



Extraction and identification methods of microplastics and nanoplastics in agricultural soil: A review

Cao Junhao^{a,b}, Zhao Xining^{b,c,**}, Gao Xiaodong^{b,c,*}, Zhang Li^{a,b}, Hu Qi^{a,b}, Kadambot H. M. Siddique^d

^a College of Water Resources and Architectural Engineering, Northwest A&F University, 712100 Yangling, China

^b Key Laboratory of Agricultural Soil and Water Engineering in Arid and Semiarid Areas, Ministry of Education, Northwest A&F University, 712100 Yangling, China

^c Institute of Soil and Water Conservation, Chinese Academy of Sciences and Ministry of Water Resources, 712100 Yangling, China

^d The UWA Institute of Agriculture and School of Agriculture & Environment, The University of Western Australia, Perth, WA, 6001, Australia

ARTICLE INFO

Keywords:

Microplastics
Nanoplastics
Soil health
Extraction
Identification

ABSTRACT

As the abundance of microplastics and nanoplastics (MPs/NPs) increases in the environment, their presence in agricultural soil has become of interest. MPs/NPs can affect soil physical and chemical properties and be absorbed by plants and soil animals, causing physical and chemical damage. Soil MPs exceeding a certain concentration cause significant harm. Therefore, the extraction and identification of MPs in soil are vital for determining soil pollution. However, soils contain many other particles of similar size to MPs/NPs, making it more difficult to distinguish them than in water bodies. No standardized extraction and identification method is available to quantify MPs/NPs in soil. Various methods have been described in the literature, but they involve many different procedures for sampling, purification, digestion, and identification. This paper reviews extraction and identification methods for MPs/NPs in soil, sediment, and water and summarizes agricultural soil sampling and preservation, MPs/NPs separation, organic matter removal, and MPs/NPs identification. We also compare the advantages and disadvantages of existing methods and propose future research topics.

1. Introduction

Plastics are widely used in industrial and agricultural production and daily life due to their excellent performance and low cost (Fred-Ahmadu et al., 2020). It is estimated that 33 billion tons of plastics will have been produced by 2050 (Sharma et al., 2020). A small proportion (6–26%) of waste plastic is recycled, with the remainder ending up in the environment (Plastics Europe, 2018). Two main sources of microplastics (MPs) occur in farmland (Eerkes-Medrano et al., 2015): (1) primary microplastics (such as industrial abrasives, cosmetics, leather goods, and shampoo) (Andrady, 2011; Browne et al., 2011; Cole et al., 2011) enter farmland through sewage irrigation, composting, wind, etc. (Huang et al., 2020); (2) secondary microplastics are formed from macroscopic fragments originating from mechanical, oxidative, and photochemical processes (Browne et al., 2007; Zhao et al., 2015) when agricultural plastics (such as plastic films, fertilizer bags, and drip irrigation pipes) enter farmland (Huang et al., 2020; Van den Berg et al., 2020; Wang

et al., 2020a; Zhang et al., 2020). Once in the farmland, these MPs are difficult to recycle and remain in the soil for a long time.

MPs are defined as plastic fragments with diameters (d) less than 5 mm (Arthur et al., 2009; Elkhatib and Oyanedel-Craver, 2020). However, some researchers believe that MPs should include NPs (Wallace, 2016), while others believe that MPs do not include NPs (Frias and Nash, 2019). In this paper, we suppose that MPs include NPs. The upper size limits of NPs are controversial. Some authors want the upper size limit for NPs defined as 1000 nm (Cole and Galloway, 2015; Da Costa et al., 2016; Gigault et al., 2018), while others prefer 100 nm (He et al., 2018a; Nguyen et al., 2019). For this study, the upper limit of NPs is 1000 nm because 200 nm plastics can be absorbed by plants (Li et al., 2020).

Research on MPs in the sea began in the early 1970s (Colton et al., 1974) but for soils, the first article was published in 2012 (Rillig, 2012), with most studies after 2016 (Helmberger et al., 2020). Despite the relatively recent research into MPs in soil, more MPs are in soil than the sea (He et al., 2018a; Rezanian et al., 2018). Residual MPs in soil can

* Corresponding author. Institute of Soil and Water Conservation, Chinese Academy of Sciences and Ministry of Water Resources, 712100 Yangling, China.

** Corresponding author. Key Laboratory of Agricultural Soil and Water Engineering in Arid and Semiarid Areas, Ministry of Education, Northwest A&F University, 712100 Yangling, China.

E-mail addresses: xiningz@aliyun.com (Z. Xining), gao_xiaodong@nwfau.edu.cn (G. Xiaodong).

<https://doi.org/10.1016/j.jenvman.2021.112997>

Received 18 February 2021; Received in revised form 25 May 2021; Accepted 1 June 2021

Available online 7 June 2021

0301-4797/© 2021 Elsevier Ltd. All rights reserved.

change soil pH (Wang et al., 2020a, 2020b), electrical conductivity, and organic matter and nutrient availability (Gong and Xie, 2020), increase soil porosity, decrease soil water holding capacity (Zhang et al., 2019a), and accelerate water evaporation (Wan et al., 2019). MPs in soil prevent downward water movement, resulting in water wastage (Cao et al., 2020). Due to their high specific surface area, MPs can adsorb toxic substances such as pesticides and heavy metals in farmland (Lan et al., 2021). MPs in soil have affected the growth of wheat, corn, cotton, and other plants (Qi et al., 2018). Moreover, the substances used to enhance plastic flexibility, expansibility, and workability release toxins into soil, causing soil pollution (Chen et al., 2013; Van Wezel et al., 2000).

MPs are ingested by animals and transferred to higher levels of the food chain, a common occurrence in marine systems (Carbery et al., 2018). MPs in soil adversely affect earthworms, springtails, enchytraeid worms, isopods, oribatid mites, snails, and microbial communities (Baeza et al., 2020; Von Moos et al., 2012). Round worm (*Caenorhabditis elegans*) can absorb MPs, accumulating in their intestines, causing a series of adverse effects (Lei et al., 2018). Laboratory tests also confirmed that MPs are absorbed by wheat and lettuce roots and transported upward (Li et al., 2020). *Murraya exotica* plants can also uptake MPs, which are mainly transported in intercellular spaces (Zhang et al., 2019b). If MPs in soil are small enough, they could be absorbed by soil invertebrates and plants, pass up through the food chain, and end up on people's tables, but this needs further research.

MPs are ubiquitous in the natural environment (Dioses-Salinas et al., 2020). To understand how MPs harm agricultural environments, they need to be sampled and analyzed from agricultural soil. However, there is no agreed standard for the extraction and identification of MPs/NPs. Indeed, there are few extraction and identification processes for MPs/NPs in agricultural soil, relative to those available in water. This paper summarizes the available methods for extracting and identifying MPs in soil and sediment and draws on the methods used in water bodies. It also presents a set of procedures for extracting and identifying MPs/NPs in agricultural soil (Fig. 1).

2. Soil sampling and pretreatment

Due to the heterogeneity and complexity of soil and the large range of MPs particle sizes, it is important to formulate appropriate sampling methods, based on the sampling purpose, to ensure sample representativeness and improve the accuracy of follow-up analysis (Möller et al., 2020; Wagner et al., 2001). The size of the sampling area depends on the objectives of the survey, while the sample size is determined by the variability of survey parameters (Schleuss and Muller, 2001). The sampling site, depth, and mass should be determined beforehand, with potential accumulation zones of MPs considered, such as abandoned areas of residual film at the head of the field.

2.1. Sampling sites and sampling points

Sampling techniques include random, systematic, stratified, and composite sampling (Barahona and Iriarte, 2001). The distribution of MPs is irregular in farmland. Random sampling avoids bias and means that each sample has the same chance of selection. Systematic sampling ensures uniform coverage, with sampling points forming a regular pattern. Stratified sampling shows significant differences among different soil layers. Composite sampling involves combining different subsamples into a single composite sample. To increase sampling accuracy, multiple sampling methods can be combined to obtain accurate data and optimize sampling strength (Table 1). Scheurer and Bigalke (2018) combined composite and systematic sampling, taking three composite samples, comprising five subsamples, from each plot along a floodplain line parallel to the river bank. Huang et al. (2020) combined random sampling and composite sampling, using five 1 m × 1 m plots selected from each site and three replicates from each plot to form a large sample. Zhang and Liu (2018) combined stratified, random, and composite sampling, with each sample comprising six subsamples from the 0–5 cm or 5–10 cm soil layers in the same six sampling sites.

The minimum required number (MRN) of sampling points is important when measuring MPs pollution in cultivated soil. Generally, a large number of sampling points improves accuracy. However, the MRN

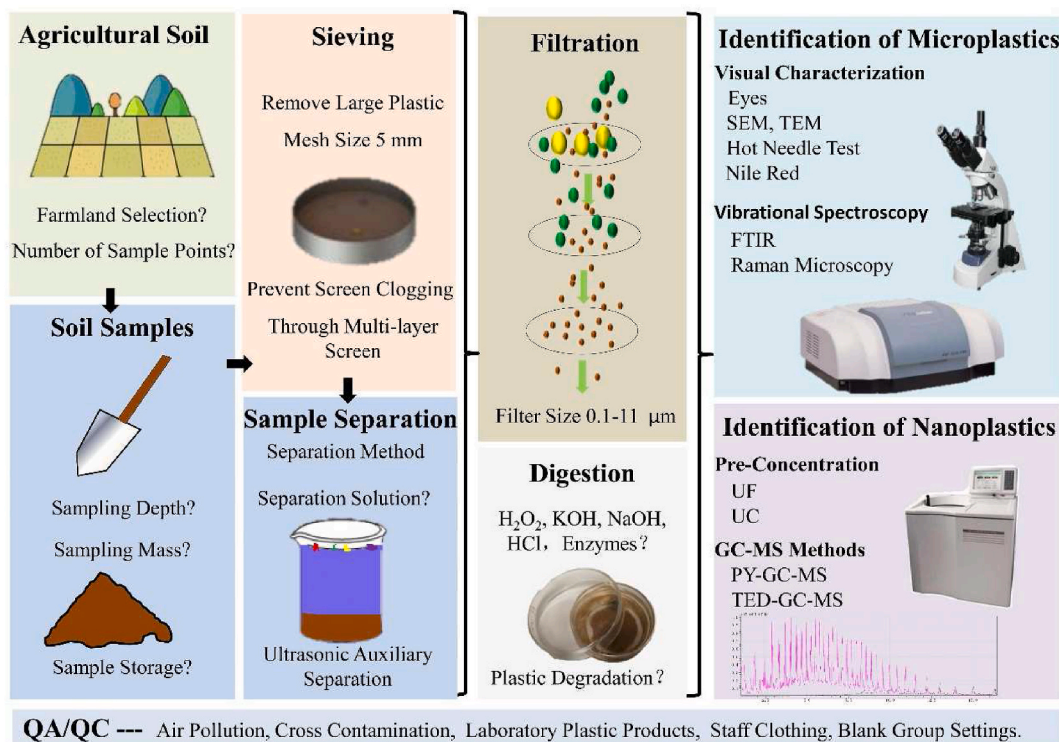


Fig. 1. Review of extraction and identification methods for MPs/NPs in agricultural soil.

Table 1
Comparison of sampling techniques, sites, points and depths in different studies.

Sampling technique	Sampling site	Sampling points	Sampling depths	Reference
Composite and systematic	Flood plain	435	0–5 cm	Scheurer and Bigalke (2018)
Random and composite	Cotton field	384	0–5, 5–20, 20–40 cm	Huang et al. (2020)
Stratified, random, and composite	Cropland and forest buffer	250	0–5, 5–10 cm	Zhang and Liu (2018)
Stratified and random	Abandoned rice paddy field	–	0–10, 10–20 cm	Chen et al. (2020a)
–	Nearshore and offshore zones	–	0–3 cm	Dai et al. (2018)
Stratified	Vegetable farmland	60	0–3, 3–6 cm	Liu et al. (2018)
Random and composite	Vegetable farmland	100	0–5 cm	Chen et al. (2020b)

should be determined according to the type of research being undertaken, the size of the research area, after costs and other factors have been considered (Weber et al., 2020).

2.2. Sampling depth

Since soil is a three-dimensional medium affected by various dynamic issues, including agricultural cultivation, different concentrations of MPs occur at different tillage layer depths (0–40 cm), so it is important to consider sampling depth (Huang et al., 2020). For no-tillage farmland, it is usual to take soil samples from the 0–5 cm layer. For tilled soil, vertical distribution must be considered. Some studies (e.g., Chen et al., 2020a) divided the soil into two layers (0–10 and 5–20 cm), while others (e.g., Huang et al., 2020) divided the soil into three layers for sampling (0–5, 5–20, and 20–40 cm). The sampling depth depends on the plowing depth. While it is believed that no MPs occur below the tillage layer, it is unknown whether they move through the soil. He et al. (2018b) found large plastic particles at depths up to 40 cm in soil tilled to 35 cm depth. Tillage practices are not the only factors that affect the vertical distribution of MPs in farmland. Other factors include runoff, soil erosion, root disturbance, animal transportation, and farmland location (Dioses-Salinas et al., 2020). For example, farmland near highways or factories, with widespread MP sources, had more small-size MPs and subsoil MPs than ordinary farmland (Zhang and Liu, 2018). Therefore, the sampling depth of farmland in certain locations should be increased appropriately. The distribution characteristics of different MPs at depth in farmland soil must be considered carefully.

2.3. Sampling mass and pretreatment

The mass of each sample should exceed that required for MPs quantification. Various studies have used sampling masses ranging from 5 g to 4 kg (Crichton et al., 2017; Dai et al., 2018; Felsing et al., 2018;

Table 2
Quality and pretreatment of microplastic samples for extraction.

Sampling mass	Drying temperature	Storage temperature	Reference
5 g	60 °C	–20 °C	Xu et al. (2020b)
10 g	Room temperature	4 °C	Zhang et al. (2018)
50 g	50 °C	–20 °C	Crichton et al. (2017)
150 g	105 °C	Room temperature	Felsing et al. (2018)
200 g	60 °C	–	Han et al. (2019)
500 g	–	–	Dai et al. (2018)
1 kg	60 °C	Room temperature	Nuelle et al. (2014)
4 kg	105 °C	Room temperature	Zhou et al. (2018)

Han et al., 2019; Nuelle et al., 2014; Xu et al., 2020b; Zhang et al., 2018; Zhou et al., 2018), as shown in Table 2. No definitive minimum amount for a soil sample has been ascertained. After sampling, most samples must be transported and stored before extraction. There is no clear standard for the transportation or storage of samples. In the literature, the choice of transport and storage temperatures appears arbitrary, ranging from –20 °C to room temperature (Crichton et al., 2017; Felsing et al., 2018); however, this may be, in part, because sampled soil in some studies may not be just for MPs analysis. A room temperature study of MPs is cheap and yields reliable results. The literature describes the need to dry samples and the corresponding drying temperatures before extracting MPs. Most researchers stated that soil drying made it easier to separate MPs from the soil and remove large plastic pieces. The recommended drying temperature is moderate to avoid MPs degradation. Air drying of soil is not recommended due to the potential for air pollution. Overall, it is suggested that soil samples are dried at around 60 °C before MPs extraction (Nuelle et al., 2014).

As agricultural soil contains numerous organic and inorganic substances (such as roots and stones), MPs can be mixed with soil aggregates or organic matter, affecting the extraction process. Therefore, before sample purification, particles larger than 5 mm need to be removed with a 5 mm sieve. We suggest using 1 mm screens because plastic larger than 1 mm is visible to the naked eye, and 1–5 mm pieces of plastic sheet will stick together when wet, usually with sand and gravel trapped between them, making them too dense to separate using the density separation method. Fig. 2a shows sand and gravel trapped between 1 and 5 mm pieces of plastic sheet.

2.4. Sample sieving

Sieves are mainly used to remove large particles in soil before MPs extraction. The conventional pretreatment step removes particles larger than 5 mm. In some studies, all soil from a sampling site was sieved to recover MPs of specific sizes. The purpose of the research determines the mesh density of the sieve. Most researchers choose a sieve with a mesh size between 20 and 500 µm (Leslie et al., 2017), made from steel or iron. Sieves can be stacked in several layers to form a sieving gradient, with the mesh density increasing from top to bottom. Some researchers use sieves with five different pore apertures (4.75, 0.85, 0.3, 0.106, 0.02 mm), stacked sequentially (Michielssen et al., 2016). A sieving gradient can prevent sieve blockage and sample loss.

3. Sample purification

To analyze MPs further, they need to be separated from the soil medium without damaging their structure.

3.1. Density separation

The density separation method is the most common method for soil MPs separation. The soil is first treated using ultrasonics (Liu et al., 2018) to ensure that each particle in the bulk sample either sinks or floats, depending on their relative density (Zhang et al., 2018). Sodium chloride is a cheap and environmentally friendly salt (Nuelle et al., 2014), widely used in suspension solutions (Zhou et al., 2018). However, the density of saturated NaCl solution is 1.2 g/cm³, meaning that large density plastics such as polyvinyl chloride (PVC, 1.35 g/cm³), polyethylene terephthalate (PET, 1.38 g/cm³), and other high-density plastics (Ruggero et al., 2020) cannot be separated in this manner. Therefore, many researchers use a saturated solution of zinc chloride (ZnCl₂), sodium iodide (NaI), sodium bromide (NaBr), calcium chloride (CaCl₂), and zinc bromide (ZnBr₂) for the suspension medium (Han et al., 2019; Imhof et al., 2012; Scheurer and Bigalke, 2018). The recycling rate of the high-density separation solution is significantly higher than that of NaCl. The choice of suspension medium should depend on the recovery rate and price and its environmental impact.

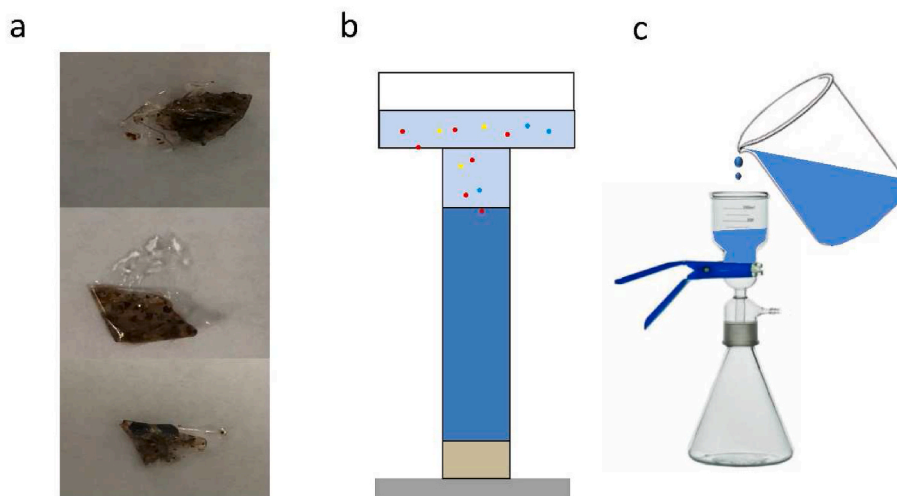


Fig. 2. Extraction process. (a) Sand and gravel trapped inside plastic film; (b) Density separation; (c) Filtering.

Many solutions, such as $ZnCl_2$ and NaI, are not environmentally friendly.

The selected suspension medium is placed in a beaker with the soil. After stirring and sedimentation, the supernatant containing MPs is sucked into another beaker and then transferred into the filtration system (Fig. 2c). In the transfer between filtration system and beakers, or during emptying, MPs can stick to the beaker wall, so smooth, transparent glassware is required for this process.

The original separating method is shown in Fig. 2b; it has since been improved due to the low recovery rate. In 2012, Imhof et al. (2012) developed the Munich Plastic Sediment Separator (MPSS). In 2017, Coppock et al. (2017) and Mahat (2017) improved the MPSS. The MPSS separator comprises three parts: stirring sediment container, standpipe, and dividing chamber with ball valve and filter holder. This device separates the MPs particles from the solution and transfers them directly to the filter. The process does not require repeated emptying and extraction, avoiding extensive MPs loss. Imhof et al. (2012) stated that the MPSS had a 95–100% recovery rate for MPs. Zobkov and Esiukova (2017) reported that the extraction efficiency significantly decreased to 13–39% when extracting MPs, which may be due to difficulties extracting organic matter from MPs. A simple and cheap separation device made by Coppock et al. (2017) had a high recovery rate of 92–98% but was made from PVC, meaning that PVC had to be excluded from the analysis range, as it is a plastic. The bauta separator developed by Mahat (2017) was made from metal and glass, with a suspension medium mixture of $ZnCl_2$ and $CaCl_2$ and recovery rate of 82–100%. The above three separators have not been used to separate MPs in soil, so it is unclear whether they are suitable for that process.

Devices for extracting MPs from soil and sediment have been developed. A two-step method for extracting MPs from sediments (Nuelle et al., 2014) improved the optimized extraction process. Sediments are pre-extracted using the air-induced overflow method, based on fluidization in NaCl solution; then, the sediment mass is reduced to about 80% of its original value and suspended in saturated NaI solution. Claessens et al. (2013) developed a new device, based on ‘Barnett’s fluidized sand bath,’ which uses upward gas and liquid flow to separate lighter particles in the soil from heavier ones, and then used NaI solution for suspension. This device is also made of PVC, meaning it cannot separately identify PVC commonly found in soil (Liu et al., 2019). Both methods can process large sample numbers. The extraction rates of these methods for MPs $>35 \mu m$ are $>90\%$, but their effectiveness for MPs $<35 \mu m$ is not clear. Moreover, these methods are applicable for loose soil; it is unknown whether they can separate MPs in cohesive soil.

3.2. Electrostatic separation

Soil minerals and other particles are electrically conductive, but plastics are not. Using this difference in electrostatic properties, the two can be separated using an external electric field. Electrostatic separation is a dry processing technique for separating primary and secondary raw materials using electric forces acting on charged particles (Deotterl et al., 2000). Felsing et al. (2018) studied the electrostatic behavior of plastic particles, then modified a small electrostatic separation device to improve the separation of MPs from sediment samples. Up to 99% of the original sample mass could be removed without the loss of MPs. This method’s advantage is that it simplifies the treatment and preparation of different field samples and is quick as almost no biological substance remains in the sample fraction after the last step. However, Felsing et al. (2018) tested this device on MPs with particle sizes ranging from $63 \mu m$ to 5 mm; its efficacy for processing smaller MPs or even NPs was not reported.

3.3. Oil separation

A new, cost-efficient oil extraction protocol (OEP) (Crichton et al., 2017) uses the lipophilic properties of MPs as an alternative to density-based oil recovery methods. The OEP had a 90–100% recovery ratio for seven polymers, indicating a higher efficiency than density separation in a salt solution. OEP is simpler, easier, and cheaper than salt solution separation. However, oil interferes with Fourier Transform Infrared Spectroscopy (FTIR) during identification, so washing with 90% ethanol after extraction is necessary.

Mani et al. (2019) recently conducted a study to separate MPs from fluvial suspended surface solids, marine suspended surface solids, marine beach sediments, and agricultural soil substrates using castor oil. In this study, 0.3–1 mm MP particles were separated using four pristine polymers [polypropylene (PP), polystyrene (PS), poly methyl-methacrylate (PMMA), and glycol-modified polyethylene terephthalate (PETG)] added to four substrates for extraction. The mean \pm SD MPs spike recovery rate was $99 \pm 4\%$ with an average matrix reduction of $95 \pm 4\%$ (dry weight, $n = 16$). This method is cheaper, lower risk, and faster than salt solution separation.

3.4. Froth flotation

Froth flotation exploits the density of the material and the hydrophobicity of its surface. It is commonly used in the recycling industry. Froth selectively attaches to hydrophobic particles, carrying them

upwards, thus separating them from hydrophilic particles. This method uses different hydrophilic characteristics to separate plastics from soil. There are three plastic flotation methods: gamma flotation, reagent adsorption, and surface modification (Fraunholz, 2004). However, the complicated surface modification procedure takes time and suffers from the unpredictable floatability of plastics, leaving a gap between the theory of surface modification and its practical application (Jiang et al., 2020). Huang et al. (2017) used pinacol (97.71% pure) as a foaming agent and potassium permanganate as a surface modifier to yield a 95% recovery rate for PVC and PMMA. Imhof et al. (2012) used froth flotation to extract MPs from sediments but reported low efficiency and significant variation among different polymers.

3.5. Magnetic extraction

Grbic et al. (2019) developed a magnetic extraction method for plastics. Hydrophobic iron nanoparticles are bound to plastic particles and then magnetized. Iron nanoparticles, once processed with hydrophobic hydrocarbon, using cetyltrimethoxysilane (HDTMS), bind to the surface of the MPs and can be extracted with a magnetic field. Iron nanoparticles were selected due to their high specific surface area, low cost, and ferromagnetic properties. Some 84% and 78% of MPs (polyethylene, polystyrene, polyurethane, PVC, and polypropylene) could be recovered from fresh water and sediment, respectively, across a particle size ranging from 200 μm to 1 mm. Although the authors stated that using ultrasound in surfactant or acid solution can remove iron nanoparticles from MPs (Löder and Gerdts, 2015), this method may further fragment MPs particles.

4. Digestion of biological material

MPs separated from agricultural soil are often mixed with organic matter (Munno et al., 2018), affecting the accurate identification and quantification of MPs. Therefore, the organic matter must be removed first; the most common method is digestion with acid, alkali, enzyme, or H_2O_2 . It is recommended to carry out filtration before digestion because there may be small amounts of unidentified impurities in the digestion agent solution.

4.1. Filtration

Before the digestion of biological material, it is necessary to filter and remove unwanted particles after extracting the MPs from the soil matrix and placing them into salt solution. The filtration method is similar to that used for seawater. The purpose of the research determines the mesh density of the filter. When selecting the filter, the minimum size identified by the methods for identifying MPs should be considered (Fig. 3). Filter pore sizes range from 0.1 to 11 μm (Murphy et al., 2016). Filters are made from various materials, including glass, paper, isopore polycarbonate membrane, and cellulose acetate (Majewsky et al., 2016). Polymer filters should not be used as there is a risk of contamination with NPs, but there is no research to support this idea.

Filters can be stacked into several layers to form a filtration gradient, with the mesh density increasing from the top to bottom. Some researchers (Talvitie et al., 2017) set up filters with three different pore sizes (300, 100, and 20 μm) to pass through the supernatant containing MPs separated from sedimentary species. Multiple filtrations can be undertaken with separate filtration steps, as described by Hernandez et al. (2017), who used a five-step extraction process, passing the sample through the following filters: (1) Whatman filter paper (20–25 μm), (2) Whatman filter paper (2.5 μm), (3) EMD Millipore Millex Sterile Syringe Filters of 0.45 and 0.1 μm applied using positive pressure from a 10 ml syringe, and (4, 5) two repeated steps of 0.1 μm syringe filtration. Filtration provides a smaller sample for the digestion of biological material.

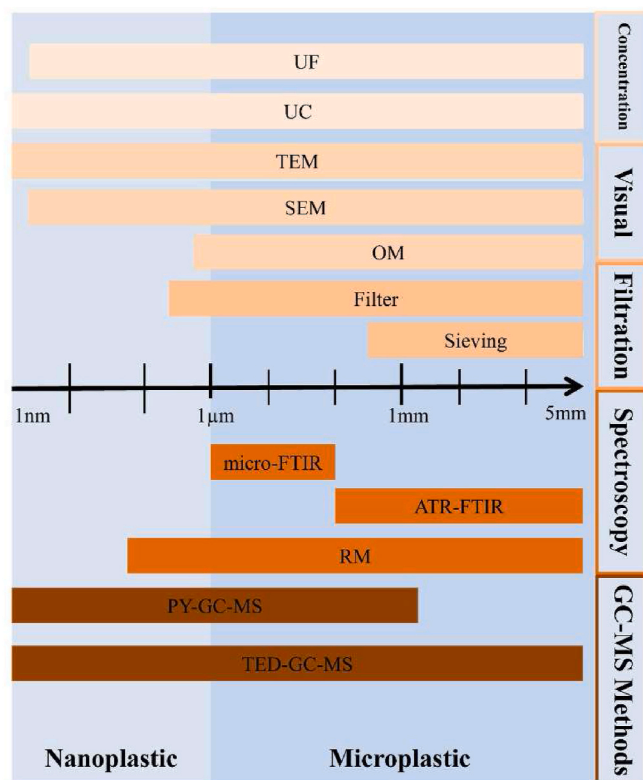


Fig. 3. Size ranges for the extraction and identification methods of MPs/NPs.

4.2. Hydrogen peroxide (H_2O_2)

H_2O_2 is commonly used to digest organic matter (He et al., 2018a; Kumar et al., 2020). While researchers have successfully digested organic matter from sediment, soil, seawater, and fish using H_2O_2 , they have only extracted large MPs particles, not those at a nanometer scale. A 30% H_2O_2 solution was used to remove organic matter from sediments, which did not affect plastic particles (Liebezeit and Dubaish, 2012), but light microscopy showed that acid, alkali, and H_2O_2 could lead to particle cohesion due to changes in the ionic strength of the solution (Nuelle et al., 2014). Rist et al. (2017) tested the effect of 30% H_2O_2 and 35% H_2O_2 solutions on 10 MPs polymers over seven days, with most becoming smaller, thinner, and more transparent. A study on MPs in natural marine snow revealed that a 30% H_2O_2 treatment for organic matter-rich samples formed denser foams (Zhao et al., 2017). The authors recommended using 15% H_2O_2 at 75 $^\circ\text{C}$ for 24 h, which has the same effect as 30% H_2O_2 . However, temperature-sensitive polymers may change their properties at such a high temperature.

Tagg et al. (2017) used Fenton's reagent (mixture of H_2O_2 and ferrous ion, Fe^{2+}) to improve H_2O_2 oxidation efficiency of organic compounds; they found no significant effect of Fenton's reagent on the surface area of PE, PP, and PVC but it did affect the surface area of nylon. The advantage of using this reagent is its speed and ability to digest many organic compounds in MPs. Hurley et al. (2018) studied four methods for removing organic material from MPs in a complex solid matrix: oxidation using H_2O_2 , Fenton's reagent, and alkaline digestion with NaOH and KOH. They confirmed that Fenton's reagent provides the highest removal rate of organic matter from soil and sludge, with no influence on any tested MPs. When Fenton's reagent was used to treat the MPs in rich organic matter (Munno et al., 2018), 35% H_2O_2 was added. The mixture reached 93 $^\circ\text{C}$ due to the violent reaction between the chemicals and organic matter, resulting in low MPs recovery rates. Thus, Munno et al. (2018) suggested that temperatures should not exceed 60 $^\circ\text{C}$ to avoid thermal degradation of MPs; this is similar to the

recommendation made by Hurley et al. (2018) that the mixture should be kept below 40 °C when using Fenton's reagent.

4.3. Alkaline digestion

Many researchers have separated organic matter and MPs using an alkaline solution, commonly KOH and NaOH. Although alkaline digestion of organic matter is not ideal, using 10% KOH solution to digest organic matter and extract MPs is effective (Foekema et al., 2013). Cole et al. (2014) tested NaOH and compared it with enzyme and acid digestion; 10 M NaOH affected nylon, PVC, and PE particles, even under optimal alkaline conditions. Dehaut et al. (2016) showed that 10% KOH and 10 M NaOH solution changed the shape and size of cellulose acetate and PE terephthalate. Munno et al. (2018) found that a more concentrated KOH solution did not improve MPs recovery rate but changed its color. NaOH had significantly better digestion efficacy on organic matter than HCl solution (Cole et al., 2014), and the use of ultrasonics further improved organic matter digestion efficiency. Using 10 M NaOH, Dehaut et al. (2016) produced different degrees of MPs degradation, including peeling off polyethylene terephthalate (PET), and the matte texture signs shown on the polycarbonate (PC). Interestingly, the use of 10% KOH increased the mass of polystyrene (PS), which is not consistent with the current understanding. Alkaline solution is not recommended.

4.4. Acid digestion

The most commonly used acids for organic matter digestion are HNO₃ and HCl (Blaesingand Amelung, 2018). When 20% HCl was used as a digester, it was less effective than H₂O₂. Strong acid can effectively remove organic matter but is not recommended due to the potential degradation of MPs (Avio et al., 2015; Catarino et al., 2017; Nuelle et al., 2014; Rocha-Santos and Duarte, 2015). Scheurer and Bigalke (2018) tested 13% KClO, 50% NaOH, 96% H₂SO₄, 65% HNO₃, and 30% H₂O₂ for organic matter removal and found that HNO₃ disintegrated ABS, PA, and PET particles. In addition, black carbon particles were not removed (Kappenberg et al., 2016; Nguyen et al., 2019).

4.5. Enzyme digestion

Enzyme digestion of organic matter is the least aggressive method, having minimal impact on MPs. One single enzyme is used in the early digestion stage, and a combination of enzymes is carefully selected to digest the organic matter in the later stage. Karlsson et al. (2017) successfully extracted MPs from organic matter using a single protease. However, biodegradable polylactic acid was degraded after protease treatment (Möller et al., 2021). Mintenig et al. (2017) digested organic matter using protease, lipase, and cellulase in succession before passing it through 35% H₂O₂. While this composite operation is better at digesting organic matter, its influence on MPs remains unclear. Another study incubated samples with sodium dodecyl sulfate to increase the contact surface for subsequent enzyme treatment and then used protease, cellulase, H₂O₂, and chitinase to treat samples—the combination of enzymes and H₂O₂ effectively digested organic matter and did not damage the MPs (Löeder et al., 2017). However, the enzyme combination may need to be changed for organic matter in soil. No studies concluded that their methods were suitable for different sample matrices or for MPs concentrated on filters.

There has been little research on the digestion of organic matter in soil compared to seawater (Nguyen et al., 2019). Most methods are either time-consuming or expensive, which limits large-scale investigations. Enzyme treatment is recommended as it is mild and selective, but a suitable enzyme for soil organic matter must be carefully determined. In addition, when combined with ultrasonic treatment, attention should be paid to avoiding the breakup of aging and catalyzed MPs, which may result in unintentional secondary MPs (Löeder and Gerds, 2015).

5. Identification and quantification of microplastics

After sampling, pretreating, purifying, and digesting soil samples, MPs need to be identified and quantified, which is a long and tedious process. MPs have different characteristics, such as size, shape, composition, quality, and so on. The granularity range of MPs/NPs extraction and identification methods also differs (Fig. 3). In early studies, MPs identification mainly occurred through visual characterization, with or without a microscope (Munno et al., 2018), with low accuracy. Later, vibrational spectroscopy technology was used to identify MPs, primarily Raman spectroscopy and Fourier transform infrared spectroscopy. However, this method is time-consuming and has a size limit for MPs. Gas chromatographic–mass spectrometric methods overcome the size limitation but impact other characteristics of MPs. Hence, each identification method only identifies some of the required characteristics of MPs. See Table 3 for the advantages and limitations of each method.

5.1. Visual characterization

Visual characterization is an inexpensive and convenient method (Nguyen et al., 2019). However, visual characterization suffers from user subjectivity, and tiny particles may be missed or misidentified. To differentiate MPs particles from other particles, some researchers use the hot needle test, which exploits the thermoplastic properties of MPs (Lusher et al., 2017; Silva et al., 2018). Zhang and Liu (2018) heated MPs and impurities extracted from soil samples (3–5 s at 130 °C) and compared the microscopic images before and after heating: the melted particles were identified as MPs. Although this method is simple, it does not consider that natural particles, such as wax, also melt at this temperature, and some high-density and thermosetting plastics do not melt under these conditions. Furthermore, this method can only determine the number of MPs, not their type. Moreover, identifying the size of MPs is limited by microscopes.

The resolution of the microscope is important for the identification of MPs. The lower limits of MPs identification using a traditional microscope is a particle size of 200 nm (Betzig et al., 2006). For smaller MPs (<200 nm), scanning electron microscopy (SEM) should be used (Silva et al., 2018). However, SEM is expensive, and the corresponding sample preparation is complex (Shim et al., 2017). Also, SEM only measures size, it cannot identify particle composition. Transmission electron microscopy is also not typically used to analyze NPs because NPs are amorphous (Gigault et al., 2016). Polarized light microscopy can be used to identify MPs, exploiting differences in microchromatism, birefringence, extraction pattern, and refraction index characteristics (Habib et al., 1998; Von Moos et al., 2012). Although microscopes can observe smaller particles, they do not reveal differences between synthetic particles and MPs. MPs dyeing seems to solve this problem. In particular, Nile red is a good fluorescent agent for detecting various polymers (Erni-Cassola et al., 2017; Shim et al., 2016). Nile red was used on samples before using a microscope to differentiate MPs from other substances (Maes et al., 2017). However, Nile red also marks the organic matter surrounding MPs (Lusher et al., 2017; Ruggero et al., 2020), so it needs to be completely digested before the dyeing process.

Visual characterization is only a preliminary identification of MPs; it can reduce the number of particles that need to be chemically characterized later (Nguyen et al., 2019). Some researchers use visual classification as the first step in MPs screening (Renner et al., 2018; Rocha-Santos and Duarte, 2015). Due to the large amount of MPs in soil, Lorenzo-Navarro et al. (2021) developed an architecture based on deep learning networks to automatically count and classify 1–5 mm MP from images >16 megapixels. However, the method first requires humans to specify MPs to practice, and its accuracy is questionable.

Table 3
Advantages and limitations of different methods.

Group	Method	Advantages	Limitations	Reference
Sample purification	Density separation	<ul style="list-style-type: none"> ◆ High separation efficiency ◆ Simple operation ◆ Inexpensive ◆ Handling large sample numbers 	<ul style="list-style-type: none"> • Low-density solution cannot separate high-density plastics • High-density solutions are expensive or toxic • Time-consuming 	Nuelle et al. (2014) Ruggero et al. (2020)
	Electrostatic separation	<ul style="list-style-type: none"> ◆ High separation efficiency ◆ Simple operation ◆ Fast ◆ Simple sample handling 	<ul style="list-style-type: none"> • Difficult to separate small-sized MPs • Samples need to be dispersed and dried 	Felsing et al. (2018)
	Oil separation	<ul style="list-style-type: none"> ◆ High separation efficiency ◆ Simple operation ◆ Inexpensive ◆ Fast 	<ul style="list-style-type: none"> • Identification of interference MPs 	Crichton et al. (2017)
	Froth flotation	<ul style="list-style-type: none"> ◆ Separation of large quantities of samples ◆ Simple sample handling 	<ul style="list-style-type: none"> • Time-consuming • Low separation efficiency • Complex procedures 	Fraunholz (2004) Jiang et al. (2020)
	Magnetic extraction	<ul style="list-style-type: none"> ◆ Separate small-sized MPs ◆ Inexpensive 	<ul style="list-style-type: none"> • Time-consuming • Complex procedures • Sample damage • Destructive to MPs 	Grbic et al. (2019)
Digestion	H ₂ O ₂	<ul style="list-style-type: none"> ◆ Inexpensive ◆ Can be used in complex environments 	<ul style="list-style-type: none"> • Time-consuming • Produce high temperature 	He et al. (2018b) Kumar et al. (2020)
	Alkaline	<ul style="list-style-type: none"> ◆ Inexpensive ◆ Suitable for biological samples ◆ Strong digestion ability 	<ul style="list-style-type: none"> • Destructive to MPs • Removal efficiency varies with the types of MPs 	Hurley et al. (2018) Cole et al. (2014) Foekema et al. (2013)
	Acid	<ul style="list-style-type: none"> ◆ Effective removal of organic matter 	<ul style="list-style-type: none"> • Destructive to MPs • Carbon black cannot be removed 	Dehaut et al. (2016) Blaesing and Amelung. (2018) Avio et al. (2015)
	Enzyme	<ul style="list-style-type: none"> ◆ Inexpensive ◆ Does not degrade plastic ◆ Suitable for biological samples ◆ Relatively gentle 	<ul style="list-style-type: none"> • Expensive • The removal efficiency of soil organic matter is unclear 	Kappenberg et al. (2016) Karlsson et al. (2017) Nguyen et al. (2019)
Identification and quantification	Visual characterization	<ul style="list-style-type: none"> ◆ Fast, easy, and quick ◆ Inexpensive ◆ Identifies shape, size, and colors ◆ Non-destructive 	<ul style="list-style-type: none"> • Judging by people's subjective consciousness • Lack of information on plastic composition • Large size 	Munno et al. (2018) Nguyen et al. (2019)
	FTIR	<ul style="list-style-type: none"> ◆ Non-destructive ◆ Fast, simple ◆ Identifies the composition of plastic ◆ Automated 	<ul style="list-style-type: none"> • Expensive • Difficult to analyze NPs • Strong interference from water 	Elert et al. (2017) Löeder and Gerdt (2015) Hufnagl et al. (2019)
	Raman	<ul style="list-style-type: none"> ◆ Identifies the composition of plastic ◆ Generates high-resolution images ◆ NPs can be analyzed ◆ Non-destructive ◆ Easy sample preparation 	<ul style="list-style-type: none"> • Expensive • Time-consuming • Samples require refinements • Small area 	Kaeppeler et al. (2015) Cabernard et al. (2018)
	UF	<ul style="list-style-type: none"> ◆ Inexpensive ◆ Easily available ◆ Large volumes ◆ Mild ◆ Little sample damage 	<ul style="list-style-type: none"> • Membrane with small pores • No separation from the particulate matrix • Low flow rates 	Schwaferts et al. (2019) Pitt et al. (2018) Pansare et al. (2017)
	UC	<ul style="list-style-type: none"> ◆ Simple ◆ Easily available ◆ Inexpensive 	<ul style="list-style-type: none"> • Small volumes • Slow • Harsh conditions • No separation from the particulate matrix • Sample damage 	Laborda et al. (2016)
	Py-GC-MS	<ul style="list-style-type: none"> ◆ Quick sample preparation ◆ Easy and reliable ◆ Identifies MPs of any size ◆ Quantification of MPs ◆ Identify any plastic additives present 	<ul style="list-style-type: none"> • Expensive • Small sample masses • Destructive to MPs • Dry sample needed • Pre-concentration 	Fischer and Scholz-Boettcher (2017) Fries et al. (2013) Kaeppeler et al. (2018)
	TED-GC-MS	<ul style="list-style-type: none"> ◆ Higher sample masses ◆ Quantification of MPs ◆ Identifies MPs of any size ◆ Fast 	<ul style="list-style-type: none"> • Expensive • Destructive to MPs • Dry sample needed • Pre-concentration 	Duemichen et al. (2017) Duemichen et al. (2015) Duemichen et al. (2014)

5.2. Vibrational spectroscopy

Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) are the most common and advanced analytical methods for studying MPs. They can distinguish between polymers and other substances in the sample and determine the type of polymer.

FTIR is a simple and low-cost MPs identification technology. The

infrared absorption depends on changes in chemical bond permanent dipole moments, so the polar functional groups in MPs are easy to detect (Elert et al., 2017). However, the size of FTIR recognition MPs is limited. To improve the accuracy of MPs identification, FTIR spectra are needed to compare with the spectrum library and manually conduct spectral analysis (Jung et al., 2018). Focal plane array (FPA) micro-Fourier transform infrared (micro-FTIR) spectroscopy can identify particle

sizes ranging from 10 to 500 μm (Löeder et al., 2015). Attenuated total reflection (ATR)-FTIR can only be used to identify particles $>500 \mu\text{m}$ (Renner et al., 2017). FTIR requires a minimum thickness of 150 nm (Mallikarjunachari and Ghosh, 2016), and the shape, size, or thickness of the detected particles affect the FTIR imaging results (Löeder et al., 2015). For black particles, FTIR is often inaccurate due to the high absorption of infrared radiation. Fuller and Gautam (2016) developed a method for detecting MPs in soil based on pressurized fluid extraction. ATR-FTIR spectroscopy was used to measure MPs in the residues after evaporation of the suspension. This method is simple and fast, and not limited by particle size. However, it can only carry out mass analysis and cannot measure MP number, size, or shape. For more information on FTIR, readers can refer to Hufnagl et al. (2019) and Primpke et al. (2017).

Raman spectroscopy can compensate for some FTIR shortcomings, as the chemical imaging line generated from Raman spectroscopy can reach a pixel resolution of 500 nm (Kaeppler et al., 2015). Surface-enhanced Raman spectroscopy (SERS) can identify MPs less than 500 nm. Xu et al. (2020a) used SERS with Klarite substrates can identify microplastics with sizes down to 450 nm. Zhou et al. (2021a) used SERS to identify NPs surrounded by SERS-active silver nanoparticles (AgNPs) with sizes down to 50 nm. The main advantages of Raman spectroscopy are its use of the complete wavelength region and ability to detect amorphous carbon (Lenz et al., 2015). Raman spectroscopy has better spectral resolution and lower interference of moisture signal than FTIR, so it is not affected by the shape and thickness of particles. These advantages make Raman spectroscopy better than FTIR for identifying MPs (Cabernard et al., 2018), but the process takes longer than FTIR (Kaeppler et al., 2016). Typically, in farmland soil, numerous particles cannot be visually characterized and require spectral identification, which can take a long time when using Raman spectroscopy.

Soil samples contain organic matter, microorganisms (Kaeppler et al., 2016), background fluorescence (Lenz et al., 2015), and inorganic material (Elert et al., 2017) that strongly interfere with the target spectrum, making them unable to be identified. When using either of the vibration spectroscopy types described, the organic matter needs to be completely digested to avoid affecting the results.

6. Identification and quantification of nanoplastics

Identifying and quantifying NPs are relatively difficult compared to MPs (1 μm –5 mm), mainly because their size is too small for ordinary test instruments to identify nanoscale particles. Most studies on the identification and quantification of NPs have used spiked environmental samples, with only five studies identifying NPs in real field samples (Cai et al., 2021). Only Wahl et al. (2021) has extracted NPs from soil, which ranged from 20 to 150 nm. In these studies, gas chromatographic–mass spectrometric methods are mainly used, as it can manage samples in batches, and there is no requirement for impurities in samples.

6.1. Pre-concentration

While studies have revealed the abundance of MPs in agricultural soil (Jambeck et al., 2015), the concentrations of NPs can be very low (Lenz et al., 2016; Ter Halle et al., 2017), even lower in the colloidal part of the solution after filtration. Therefore, to measure the concentration of NPs in filtered solutions, a pre-concentration step is necessary.

6.1.1. Ultrafiltration

Ultrafiltration (UF) uses a type of porous membrane (Fig. 4), with a molecular weight cutoff ranging from 10 to 100 kDa, equivalent to 5–50 nm pore size (Schwaferts et al., 2019). The solution penetrates the ultrafiltration membrane, with pressure applied to encourage flow and improve filtration efficiency. Due to the small pore size of the ultrafiltration membrane, the remaining particles are left suspended in solution (Pitt et al., 2018). Ultrafiltration can be carried out in a stirred tank (Ter

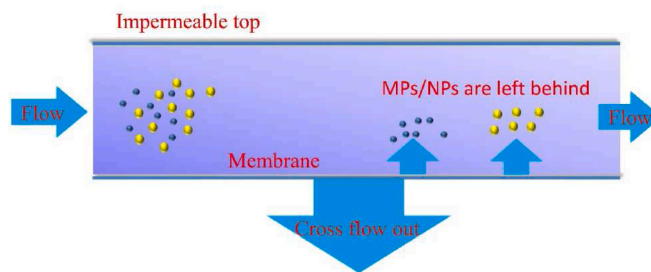


Fig. 4. Diagram of ultrafiltration process.

Halle et al., 2017), centrifugal field (Pitt et al., 2018), or cross-flow filtration (Mintening et al., 2018). Ultrafiltration using a stirred tank (Ter Halle et al., 2017) may damage the NPs in the solution. Mintening et al. (2018) concentrated a suspension containing PS (50–1000 nm) using cross-flow UF with a 40–60 kDa cutoff flow, as cross-flow UF is relatively gentle, has low particle loss and sample damage, and can process many solutions. Cross-flow can also create a focusing flow to collect up to 50 ml of suspension at the beginning of the channel for pre-concentration (Prestel et al., 2006). Therefore, cross-flow UF is a promising method for soil sample treatment (Laborda et al., 2016; Vauthier and Bouchemal, 2009).

6.1.2. Ultracentrifugation

As NPs are insoluble, they can be sediment particles from solution by centrifugation and ultracentrifugation (UC). UC uses faster spinning speeds, which can collect dispersed particles in the solution, irrespective of whether they are plastic or not; however, it may damage the NPs (Laborda et al., 2016; Vauthier and Bouchemal, 2009), which is irrelevant if you only need to know the quality and composition of NPs. UC is relatively easy to operate, but it can only process a small volume (10–100 ml) of solution, limiting its use with water samples. The volume of suspension obtained from soil samples should be smaller; however, there is no research on the use of UC for soil MPs extraction. Taking the density gradient UC (Kumar et al., 2018), you can directly separate NPs from soil (Von der Kammer et al., 2012). In a recent study, NaCl and bovine serum albumin were added to the nanoplastic solution, which obtained protein with concentrated nanoplastics at a centrifugation speed of 8000 rpm for 15 min (Zhou et al., 2021b).

6.1.3. Solution evaporation

The rotary evaporator (Vauthier and Bouchemal, 2009) is mainly used for solution evaporation. Its working principle is to sublimate the solid at $-70 \text{ }^\circ\text{C}$ under negative pressure, which is especially useful for organic solutions. At present, this technology has been successfully used to extract NPs from the ocean (Ter Halle et al., 2017). This technology cannot remove dissolved substances and is not economical to deal with numerous suspensions, so it is usually combined with the above two pre-concentration methods.

6.2. Gas chromatographic–mass spectrometric methods

Mass spectrometry is the most commonly used method for analyzing MPs/NPs in the environment. Its analysis method differs from vibrational spectroscopy in that it attains mass fraction information through sample destruction, so it cannot identify particle quantities or shapes.

Pyrolysis coupled with gas chromatography–mass spectrometry (Py-GC–MS) is a sensitive and ideal method for characterizing and quantifying MPs and other organic additives (Fischer and Schloz-Boettcher, 2017; Fries et al., 2013; Hendrickson et al., 2018; Li et al., 2018). The combination of Py-GC–MS, and FTIR is suitable for determining MPs in samples (Kaeppler et al., 2018). In Py-GC–MS, samples are first decomposed in inert gas at high temperature, then separated using gas chromatography, and finally analyzed with mass spectrometry (Roussis

and Fedora, 1996). Polymers are identified by their unique pyrolysis products (Kaeppeler et al., 2018). However, the method requires sample preparation and choice of pyrolysis type (Dworzanski and Muezelaar, 2017), so it is difficult for researchers to obtain similar results. Due to the size of the pyrolyzer, the amount of sample that can be added each time is limited to 0.5 mg (Duemichen et al., 2017), with detected particle sizes limited to 1.5 mm (Fries et al., 2013), making it unsuitable for large volume samples. Ter Halle et al. (2017) used Py-GC-MS to detect the presence of NPs for the first time in the subtropical circulation of the Atlantic Ocean.

Compared with Py-GC-MS, thermal extraction–desorption coupled with gas chromatography–mass spectroscopy (TED-GC-MS) has a higher sample capacity, up to 20 mg (Duemichen et al., 2017) at a time, with no sample pretreatment required. After placing the product of thermal extraction from the thermogravimetric analysis into a solid phase adsorber, it is pyrolyzed under 1000 °C and sucked into a gas chromatography–mass spectrometer for polymer identification (Duemichen et al., 2015, 2017). It takes 2–3 h for the sample to be processed by TED-GC-MS, which is less than most vibrational spectroscopy methods (Duemichen et al., 2014). Eisentraut et al. (2018) successfully identified NPs from tire wear in environmental samples using TED-GC-MS.

These two technologies require a high concentration of NPs in samples, so they are generally combined with pre-concentration to reduce labor and material resources and ensure NPs detection. These two methods only detect the percentage of NPs in the sample, not their size, shape, or color; however, this information is important for evaluating the impact of NPs particles on soil. Additionally, NPs in soil samples can be embedded or attached to other particles, so sensitivity can be an obstacle. The number of samples that can be injected is limited. While the sample volume of TED-GC-MS is higher than Py-GC-MS, it has potential for improvement.

6.3. Other methods

Thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) can be used to analyze NPs. However, only PE and PP can be identified (Majewsky et al., 2016). TGA combined with MS can be used to analyze MPs in soil samples, but this method is limited to PET analysis (David et al., 2018). At present, TGA is rarely used to identify MPs, but it has good application prospects.

X-ray photoelectron spectroscopy (XPS)—using X-ray radiation on a sample resulting in the emission of photoelectrons—can give specific characteristic bands. XPS has been used for the chemical composition of PS latex (Simon et al., 2018) and polyethylene NPs (Hernandez et al., 2017). However, XPS alone cannot identify the polymer type. It mainly reveals changes in oxidation on the surface of NPs through changes in the oxygen content of the sample (Lu et al., 2018).

Plastic particles and particle size distribution characteristics can be measured by laser scattering; the most widely used is dynamic light scattering (DLS) (Xu, 2015), measuring particle sizes between 1 nm and 3 μm. The theoretical model used in DLS is sphere-based, which works best with monodisperse suspensions. This method does not provide the composition of particles, only the size.

7. Quality assurance/quality control (QA/QC)

MPs are ubiquitous in our environment. Samples taken from farmland, for example, and analyzed in the laboratory may be polluted by the environment, e.g., from MPs in the air, synthetic fibers in staff clothes, and laboratory plastic products.

During field sampling, all tools must be metal and clean. Samples must be stored in covered non-plastic (e.g., metal) containers. When handling samples in the laboratory, staff should wear clothes made from natural fibers; outside, they should wear 100% cotton clothes when sampling (Murphy et al., 2016). The number of staff should be small, with entry and exit to/from the laboratory minimized (Woodall et al.,

2015). All equipment and materials in the laboratory should be cleaned with deionized water before use (Löeder et al., 2017; Piehl et al., 2018). All tools must be rinsed with deionized water before and after contact with each sample to prevent cross-contamination. The sample treatment process should be carried out in a laboratory laminar flow hood (Murphy et al., 2016) to prevent air pollution. Equipment and materials should be cleaned with deionized water after the first cleaning for use as a blank group for subsequent analysis. All experimental equipment should be non-plastic; if unavoidable, it must not affect experimental results. In addition, it is necessary to analyze blank samples to evaluate systematic errors of the experiment (Carter and Gregorich, 2007).

8. Conclusions and outlook

In the above chapters, we discuss the extraction and identification methods of MPs/NPs and suggest combining different technologies to make full use of their advantages because a single technology is unlikely to provide the required information. Due to the large sample size of agricultural soil, an analysis method with low cost and high efficiency should be selected to facilitate pollution evaluation. At present, a large gap exists between different laboratories on the extraction and identification of MPs (Van Mourik et al., 2021). Therefore, the method must be optimized to expedite the sample information. The selection of sampling site, depth, and quality should be based on the primary test purpose and test conditions. After sampling, the samples must be purified; there are numerous purification methods, including density separation, electrostatic separation, oil separation, froth flotation, and magnetic extraction. At present, density separation is more commonly used because it is simple and easy to do. It is important not to use a salt solution that contains chemicals in the environment. After extracting the MPs/NPs, they need to be digested; the commonly used methods are H₂O₂, alkaline, acid, and enzyme digestion, which can be used in combination. Visual characterization, vibrational spectroscopy, and GC-MS methods are the main methods for identifying MPs/NPs. Visual characterization is generally used as the first step to identify MPs with particles >1 μm. If the identified MPs do not contain NPs, you can use vibrational spectroscopy because it is simpler and takes less time than GC-MS methods. NPs can only be identified by GC-MS methods. Pre-concentration is needed before using GC-MS methods. However, GC-MS methods can only obtain the quality of NPs.

This review introduced MPs/NPs analysis techniques and a road map for the analysis process (Fig. 1). We listed the advantages and limitations of the methods described (Table 3) to help select appropriate methods. We believe that the following aspects need further investigation:

- At present, the extraction and identification methods of MPs in soil do not accurately extract and identify NPs, and the content and type of NPs in soil are unknown. Therefore, future research should strengthen the extraction and identification of NPs in soil and plants to understand whether NPs can enter the human food chain through soil.
- The transport mechanism of MPs in soil is not clear and may be affected by water transport, tillage methods, plant root growth, and other factors. It is important to understand the transport mechanism of MPs in different soil textures to know how deep MPs can be transported and whether it will affect groundwater.
- There are few studies on the source and fate of MPs in soil. Understanding the source of MPs in soil can be controlled from the source. Microorganisms can degrade MPs in soil, which is significant for breeding microorganisms that can degrade MPs without adversely affecting the agricultural environment.
- Design a standard procedure that is fast, convenient, and practical for MPs/NPs extraction and identification that can be used to analyze the source of MPs/NPs in agricultural soil and the degree of soil pollution, thus improving the soil environment and food security.

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.

Acknowledgements

This work was jointly supported by the National Key Research and Development Program (2016YFC0400204), the National Natural Science Foundation of China (41771316), the Shaanxi Innovative Research Team for Key Science and Technology (No. 2017KCT-15), and the '111' Project (No. B12007).

References

- Andrady, A.L., 2011. Microplastics in the marine environment. *Mar. Pollut. Bull.* 62, 1596–1605.
- Arthur, C., Baker, J., Bamford, H., 2009. *Proceedings of the International Research Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris*; NOAA Marine Debris Program, National Oceanic and Atmospheric Administration. U.S. Department of Commerce: Silver Spring, MD.
- Avio, C.G., Gorbi, S., Regoli, F., 2015. Experimental development of a new protocol for extraction and characterization of microplastics in fish tissues: first observations in commercial species from Adriatic Sea. *Mar. Environ. Res.* 111, 18–26. <https://doi.org/10.1016/j.marenvres.2015.06.014>.
- Baeza, C., Cifuentes, C., Gonzalez, P., Aranedo, A., Barra, R., 2020. Experimental exposure of lumbricus terrestris to microplastics. *Water, Air, Soil Pollut.* 231 (6) <https://doi.org/10.1007/s11270-020-04673-0>.
- Barahona, E., Iriarte, A., 2001. An overview of the present state of standardization of soil sampling in Spain. *Sci. Total Environ.* 264 (1–2), 169–174. [https://doi.org/10.1016/S0048-9697\(00\)00620-3](https://doi.org/10.1016/S0048-9697(00)00620-3).
- Betzig, E., Patterson, G.H., Sougrat, R., Lindwasser, O.W., Olenych, S., Bonifacino, J.S., Hess, H.F., 2006. Imaging intracellular fluorescent proteins at nanometer resolution. *Science* 313 (5793), 1642–1645. <https://doi.org/10.1126/science.1127344>.
- Blaesing, M., Amelung, W., 2018. Plastics in soil: analytical methods and possible sources. *Sci. Total Environ.* 612, 422–435. <https://doi.org/10.1016/j.scitotenv.2017.08.086>.
- Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., Thompson, R., 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environ. Sci. Technol.* 45, 9175–9179.
- Browne, M.A., Galloway, T., Thompson, R., 2007. Microplastic-an emerging contaminant of potential concern? *Integrated Environ. Assess. Manag.* 3, 559–566.
- Cabernard, L., Roscher, L., Lorenz, C., Gerdt, G., Primpke, S., 2018. Comparison of Raman and Fourier transform infrared spectroscopy for the quantification of microplastics in the aquatic environment. *Environ. Sci. Technol.* 52 (22), 13279–13288. <https://doi.org/10.1021/acs.est.8b03438>.
- Cai, H., Xu, E.G., Du, F., Li, R., Liu, J., Shi, H., 2021. Analysis of environmental nanoplastics: progress and challenges. *Chem. Eng. J.* 410 <https://doi.org/10.1016/j.cej.2020.128208>.
- Cao, J., Chen, P., Li, Y., Fang, H., Gu, X., Li, Y., 2020. Effect of plastic film residue on vertical infiltration under different initial soil moisture contents and dry bulk densities. *Water* 12 (5). <https://doi.org/10.3390/w12051346>.
- Carbery, M., Connor, W.O., Thavamani, P., 2018. Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. *Environ. Int.* 115, 400–409. <https://doi.org/10.1016/j.envint.2018.03.007>.
- Carter, M.R., Gregorich, E.G., 2007. *Soil Sampling and Methods of Analysis*. CRC Press, Boca Raton.
- Catarino, A.I., Thompson, R., Sanderson, W., Henry, T.B., 2017. Development and optimization of a standard method for extraction of microplastics in mussels by enzyme digestion of soft tissues. *Environ. Toxicol. Chem.* 36 (4), 947–951. <https://doi.org/10.1002/etc.3608>.
- Chen, H., Wang, Y., Sun, X., Peng, Y., Xiao, L., 2020a. Mixing effect of polylactic acid microplastic and straw residue on soil property and ecological function. *Chemosphere* 243.
- Chen, Y., Leng, Y., Liu, X., Wang, J., 2020b. Microplastic pollution in vegetable farmlands of suburb Wuhan, central China. *Environ. Pollut.* 257 <https://doi.org/10.1016/j.envpol.2019.113449>.
- Chen, Y., Wu, C., Zhang, H., Lin, Q., Hong, Y., Luo, Y., 2013. Empirical estimation of pollution load and contamination levels of phthalate esters in agricultural soils from plastic film mulching in China. *Environ. Earth Sci.* 70 (1), 239–247. <https://doi.org/10.1007/s12665-012-2119-8>.
- Claessens, M., Van Cauwenbergh, L., Vandegehuchte, M.B., Janssen, C.R., 2013. New techniques for the detection of microplastics in sediments and field collected organisms. *Mar. Pollut. Bull.* 70 (1–2), 227–233. <https://doi.org/10.1016/j.marpolbul.2013.03.009>.
- Cole, M., Galloway, T.S., 2015. Ingestion of nanoplastics and microplastics by pacific oyster larvae. *Environ. Sci. Technol.* 49 (24), 14625–14632. <https://doi.org/10.1021/acs.est.5b04099>.
- Cole, M., Lindeque, P., Halsband, C., Galloway, T.S., 2011. Microplastics as contaminants in the marine environment: a review. *Mar. Pollut. Bull.* 62, 2588–2597.
- Cole, M., Webb, H., Lindeque, P.K., Fileman, E.S., Halsband, C., Galloway, T.S., 2014. Isolation of microplastics in biota-rich seawater samples and marine organisms. *Sci. Rep.-UK* 4. <https://doi.org/10.1038/srep04528>.
- Colton, J.B., Knapp, F.D., Burns, B.R., 1974. Plastic particles in surface waters of the northwestern Atlantic. *Science* 185, 491–497. <https://doi.org/10.1126/science.185.4150.491>.
- Coppock, R.L., Cole, M., Lindeque, P.K., Queiros, A.M., Galloway, T.S., 2017. A small-scale, portable method for extracting microplastics from marine sediments. *Environ. Pollut.* 230, 829–837. <https://doi.org/10.1016/j.envpol.2017.07.017>.
- Crichton, E.M., Noel, M., Gies, E.A., Ross, P.S., 2017. A novel, density-independent and FTIR-compatible approach for the rapid extraction of microplastics from aquatic sediments. *Anal. Methods-UK* 9 (9), 1419–1428. <https://doi.org/10.1039/c6ay02733d>.
- Da Costa, J.P., Santos, P.S.M., Duarte, A.C., Rocha-Santos, T., 2016. Nano) plastics in the environment - sources, fates and effects. *Sci. Total Environ.* 566, 15–26. <https://doi.org/10.1016/j.scitotenv.2016.05.041>.
- Dai, Z., Zhang, H., Zhou, Q., Tian, Y., Chen, T., Tu, C., Luo, Y., 2018. Occurrence of microplastics in the water column and sediment in an inland sea affected by intensive anthropogenic activities. *Environ. Pollut.* 242, 1557–1565. <https://doi.org/10.1016/j.envpol.2018.07.131>.
- David, J., Steinmetz, Z., Kucerik, J., Schaumann, G.E., 2018. Quantitative analysis of poly(ethylene terephthalate) microplastics in soil via thermogravimetry-mass spectrometry. *Anal. Chem.* 90, 8793–8799.
- Dehaut, A., Cassone, A.L., Frere, L., Hermabessiere, L., Himber, C., Rinnert, E., Paul-Pont, I., 2016. Microplastics in seafood: benchmark protocol for their extraction and characterization. *Environ. Pollut.* 215, 223–233. <https://doi.org/10.1016/j.envpol.2016.05.018>.
- Deotterl, M., Wachsmuth, U., Waldmann, L., Flachberger, H., Mirkowska, M., Brands, L., Beier, P.-M., Stahl, I., 2000. *Electrostatic Separation, Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co (KGaA).
- Dioses-Salinas, D.C., Pizarro-Ortega, C.I., De-la-Torre, G.E., 2020. A methodological approach of the current literature on microplastic contamination in terrestrial environments: current knowledge and baseline considerations. *Sci. Total Environ.* 730 <https://doi.org/10.1016/j.scitotenv.2020.139164>.
- Duemichen, E., Barthel, A.-K., Braun, U., Bannick, C.G., Brand, K., Jekel, M., Senz, R., 2015. Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method. *Water Res.* 85, 451–457. <https://doi.org/10.1016/j.watres.2015.09.002>.
- Duemichen, E., Braun, U., Senz, R., Fabian, G., Sturm, H., 2014. Assessment of a new method for the analysis of decomposition gases of polymers by a combining thermogravimetric solid-phase extraction and thermal desorption gas chromatography mass spectrometry. *J. Chromatogr. A* 1354, 117–128. <https://doi.org/10.1016/j.chroma.2014.05.057>.
- Duemichen, E., Eisentraut, P., Bannick, C.G., Barthel, A.K., Senz, R., Braun, U., 2017. Fast identification of microplastics in complex environmental samples by a thermal degradation method. *Chemosphere* 174, 572–584. <https://doi.org/10.1016/j.chemosphere.2017.02.010>.
- Dworzanski, J.P., Meuzelaar, H.L.C., 2017. *Pyrolysis mass spectrometry, methods*. Encyclopedia of Spectroscopy and Spectrometry. Elsevier, pp. 789–801.
- Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* 75, 63–82.
- Eisentraut, P., Duemichen, E., Ruhl, A.S., Jekel, M., Albrecht, M., Gehde, M., Braun, U., 2018. Two birds with one stone-fast and simultaneous analysis of microplastics: microparticles derived from thermoplastics and tire wear. *Environ. Sci. Technol. Lett.* 5 (10), 608–613. <https://doi.org/10.1021/acs.estlett.8b00446>.
- Elert, A.M., Becker, R., Duemichen, E., Eisentraut, P., Falkenhagen, J., Sturm, H., Braun, U., 2017. Comparison of different methods for MP detection: what can we learn from them, and why asking the right question before measurements matters? *Environ. Pollut.* 231, 1256–1264. <https://doi.org/10.1016/j.envpol.2017.08.074>.
- Elkhatib, D., Oyanedel-Craver, V., 2020. A critical review of extraction and identification methods of microplastics in wastewater and drinking water. *Environ. Sci. Technol.* 54 (12), 7037–7049. <https://doi.org/10.1021/acs.est.9b06672>.
- Erni-Cassola, G., Gibson, M.I., Thompson, R.C., Christie-Olea, J.A., 2017. Lost, but found with Nile red: a novel method for detecting and quantifying small microplastics (1 mm to 20 μm) in environmental samples. *Environ. Sci. Technol.* 51 (23), 13641–13648. <https://doi.org/10.1021/acs.est.7b04512>.
- Felsing, S., Kochleus, C., Buchinger, S., Brennholt, N., Stock, F., Reifferscheid, G., 2018. A new approach in separating microplastics from environmental samples based on their electrostatic behavior. *Environ. Pollut.* 234, 20–28. <https://doi.org/10.1016/j.envpol.2017.11.013>.
- Fischer, M., Scholz-Boettcher, B.M., 2017. Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography-mass spectrometry. *Environ. Sci. Technol.* 51 (9), 5052–5060. <https://doi.org/10.1021/acs.est.6b06362>.
- Foekema, E.M., De Gruijter, C., Mergia, M.T., van Franeker, J.A., Murk, A.J., Koelmans, A.A., 2013. Plastic in north sea fish. *Environ. Sci. Technol.* 47 (15), 8818–8824. <https://doi.org/10.1021/acs.est.400931b>.
- Fraunholz, N., 2004. Separation of waste plastics by froth flotation - a review, part I. *Miner. Eng.* 17 (2), 261–268. <https://doi.org/10.1016/j.mineng.2003.10.028>.
- Fred-Ahmadu, O.H., Bhagwat, G., Oluyoye, I., Benson, N.U., Ayejuy, O.O., Palanisami, T., 2020. Interaction of chemical contaminants with microplastics: principles and perspectives. *Sci. Total Environ.* 706.
- Fries, E., Dekiff, J.H., Willmeyer, J., Nuelle, M.T., Ebert, M., Remy, D., 2013. Identification of polymer types and additives in marine microplastic particles using

- pyrolysis-GC/MS and scanning electron microscopy. *Environ Sci-Proc Imp.* 15 (10), 1949–1956. <https://doi.org/10.1039/c3em00214d>.
- Frias, J.P.G.L., Nash, R., 2019. Microplastics: finding a consensus on the definition. *Mar. Pollut. Bull.* 138 (2019), 145–147.
- Fuller, S., Gautam, A., 2016. A procedure for measuring microplastics using pressurized fluid extraction. *Environ. Sci. Technol.* 50 (11), 5774–5780. <https://doi.org/10.1021/acs.est.6b00816>.
- Gigault, J., Pedrono, B., Maxit, B., Ter Halle, A., 2016. Marine plastic litter: the unanalyzed nano-fraction. *Environ Sci-Nano.* 3 (2), 346–350. <https://doi.org/10.1039/c6en00008h>.
- Gigault, J., ter Halle, A., Baudrimont, M., Pascal, P.Y., Gaufré, F., Thuy-Linh, P., Reynaud, S., 2018. Current opinion: what is a nanoplastic? *Environ. Pollut.* 235, 1030–1034. <https://doi.org/10.1016/j.envpol.2018.01.024>.
- Gong, J., Xie, P., 2020. Research progress in sources, analytical methods, eco-environmental effects, and control measures of microplastics. *Chemosphere* 254, 126790.
- Grbic, J., Nguyen, B., Guo, E., You, J.B., Sinton, D., Rochman, C.M., 2019. Magnetic extraction of microplastics from environmental samples. *Environ. Sci. Technol. Lett.* 6 (2), 68. <https://doi.org/10.1021/acs.estlett.8b00671>.
- Habib, D., Locke, D.C., Cannone, L.J., 1998. Synthetic fibers as indicators of municipal sewage sludge, sludge products, and sewage treatment plant effluents. *Water Air Soil Pollut.* 103 (1–4), 1–8. <https://doi.org/10.1023/a:1004908110793>.
- Han, X.X., Lu, X.Q., Vogt, R.D., 2019. An optimized density-based approach for extracting microplastics from soil and sediment samples. *Environ. Pollut.* 254, 7. <https://doi.org/10.1016/j.envpol.2019.113009>.
- He, D., Luo, Y., Lu, S., Liu, M., Song, Y., Lei, L., 2018a. Microplastics in soils: analytical methods, pollution characteristics and ecological risks. *Trac. Trends Anal. Chem.* 109, 163–172. <https://doi.org/10.1016/j.trac.2018.10.006>.
- He, H.J., Wang, Z.H., Guo, L., Zheng, X.R., Zhang, J.Z., Li, W.H., Fan, B.H., 2018b. Distribution characteristics of residual film over a cotton field under long-term film mulching and drip irrigation in an oasis agroecosystem. *Soil. Till. Res.* 180, 194–203. <https://doi.org/10.1016/j.still.2018.03.013>.
- Helmberger, M.S., Tiemann, L.K., Grieshop, M.J., 2020. Towards an ecology of soil microplastics. *Funct. Ecol.* 34 (3), 550–560. <https://doi.org/10.1111/1365-2435.13495>.
- Hendrickson, E., Minor, E.C., Schreiner, K., 2018. Microplastic abundance and composition in western lake superior as determined via microscopy, pyr-GC/MS, and FTIR. *Environ. Sci. Technol.* 52 (4), 1787–1796. <https://doi.org/10.1021/acs.est.7b05829>.
- Hernandez, L.M., Yousefi, N., Tufenkji, N., 2017. Are there nanoplastics in your personal care products? *Environ. Sci. Technol. Lett.* 4, 280–285. <https://doi.org/10.1021/acs.estlett.7b00187>.
- Huang, L., Wang, H., Wang, C., Zhao, J., Zhang, B., 2017. Microwave-assisted surface modification for the separation of polycarbonate from polymethylmethacrylate and polyvinyl chloride waste plastics by flotation. *Waste Manag. Res.* 35 (3), 294–300. <https://doi.org/10.1177/0734242x16682078>.
- Huang, Y., Liu, Q., Jia, W., Yan, C., Wang, J., 2020. Agricultural plastic mulching as a source of microplastics in the terrestrial environment. *Environ. Pollut.* 260, 114096. <https://doi.org/10.1016/j.envpol.2020.114096>.
- Hufnagl, B., Steiner, D., Renner, E., Löder, M.G.J., Laforsch, C., Löhniger, H., 2019. A methodology for the fast identification and monitoring of microplastics in environmental samples using random decision forest classifiers. *Anal. Method. UK* 11 (17), 2277–2285. <https://doi.org/10.1039/c9ay00252a>.
- Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. *Environ. Sci. Technol.* 52 (13), 7409–7417. <https://doi.org/10.1021/acs.est.8b01517>.
- Imhof, H.K., Schmid, J., Niessner, R., Ivleva, N.P., Laforsch, C., 2012. A novel, highly efficient method for the separation and quantification of plastic particles in sediments of aquatic environments. *Limnol Oceanogr. Methods* 10, 524–537. <https://doi.org/10.4319/lom.2012.10.524>.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. *Science (New York, N.Y.)*. *Mar. Pollut.* 347, 768–771. <https://doi.org/10.1126/science.1260352>.
- Jiang, H., Zhang, Y., Wang, H., 2020. Surface reactions in selective modification: the prerequisite for plastic flotation. *Environ. Sci. Technol.* 54 (16), 9742–9756. <https://doi.org/10.1021/acs.est.9b07861>.
- Jung, M.R., Horgen, F.D., Orski, S.V., Rodriguez, C.V., Beers, K.L., Balazs, G.H., Todd Jones, T., Work, T.M., Brignac, K.C., Royer, S.J., Hyrenbach, K.D., Jensen, B.A., Lynch, J.M., 2018. Validation of ATR-FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. *Mar. Pollut. Bull.* 127, 704–716. <https://doi.org/10.1016/j.marpolbul.2017.12.061>.
- Kaeppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K.-J., Voit, B., 2016. Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both? *Anal. Bioanal. Chem.* 408 (29), 8377–8391. <https://doi.org/10.1007/s00216-016-9956-3>.
- Kaeppler, A., Fischer, M., Scholz-Boettcher, B.M., Oberbeckmann, S., Labrenz, M., Fischer, D., Voit, B., 2018. Comparison of mu-ATR-FTIR spectroscopy and py-GCMS as identification tools for microplastic particles and fibers isolated from river sediments. *Anal. Bioanal. Chem.* 410 (21), 5313–5327. <https://doi.org/10.1007/s00216-018-1185-5>.
- Kaeppler, A., Windrich, F., Löder, M.G.J., Malanin, M., Fischer, D., Labrenz, M., Voit, B., 2015. Identification of microplastics by FTIR and Raman microscopy: a novel silicon filter substrate opens the important spectral range below 1300 cm⁻¹ for FTIR transmission measurements. *Anal. Bioanal. Chem.* 407 (22), 6791–6801. <https://doi.org/10.1007/s00216-015-8850-8>.
- Kappenberg, A., Blaesing, M., Lehndorff, E., Amelung, W., 2016. Black carbon assessment using benzene polycarboxylic acids: limitations for organic-rich matrices. *Org. Geochem.* 94, 47–51. <https://doi.org/10.1016/j.orggeochem.2016.01.009>.
- Karlsson, T.M., Vethaak, A.D., Almroth, B.C., Ariese, F., van Velzen, M., Hasselov, M., Leslie, H.A., 2017. Screening for microplastics in sediment, water, marine invertebrates and fish: method development and microplastic accumulation. *Mar. Pollut. Bull.* 122 (1–2), 403–408. <https://doi.org/10.1016/j.marpolbul.2017.06.081>.
- Kumar, M., Xiong, X., He, M., Tsang, D.C.W., Gupta, J., Khan, E., Bolan, N.S., 2020. Microplastics as pollutants in agricultural soils. *Environ. Pollut.* 265 (PTA) <https://doi.org/10.1016/j.envpol.2020.114980>.
- Kumar, P., Li, A., Ma, J., Kuang, Y., Luo, L., Sun, X., 2018. Density gradient ultracentrifugation for colloidal nanostructures separation and investigation. *Sci. Bull.* 63, 645–662. <https://doi.org/10.1016/j.scib.2018.04.014>.
- Laborda, F., Bolea, E., Cepria, G., Gomez, M.T., Jimenez, M.S., Perez-Arantegui, J., Castillo, J.R., 2016. Detection, characterization and quantification of inorganic engineered nanomaterials: a review of techniques and methodological approaches for the analysis of complex samples. *Anal. Chim. Acta* 904, 10–32. <https://doi.org/10.1016/j.aca.2015.11.008>.
- Lan, T., Wang, T., Cao, F., Yu, C., Chu, Q., Wang, F., 2021. A comparative study on the adsorption behavior of pesticides by pristine and aged microplastics from agricultural polyethylene soil films. *Ecotoxicol. Environ. Saf.* 209 <https://doi.org/10.1016/j.ecoenv.2020.111781>.
- Lei, L., Wu, S., Lu, S., Liu, M., Song, Y., Fu, Z., Shi, H., Kathleen, M.R.S., He, D., 2018. Microplastic particles cause intestinal damage and other adverse effects in zebrafish *Danio rerio* and nematode *Caenorhabditis elegans*. *Sci. Total Environ.* 619–620, 1–8.
- Lenz, R., Enders, K., Nielsen, T.G., 2016. Microplastic exposure studies should be environmentally realistic. *Proc. Natl. Acad. Sci. U.S.A.* 113 (29), E4121–E4122. [doi:10.1073/pnas.1606615113](https://doi.org/10.1073/pnas.1606615113).
- Lenz, R., Enders, K., Stedmon, C.A., Mackenzie, D.M.A., Nielsen, T.G., 2015. A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. *Mar. Pollut. Bull.* 100 (1), 82–91. <https://doi.org/10.1016/j.marpolbul.2015.09.026>.
- Leslie, H.A., Brandsma, S.H., van Velzen, M.J.M., Vethaak, A.D., 2017. Microplastics en route: field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. *Environ. Int.* 101, 133–142. <https://doi.org/10.1016/j.envint.2017.01.018>.
- Li, J., Liu, H., Chen, J.P., 2018. Microplastics in freshwater systems: a review on occurrence, environmental effects, and methods for microplastics detection. *Water Res.* 137, 362–374. <https://doi.org/10.1016/j.watres.2017.12.056>.
- Li, L., Luo, Y., Li, R., Zhou, Q., Peijnenburg, W.J.G.M., Yin, N., Zhang, Y., 2020. Effective uptake of submicrometre plastics by crop plants via a crack-entry mode. *Nat. Sustain.* 3 (11), 929–937. <https://doi.org/10.1038/s41893-020-0567-9>.
- Liebezeit, G., Dubaish, F., 2012. Microplastics in beaches of the east Frisian islands spiekeroog and kachelotplate. *Bull. Environ. Contam. Toxicol.* 89 (1), 213–217. <https://doi.org/10.1007/s00128-012-0642-7>.
- Liu, M., Lu, S., Song, Y., Lei, L., Hu, J., Lv, W., He, D., 2018. Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai, China. *Environ. Pollut.* 242, 855–862. <https://doi.org/10.1016/j.envpol.2018.07.051>.
- Liu, M., Song, Y., Lu, S., Qiu, R., Hu, J., Li, X., He, D., 2019. A method for extracting soil microplastics through circulation of sodium bromide solutions. *Sci. Total Environ.* 691, 341–347. <https://doi.org/10.1016/j.scitotenv.2019.07.144>.
- Löder, M.G.J., Gerds, G., 2015. Methodology used for the detection and identification of microplastics—a critical appraisal. *Mari. Anthropol. Lit.* 201–227. https://doi.org/10.1007/978-3-319-16510-3_8.
- Löder, M.G.J., Imhof, H.K., Ladehoff, M., Loeschel, L.A., Lorenz, C., Mintenig, S., Gerds, G., 2017. Enzymatic purification of microplastics in environmental samples. *Environ. Sci. Technol.* 51 (24), 14283–14292. <https://doi.org/10.1021/acs.est.7b03055>.
- Löder, M.G.J., Kuczera, M., Mintenig, S., Lorenz, C., Gerds, G., 2015. Focal plane array detector-based micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples. *Environ. Chem.* 12 (5), 563–581. <https://doi.org/10.1071/en14205>.
- Lorenzo-Navarro, J., Castrillon-Santana, M., Sanchez-Nielsen, E., Zarco, B., Herrera, A., Martinez, I., Gomez, M., 2021. Deep learning approach for automatic microplastics counting and classification. *Sci. Total Environ.* 765 <https://doi.org/10.1016/j.scitotenv.2020.142728>.
- Lu, S., Zhu, K., Song, W., Song, G., Chen, D., Hayat, T., Alharbi, N.S., Chen, C., Sun, Y., 2018. Impact of water chemistry on surface charge and aggregation of polystyrene microspheres suspensions. *Sci. Total Environ.* 630, 951–959. <https://doi.org/10.1016/j.scitotenv.2018.02.296>.
- Lusher, A.L., Welden, N.A., Sobral, P., Cole, M., 2017. Sampling, isolating and identifying microplastics ingested by fish and invertebrates. *Anal. Method. UK* 9 (9), 1346–1360. <https://doi.org/10.1039/c6ay02415g>.
- Maes, T., Jessop, R., Wellner, N., Haupt, K., Mayes, A.G., 2017. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. *Sci. Rep-UK* 7. <https://doi.org/10.1038/srep44501>.
- Mahat, S., 2017. Separation and quantification of microplastics from beach and sediment samples using the Bauta microplastic-sediment separator. Masters Thesis. Norwegian University of Life Sciences.
- Majewsky, M., Bitter, H., Eiche, E., Horn, H., 2016. Determination of microplastic polyethylene (PE) and polypropylene (PP) in environmental samples using thermal analysis (TGA-DSC). *Sci. Total Environ.* 568, 507–511.

- Mallikarjunachari, G., Ghosh, P., 2016. Analysis of strength and response of polymer nano thin film interfaces applying nanoindentation and nanoscratch techniques. *Polymer* 90, 53–66. <https://doi.org/10.1016/j.polymer.2016.02.042>.
- Mani, T., Frehland, S., Kalberer, A., Burkhardt-Holm, P., 2019. Using castor oil to separate microplastics from four different environmental matrices. *Anal. Method. UK* 11 (13), 1788–1794. <https://doi.org/10.1039/c8ay02559b>.
- Michielssen, M.R., Michielssen, E.R., Ni, J., Duhaime, M.B., 2016. Fate of microplastics and other small anthropogenic litter (SAL) in wastewater treatment plants depends on unit processes employed. *Environ. Sci. Wat. Res.* 2 (6), 1064–1073. <https://doi.org/10.1039/c6ew00207b>.
- Mintenig, S.M., Int-Veen, I., Loder, M.G.J., Primpke, S., Gerdt, G., 2017. Identification of microplastic in effluents of waste water treatment plants using focal plane arraybased micro-Fourier-transform infrared imaging. *Water Res.* 365–372 <http://dx.doi.org/10.1016/j.watres.2016.11.015>.
- Mintenig, S.M., Bduerlein, P.S., Koelmans, A.A., Dekker, S.C., van Wezel, A.P., 2018. Closing the gap between small and smaller: towards a framework to analyse nano- and microplastics in aqueous environmental samples. *Environ. Sci. Nano.* 5 <https://doi.org/10.1039/C8EN00186C>.
- Möller, J.N., Löder, M.G.J., Laforsch, C., 2020. Laforsch. Finding microplastics in soils: a review of analytical methods. *Environ. Sci. Technol.* 54 (4), 2078–2090.
- Möller, J.N., Heisel, I., Satzger, A., Vizsolyi, E.C., Oster, S.D.J., Agarwal, S., Löder, M.G.J., 2021. Tackling the challenge of extracting microplastics from soils: a protocol to purify soil samples for spectroscopic analysis. *Environ. Toxicol. Chem.* <https://doi.org/10.1002/etc.5024>.
- Munno, K., Helm, P.A., Jackson, D.A., Rochman, C., Sims, A., 2018. Impacts of temperature and selected chemical digestion methods on microplastic particles. *Environ. Toxicol. Chem.* 37 (1), 91–98. <https://doi.org/10.1002/etc.3935>.
- Murphy, F., Ewins, C., Carbonnier, F., Quinn, B., 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. *Environ. Sci. Technol.* 50 (11), 5800–5808. <https://doi.org/10.1021/acs.est.5b05416>.
- Nguyen, B., Claveau-Mallet, D., Hernandez, L.M., Xu, E.G., Farmer, J.M., Tufenkji, N., 2019. Separation and analysis of microplastics and nanoplastics in complex environmental samples. *Acc. Chem. Res.* 52 (4), 858–866. <https://doi.org/10.1021/acs.accounts.8b00602>.
- Nuelle, M.T., Dekiff, J.H., Remy, D., Fries, E., 2014. A new analytical approach for monitoring microplastics in marine sediments. *Environ. Pollut.* 184, 161–169. <https://doi.org/10.1016/j.envpol.2013.07.027>.
- Pansare, V.J., Tien, D., Thoniyot, P., Prud'homme, R.K., 2017. Ultrafiltration of nanoparticle colloids. *J. Membr. Sci.* 538, 41–49. <https://doi.org/10.1016/j.memsci.2017.03.041>.
- Piehl, S., Leibner, A., Löder, M.G.J., Dris, R., Bogner, C., Laforsch, C., 2018. Identification and quantification of macro- and microplastics on an agricultural farmland. *Sci Rep-UK* 8. <https://doi.org/10.1038/s41598-018-36172-y>.
- Pitt, J.A., Trevisan, R., Massarsky, A., Kozal, J.S., Levin, E.D., Di Giulio, R.T., 2018. Maternal transfer of nanoplastics to offspring in zebrafish (*Danio rerio*): a case study with nanopolystyrene. *Sci. Total Environ.* 643, 324–334. <https://doi.org/10.1016/j.scitotenv.2018.06.186>.
- Plastics Europe, 2018. Plastics-the Facts 2019: an Analysis of European Plastics Production, Demand and Waste Data. www.plasticseurope.org.
- Prestel, H., Niessner, R., Panne, U., 2006. Increasing the sensitivity of asymmetrical flow field-flow fractionation: slot outlet technique. *Anal. Chem.* 78, 6664–6669. <https://doi.org/10.1021/ac060259l>.
- Primpke, S., Lorenz, C., Rascher-Friesenhausen, R., Gerdt, G., 2017. An automated approach for microplastics analysis using focal plane array (FPA) FTIR microscopy and image analysis. *Anal. Method. UK* 9 (9), 1499–1511. <https://doi.org/10.1039/c6ay02476a>.
- Qi, Y., Yang, X., Mejia Pelaez, A., Huerta Lwanga, E., Beriot, N., Gertsen, H., Geissen, V., 2018. Macro- and micro- plastics in soil-plant system: effects of plastic mulch film residues on wheat (*Triticum aestivum*) growth. *Sci. Total Environ.* 645, 1048–1056. <https://doi.org/10.1016/j.scitotenv.2018.07.229>.
- Renner, G., Schmidt, T.C., Schram, J., 2017. Characterization and quantification of microplastics by infrared spectroscopy. *Compr. Anal. Chem.* 75, 67–118.
- Renner, G., Schmidt, T.C., Schram, J., 2018. Analytical methodologies for monitoring micro(nano)plastics: which are fit for purpose? *Curr. Opin. Environ. Sci. Health* 1 (Sp. Iss. SI), 55–61. <https://doi.org/10.1016/j.coesh.2017.11.001>.
- Rezania, S., Park, J., Md Din, M.F., Mat Taib, S., Talaiekhosani, A., Kumar Yadav, K., Kamyab, H., 2018. Microplastics pollution in different aquatic environments and biota: a review of recent studies. *Mar. Pollut. Bull.* 133, 191–208. <https://doi.org/10.1016/j.marpolbul.2018.05.022>.
- Rillig, M.C., 2012. Microplastic in terrestrial ecosystems and the soil? *Environ. Sci. Technol.* 46 (12), 6453–6454. <https://doi.org/10.1021/es302.011r>.
- Rist, S., Baun, A., Hartmann, N.B., 2017. Ingestion of micro- and nanoplastics in *Daphnia magna* - quantification of body burdens and assessment of feeding rates and reproduction. *Environ. Pollut.* 228, 398–407. <https://doi.org/10.1016/j.envpol.2017.05.048>.
- Rocha-Santos, T., Duarte, A.C., 2015. A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. *Trac. Trends Anal. Chem.* 65, 47–53. <https://doi.org/10.1016/j.trac.2014.10.011>.
- Roussis, S.G., Fedora, J.W., 1996. Use of a thermal extraction unit for furnace-type pyrolysis: suitability for the analysis of polymers by pyrolysis/GC/MS. *Rapid Commun. Mass Spectrom.* 10 (1), 82–90. [https://doi.org/10.1002/\(sici\)1097-0231\(19960115\)](https://doi.org/10.1002/(sici)1097-0231(19960115)).
- Ruggero, F., Gori, R., Lubello, C., 2020. Methodologies for microplastics recovery and identification in heterogeneous solid matrices: a review. *J. Polym. Environ.* 28 (3), 739–748. <https://doi.org/10.1007/s10924-019-01644-3>.
- Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss floodplain soils. *Environ. Sci. Technol.* 52 (6), 3591–3598. <https://doi.org/10.1021/acs.est.7b06003>.
- Schleuss, U., Muller, F., 2001. Requirements for soil sampling in the context of ecosystem research. *Sci. Total Environ.* 264 (1–2), 193–197. [https://doi.org/10.1016/S0048-9697\(00\)00624-0](https://doi.org/10.1016/S0048-9697(00)00624-0).
- Schwaferts, C., Niessner, R., Elsner, M., Ivleva, N.P., 2019. Methods for the analysis of submicrometer- and nanoplastic particles in the environment. *Trac. Trends Anal. Chem.* 112, 52–65. <https://doi.org/10.1016/j.trac.2018.12.014>.
- Sharma, M.D., Elanjickal, A.L., Mankar, J.S., Krupadam, R.J., 2020. Assessment of cancer risk of microplastics enriched with polycyclic aromatic hydrocarbons. *J. Hazard Mater.* 398, 122994.
- Shim, W.J., Hong, S.H., Eo, S.E., 2017. Identification methods in microplastic analysis: a review. *Anal. Method. UK* 9 (9), 1384–1391. <https://doi.org/10.1039/c6ay02558g>.
- Shim, W.J., Song, Y.K., Hong, S.H., Jang, M., 2016. Identification and quantification of microplastics using Nile Red staining. *Mar. Pollut. Bull.* 113 (1–2), 469–476. <https://doi.org/10.1016/j.marpolbul.2016.10.049>.
- Silva, A.B., Bastos, A.S., Justino, C.L.L., da Costa, J.A.P., Duarte, A.C., Rocha-Santos, T.A.P., 2018. Microplastics in the environment: challenges in analytical chemistry A review. *Anal. Chim. Acta* 1017, 1–19. <https://doi.org/10.1016/j.aca.2018.02.043>.
- Simon, M., van Alst, N., Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. *Water Res.* 142, 1–9. <https://doi.org/10.1016/j.watres.2018.05.019>.
- Tagg, A.S., Harrison, J.P., Ju-Nam, Y., Sapp, M., Bradley, E.L., Sinclair, C.J., Ojeda, J.J., 2017. Fenton's reagent for the rapid and efficient isolation of microplastics from wastewater. *Chem. Commun.* 53 (2), 372–375. <https://doi.org/10.1039/c6cc08798a>.
- Talvitie, J., Mikola, A., Koistinen, A., Setälä, O., 2017. Solutions to microplastic pollution - removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. *Water Res.* 123, 401–407. <https://doi.org/10.1016/j.watres.2017.07.005>.
- Ter Halle, A., Jeanneau, L., Martignac, M., Jarde, E., Pedrono, B., Brach, L., Gigault, J., 2017. Nanoplastic in the north atlantic subtropical gyre. *Environ. Sci. Technol.* 51 (23), 13689–13697. <https://doi.org/10.1021/acs.est.7b03667>.
- Van den Berg, P., Huerta-Lwanga, E., Corradini, F., Violette, G., 2020. Sewage sludge application as a vehicle for microplastics in eastern Spanish agricultural soils. *Environ. Pollut.* 261, 114198. <https://doi.org/10.1016/j.envpol.2020.114198>.
- Van Mourik, L.M., Crum, S., Martinez-Frances, E., van Bavel, B., Leslie, H.A., de Boer, J., Cofino, W.P., 2021. Results of WEPAL-QUASIMEME/NORMANs first global interlaboratory study on microplastics reveal urgent need for harmonization. *Sci. Total Environ.* 772 <https://doi.org/10.1016/j.scitotenv.2021.145071>.
- Van Wezel, A.P., Van Vlaardingen, P., Posthumus, R., Crommentuijn, G.H., Sijm, D., 2000. Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties. *Ecotoxicol. Environ. Saf.* 46 (3), 305–321. <https://doi.org/10.1006/eesa.2000.1930>.
- Vauthier, C., Bouchemal, K., 2009. Methods for the preparation and manufacture of polymeric nanoparticles. *Pharm. Res. (N. Y.)* 26 (5), 1025–1058. <https://doi.org/10.1007/s11095-008-9800-3>.
- Von der Kammer, F., Ferguson, P.L., Holden, P.A., Mason, A., Rogers, K.R., Klaine, S.J., Koelmans, A.A., Horne, N., Unrine, J.M., 2012. Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies. *Environ. Toxicol. Chem.* 31, 32–49. <https://doi.org/10.1002/etc.723>.
- Von Moos, N., Burkhardt-Holm, P., Koehler, A., 2012. Uptake and effects of microplastics on cells and tissue of the blue mussel *Mytilus edulis* L. after an experimental exposure. *Environ. Sci. Technol.* 46 (20), 11327–11335. <https://doi.org/10.1021/es302332w>.
- Wagner, G., Desaulles, A., Muntau, H., Theocharopoulos, S., Quevaullier, P., 2001. Harmonisation and quality assurance in pre-analytical steps of soil contamination studies - conclusions and recommendations of the CEEM Soil project. *Sci. Total Environ.* 264 (1–2), 103–117. [https://doi.org/10.1016/S0048-9697\(00\)00614-8](https://doi.org/10.1016/S0048-9697(00)00614-8).
- Wahl, A., Le Juge, C., Davranche, M., El Hadri, H., Grassl, B., Reynaud, S., Gigault, J., 2021. Nanoplastic occurrence in a soil amended with plastic debris. *Chemosphere* 262. <https://doi.org/10.1016/j.chemosphere.2020.127784>.
- Wallace, H., 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. *EFSA J.* 14, e04501.
- Wan, Y., Wu, C.X., Xue, Q., Hui, X.M.N., 2019. Effects of plastic contamination on water evaporation and desiccation cracking in soil. *Sci. Total Environ.* 654, 576–582.
- Wang, F.Y., Zhang, X.Q., Zhang, S.Q., Zhang, S.W., Sun, Y.H., 2020a. Interactions of microplastics and cadmium on plant growth and arbuscular mycorrhizal fungal communities in an agricultural soil. *Chemosphere* 254, 126791.
- Wang, W., Ge, J., Yu, X., Li, H., 2020b. Environmental fate and impacts of microplastics in soil ecosystems: progress and perspective. *Sci. Total Environ.* 708, 134841 <https://doi.org/10.1016/j.scitotenv.2019.134841>.
- Weber, C.J., Weihrach, C., Opp, C., Chiffard, P., 2020. Investigating microplastic dynamics in soils: orientation for sampling strategies and sample pre-processing. *Land Degrad. Dev.* 32 (1), 270–284.
- Woodall, L.C., Gwinnett, C., Packer, M., Thompson, R.C., Robinson, L.F., Paterson, G.L.J., 2015. Using a forensic science approach to minimize environmental contamination and to identify microfibrils in marine sediments. *Mar. Pollut. Bull.* 95 (1), 40–46. <https://doi.org/10.1016/j.marpolbul.2015.04.044>.
- Xu, G., Cheng, H., Jones, R., Feng, Y., Gong, K., Li, K., Fang, X., Tahir, M.A., Valev, V.K., Zhang, L., 2020a. Surface-enhanced Raman spectroscopy facilitates the detection of microplastics <1 μm in the environment. *Environ. Sci. Technol.* 0c02317 <https://doi.org/10.1021/acs.est.0c02317>.
- Xu, Q., Gao, Y., Xu, L., Shi, W., Wang, F., LeBlanc, G.A., Lei, K., 2020b. Investigation of the microplastics profile in sludge from China's largest water reclamation plant

- using a feasible isolation device. *J. Hazard Mater.* 388 <https://doi.org/10.1016/j.jhazmat.2020.122067>.
- Xu, R., 2015. Light scattering: a review of particle characterization applications. *Particuology* 18, 11–21. <https://doi.org/10.1016/j.partic.2014.05.002>.
- Zhang, B., Yang, X., Chen, L., Chao, J., Teng, J., Wang, Q., 2020. Microplastics in soil: a review of possible sources, analytical methods and ecological impacts. *J. Chem. Technol. Biotechnol.* <https://doi.org/10.1002/jctb.6334>.
- Zhang, G.S., Liu, Y.F., 2018. The distribution of microplastics in soil aggregate fractions in southwestern China. *Sci. Total Environ.* 642, 12–20. <https://doi.org/10.1016/j.scitotenv.2018.06.004>.
- Zhang, G.S., Zhang, F.X., Li, X.T., 2019a. Effects of polyester microfibers on soil physical properties: perception from a field and a pot experiment. *Sci. Total Environ.* 670, 1–7.
- Zhang, S., Yang, X., Gertsen, H., Peters, P., Salanki, T., Geissen, V., 2018. A simple method for the extraction and identification of light density microplastics from soil. *Sci. Total Environ.* 616, 1056–1065. <https://doi.org/10.1016/j.scitotenv.2017.10.213>.
- Zhang, T.R., Wang, C.X., Dong, F.Q., Gao, Z.Y., Zhang, C.J., Zhang, X.J., Zhang, J.P., 2019b. Uptake and translocation of styrene maleic anhydride nanoparticles in *Murraya exotica* plants as revealed by noninvasive, real-time optical bioimaging. *Environ. Sci. Technol.* 53 (3), 1471–1481. <https://doi.org/10.1021/acs.est.8b05689>.
- Zhao, S., Danley, M., Ward, J.E., Li, D., Mincer, T.J., 2017. An approach for extraction, characterization and quantitation of microplastic in natural marine snow using Raman microscopy. *Anal. Method.* UK 9 (9), 1470–1478. <https://doi.org/10.1039/c6ay02302a>.
- Zhao, S., Zhu, L., Li, D., 2015. Microplastic in three urban estuaries. *China. Environ. Pollut.* 206, 597–604.
- Zhou, Q., Zhang, H., Fu, C., Zhou, Y., Dai, Z., Li, Y., Luo, Y., 2018. The distribution and morphology of microplastics in coastal soils adjacent to the Bohai Sea and the Yellow Sea. *Geoderma* 322, 201–208. <https://doi.org/10.1016/j.geoderma.2018.02.015>.
- Zhou, X.X., Liu, R., Hao, L.T., Liu, J.F., 2021a. Identification of polystyrene nanoplastics using surface enhanced Raman spectroscopy. *Talanta* 221. <https://doi.org/10.1016/j.talanta.2020.121552>.
- Zhou, X.X., He, S., Gao, Y., Li, Z.C., Chi, H.Y., Li, C.J., 2021b. Protein corona-mediated extraction for quantitative analysis of nanoplastics in environmental waters by pyrolysis gas chromatography/mass spectrometry. *Anal. Chem.* 93 (17), 6698–6705. <https://doi.org/10.1021/acs.analchem.1c00156>.
- Zobkov, M.B., Esiukova, E.E., 2017. Evaluation of the Munich Plastic Sediment Separator efficiency in extraction of microplastics from natural marine bottom sediments. *Limnol Oceanogr. Methods* 15 (11), 967–978. <https://doi.org/10.1002/lom3.10217>.