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REVIEW

The Emerging of Microplastic and Nanoplastic as Pollutants and their Characterization and Analysis

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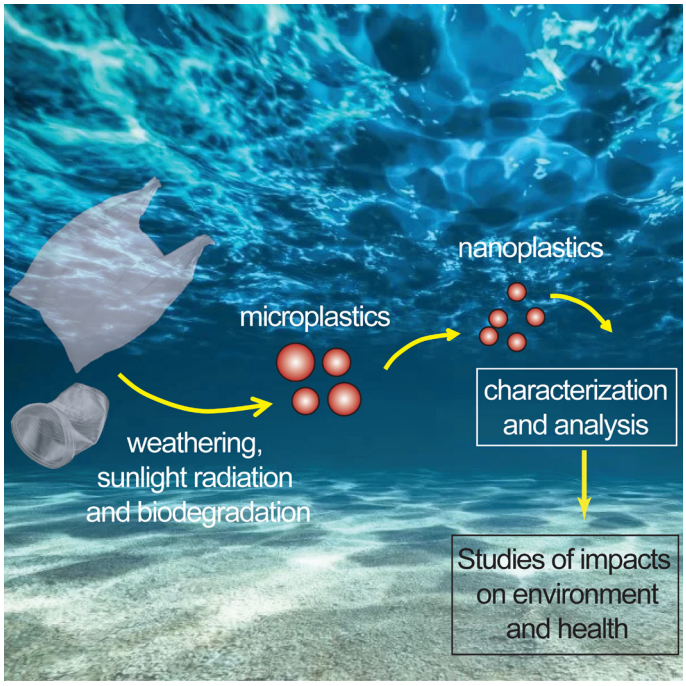

Global plastic pollution is a serious problem that is increasing over the years since millions of tons of plastics end up in the environment. These plastics are fragmented due to sunlight radiation, biodegradation, and other environmental factors leading to small debris which can be transformed into microplastics and nanoplastics. Due to their small size and high surface area, these materials can be easily absorbed by organisms besides being able to adsorb toxic pollutants. Considering these issues, studies about their toxicity and fate in the environment are of great importance, however, the success of these studies depends on the methods of sampling, sample preparation, and also analysis, which need to be developed and improved. Thus, the current review proposes an integrated approach of methodologies of sampling, sample preparation, and analysis of solid and aqueous samples with microplastics and nanoplastics besides discussing the challenges and new methodologies for microplastics and nanoplastics analysis.

Keywords: microplastic, nanoplastic, environmental pollution, nanoplastic analysis, sample preparation

INTRODUCTION

Over the past decades, Earth is polluted with plastic waste since its production has been massively employed for a wide range of applications in order to improve life quality, however, this extensive use of plastics has resulted in severe environmental pollution which is getting concerned of the scientific community.[1] Plastic pollution achieved alarming levels in the environment and it is estimated that this pollution on land and in freshwater could be many times greater than the estimated 4.8 to 12.7 million tonnes.[2] Consequently, the large plastic debris is like to break down into small debris due to weathering, sunlight radiation, and biodegradation: the microplastics (MP) and even the nanoplastics (NP) (Figure 1).[1]

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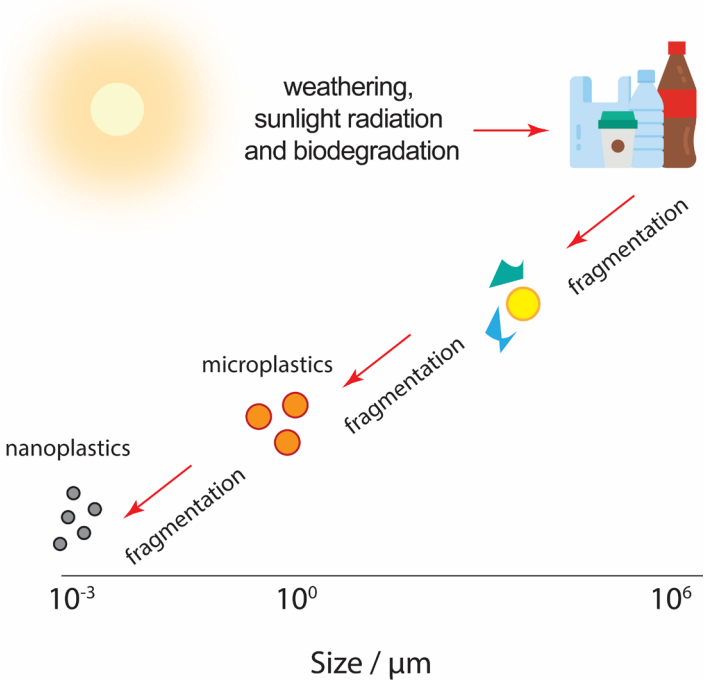

Figure 1. Schematic representation of the fragmentation of plastics and nanoplastic formation.

Since this is an emerging issue in the environment, some distinctions are necessary to be made for these terminologies. Firstly, it is common the association of polymers and plastics, and consequently the association of nanopolymers as NPs. However, it must be taken into account that all plastics are polymer-based, however, not all polymers are plastics and consequently, there is a distinction between NPs and nanopolymers.[2] The second consideration is about the size and characteristics of these materials since the properties and behavior of nanomaterials cannot be extrapolated for a bulk counterpart, and due to this, it can be made a separation of NPs and MPs regardless of the size range.[2] With these considerations in mind and the inaccuracy in the definition, it can be assumed that MPs can be further degraded to NPs, which have a particle size between 1 nm and 100 nm.[3] These characteristics enable MPs and NPs to escape from the wastewater treatment process and enter the environment (aquatic ecosystem, soil, and sediments)[3] and also in the food chain.

The reach of MPs and NPs achieved alarming consequences since studies have demonstrated that these materials can be translocated across the placenta into the fetal kidney, heart, lung, liver, and brain in the late-stage of pregnancy, besides these materials have also been found in breast milk.[4]

Furthermore, some studies have demonstrated that MPs and NPs are able to bind toxic metals such as Pb and Cu,[5,6] which can enhance the problem of toxicity of these metals since they can be spread in different environments and contaminate them.

Although these studies about nano and microplastics are getting attention, compared with the vast literature about nanoparticles (toxicity, analysis, and characterization), the MPs and NPs investigation is at the infancy stage (Figure 2), and protocols are still under development.[1]

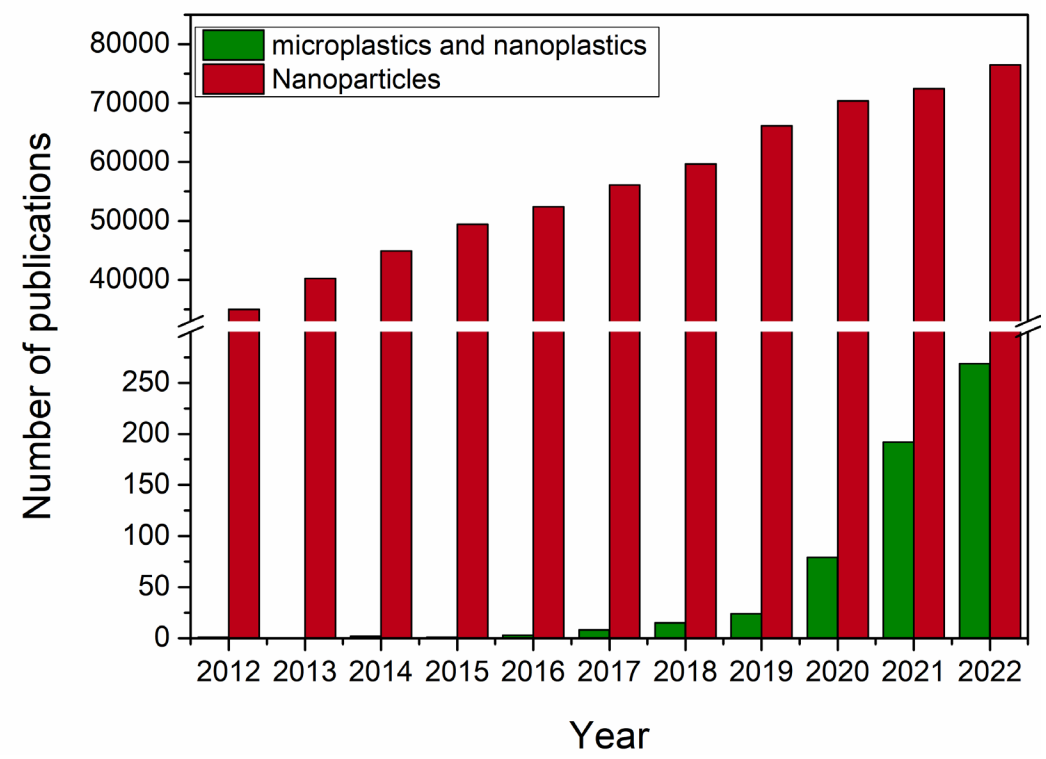

Figure 2. Comparison of the number of publications between microplastics and nanoplastics and nanoparticles (source: Scopus)

The success of studies about the toxicity of MPs and NPs as well as their fate in the environment depends on the methods of sampling, sample treatments, separation, and analysis, therefore the development of these methodologies is undoubtedly of great importance.

Considering this challenge, this review aims to provide a recent overview of the methods for the determination of micro and nanoplastics and also the methods of sample treatments considering the challenges that have to be overcome.

SAMPLING AND SAMPLE TREATMENT

The sampling and processing methods for water samples are similar for both fresh and saltwater, although differences can be noted in the distribution of MPs since it is influenced by density (since generally, MPs will be deeper in freshwater) and hydrodynamic profile of the samples.[7] The water samples are collected directly from the area in which the study will be performed and nets are frequently used to collect MPs from water samples. Different nets can be employed according to the deep and also the pore diameters (for example, for superficial collection, neuston or manta can be employed with approximately 333 μm). Pumps are also used for sampling since it is possible to obtain several cubic meters of water per hour and is used for a specific depth where extraction is guaranteed.[8] Crew and co-workers employed specific bottles for water sampling in which the 4 L plastic jugs were acid-washed and used to collect water at a depth of 0-5 cm. This procedure was repeated 25 times to filter 100 L of water sample through a piece of 100 mm nylon mesh.[9]

The sampling of soil and sediment samples depends on the distribution of MPs and NPs which is influenced by different factors such as meteorological, temporal, and dependent on the sampling area and can compromise the reproducibility of the results.[7] The collection of MPs on beaches is easy to implement by using forceps, and sieving and allows the collection of large volumes of the sample or replicates while the collection of samples from seabed requires the use of specialized equipment such as box corer and

grab samples, furthermore, since the deep is an important factor, the number of replicates can vary in order to ensure the representativity.[7] The collection of soil can correspond to the uppermost horizon (0-10 cm, organo-mineral horizon) and can be collected using stainless steel shovel, stainless steel corer, and Lenz sampler. Due to the heterogeneous matrix, soil samples are easily affected by human interaction and making it difficult to obtain representative samples. It is also important that the sampling amount of soil should exceed the amount essential for the analysis of MPs allowing additional repetitions when needed.[10,11] As MPs particles are particulates with a wide range of size, their distribution in soil also can be significantly variable.[12] In order to overcome this problem, some authors[13,14] employed composite samples taken from defined subunits within a sampling site to get a representative sample from the contaminated site.

Different sample preparation can be employed for aqueous samples such as seawater, river water, or other aqueous sources. Filtration is commonly the first step that concentrates the MPs and NPs and enables an increase in the quality of analysis. The sieving is another treatment that differs from filtration by the use of a sieve (usually with a mesh size between 0.038 and 4.750 mm) to separate the MPs.[8] The preconcentration treatments is a tool to improve the limit of detection (LOD) and limit of quantification (LOQ) of analysis and different methodologies can be employed in this step such as ultrafiltration,[15–17] crossflow ultrafiltration,[15,17] ultracentrifugation,[17] and cloud point extraction.[1,18–20] In ultrafiltration, is employed a porous membrane ranging from 10 to 100 kDa of molecular weight cutoff where the solution penetrates by an applied pressure.[17] The ultracentrifugation uses faster spinning speeds able to collect dispersed particles, and since MPs and NPs are insoluble, they can be sedimented. However, this technique may damage the MPs, thus if the composition of MPs is the only information required, this will not be a problem.[17] Cai et al. employed ultracentrifugation for separation and enrichment in river water samples and they reported that NPs fragments were successfully separated and enriched by a factor of nearly 50 times with a high recovery rate (87.1%).[21] Cloud point extraction is a technique based on the formation of micelles from a nonionic surfactant abbe to bind and concentrate the analyte or particle of interest when they are heated above its cloud point temperature.[18]

For solid samples such as sediments and soil, the extraction procedure is one of the most employed methodologies for sample preparation. Wahl and co-workers performed a water-soil extraction with ultrapure water added to soil at a soil/water ratio of 1:4 and stirred at 300 r min^{-1} for 72 h and after, samples were filtered to 0.8 mm (Sartorius filters).[10] Junhao et al. recommend that drying made easier the separation of MP from the soil, however, the temperature must be moderate in order to avoid MPs degradation, therefore, it is suggested that drying takes place at a temperature close to 60 ºC.[17] Crew and co-workers employed sieving (in order to separate in 8 different sediment size fractions) and also dried the sediment samples in order to perform the extraction of microplastics.[9] In the density separation, the soil is treated using ultrasonic, and after is added a saturated solution of zinc chloride, calcium chloride, sodium bromide, or zinc bromide is for the suspension medium. After, stirring and sedimentation of the mixture, the supernatant with MPs is filtered.[17] Recently, Schütze and co-workers performed a systematic study of the different solutions (NaBr, H_2O, NaCl, and sodium hexametaphosphate) with different densities in order to separate a mixture of microplastics, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate, and three biodegradable polymers (PLA, PBS, MB), achieving recovery rates of 87.3–100.3% for conventional polymers, and 38.2–78.2% for biodegradable polymers for NaBr solution.[22] Electrostatic separation is a dry processing technique and can be employed since the soil constituents are electrically conductive and MPs and NPs are not this method has the advantage to be quick, simple and up to 99% of the original mass can be removed without the loss of MPs.[17] The digestion of organic matter is sometimes desired (if the proposal of the study is not to investigate the interaction of MPs and organic matter in the environment) since it can affect the accurate identification and quantification of MPs and NPs. Different digestion methods can be used for this proposal such as digestion with acid (commonly with HNO_3 and/or HCl), alkali (commonly with KOH and NaOH), H_2O_2, and enzyme which is the least aggressive method with low impact on MPs.[17] The combination of density separation and removal

of organic matter was also employed by Hurley et al.[23] to separate the microplastics from a complex solid matrix. Oxidation methods using H_2O_2, Fenton's reagent (identified as the optimum protocol), and alkaline digestion with NaOH and KOH were employed to remove the organic matter, and water and NaI were employed for density separation of the microplastics.[23]

The different sample treatments for solid and liquid samples are summarized in Table I.

Table I. Some methodologies for sample treatment for MPs and NPs analysis

Methodology	Characteristic	Reference
	Liquid samples	
Filtration	Large volumes of water can be filtered and the particles are directly concentrated during the sampling	24
Sieving	Simple and employs sieves with a mesh size between 0.038 and 4.750 mm	8
Preconcentration	Different methodologies such as ultrafiltration, crossflow ultrafiltration, ultracentrifugation, and cloud point extraction.	1,15–20
	Solid samples	
Digestion	Can be performed with acid and alkali solutions, H_2O_2, and enzymes	17
Electrostatic separation	High separation efficiency, quick, and simple	17
Density separation	Simple, different salt solutions can be employed	17
Extraction	Simple, can employ different solutions and solvents such as water	10
Drying	Avoiding temperatures above 60 ºC	17

Another technique for MPs and NPs separation has been widely used: field flow fractionation (FFF). The FFF is a fluid-assisted hydrodynamic separation method that is used to separate macromolecular particles (proteins, nanomaterials) from colloidal particles. The principle of the method is based on the distinct diffusivity of the particles in which when the particles pass through the FFF, a perpendicular field is applied and the particles stay at different distances from the channel wall and present different retention times, enabling the fractionation of the particles in the sample.[25] The most used FFF for MPs and NPs is the asymmetrical flow field-flow fractionation (AF4).[1] In this mode, the sample sorting is achieved by sample circulation in the channel, where the particles stabilize at different heights, according to the difference in diameters, after introducing two opposite flow streams.[25] Pashaei et al. employed the AF4 for the characterization and determination of NPs and MPs in hypersaline lakes and they found that MPs and NPs have different transport mechanisms in this environment and fate compared to lake and ocean.[26] Correia and Loeschner coupled multi-angle light scattering (MALS) with AF4 for the detection of NPs in food and reported that although polystyrene NPs could be detected and characterized, the determination and characterization of polyethylene NPs in fish samples were not possible and consequently new methodologies need to be developed to improve this determination.[27] Recently, Müller and co-workers employed the AF4 to investigate the impact of MPs and NPs presented in paints on *Daphnia magna* and on the murine cell line which was strongly affected by the polymers of MPs and NPs.[28]

ANALYSIS OF MICROPLASTICS AND NANOPLASTICS

Identification and quantification of microplastics can be made by spectroscopy methods, microscopy images, and also by visual analysis. Plastics with a size ranging from centimeters and millimeters are

easy to be detected by the naked eye after the collection of samples. Optical microscopes (OMs) are widely employed as an identification tool for smaller plastic particles especially when they are colored. However, the determination of smaller microplastics with no color or specific shape is difficult.[29] Given this, the scanning electron microscope (SEM) can overcome this problem, since it is possible to visualize at nanometer size. Furthermore, SEM equipped with energy-dispersive X-ray (SEM/EDX) also can provide information about the composition and surface structure of the MPs and NPs which is a useful tool for the identification of the MPs and NPs.[29] The SEM/EDX can identify some MPs and NPs due to the elemental signatures. In view of this, Wang et al. easily identified PVC MPs due to the unique elemental signature pf PVC including chlorine.[30] Besides the identification of the type of MPs due to the elemental signature, it is also possible to evaluate the aging of the MP in the environment. This was observed by Tiwari et al., the authors observed characteristics cracks in MPs surfaces, suggesting polymer aging, mechanical and oxidative weathering.[31]

Vibrational techniques such as Fourier-transform infrared (FT-IR) and Raman spectroscopy are widely used for identifying the chemical composition of MPs and NPs, since they can provide information about the functional groups and molecular structure besides the information about size, size distribution, and morphology.[29,32,33]

The micro-FTIR spectroscopy (μ-(FT)IR spectroscopy) is the most employed method for MPs analysis, in which the FTIR spectrometer is coupled to an optical microscope and can be performed in reflectance or transmission mode. The reflectance mode allows an investigation of the particle surface MPs modifications due to aging effects, however, this mode can suffer undesired light-scattering effects on the particle surface that decrease the spectral quality. The transmission mode presents high-quality spectra, however, the thickness or color of MPs influences the analysis since it may lead to total absorption causing unidentifiable spectra due to the convergence of the bands.[33] A small size of MPs (20 μm) present in bottled drinking water was identified using using FTIR microscope as reported by Zainuddin and Syuhada.[34]

Raman microspectroscopy (RM), a non-destructive method based on the effect of inelastic light scattering on molecules, can also be coupled with confocal optical microscopy. This configuration provides a resolution lower than 1 μm, which is better than μ-(FT)IR spectroscopy (with a resolution of about 10 μm). This technique allows analysis of MPs in aqueous and wet samples since it is insensitive to water, however, it may suffer interference due to fluorescence of inorganic and organic impurities in the samples.[33] The surface-enhanced Raman spectroscopy (SERS) is also a technique employed for MPs and NPs characterization. This technique amplifies the Raman signal using a laser source combining the advantages of both plasmonics and Raman scattering.[35] Hu et al. employed this technique in order to analyze polystyrene NP and they reported a high sensitivity (detection limit of 6.25 μg/mL for 100 nm PS NP), interference resistance, good repeatability, and quantitative analysis ability ($R2 > 0.970$).[36] Furthermore, the combination of preconcentration methods and these techniques for analysis can enhance the limits of detection improving the analysis. According to Yang et al, the combination of bifunctional Ag nanowire membranes was employed to enrich NPs and enhance the surface-enhanced Raman spectroscopy (SERS) spectra. Good retention rates (86.7% for 50 nm and approximately 95.0% for 100–1000 nm) and high sensitivity (down to 10–7 g/L for 50–1000 nm and up to 105 SERS enhancement factor) of standard polystyrene (PS) NPs were achieved.[37]

In contrast to spectroscopic methods, thermoanalytical methods are destructive techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and pyrolysis-gas chromatography-mass spectrometry, and the sample is thermally decomposed under defined conditions.[38] The TGA measures the mass change as a function of thermolysis temperature and although it is a useful tool, it can be a challenge to quantify the fraction of different types of plastics in a mixture.[29] TGA has long been used in the investigation of the thermal properties of plastics since it is an easy and quick technique, moreover, when combined with FTIR and CG-MS the characterization of polymers based on the gaseous decomposition products can be improved.[39] Dümichen et al. compared the polyethylene MPs analysis from TGA and pyrolyze gas chromatography-mass spectrometry and reported that high sample masses in TGA

(200 times higher than used in the chromatography technique) were able to be analyzed from complex non-homogenous matrices.[40] The combination of TGA and FTIR could distinguish and also quantify MPs of PVC and PS in mussels and seawater samples as reported by Yu et al.[41]

Differential scanning calorimetry (DSC) is another thermal analysis that measures the amount of energy required to increase the temperature of the sample as a function of temperature, and the identification of the type of plastic can be made using established libraries of the thermal degradation patterns.[29] This technique requires reference materials to identify the polymer and due to this, it is useful for identifying primary MPs.[42] According to Shabaka et al., this technique was able to reveal the presence of ten polymers ranging from 0.5 mm to 5 mm and with a variety of shapes and colors in seawater and shoreline sediments.[43] Chialanza and co-workers coupled optical microscopy with image analysis (IA) and DSC and these combined techniques provided particle characterization and counting procedures based on image analysis chemical identification of MPs based on DSC signal processing.[44]

Pyrolysis-gas chromatography-mass spectrometry has been one of the techniques employed to explore the characteristics of MPs and NPs since non or minimum pretreatment is needed, it has high sensitivity, it can analyze mixtures of different polymers, it is a fast technique, and also it is possible to analyze the samples quantitatively.[45] The quantification and detection of MPs and NPs are accomplished by characteristic pyrolysis products and their respective indicator ions.[38] Blancho and co-workers employed this technique to analyze polypropylene and polystyrene NP in suspensions and also explored different matrix effects by spiking the NP in different organic matter suspensions (i.e., algae, soil natural organic matter, and soil humic acid). They reported that polypropylene NP identification was validated while polystyrene NP requires preliminary treatment.[46] Coupling the tandem mass spectrometry to pyrolysis-gas chromatography, the detection of MPs was improved according to Albignac et al. since besides this method was employed to analyze MPs from 500 µm down to 0.7 µm, the quantification of six common polymers was possible in one run.[47]

Table II. The most employed techniques for MPs and NPs analysis

Technique	Characteristic	Reference
Optical microscope	Determination of smaller microplastics with no color or specific shape is difficult	29
SEM	Possibility to visualize at nanometer-size	29
SEM/EDX	Provide information about the composition and surface structure	29
Raman microspectroscopy	Allows analysis of MPs in aqueous and wet samples, may suffer interferences due to fluorescence	33
Micro-FTIR spectroscopy	Resolution limited to approximately 10 µm, performed in reflectance or transmission mode	33
Thermogravimetric analysis	Easy and quick technique, difficult to analyze mixtures of plastics	29,39
Differential scanning calorimetry	Requires a reference material to identify the polymer	42
Pyrolysis-gas chromatography-mass spectrometry	High sensitivity, possibility to analyze mixtures of different polymers, and analyze the samples quantitatively	45

These techniques can be combined to provide more accurate information about the MPs and NPs in samples. The FTIR, AFM-IR and Pyr-GC/MS were employed by Li et al. for the characterization of NPs in tap water samples which were polyolefins, polystyrene, polyvinyl chloride, polyamide, and some plastic additives. Furthermore, besides the identification of the polymer present in MPs samples, the size was also identified: the abundance of NPs with the most frequent particle sizes in a range of 58–255 nm was 1.67–2.08 μg L^{-1} in tap water.[48]

FUTURE PERSPECTIVES

Considering that there is a lack of information about the toxic effects and fate of MPs and NPs, the development of these studies needs improvements in the sample preparation and mostly in the analysis of the samples. A new strategy of the methodology of analysis is emerging which is the use of Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS). According to Jiménez-Lamana, the possibility to associate metals such as nanoparticles (gold nanoparticles) in NPs and MPs make the analysis possible since the adsorbed Au produced a SP-ICP-MS signal allows the counting of individual NPs particles, and hence their accurate quantification.[49] This possibility of analysis can be an important tool for the investigation of metals adsorbed in MPs and NPs, allowing their direct characterization.

Although this new possibility of analysis emerged, there are challenges to be overcome such as (i) ensuring the sampling is representative as possible, since representative MPs and NPs samples are essential for the interpretation of the analysis, and also the consequences of the presence of these materials in the environment. In view of this, the improvement of the sampling technique considering the spatial and temporal variation is critical. (ii) Understand the complex composition of NPs and MPs, since in the environment, these materials can be associated with toxic metals (and other compounds) and also organic matter and these compositions can affect the fate and toxicity of these materials. (iii) Improve the techniques of sampling and analysis of small NPs to avoid loss of these materials and obtain more complete information about the presence of these materials in the environment.[50,51]

Furthermore, compared with the studies about nanoparticles, the investigation of MPs and NPs is in the beginning and due to this, this is a wide field of study to be explored.

Conflicts of interest

No conflicts to declare.

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