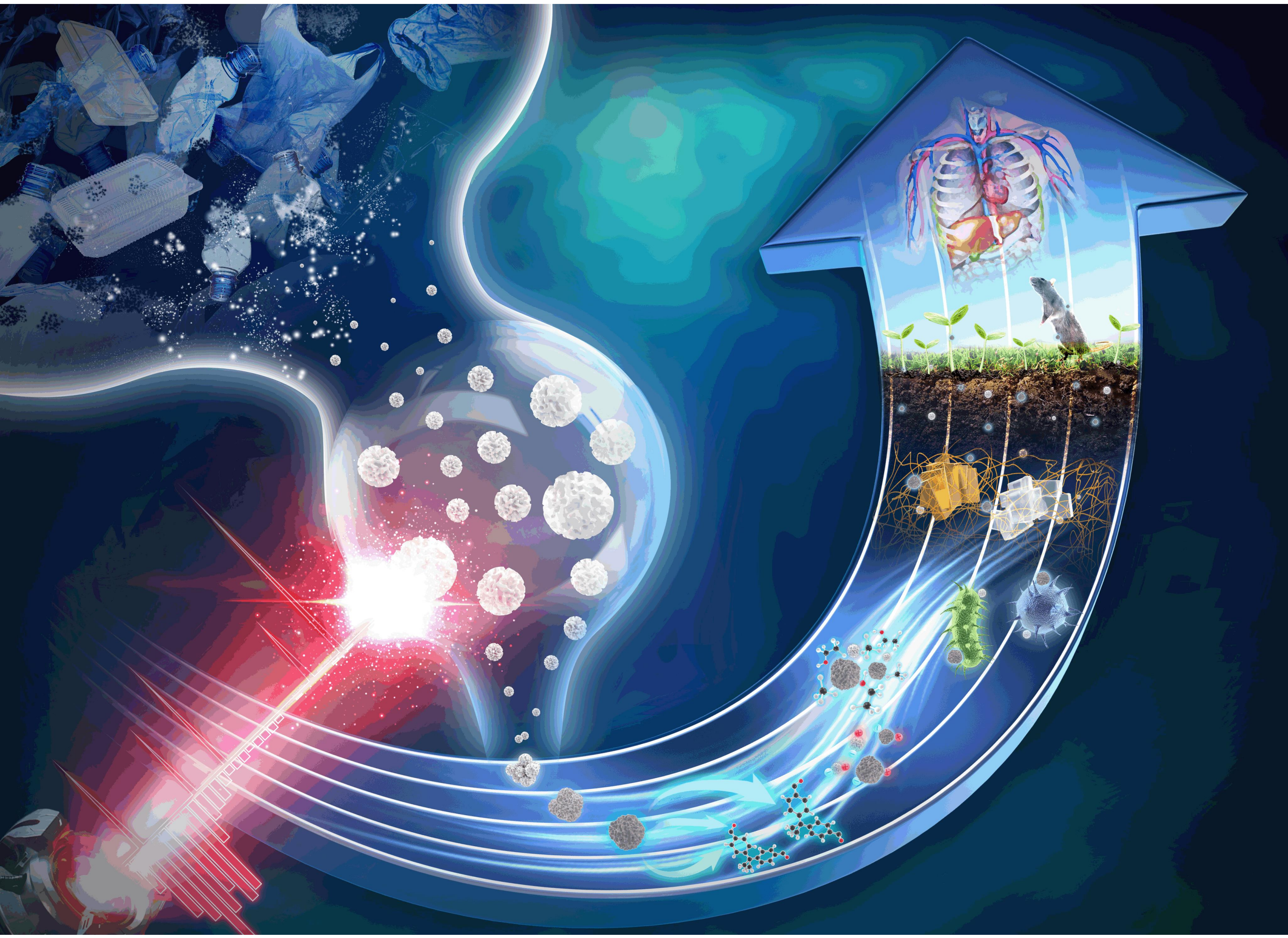
Atomic Spectroscopy

ISSN: 0195-5373
e-ISSN: 2708-521X
Vo. 44 No. 5
SEP/OCT 2023

www.at-spectrosc.com



Cover Feature:

A Progress Review on Characterization, Environmental Behaviors and Toxicity Effects of Micro (Nano) Plastics Using Atomic Spectrometry

Xinyi Wu, Zhangguo Wu, Meseret Amde, Weichen Zhao, Gang Li, Shixiang Gao, Maoyong Song, Yan Ma, Zhiqiang Tan, Yongguang Yin, and Qinghua Zhang

Atomic Spectroscopy Press

Atomic Spectroscopy

Review

A Progress Review on Characterization, Environmental Behaviors and Toxicity Effects of Micro (Nano) Plastics Using Atomic Spectrometry

Xinyi Wu,[a,b] Zhangguo Wu,[a,e] Meseret Amde,[c] Weichen Zhao,[a,f] Gang Li,[a,f] Shixiang Gao,[g] Maoyong Song,[d,f] Yan Ma,[b] Zhiqiang Tan,[a,e,f,*] Yongguang Yin,[d,e,f,*] and Qinghua Zhang[a,e,f]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China

[b] School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, P. R. China

[c] Department of Chemistry, College of Natural and Computational Sciences, Haramaya University, Oromia, Ethiopia

[d] Key Laboratory of Environmental Nanotechnology and Health Effects, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China

[e] School of Environment, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, P. R. China

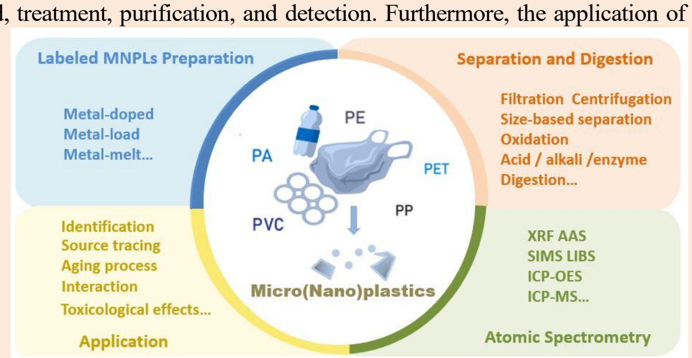
[f] College of Resource and Environment, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[g] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, P. R. China

Received: *December 14, 2023;* ***Revised:*** *January 07, 2024;* ***Accepted:*** *January 08, 2024;* ***Available online:*** *January 08, 2024.*

DOI: 10.46770/AS.2023.302

ABSTRACT: Micro (nano) plastics, MNPLs, have become emerging particulate human-made pollutants, and quickly become the fields of increasing concern of the public. Due to the lack of analytical technology with sufficient sensitivity and selectivity, it is difficult to fully detect and determine the characteristics of MNPLs in the environment and biological matrix. Atomic spectrometry has many advantages, such as low detection limit and high sensitivity, and shows great potential in the analysis of MNPLs. However, there is a lack of systematic summary in this field at present in order to give full play to its advantages in the analysis of plastics. In this review, the whole process of analyzing MNPLs in complex matrix based on various atomic spectroscopy techniques have been discussed, including sample labeled, treatment, purification, and detection. Furthermore, the application of atomic spectrometry in tracing the source of MNPLs in the environment, *in situ* identification and classification, analysis surface morphology and functional groups changes during aging process, assessments of environmental ecological risk assessment and toxicological effects were addressed aiming to improve our understanding on the environmental fate and transport of the fragments. Finally, future outlooks and research directions have been recommended based on the existing research gaps in the area.



INTRODUCTION

Micro (nano) plastics (MNPLs) are tiny fragments of plastic polymers, which widely exist in various environmental media (ocean, sediment, soil, and atmosphere). MNPLs can migrate through the environmental systems and can accumulate in plants and organisms, even detected in human blood and milk samples.[1] MNPLs have been considered as emerging particulate man-made pollutants. Microplastics (MPLs) are a variety of plastic particles with the size ranging from 1 μm to 5 mm.[2] Primary MPLs refer to those plastics with a size less than 5 mm that are intentionally produced for industrial applications, cosmetics and cleaning products. Secondary MPLs are formed from larger plastics in the environment due to UV-induced degradation, hydrolysis and biodegradation processes, or during use.[3] Due to the potential ecological and health impacts of MPLs in the environment, researchers have suggested to consider mechanical breaking down plastic fragments to a lower scale (sub-micron scale). Nanoplastics (NPLs) are defined as unintentionally produced particles during the manufacture and degradation of plastic objects and exhibit colloidal behavior, with sizes ranging from 1 to 1000 nm.[4] The colloidal characteristics of NPLs, Brown motion and high surface reactivity, make them to easily undergo homo- and hetero-aggregation in the environment. NPLs can also easily pass through physiological barriers at a faster rate than that of larger plastic particles. This indicate that NPLs can have higher environmental risks, and their environmental fate and impacts should be delineated urgently.[5]

It is reported that MNPLs may have adverse effects on soil properties, soil processes, aquatic organisms and terrestrial plants.[6,7] In aquatic and terrestrial environment, MNPLs may accumulate in different species such as fish, crabs and crops, and eventually enter the human body through the food chain.[8,9] Using different experimental animals under laboratory conditions, it was reported that MNPLs leads to free radical production, immune changes, gene expression changes, genotoxicity, endocrine interference, neurotoxicity, reproductive abnormalities, and behavioral abnormalities.[10] These effects may be related to the possible leaching of polymer monomers and additives, some of which have been proven to be toxic, carcinogenic or endocrine-disrupting, which can cause cancer, and several reproductive diseases to humans and other organisms.[11,12] In addition, MNPLs can absorb persistent organic pollutants or toxic metals from the environment and serve as carriers of pathogenic or antibiotic-resistant microorganisms.[13]

However, MNPLs are extremely complex and diverse in size, shape, density, polymer type and surface properties. The analysis of MNPLs may be like looking for a needle in a haystack. This highlights the importance of choosing appropriate methods to analyze and study the environmental processes and interactions of MNPLs with other pollutants. At present, due to the lack of analytical technology with sufficient sensitivity and selectivity, it is difficult to accurately detect and determine the characteristics of MNPLs in the environment matrix.[14]

To assess the actual risks associated with MNPLs, reliable data on the occurrence of these particles in various environmental and biological samples are needed and powerful analytical techniques are required to do so. The commonly used analytical methods for the analysis of MNPLs include pyrolysis-gas mass spectrometry (Py-GC/MS),[15] Fourier transform infrared spectroscopy (FTIR),[16] Raman spectroscopy,[17] and inductively coupled plasma mass spectrometry (ICP-MS).[18] The MNPLs surface morphology and composition are usually characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). As a mass-based method, Py-GC/MS is the most commonly used method in analyzing MNPLs at present. This method can identify different types of plastics in complex matrix according to the analysis of pyrolysis products. Py-GC/MS has the advantages of high sensitivity, small sample consumption, and fast analysis speed. But it is troublesome to identify a large number of pyrolysis products, and the spectral characteristics obtained cannot fully reflect the composition and structure of the samples. Raman technique is suitable for MNPLs analysis having different size ranges, and particles with similar size ranges can be detected in good accuracy. Raman spectroscopy is a nondestructive analysis method, which can obtain the vibration fingerprint spectrum of MNPLs, and further identify by using self-made and commercial spectrum databases. On the other hand, this method is relatively time-consuming and often interfered by fluorescence.

Atomic spectrometry has the advantages of low detection limit and high sensitivity, and shows great potential in the analysis of MNPLs. Atomic spectrum is a spectrum composed of a series of wavelengths of light emitted or absorbed by electrons in atoms when their energy changes, which can be used for qualitative and quantitative analysis.[19,20] There are many kinds of analytical methods of atomic spectroscopy, including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and X-ray fluorescence spectrometry (XFS), which can be used for quantitative analysis of trace single elements.[21] ICP-MS and inductively coupled plasma optical emission spectrometery (ICP-OES) have been widely used in various research fields because of their short analysis time and sensitivity. For example, after the MNPLs is labeled with metal, the element can be analyzed by ICP-MS and ICP-OES to realize the quantification of MNPLs.[22] ICP-MS can detect a variety of metals to ng level , including Cd (2.34 ng/g), Cu (180.64 ng/g), Ni (12.69 ng/g), Pb (1.17 ng/g), Sb (14.43 ng/g), and Zn (178.03 ng/g).[23] In addition to quantification, laser-induced breakdown spectroscopy (LIBS) and secondary ion mass spectroscopy (SIMS) have other advantages, in realizing the visualization of particles and exploring their spatial distribution.[24] In the *Web of Science*, “microplastic” or “nanoplastic” AND “atomic spectrometry” or “ICP-MS” or “ICP-OES” or “LIBS” or “SIMS” or “XRF” or “AAS” were used as search terms, and a total of 117 most relevant articles were retrieved. After excluding duplicated and meaningless keywords, a co-occurrence analysis of these papers was conducted (Fig. 1). The research on the analysis of MNPLs by atomic spectrometry is mainly concentrated in the recent three years, including identification, characterization and migration in the environment. The results have the following characteristics: (1) With the development of various characterization methods such as atomic spectrometry, the analysis

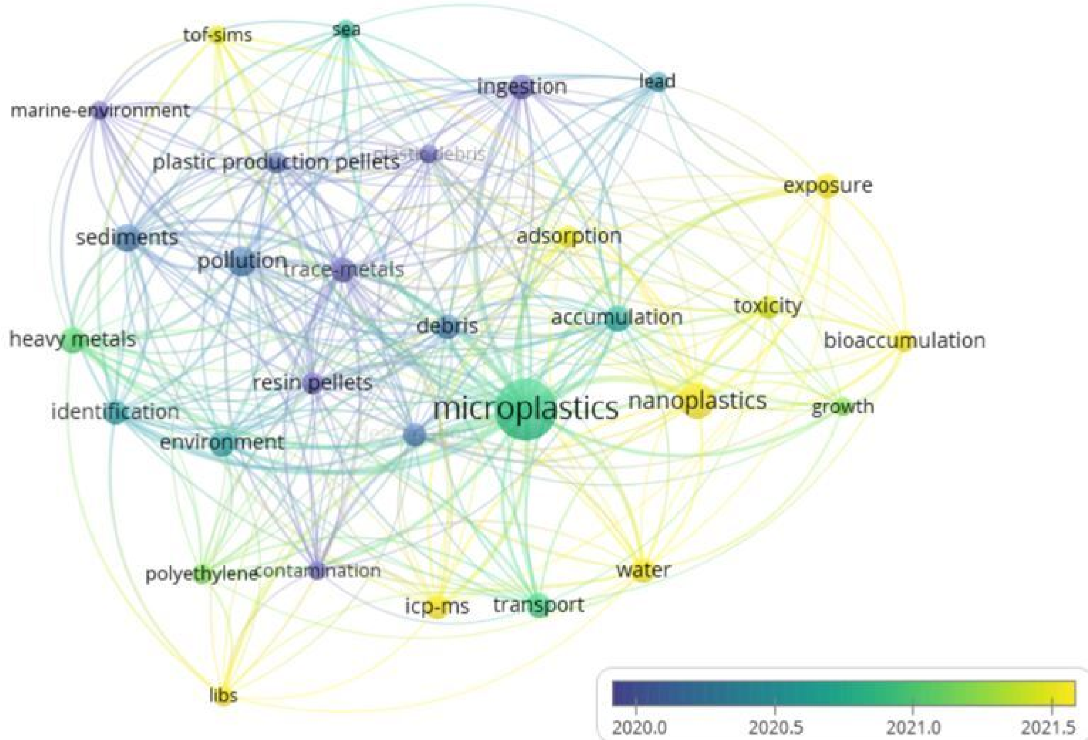


Fig. 1 Overlay visualization of the most frequent terms in "application of Atomic Spectrometry in MNPLs" co-occurrence analysis (at least 6 occurrences). Data was collected from Web of Science on October 30, 2023. The size of the circle indicates the occurrences of the keywords, and the thickness of the links reflects the strength of relevance between the keywords. As shown in the color bar, the co-citation circles and links in the same period are shown in special colors.

analysis of smaller plastics can be realized, and it gradually develops from MPLs to NPLs; (2) In the past, the main research scenes of MNPLs focused on water and sediments, but in recent studies, it began to explore its scenes in soil and organisms (including biological accumulation and toxicity); (3) The study of MNPLs by atomic spectroscopy has developed rapidly and LIBS, ICP-MS and TOF-SIMS are all effective analytical methods at present.

In the pool of literature, there are many studies on the analysis of MNPLs by atomic spectroscopy, but there is no comprehensive review article on the area to the best of our knowledge. In this review, sample pretreatment methods for MNPLs analysis, application of atomic spectrometry in the analysis of MNPLs in complex matrix, and summary and prospect of atomic spectroscopy in MNPLs analysis has been covered. When discussing the pretreatment methods, the different labeling methods of MNPLs and the appropriate separation and digestion methods for the different analysis needs are addressed. The whole process of identification, traceability, aging process, and ecological risk caused by migration and transformation of MNPLs by atomic spectrometry is introduced.

PREPARATION AND PRETREATMENT OF MNPLs BEFORE ANALYSIS

MNPLs are widely distributed in various complex matrices where various interfering entities exist. Hence, selecting appropriate sample collection and handling methods which may differ according to the considered environmental media is mandatory before the qualitative and quantitative analysis. In addition, to explore the environmental behavior of MNPLs and reveal the complex mechanisms, it is usually necessary to prepare functional MNPLs in experimental research, such as modifying or labeling standard plastic particles. Whether they are naturally existing in the environment or model particles, it is necessary to remove the interference of organic matter and other co-existing substances and separate them before analysis.

Preparation of labeled MNPLs. It remains challenging to utilize sensitive atomic spectrometry techniques to characterize the concentration of MNPLs. Plastics are polymers composed of carbon chains, and many atomic spectrometry techniques such as ICP-MS have certain difficulties in detecting carbon directly. The

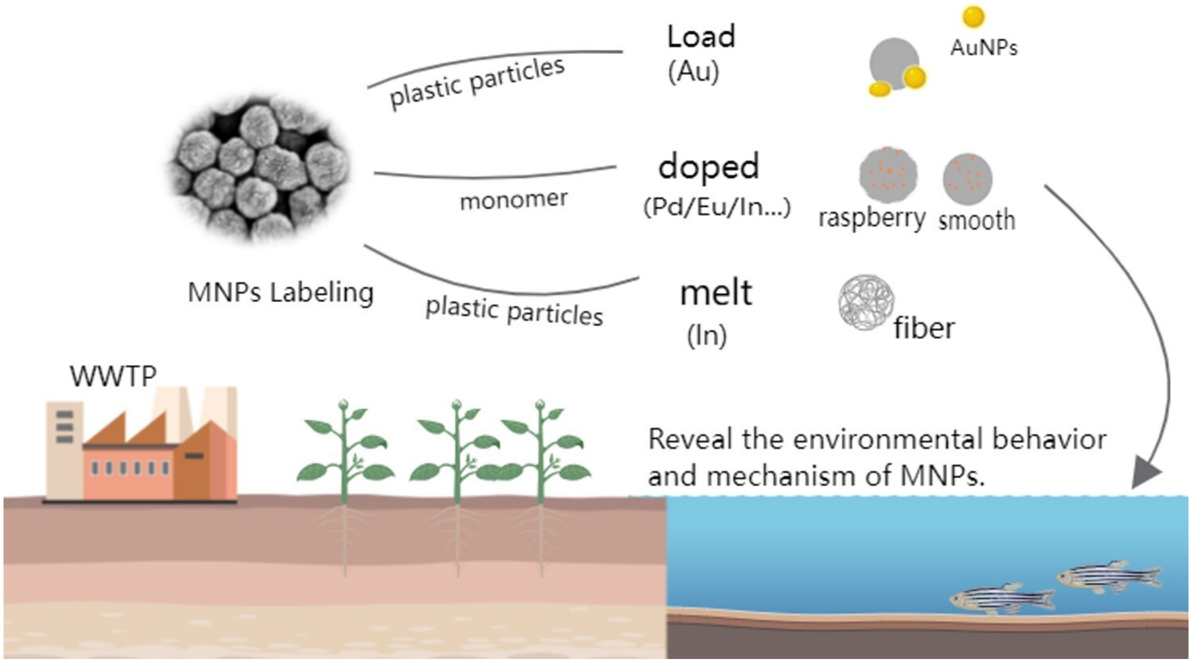


Fig. 2 Different ways of MNPLs labeling.

ionization potential of carbon element is high (11.3 eV), and it exists in argon (mainly as impurities in the form of CO_2) and in reagents (including acid and water) used to generate plasma.[25,26] This indicate that there is high background interference which leads to a high detection limit and a certain difficulty in direct carbon analysis. The background value of carbon can be greatly reduced by shortening the measurement time by using the residence time in the microsecond range, such as single particle ICP-MS (spICP-MS) and single cell ICP-MS (scICP-MS) to measure carbon-containing particles. However, this direct analysis method is mainly aimed at MPLs, and NPLs is not suitable. In addition, using a tracer is a good choice in the study of the potential mechanisms, processes, and principles of the environmental behavior of MNPLs. The application of this method is very extensive, and it can be applied to a variety of complex matrices and there is no limit to the types of quantitative instruments. Therefore, using a tracer is a good choice in the study of the potential mechanisms, processes, and principles of the environmental behavior of MNPLs. The common marking methods reported so far include metal loading, doping, and melting (Fig. 2).

The principle of metal labeling is mainly based on the advantages of MNPLs (especially NPLs) high adsorption capacity to metallic compounds. The common existing chemical forms of metals are metal ions, organometallic compounds, and metal nanoparticles (NPs), and not all metals have good labeling effects. Previous studies have shown that it is difficult to mark MNPLs by metal ions because the quality of metal adsorbed on the surface of particles in the detection process is not enough to compensate for the background signal.[27] Hydrophobic organometallic compounds and positively charged nanoparticles are more effective for marking MNPLs. Lamana *et al.* put forward a new method for the determination of polystyrene NPLs (PS-NPLs) by using single particle ICP-MS (spICP-MS) to detect conjugated gold nanoparticles (AuNPs).[28] It is possible to measure the distribution of the number of particles with different particle sizes. This labeling strategy has shown good results in both detection and quantification and has been optimized for calculating MNPLs in environmental water. However, the method is not suitable for complex matrices as the comprising negatively charged substances or particles may adsorb AuNPs, which leads to the analysis overestimation. In addition, synthetic NPLs usually contain a large number of carboxyl groups which makes the positively charged AuNPs are easily labelled by electrostatic adsorption. But it is not clear whether the original NPLs in real environmental samples have enough carboxyl groups to adsorb AuNPs. The *in situ* growth of AuNPs on NPLs can be optimized by adding surfactants. For instance, in the presence of 100 μM cetyltrimethyl ammonium bromide (CTAB), significant improvement (about 70%) of the labeling efficiency of gold on the surface of PS-NPLs is reported.[29] The use of organometallic compounds, such as $[Au(en)_2]^{3+}$ precursors (an ethylenediamine complex of Au), can effectively mark *in situ* on almost all common environmental NPLs (polyethylene, polyvinyl chloride, polypropylene, polyethylene glycol terephthalate, polystyrene and polymethyl methacrylate), with the size of 50 – 1200 nm.[30] Luo *et al.* used europium chelate Eu-β-diketonate (PS-Eu) with

Table 1. Different MNPLs labeling methods and their applications

Labeling mode	Metal type	Average diameter	Metal content (wt %)	Sample	Addition concentration	Ref.
Internal doping	Pd	160 nm	0.5	wheat	3/30 mg/L	29
Internal doping	Pd	159±0.9 nm (smooth) 186±1.1 nm (raspberry)	0.49	activated sludge	/	27
Surface loading	Eu	244±12 nm	1.6	Wheat and lettuce	1 mg/kg; 10 mg/kg	26
Internal doping	Pd In	187±22 nm (particle) Ø30 μm 510±12 μm (fibre)	0.5 0.213 ± 0.05	Sewage Sludge	/	37
Internal doping	Pd	164±11 nm (smooth) 151±12 nm (raspberry)	0.49	*Oysters*	0.8 mg/L	33
Surface loading	Au	50-1200 nm	/	water	/	25
Internal doping	Pd	160 nm	0.49	Bacteria *Shewanella oneidensis*	18.75-300 mg/L	38
Internal doping	Pd	200 nm	0.3	*D. magna*	0.1 mg/L; 1 mg/L	35
Melt mixing	In	125-250 μm	0.2	soil	/	29
Internal doping	Eu Fe	640 nm 270 nm	<0.2 <40	microalgae	1 mg/L 7 mg/L	30
Internal doping	Pd	205±15 nm	0.49	rainbow trout	10 mg/kg	36
Internal doping / Melt mixing	Pd In	160 nm (particle); 500 ±12.2 mm; Ø30 μm (fibre)	0.49 0.25	WWTP	13.78 mg/L; 2.5 mg/L	28

fluorescent groups to load PS particles with a particle size of 200 nm. They measured the absorption of PS-Eu particles by plants, realizing quantitative and visual dual-function labeling.[31] However, it is necessary to optimize the removal of insoluble residues in the solution and eliminate the interference effects of salt, NOM, inorganic, and hydrophilic organic nanoparticles in environmental water to accurately quantify the MNPLs.

The above method is to mark the pre-existing MNPLs, but doping with scarce elements is realized in the preparation stage of MNPLs, which can be prepared in particle or fiber forms. When scarce metals are used, the tracer will not be quenched by homogenization or digestion of the complex samples. The particles can be directly added to various environmental and biological samples Without concern for background interference. In the work of Mitrano *et al*., a method to synthesize NPLs doped with chemically coated metal Pd as a tracer.[32] It can easily detect and more accurately quantify NPLs with low detection limit in complex media. Using simulated activated sludge process of urban sewage treatment plant, the authors demonstrated the practicability of the method in environmental matrix with batch experiment. Pd can be directly measured by ICP-MS and indicating the NPLs. The NPLs recovery across all the spiked samples were around $93 \pm 3\%$. The particles synthesized were polyacrylonitrile (PAN) core materials containing metal tracers, and then cross-linked polystyrene shells were added to form a core-shell structure. This way of doping metal into the particles further reduced its leaching. The surface of NPLs can be controlled by the composition and speed of feeding the shell polymer material into the reaction vessel. (1) When the mixture of shell raw materials is slowly transitioned between two polymers in gradient to form a shell, a smooth surface will be produced. (2) By directly adding styrene and divinylbenzene to the seeds of PAN core, the phase separation of polymer is carried out in the whole polymerization process, which leads to the appearance of "raspberry". It is verified that the shape of the shell will not affect the function of Pd as a tracer. In addition to Pd, other metals such as In and Fe have also been developed as doping elements.[33-35] Rare earth elements (REEs) are composed of lanthanides plus Sc and Y, and because of their unique properties, REEs have various indispensable applications in modern electronic equipment. Consequently, researchers suggested that REEs may be used as tracers of electronic plastics.[36]

Through the preparation of labelled MNPLs, their application in a variety of complex substrates has been realized. To mention few, their application to study the absorption, migration and transformation of MNPLs by animals and plants,[37-41] evaluation of treatment performance of sewage treatment plants,[30,33,42] their influence of growth activity of bacteria,[43,44] and for quantitative detection of MNPLs in soil[34] can be mentioned (Table 1). Among the three different labeling methods, it needs to be determined according to the actual situation. The synthesis of labeled MNPLs from monomers has good stability and low leaching risk of labeled metals. The particle size and surface morphology can be controlled by adjusting the synthesis time and mode. However, the synthesis steps are complicated and take a long time. The method of marking on the surface of existing particles has the advantages of easy operation and being suitable for various sizes, but there may be a risk of leaching of metals. The above two methods can be applied in both environmental and biological matrix. The last method is marking by melting, and the particles synthesized by this method are usually large-sized plastics of micron or millimeter level, and the shape is usually Fibrous shaped. This method is usually used in environmental matrix.

Separation of MNPLs in environmental samples. The methods of separating MNPLs from the environmental matrix mainly include filtration, centrifugation and size-based separation. The choice of specific methods needs to be determined according to the type of matrix and particle size of the MNPLs.[30,45]

Filtration-based separation is the most common method to extract plastics in the environment, mainly for water samples.[34] Membrane filtration is a very convenient way in actual operation. Plastic particles with different particle sizes can be filtered out according to the pore size of the membrane. However, environmental samples are usually complex, and may contain a large number of other suspended substances that may cause blockage during filtration and thus affecting the separation of MNPLs. Membrane filtration can also be combined with other methods in the actual sampling and separation process. For example, Haque *et al.* digested the collected samples in the step of separating samples from sediments, and then added saturated NaCl solution (1.2 g/cm^3) to the samples for centrifugal separation prior to the liquid part separation by filtration through 0.45 μm Whatman microfiber glass filter paper.[46] Salts such as NaCl and $CaCl_2$ are often added in centrifugal separation to enhance the separation, but their biodegradability is poor and limited their application. To address this issue, Jarosz *et al.* developed a new method, using potassium formate aqueous solution (H_2O/KCOOH) as a salt substitute due to its biodegradability in the environment besides to its role in marking the separation process fast and very effective.[47]

The other separation methods include size exclusion chromatography (SEC), field-flow fractionation (FFF), and capillary electrophoresis (CE). These methods can effectively separate MNPLs in a short time. At the same time, they can be coupled online with detectors to realize the separation and quantification, and provide real-time information of MNPLs. Separation by SEC requires almost no sample preparation for water samples, and cheap and non-toxic mobile phases can be used.[48] In SEC, a solute is eluted according to its hydrodynamic volume, and a polymer often shows multiple distributions of its physical and chemical properties at the same time. However, co-elution may occur, leading to inaccurate conclusions about the size or molecular weight of analytes.[49] CE is a new type of liquid phase separation technology with capillary as separation channel and high voltage DC electric field as driving force, which can realize the effective separation of NPLs. It has high resolution, high sensitivity and short processing time.[50] FFF is a chromatography like technique in which a force field perpendicular to the laminar flow direction is applied to particles in a narrow channel (100 – 500 μm), which has no stationary phase and separates particles according to their sizes which have different retention time in the channel.[51,52] The classification of FFF can be distinguished according to the type of the driving force applied for separation which can be flow field, electric field, centrifugal field, thermal field, sedimentation field, and magnetic field. FFF can realize the separation of NPLs, and has been applied to the separation of MNPLs.[53,54] The FFF technique can be hyphenated with MS, ultraviolet, refractive index, or fluorescence detectors, and can also provide quantitative information about the particles.[55]

Digestion of the samples before MNPLs detection. Actual samples which may comprise MNPLs can be either environmental samples (e.g. water, sediment, and soil) or biological samples (e.g. animals and plants). MNPLs extracted from complex environment matrix may contain other organic/inorganic residues along with the plastic particles which may interfere the characterization and quantification of the MNPLs. This indicate that it is necessary to digest the samples and remove the interfering entities. The most common digestion methods are oxidation, acid digestion[56], alkali digestion[57], and enzyme digestion.[58,59] The choice of specific digestion method needs to be based on the type of matrix and the size of plastic particles. It should be noted that the order of separation and digestion is not fixed, and it needs to be determined according to the actual situation of the sample.

Acid digestion can destroy the complex matrix of samples and remove organic matter, thus minimizing interference. In water and soil samples, nitric acid (65%) is often used for digestion. In addition to using one acid alone, it can also be mixed with hydrogen peroxide (combined with oxidation method) or other acids (sulfuric acid, or hydrochloric acid, hydrofluoric acid) to make the digestion more thorough. For example, adding hydrofluoric acid to digest soil samples can remove not only organic matter but also siliceous particles. Muniasamy *et al.* compared several different acid digestion methods.[57] By summarizing the acid digestion methods in the literature, the reagents that can be used are: HNO_3, H_2SO_4, HF, $H_2O_2$and the mixture of two of them. Among them, aqua regia (HNO_3-HCl combination) is the most commonly used acid digestion method at present. The aqua regia method is widely used in the determination of metals in MPLs because of its simplicity and strong adaptability.

Alkaline digestion is usually suitable for removing organic matter from plants or biological samples. Besides the traditional inorganic alkali potassium hydroxide, some alkaline digestive juices of biological substrates, such as 25% tetramethylammonium hydroxide solution are also a good choice.[44] In addition, there are green methods with less harm, such as H_2O_2, Fenton reagent and enzyme digestion.[56]

APPLICATION OF ATOMIC SPECTROMETRY IN MNPLS ANALYSIS

***In situ* identification, characterization and classification.**

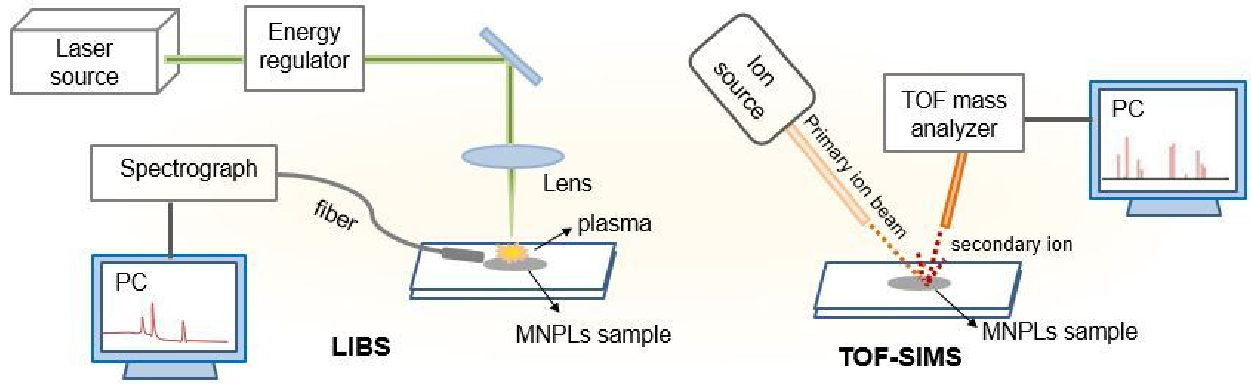


Fig. 3 Basic principles of LIBS and TOF-SIMS. (The green line in LIBS indicates the laser path. Ions emitted by ion sources in TOF-SIMS form secondary ions on the surface of MNPLs.)

Spectroscopic techniques, especially Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR), have been widely used in the characterization of MNPLs. However, these methods have some problems when analyzing actual samples. Raman spectroscopy requires pretreatment of samples and a lot of data processing, and each sample needs to be scanned several times, which takes a long time. Even though FTIR can be used without sample pretreatment, it is difficult to utilize it for the analysis of dark or black samples.[60] Therefore, it is necessary to develop other technologies to optimize the analysis methods. In order to explore the quantity, migration, and environmental effects of MNPLs in the environment, it is necessary to identify and characterize them in situ. The *in situ* techniques have two advantages, rapid analysis and can be used as a handheld system or a small portable device for on-site measurement.

Different types of plastics have certain differences in form and composition. Compared with other MPLs, Polyethylene has a more complex structural surface morphology. The elements that usually exist as additives in MNPLs are used as markers to distinguish different polymer types, so specific elements can be analyzed by ICP-MS, LIBS and other methods. In addition, the classification of MNPLs can be realized by combining spectrogram with machine learning. LIBS technology based on atomic spectrum is a potential choice for *in situ* identification of MNPLs. The cost of LIBS experimental equipment is relatively low, and it does not need complicated sample preparation. There is no need to consider the surface shape and physical state of the sample when detecting. Plasma is generated on the surface of the sample by laser ablation, and after the plasma is cooled, the unique radiation emitted by the elements is detected by a spectrometer (Fig. 3). It can provide the chemical composition and information on molecular structure of the samples and the analysis can also be completed in only a few seconds.[61] Another advantage of this method is the possibility of real time characterization of the samples which is convenient to re-collect the sample if there is a problem. Previous studies have shown that LIBS can be used to distinguish plastics from natural materials and identify the types of basic polymers, especially in distinguishing C-O and C-C skeleton, PE, and PP particles. LIBS techniques are also suitable for *in situ* measurement in field researches.[62] On the other hand, their limited application on analyzing uneven and rough surfaces should be mentioned.

In order to overcome the limitation of analyzing samples in a complex environment, two or more complementary spectral methods and machine learning models are usually used in the application process to realize the rapid and accurate identification and classification of plastics. Combining analytical instruments with multivariate data analysis, such as principal component analysis (PCA), artificial neural network (ANN), and partial least squares discriminant analysis (PLS-DA), increased success rate of LIBS application (36% to 99%) for different types of plastics were reported.[63] LIBS and Raman spectroscopy can be also combined in a system to establish a multimode optical spectrum system.[64] The compactness and robustness of efficient optical alignment make it a portable system that can be operated in a non-laboratory environment. By combining LIBS and Raman spectrum data with PCA, different variants of consumer plastic samples under different physical conditions (such as color and surface conditions) were analyzed. It was found that data clustering based on plastic categories had good classification effect.[65] For example, when analyzing samples from soil, the element and molecular information of LIBS and Raman spectroscopy can complement each other, reducing the number of drop-out in the identification-sorting process.

SIMS is one of the most popular surface imaging technologies, which has the advantages of allowing monoatomic analysis of molecular structure, low molecular weight compounds (＜1000 Da), μg level and high spatial resolution.[66] When the high-energy primary ion beam hits the plastic particles, the polymer molecules on the surface split into smaller fragments and form secondary ions, which correspond to the unique chemical composition of different plastics. Secondary ions are collected by a mass spectrometer (e.g. TOF), and *in situ* mass spectrometry imaging (MSI) is formed by separating and detecting each m/z when the sample is scanned by a focused ion beam (Fig. 3). Time-of-flight SIMS (TOF-SIMS) can realize *in situ* chemical analysis and spatial location at the same time.[67,68] The high detection sensitivity and high spatial resolution (~ 100 nm) of its imaging allow MPLs as small as 1 μm to be detected, and the detection limit is 10~100 ng.[69] TOF-SIMS imaging has the advantages of high chemical specificity and high detection sensitivity. It can identify and locate a large number of MPLs at the same time, and quickly obtain the physical and chemical properties and distribution of the MPLs. The main limitation of this technology is that the area covered by each analysis is small.

TOF-SIMS is applicable to many scenarios, including the analysis of MNPLs in farmland soil, beaches, sediments and biological communities, and even in food samples. This method can be used to characterize different types of MNPLs in farmland soil. For instance, Du *et al*. used TOF-SIMS combined with mass high resolution and positive and negative ion imaging modes.[70] The particle size and abundance of four kinds of MPLs in farmland soil were successfully identified, and the particle size range of MPLs was 0 ~ 35 μm. The fragment ions used for detection were found: the m/z of polypropylene was 71.086 ($C_5H_{11}^+$), the m/z of polyamide was 30.036 (CH_4N^+), the m/z of polyethylene terephthalate was 149.024 ($C_8H_5O_3^+$), and the m/z of polyethylene terephthalate was 83.977(C_4HCl^+). When analyzed in normal mode, the main fragment ions of PE obtained are $[C_3H_3(CH_2)_n]^+$, $[C_nH_{2n}]^+$ and $[C_nH_{2n+1}]^+$.[65] The fragment ion m/z=113 is considered to be suitable for PE identification. This method shows application potential in analyzing more complex plastic particles released from food contact materials.[71] TOF-SIMS further confirmed the quantity ratio of different particles in the leachate of PET/PE composite tea bag. This technology is suitable for 0.195 ~ 1.04 μm PS, 0.311 μm PET and 0.344 μm PE, and the minimum concentration of 2.49×10^9 particles/mL. But a common food contact material PP is not involved here since its mass spectrum is that of PE and the TOF-SIMS cannot distinguish it. In addition, TOF-SIMS can also be used in biological samples. *In situ* chemical analysis and spatial location of MPLs with different chemical components in paramecium were carried out by TOF-SIMS and six different types of MPLs (size, 1 to 50 μm) were simultaneously identified and imaged in the report.[72] The chemical information generated from paramecium and MPLs has been used to identify and visualize the cell structure of paramecium and MPLs.

Traceability of MNPLs in Environment. MNPLs have become ubiquitous in the environment, even in places where human activities are less.[3] Identifying the possible sources of MNPLs is also important to reduce their environmental risks. In the manufacturing process of commercial MNPLs, some additives such as inorganic and organometallic compounds are usually added to broaden their application as heat stabilizers, fillers, pigments, fungicides, and flame retardants.[73] Investigating the characteristics of trace metals in MNPLs is an effective method to trace source of the pollutants. Combining micro-X-ray fluorescence (μXRF) and FTIR has become a well-established method to analyze the source of paint particles.[74] By analyzing the elements of paint fragments in the ocean and comparing them with the samples of existing ships, the source of the fragments can be determined by evaluating their similarity. The determination of the elemental composition of paint particles can also provide tiny but important information about inorganic additives. Similarly, through this combination method, the source of MNPLs in the environment can be explored, which is helpful for targeted prevention of pollution. After collecting samples from the environment, the analysis steps are as follows: (1) analyzing the spectral information by FTIR and comparing it with the known spectral information to preliminarily determine the composition of the polymer; (2) using non-destructive analysis techniques (e.g. μXRF, and LIBS) and carrying out qualitative and quantitative analysis of element composition to distinguish its sources.

X-ray fluorescence (XRF) is an elemental analysis technique in which direct X-ray excitation is used to induce fluorescence emission from a sample for analysis.[75] It has high excitation energy and a large irradiation area, which makes it more suitable for the analysis of uneven samples with low analyte concentration. On-site portable XRF spectrometry is a non-destructive and very useful technique to characterize the composition of synthetic polymers. For example, XRF can be used to evaluate the degree of chlorination, determine whether brominated flame retardants have been added, identify inorganic pigments and detect the presence of harmful and restricted metals.[76] However, the traditional XRF has shortcomings when utilized in plastics analysis. To mention few, the incident flux on the sample is low (which affects the sensitivity of analyzing trace elements) and due to the low density of the plastic materials, the absorption capacity of plastics to radiation is relatively poor (which has an impact on the generation and detection of fluorescent X-rays). Therefore, improved XRF techniques such as μXRF, Energy Dispersion XRF (ED-XRF) among others have been proposed for the actual analysis.

Unlike the traditional XRF, μXRF uses X-ray optical crystals to limit size of the excitation beam or focus the excitation beam on the surface of the sample to form a small spot, which can detect a very small sample area and analyze the tiny characteristics on the sample. In addition, a portable test bench has been developed, in which XRF can be operated remotely through a laptop. The sample is shielded by a tungsten PVC shell, and the direct element characteristics of the stranded MPLs are tested.[77] ED-XRF analysis uses a portable instrument, which is remotely activated by a laptop. The sheet is placed in the center of the detector window

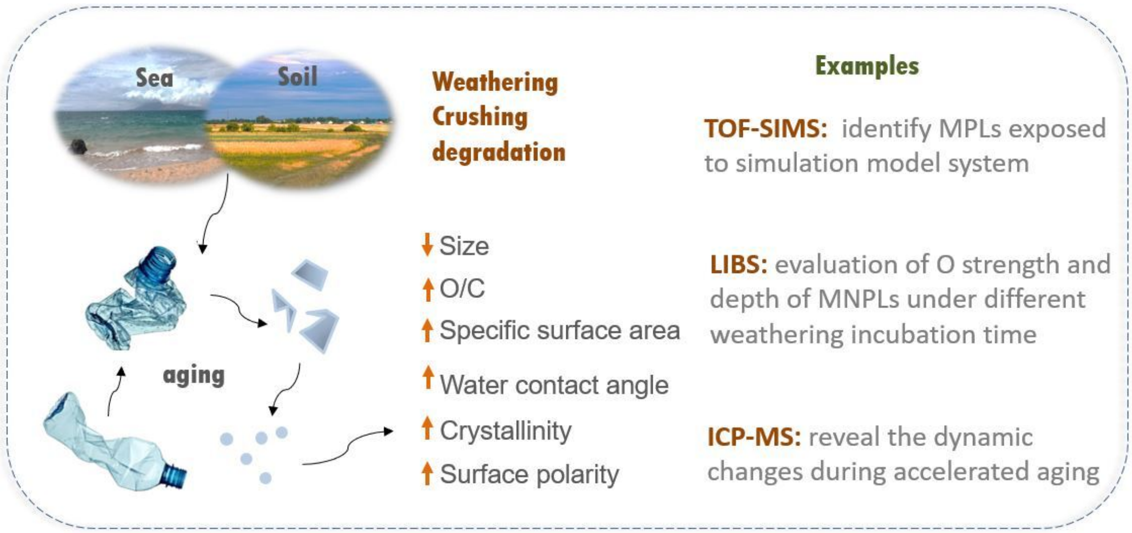


Fig. 4 Quantitative analysis of aging behavior of MNPLs in the environment by atomic spectrometry. (The black arrows show the transformation process of MNPLs aging in the environment; The orange arrows show the changing trend of various properties of MNPLs during the aging process.)

and real-time images generated by CCD camera in the detector window and 3 mm circular grid is projected on the notebook computer by Niton software.[78] It is helpful to locate and estimate the particle size independently.

One applications area of traceability of MNPLs is the analysis MNPLs produced by the wear of ship paint in the ocean. The wear of ship paint surface is a potential source of MPLs. Paint flakes have been found in MPLs sampled from marine environment and digestive tract of marine organisms. The combination of FTIR and μXRF techniques can help to identify the source of coatings, and understand the coating fragments contribution on MPLs content in the environment.[79] Taking the case of Geldet River as an example, 7% of plastic waste (n = 883) collected in the Geldet Estuary of Hayes was analyzed by FTIR.[79] It was found that PP, PE and PS were the most abundant polymer types from disposable packaging materials. A limited amount of plastic waste (n = 100) was selected, and its mineral element composition was non-destructively screened by μXRF. The results showed that S, Ca, Si, P, Al, and Fe are the main constituting mineral elements. These elements come from flame retardants, mineral fillers, and catalysts commonly used in plastic production, so as to infer the possible sources of plastics.

The relative intensity of fingerprint peak in LIBS spectrum is used to express the semi-quantitative analysis of target metal.[80] This method was successfully applied to the simultaneous determination of various metals in MPLs samples. The content of each metal (including Cu, Pb, Fe, Cd, Zn, Mn, and Cr, *etc.*) was determined by using the linear relationship between LIBS signal intensity and element concentration. Based on the statistical analysis of the characteristics of trace metals in MPLs, the sources and possible sources of the detected metals can be described. Although LIBS has been widely used to quantify the content of heavy metals, this technology is affected by the negative matrix interference caused by physical scattering of samples. In addition to tracing the trace metals, this non-destructive technique based on single particle level analysis can be used to study the plastic-metal interaction and explore the complex environmental factors affecting the absorption process.

Analysis of the aging process and property change. In the process of long-term environmental action, plastics will undergo weathering, aging and degradation, forming smaller particles or becoming carriers of some pollutants in the process (Fig. 4). Therefore, it is necessary to explore the long-term environmental impact of MNPLs and formulate mitigation plans to minimize their potential effects. Weathering and degradation along the coast are considered to be the main reasons for polymer embrittlement, which may eventually lead to MNPLs. Jungnickel *et al*. analyzed the degradation of PE, a common plastic type in the environment based on the composition and size of the new debris using TOF-SIMS.[81] The artificial seawater was used to simulate the waves in the laboratory, and it was observed that the primary PE pellets suffered serious surface damage and secondary MPLs particles were formed at the same time. Without any pretreatment, TOF-SIMS imaging has been also successfully used to identify MPLs in Ottawa sand model system exposed to ocean wave simulation for 14 days. In addition, TOF-SIMS observations provided direct evidence for the conditional fragmentation process.[82]

LIBS can identify the sample material and determine the chemical composition layer by layer at the same time, which has been proved to be a tool for depth profile analysis in metal research. LIBS was used to evaluate the O intensity and depth of PS at different weathering incubation times.[83] The weathering-induced oxidation effect after artificial weathering for about 400 h was observed by detecting the spectral characteristics of oxidation and laser ablation. The depth profile shows that the oxidation of all samples requires 800 h, and the oxidation extends to the second layer with a depth of about 51.23 μm. For the sample weathered for 2000 h, the oxidation penetrated into the third layer, and the depth was 57.98 μm. This proves that the oxygen content and its penetration depth change with the weathering time. LIBS technology can combine plastic identification, trace element detection and weathering and oxidation detection, and hence it has great potential in plastic waste identification and analysis.

The content of metal-based NPLs in the environment or metal-labeled MNPLs prepared in the laboratory can be determined by ICP-MS. Specifically, spICP-MS was used to quantify the size (0.8~ 5 μm) and concentration of MPLs labeled with Au. The occurring dynamic changes during accelerated aging were revealed with a relatively low detection limit (8.4×10^5 particles /L).[84]

Interaction between MNPLs and pollutants. With rapid urbanization and the development of industrialization, various anthropogenic activities such as mining, smelting, and agriculture intensify the release of heavy metals which make them important environmental pollutants.[85] When heavy metals and MNPLs co-exist in environmental media, they may interact and will have a greater negative effect on the ecological environment. Therefore, it is necessary to find/develop suitable methods to explore their interaction behavior and mechanisms. The adsorption mechanisms of heavy metals on MNPLs in water include complexation, electrostatic attraction, cation-π bond interaction, and physical adsorption.[86] The adsorption capacity of MNPLs for heavy metals is related to the functional groups and hydrophobicity of the MNPLs. The existence of C-O and N-H in MPLs leads to their high adsorption capacity towards heavy metals.[87]

After collecting MNPLs from actual environmental samples, seawater, sediments, soil, and wetlands, samples are pretreated by separation and digestion, and then, the metal content on the surface of MNPLs can be quantitatively analyzed and the correlation of spatial distribution can be obtained by ICP-MS and ICP-OES.[88-91] This approach can be followed to explore the interaction between MNPLs and inorganic metals and assess their possible environmental impact. Jian et al. systematically studied the effects of internal factors (polymer type and particle size of MPLs) and external factors (pH, organic matter, ionic strength, and sediment of water) on metal adsorption in Poyang Lake.[92] The metal adsorption reached the highest equilibrium at 72 h, and the adsorption capacity decreased with the increase of MPLs particle size and followed a decreasing order of PP > PE > PS and Cu > Pb > Cd for the heavy metals. In addition, factors affecting the adsorption procedure are also different in different environments. Dissolved organic matter fulvic acid (FA) consisting of C, H, O, N, and S naturally exists in the Poyang Lake wetland. This natural FA contains many phenolic hydroxyl groups and carboxyl groups, which can interact with oxides, metal ions, and other organic substances. The adsorbed metals were quantified by ICP-MS, and it was found that the adsorption of Cu, Cd, and Pb by all MPLs in the experiment increased with the increase of FA concentration in water. FA can also adhere to the MPLs surface, which leads to the increase of zeta potential (negative charge) on the MPLs surface and enhances their electrostatic interaction with Cu, Cd, and Pb.

Biofilm may be also form on the surface of MNPLs during the aging process. Compared with the original MPLs, due to the formation of biofilm on MPLs, increased adsorption of heavy metals was observed.[93] At the same time, due to the cracks on the aging MPLs, the surface area increases, providing more sites for adsorption.[94] Using NanoSIMS and SEM-EDX for visualization and ICP-MS for quantitative analysis, Zhou et al. investigated the contribution of biofilm to the adsorption of Cu on MPL surface.[95] Based on NanoSIMS visualization, the distribution of biofilm and Cu on the MPLs surface was located at different Cu concentrations (10, 100, and 1000 μg/L) and the results indicated that Cu and biofilm coexisted in the same position on the MPLs surface, and biofilm could promote the adsorption of Cu. In addition to traditional plastics, biodegradable plastics have begun to rise in recent years. They have replaced traditional plastics, but their environmental risks in the aging process may be greater than traditional plastics. To this end, Shi et al. studied the aging of biodegradable MPLs and conventional MPLs in the Pearl River Estuary after long-term exposure and their effects on the adsorption of heavy metals in seawater.[96] Their results showed that the changes in surface characteristics of biodegradable MPLs after aging are more obvious than those of traditional MPLs, which may indicate that they may pose higher risks to environmental. After 9 – 12 months of aging, the characteristic changes and adsorption capacity (towards Cu, Pb, and As) of biodegradable MPLs were found to be more prominent than that of conventional MPLs.

Interactions between plastics and metals are speculated to occur on the surface and the classical isotherm theory has been used to reveal the adsorption capacity of MNPLs. Some atomic spectroscopy techniques can be also used to investigate the adsorption capacity and diffusion of metals by MNPLs. For instance, Aynard *et al*. developed an advanced method, using complementary surface analysis techniques: TOF-SIMS, XPS, and ICP-MS to quantify the total mass of Cu metal adsorbed by NPLs.[97] The interaction between NPLs and Cu in the surface layer is analyzed, and the ability of the NPLs to adsorb metals in their core is revealed. After being exposed for 24 – 144 h, the surface chemical composition of the samples was analyzed by TOF-SIMS and XPS, and the Cu content of the whole NPLs was determined by ICP-MS. The results show that after 24 h exposure, the Cu concentration on the surface of NPLs remains unchanged due to saturation, while the Cu concentration inside the NPLs increases as time increases. Organic fragments peculiar to the polymer

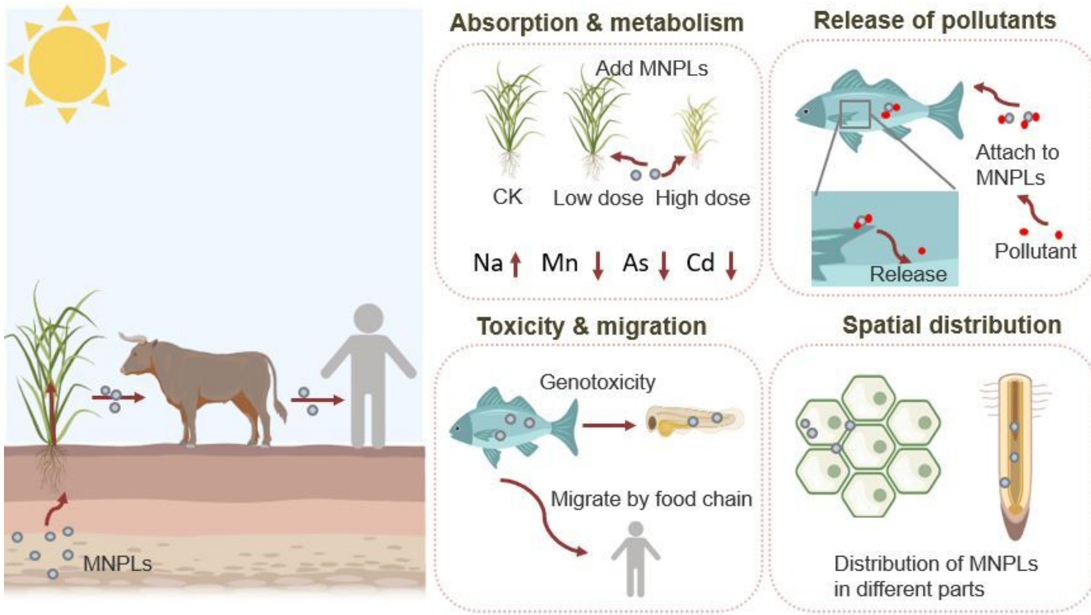


Fig. 5 Environmental and ecological risk assessment and toxicological effects of MNPLs.

structure of NPLs were observed, such as $C_2H_3^+$, $C_3H_3^+$, $C_6H_5^+$, $C_7H_7^+$ or C_9H_7. More interestingly, molecular fragments of copper oxide, such as $Cu_2(OH)^+$ and $C_4H_8O_3Cu^+$ were also observed. It confirmed the interaction between NPLs containing carboxyl groups and Cu. In addition to analyzing the light beam, TOF-SIMS also removes samples layer by layer by using sputtering ion beam, thus providing local resolution depth profile and complete three-dimensional analysis data. According to Fick's second diffusion law, Kern et al. determined the diffusion coefficients of Cu^{2+} and Ni^{2+} in PP in the frozen state ($T < -130$ °C) by using the classical SIMS depth spectrum method.[98] The results showed that the diffusion rate of Cu^{2+} in dried PP is faster than that of Ni^{2+} and relative to the dry PP, the diffusion rate of Cu^{2+} ion in water-saturated PP is slower.

Through the adsorption process, MNPLs become host of pollutants and share the environmental niche.[99] The potential interaction between them can alter their environmental behaviors. As an example, high contents of trace metals in oysters (30.5, 4.4, 0.40 and 181 μg/g dry weight of Cr, Cd, Pb and Cu, respectively) all exceeding the standard were reported.[100] In the report, strong correlation between *in vivo* concentrations of MPLs and the four trace metals Cd, Cr, Cu, and Pb were observed which indicating their potential interactions *in vivo*. It is also found that MPLs fiber can easily enrich metal elements, especially Ni, Mn, Cu and Cd. Besides being the carrier of pollutants, the adsorption of some pollutants on MNPLs can slow down its biological toxicity. Li et al. observed the surface of PEMP (150 μm) separated from ZnO nanoparticles (nZnO, 20 – 30 nm) suspension by SEM, determined their Zn concentration by ICP-MS, and determined the crystal morphology of Zn on the surface by XRD.[101] The results revealed that the suspended nZnO aggregates are adsorbed by PEMP and its toxic effects on the growth of marine microalgae was significantly reduced (~14.4%). Similar observation was reported in another study in which the potential interaction between two kinds of PS-NPLs (size, 50 and 500 nm) and two kinds of silver compounds, AgNPs (size, 10 nm) and silver nitrate.[102] Exposure to silver compounds, PS-NPLs, or their joint exposure did not affect the survival of eggs to adults. The combined treatment successfully restored the delay of fly emergence induced by silver compounds. The antagonistic interaction between PS-NPLs and silver compounds (whatever its form) was confirmed, which improved the harmful effects related to silver exposure. In addition, the interaction between MNPLs and pollutants can affect the biogeochemical cycle of pollutants and promote pollutants to sink into deeper water layers and sediments.[103]

Environmental and ecological risk assessment and toxicological effects. MNPLs will undergo migrations and various transformations in the environment and be absorbed by animals and plants. The main biological effects involved are as follows: (1) the absorption, metabolism and growth of MNPLs in organisms; (2) the release of pollutants carried by MNPLs after they enter the organism; (3) reproductive toxicity, genetic toxicity and enrichment effect of MNPLs in the food chain; (4) Spatial distribution of MNPLs in organisms (Fig. 5). These contents can be analyzed in all directions by atomic spectroscopy.

As mentioned in the previous chapter, the labeling of MNPLs is the best means to study their migration, absorption, and transformations in the environment and organisms, animals and plants. In such cases, animals/plants are exposed to the solution containing labeled plastics for culture, and the labeled elements are analyzed by ICP-MS or ICP-OES to realize the quantification of MNPLs.[56,104,105] Hasselerharm *et al.* exposed *Gammarus pulex* to different concentrations of Pd-doped NPLs through natural sediments, and evaluated their absorption and chronic effects through 28-day standardized single species toxicity test.[101] NPLs concentration is quantified according to the Pd concentration measured by ICP-MS of exposed organism digests and excreted fecal particles during purification 24 hours after exposure. Ribeiro et al. also used the same method to evaluate the NPLs concentration in exposed oysters. They inferred the accumulation and elimination speed of Pd-NPLs, and understood the metabolism of Pd-NPLs during purification.[107] In addition to the traditional ICP-MS, different modes such as single-cell ICP-MS (scICP-MS) can be used in practical applications. Cassano *et al*. prepared Au-containing NPLs and established a rapid and high-throughput qualitative method to study their cell interaction.[108] The interaction and uptake of NPLs by mouse macrophages were quantified by scICP-MS and electron microscope. The applicability of rapid detection of doped particles by scICP-MS was proved, and it was applied to the analysis of NPLs (size, 50 – 350 nm). ICP-OES or ICP-MS can also be used study the relationship between the characteristics of nutrient elements (ionome) of rice seedlings and MPLs.[109] After 21 days of experimental treatment, different doses of PE-MPLs had no significant effect on the growth of seedlings, but middle and high doses of PE-MPLs had significant inhibition on the root growth of the seedlings. Further analysis showed that PE-MPLs treatment reduced the accumulation of essential, Mn, and non-essential, As and Cd, mineral elements but increased the accumulation of essential mineral elements Na in rice seedlings.

MNPLs interact with metal or organic pollutants in the environment, and pollutants may be released in the body after being absorbed by animals and plants, resulting in greater ecological risks. Therefore, it is necessary to explore the process in detail. Some studies have simulated the *in vitro* gastric conditions of marine birds, and investigated the bioavailability of autogenous metals (Fe, Mn) and trace metals (Co, Pb) obtained from the environment by PE-MPLs.[110] The plastic after metal adsorption was exposed to acidified pepsin salt solution (pH, ~ 2.5) at 40 °C for 168 h, and the extracted metal and residual metal were analyzed by ICP-MS. The metabolism of plastics and heavy metal pollutants often takes a long time. Once ingested, pollutants may stay in the body for a long time. Short-term exposure is not enough to reflect the real situation, so long-term research is needed. Jang *et al.* quantified the transfer of trace metal Cu and Pb from MPLs (PA and biodegradable plastic PLA) to catfish at environmentally relevant concentrations.[111] Fish were exposed to seven different feed combinations and kept for three months. Every other month, the concentrations of Cu and Pb in gill, intestine, liver and edible muscle were analyzed by ICP-OES. The results showed that there were significant differences in the accumulation of trace metals in different tissues, with the highest content in gill, followed by liver, intestine and edible muscle. At the same time, like the research on biodegradable plastics mentioned in the previous section, a large amount of metal of biodegradable PLA is transferred to catfish, which may pose a greater threat to the environment when ingested.

In the environment, MNPLs may interact with organisms, be absorbed by biota, and then transfer in the food chain.[41,112-115] Understanding the nutrient transfer of MNPLs is the basic element to evaluate its possible risks. Due to the limitations of the analysis, this nutrient transfer is difficult to quantify and can only be determined by using fluorescent-labeled plastic particles. Recently, scICP-MS was introduced to measure the concentration of elements in cells on a cell-by-cell basis. The concentration was as low as one gram per liter. It is possible to measure the transfer concentration of metal-doped MNPLs in the food chain at trace level by these technologies. Monikh *et al.* used 270 nm iron oxide doped PS-NPLs and 640 nm Eu doped PS-NPLs (Eu-PS-NPLs) to evaluate the effect of particle size on the nutrient transfer of MNPLs along the food chain of algae-*Daphnia magna,* and the effect on the reproduction of *Daphnia magna* that feeds on the algae exposed to MNPLs.[116] The results show that MNPLs may be transferred to a higher nutritional level. MNPLs may have an impact on the offspring of organisms in addition to transfer of the food chain. Heinlaan *et al.* used Pd-doped PS to evaluate the multi-generation (F0 – F3) impact of NPLs for the first time.[40] The rigor of this article is to explore whether the impact of plastics on biology is specific by comparing other nanoparticles. The results showed that 0.1 mg/L NPLs did not affect on F3 adult *Daphnia magna*, but 1mg NPLs/L had a stimulating effect on F3 adult *Daphnia magna* (higher fertility). In contrast, 1 mg/L SiO_2 has a significant effect on the mortality, body shape and fertility of F3 adults. Both NPLs and SiO_2 have effects on offspring, resulting in the decrease of body shape and fat content of F3 cubs. Importantly, the effects of NPLs on rats' adults and offspring only began after multiple generations of exposure.

The use of metal-doped MNPLs extends our analysis possibilities to μXRF and ICP-MS.[117-119] XRF has been proven to be a unique technology to study the interaction between plants and engineered nanomaterials, which provides multi-element detection with lateral resolution and important information for understanding the absorption, transportation and storage mechanisms.[120] In addition to the basic quantification of elements, visualization can provide more effective information for the spatial distribution of NPLs. μXRF technique was used to observe the NPLs in the root system.[37] NPLs accumulate on the root epidermis, especially in the root tip and root mature area. The close relationship between plant roots, root deposits and the behavior of NPLs is obvious. Using Pd signal, the localization of NPLs was studied by μXRF on the whole root tip and root frozen section of mature area of plants exposed to 30 mg/L NPLs. Combined with the evidence of absorption and transport, root cap is shown to be the entry point of NPLs in wheat plants. For ICP-MS, fluorescence imaging and quantitative bioanalysis can also be realized by combining time-gated technology, and the absorption pathway of NPLs by edible plants is qualitatively studied.[31] The absorption of PS-Eu particles by hydroponic wheat (*Triticum aestivum*) and sandy lettuce (*Lactuca sativa*) was determined by ICP-MS. PS-Eu particles mainly accumulate in the root system, but the transport to the stem is limited (the transport amount is less than 3% when 5000 μg PS are exposed per liter). Through the time-resolved fluorescence of Eu chelate, PS-Eu particles in roots and buds were visualized by time-gated luminescence technology.

CONCLUSIONS AND OUTLOOKS

The number of articles on MNPLs has increased, especially more new researchers have come onboard and paying attention to MNPLs. The basis of studying various environmental behaviors of MNPLs starts from developing/adopting appropriate analytical methods. In this paper, the application of atomic spectrometry in MNPLs is reviewed. Atomic spectrometry has numerous advantages such as accuracy, rapidity, simple operation, low detection limit, and applicable on wide particle size range. It also provides more spatial distribution information besides to the traditional quantification. At the same time, the method of marking plastics is presented in detail to further clarify the limitation of carbon element in some instrumental analysis. The combination of atomic spectroscopy and other methods can help to identify, characterize, and analyze the whole life cycle of MNPLs, fully understand their transportation and fate, and have great application prospects in reducing their ecological and environmental risks.

There are still some challenges in the application of atomic spectrometry in MNPLs: (1) At present, expensive rare metals such as gold, palladium, and europium are usually used to mark MNPLs. Hence, developing marking methods with high detection sensitivity and low prices is urgent demand. In addition, the ionization efficiency of carbon elements should be improved to realize the direct quantification of C without labeling other elements. (2) Miniaturized atomic spectrometers should be actively developed for quick and in situ measurement of MNPLs and to realize large-scale application and popularization such analysis. (3) Another research gap to be addressed in the future is developing a high-throughput nano-analysis system, which can simultaneously determine the chemical characteristics and morphology of MNPLs, and has an automatic quantitative algorithm to realize the systematic analysis of MNPLs. (4) To ensure the reliable results of MNPLs analysis in different media, well-validated techniques have to be there. Therefore, it is necessary to verify and compare the methods in the future and form a unified standard method. It is urgent to add new management regulations from the aspect of policy formulation in order to manage MNPLs in the process of use.

AUTHOR INFORMATION

Zhiqiang Tan obtained his B.Sc. in environmental sciences at Hebei University, China, in 2005, and then received his M.Sc. in environmental sciences under the supervision of Professor Xiandeng Hou from Sichuan University, China, in 2008. He obtained his Ph.D. in environmental sciences in 2011 under the supervision of Professor Jingfu Liu at Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences (CAS), Beijing, China, and then became a postdoctoral researcher with Professor Guibin Jiang from 2011 to 2013. He has successively conducted research at Yonsei University, the University of Utah, and University of Massachusetts as a visiting scholar from 2013 to 2018. He is currently a full professor at RCEES, CAS. His research interests focus on the development of new instruments for the identification and characterization of low-concentration micro/nanoparticles and their applications in environmental chemistry, nano-agriculture, and biomedicine. He has been working as member of editorial board for *Atomic Spectroscopy*.

Yongguang Yin received his B.Sc. in chemistry at Chongqing University, China, in 2002 and then received his M.Sc. in analytical chemistry under the supervision of Professor Zhining Xia from Chongqing University in 2005. He obtained his Ph.D. in environmental sciences in 2008 with the guidance of Professor Guibin Jiang at RCEES, CAS, Beijing, China. Currently, he is a full professor at RCEES, CAS. His research interests include the environmental behaviors and geochemical cycling of toxic metals. He has been working as member of editorial board for *Atomic Spectroscopy* since Jan. 2020.

Corresponding Author

* Z. Q. Tan

Email address: zqtan@rcees.ac.cn

*Y. G. Yin

Email address: ygyin@rcees.ac.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 22241601 and No. 22076199).

REFERENCES

1. F. Laborda, C. Trujillo, and R. Lobinski, *Talanta*, 2021, **221**, 121486. https://doi.org/10.1016/j.talanta.2020.121486
2. J. Caldwell, C. L. Fonta, G. Toullec, N. H. Lyndby, B. Haenni, P. T. Blanco, B. Espiña, B. R. Rutishauser, and A. P. Fink, *Environ. Sci. Technol*., 2023, **57**, 6664-6672. https://doi.org/10.1021/acs.est.2c09233
3. L.-P. Yang, B.-Z. Tang, and W.-X. Wang, *ACS Nano*, 2023, **17,** 19410-19420. https://doi.org/10.1021/acsnano.3c07571
4. J. Gigault, A. Halle, M. Baudrimont, P. Y. P. F. Gauffre, T. L. Phi, H. E. Hadri, B. Grasslf, S. Reynaud, *Environ. Pollut*., 2018, **235**, 1030-1034. https://doi.org/10.1016/j.envpol.2018.01.024
5. P. Li, Y.-J. Lai, Qingcun Li, L.-J. Dong, Z.-Q. Tan, S.-J. Yu, Yongsheng Chen, V. K. Sharma, J.-F. Liu, and G.-B. Jiang, *Anal. Chem*., 2022, **94**, 740-747. https://doi.org/10.1021/acs.analchem.1c03114
6. F. Blancho, M. Davranche, R. Marsac, B. Grassl, S. R. A. Léon, A. Dia, and J. Gigault, *Environ. Sci.: Nano*, 2022, **9**, 2094. https://doi.org/10.1039/d2en00048b
7. F. Dang, Q.-Y. Wang, X.-L. Yan, Y.-Y. Zhang, J.-C. Yan, H. Zhong, D.-M. Zhou, Y.-M. Luo, Y.-G. Zhu, B.-S. Xing, and Y.-J. Wang, *ACS Nano*, 2022, **16**, 10, 17157–17167. http://doi.org/10.1021/acsnano.2c07627
8. M.-M. Teng, X.-L. Zhao, C.-G. Wang, C. Wang, J. C. White, W.-T. Zhao, L.-F. Zhou, M. Duan, and F.-C. Wu, *ACS Nano*, 2022, **16**, 8190-8204. https://doi.org/10.1021/acsnano.2c01872
9. F. Dang, Q.-Y. Wang, Y.-N. Huang, Y.-J. Wang, and B.-S. Xing. *Eco-Environ. & Health*. 2022,**1**,11-22. https://doi.org/10.1016/j.eehl.2022.02.001
10. M.-C. Shen, Y.-X. Zhang, Y. Zhu, B. Song, G.-M. Zeng, D.-F. Hu, X.-F. Wen, and X.-Y. Ren, *Environ. Pollut*., 2019, **257**, 511-521. https://doi.org/10.1016/j.envpol.2019.05.102
11. Y. Li, L.Tao, Q. Wang, F.-B. Wang, G. Li, and M.-Y. Song. *Environ. & Health*, 2023, **1**, 4, 249-257. http://doi.org/10.1021/envhealth.3c00052
12. Y.-Y. Zhang and G. G. Goss, *Environ. Sci.: Nano*, 2021, **8**, 3685-3698. https://doi.org/10.1039/d1en00738f
13. A. Aynard, C. Courrèges, C. J. J. Lamana, A. Raad, Miqueu, B. Grassl, and S. Reynaud, *Environ. Pollut.*, 2023, **323**, 121229. https://doi.org/10.1016/j.envpol.2023.121229
14. S. M. Mintenig, S. C. Dekker, P. S. Bäuerlein, A. A. Koelmans, and A. P. van Wezel, *Environ. Sci.: Nano*, 2018, **5**, 1640. https://doi.org/10.1039/c8en00186c
15. Y. Wang, L.-L. Xiang, F. Wang, Z.- Q. Wang, Y.-R. Bian, C.-G. Gu, X. Wen, F. O. Kengara, A. Schäffer, X. Jiang, and B.-S. Xing. *Environ. Sci. Technol*., 2022, **56**, 16907-16918. https://doi.org/10.1021/acs.est.2c06054
16. S. Y. Lee, J. An, and J. H. Kwon, *Environ. Pollut*., 2023, **336**, 122452. https://doi.org/10.1016/j.envpol.2023.122452
17. L. Cabernard, L. Roscher, C. Lorenz, G. Gerdts, and S. Primpke, *Environ. Sci. Technol*., 2018, **52**, 13279-13288. https://doi.org/10.1021/acs.est.8b03438
18. M. Trainic, J. M. Flores, I. Pinkas, M. L Pedrotti, F. Lombard, G. Bourdin, G. Gorsky, E. Boss, Y. Rudich, A. Vardi, and I. Kore, *Commun. Earth Environ*., 2020, **1**, 64. https://doi.org/10.1038/s43247-021-00119-5
19. P.-P. Chang, L.-Na. Zheng, B. Wang, M.-Li. Chen, M. Wang, J.-H. Wang, and W.-Y. Feng, *Atom. Spectrosc*., 2022, **43**, 255-265. https://doi.org/10.46770/AS.2022.108
20. J.-H. Liu, L.-N. Zheng, J.-W. Shi, X. Wei, X. Li, M.-L. Chen, M. Wang, J.-H. Wang, and W.-Y. Feng, *Atom. Spectrosc*., 2021, **42**, 114-119. https://doi.org/10.46770/AS.2021.102
21. B. K. Adji, I. Octodhiyanto, R. Rahmayanti, and A. P. Nugroho, *Water Air Soil Pollut*., 2022, **233**, 112. https://doi.org/10.1007/s11270-022-05572-2
22. S. Kühn, A. van Oyen, A. M. Booth, A Meijboom, J. A. van Franeker, *Chemosphere*, 2018, **213**, 103-113. https://doi.org/10.1016/j.chemosphere.2018.09.032
23. H. Wijesekara, N. S. Bolan, L. Bradney, N. Obadamudalige, B. Seshadri, A. Kunhikrishnan, R. Dharmarajan, Y. S. Ok, J. Rinklebe, M. B. Kirkham, and M. Vithanage, *Chemosphere*, 2018, **199**, 331-339. https://doi.org/10.1016/j.chemosphere.2018.01.166
24. D. Chen, T. Wang, Y.-W. Ma, G. W. Wang, Q.-W. Kong, P.-F. Zhang, and R.-L. Li, *Sci. Total Environ*., 2020, **743**, 140850. https://doi.org/10.1016/j.scitotenv.2020.140850
25. L. Hendriks and D. M. Mitrano, *Environ. Sci. Technol*., 2023, **57**, 7263-7272. https://doi.org/10.1021/acs.est.3c01192
26. Z.-Q. Tan, B.-W. Wang, Y.-G. Yin, Q. Liu, X. Li, and J.-F. Liu, *Anal. Chem.*, 2020, **92**, 1549-1556, http://dx.doi.org/10.1021/acs.analchem.9b04837
27. L. Marigliano, B. Grassl, J. Szpunar, S. Reynaud, and J. J. Lamana, *Molecul*es, 2021, **26**, 7093. https://doi.org/10.3390/molecules26237093
28. J. J. Lamana, L. Marigliano, J. Allouche, B. Grassl, J. Szpunar, and S. Reynaud, *Anal. Chem*., 2020, **92**, 11664-11672. https://doi.org/10.1021/acs.analchem.0c01536
29. P. Li, C.-J. He, and D.-H. Lin, *Environ. Pollut*., 2022, **314**, 120267. https://doi.org/10.1016/j.envpol.2022.120267
30. Y.-J. Lai, L.-J. Dong, Q.-C. Li, P. Li, Z.-N. Hao, S.-J. Yu, and J.-F. Liu, *Environ. Sci. Technol.*, 2021, **55**, 4783-4791. https://doi.org/10.1021/acs.est.0c06839
31. Y.-M. Luo, L.-Z. Li, Y.-D. Feng, R.-J. Li, J. Yang, W. J. G. M. Peijnenburg, and C. Tu, *Nat. Nanotechnol.*, 2022,**17**, 424-431. https://doi.org/10.1038/s41565-021-01063-3
32. D. M. Mitrano, A. Beltzung, S. Frehland, M. Schmiedgruber, A. Cingolani, and F. Schmidt, *Nat. Nanotechnol*., 2019, **14**, 362-368. https://doi.org/10.1038/s41565-018-0360-3
33. S. Frehland, R. Kaegi, R. Hufenus, and D. M. Mitrano, *Water Res.*, 2020, **182**, 115860. http://doi.org/10.1016/j.watres.2020.115860
34. A. H. Tophinke, A. Joshi, U. Baier, R. Hufenus, and D. M. Mitrano, *Environ. Pollut*., 2022, **311**, 119933. https://doi.org/10.1016/j.envpol.2022.119933
35. A. F. Monikh, L. Chupani, M. G. Vijver, and W. J. G. M. Peijnenburg, *Environ. Pollut*., 2021, **269**, 116066. https://doi.org/10.1016/j.envpol.2020.116066
36. A. Turner, J. W. Scott, and L. A. Green, *Sci. Total Environ.*, 2021, **774**, 145405. https://doi.org/10.1016/j.scitotenv.2021.145405
37. A. E. P. D. Real, D. M. Mitrano, H. C. Michel, M.Wazne, J. R. Herrera, E. Bortel, B. Hesse, J. Villanova, and G. Sarret, *J. Hazard. Mater.*, 2022, **430**, 128356. https://doi.org/10.1016/j.jhazmat.2022.128356
38. T.-Y. Jin, J.-C. Tang, H. H. Lyu, L. Wang, A. B. Gillmore, and S. M. Schaeffer, *J. Agric. Food Chem.*, 2022, **70**, 14, 4182-4201. https://doi.org/10.1021/acs.jafc.1c07849

39. N. R. Bruna, M. M. T. Beenakker, E. R. Hunting, D. Ebert, and M. G. Vijver. *Nanotoxicology*, 2017, **11**, 1059-1069. https://doi.org/10.1080/17435390.2017.1391344
40. M. Heinlaan, K. Viljalo, J. Richter, A. Ingwersen, H. Vija, and D. M. Mitrano, *Environ. Pollut.*, 2023, **323**, 121213. https://doi.org/10.1016/j.envpol.2023.121213
41. N. J. Clark, F. R. Khan, C. Crowther, D. M. Mitrano, and R. C. Thompson, *Sci. Total Environ.*, 2023, **854**, 158765. https://doi.org/10.1016/j.scitotenv.2022.158765
42. A. S. Keller, J. J. Martinez, and D. M. Mitrano, *Environ. Sci. Technol.*, 2020, **54**, 911-920. http://doi.org/10.1021/acs.est.9b06483
43. V. S. Fringer, L. P. Fawcett, D. M. Mitrano, and M. A. M. Jones, *Front. Environ. Sci.*, 2020, **8**: 97. http://doi.org/10.3389/fenvs.2020.00097
44. K. Manoli, A. Naziri, I. Ttofi, C. Michael. I. J. Allan, and D. F. Kassinos, *Water Res.*, 2022, **222**, 118906. https://doi.org/10.1016/j.watres.2022.118906
45. F. Barbosa, J. A. Adeyemi, M. Z. Bocato, A. Comas, A. Campiglia, *Environ. Res.*, 2020, **182**, 109089. https://doi.org/10.1016/j.envres.2019.109089
46. M. R. Haque, M. M. Ali, W. Ahmed, M. A. B. Siddique, M. A. Akbor, M. S. Islam, and M. M. Rahman, *Sci. Total Environ.*, 2023, **857**, 159344. http://doi.org/10.1016/j.scitotenv.2022.159344
47. K. Jarosz, P. Natkanski, and M. Michalik, *Minerals*, 2022, **12**, 269. https://doi.org/10.3390/min12020269
48. Y. K. Lee, C. R. Castillo, S. Hong, and J. Hur. *Water Res.*, 2023, **175**, 115678. https://doi.org/10.1016/j.watres.2020.115678
49. S. K. Wysor and R. K. Marcus, *J. Chromatogr. A*, 2023, **1701**, 464051. https://doi.org/10.1016/j.chroma.2023.464051
50. B. H. L. Encinas, Y. V. Zhang, P. P. Gqamana, J. Lavicka, and F. Foret, *TrAC, Trends Anal. Chem.*, 2023, **164**, 117093. https://doi.org/10.1016/j.trac.2023.117093
51. J. C. Giddings, *Science*, 1993, **260**, 4.
52. Z.-G. Wu, W.-C. Zhao, Y.-G. Yin, Y.-J. Wei, Y.- W.- J. Liu, N.-L. Zhu, Z.-Q. Tan, Q.-H. Zhang, and J.-F. Liu, *TrAC Trends Anal. Chem.*, 2023,**164**,117114. http://dx.doi.org/10.1016/j.trac.2023.117114.
53. B. Battistini, F. Petrucci, and B. Bocca, *Anal. Bioanal. Chem.*, 2021, **413**, 3027-3039. https://doi.org/10.1007/s00216-021-03238-2
54. Z.-Q. Tan, W.-C. Zhao, Y.-G. Yin, M. Xu, W.-X. Pan, Y.- W.- J. Liu, Q.-H. Zhang, B. K. Gale, Y.- K. Rui, and J.-F. Liu, *Water Res.*, 2023, **228**, 119355. http://dx.doi.org/10.1016/j.watres.2022.119355
55. Q.-S. Bai, Y.-G. Yin, Y.- W.- J. Liu, H.-W. Jiang, M.-X. Wu, W.-D. Wang, Z.-Q. Tan, J.-F. Liu, M. H. Moon, and B.-S. Xing, *Appl. Spectrosc. Rev.*, 2021,**58**,110-131. http://dx.doi.org/10.1080/05704928.2021.1935272
56. C.-J. Li, Y. Gao, S. He, H.-Y. Chi, Z.-C. Li, X.-X. Zhou, and B. Yan, *Environ. Sci. Technol. Lett.*, 2021, **8**, 633-638. http://doi.org/10.1021/acs.estlett.1c00369
57. G. K. Muniasamy, F. P. Guevara, I. E. Martínez, and V. C. Shruti, *J. Hazard. Mater.*, 2021, **415**, 125755. https://doi.org/10.1016/j.jhazmat.2021.125755
58. L. W. Friesen, M. E. Granberg, M. Hassellöv, G. W. Gabrielsen, and K. Magnusson, *Mar. Pollut. Bull.*, 2019, **142**, 129-134. https://doi.org/10.1016/j.marpolbul.2019.03.016
59. C. D. Fiore, Y. Ishikawa, and S. L. Wright, *J. Hazard. Mater.*, 2024, **464**, 132991. https://doi.org/10.1016/j.jhazmat.2023.132991
60. N. P. Ivleva, *Chem. Rev.*, 2021, **121**, 19, 11886-11936. https://doi.org/10.1021/acs.chemrev.1c00178
61. V. K. Singh, N. Sharma, O. N. Verma, V. K. Singh, D. K. Tripathi, Y. Lee, S. Kumar, P. K. Rai, and M. A. Gondal. *Atom. Spectrosc.*, 2021, **42**, 99-113. https://doi.org/10.46770/AS.2020.201
62. R. Giugliano, B. Cocciaro, F. Poggialini, S. Legnaioli, V. Palleschi, M. Locritani, and S. Merlino, *Sensors*, 2022, **22**, 6910. http://doi.org/10.3390/s22186910
63. A. Michel, A. E. Morrison, V. L. Preston, C. T. Marx, B. C. Colson, H. K. White, *Environ. Sci. Technol.*, 2020, **54**, 10630-10637. https://doi.org/10.1021/acs.est.0c02099
64. U. K. Adarsh, E. B. Gowd, A. Bankapur, V. B. Kartha, S. Chidangil, and V. K. Unnikrishnan, *Waste Manage.*, 2022, **150**, 339-351. https://doi.org/10.1016/j.wasman.2022.07.025
65. P. Pořízka, L. Brunnbauer, M. Porkert, U. Rozman, G. Marolt, D. Holub, M. Kizovský, M. Benešová, O. Samek, A. Limbeck, J. Kaiser, and G. Kalčíková, *Chemosphere*, 2023, **313**, 137373. http://doi.org/10.1016/j.chemosphere.2022.137373
66. A. Kundu, N. P. Shetti, S. Basu, K. R. Reddy, M. N. Nadagouda, and T. M. Aminabhavi, *Chem. Eng. J.*, 2021, **421,** 129816. http://doi.org/10.1016/j.cej.2021.129816
67. I. Jakubowicz, J. Enebro, and N. Yarahmadi, *Polym. Test.*, 2021, **93**, 106953. http://doi.org/10.1016/j.polymertesting.2020.106953
68. F.-F. Jia, Q. Luo, Y.-Y. Zhang, Y. Zhao, K. Wu, and F.-Y. Wang. *Atom. Spectrosc.*, 2021, **42**, 166-174. http://doi.org/10.46770/AS.2021.106
69. S. H. Chou, Y. K. Chuang, C. M. Lee, Y. S. Chang, Y. J. Jhang, C. W. Yeh, T. S. Wu, C. Y. Chuang, and I. L. Hsiao, *Environ. Pollut.*, 2022, **300**, 118964. http://doi.org/10.1016/j.envpol.2022.118964
70. C. Du, J. Wu, J. Gong, H.-D. Liang, and Z.-P. Li. *Surf. Interface Anal.*, 2020, **52**, 293-300. http://doi.org/10.1002/sia.6742
71. D. S. Francischini and M. A. Z. Arruda, *Microchem. J.*, 2021, **169**, 106526. https://doi.org/10.1016/j.microc.2021.106526
72. J. Feng, H. Zhao, X. Gong, M.- C. Xia, L. Cai, H.Yao, X.Zhao, Z.Yan, Z. Li, H. Nie, X. Ma, and S. Zhang, *Anal. Chem.*, 2021, **93**, 5521-5528. http://doi.org/10.1021/acs.analchem.0c05383
73. L. Hildebrandt, M. Au, T. Zimmermann, A. Reese, J. Ludwig, and D. Profrock, *PLoS One*, 2020, **15**, e0236120. http://doi.org/10.1371/journal.pone.0236120
74. C. Eistenschneider, P. B. Holm, T. Mani, S. Primpke, H. Taubner, and G. Gerdts, *Environ. Sci. Technol.*, 2021, **55**, 15900-15911. http://doi.org/10.1021/acs.est.1c05207
75. Y.-Y. Chen, X.-B. Li, F.-F. Teng, J. Chen, and R. R. Robert, *Atom. Spectrosc.*, 2023, **44**, 24-31. http://doi.org/10.46770/AS.2022.246
76. A. Massos and A. Turner, *Environ. Pollut.*, 2017, **227**, 139-145. https://doi.org/10.1016/j.envpol.2017.04.034
77. A. Turner, *Mar. Pollut. Bull.*, 2017, **124**, 286-291. http://doi.org/10.1016/j.marpolbul.2017.07.045
78. A. Turner, C. Ostle, and M. Wootton, *Sci. Total Environ.*, 2022, **806**, 150375. http://doi.org/10.1016/j.scitotenv.2021.150375
79. M. Velimirovic, B. Teunkens, H. Ghorbanfekr, B. Buelens, T. Hermans, S. V. Damme, K. Tirez, and F. Vanhaecke, *Sci. Total Environ.*, 2022, **851**, 158226. http://doi.org/10.1016/j.scitotenv.2022.158226
80. X. Chen, S. Ali, L. Yuan, F. Guo, G. Huang, W. Shi, and X. Chen, *Chemosphere*, 2022, **287**, 132172. http://doi.org/10.1016/j.chemosphere.2021.132172
81. H. Jungnickel, R. Pund, J. Tentschert, P. Reichardt, P. Laux,

H. Harbach, and A. Luch, *Sci. Total Environ.*, 2016, **563-564**, 261-266. http://doi.org/10.1016/j.scitotenv.2016.04.025

82. L. Wang, P. Li, Q. Zhang, M. Wu, J. Luo, and D. Hou, *Environ. Sci. Technol.*, 2021, **55**, 6012-6021. http://doi.org/10.1021/acs.est.1c01042
83. C. Sommer, J. Nguyen, T. Menzel, J. A. Prume, H. Ruckdäschel, and M. Koch, *Polym. Test.*, 2022, **112**, 107623. https://doi.org/10.1016/j.polymertesting.2022.107623
84. Z. Liu, Y. Zhu, S. Lv, Y. Shi, S. Dong, D. Yan, X. Zhu, R. Peng, A. A. Keller, and Y. Huang, *Environ. Sci. Technol. Lett*., 2022, **9**, 50-56. http://doi.org/10.1021/acs.estlett.1c00888
85. G. L. Sullivan, J. D. Gallardo, T. M. Watson, and S. Sarp, *Water Res.*, 2021, **196**, 117033. https://doi.org/10.1016/j.watres.2021.117033.
86. U. L. H. P. Perera, H. C. S. Subasinghe, A. S. Ratnayake, W. A. D. B. Weerasingha, and T. D. U. Wijewardhana, *Mar. Pollut. Bull*., 2022, **185**, 114301. https://doi.org/10.1016/j.marpolbul.2022.114301
87. S. Kuhn, A. Oyen, A. M. Booth, A. Meijboom, and J. A. Franeker, *Chemosphere*, 2018, **213**, 103-113. http://doi.org/10.1016/j.chemosphere.2018.09.032
88. M. K. Nguyen, M. R. J. Rakib, C. Lin, N. T. Q. Hung, V. G. Le, H. L. Nguyen, G. Malafaia, and A. M. Idris, *TrAC Trends Anal. Chem.*, 2023, **168**, 117294. https://doi.org/10.1016/j.trac.2023.117294
89. M. C. Vedolin, C. Teophilo, A. Turra, and R. Figueira, *Mar. Pollut. Bull.*, 2018, **129**, 487-493. http://doi.org/10.1016/j.marpolbul.2017.10.019
90. J. Wang, J. Peng, Z. Tan, Y. Gao, Z. Zhan, Q. Chen, and L. Cai, *Chemosphere*, 2017, **171**, 248-258. http://doi.org/10.1016/j.chemosphere.2016.12.074
91. A. Bellingeri, E. Bergami, G. Grassi, C. Faleri, P. R. Hasselerharm, A. A. Koelmans, and I. Corsi, *Aquat. Toxicol*., 2019, **210**, 179-187. http://doi.org/10.1016/j.aquatox.2019.02.022
92. M. Jian, J. Niu, W. Li, Y. Huang, H. Yu, Z. Lai, S. Liu, and E.-G. Xu, *Chemosphere*, 2022, **309**, 136547. http://doi.org/10.1016/j.chemosphere.2022.136547
93. Y. Lin, J. Xie, Q. Xiang, Y. Liu, P. Wang, Y. Wu, and Y. Zhou, *Sci. Total Environ.*, 2022, **822**, 153609. http://doi.org/10.1016/j.scitotenv.2022.153609
94. H. Aslam, T. Ali, M. M. Mortula, and A. G. Attaelmanan, *Mar. Pollut. Bull.*, 2020, **150**, 110739. http://doi.org/10.1016/j.marpolbul.2019.110739
95. Q. Zhou, C. Tu, Y. Liu, Y. Li, H. Zhang, A. Vogts, S. Plewe, X. Pan, Y. Luo, and J. J. Waniek, *Sci. Total Environ.*, 2022, **853**, 158217. http://doi.org/10.1016/j.scitotenv.2022.158217
96. M. Shi, Q. Xie, Z.- L Li., Y.- F. Pan, Z. Yuan, L. Lin, X.- R. Xu, and H.- X. Li, *Environ. Pollut.*, 2023, **322**, 121158. http://doi.org/10.1016/j.envpol.2023.121158
97. F. Glaubitz, A. R. Vogel, Y. Kolberg, W. Tümpling, and H. Kahlert, *Environ. Pollut.*, 2023, **335**, 122293. https://doi.org/10.1016/j.envpol.2023.122293
98. S. Kern, C. Kern, M. M. Pradja, R. A. Düring, and M Rohnke, *J. Appl. Polym. Sci.*, 2021, **138,** 49655. http://doi.org/10.1002/app.49655
99. A. T. Ta and S. Babel, *Chemosphere*, 2020, **257**, 127234. https://doi.org/10.1016/j.chemosphere.2020.127234
100. X. Zhu, L. Qiang, H. Shi, and J. Cheng, *Mar. Pollut. Bull.*, 2020, **154**, 111079. http://doi.org/10.1016/j.marpolbul.2020.111079
101. J. Li, S. Mao, Y. Ye, J. Lu, F. Jing, Y. Guo, H. Liu, P. Wang, W. Ma, P. Qi, J Zheng, and C. Qu, *Environ. Pollut.*, 2021, **290**, 118042. http://doi.org/10.1016/j.envpol.2021.118042
102. M. Alaraby, D. Abass, A. Villacorta, A. Hernández, and R. Marcos, *Sci. Total Environ*., 2022, **842**, 156923. https://doi.org/10.1016/j.scitotenv.2022.156923
103. Y.-N. Huang, F. Dang, Y.-G. Yin, G.-D. Fang, Y.-J. Wang, G.-H. Yu, D.-M. Zhou, and B.-S. Xing, *Environ. Sci. Technol. Lett.* 2022, **9**, 2, 179–185. https://doi.org/10.1021/acs.estlett.1c00766
104. S. Gangadoo, S. Owen, P. Rajapaksha, K. Plaisted, S. Cheeseman, and H. Haddara, *Sci. Total Environ*., 2020, **732**, 138792. http://doi.org/10.1016/j.scitotenv.2020.138792
105. S. He, H. Chi, C. Li, Y. Gao, Z. Li, X. Zhou, and B. Yan, *Environ. Sci.: Nano*, 2022, **9**, 1353-1363. http://doi.org/10.1039/d1en00940k
106. E. B. Fernandez, A. R. Ibarz, M. Velimirovic, K. Tirez, and F. Vanhaecke, *J. Anal. At. Spectrom.*, 2020, **35**, 455-466. http://doi.org/10.1039/c9ja00379g
107. F. Ribeiro, D. M. Mitrano, C. Hacker, P. Cherek, K. Brigden, S. L. Kaserzon, K.V. Thomas, and T. S. Galloway, *Environ. Sci. Technol.*, 2022, **56**, 16716-16725. http://doi.org/10.1021/acs.est.2c02269
108. D. Cassano, A. Bogni, R. L. Spina, D. Gilliland, and J. Ponti, *Nanomaterials*, 2023, **13**. http://doi.org/10.3390/nano13030594
109. M. Tang, Y. Huang, W. Zhang, T. Fu, T. Zeng, Y. Huang, and X. Yang, *Bull. Environ. Contam. Toxicol*., 2022, **108**, 949-955. http://doi.org/10.1007/s00128-021-03453-8
110. L. A. Holmes, R. C. Thompson, and A. Turner, *Environ. Pollut.*, 2020, **261**, 114107. https://doi.org/10.1016/j.envpol.2020.114107
111. F. H. Jang, C. Wong, J. Choo, E. S. A. Sia, A. Mujahid, and M. Müller, *Environ. Pollut.*, 2022, **298**, 118850. https://doi.org/10.1016/j.envpol.2022.118850
112. P. K. Lindeque, M. Cole, R. L. Coppock, C. N. Lewis, R. Z. Miller, and A. J. R. Watts, *Environ. Pollut.*, 2020, **2020**, 114721. https://doi.org/10.1016/j.envpol.2020.114721
113. H. K. Imhof, C. Laforsch, A.C. Wiesheu, J. Schmid, P. M. Anger, R. Niessner, and N. P. Ivleva, *Water Res.*,2016, **98**, 64-74. https://doi.org/10.1016/j.watres.2016.03.015
114. S. Squadrone, S. Pederiva, T. Bezzo, R. M. Sartor, M. Battuello, N. Nurra, A. Griglione, P. Brizio, and M. C. Abete, *Environ. Sci. Pollut. Res.*, 2022, **29**, 29529-29534. http://doi.org/10.1007/s11356-021-13662-7
115. E. Besseling, P. R. Hasselerharm, E. M. Foekema, and A. A. Koelmans, *Environ. Sci. Technol*., 2019, 49, 32- 80. https://doi.org/10.1080/10643389.2018.1531688
116. K. Chouchene, T. Nacci, F. Modugno, V. Castelvetro, and M. Ksibi, *Environ. Pollut*., 2022, **30**, 119016. https://doi.org/10.1016/j.envpol.2022.119016
117. M. Mansor, S. Drabesch, T. Bayer, A. V. Le, A. Chauhan, J. Schmidtmann, S. Peiffer, and A. Kappler, *Environ. Sci. Techno. Lett*., 2021, **8**, 589-595. http://doi.org/10.1021/acs.estlett.1c00314.
118. G. Somdeep, D. Ranjan, B. Madhuruma, M. Shouvik, and C. Punarbasu, *J. Earth Syst. Sci.*, 2021, **130**, 236. https://doi.org/10.1007/s12040-021-01733-9
119. Q. Chen, M. Gundlach, S. Yang, J. Jiang, M. Velki, D. Yin, and H. Hollert, *Sci. Total Environ.*, 2017, **584–585**, 1022-1031. https://doi.org/10.1016/j.scitotenv.2017.01.156
120. H. Du, Y. Wang, P. Zhang, R. Mei, Y. Ji, X. Zhao, Z. Zhang, J. Ma, and L. Chen, *Nanoscale*, 2022, **14**, 7807-7816. http://doi.org/10.1039/d2nr00157h