




Advancing microplastic and associated pollutants detection: A comprehensive review on high-sensitivity analysis using mass spectrometry techniques

R. González Herrera^{a,b,1}, A. Doblado-Onieva^{a,b,1}, P. Montoro-Leal^{c,d,*},
M.M. López Guerrero^{a,b,**} 

^a Department of Analytical Chemistry, Faculty of Sciences, University of Malaga, Campus de Teatinos, Malaga, 29071, Spain

^b Instituto Universitario de Materiales y Nanotecnología, IMANA, University of Malaga, Campus de Teatinos, Málaga, 29071, Spain

^c Regional Institute of Applied Scientific Research, IRICA, University of Castilla-La Mancha, Ciudad Real, 13005, Spain

^d Department of Analytical Chemistry and Food Technology, Faculty of Science and Chemical Technologies, University of Castilla-La Mancha, Ciudad Real, 13005, Spain

ABSTRACT

The accumulation of plastic waste in the environment, coupled with its prolonged persistence, has led to alarmingly high concentrations. Over time, these plastics degrade into microscopic particles, known as ‘microplastics’ (MPs), which are considered potential pollutants that threaten ecosystems and human health. Current research not only focuses on the identification and monitoring of MPs but also the determination of associated inorganic and organic pollutants since these particles can act as transport vectors of trace elements (TEs) and volatile organic compounds (VOCs). Although spectroscopic techniques have been employed, mass spectrometry has been postulated as the most promising to achieve this purpose. This review discusses the use of MS-based techniques for detecting MPs and quantifying TE and VOCs in MPs, including their bioaccessible fraction. Recent approaches such as gold nanoparticle (AuNPs) labeling for SP-ICP-MS and LA-ICP-MS mapping are also discussed for evaluating biological and environmental risks.

1. Introduction

The accumulation of plastic waste in the environment, coupled with its prolonged persistence and insufficient monitoring, has led to alarmingly high concentrations. Over time, these plastics degrade into microscopic particles [1]. Although marine plastic pollution remains a significant societal concern, the increasing prevalence of microplastics (MPs) in freshwater ecosystems also requires attention [2].

MPs can enter the human body through ingestion, dermal contact, and inhalation [3]. As microplastic size decreases, their potential for bioaccumulation increases, indicating a growing risk to human health [4]. Additionally, MPs can adsorb environmental contaminants, including pesticides, heavy metals, and persistent organic pollutants. When ingested by organisms, the adsorbed contaminants can be released, leading to toxicity and further environmental harm [5]. For instance, marine organisms often mistake MPs for food, facilitating their bioaccumulation along the food chain [6,7]. MPs toxicity studies have demonstrated adverse effects on marine organisms, particularly in relation to oxidative stress and reproductive health. Additional research

has focused on detecting, identifying, and quantifying MPs in commercially significant marine species [8,9].

Identifying MPs in environmental contexts is essential for assessing pollution levels and potential exposure risks, preserving ecosystems, aiding food producers in meeting regulatory standards, safeguarding consumer health, increasing public awareness of ingestion risks, and providing data to inform regulations and scientific research [10]. However, effective monitoring requires the integration of comparable and reliable analytical techniques, as accurately identifying MPs of different shapes, compositions, and sizes (typically measuring ≤ 5 mm are classified as MPs [1], and $< 1 \mu\text{m}$ as nanoplastics (NPTs) [11]), using a single methodology presents significant challenges. MPs in the environment are typically monitored using both physical and chemical detection methods. Physical detection serves as a cost-effective and rapid initial assessment for larger particles, however, chemical techniques such as Fourier Transform Infrared Spectroscopy (FT-IR), and mass spectrometry techniques (Gas Chromatography-Mass Spectrometry (GC-MS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)) are necessary for the identification and removal of smaller

* Corresponding author. Regional Institute of Applied Scientific Research, IRICA, University of Castilla-La Mancha, Ciudad Real, 13005, Spain.

** Corresponding author. Department of Analytical Chemistry, Faculty of Sciences, University of Malaga, Campus de Teatinos, Malaga, 29071, Spain.

E-mail addresses: Pablo.Montoro@uclm.es (P. Montoro-Leal), mmlopez@uma.es (M.M. López Guerrero).

¹ Equally contribution.

microplastics [12,13].

Common physical detection methods include optical microscopy, stereomicroscopy, and flow cytometry, which allow rapid visualization and counting of microplastics, particularly those larger than 100 μm [14, 15]. Filtration combined with sieving or density separation is often employed to concentrate particles prior to analysis, providing an efficient preliminary assessment of microplastic abundance and size distribution. While these methods are useful for larger particles, their resolution is limited for NPTs or chemically complex samples, highlighting the need for complementary chemical and mass spectrometry-based techniques.

Mass spectrometry (MS) has emerged as a superior analytical approach for MPs and NPTs detection due to its exceptional sensitivity, precision, and versatility. Unlike traditional spectroscopic techniques, MS enables the simultaneous quantification of particle size, mass, and elemental composition, even at ultra-trace environmental concentrations [16–20]. For example, mass spectrometry and thermal analysis combination proved to be an effective technique for detecting MPs in food samples [20]; the MPs analysis includes methods such as Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC-MS), Thermo-Extraction and Desorption (TED) coupled with GC-MS, TGA-Differential Scanning Calorimetry (TGA-DSC), and TGA-Thermal Desorption-Gas Chromatography-Mass Spectrometry (TGA-TD-GC-MS).

Besides, advanced ICP-MS based methodologies such as Single Particle ICP-MS (SP-ICP-MS) and ICP Time-of-Flight MS (ICP-TOF-MS) allow real-time single-particle analysis with high-throughput and reproducible data across diverse matrices [18,21]. SP-ICP-MS offers valuable insights into their size distribution and mass concentration [17], and ICP-TOF-MS enables high-sensitivity single-particle analysis by capturing transient ion signals from diluted suspensions [18]. Moreover, Laser-Ablation ICP-MS (LA-ICP-MS) and metal nanoparticle tagging approaches enable precise surface characterization and detection of NPTs with minimal error, surpassing conventional FT-IR or Raman microscopy in both sensitivity and applicability [19,22]. For these reasons, MS rises as the gold standard for comprehensive microplastic research, effectively overcoming the limitations of other analytical methods.

Regarding ICP-MS analysis, two primary methodologies are commonly used: one measures signal intensity at specific mass-to-charge ratios (m/z), such as 13 (^{13}C), and the other detects metals tagged onto NPTs [16]. A novel technique for NPTs detection employs gold-based nanoparticles (AuNPs) that bind to their surface, allowing precise quantification with an error margin below 5 % [19]. Nevertheless, it should be emphasized that ICP-MS also presents inherent limitations for the direct characterization of polymeric structures, as it cannot differentiate between metal-free plastics or determine polymer composition [16–19]. For unequivocal polymer identification, complementary analytical approaches are required. In this way, techniques such as pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), thermal extraction–desorption GC-MS, and high-resolution vibrational spectroscopy (e.g., Raman and FT-IR microscopy) are considered gold standards for polymer characterization, allowing accurate discrimination among polyethylene (PE), polypropylene (PP), polystyrene (PS), and other common polymers in environmental samples [20]. The integration of such methods is therefore essential to obtain a comprehensive understanding of MPs occurrence, composition, and their environmental fate.

Furthermore, beyond their primary impact as pollutants, MPs have demonstrated the ability to act as vectors for trace elements, adsorbing and transporting these contaminants across various environmental compartments. Godoy et al. examined the adsorption of metals as Cd, Co, Cr, Cu, Ni, Pb, and Zn by five different types of MPs in Milli-Q and natural waters [23]. The results showed that PE and PVC effectively absorbed Pb, Cr, and Zn on their surfaces. Consequently, MPs loaded with trace elements pose a dual threat: they serve as carriers for toxic elements and, upon ingestion by aquatic organisms, facilitate the

bioaccumulation and biomagnification of contaminants in the food chain [23,24]. Besides, Godoy et al. provided a comprehensive assessment of marine plastic pollution in Spain, integrating data on MPs abundance, sources, and associated contaminants, with an emphasis on policy and management implications [25]. This author expanded the scope to other environmental compartments, reporting the presence of MPs in sandy beaches of Portugal and the first evidence of MPs in remote high-mountain lakes of Sierra Nevada, where particle morphology, size distribution, and potential sources were studied, highlighting the role of MPs as vectors even in pristine environments [26,27].

Apart from trace elements, recent research has revealed that volatile organic compounds (VOCs) are also pollutants associated to the presence of MPs. VOCs are substances that can be released into the environment from both natural and anthropogenic sources [28], including aromatic hydrocarbons, alkanes, aldehydes, aliphatic hydrocarbons, terpenes, chlorinated hydrocarbons, glycol ethers, and esters [29]. In the last years, the release of harmful VOCs from plastic waste to the environment because of chemical and physical degradation has been studied [30,31], indicating that the evaluation of environmental impact of MPs pollution should also consider the VOCs emitted. A comprehensive analysis of VOC emissions would help researchers gain deeper insights into the degradation process of plastics and assess their overall environmental impact more thoroughly. In line with green chemistry principles, a Headspace Solid-Phase Microextraction Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS) method was developed to study the profile of volatile organic compounds (VOCs) [32–34]. However, studies specifically addressing the accumulation of VOCs released by MPs in animal organs remain scarce. The existing literature includes only two studies that have investigated VOCs in plastic-packaged meat using purge-and-trap and solid-phase microextraction in combination with GC-MS [35,36].

As can be observed in Fig. 1, this review provides a comprehensive examination of the occurrence, detection, and environmental implications of MPs and NPTs, with a particular emphasis on their role as vectors for trace elements and VOCs. Furthermore, latest advancements in mass spectrometry for the determination of MPs, NPTs, and their associated pollutants are also highlighted, underscoring the need for standardized, real-time monitoring tools.

2. Analysis of microplastics in the environment by ICP-MS

Since microplastics represent a global issue due to their persistence and toxicity, affecting both terrestrial and aquatic ecosystems, it is essential to establish a standardized analytical method. A recent study in the North Persian Gulf (Bushehr Province, Iran) found MPs in the gastrointestinal tracts of various fish and crustaceans, including *Psettodes erumei*, *Sphyræna jello*, *Sillago sihama*, *Metapenæus affinis*, and *Portunus segnis* [37,38]. These findings, along with others, underscore the widespread presence of MPs in marine food and their potential implications for both marine ecosystems and human health. In this review, we aim to explain why ICP-MS is not only an analytical technique but the most effective method for the detection and quantification of MPs and NPTs.

Table 1 summarizes the main analytical techniques currently used for the detection and characterization of MPs and NPTs in different environmental matrices. It compares their applicability, polymer identification capability, size range, and main advantages and limitations.

The detection and quantification of MPs and NPTs in environmental matrices remain analytically challenging due to their small size, heterogeneous compositions, and complex surrounding matrices. Among the existing methods, spectroscopic approaches such as μ -FTIR and Raman microscopy are the most established for microplastic identification, providing reliable chemical characterization for particles above 10 μm (FTIR) and 1 μm (Raman). However, their applicability decreases significantly at the nanoscale, and throughput is constrained by time-intensive imaging and data processing [39–41].

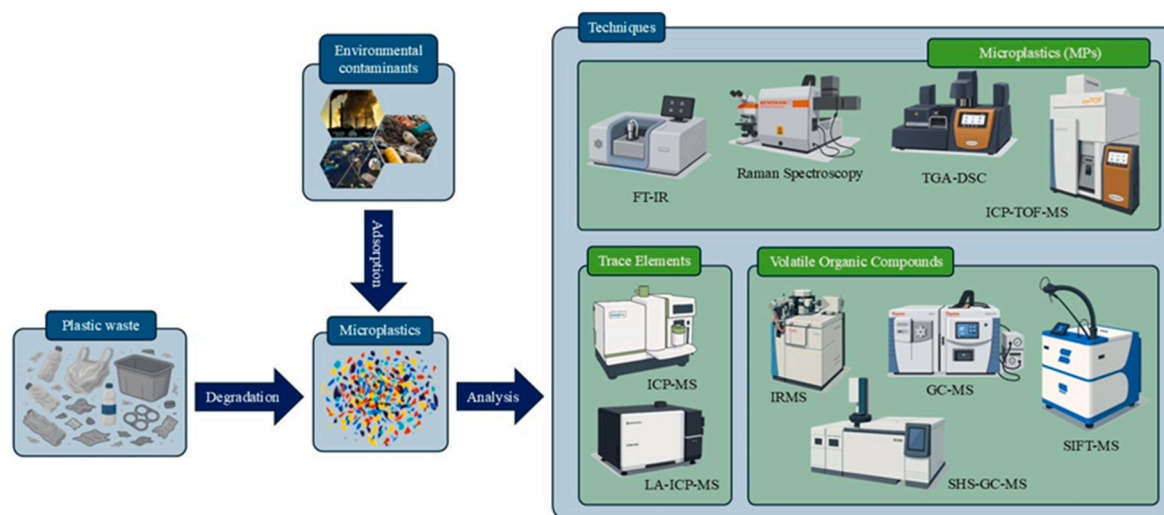


Fig. 1. Schematic representation of the origin of MPs and NPTs through the degradation of plastic waste, along with the adsorption of environmental pollutants. Conventional spectroscopic techniques commonly applied for MPs analysis are shown, as well as mass spectrometry-based approaches for the analysis of MPs, NPTs, and their associated contaminants (trace elements and VOCs).

Table 1

Current methods for the detection of MPs and NPTs in different environments, including composition, size range, and main considerations.

Methods	Environmental Samples	MPs composition	Size range (approx.)	Advantages/Limitations	Ref.
μ -FT-IR/FT-IR-Imaging	Water (filters), sediments, biota, air	Common polymers (PE, PP, PS, PET, PVC, etc.)	$\sim 20 \mu\text{m}$ and above (down to $\sim 10 \mu\text{m}$ with optimized μ -FTIR)	Direct chemical identification; non-destructive; limited for $< 10 \mu\text{m}$; requires pretreatment	[39,40]
Raman spectroscopy (μ -Raman, Raman mapping)	Water, sediments, air, biota	Common polymers; suitable for colored particles	$\sim 1 \mu\text{m}$; in ideal cases down to hundreds of nm	Higher spatial resolution than FTIR; affected by fluorescence; weak signal in some polymers	[40,41]
Py-GC-MS	Water extracts, sediments, biota, food	Identifies polymer type and additives (PE, PP, PS, PET, PVC, PMMA)	Mass-based, not particle-resolved	High specificity; suitable for complex matrices; destructive; no particle size/shape info	[42,43]
SP-ICP-MS, incl. metal labelling/SP-ICP-TOF-MS	Water (drinking, surface), biota digests/seawater, complex system	Detects labelled NPTs (e.g., Au-, Ag-labelled plastics)/Labelling not required if NPTs contain metals or additives	$\sim 50 \text{ nm}$ – several μm (depending on labelling efficiency)	High sensitivity; allows counting and sizing if labelled; requires complex labelling and pretreatment	[44–46]/[47–49]
NTA/DLS	Laboratory suspensions, clear waters	Physical sizing only, no chemical ID	NTA: $\sim 50 \text{ nm}$ – $1 \mu\text{m}$; DLS: $\sim 1 \text{ nm}$ – $1 \mu\text{m}$	Good for size/concentration; no polymer ID; affected by aggregation	[50,51]
SEM/TEM (+EDX)	Lab (filters, tissues)	Morphology; elemental info with EDX (not polymer-specific)	SEM: $\sim 10 \text{ nm}$ – μm ; TEM: sub-nm to 100 nm	Excellent morphology; can detect additives/metals; destructive prep; no direct polymer ID	[40,50,52–54]
TGA/TGA-MS/TGA-GC-MS	Preconcentrated samples (sediments, filters, tissues)	Identifies polymers by thermal/fragment patterns	Mass-based	Useful for composition by weight; no particle-level info; requires calibration	[20,42,43,55]
Surface-Enhanced Raman Scattering (SERS)/Biosensors (optical/electrochemical)	Emerging applications in water, in situ sensors	Depends on probe; potential polymer-specific	Variable; sub- μm possible	High sensitivity; rapid detection; still in development for complex matrices	[50,56,57]

Thermal techniques such as Py-GC-MS are highly valuable for polymer identification and quantification, particularly in complex matrices. Nevertheless, they are destructive and mass-based and therefore cannot resolve particle size distribution or morphology [42,43]. Similarly, physical sizing techniques (Nanoparticle Tracking Analysis (NTA), Dynamic Light Scattering (DLS), SEM/TEM) provide valuable information on particle size and morphology but lack chemical specificity [40,50,51].

In contrast, SP-ICP-MS, particularly when combined with innovative labelling strategies (e.g., in situ growth of gold nanoparticles, cloud-point extraction, or microdroplet calibration), emerges as the most versatile and promising method for NPTs. This technique enables simultaneous quantification, sizing, and counting of particles down to tens of nanometers, addressing the limitations of FTIR and Raman at

smaller scales [44–46]. Furthermore, when integrated with ICP-TOFMS, it allows multiplexed, high-throughput analysis, making it suitable for heterogeneous environmental samples with pronounced matrix effects [47–49].

Overall, FTIR and Raman remain indispensable for standardized microplastic monitoring and Py-GC-MS excels in compositional mass analysis, SP-ICP-MS with metal labelling currently represents the most powerful tool for NPTs research, offering the sensitivity, versatility, and scalability needed to advance environmental and biological studies of plastic pollution.

Various spectroscopy techniques, such as Raman [58] and FT-IR [59], have been employed for the detection of MPs. Although both are non-destructive methods, they present limitations in identifying MPs in environmental samples. In Raman spectroscopy, the presence of water

and humidity can interfere with incident light dispersion, affecting detection, making sample purification crucial [60], while the laser power may degrade the sample [52]. Additionally, the additives and pigments incorporated into plastics may interfere with the identification of microplastics using this technique [61]. Conversely, FT-IR spectroscopy, despite its effectiveness, may exhibit an increased signal-to-noise ratio due to prolonged analysis time, complicating result accuracy [62]. This spectroscopic technique is not suitable for detecting microplastics of a size $<20\ \mu\text{m}$ [60]; consequently, it cannot be used for NPTs. Furthermore, in both techniques, reference spectra are often derived from standard samples, which are cleaner and easier to identify than real samples [63], thus hindering accurate MP detection under environmental conditions. Due to these limitations, ICP-MS has been proposed as an effective alternative, offering simpler and more precise interpretation for MPs detection.

Before the detection and quantification by ICP-MS of MPs and NPTs in biological samples, soil and environmental waters, or even from the atmosphere, a series of preliminary processes must be conducted, including sampling, pretreatment, extraction and separation (Fig. 2).

2.1. Pretreatment and separation of MPs and NPTs from samples

The collected samples often contain high organic matter content or may originate from gastrointestinal systems. Before analysis, sample pretreatment is typically required for the extraction of MPs. The digestion step can be skipped for simpler environmental matrices, such as drinking water and seawater. The digestion method must be carefully selected to avoid compromising the structural or chemical integrity of microplastics. To date, various digestion techniques have been implemented, involving distinct types of digestion: oxidative digestion, acid digestion, alkaline digestion, enzyme digestion and mixed digestion [64].

Oxidative digestion is a widely used method for the pretreatment of soil, biological, and atmospheric samples. Reagents such as Fenton's reagent [65], hydrogen peroxide (H_2O_2) [66] and sodium hypochlorite (NaClO) can be used. When these agents are insufficient to remove stable polymers, strong oxidizing agents, such as nitric acid (HNO_3), are used due to their high efficiency in removing organic matter ($>98\%$) [67]. However, they can significantly affect the physical and chemical properties of MPs [68,69]. Other acids such as HCl , H_2SO_4 and CH_2O_2 are also frequently used, especially for biological tissues [70]. The

alkaline $\text{K}_2\text{S}_2\text{O}_8$ digestion enhances reaction efficiency and minimizes functional group damage during microplastic pretreatment. Thus, a digestion protocol based on alkaline $\text{K}_2\text{S}_2\text{O}_8$ offers an effective approach for isolating seawater MPs from biologically rich samples [71]. Finally, enzymatic digestion is a specific method for the hydroxylation of proteins and the decomposition of tissues; however, its cost is significantly high, and it tends to be time-consuming [72]. Enzymatic digestion ensures that MPs degradation is avoided, as MPs surfaces cannot be affected by this treatment (e.g. proteinase-K), being less harmful to human health [73].

Separation techniques are commonly employed to enhance the concentration and purification of environmental MPs and NPTs. Various methods are available, including magnetic, density, and electrostatic separation, as well as filtration, field-flow fractionation, and size-exclusion chromatography [74]. The separation of MPs and NPTs from environmental matrices is a critical step prior to their identification and quantification. Different methods have been developed, whose applicability depends on the size of the particles, the complexity of the sample, and the analytical objectives. An overview of the main separation methods is presented in Fig. 2. Filtration and density separation remain the primary tools for MPs, especially in sediments and soils, while preconcentration, field-flow-fractionation, and chromatographic approaches are essential for handling NPTs due to their smaller size and lower abundance. Magnetic and electrostatic separation provide complementary strategies, particularly for complex matrices where conventional approaches may be insufficient [64].

2.2. Detection of MPs by ICP-MS

The feasibility of detecting MPs using ICP-MS operated in SP-ICP-MS was evaluated by Bolea-Fernández et al. [17]. PS microspheres doped with lanthanide nuclides ($2.5\ \mu\text{m}$) were used to prepare dilutions in ultrapure water, with three measurement replicates in which microspheres were monitored through the signal intensities of ^{13}C and ^{165}Ho . Detection was based on monitoring the ^{13}C minor isotope instead of ^{12}C to minimize spectral interferences and to avoid high background. Additionally, the sample introduction flow rate and dwell time were optimized to $100\ \mu\text{s}$. It was demonstrated that the number of ^{13}C peaks is directly correlated with the concentration of MPs in solution, with results validated by comparison to the ^{165}Ho signal from the same microspheres. These findings confirmed the feasibility of SP-ICP-MS as a

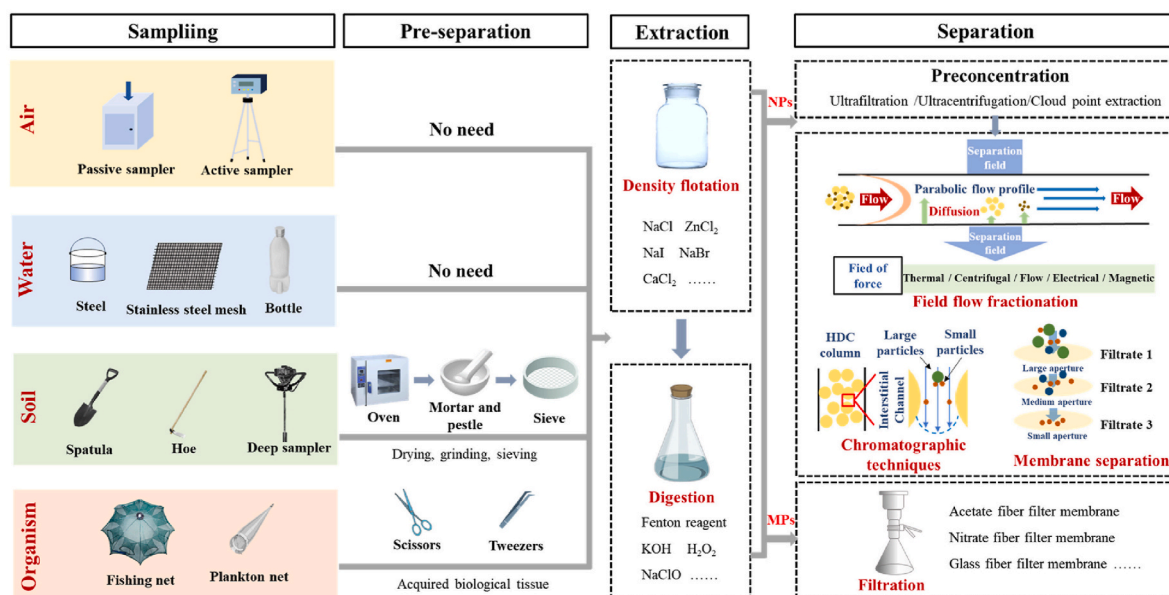


Fig. 2. Protocols for sampling, pre-separation, extraction and separation of MPs and NPTs in different environmental compartments [64].

promising technique for the detection, quantification, and characterization of MPs [17]. Laborda et al. also monitored the ^{13}C isotope for the identification and quantification of PS microparticles down to 1.2 μm in personal care products and released from food packaging materials, demonstrating the wide applicability of this technique [75].

As previously mentioned, ^{13}C can be used for the monitorization of MPs by SP-ICP-MS in relatively simple matrices. However, most MPs are found in more complex matrices such as seawater. Fig. 3A illustrates the reduced sensitivity of the signal intensity of ^{13}C from PS-based MPs particles in seawater (red) compared to those obtained from PS-based MPs in ultrapure water (blue), causing an underestimation of MPs sizes of 28 %. Despite this, the adequate calibration of MPs reference materials in high-ionic strength matrices is possible. The size distribution of a 4 μm MP standard in seawater was calibrated with a 3 μm MP standard in seawater (Fig. 3B). These matrix effects result from the high ion concentration in seawater, which induces defocusing of the extracted ion beam and causes salt deposition on the lenses and vacuum interface. To solve the challenges, Gonzalez de Vega et al. introduced several methodological innovations [76]. In this study, the spectral interferences and background noise generated during the analysis of the ^{12}C isotope signal were reduced using tandem MS (ICP-MS/MS) and collision/reaction gases. To evaluate the effectiveness of ^{12}C and ^{13}C analysis, different methods were compared, studying the use of cell gases such as H_2 , O_2 , and NH_3 . The study included the direct analysis of both isotopes with and without H_2 to reduce spectral interferences, showing that the lowest size detection limits (sDL) were obtained using this cell gas in ultra-pure water (0.62 μm) and seawater (0.96 μm). The results demonstrated that the analysis of MPs via SP-ICP-MS in complex matrices, such as seawater, is more accurate when employing online gas dilution due to the improvement of size calibration. Furthermore, the monitorization of ^{12}C instead of ^{13}C enhanced ion transmission, reduced background noise, and improved sDLs, supporting its application in environmental studies [76].

A method for the detection and quantification of NPTs in drinking,

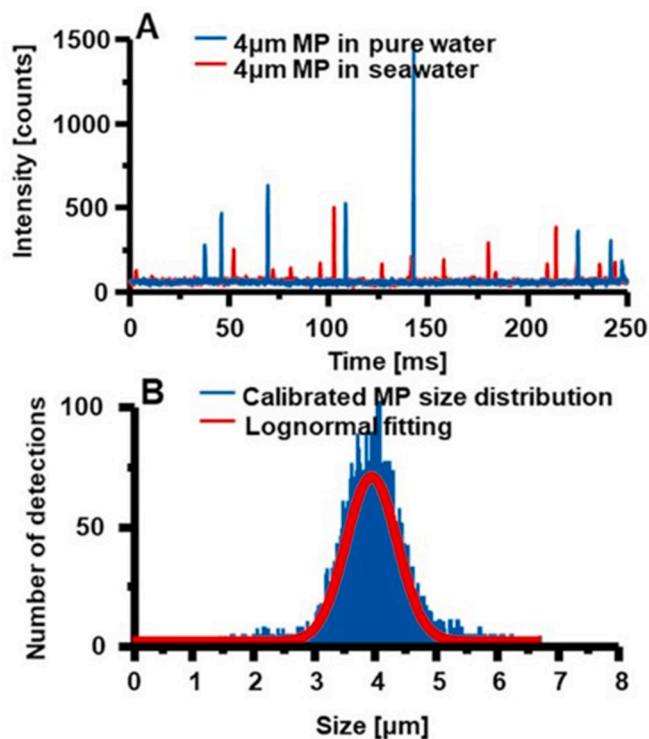


Fig. 3. Analysis of 4 mm polystyrene-based MPs in ultra-pure and seawater. The high ion strength of seawater reduced ion transmission leading to reduced sensitivity. B) Signal calibration using a 3 μm MP standard in seawater [76].

tap, and river water was developed, based on the conjugation of NPTs with functionalized gold-containing nanoparticles (AuNPs). The proposed labelling strategy is illustrated in Fig. 4, which encompassed the following experimental protocol: 1) modification of AuNPs to obtain a positively charged surface, AuNPs(+), 2) modification of NPTs to obtain negatively charged surface, NPTs(-), 3) coupling of AuNPs(+) and NPTs(-) via electrostatic interactions, 4) washing and stabilization of the resulting nanocomposite, and 5) detection and quantification by SP-ICP-MS. The selectivity of the method was achieved through the interaction between negatively charged carboxylate groups on the NPTs(-) surface and positively charged gelatine attached to custom-synthesized AuNPs(+) prior to SP-ICP-MS analysis. The adsorbed Au generated an SP-ICP-MS signal, allowing for the counting of individual NPs particles and their accurate quantification, with an error below 5 % [19].

In follow-up research, a comprehensive method was developed, from sample pretreatment to the quantitative detection of NPTs in environmental waters. The pretreatment involved filtration through a 1 μm pore-size glass fiber membrane and acid digestion with a mixture of 5 mM HNO_3 and 40 mM HF, which effectively removed coexisting inorganic nanoparticles. The subsequent dual cloud-point extraction efficiently isolated NPTs from various matrices. Following this, labelling was performed by in-situ growth of AuNPs, and the NPTs (50–1200 nm) were determined using SP-ICP-MS as illustrated in Fig. 5 [44].

In a subsequent study, three different strategies for the analysis of PS NPTs by SP-ICP-MS based on the use of metal species (ions, hydrophobic organometallic compounds, and nanoparticles) were studied and discussed [77]. As summarized in Fig. 6, three labelling strategies were evaluated: metal ions, hydrophobic organometallic compounds, and functionalized metal nanoparticles. Metal ion labelling (e.g., Ag^+) proved limited, as the adsorbed mass per particle was insufficient for reliable quantification and prone to desorption during dilution. Hydrophobic organometallic probes, such as lead (II) phthalocyanine, enabled NPTs detection through strong hydrophobic and π - π interactions, though the need for additional purification reduced their efficiency. In contrast, functionalized gold nanoparticles demonstrated the most promising results. Electrostatic interactions between surface carboxyl groups on NPTs and positively charged AuNPs allowed both sensitive detection and accurate quantification, particularly for highly functionalized NPTs.

The work published by Li et al. introduced improvements to the method for extracting and quantifying PS NPTs from biological samples, including bacteria, algae, nematodes, and earthworms. The process combined alkaline digestion, centrifugation, and CPE, and quantification was achieved through gold nanoparticle labelling and SP-ICP-MS. The method effectively digested biological matrices using 25 % tetramethylammonium hydroxide and purified PS NPTs of different sizes and surface functionalities via CPE. The Au labeling efficiency improved by 70 % with cetyltrimethylammonium bromide, achieving a detection limit of 3.7×10^7 particles g^{-1} , corresponding to 0.02–2.5 $\mu\text{g g}^{-1}$ for 100–500 nm PS NPTs [45].

Besides, MPs in the range from 1 μm to 6 μm were analyzed by Sakanupongkul et al. developing a simple SP-ICP-MS approach to analyze. This system was used to estimate the size of laboratory-synthesized polystyrene latex particles, showing that SP-ICP-MS sizes were larger than Scanning Electron Microscope (SEM) reference sizes, needing particle washing for accurate results. After washing, SP-ICP-MS results matched SEM sizes, confirming its reliability. The method was subsequently applied to analyze microplastics from consumer products (teabags, face masks), with DLS and SEM also used for comparison. SP-ICP-MS provided effective microplastic size data, though further development is needed for NPTs detection [78].

3. Determination of trace elements in MPs

Despite the recent approaches exposed for the monitorization of MPs, the negative effects of these pollutants on health and environment

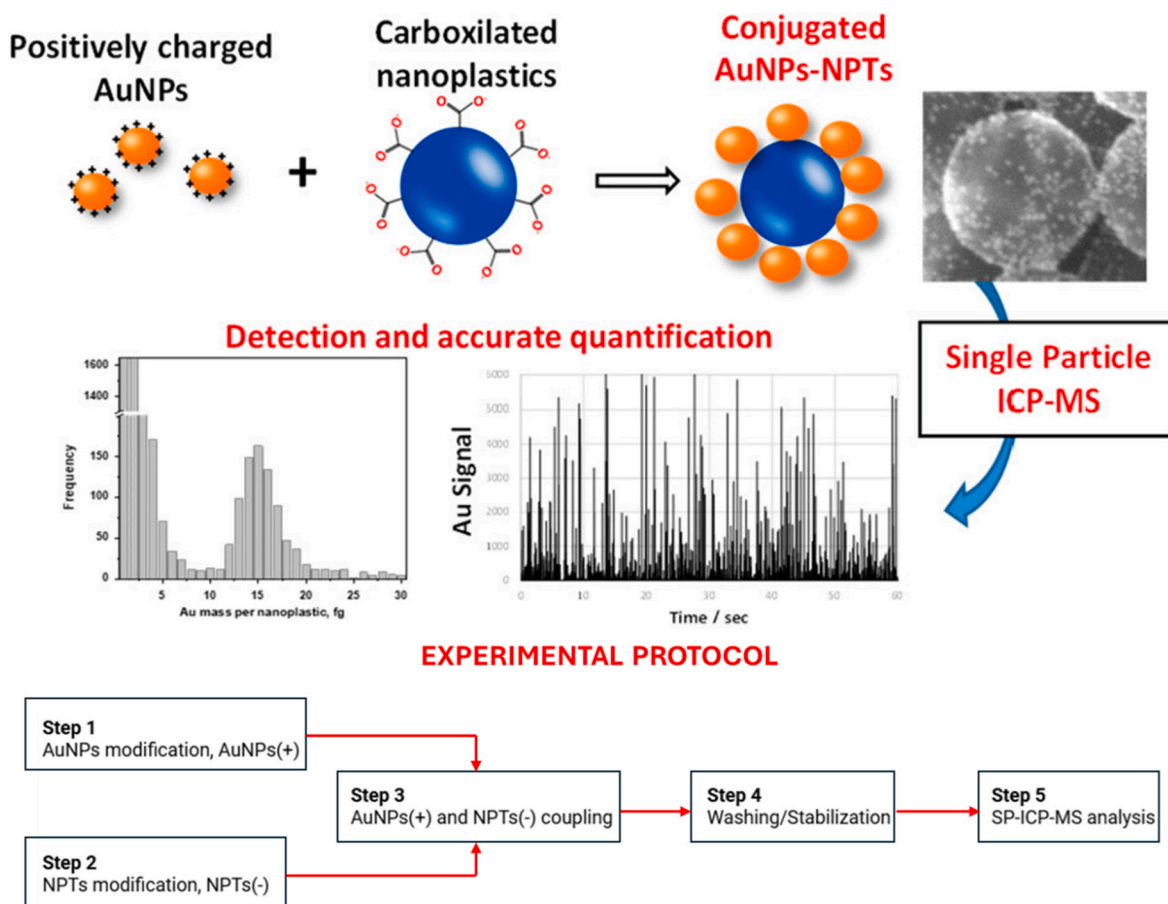


Fig. 4. Schematic representation of the labelling strategy and experimental protocol. Conjugating NPTs with functionalized AuNPs represents a critical preparatory step that enables their subsequent detection and quantification by ICP-MS. The labelling strategy relies on the interaction between the NPTs' surface groups and the functionalized gold nanoparticles, thereby providing a detectable elemental signal for SP-ICP-MS analysis [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

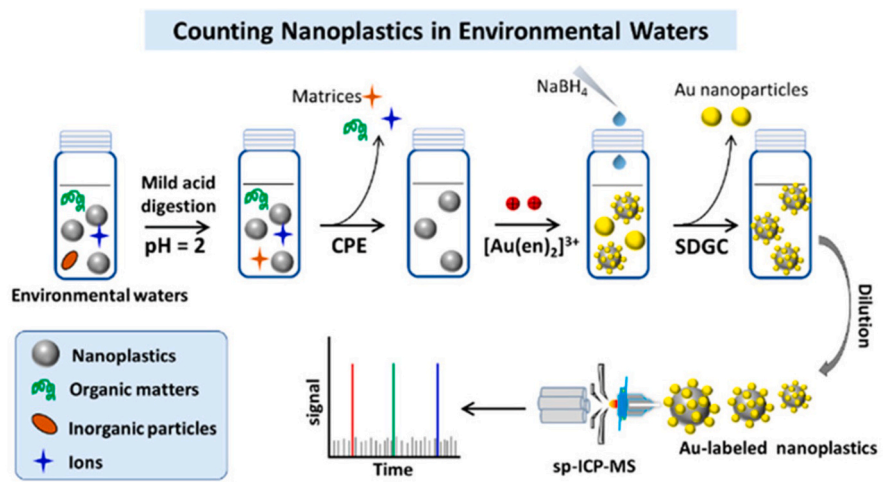


Fig. 5. Schematic diagram of counting NPTs by SP-ICP-MSs in environmental water by SP-ICP-MS. After mild acid digestion and cloud-point extraction (CPE), NPTs were labelled with gold nanoparticles through in situ reduction and subsequently purified by sucrose density gradient centrifugation (SDGC) [44]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

must be also evaluated by studying the content of heavy metals and other trace elements. Their presence in MPs can be justified regarding two main factors: First, the addition of these compounds as additives during plastic manufacturing in order to improve physicochemical

properties and minimize production costs, which are located inside MPs structure, and second, their adsorption on the MPs surface due to their micrometric size, high specific surface area and hydrophobic nature [24, 79]. This adsorption can occur via various mechanisms, including

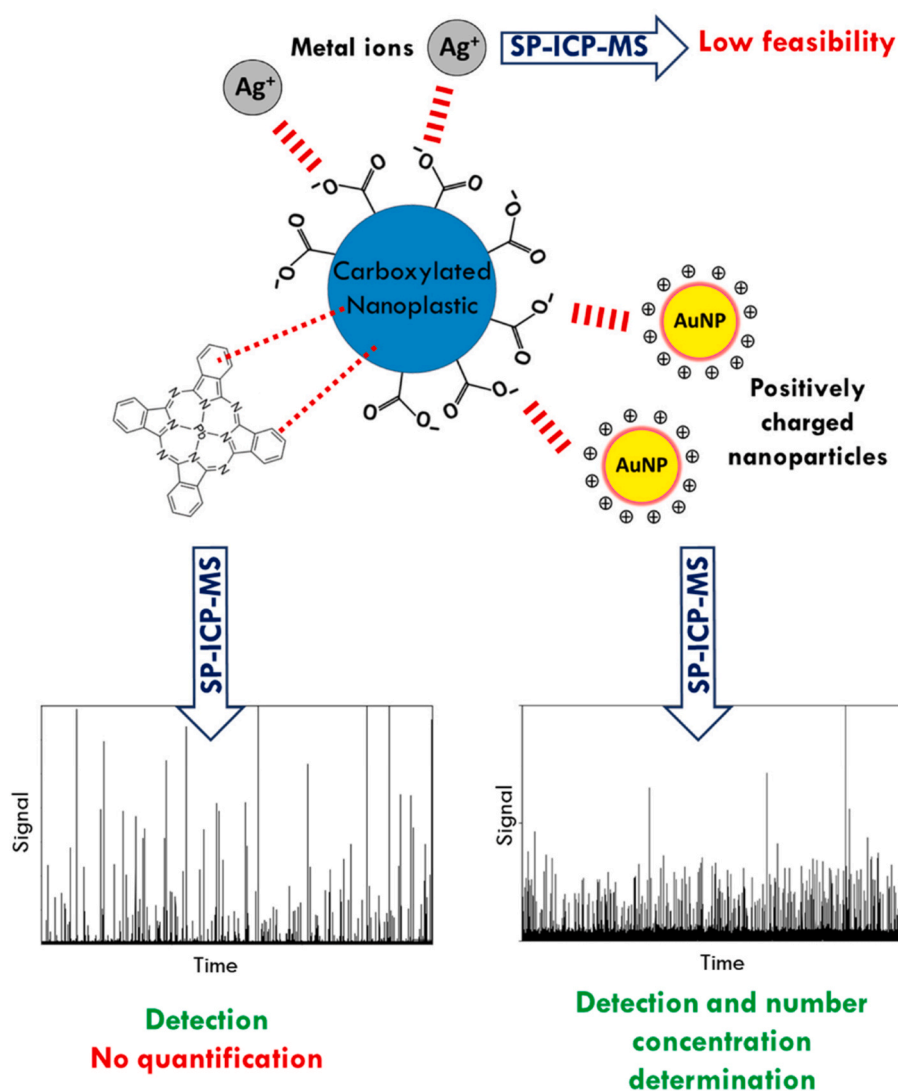


Fig. 6. Summary of three labelling strategies: metal ions (Ag^+), hydrophobic organometallic compounds (Pb(II) phthalocyanine), and functionalized metal nanoparticles (AuNPs) to the detection and quantification of NPTs by SP-ICP-MS [77].

physical adsorption, electrostatic interaction, hydrogen bonding, complexation, and π -cation bonding interaction (Fig. 7), depending on the composition of the MPs and environmental factors such as pH, temperature, salinity, and the presence of other pollutants [80,81].

Consequently, the intake of MPs can release heavy metals and other toxic compounds into the organism, resulting in bioaccumulation and biomagnification across the trophic chain. Therefore, the determination of these pollutants in MPs is essential to study and evaluate the transport pathways of toxic elements, discharge sources of pollutants, and potential environmental risks. To address their analysis, the determination of the released concentration from MPs is considered more appropriate than the total quantity, since just part of the total concentration can be released within a timeframe [79]. However, the determination of total concentration in MPs is also addressed since this data is also relevant for the estimation of bioaccessible fraction of pollutants.

MPs samples are considered complex due to the wide diversity of matrices and their heterogeneous composition containing a variable concentration of different trace elements. Inductively Coupled Optical Emission Spectrometry (ICP-OES), Atomic Absorption Spectrometry (AAS), and ICP-MS are the most frequently used techniques for their identification [79]. These techniques necessitate aqueous samples for detection, so sample preparation protocols are required to extract the

analytes from the solid-state samples prior to analysis.

In the last decades, the United States Environmental Protection Agency (US EPA) method 3052 has been widely employed as acid digestion pretreatment for organic and other complex matrices, achieving complete disintegration of the sample and the efficient extraction of trace elements into the solution. This digestion protocol uses HF in conjunction with HNO_3 , followed by heating the sample in a microwave oven [82]. An alternative procedure to this protocol is the ultrasound (US), which is considered an efficient pretreatment method for being fast and simple, minimizing waste and reagent consumption. This protocol is based on the phenomenon "cold boiling", consisting in the formation and collapse of microbubbles within the liquid. The "cold boiling" effect favors chemical and physical reactions due to localized temperature and pressure incrementation on the solid surface. In combination with strong acids, this process presents a high extraction efficiency [83,84].

Besides, although direct analysis of MPs with no pretreatment can be also performed using LA-ICP-MS, X-ray fluorescence (XRF), and Laser-Induced Breakdown Spectroscopy (LIBS), the direct determination of metals in MPs presents significant problematics due to the high salt content of the matrix and the low concentration of analytes [85,86]. Therefore, highly sensitive analytical techniques with very low

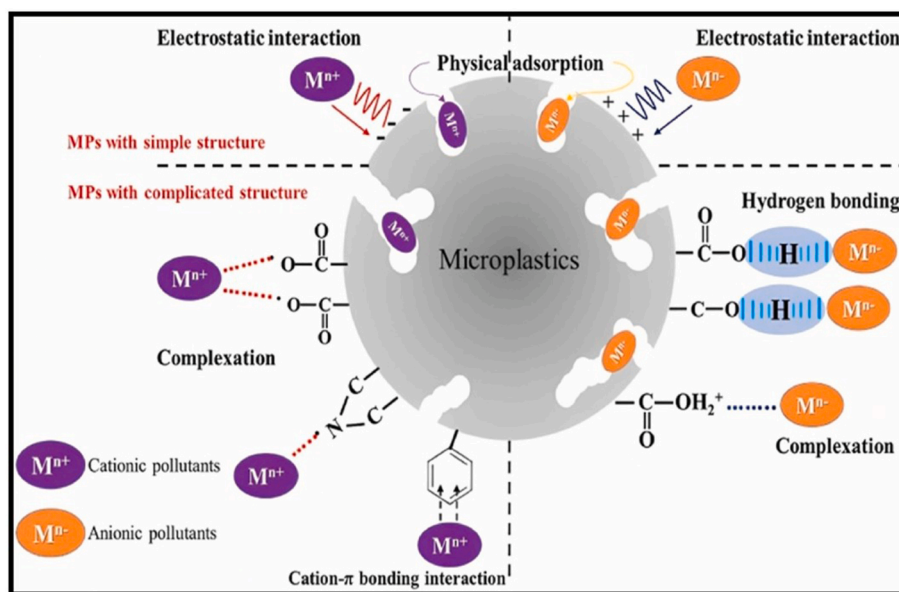


Fig. 7. Illustration of the mechanism for ions and MPs interactions [81].

detection limits are required. For these reasons, ICP-MS is the most employed technique for metal determination in MPs.

3.1. Determination of trace elements in MPs by ICP-MS

In the study developed by Zhou et al., the heavy metal content in MP particles was determined and compared with the concentration of heavy metals present in soil samples. Initially, 400 microplastic particles were selected for heavy metal extraction, and sonicated to eliminate any adhered impurity. Then, the samples were transferred to centrifuge tubes with 2.5 mL of 20 % aqua regia. The tubes were centrifuged at 150 rpm for 24 h at RT. A separate preparation process was performed with soil samples. 0.1 g of dry soil was subjected to microwave digestion using 4 mL of HNO₃ and 2 mL of HF. After samples preparation, the analysis of heavy metals was performed by ICP-MS. The found concentrations of Cd, Cr, Pb, Ag, Cu, Sb, Hg, Fe, and Mn in MP particles were 0.6, 14.2, 13.1, 0.2, 13.7, 0.5, 0.1, 3367.4, and 14.5 μg g⁻¹, respectively, while the corresponding concentrations in soil samples of these elements were 0.5, 74.9, 23.9, 1.5, 21.2, 1.2, 0.2, 37, 330.1, and 121.5 μg g⁻¹ [87].

In general, the values obtained in soils were considerably higher. These data may be justified attending to the larger surface area, porosity and density of charged surface sites in soil organic matter, facilitating metal retention and accumulation. Furthermore, the adsorption efficiency of heavy metals onto MPs surface is influenced by several factors, including polymer type and environmental conditions. The results showed a strong correlation between the concentration of heavy metal in MPs and soil samples, suggesting that the heavy metal content in MPs could be used as indicators of heavy metal contamination grade in soils. Moreover, MPs can be considered as vectors for heavy metal transport and distribution within the environment [87].

Deng et al. also provided data on the concentration of metals in MPs and sediments. For this purpose, 0.1 g of MPs were weighed and transferred to polytetrafluoroethylene (PTFE) containers, conducting a microwave-assisted digestion by adding 2 mL of 30 % H₂O₂, 5 mL of 65–68 % HNO₃, and 5 mL of 95–98 % H₂SO₄. The solution was then transferred to 50 mL volumetric PTFE flasks, filtered through 0.22 μm membrane filters and stored at -4 °C until analysis by ICP-MS. The detected trace elements were Cr, Ni, Cu, Zn, Pb, As, Cd, and Hg. To determine the concentration of these elements in sediments, 0.2 g of dried and ground sediment was first weighed into a PTFE vessel and

digested with 8 mL of 65–68 % HNO₃ and 2 mL of HF (≥40 %). After digestion using a microwave system, 0.5 mL of HClO₄ was added, followed by heating to 130 °C until 2 mL of the solution remained. Subsequently, the procedure for MPs digestion was the same as described above [88].

The concentrations of heavy metals accumulated in MPs and sediments were the following (μg g⁻¹): Cr: 4.79–15.70 (11–46 %), Ni: 2.11–6.00 (10–27 %), Cu: 2.42–23.25 (8–65 %), Zn: 7.16–185.39 (4–93 %), Pb: 13.42–51.58 (14–110 %), As: 0.64–6.53 (8–80 %), Cd: 0.02–0.78 (2–153 %), and Hg: 0.00–0.076 (0–12 %, Hg not detected in some MPs batches). As can be noted, these results indicated that the concentrations of heavy metals accumulated in MPs were generally lower than those present in sediments. Therefore, although MPs can not be considered the main contamination source of soils, these could act as carriers of heavy metals, spreading the pollutants and increasing their concentration in the environment [88].

Zhu et al. investigated the contamination of MPs and trace elements in vivo, allowing for a better understanding of the behavior of these pollutants. For this study, oysters were used as model organisms to study the interactions between heavy metals and MPs after bioaccumulation of the second. The oyster tissues were homogeneously powdered using a freeze-drying protocol, and 0.2 g were taken to determine metal concentrations. To achieve this, the samples were added to a digestion tube containing 2 mL of 67 % HNO₃ and kept in an oscillating incubator for 2 h at 180 °C until complete digestion. Then, 1 mL of 30 % H₂O₂ was added to the solution and heated to 120 °C until only 0.2 mL remained. To finish sample preparation, 4.8 mL of deionized water was added for further analysis by ICP-MS [89].

Cd, Cr, Pb, Cu were selected as target analytes, and the results indicated that Cu presented the highest concentration in oyster tissues, and Pb the lowest. Furthermore, a significant correlation between the content of MPs in oysters and the concentration of trace metals was found, increasing the values of Cd, Cr, Pb, and Cu when MPs content was raised. These results suggested that MPs could be responsible for the in vivo absorption of trace metals in oysters. The main entrance of MPs into the oyster organism is through the gills, being responsible for filtering seawater and, consequently, transferring organic matter and other substances to the tissues [89].

Smith and Turner studied the mobility of a variety of potentially hazardous elements present in MPs using both the physiologically based extraction test (PBET) and a diet-adapted PBET (DA-PBET), in which fish

oil was added. For its development, hazardous elements were first extracted through different protocols, consisting of a 0.1 M NaCl solution, a PBET, inspired by the chemistry of the digestive system of the northern fulmar (a procellariiform known for ingesting substantial amounts of MPs), and the diet-adapted PBET (DA-PBET), designed to simulate digestive conditions that include dietary oils. For this purpose, 100 mg of MPs was added in centrifuge tubes with 50 mL of 0.1 M NaCl solution in one tube, 50 mL of PBET solution in another, and finally, 40 mL of PBET plus 10 mL of anchovy oil in the last tube. These samples were incubated under continuous lateral at 100 rpm and 40 °C. Once prepared, 4 mL aliquots of solution filtered through 0.45 µm membrane, and the filtrates were transferred to individual tubes, where 80 µL of 2 % HNO₃ was added. Additionally, the extractions were performed in the absence of MPs as controls [90].

The samples NaCl, PBET and DA-PBET were then analyzed for Br, Cd, Cr, Hg, Pb, and Sb using ICP-MS. In general, the mobilization of the elements was enhanced under the acidic conditions of PBET and DA-PBET, compared to the non-acidified NaCl solution. For example, the Cr results can be observed in Fig. 8, increasing concentration values of this element at higher times following this tendency. In the case of DA-PBET test, the hydrophobic anchovy-oil presented a double role, modifying the integrity of the plastic structure and facilitating the extraction of relatively hydrophobic brominated organic compounds. So, it was demonstrated that bioaccessibility of metals from MPs depended on several factors, including gastric fluid composition, extraction conditions and diet [90].

In the study conducted by Holmes et al., the bioaccessibility of metals from MP pellets in the was investigated using a modified standard PBET for aquatic birds. To achieve this, a synthetic gastric fluid was prepared adding 5.844 g of NaCl, 10 g of pepsin, and HCl 1 M for pH adjustment to a 1L flask containing deionized water. Then, 40 mL of the synthetic gastric fluid was introduced into centrifuge tubes, which were sealed and placed in a hot water bath. After conditioning, 20 polystyrene pellets of different categories in size, weight and color were transferred, and the mix was maintained at 100 rpm for one week at 40 °C. Subsequently, an aliquot was taken for analysis and diluted with 2 % HNO₃ for further analysis. To obtain the remaining concentration of metals in MPs, the pellets were washed with deionized water to remove any residual gastric solution from the surface and air-dried prior to complete digestion using

2.5 mL of 20 % aqua regia solution. Metal concentrations in both samples were analyzed using ICP-MS. The maximum total concentrations of Fe, Mn, Co, and Pb in the studied MPs were 38.9, 0.81, 0.014, and 0.10 µg g⁻¹, while their maximum bioaccessibility percentage were 62.6, 78.4, 48.7, and 77.7 %, respectively. Attending to the limit toxicity values for seabirds, these concentrations were considered insufficient to produce negative effects in their organism. However, a relevant fraction of metals can be released from MPs and, depending on the composition, the risk may become significant [91].

Table 2 shows a compilation of recent works based on the determination of metals contained in MPs using ICP-MS. Samples, MPs composition, pretreatment and maximum relevant metal concentration found in MPs can also be observed. Most methodologies are focused on the determination of heavy metals in polypropylene (PP) and PE, presenting excellent limits of detection (LODs ≤ 0.18 µg g⁻¹). Besides, the approaches are generally multielemental, so only information of relevant elements based on concentration and/or toxicity criteria has been included to simplify data discussion. Authors usually use complete digestion protocols, without evaluating the bioaccessible fraction of the analytes. It should be noted that MPs exhibit a wide variety of polymer types since these samples typically originate from the degradation of diverse materials with distinct chemical compositions [20]. Consequently, the interpretation of analytical results according to samples variability is a challenge. For this reason, and to provide clear and reliable information, an overview expressed as the maximum found concentration of the elements studied in MPs is included. Attending to the found concentrations of trace elements in MPs, different orders of magnitude depending on the analyte and the MPs composition are observed. The minimum value was obtained for the rare earth elements Sc, Y, La, Ce (< 0.1 µg g⁻¹) [92], while the maximum concentrations were found in paint particles in the 15-1800 µg g⁻¹ range for Ni, As, Cd and Pb [93]. Besides, these results showed that most trace elements present in MPs can be found in the 0.01–500 µg g⁻¹ range.

3.2. Determination of trace elements in MPs by LA-ICP-MS

Despite the limitations associated with the solid direct analysis mentioned above, LA-ICP-MS has been postulated in recent years as a promising technique for the analysis of trace elements in MPs. This is

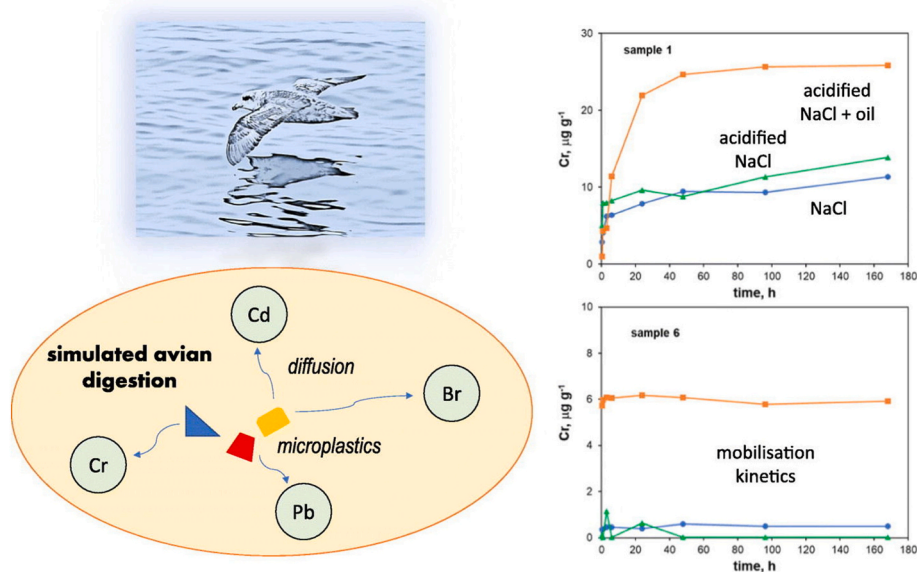


Fig. 8. Diffusion of contaminants (Cr, Cd, Pb, and Br) from MPs to the organism. Mobilization of Cr under three different conditions: NaCl solution (blue line), an avian physiologically-based extraction test (PBET, green line) and avian-based dietary-adapted PBET (DA-PBET, orange line), incorporating fish oil to the mix as part of their diet [90]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Determination of trace elements in MPs using ICP-MS.

Sample	MPs composition	Pretreatment	Trace elements	LOD $\mu\text{g g}^{-1}$	Total concentration $\mu\text{g g}^{-1}$	Ref.
Coastal plastic litter	PP, PS, PE, PET, ABS	Complete acid digestion	Ba, Zn, Ti, Fe, Pb, B	–	41.0, 32.0, 40.0, 69.0, 15.0	[94]
Plastic litter	PP	UV Photo-aging, complete digestion and acid leaching	Al, Fe, Zn, Ba	–	112.39, 23.38, 0.901, 323.6 (leached fraction 11.51, 4.45, 99.86, 83.04 %)	[95]
River estuary water	PE, PLA, PBAT ^a , PCL ^b	Complete acid digestion	Cu, Pb, As, Mn, Cr, Co	0.008–0.18	0.4, 2.0, 1.0, 16.0, 13.0, 0.25	[96]
Marine zooplacton	–	Complete acid digestion	Al, Cr, Fe, Mn, Ni, Pb, Cu, Zn	0.01	30, 7.0, 16, 1.6, 3.2, 1.5, 1.0, 4.5	[97]
Floodplain soils	PE, PP, CSM ^c , PA ^d , PMMA ^e	Complete acid digestion	Zn, Ni, Cr, Pb, Cu	–	94.6, 23.5, 67.6, 34.2, 28.1	[98]
Coastal plastic litter	PS	Complete and partial acid digestion	Pb, Cr, As	–	24.8, 15.0, 5.50 (>20 % bioaccessibility)	[99]
Disposable face masks	PP	UV Photo-aging	Zn	–	0.08 ^f	[100]
Consumer plastics	PP, PE, PS, among others	Complete acid digestion	Sc, Y, La, Ce	0.002–0.3	0.34, 0.47, 0.49, 1.13	[92]
Seawater	PP, PE, PS, PET	Complete acid digestion	Al, Si, Ti, Sr, Fe, Ba, Cu, Cd, Pb	–	450, 5000, 200, 350, 220, 180, 150, 120, 100	[101]
Disposable face masks	PP	Stirring in artificial seawater under simulated conditions	Al, Si, Mn, Zn	0.00006–0.003	0.06, 0.05, 0.06, 0.59 ^f	[102]
Paint particles	PES, PVA	Complete acid digestion	Ni, As, Cd, Pb	–	30, 15, 30, 1800	[93]

^a Poly (butylene adipate-co-terephthalate).

^b Polycaprolactone.

^c Chlorosulfonated polyethylene.

^d Polyamide.

^e Polymethylmethacrylate.

^f Calculated as the concentration of the trace element released into the solution from face masks MPs ($\mu\text{g mL}^{-1}$).

due to its capacity to perform mapping analysis of MPs with relatively good sensitivity and precision to identify MPs and distinguish between the inner additives from the core, and the trace elements located on the MPs surface corresponding to adsorbed species [86].

Porizka et al. selected five types of MPs (PA, PE, PET, PP and PVC) and aged under controlled conditions in freshwater and wastewater prior to the analysis by several techniques such as ICP-MS, LA-ICP-MS and Raman spectroscopy. Typical trace elements usually found in MPs were monitored by LA-ICP-MS analysis (Al, Sb and Zn). Comparing the distributions of the Al, Zn, and Sb in a mix of MPs, their identity and morphology (size and shape) were studied. As can be observed in Fig. 9, the size and shape of MPs were highly heterogeneous, indicating a high level of polydispersity. Regarding composition, Al is usually used as flame retardant in PP, Zn is a typical additive in PVC and Sb is normally

added in PET manufacturing, so their respective presence in the MPs core revealed their identity. Furthermore, the presence of Al on the surface can be justified through the adsorption mechanism, being considerably more bioaccessible than the intern additives [86].

In the study developed by El Hadri et al., LA-ICP-MS was applied for the analysis of trace elements (Fe, Cu, Zn, As, Cd, Sn, Sb, Pb, and U) in the microplastic subsurface (200 μm) of PE and PP, corresponding to more than half distance between the surface and core. It was also demonstrated that the discrimination of the presence of additives such as Pb, Cu and Sb, and the presence of adsorbed metals (Fe, Cu, Zn, As, Cd, Sn, Sb, Pb and U) was possible. Consequently, the obtained mapping by LA-ICP-MS of the sorption or additives content allowed the establishment of concentration profiles characteristics for every type of MPs, considered as a fingerprint. Besides, these results showed high potential

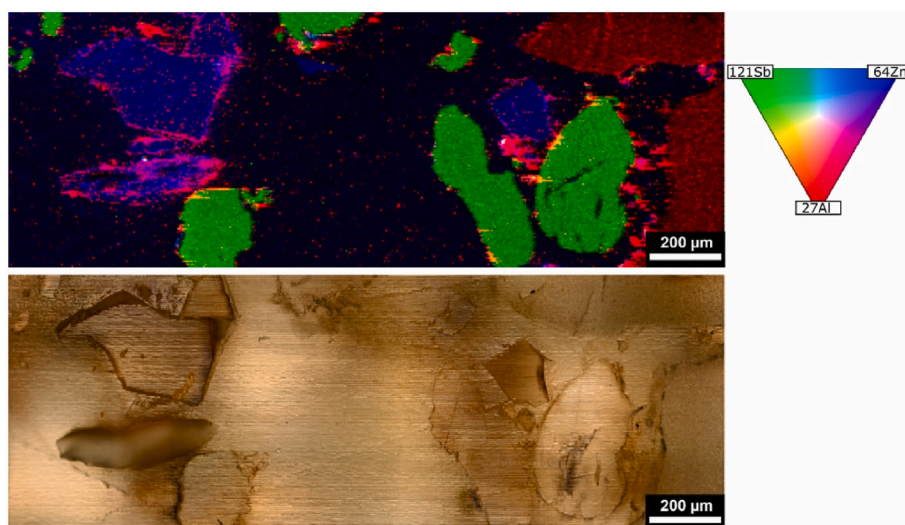


Fig. 9. Mapping of Sb, Zn and Al in MPs obtained by LA-ICP-MS after aging in freshwater. Distribution of analyzed marker elements allowed the identification of the polymeric mix, their distribution in the sample, and particle morphology (size and shape). The identity of the polymers present in samples were the following: PP (Al), PVC (Zn), and PET (Sb). The sample was mounted in epoxy resin prior to analysis [86].

to identify the trace elements more susceptible to being released into the environment and organisms [103]. This study also demonstrated the benefits of using LA-ICP-MS for the identification of MPs and the elucidation of their impact on the environment and living beings.

The interaction between nanoparticles (NPs) with pollutants affects their bioavailability and toxicity, including metallic-derived NPs and NPTs. However, the processes by which these nanomaterials change in vivo have rarely been explored. In the work developed by Chen et al. it was concluded from LA-ICP-MS mapping results that both ZnO NPs and nanometric PS caused more Cd to accumulate in zebrafish larvae, but with distinct pathways. In the PS + Cd²⁺ co-exposure, Cd was absorbed by larvae through the "Trojan horse" effect and remained in the abdomen where PS was located, avoiding toxic effects in other systems. On the contrary, the exposition to ZnO NPs + Cd²⁺ caused a general intoxication in the organism (Fig. 10). This effect could explain why PS + Cd²⁺ co-exposure could increase the tolerance limit of larvae towards Cd, causing lower toxic effects than Cd²⁺ exposure alone [104].

Therefore, it was demonstrated that the interaction between PS and metals in vivo had a considerable impact on bioaccessibility and toxicity. Nevertheless, this does not mean that co-exposure to nanometric plastics or MPs along with Cd²⁺ is safe. In fact, it is still unknown whether long-term exposure could produce the opposite effect, releasing a higher concentration of Cd by dissociation from plastic materials. This study revealed that LA-ICP-MS can help to explain the consequences derived from co-exposure of MPs and associated pollutants such as trace metals, showing great potential in environmental health applications [104].

Similar behaviour was observed by Wu et al. when the co-exposure to aged PS-COOH MPs and Cd²⁺ on rice leaves as model organism via the foliar route was investigated. Thirty-day-old rice seedlings grown in soil were exposed to Cd(NO₃)₂ using foliar spraying at 1, 10, 50, 100, and 500 µM, with or without MPs at 30 µg d⁻¹ rate. The results of this study suggested that Cd accumulation on rice leaves had a higher toxic impact than MPs-Cd co-exposure. In fact, the authors demonstrated by LA-ICP-MS mapping that Cd accumulation was significantly reduced in the co-exposed leaves (29.3 – 77.9 %). The main hypothesis to explain this was the ability of aged negatively charged PS-COOH MPs to capture Cd²⁺, minimizing the concentration of free Cd²⁺ that finally penetrates inducing oxidative and chloroplast damage. The present study could be useful to evaluate the impact of Cd and MPs on rice growth and to identify the molecular mechanisms behind toxic effects caused by heavy metals and MPs [105]. Consequently, mitigation strategies to protect plants and animals from these pollutants could be developed.

4. Determination of VOCs in MPs

As in the case of trace elements, VOCs are pollutants associated with the presence of MPs. The natural emissions sources of VOCs include plants, forest fires, and anaerobic moors processes, and anthropogenic sources originate from domestic and industrial processes as ingredients for paints, varnishes, waxes, disinfecting products, cosmetics, hydrocarbon fuels burning, petroleum storage and distribution, etc. (Fig. 11)

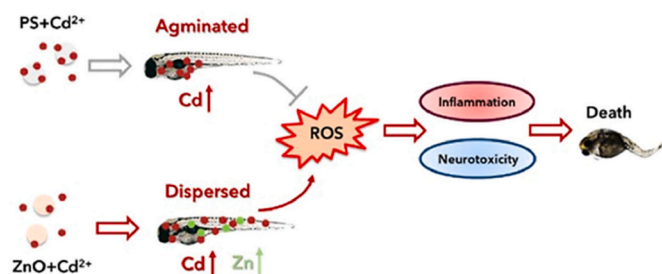


Fig. 10. Possible schematic diagram of the toxic effects caused by bioavailability of Cd on larvae co-exposed to PS/ZnO NPs and Cd²⁺ [104].

[28,106–108]. The most common VOCs present in daily life include aromatic hydrocarbons, alkanes, aldehydes, aliphatic hydrocarbons, terpenes, chlorinated hydrocarbons and glycol ethers and esters [29].

As VOCs exhibit high reactivity, they tend to form radicals easily, leading to rapid chemical reactions that contribute to atmospheric pollution and secondary organic aerosol formation [28,109]. The breakdown of organic matter in sludge during the hydrothermal process can generate VOCs, which aged microplastics, due to their altered surface characteristics, could potentially adsorb and transport, thereby increasing ecological risks once released into the environment [110]. Their impact not only affects air quality and environmental balance but also poses significant risks to human health, contributing to respiratory diseases, neurotoxic effects and endocrine system disorders [28,29,111, 112].

A general workflow for the determination of VOCs in microplastics is summarized in Fig. 12, comprising four main steps: sampling, pre-separation, extraction, and separation/detection. Sampling involves the collection of MPs from environmental matrices (water, sediments, or biota) under controlled conditions to minimize contamination. Pre-separation aims to isolate MPs from organic matter and mineral particles, typically through density separation, flotation, and filtration [113]. Extraction techniques, such as headspace solid-phase microextraction (HS-SPME), purge-and-trap, or thermal desorption, are then applied to release VOCs adsorbed onto or embedded within polymers [114]. Finally, separation and detection are achieved using advanced chromatographic and mass spectrometric methods.

Among the techniques used for determining VOCs, GC-MS are the most widely applied [115]. However, the need for in situ analyses requires portable and efficient tools for real-time monitoring. Developing a sensitive and transportable instrument to detect VOC emissions from plastic debris would enhance the ability to identify macro and MPs in specific environments. Additionally, it would help establish links between these emissions and the growing evidence of harmful interactions between MPs and living organisms.

Among the portable technologies currently available, Selected Ion Flow Tube-mass Spectrometry (SIFT-MS) stands out as one of the few capable of conducting real-time qualitative and quantitative analyses of VOCs at trace levels in air or sample headspaces. This technique utilizes precisely controlled ultra-soft chemical ionization with various reagent ions (e.g., H₃O⁺, NO⁺, and O₂⁺), enabling high chemical selectivity for different classes of compounds without requiring chromatographic separation systems [116,117].

Carrying out a literature review of VOC determination in MPs, researchers have focused on three key areas: optimizing analytical methods for detecting VOCs associated with MPs, investigating their presence and distribution in environment and living organisms, and evaluating their toxicity and biological impact.

Peñalver et al. developed a methodology based on GC coupled with Static Headspace MS (SHS-GC-MS) for detecting VOCs associated with MPs in animal tissues. This approach, which integrates VOC extraction via static headspace with the high resolution and sensitivity of GC-MS, facilitated both the identification and quantification of a wide range of compounds and as well as the assessment of their accumulation in different organs. Chemometric analysis, along with verification of VOC sources through Thermogravimetric Analysis-Mass Spectrometry (TGA-MS), provided valuable insights into contamination sources and bio-accumulation processes. This methodology demonstrated high sensitivity, reproducibility, and accuracy, allowing the tentative identification of 60 compounds associated with MPs through a non-targeted approach in 48 organ samples from different animals [118].

Additionally, 25 of these VOCs were quantified in this work through targeted analysis, with concentrations ranging from 1.12 to 920 ng g⁻¹. The findings confirmed the presence of certain compounds linked to MPs in the analyzed samples. To confirm the origin of the detected VOCs, a TGA-MS study was conducted. The analysis revealed that samples in which no VOCs were detected showed no signals corresponding to the

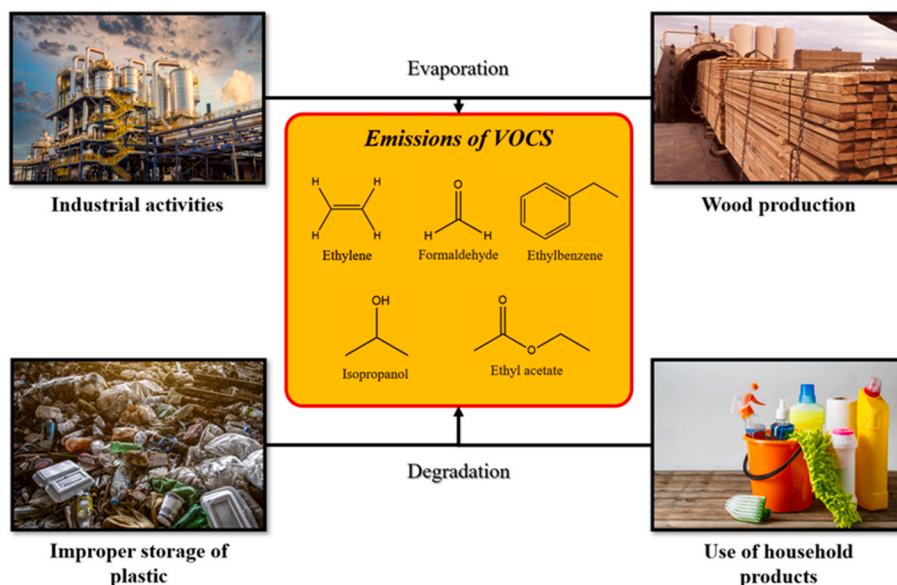


Fig. 11. Common emission sources of VOCs by degradation and evaporation.

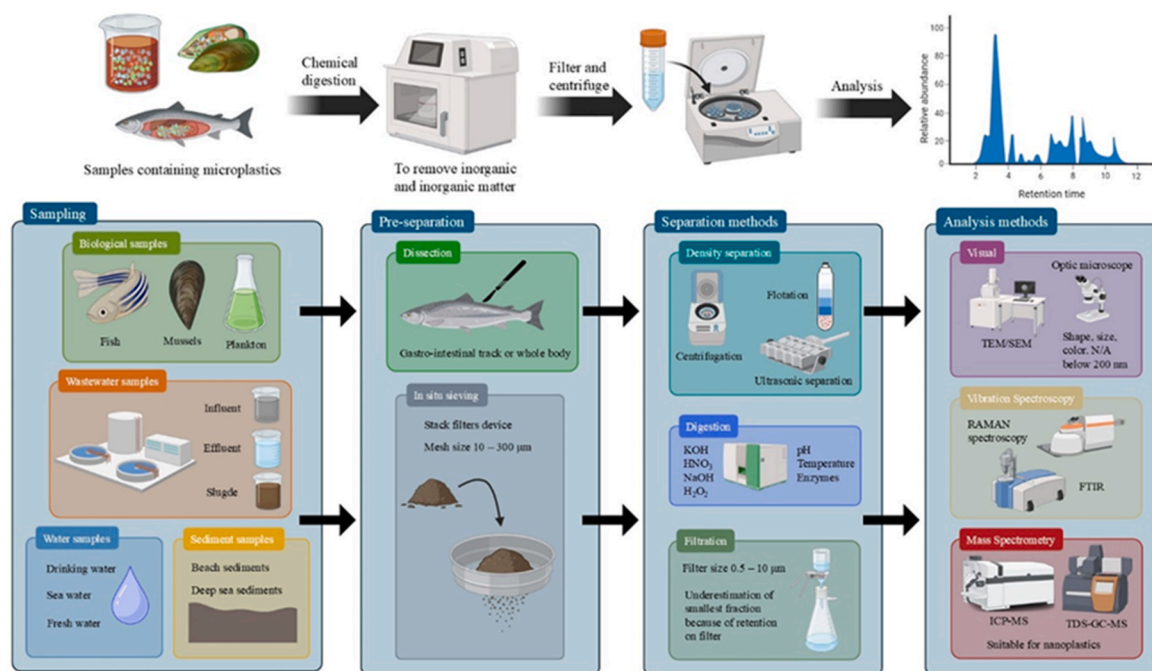


Fig. 12. Schematic workflow for the processing and analysis of microplastic samples for VOC determination.

characteristic ions of PS (m/z 78, 104). In contrast, samples with higher concentrations of volatiles exhibited a greater release of PS-related monomers, demonstrating a correlation with the HS-GC-MS results [118].

To determine the stable isotopic composition ($\delta^{13}\text{C}$) of VOCs embedded in MPs, Le Juge et al. introduced a novel analytical approach [119]. The researchers developed a precise and sensitive method capable of detecting VOCs at trace concentration levels and simultaneously analysing their isotopic signatures utilizing Purge-&Trap GC-MS and Combustion Isotope Ratio Mass Spectrometry (PT-GC-MS-C-IRMS). The methodology involves heating MP samples to release VOCs, which are then extracted through purging and cryo-trapped on a Tenax sorbent for further analysis. This technique was applied to different plastic materials, including PS, PET, and PLA,

revealing distinct $\delta^{13}\text{C}$ patterns for specific VOCs. These findings suggest that isotopic analysis can serve as a valuable tool for tracing plastic pollution sources and understanding MPs' environmental transformation processes.

A key finding of the study was the significant isotopic variation between the styrene monomer and the bulk PS polymer. The $\delta^{13}\text{C}$ value of styrene was notably different from that of the polymer, indicating the potential for isotopic fractionation during synthesis or diffusion processes. This suggests that isotopic analysis can provide critical insights into the production, degradation, and environmental behaviour of MPs. To ensure the accuracy and reliability of the results, the temperature and sample mass parameters were optimized. The findings demonstrated that increasing these factors enhanced sensitivity without altering the $\delta^{13}\text{C}$ values of VOCs, confirming the robustness of the VOC detection

and analysis method at ultra-low concentrations. Overall, this research underscored the potential of VOC $\delta^{13}\text{C}$ Compound-Specific Isotope Analysis (CSIA) as a complementary technique for the characterization of MPs. By enabling plastic fingerprinting and providing insights into degradation pathways, this approach can contribute to a deeper understanding of MPs pollution. Future studies should focus on refining the methodology and exploring isotopic fractionation mechanisms under various environmental conditions [119].

Table 3 summarizes recent studies analysing VOCs in MPs, detailing the samples investigated, the composition of the MPs and the analytes detected. The most analyzed plastics are PS, PP, PET, LDPE and HDPE. The analytes studied include a wide range of compounds in MPs of different compositions, from aromatic hydrocarbons to aldehydes, ketones and halogenated esters. Consequently, found concentration (e.g. $0.0002\text{--}30\ \mu\text{g g}^{-1}$) and LODs (e.g. $2\text{--}1000\ \text{ng L}^{-1}$) can range over several orders of magnitude [120,121]. In most cases, LODs are not calculated by authors since these works are mainly focused on VOCs extraction and reliable identification. Instruments were adequately calibrated, ensuring suitable quantitative or semiquantitative analysis. Analyzed samples include marine debris, sand and sediments, food packaging, play mats, biological tissues, fecal material, and air. This information highlights the diversity of approaches in the investigation of VOCs in MPs, underlining the importance of considering sample type, composition of the MPs, and specific analytes to better understand the environmental impact of these pollutants [118].

5. Perspectives and Future challenges

Future research should prioritize enhancing the sensitivity and specificity of SP-ICP-MS to detect even smaller NPTs within complex environmental and biological matrices, such as atmospheric samples and biological tissues. The development of standardized protocols for

sample preparation and detection is essential to ensure global comparability of data. Additionally, integrating SP-ICP-MS with emerging technologies, such as machine learning and automated analysis, presents a promising avenue for improving the accuracy, efficiency, and scalability of microplastic monitoring in environmental and human health studies [131].

Current research trends emphasize the adsorption capacity of MPs for trace elements, particularly their role as carriers of heavy metals, which amplifies their potential environmental impact. To accurately assess the biological risks associated with MPs and their adsorbed contaminants, it is crucial to not only determine their total pollutant content but also evaluate their bioaccessible fraction. Future challenges include a comprehensive assessment of MP toxicity and the environmental impact of associated metallic species across different ecosystems, including soils, river water, and seawater [132,133]. Furthermore, the development of advanced sample pretreatment protocols will be critical to improving analytical accuracy and extraction efficiency. The interaction mechanisms between MPs and living organisms remain an important area of investigation, particularly through in vivo studies assessing bioaccumulation effects and the consequences of long-term co-exposure to MPs and their associated pollutants.

Advances in the detection and analysis of VOCs associated with MPs are leading to more effective strategies for evaluating environmental and toxicological risks. Addressing these challenges requires an interdisciplinary approach which integrates experimental studies with predictive modelling and the analysis of MP degradation under real environmental conditions, leading to a better understanding of their ecosystem impact. At the same time, the implementation of more efficient and sustainable analytical techniques, such as methodologies based on isotopic ratios (particularly fractionation studies) is gaining relevance. In this context, CSIA of VOCs embedded in MPs is emerging as a powerful tool for fingerprinting plastic materials and tracing their

Table 3
Determination of volatile organic compounds in MPs.

Sample	MPs composition	Analyte/s	Concentration	LOD	Ref
Macro- and microplastic (1–5 mm) marine debris	PP, LDPE, HDPE, PS, PET	Aldehydes, ketones, thiols, disulphide, alkanes, alkenes, aromatic hydrocarbons and alkyl or aryl halides	$0.02\text{--}825\ \text{ng g}^{-1}$	$2\text{--}1000\ \text{ng L}^{-1}$	[120]
Macro- and microplastic (up to 1 cm) debris from sand	LDPE, PP, PET	Alcohols, carboxylic acids, aldehydes, esters and ketones	$0\text{--}1.9\ \text{mg L}^{-1}$ range for LDPE, $0.08\text{--}2.1\ \text{mg L}^{-1}$ range for PP and $0.02\text{--}0.96\ \text{mg L}^{-1}$ range for PET	–	[122]
Self-heating food packaging	PP	Saturated hydrocarbons, fatty acyls, organoxygen compounds, unsaturated hydrocarbons, aromatic hydrocarbons, and phenol ethers, with saturated hydrocarbons and fatty acyls	Semiquantitative analysis	–	[30]
Biodegradable microplastics	PBAT ^b , PLA, PBS	Small hydrocarbons, aldehydes, alcohols, and ketones	–	$0.14\text{--}1.8\ \text{mg L}^{-1}$	[123]
Human Coronary Artery Smooth Muscle Cells	PS, HDPE, LDPE	Aldehydes, ketones, esters, alcohols, alkanes and alkenes	–	$1.5\ \mu\text{g L}^{-1}$	[124]
Sediment from lake and marine sediments from a sandy beach	PP, LDPE, HDPE, PS, PET	Aldehydes ^c and carboxylic acids ^c together with a predominance of acetone and alcohols ^d	$0.06\text{--}25\ \text{mg g}^{-1}$	–	[125]
Microplastic sample	LDPE, PP, PLA, PET	Ketones, esters, aromatic hydrocarbons and quinones.	$0.0002\text{--}30\ \mu\text{g g}^{-1}$	–	[121]
Play mats	PVC, PE, PP, PET	Alkanes, alkenes, alcohols, aldehydes, chloride, esters, ether, ketones, nitride compounds and aromatic hydrocarbon.	–	–	[126]
Water treatments	PP, PS and PVC	Alkanes, alkenes, alcohols, aromatic hydrocarbon and aldehydes	$40\text{--}216\ \mu\text{g g}^{-1}$	–	[127]
Indoor air	PMMA, N66 ^e , PP, NBR ^f , PVC, PET, PC, ABS, PE, and PS	Ketones, lactones, oxygenated heterocycles	$0.01\text{--}0.36\ \mu\text{g m}^{-3}$	–	[128]
Fecal samples	PE	Alcohols, aldehydes, ketones, esters	–	–	[129]
Air	PE, PET	Esters, alkanes, alcohols, aldehydes, aromatic hydrocarbon, acids	$34\text{--}6315\ \mu\text{g g}^{-1}$	–	[130]

a Compounds with 2, 4, 6, and 8 carbon atoms chain lengths.

^bPolybutylene adipate terephthalate.

^cCompounds in the C₂–C₁₂ range.

^dCompounds up to C₆.

^eNylon-6,6.

^fNitrile butadiene rubber.

sources [134].

Nevertheless, significant technical constraints remain. For instance, natural background VOCs can generate strong spectral interferences that obscure the identification of plastic-derived compounds. Differentiating these overlapping signals requires more systematic use of advanced pre-treatment methods (e.g., selective extraction or thermal desorption coupled with clean-up steps), as well as the development of reference spectral libraries that integrate both polymer-derived and natural VOCs [135]. Additionally, coupling CSIA with multidimensional separation techniques such as high-resolution mass spectrometry offers promising avenues to resolve complex mixtures and enhance source discrimination [136]. Beyond these analytical advances, establishing standardized protocols for environmental samples and conducting controlled degradation experiments under realistic conditions should be prioritized [137]. These approaches would not only improve reliability in distinguishing MP-related VOCs from environmental backgrounds but also provide actionable research priorities to bridge current methodological gaps.

Addressing these challenges requires an interdisciplinary approach that combines experimental research, predictive modelling, and the study of MP degradation under real environmental conditions to gain a deeper understanding of their long-term ecological impact. In parallel, the implementation of more efficient and sustainable analytical techniques, alongside increased collaboration between researchers, policy-makers, and industry stakeholders, will be key to developing innovative regulations aimed at minimizing the release of pollutants from MPs. These synergies will not only enhance risk management strategies for human health but also promote technological solutions that align with environmental sustainability and the principles of the circular economy.

6. Conclusions

MPs and NPTs are pervasive environmental pollutants with significant ecological and human health implications. Their environmental risk extends beyond their mere presence, as they serve as carriers for heavy metals, VOCs, and other toxic substances, either through adsorption mechanisms or as internal additives.

Among the various techniques available, SP-ICP-MS has emerged as a powerful tool for MPs and NPs analysis due to its high sensitivity, accuracy, and capacity for real-time quantification. The integration of ICP-MS/MS and collision/reaction gases (e.g., H₂, O₂, NH₃) significantly enhanced analytical performance by reducing spectral interferences. Additionally, recent advancements in SP-ICP-MS have enabled the precise detection and quantification of NPs through functionalized gold nanoparticle labeling, ensuring high sensitivity and selectivity. These methodological improvements position SP-ICP-MS as a promising approach for comprehensive MP monitoring across aquatic environments and consumer products.

The ability of MPs to transport pollutants underscores their role as secondary contamination vectors, necessitating reliable analytical methods for their detection, characterization, and risk assessment. In this context, researchers successfully studied the combination of sample pretreatments for complete extraction and partial digestions based on PBET and DA-PBET prior to ICP-MS analysis, while the mobility of trace metals inside the organisms was observed by LA-ICP-MS mapping with direct solid-state analysis. The combination of both allowed a deeper understanding of potential environmental impact and contamination pathways between ecosystems, pollutants carriers and organisms.

Besides, the analysis of VOCs in MPs plays an important role for understanding the environmental and toxicological impact of these compounds. GC-MS and its variants, SHS-GC-MS and PT-GC-MS-C-IRMS, have shown high sensitivity and accuracy in the identification and quantification of VOCs in different types of MPs and environmental matrices, providing valuable information on their origin, distribution and transformation. The studies reviewed have identified a wide range of VOCs associated with MPs, highlighting the presence of aromatic

hydrocarbons, aldehydes, ketones, esters and halogenated compounds. The results indicated that MPs can also serve as carriers for VOCs, thereby enhancing their potential toxicity and impact on human health and ecosystems.

To the best of our knowledge, no previous review has rigorously and simultaneously addressed recent advances in the analysis of MPs alongside trace elements and VOCs as associated pollutants, also considering bioaccessibility assessments. This work pioneers the field by filling this gap and providing a focused, up-to-date overview of cutting-edge mass spectrometry techniques and their implications for environmental and toxicological research.

CRedit authorship contribution statement

R. González Herrera: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **A. Doblado-Onieva:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization. **P. Montoro-Leal:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M.M. López Guerrero:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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