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Review

Analytical methods and environmental processes of nanoplastics

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ABSTRACT

The degradation of plastic debris may result in the generation of nanoplastics (NPs). Their high specific surface area for the sorption of organic pollutions and toxic heavy metals and possible transfer between organisms at different nutrient levels make the study of NPs an urgent priority. However, there is very limited understanding on the occurrence, distribution, abundant, and fate of NPs in the environment, partially due to the lack of suitable techniques for the separation and identification of NPs from complex environmental matrices. In this review, we first overviewed the state-of-the-art methods for the extraction, separation, identification and quantification of NPs in the environment. Some of them have been successfully applied for the field determination of NPs, while some are borrowed from the detection of microplastics or engineered nanomaterials. Then the possible fate and transport of NPs in the environment are thoroughly described. Although great efforts have been made during the recent years, large knowledge gaps still exist, such as the relatively high detection limit of existing method failing to detect ultralow masses of NPs in the environment, and spherical polystyrene NP models failing to represent the various compositions of NPs with different irregular shapes, which needs further investigation.

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Introduction

Plastics are cheap, lightweight and kind of durable, which made them useful in a wide range of applications. Especially in the field of packaging, plastic items such as the disposable plastic bags make our life much more convenient, and can be found in every corner of our everyday life. The world's production of plastics is growing exponentially since the large-scale manufacture in the 1950s, which reached about 335 mil-

lion metric tons in 2016 (Geyer et al., 2017). At the same time, large amounts of plastic wastes were generated, of which only about 9% were recycled, and the vast majority of them were ended up in the landfills or directly released into the natural system (Geyer et al., 2017). For example, it is calculated that about 275 million metric tons of plastic wastes were produced in 192 coastal countries in 2010, of which 4.8 to 12.7 million metric tons entered the ocean (Jambeck et al., 2015). The photo-oxidation by UV radiation, mechanical abrasion by sand and sea wave, and biological degradation by organisms may make the plastics brittle, resulting in the formation of small debris (Ivleva et al., 2017). In a previous study that simulating a beach environment in the laboratory by expos-

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ing different plastic fragmentations to UV irradiation and mechanical abrasion with sand, it was found that tens of thousands of plastic particles were produced per pellet after 12-month UV exposure and 2-month mechanical abrasion, indicating the generation of small plastic particles in the environment (Song et al., 2017). Meanwhile, plastic beads are also widely incorporated in our daily personal care products, such as shampoos, facial and body scrubs, and toothpaste (Ivleva et al., 2017). The production and use of these items also lead to the release of plastic pellets into the environment. It is estimated that more than 5 trillion plastic pieces weighing over 250,000 tons were floating on the global oceans (Eriksen et al., 2014), which pose a great threat to the natural ecosystem.

Of the plastic debris, particles with the size smaller than 5 mm have been paid special attention, due to the fact that small pellets are more easily swallowed or filter-fed by marine biota (Law and Thompson, 2014). Due to the irregular shape of plastic fragments, they may cause adverse effects on the ingesting organisms such as the internal abrasions or the blockage of gastrointestinal tracts, leading to the organisms starving to death (Ivleva et al., 2017). The decreased feeding, reduced growth rates, inhibited hatching, and abnormal behaviors were also reported (Besseling et al., 2014; Lei et al., 2018; Pikuda et al., 2019). The large surface area facilitates the adsorption and accumulation of organic pollutions and toxic heavy metals (Law and Thompson, 2014; Wang et al., 2020), such as polychlorinated biphenyls, dichlorodiphenyltrichloroethane, polybrominated diphenyl ethers, Cd^{2+} , Cu^{2+} , and Zn^{2+} , making the plastic pieces act as vectors to enhance the transfer of harmful chemicals. Additionally, different kinds of additives are incorporated in plastics, such as plasticizers and flame retardants (Chen et al., 2018; Guo et al., 2019; Morin et al., 2017), and the release of these toxic contaminants is also a concern.

Typically, plastic particles with the size ranging from 5 mm to 1 μm are referred to microplastics (MPs) (Ivleva et al., 2017) and with the size between 1000 nm and 1 nm are called nanoplastics (NPs) (Gigault et al., 2018). However, the clear definition of MPs and NPs is still under debate. In some studies, the classification of NPs followed the European Commission's definitions for engineered nanomaterials (ENMs) that with at least one dimension between 1 and 100 nm (Alimi et al., 2018; Schwaferts et al., 2019). In this study, NPs are defined as particles within a size ranging from 1 to 1000 nm, which is most frequently used in the literature. Currently, much emphasis has been focused on the generation, analysis, fate, effects and removal of MPs in the environment (Ivleva et al., 2017; Ma et al., 2019). Just search the key word of “microplastics” on the website of “Web of Science”, and more than 3100 items were listed, while studies on the topic of NPs are much less. MPs have been widely detected in natural waters (McCormick et al., 2014; Su et al., 2016), marine organisms (Li et al., 2016; Li et al., 2015), sediments (Klein et al., 2015; Peng et al., 2017a), even in the table salts (Kim et al., 2018; Yang et al., 2015), and tap water (Kniggendorf et al., 2019). However, the detection of NPs in the environment is rare, which raises the question that whether the plastic pieces fragmenting into NPs occurs (Bouwmeester et al., 2015). Theoretically, the degradation process of plastics does not stop just at the mm or the μm range, the ongoing external weathering would make MPs continue to break down to generate NPs (Lehner et al., 2019). Actually, recent studies found that several polymer nanoparticles including polyethylene terephthalate (PET), polystyrene (PS), polyethylene (PE), and polyvinyl chloride (PVC) were present in the North Atlantic subtropical gyre (Ter Halle et al., 2017) and the high-altitude Alpine snow (Materić et al., 2020), proving the existence of NPs in the environment.

One of the key reasons for the limited reports on NPs is the lack of practical methods for the analysis of NPs in the environment, which further hinders the accurate prediction of the potential risks of NPs and their possible effects on the human health. Although multiple techniques have been developed for the separation, identification and quantification of MPs in different matrices, and several reviews have extensively summarized the analysis of MPs in the environment (Möller et al., 2020; Nguyen et al., 2019; Schwaferts et al., 2019; Zarfl, 2019), majority of the methods are not suitable for the determination of NPs due to the size discrimination of MPs and NPs. Even for the same type of plastics, when the size drops down to the nano-scale, the chemical and physical properties would change significantly compared with their micron-sized counterparts, making the capture of these pellets much more difficult. For example, flotation is frequently used to separate MPs from denser sediment with high efficiency; however, the buoyant force for NPs is too low to achieve the separation, and the small size of NPs also hinders their recovery from the air-liquid interface, making this method fail to isolate NPs (Nguyen et al., 2019). In this review, we aim to give a critical overview over the methods developed specially for the separation, determination and quantification of NPs in the environment, and the potential solutions that can be possibly used in the NP analysis are also included. Then, we summarized the fate and transport of NPs reported in previous studies, which would be effective to elucidate possible environmental behaviors in the environment.

1. Pretreatment of the samples

1.1. Sample digestion

Environmental samples may contain abundant organic matters, especially for the complex matrices such as wastewater, biota, soil, and sediments. Even in the freshwater system, NPs are always covered by biofilms or associated with organisms, which makes the analysis of NPs very difficult. Therefore, a pretreatment process to remove the organic fractions in the samples is always needed. Although studies on the determination of NPs are really scarce, some purification methods for MPs are also applicable due to the similar chemical constitutions. Two main approaches have been extensively reported in the literature, i.e. chemical degradation and enzymatic digestion (Zarfl, 2019).

In the first method, different chemicals, including acids (HCl and HNO_3), alkalis (NaOH and KOH), oxidizing agents (H_2O_2), and surfactants (sodium dodecylsulfate, SDS) are frequently used to treat the samples. However, most of the studies just mentioned in the Methods section that a certain chemical was used to digest the samples, and the digestion efficiency and whether the chemicals damage the MPs were not evaluated. Only several reports thoroughly assessed the applicability of each protocols (Cole et al., 2014; Dehaut et al., 2016; Hurley et al., 2018; Prata et al., 2019; Tagg et al., 2015). Strong acids, such as HCl and HNO_3 , and SDS showed insufficient reduction in organic matter contents (Cole et al., 2014; Prata et al., 2019). Even conducted at a high temperature (50 °C) for 1 hr, HNO_3 and SDS solutions could degrade about 40% and 30% of a pool of natural organic matter, including vegetable matters, animal matters, oils and paraffins, only a little higher or even lower than the control (Prata et al., 2019). Alkalis (NaOH and KOH) are more efficient for the digestion of animal tissues (Dehaut et al., 2016; Prata et al., 2019), and the digestion efficiency is much higher, especially at a high concentration and temperature. Cole et al. reported that 91.3% of natural plankton samples could be digested at an

optimized alkaline decomposition protocol (10 M NaOH at 60 °C, 24 hr) (Cole et al., 2014). However, partial degradation of Nylon fibres, PET and polycarbonate (PC) particles, melting of PE fragments, and weathering of PVC granules were observed for the alkaline treatment (Cole et al., 2014; Hurley et al., 2018).

The hydrogen peroxide solution (30%) was widely adapted for the digestion of organic matrix in wastewater (Dyachenko et al., 2017; Mason et al., 2016; Mintenig et al., 2017). According to Tagg et al. (2015), a 30% H₂O₂ pretreatment step (7 days) could efficiently remove the organic matter content in wastewater, resulting in a dramatic improvement of the filtration rate. Moreover, the Fourier-transform infrared (FTIR) spectra of MPs unchanged after H₂O₂ digestion, which did not influence the following identification. Another study (Hurley et al., 2018) showed that polyamide 66 (PA 66) could be damaged after exposed to H₂O₂ at concentrations higher than 30%, and treating polypropylene (PP) with 30% H₂O₂ at 70 °C also resulted in significant size reduction. Thus, for samples contained these target materials, special care should be taken when using H₂O₂ as the digestion solution. Fenton's reagent (H₂O₂ + Fe²⁺) was identified as the most suitable protocol to degrade complex matrices of environmental samples (Hurley et al., 2018; Prata et al., 2019). Even for soils and sludges, more than 86% of organic contents can be readily removed after the treatment, which was much higher than other acid or alkali based methods. Moreover, the commonly used polymer types, including PP, low density PE, high density PE, PS, PET, PA 66, PC, and poly(methyl-methacrylate) (PMMA), could escape from the digestion, and did not show any form of physical disintegration (Hurley et al., 2018).

Enzymatic digestion is proved to be a useful approach to purify plastic particles from complex environmental samples. After optimizing the digestion procedure, Cole et al. (2014) revealed that >97% (by weight) of the matrices in plankton-rich seawater samples can be digested by using an efficient enzyme Proteinase-K without damaging the MPs present. Similar digestion efficiency was also reported in the separation of MPs in mussels (Karlsson et al., 2017). However, the main problem of this method is the high price of Proteinase-K that is widely used in molecular biology applications. Although other inexpensive enzymes such as protease and trypsin are also identified to be efficient to decompose organic components (Catarino et al., 2017; Courtenne-Jones et al., 2017), the main targets of these enzyme are animal tissues. Löder et al. developed a sequential enzymatic purification method (Löder et al., 2017) which is suitable for the digestion of different types of environmental samples, such as wastewater, sediment, biota and food samples. In this study, based on the specific organic compounds, different sets of enzymes can be used, and the multi-step of enzymatic digestion followed by H₂O₂ treatment can significantly improve the digestion efficiency. However, the complicated procedures and the relative long digestion time (several days) may resist the widespread use of this approach.

1.2. Membrane filtration

Membrane filtration is commonly used for the separation of particulate matters from water samples, due to its easy-handling, high efficiency, and desirable enrichment factors. Membranes with varying pore sizes (from several µm to dozens of nm) enable the fractionation of different sized NPs. By using a 2.5 µm cellulose filter, Hernandez et al. (2019) readily separated MPs and NPs in the teabag leachate after plastic teabags were steeped at 95 °C. Polytetrafluoroethylene (PTFE) filters with a pore size of 0.2 µm were also utilized to sort NPs from MPs in the melted Alpine snow samples (Materić et al., 2020). One of the main advantages is that the size and morphology of NPs kept on the filter could be conserved, and fur-

ther identification and quantification are available. However, when the pore size is down to the nm range, the membrane fouling would slow down the filtration process (Abdelrasoul et al., 2017), and the possible damage of pore structures makes the valid volume of samples that can be filtered largely decreased. Commonly, the cost is much higher for smaller pore sized membranes of the same materials, which makes the analysis of samples with large volumes impossible. An expedient approach is a sequential filtration process with diverse pore sized membranes. Hernandez et al. (2017) conducted a five-step filtration by using membranes with pore sizes of 25 µm, 2.5 µm, 0.45 µm and two times of 0.1 µm for the size selection of PE NPs in facial scrubs (Fig. 1), which would reduce the clogging of pores to some extent.

As several membrane materials can strongly adsorb ENMs (Zhou et al., 2017), the adsorption of NPs should also be considered. However, the filtration efficiency and recoveries of NPs are seldom evaluated, which may affect the accurate quantification of NPs in the following analysis.

1.3. Ultrafiltration

Ultrafiltration is another noteworthy method allowing the pre-concentration, separation, and purification of NPs at the same time. A hydrostatic force is applied on a nano-porous membrane to allow the isolation of particles from the solution (Majedi and Lee, 2016). After ultrafiltration, a low volume of the solvent is retained, which facilitates the particle collection and largely reduces sample loss and particle alteration or aggregation. When analyzing NPs in the North Atlantic subtropical gyre (Ter Halle et al., 2017), 1 L of filtered seawater can be concentrated to a volume of 10 mL by using an 8200-Amicon-stirred polysulfone (10 kDa)-based cell, with an enrichment factor of 100. Crossflow ultrafiltration is also used for the separation of NPs in drinking water samples. Although reproducible, the recovery of the 50 nm PS spheres was extremely low (only 12.7%) (Mintenig et al., 2018), which needs further optimization to increase the method efficacy.

1.4. Field flow fractionation

Field flow fractionation (FFF) is a powerful tool for the separation of ENMs (Tan et al., 2015, 2017), and can also be adapted for the size discrimination of NPs in the environment. Gigault et al. (2017) proposed an optimized asymmetrical flow FFF (AF4) method that can sort PS NPs with the whole colloidal size range from 1 to 800 nm. Adjusting the relaxation and elution parameters (without changing the mobile phase composition and channel components) could also allow high-resolution discrimination of the subfractions: 10–100 nm, 100–200 nm, 200–450 nm, and 450–800 nm in diameter, showing the powerful separation capability of AF4. The method is also applied for the isolation of NPs in environmental waters and marine food products (Correia and Loeschner, 2018; Mintenig et al., 2018). After enzymatic digestion, PS NPs (100 nm) in fish can be successfully separated and further characterized by AF4 coupled to multi-angle light scattering with a limit of detection of 52 µg/g fish (Correia and Loeschner, 2018). However, the optimized method failed to detect PE NPs in fish samples due to the high light scattering background, implying that the analysis of different polymers by AF4 should be operated on a case-by-case basis. Overall, it is still a complex technique that requires multistep parameter optimization and lots of user experience (Gigault et al., 2017), which would be difficult for new operators.

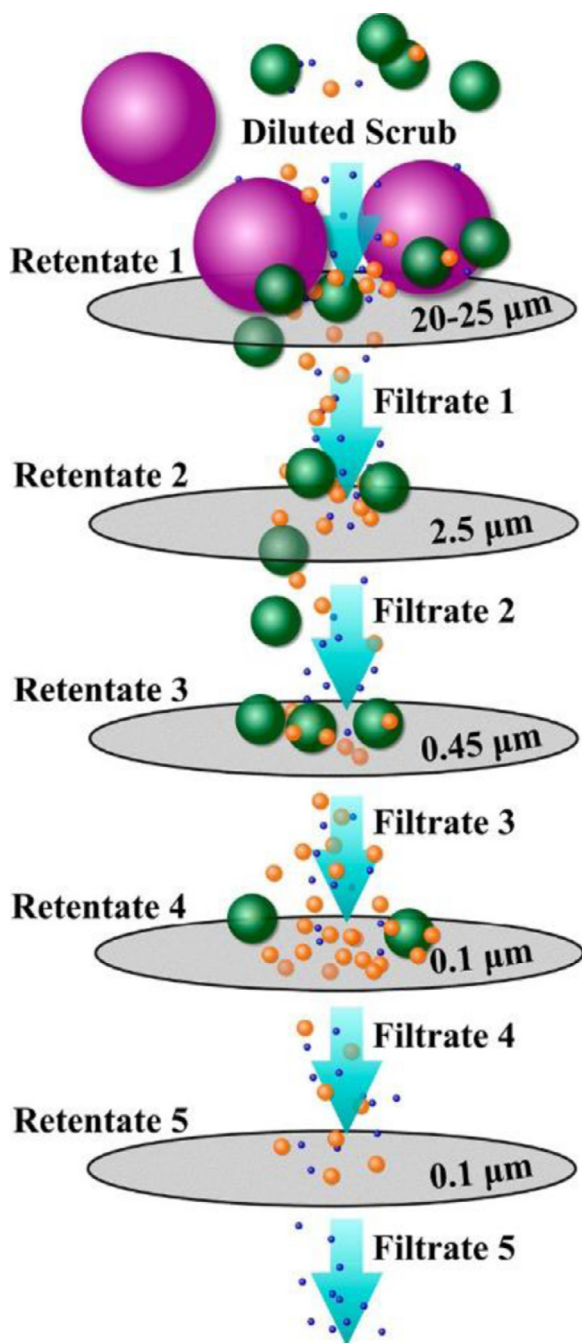


Fig. 1 – Scheme of the sequential filtration process of polyethylene nanoparticles in commercial facial scrubs. Reprinted with permission from reference (Hernandez et al., 2017). Copyright 2017 American Chemical Society.

1.5. Cloud point extraction

Based on the solubilization ability and cloud points of non-ionic surfactants, cloud point extraction (CPE) is widely applied for the concentration and isolation of ENMs from environmental samples (Chao et al., 2011; Liu et al., 2009a; Liu et al., 2009b; Liu et al., 2012; Yu et al., 2013). Recently, a Triton X-45 (TX-45) based CPE method was firstly proposed for the enrichment of NPs in real waters (Fig. 2) (Zhou et al., 2019). By using PS and PMMA NPs as the models, the target NPs can be

readily captured in the surfactant micelle above cloud points, and be well separated from the matrices after centrifugation. Under optimal conditions, an enrichment factor of 500 can be acquired without damaging the original size and morphology of NPs in the pristine samples. Meanwhile, TX-45 in the selected surfactant-rich phase can be degraded at 190 °C for 3 hr, which did not disturb the further quantification. By spiking 8.47–12.1 μg/L of model NPs into river water, sea water, influent and effluent from a waste water treatment plant (WWTP), recoveries of 76.6%–96.6% can be obtained, showing that the method is feasible for the determination of NPs in a wide range of environmental waters.

Due to the ultralow mass of NPs in the aquatic system, an enrichment factor of 500 may be not enough. As only 10 mL of each sample was used for optimization of the CPE method in the study (Zhou et al., 2019), using a larger volume of samples for the extraction (Hartmann and Schuster, 2013), or a multi-step extraction may further increase the enrichment factor.

1.6. Pressurized fluid extraction

Pressurized fluid extraction (PFE) appeared to be an alternative method for the extraction of plastic fragments in complex environmental samples. Two steps were included in the procedure: the samples were firstly extracted with methanol at 100 °C to remove all the extractable semivolatile organic compounds; and then selected plastics were recovered by using dichloromethane at 180 °C. It is demonstrated that five commonly used plastics including PS, PVC, PET, PP, and high density PE can be quantitatively harvested from municipal waste and soils (Fuller and Gautam, 2016).

Though PFE is simple and quick, the shortcoming is that this method is destructive and would extract all the plastics with different sizes in principle. Therefore, for the specific analysis of NPs, an initial separation step should be performed to remove large plastic fragments in the samples. It is impossible to characterize the original size and shape of NPs in the samples, making it hard to trace the source of NPs. Moreover, all the types of plastics extracted would mixed homogeneously in the plastic residue after solvent evaporation, which is a big challenge for the subsequent identification and quantification.

1.7. Alkali-assisted thermal hydrolysis

Plastics are polymers with different degrees of polymerization. Theoretically, the determination of plastics can be conducted by analyzing the typical building block compounds after depolymerization. However, the degradation of polymers with a carbon-carbon backbone is very difficult except the hydrolysis of ester groups (Gewert et al., 2015). Wang et al. (2017b) performed an alkali-assisted thermal hydrolysis method for the depolymerization of PET and PC that containing ester groups. After incubated at 135 °C or 115 °C in a pentanol or butanol system for 30 min in the presence of KOH, PET and PC plastics were well depolymerized, while the amounts of PET and PC can be calculated by analyzing the contents of the hydrolysis products, i.e., p-phthalic acid (PTA) and bisphenol A (BPA) in the system by liquid chromatography–tandem mass spectrometry (LC–MS/MS) (Fig. 3). The successful quantification of PET and PC particles in sewage sludge, pet food and feces from the United States (Zhang et al., 2019a, 2019b) implied that this indirect measuring approach is effective to assess the pollution, transport and potential impacts of PET and PC in the environment.

However, this method is only applicable for PET and PC with ester groups in the main chain, which resists its wide application. The hydrolysis procedure obliterates the original size and morphology of plastic pieces, and MPs and NPs in the

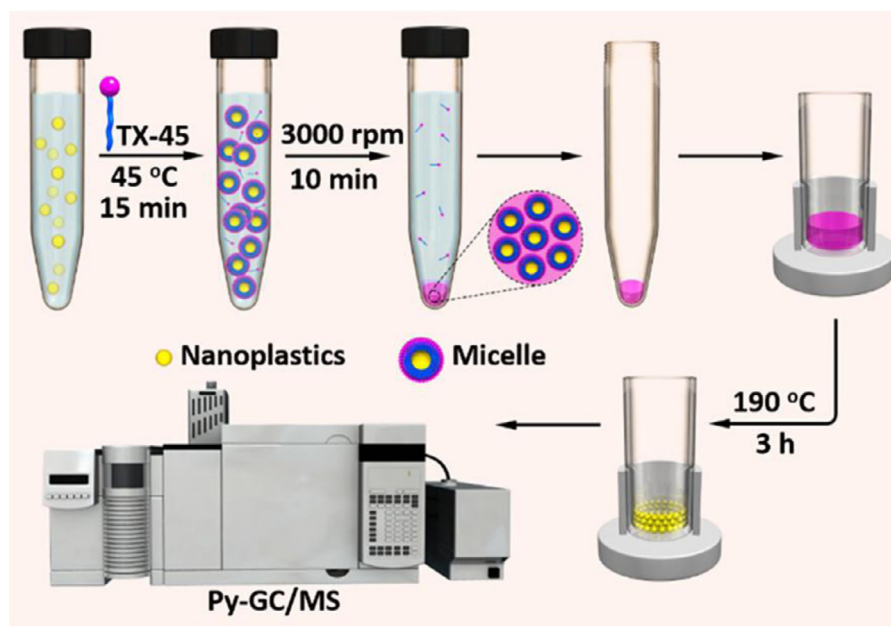


Fig. 2 – Preconcentration of nanoplastics by cloud point extraction for mass quantification and composition identification with pyrolysis gas chromatography–mass spectrometry. Reprinted with permission from reference (Zhou et al., 2019). Copyright 2019 American Chemical Society.

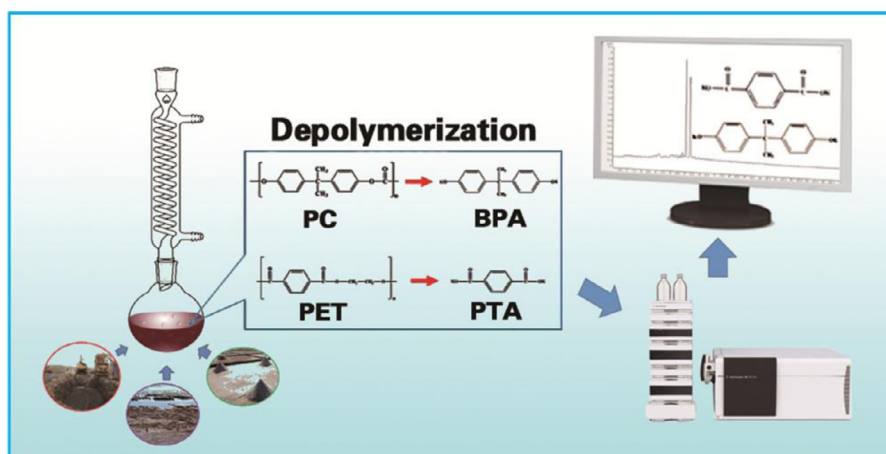


Fig. 3 – Scheme of the quantification of polycarbonate and polyethylene terephthalate plastics by depolymerization coupled with liquid chromatography–tandem mass spectrometry determination. Reprinted with permission from reference (Wang et al., 2017b). Copyright 2017 American Chemical Society.

samples would be quantified together. Therefore, the contribution of large plastic debris should be subtracted by proper methods if the separate analysis of MPs and NPs is demanded.

2. Identification and quantification of NPs

For the accurate evaluation of the potential risks of NPs in the environment, further information on the abundance, size distribution and chemical composition of NPs is needed after sample digestion and purification. Different methods for the qualitative, quantitative, or combined determination of NPs have been reported.

2.1. Visual identification of the size and morphology

Multiple techniques for the characterization of ENMs, including light scattering, electron microscopy, and nanoparticle tracking analysis, can also be adapted to identify the presence of NPs in the environment (Correia and Loeschner, 2018; Gigault et al., 2016b; Hernandez et al., 2017; Lambert and Wagner, 2016). Previous studies have described these methods in details (Gunsolus and Haynes, 2016; Luo et al., 2018; Schwaferts et al., 2019), and we do not aim to discuss here. It is worth noting that these techniques are not specific to NPs, therefore, subsequent chemical identification are required to confirm the existence of NPs.

2.2. Chemical identification

2.2.1. Spectroscopy

Spectroscopic techniques such as FTIR and Raman spectroscopy are extensively used for the identification of MPs, however, the smallest plastic particle that can be measured by these methods are around μm levels (Ivleva et al., 2017). Until recently, Raman Tweezers, a technique combining optical tweezers with Raman spectroscopy, is introduced for the study of MPs and NPs in seawater. It allowed the optical trapping and chemical identification of common NPs (including PP, PE, PS and nylon) down to the 50 nm range (Gillibert et al., 2019), which would be a potential tool to monitor the pollution of MPs and NPs in the marine system.

2.2.2. Mass spectrometry methods

Several mass-spectrometry (MS)-based methods have been presented for the analysis of MPs, which also enables the detection of NPs, since samples are determined in bulk regardless of the particle size (Nguyen et al., 2019). Plastic pieces can be identified by the characteristic mass pattern in MS, while the signal intensity of the indicative fragment ions also gives information on the relative weight of the target, which allows the qualitative and quantitative characterization of plastics simultaneously.

Pyrolysis coupled with gas chromatography–mass spectrometry: Pyrolysis gas chromatography mass spectrometry (py-GC-MS) is a well-developed method for the identification and mass quantification of polymers. In the method, samples are placed on a filament or in a furnace, and thermally treated to a programmed temperature under inert conditions. The degraded gaseous products are trapped by cooling or transferred directly to a gas chromatography column for separation, and then analyzed by a quadrupole MS (Ivleva et al., 2017; Nguyen et al., 2019). By using a Curie-Point py-GC-MS, eight common polymers including PE, PP, PS, PET, PVC, PMMA, PC, and PA 66, can be readily detected simultaneously in a single run, showing that this method is sensitive and reliable for the identification of plastics (Fischer and Scholz-Böttcher, 2017). This method allows the analysis of NPs in the environment with proper enrichment and separation procedures. After concentrated by ultrafiltration (a concentration factor of 100), PVC, PE, PS, and PET NPs were detected by py-GC-MS in the North Atlantic subtropical gyre (Ter Halle et al., 2017). Other studies also showed that py-GC-MS was suitable for the determination of plastics in wastewaters, beach sediments, and fish samples (Fischer and Scholz-Böttcher, 2017; Hermabessiere et al., 2018; Zhou et al., 2019).

However, the limit of detection (LOD) of py-GC-MS needs to be improved for the routine determination of plastics. As reported by Mintenig et al. (2018), the LOD was 4 mg/L for the direct analysis of PS NP suspensions, which could reduce to 20 $\mu\text{g/L}$ after subjected to cross-flow ultrafiltration with an enrichment factor of 200. After CPE, a LOD of 1.1 $\mu\text{g/L}$ was presented for PS NPs that were concentrated by a factor of 500 (Zhou et al., 2019). As the mass of NPs in the environment is extremely low, proper concentration is highly demanded. Since each pyrolysis type has a specific temperature behavior, poor reproducibility over different laboratories were reported (Nguyen et al., 2019). Py-GC-MS is sensitive to impurities, and sample masses allowed for analysis are very small (<0.5 mg); therefore, for complex environmental samples such as soils, sediment and organisms, the organic and inorganic composites must be carefully removed before analysis (Duemichen et al., 2015). In addition, the capillaries and injected system are easily polluted or even blocked by high boiling compounds, which largely enhances the maintenance cost (Duemichen et al., 2017).

Thermoextraction and desorption coupled with gas chromatography mass spectrometry: Thermoextraction and desorption coupled with gas chromatography mass spectrometry (TED-GC-MS) is another thermoanalytical method that is first proposed by Dümichen et al. (2014). Two steps are involved in the procedure. Samples are firstly exposed to a thermogravimetric analyzer (TGA), and the gaseous decomposition products are trapped by a connected solid-phase adsorber. The adsorbents are then analyzed by thermal desorption gas chromatography mass spectrometry for polymer identification. Unlike py-GC-MS that the thermal degradation of samples is restricted within a small pyrolyzer, a TGA is used for the pyrolysis, thus samples with higher masses (up to 100 mg) can be used, which would be attractive for the analysis of heterogeneous samples on a small scale (Dümichen et al., 2017). Additionally, as the degradation compounds are first caught by the solid-phase adsorber and then thermal desorbed by TDS-GC-MS, contamination or blockage of the transfer capillary would be significantly hindered (Duemichen et al., 2015). Common polymers such as PE, PP, PS, PET, and PA spiked into soil, digested sludge and suspended solids can be unambiguous distinguished (Dümichen et al., 2017). Real sample analysis revealed that PP, PE and PS were detected in ferment residues from a biogas plant and PE and PS were identified in river waters (Dümichen et al., 2017). Polymer debris derived from thermoplastics and tire wear abrasion could also be determined in environmental samples from street runoff by TED-GC-MS (Eisentraut et al., 2018), showing that this method is appealing to monitor the polymer pollution in the environment. Although TED-GC-MS showed as a semi-quantitative method (Duemichen et al., 2014), it is an excellent complement to py-GC-MS for the distinguish of plastics in the environment.

Thermal desorption-proton transfer reaction-mass spectrometry: Recently, a new method named thermal desorption-proton transfer reaction-mass spectrometry (TD-PTR-MS) is introduced for the sensitive identification and quantification of plastics. PET, PVC and polypropylene carbonate MPs and PET NPs are detected in Alpine snow without complex digestion or separation by this method (Materić et al., 2020). The small sample requirement (1 mL), low detection limit (1 ng for PS without any preconcentration), and high-mass resolution make it very suitable for ultratrace determination of different NPs in the environment, especially in air, snow, and natural and drinking water (Materić et al., 2020).

Liquid chromatography-tandem mass spectrometry: For polymers that contained ester groups, such as PET and PC, the alkali-assisted thermal hydrolysis method is more appealing to separate these polymers from complex matrices. The hydrolysis products, i.e. PTA and BPA, can be determined by LC-MS/MS for the polymer quantification (Wang et al., 2017b). According to the structural formulas of PET and PC, units of PTA- H_2O and BPA-2H account for about 77.4% and 89.5% in PET and PC polymers respectively, thus amounts of the two plastics in samples can be calculated. However, since neither PTA nor BPA are specific building block compounds to PET and PC, if other polymers involving the same hydrolysis product existed in the sample, the results determined would be biased (Wang et al., 2017b).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry: Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) is a robust technique for the analysis of polymers, which can also be used for the distinguish of plastics. Targets are softly ionized after laser desorption/ionization, so ion peaks in both high-mass and low-mass regions can be detected, which is suitable for the identification of different types of plastics based on their own ionization behaviors. For example, fingerprint peaks of m/z 90, 104, 128, 130, 312–318 and repeated peaks with $\Delta m/z$

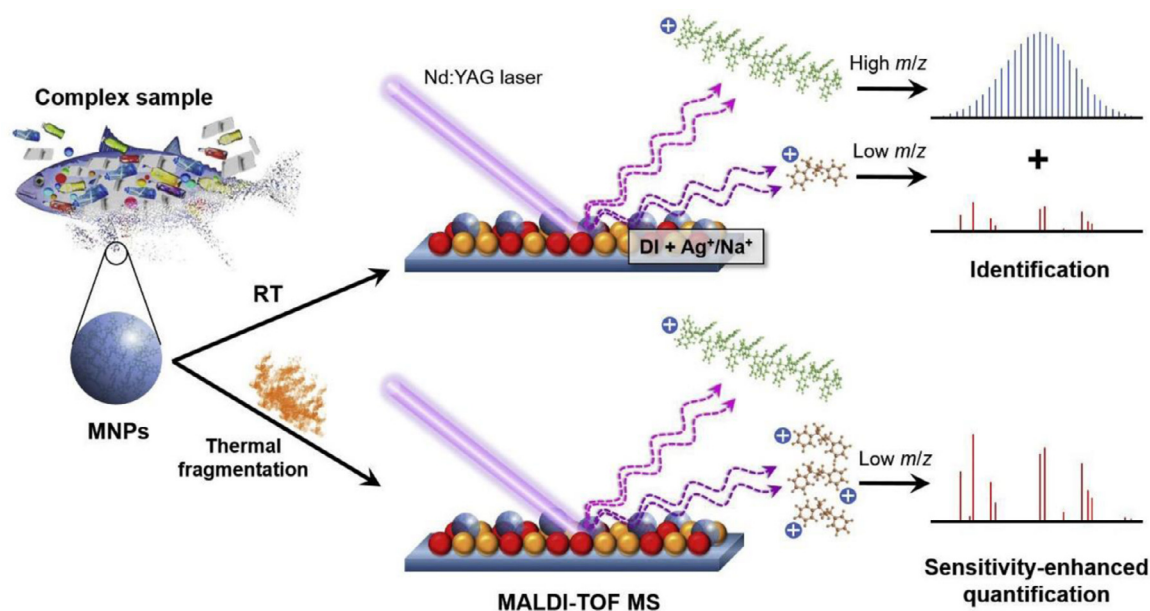


Fig. 4 – Scheme showing the mechanism and procedures for thermal enhanced identification and quantification of polystyrene micro/nanoplastics by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Reprinted with permission from reference (Lin et al., 2020). Copyright 2019 Elsevier.

104 in the m/z range 350–5000 can be used for the unambiguous distinguish of PS. Meanwhile, thermal treatment (380 °C for 10 min) accelerated the chain scission of PS, resulting in the intensity of specific ions in the low m/z ranges significantly increased, which allowed the quantification of PS plastics (Fig. 4) (Lin et al., 2020). The analysis of PS in complex samples such as fish meat and river water was also available, although a relative high LOD of 25 mg/L was represented (Lin et al., 2020). The feasibility of the method for screening of other plastics also needs verification, as only PS and PET are reported in the literature.

Thermogravimetry–mass spectrometry:
Thermogravimetry–mass spectrometry (TGA-MS) can also be used for the measurement of plastics. Different heating processes can be programmed in TGA, thus though the gaseous degradation compounds are transferred into a quadrupole mass spectrometer without chromatographic separation, the target analytes can be differentiated from the matrix due to the different decomposition temperatures. PET MPs spiked in standard loamy sand were quantitatively analyzed by TGA-MS with high efficiency (David et al., 2018), showing the potential application in the determination of plastics. However, this method is challenging to measure environmental samples that contained high contents of organic substances such as sludge and soils (David et al., 2018), and still restricted to the identification of PET.

2.2.3. Other methods

Other thermal analysis method such as thermogravimetry coupled to differential scanning calorimetry (TGA-DSC) was also reported for the analysis of PP and PE in environmental samples. Among the commonly used plastics, including PET, PVC, PA, PUS, PP, and PE, only PP and PE have low melting points below 200 °C with no endothermic peaks overlapping with other plastics (Majewsky et al., 2016). Therefore, only PP and PE can be clearly identified by the method. Overall, TGA-DSC is much cheaper compared with these MS based method,

which would be an attractive supplement for the determination of PE and PP in the environment.

The main drawback of these MS and thermal based methods is that all the analytes are damaged during analysis, which makes it impossible to trace their original size and shape, though the initial information is vital to predict the hazards of NPs on organisms and the eco-system. Therefore, the combination of different visual and chemical methods is demanded to answer the specific analytical questions. A summary of the existing literature reported the analysis of NPs is shown in Table 1.

3. Environmental processes of NPs

As the size is down to the nano-scale, the behaviors of NPs obey the colloidal theory, which shows some similarities with ENMs. PS NPs are also used as the model colloid to study environmental processes of ENMs because of the inertness (Bouchard et al., 2013). On the other hand, ENMs are intentionally produced with regular sizes and shapes, while real NPs in the environment are generated naturally from the fragmentation of plastic pieces with high heterogeneity. Due to the totally different sources and compositions of NPs compared with ENMs, their final fate in the environment would be largely varied.

3.1. Aggregation and settling of NPs

Aggregation behaviors of colloids involve homoaggregation (particles attaching with each other) and heteroaggregation (particles attaching with other species), which can be well described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Alimi et al., 2018). The stability of NPs can also be explained by the theory.

Typically, the solution pH, electrolyte concentration and valence significantly affect the aggregation of nanoparticles (He

Table 1 – Methods of the pretreatment, separation, identification and quantification of nanoplastics.

Type of sample	Pretreatment	Plastics	Separation	Identification and quantification	Limit of detection	Reference
Commercial facial scrubs	Samples (0.2 g) were diluted with 10 ml of water.	Polyethylene (PE) nanoplastics (NPs)	A five-step filtration by using membranes with pore sizes of 25 µm, 2.5 µm, 0.45 µm and two times of 0.1 µm	Scanning electron microscope (SEM), dynamic light scattering (DLS), and Fourier transform infrared spectroscopy (FTIR)	/	(Hernandez et al., 2017)
Plastic teabag leachate	Steeping plastic teabags at brewing temperature (95 °C)	nylon and polyethylene terephthalate (PET) NPs	Cellulose filters with 2.5 µm pore sizes	SEM, Nanoparticle Tracking Analysis (NTA), X-ray photoelectron spectroscopy (XPS), FTIR	/	(Hernandez et al., 2019)
Alpine snow	Melted at room temperature	PET NPs	Polytetrafluoroethylene (PTFE) filters with 0.2 µm pore sizes	Thermal desorption–proton transfer reaction–mass spectrometry (TD-PTR-MS)	< 1 ng/mL	(Materić et al., 2020)
North Atlantic subtropical gyre water	Filtered through a 1.2 µm poly(ether sulfone) membrane	PE, PET, polystyrene (PS) and polyvinyl chloride (PVC) NPs	Ultrafiltration at 10 kDa using an 8200-Amicon-stirred polysulfone-based cell	DLS and pyrolysis gas chromatography mass spectrometry (py-GC-MS)	/	(Ter Halle et al., 2017)
Drinking water samples.	/	PS NPs	Crossflow ultrafiltration with molecular weight cut-off between 40 and 60 kDa, asymmetrical flow fieldflow fractionation (AF4)	py-GC-MS	20 µg/L	(Mintenig et al., 2018)
Fish meat	Acid digestion with HNO ₃ and H ₂ O ₂ , and enzymatic digestion with proteinase K	PS NPs	AF4	Multi-angle light scattering	52 µg/g	(Correia and Loeschner, 2018)
Environmental waters	Filtrated with a 1 µm glass-microfiber filter	PS and poly(methyl methacrylate) (PMMA) NPs	Cloud point extraction	Transmission electron microscopy and py-GC-MS	1.1 and 0.6 µg/L for PS and PMMA	(Zhou et al., 2019)
Composted municipal waste samples and soils	/	PS, PVC, PET, high density PE, and polypropylene (PP) microplastics (MPs) (can be used for NPs)	Pressurized fluid extraction	FTIR	/	(Fuller and Gautam, 2016)
Sludge, sediments, indoor dust, digestive residues in mussel and clam, salts, pet food and feces	/	PET and polycarbonate (PC) MPs (can be used for NPs)	Alkali-assisted thermal hydrolysis	Liquid chromatography–tandem mass spectrometry (LC–MS/MS)	2.50 and 15.9 µg/kg for PC and PET	(Wang et al., 2017b; Zhang et al., 2019a, 2019b)

et al., 2017; Sun et al., 2019; Wang et al., 2017a). The presence of electrolytes can compress the electrical double-layer repulsion, inducing the attachment of adjacent particles. The charge screening effect is higher for multivalent electrolytes (Cai et al., 2018), thus the critical coagulation concentrations would be much lower in the presence of multivalent electrolytes (Singh et al., 2019; Yu et al., 2019). Natural organic matter (NOM) and surface functionalization also appeared to influence the aggregation behaviors of NPs, but it depends

on NOM concentration, surface charges of NPs and the electrolytes in the system (Tallec et al., 2019; Wu et al., 2019). For NPs with negative charges, NOM could enhance the stability by steric repulsion in the presence of Na⁺ or low concentrations of Ca²⁺, while accelerate the aggregation by cation bridging effects with high concentrations of Ca²⁺, which is also reported for ENMs (Shen et al., 2015, 2019; Yin et al., 2015). However, NOM can induce the fast attachment of positively charged NPs due to the charge neutralization effect, and high

concentrations of NOM can even reverse the surface charge (Yu et al., 2019). As NPs may be frequently exposed to sunlight in the environment, the aggregation of UV irradiated NPs is also studied. Liu et al. (2019b) showed that the aging process induced the production of O-containing functional groups on the surface of NPs, which increased the stability of NPs in NaCl solutions. However, the aggregation of aged NPs in CaCl₂ solutions was aggravated due to the bridging between Ca²⁺ and the carboxyl groups, which calls for the consideration of variable environmental conditions in the studies.

Since natural colloids and other suspended matters such as clays, metal oxide particles, and minerals, are ubiquitous in the natural system, the collision frequency of NPs with natural colloids would be much higher than the interaction with each other. Thus, the heteroaggregation of NPs is more likely to take place. Since natural colloids are generally negatively charged in the aquatic environment, the charge neutralization mechanism is the overwhelming factor leading to the heteroaggregation of positively charged NPs (Oriekhova and Stoll, 2018). NOM and electrolytes in rivers, such as Ca²⁺ and Mg²⁺, induced a bridging effect between NPs, causing the formation of large heteroaggregates. Even for NPs with negative charges, high concentrations of electrolytes reduce the electrostatic repulsion between NPs and suspended particles, inducing the attachment (Li et al., 2019b). The presence of NOM can reduce the heteroaggregation to some extent due to the steric hindrance. The formation of large agglomerations between NPs and large suspended particles may carry and settle NPs down to the deep water (Li et al., 2019b). Additionally, the microalgae and bacteria in the aquatic environment can excrete polysaccharides to form cell aggregates with sufficient stickiness (Long et al., 2015; Priya et al., 2018), and the collision between of NPs and the cells makes the heteroaggregation with microalgae and bacteria possible. The biofouling of NPs can modify the density of these particles and the increase of the density may facilitate the vertical settling of NPs in the water column (Lagarde et al., 2016; Long et al., 2015; Long et al., 2017).

3.2. Transport of NPs

The transport of NPs is commonly conducted based on the column experiments, and granular media such as glass beads, quartz sand and soils are filled into the column to simulate the mobility of NPs in the groundwater aquifer, riverbank filtration and soil environments. According to the experience from ENMs, the porewater flow rate, porewater conditions, and types of granular media significantly affect the transport of NPs in porous media, and thus the final fate in the environment (Alimi et al., 2018). Related studies also revealed that the size, surface functionalities, aging process of NPs and the presence of biofilm coated on porous media also influence the behaviors of NPs in the laboratory column experiments.

The retention of different sized PS NPs in natural sand saturated with seawater was thoroughly investigated. It was showed that smaller NPs (100, 400, and 600 nm) aggregated quickly in simulated seawater (35 practical salinity units, PSU) due to the low energy barriers, resulting in a much weaker mobility, with only about 10% of the particles in the effluent compared to 41.3% for 800 nm NPs. However, the aggregation of smaller NPs (100–600 nm) was significantly inhibited in simulated estuarine environments (3.5 PSU), resulting in enhanced transport of NPs, while the transport of larger NPs (800 nm) did not alter much, showing the size-dependent mobility of NPs in sandy marine environments (Dong et al., 2018a). The functional groups of NPs determine the surface charges and stability, which would greatly influence their transport. Dong et al. (2019) studied the retention of PS NPs (200 nm) functionalized with surface carboxyl (NPC), sulfonic (NPS), low-density amino (negatively charged, NPA⁻), and high-density amino

(positively charged, NPA⁺) groups in seawater-saturated sand. NPC particles remained stable in simulated seawater, which exhibited highest mobility rates in the column. The aggregation of NPS and NPA⁻ particles inhibited their transport, resulting in high retention in the sand. The electrostatic attraction between negatively charged sand and positively charged NPA⁺ particles also enhance their retention. Additionally, the presence of humic acid could suppress the retention of NPC, NPS, NPA⁻ by steric repulsion. Pristine PS NPs cannot fully represent NPs formed in the real environment. Therefore, the transport of PS NPs aged by UV or O₃ exposure were also assessed. It is showed that the aging process induced the surface oxidation of NPs, resulting in increased hydrophilicity and more negative surface charges, thus improved the mobility of PS NPs in porous columns (Liu et al., 2019a). Microalgae and bacteria are ubiquitous in the environment, and biofilms coated on the porous media can also dramatically increase the retention of PS NPs, thus inhibited their transport (Mitzel et al., 2016; Peulen and Wilkinson, 2011; Tripathi et al., 2012).

Due to the widespread production and application of ENMs, the release of ENMs into the environment is inevitable. The interaction and cotransport of NPs with ENMs, the abundant natural colloids and bacteria are expected. The cotransport or deposition behavior is far more complex than the individual colloid mobility, depending on the size, surface functional groups, hydrochemical characteristics, mass concentration ratios of both materials (Dong et al., 2018b; He et al., 2018; Li et al., 2019a; Peng et al., 2017b), which needs a case-by-case investigation. The large surface area of NPs enables the adsorption of pollutions, and the transport of NPs in porous media influence the mobility of these contaminants as well. PS NPs at low concentrations were shown to facilitate the transport of nonpolar and weakly polar compounds as contaminant carriers, while hardly affect the behavior of polar compounds due to the reversible desorption (Liu et al., 2018). The aging of PS NPs resulted in the surface oxidation of NPs, which significantly enhanced the binding of both nonpolar and polar pollutions through different mechanisms. Increased transport of the adsorbed contaminants were observed due to the greater mobility of aged PS NPs (Liu et al., 2019a).

Due to the lack of proper analytical methods for the sensitive determination of NPs, standard fluorescent NPs are always used to evaluate the transport of NPs. The high LOD of fluorescence detection hindered the operation at environmentally relevant conditions. NP concentrations as high as dozens of mg/L are used in these studies, and the transport of NPs in complex matrices such as soils and WWTP systems is impossible to track. Mitrano et al. (2019) reported a novel method for the synthesis of Pt-doped NPs, and the metal Pt can be used as a tracer to quantify NPs in complex media. It was found that vast majority of NPs spiked in the activated sludge process of a WWTP were associated with the sludge, which can be transferred to soils by the direct application of sewage sludge onto agricultural fields as fertilizers.

3.3. Degradation of NPs

Plastics are polymers made from small molecular organic compounds with different degrees of polymerization. Different from ENMs, the exposure of plastics to environmental factors, such as solar irradiation, wind, and biota may cause the breakdown or even mineralization of plastics. For plastics with a carbon-carbon backbone, including PE, PP, PS and PVC, chain scission is regarded as the main pathway for degradation. Other plastics with heteroatoms in the main chain, such as PET and polyurethane, hydrolysis of ester or amide bonds can considerably facilitate the disintegrate (Gewert et al., 2015). Meanwhile, the attack by bacteria and microbial

enzymes also results in the surface erosion and biodegradation of some polymers, such as PE, PS and Nylon 6 (Min et al., 2020). It is shown that plastics can release dissolved organic carbon into the seawater during degradation, and thus promote the growth of heterotrophic bacteria in the sea (Romera-Castillo et al., 2018). Laboratory weathering experiments also reveal that UV radiation could induce the chain scission of plastics, resulting in the production of abundant low-molecular weight compounds with oxidized end groups (Gewert et al., 2018). Along with the breakdown of plastics, a great number of environmentally persistent free radicals and reactive oxygen free radicals were also detected on the surface of irradiated PS and phenolformaldehyde resin MPs (Zhu et al., 2019), which may increase the potential hazards of plastics. For most cases, the degradation first takes place at the polymer surface, which is exposed to external environments for chemical or biotic attack. Therefore, degradation of NPs would be much faster than other macroplastic due to the higher surface areas (Gewert et al., 2015).

Labeling polymers with a radiotracer would be an effective way to assess the fate of NPs in the environment. Recently, ^{14}C -labeled PS NPs (^{14}C -PS) are used to study the photo-transformation of PS NPs. UV irradiation induced the oxidation of ^{14}C -PS in air, resulting in the C-O group formation on the surface and the cross-linking of the PS chains. The mineralization of the ^{14}C -PS was also observed, and ^{14}C -PS suspended in water showed much severer mineralization than that exposed in air, indicating a higher photoreactivity for ^{14}C -PS in water (Tian et al., 2019).

4. Summary and outlook

In this review, different methods for the analysis of NPs and their possible fate and transport in the environment are overviewed. Although the outlined methods have the potential for the separation and determination of NPs in environmental samples, the research is still in its infancy. To the best of our knowledge, only two studies reported the detection and identification of NPs in the real environment up to now. One is in water samples collected from North Atlantic subtropical gyre (Ter Halle et al., 2017) and the other is in Alpine snow samples (Materić et al., 2020). However, according to some published results that simulated the degradation of plastics under UV irradiation (Gigault et al., 2016a; Lambert and Wagner, 2016), numerous NPs could be generated after UV exposure. It is speculated that NPs are ubiquitous in the ecosystem even though that they are present with a relatively low mass. Therefore, more efforts should be taken to improve the resolution and sensitivity of the analytical techniques. Though some separation and concentration methods such as membrane filtration and ultrafiltration, are conducted for the real sample isolation, the poor filtration efficiency and low recoveries hinder the quantitative analysis of NPs. The development of novel and efficient separation and enrichment approaches or preparation of suitable membrane materials are urgently needed.

Spectroscopic techniques, like FTIR and Raman spectroscopy, allow the unambiguous identification of plastic types, their abundance, size and shapes, which plays an important role in the detection of MPs. Further developments of the nano-FTIR absorption spectroscopy (Huth et al., 2012) and nano-Raman Tweezers (Gillibert et al., 2019) that enable the nano-scale resolution of plastics are promising for the nondestructive identification of NPs.

The detection of NPs in Alpine snow samples revealed that the airborne transport of NPs is also possible. Since the plastic pollution is becoming a global problem, to accurately evaluate

their environmental risks and health effects, the researchers should work together for the method improvement and real sample collection and determination in the environment.

When evaluating the fate and transport of NPs, PS NPs are always used to study the behaviors of NPs in the environment. However, real NPs in the environment are produced naturally with irregular shapes, varied sizes and different compositions, so spherical PS nanoparticles are not the ideal model. Other commonly used polymer types, such as PP, PE, PVC, and PET, with different shapes also warrant consideration in future studies to better understand the ultimate fate and potential hazards of NPs.

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