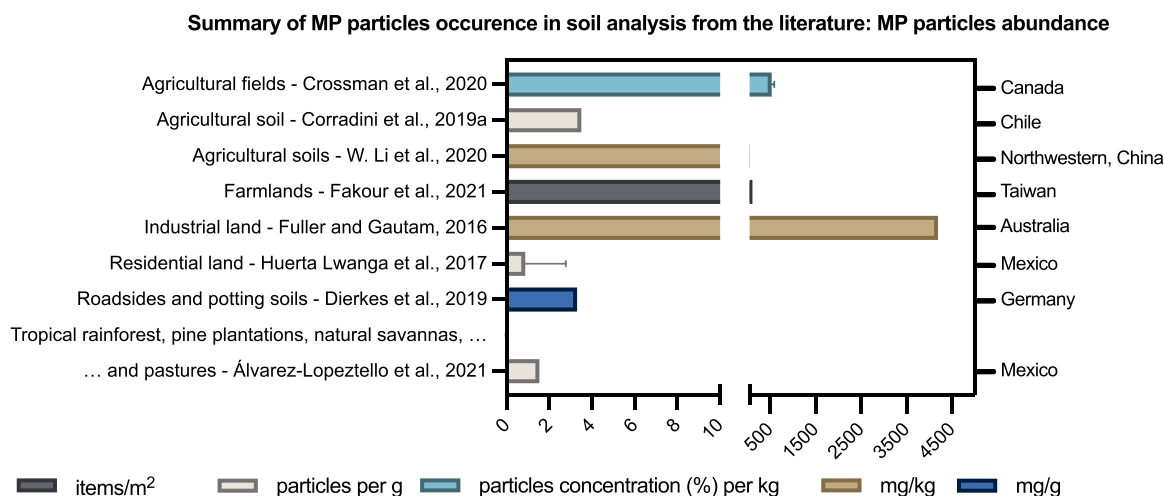


Fig. 6. Summary of MP particles abundance (given in items/m², particles per g, particles concentration (% per kg, mg/kg, and mg/g) in soil analysis from the literature (Tables S5 and S6), corresponding to their soil source(s)/type(s) (left y-axis) or location (right y-axis).

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2022.107421](https://doi.org/10.1016/j.jece.2022.107421).

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