Science of the Total Environment 913 (2024) 169678

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A reliable method to determine airborne microplastics using quantum cascade laser infrared spectrometry

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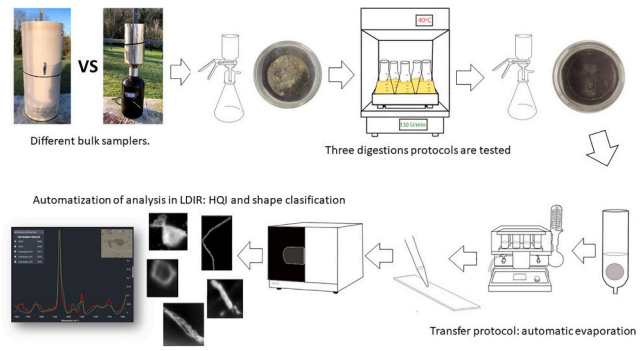
HIGHLIGHTS

- Passive sampling devices to collect atmospheric bulk deposition
- An alkaline-oxidative method allows excellent recoveries for particles (82–90 %).
- An automatic LDIR approach to differentiate fibres from particles (>90 % success)
- An LDIR identification criterion to positive matches is proposed.
- Deposition rates 98–1220 MP/m^2/day (1.7 % of total collected particles)

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dimitra A Lambropoulou

Keywords:
Atmospheric microplastics
Passive air samplers
Quantum cascade laser
Infrared spectrometry
LDIR
Bulk deposition

ABSTRACT

The number of studies dealing with airborne microplastics (MPs) is increasing but sampling and sample treatment are not standardized, yet. Here, a fast and reliable method to characterize MPs is presented. It involves the study of two passive sampling devices to collect atmospheric bulk deposition (wet and dry deposition) and three digestion methods (two alkaline-oxidative and an oxidative) to treat the samples. The alkaline-oxidative method based on KOH and NaClO was selected for a mild organic matrix digestion. In addition, some operational parameters of a high-throughput quantum cascade laser-based infrared device (LDIR) were optimized: an effective automatic tiered approach to differentiate fibres from particles (>90 % success in validation) and a criterion to establish positive matches when comparing an unknown spectrum against the spectral database (proposed match index > 0.85). The procedural analytical recoveries were very good for particles (82–90 %) and slightly lower for fibres (62–73 %). Finally, the amount and type of MPs deposited at a sub-urban area NW Spain were evaluated. Most common polymers were Polyethylene (PE), Polypropylene (PP) and Polyethylene terephthalate (PET). The deposition rates ranged 98–1220 MP/m^2/day, ca. 1.7 % of the total collected particles. More than 50 % of the total MPs deposited were in the 20–50 μm size range, whereas fibres were mostly in the 50–500 μm size range.

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https://doi.org/10.1016/j.scitotenv.2023.169678
Received 29 August 2023; Received in revised form 11 December 2023; Accepted 23 December 2023
Available online 28 December 2023

1. Introduction

Microplastics (MPs) constitute a worldwide, rising environmental problem. It is estimated that by 2050 they will be present in the ecosystems at levels in excess of 25 billion metric tons (Geyer et al., 2017) and they are being encountered in almost all natural environments (Priya et al., 2022). Currently, most studies focus on marine and terrestrial environments (dos Santos Galvão et al., 2022) whereas the atmospheric compartment has been studied much less. In particular, Dris et al. (2015) reported the first work on atmospheric (or airborne) MPs pollution, or hereinafter atmospheric microplastics (AMPs). Since then, more atmospheric studies were performed (Can-Güven, 2021; Munyaneza et al., 2022), both in urban and sub-urban areas in France (Dris et al., 2016, 2015), China (Cai et al., 2017; Liu et al., 2019b; Zhou et al., 2017), Germany (Klein and Fischer, 2019), UK (Stanton et al., 2019; Wright et al., 2020); and natural areas such as the Baltic shore (Szewc et al., 2021), Atlantic Sea (Allen et al., 2020) or the Pyrenees (Allen et al., 2019).

The fact that MPs are found even in remote areas (such as the Pyrenees, the Sahara or in the Atlantic marine atmosphere) indicates that AMPs can be transported many kilometres away through air streams (Li et al., 2020; Wieland et al., 2022). The origin of the AMPs cannot be determined precisely because of their very many inputs (dos Santos Galvão et al., 2022), including diffuse road traffic. It is thought that two relevant sources are the transport of MPs through atmospheric events, including the water cycle (Allen et al., 2020, 2019; Bergmann et al., 2019; Brahney et al., 2021, 2020), and aerosols from seawater, which bring the possibility that low-density microplastics get introduced into the air (Allen et al., 2020; Brahney et al., 2021). Overall, the main sources of AMPs seem to be road traffic (Brahney et al., 2021; Evangeliou et al., 2020), followed by plastics from oceanic emissions, wear and tear from agricultural plastics and dust generated in urban environments (Beaurepaire et al., 2021; Brahney et al., 2021).

AMPs could bring consequences for human health as breathing might be a main route of entry of MPs in the human body (Enyoh et al., 2019; Vianello et al., 2019), even more than the ingestion of marine fish (Catarino et al., 2018). The presence of AMPs has been detected in lung tissue (Prata et al., 2020b; Wang et al., 2021) and some studies have already shown a relation between the presence of MPs in the human body and respiratory diseases, which could cause lung fibrosis or even cancer (Chen et al., 2020a; Shuo et al., 2021). In addition, smaller AMPs (usually nanoplastics) could pass through epithelial cells eventually reaching blood (Wieland et al., 2022).

The sampling systems used to monitor AMPs can be classified in two main types: passive (gravity-based) and active (pumping-based). The latter are used to collect suspended aerosols samples through a filter membrane of a specific pore size and a known flow rate for a prefixed time, allowing the calculation of airborne particulate concentrations per sampled air volume (Abbasi et al., 2019; Allen et al., 2020; Dris et al., 2017; Li et al., 2020; Liu et al., 2019b; Prata et al., 2020a; Vianello et al., 2019; Wang et al., 2020).

Passive samplers collect the atmospheric particulate matter fallout (dry and/or wet deposition). They were used in most airborne studies because they are much simpler and more accessible than the active ones (Zhang et al., 2020). Most passive collectors are based on a glass or metal funnel and a collecting container where the deposited particles are recovered by rinsing the funnel with ultrapure water or a specific solution and filtering. This was first used by Dris et al. (2016; 2015) for AMPs monitoring in Paris and other authors developed similar systems (Abbasi et al., 2019; Allen et al., 2019; Cai et al., 2017; Catarino et al., 2018; Klein and Fischer, 2019; Stanton et al., 2019; Szewc et al., 2021; Thinh et al., 2020; Wright et al., 2020; Zhou et al., 2017). Some other authors used systems like ACM (Aerosol Collection Module) which collected wet and dry depositions using wet and dry buckets, respectively, activated by precipitation sensors or NILU (Norwegian Institute for Air Research) precipitation collectors (Brahney et al., 2020; Roblin et al., 2020). Passive sampling would simplify the comparison of results obtained in different studies (Beaurepaire et al., 2021; Chen et al., 2020b; Szewc et al., 2021; Can-Güven, 2021) although it is worth noting that the sampling time and surface of sampling is very variable across studies and should be harmonized. In fact, the deposition area in passive samplers is an important parameter when calculating the number of AMPs deposited per unit area (e.g. MPs/m^2/d). These samplers yield a small area being sampled, causing the extrapolation to a larger area (typically, 1 m^2) cumbersome, with a corresponding increase on the overall uncertainty. Therefore, optimizing the sampling surface area is an important consideration when evaluating deposition rates. Further, the application of duplicate samplings may also help strengthen the understanding of local scale variations with respect to deposition rates (Wright et al., 2021).

After collecting the sample, analytical digestion protocols should be applied to get rid of the organic material (that can be abundant in some locations or seasons), although that was not done extensively in early works. As sample digestion may be time-consuming it is important to set a trade-off between cost, time and integrity preservation of MPs. In the last years acid digestions have been almost discarded because they destroy many types of MPs (Enders et al., 2017; Karami et al., 2017; Pfeiffer and Fischer, 2020; Thiele et al., 2019). On the contrary, alkaline digestions based on approx. 10 % KOH are used frequently because of their acceptable cost and moderate risk of MPs destruction (Alfonso et al., 2021; Lusher and Hernandez-Milian, 2018; Prata et al., 2019). Also, oxidative digestion with H_2O_2 (either alone or combined with Fe (II) as catalyst) is used commonly (Hurley et al., 2018; López-Rosales et al., 2022b; Tagg et al., 2016; Treilles et al., 2020). Enzymes are the safest digestion media in terms of MPs preservation, but they involve high expenses and large operation times.

The most common analytical techniques to characterize chemically potential polymers are infrared (IR) and Raman spectroscopy, which are non-destructive methods. Their major disadvantage is that they are time-consuming when many particles have to be studied. However, a novel technology is playing an increasingly relevant role: the tunable quantum cascade laser (QCL) IR spectrometry (commercialized by Agilent as '*Laser Direct Infrared Imaging*', LDIR). Its characteristics make it an excellent choice for monitoring studies due to its ability to identify many particles in a relatively short time (Hildebrandt et al., 2020). In fact, it was used already by Liu et al. (2022) to monitor atmospheric dust in Beijing (China). However, its working parameters still need to be optimized to apply it to identify AMPs in field samples and some setting parameters deserve careful attention. In particular, how to automatically discriminate between fibres and fragments and to set a threshold to match positively a spectrum against a database, avoiding overestimations.

Accordingly, the major objective of the present work is to implement a fast and reliable analytical method to determine microplastics in deposited atmospheric particulate matter. For this, the following partial objectives are set: (i) to compare two passive samplers; namely, an EnviroPlaNet sampler prototype from the Spanish Network of Researchers working on plastic pollution [www.enviroplanet.net], and a commercial sampler (Depobulk®); (ii) to compare 3 types of digestions: two alkaline-oxidative ones (based on KOH plus NaClO, and KOH plus H_2O_2), and an oxidative one (using H_2O_2); (iii) to establish criteria to both get high confidence spectral identifications of MPs and to automatically classify them as fibres or particles, using a QCL-based instrument; and (iv) to apply those procedures to monitor airborne MPs in a sub-urban area at Northwestern Spain in different seasons.

2. Materials and methods

2.1. Samples and processing

The sampling location (Oleiros, A Coruña, NW Spain) is shown in Fig. SM1 (supplementary material). It corresponds to a suburban area

Fig. 1. Photographs of the samplers used in this study: (a) commercial Depobulk®, and (b) EnviroPlaNet sampling device.

with moderate traffic density (15,000–20,000 vehicles per day), 5 km SE from the main urban area (A Coruña, ca. 250,000 inhabitants, plus 250,000 inhabitants in the surrounding metropolitan area). At its Western side, the metropolitan area includes 3 industrial sites: Pocomaco (at 10 km) is an area with many warehouses, some garages and tertiary activities; A Grela-Bens (at 8 km) is a site with warehouses, a petrochemical refinery, construction-related works and coal-coke and metal works; and Sabon (at 13 km), housing warehouses, construction-related works, some textile activities and garages. The sampling site is very close to the sea (<1 km), an airport (SSW, 6 km away) and a harbour (NNW, 4 km away) (Gómez-Carracedo et al., 2015; Piñeiro-Iglesias et al., 2021). The area of A Coruña has an Atlantic climate, with rain events spread throughout the whole year which yielded a total annual precipitation ca. 1000 mm, though less frequent in summer (July–September, 74.2–148.8 mm). The region is often overcast, with moderate-strong winds from the Atlantic depression. In autumn and winter the winds blow predominantly from the South whereas in spring/summer they blow from the North. In general, winds are weaker during the night than during the day, with maximum values around noon.

The passive samplers were placed at a 2.5 m height, on top of an air monitoring station (Fig. SM1, supplementary material) and they collected the total atmospheric deposition (dry and wet) for a month. Three different seasons were studied: summer, 'July' (22-06-2021 to 22-07-2021); autumn, 'November' (16-11-2021 to 16-12-2021); and winter, 'January' (18/01/2022 to 18/02/2022).

In total, five samplers were used: three consisted of 11 cm diameter (circular collecting surface = 0.009 m^2) metal funnels over 2.5 L opaque glass collecting bottles (Fig. 1), as proposed by the Spanish Network of Plastics in the Environment ('EnviroPlaNet'). Another two commercial samplers, with 22 mm diameter (circular collecting surface = 0.038 m^2) glass funnels over 10 L ISO glass collection bottles (Fig. 1), surrounded by a Teflon shield (they are commercialized by LAbService Analytica as 'Depobulk®' samplers). All components of the collectors were plastic-free.

The first type of samplers is similar in size to those used by Klein and Fischer (2019), Zhou et al. (2017), Cai et al. (2017) and Allen et al. (2019), whereas the second type is similar in size to those used by Allen et al. (2019), Wright et al. (2020) or Thinh et al. (2020). Other studies used larger sampling areas (e.g. Dris et al., 2016; Dris et al., 2015; Szewc et al., 2021).

Collected samples were filtered through 20 μm stainless steel filters, the funnel and glass bottle were washed with abundant Milli-Q water, containing 0.1 % Triton X-100 as surfactant. For the 2.5 L glass container ('EnviroPlaNet'), 3 L of the washing solution were needed to get the best recoveries, while for the 10 L container (Depobulk®), 5 L were required. The resulting filters required a mild digestion because they clearly had organic contents. Full details on the three digestion procedures studied in this work are given in Section 3.1.

The digestates were vacuum filtered through 20 μm stainless steel filters, washed with abundant Milli-Q water and dried at room temperature. To transfer the particles from the filter to the reflecting slides for their LDIR characterization an automatic evaporation system (Syncore) was used as reported previously (López-Rosales et al., 2022a, 2022b), see Fig. SM2 (supplementary material). The enormous advantage of this procedure is that the entire filter contents are transferred to the slide so that representativeness of potential aliquots is not an issue. In brief, the filter is washed with 50 mL of 96 % ethanol into a Büchi glass tube and sonicated for 15 min, ≤40 °C. Then, the filter was washed with another 10 mL (5 mL/side) and removed. The whole solvent volume was reduced to 1.0 mL in the Syncore system (40 °C, 180 rpm) employing a pressure gradient (López-Rosales et al., 2022a). The small remnant volume at the Syncore tube was sonicated for 10 s and a volume between 0.3 and 0.7 mL was quickly collected, carefully poured on the reflective slide and the solvent allowed to evaporate. This step is repeated until all the volume is transferred to the slide. The Syncore containers were washed twice with 20 mL of ethanol, repeating the evaporation and transfer processes.

2.2. Materials and reagents

The polymers used throughout this work: PS, PP, PVC, PET, PE and PA6.6, were provided by the Universität of Bayreuth (Germany), within the framework of the JPI-Oceans-funded Baseman EU project. They were fabricated by INEOS Styrolution (PS, commercial name: Styrolution PS 158 N/L); Borealis (PP, commercial name: HL508FB); Vinnolit Gmbh (PVC, commercial name: Vinnolit S3268) Neogroup (PET, commercial name: Neopet 80); LyondellBasell (PE, low density polyethylene, commercial name: Lupolen 1800P); and BASF (PA6.6, commercial name: 'Ultramid').

They contained no additives but for the indispensable ones to get the polymers themselves, no additional preservatives were added. Their size was around 200–300 μm, although PVC particles were around 70 μm. The PET fibres (Korntex X217O) were prepared in the laboratory from a commercial fabric, and they were ca. 1 mm length and ca. 10 μm diameter. These polymers were chosen because they represent ca. 74 % of the global polymer demand (Plastics Europe, 2022) and, so, they

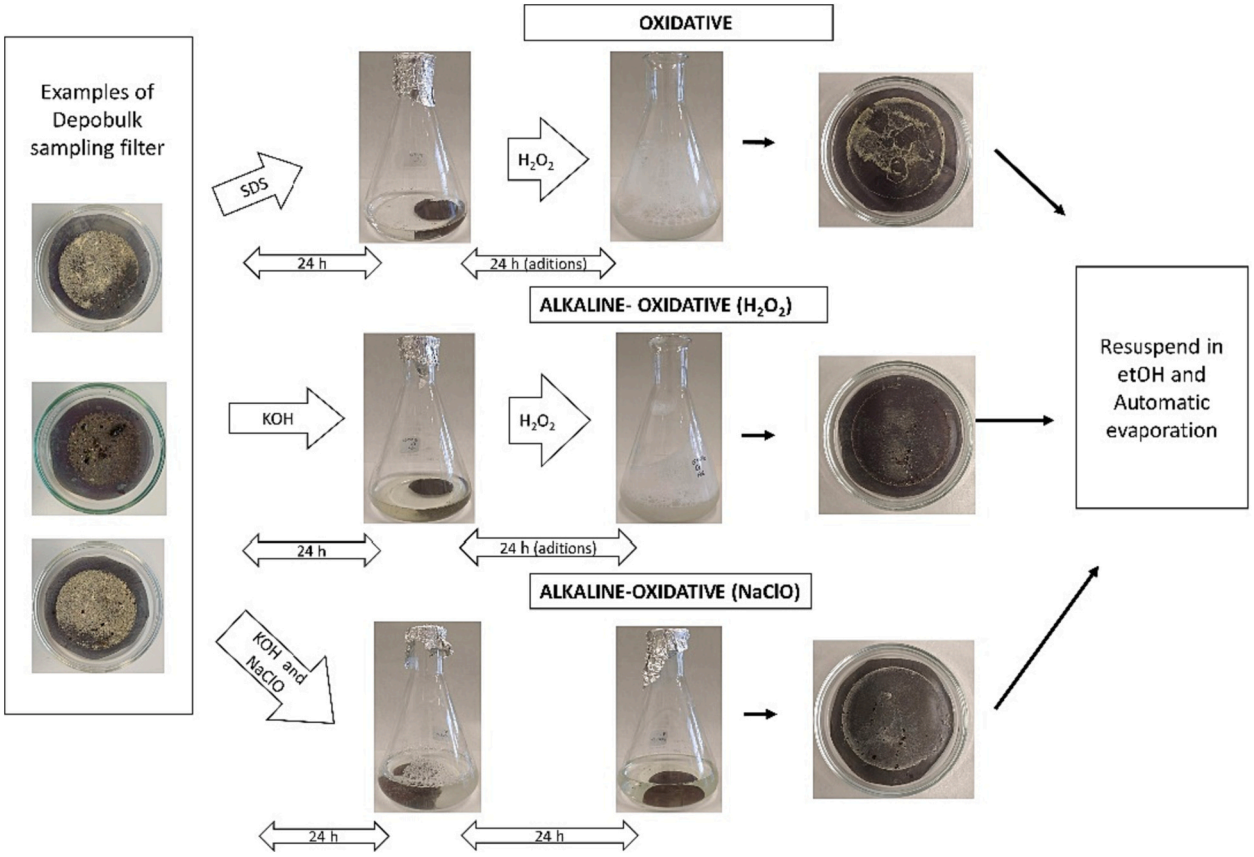

Fig. 2. Scheme of the three digestion protocols studied in this work.

appear more frequently in environmental studies.

The reagents for the alkaline treatment were potassium hydroxide (KOH 100 % purity, Merck Millipore), and Triton X-100 (Sigma-Aldrich); the oxidative treatment required sodium dodecyl sulphate (SDS ≥ 98.5 % purity), and hydrogen peroxide (H_2O_2 ≥ 30 %), both from Sigma-Aldrich, and sodium hypochlorite (NaClO 6–14 % active chloride, Merck Millipore), 96 % ethanol was from Ensure. Ultrapure Milli-Q-type water (18 MΩ·cm resistivity) was from a Direct-Q 3-V Millipore (Molsheim, France) device, collected and used daily.

The 20 μm mesh size (open bore, square weave mesh type) metallic filters were from Bopp & Co. A.G: (Switzerland) and the 1000 μL pipette tips were from Eppendorf (Hamburg, Germany).

Hence, in this study three methods validated previously for other purposes are evaluated for AMPs. One combines KOH and H_2O_2 (López-Rosales et al., 2022a). Another combines KOH and (NaClO), following Enders et al. (2020, 2017), although we reduced the concentration of KOH to 10 % to preserve the polymers best. In this treatment, NaClO replaces H_2O_2 to avoid foaming. The third is based on SDS and H_2O_2 (López-Rosales et al., 2021).

For the first alkaline-oxidative treatment, 100 mL of 10 % KOH and 0.1 mL of Triton X-100 were added to the containers with the metallic filters (see Section 2.1). After 24 h of incubation 30 % H_2O_2 was added gradually in 5 mL or 10 mL increments, until obtaining 15 % H_2O_2 in the total volume (a total of 100 mL). In some cases agitation must be interrupted due to foam, to avoid losing sample (Avio et al., 2015; López-Rosales et al., 2021). This process lasted for 48 h (Fig. 2).

In the second alkaline-oxidative treatment, 150 mL of a mixture of 10 % KOH, 15 % NaClO (14 % active chloride) and 75 % Milli-Q water, were added to containers with the filters and incubated for 48 h (Fig. 2).

The third oxidative process consisted of a first step using 100 mL of 2 % SDS to predigest the organic matter (Löder et al., 2017) from the filters and a second stage where 30 % H_2O_2 was added until reaching 15 % H_2O_2 in the total volume (Fig. 2). Incubation conditions were always 130 U/min and 40 °C.

2.3. Instruments and apparatus

An automatic evaporation system composed of a V-800/805 vacuum controller, Vacuum line and R-12 analyst Syncore Plus Line plus dedicated glass containers (residual volume 1.0 mL) (Büchi, Switzerland); a Rotabit P incubation system (Selecta, Spain), with temperature and agitation controls; a Pobel vacuum filtration system combined with a Millipore vacuum pump (Millipore, Ballerica, MA, model WP6122050); a 3,000,867 Selecta ultrasonic bath (Barcelona, Spain); and a 2001 pH-meter from Crison (Barcelona, Spain), were employed throughout.

A Leitz Wetzlar stereomicroscope (10× ocular and manual adjustment of the objective zoom up to 5×, total magnification 50×) was employed to spike samples.

An 8700 quantum cascade laser-based (in brief, QCL) IR system (LDIR, Laser Direct Infrared, Agilent) working in the 1800–975 cm^{-1} mid-IR region and using flat reflective slides (MiRR, Kevley Technologies, Chesterland, USA), was used. The same parameters were set for all samples, including the blanks. The measuring size range was set from 20 μm to 5000 μm, and sensitivity to 3 (Agilent Clarity Software, v.1.0.). These parameters were fixed after preliminary tests carried out to optimise their use. The QCL-LDIR system identifies the presence of particles over the reflective surface (whose size is that of typical optical microscope slides) and measures the absorbance-reflectance (transflectance) spectrum of each of them. The final output includes matching each spectrum to a database with different polymers so that positive matches (above a user-selected threshold) are identified as microplastics. Further, the system indicates the total number of particles, a classification of the identified MPs by size and type and it stores physical parameters as the width, height, diameter, perimeter, eccentricity (a

circle has an eccentricity value of 0 while ellipses show values from 0 to 1), solidity (defined as the ratio of the particle area over the area of its convex hull), circularity (a perfect circle has a circularity 1), and aspect ratio (relates width/height) of the item (Agilent, 2019) which eventually allow the researcher to differentiate fragments ('particles') and fibres. But this task has to be done by manual processing in an external spreadsheet after exporting the associated data to a text-compatible file.

After the QCL-LDIR measurements the spectrum of each and every particle has to be compared to a dedicated spectral library in order to assign them to the closest known polymer. For this, the use of a similarity measurement (match quality, correlation index, Hit Quality Index or any similar denomination) is required. Each instrumentation company has its own algorithms but all of them report values between 0 and 1 (or 100 %). Many published reports consider that an identification would be positive if such an index is higher than 0.65 (Cheng et al., 2021; Deng et al., 2023; Dong et al., 2022; Jia et al., 2022; Tian et al., 2021). This seems to be a too loose criterion because spectral correlations around 0.65 are easy to obtain –even for disparate spectra– and, thus, too many false positives appear. Other authors consider higher values; such as 0.7 (Ferreira et al., 2022; Whiting et al., 2022), 0.8 (Liu et al., 2022) or 0.9 (Hansen et al., 2023). Disappointingly, in many other reports this issue is not even discussed despite it clearly deserves more attention. In Section 3.2, a study is presented to fix this parameter in a LDIR system.

2.4. Quality assurance and quality control

Procedural blanks, carried out throughout the entire measurement procedure, including sample treatment (in the same manner as a test sample) were done. The metal filters were calcined at 450 °C before use and all glassware was washed with HCl > 15 % for a minimum of 24 h (Prata et al., 2021). Before use all material was washed with a 1:1 mixture of Milli-Q Water and 96 % ethanol, and then with abundant Milli-Q water. Every material was covered with aluminium foil during all stages (including storage) and sample preparation was done in a laminar flow cabinet.

Airborne studies stress the importance of including procedural blanks. For example, the contamination found by Prata et al. (2020a) in procedural blanks was composed of an average of 89 fibres and particles after 3 weeks of treatment (these contents were very similar to those of the sample) and Vianello et al. (2019) reported similar contamination levels. Song et al. (2021) found fibres even after burning the glass material.

It is important to underline the difficulty in maintaining low levels of particles in blanks. It was reported that indoor air contains (much) more MPs than outdoor environments (Beaurepaire et al., 2021), from twice (Gaston et al., 2020), to six- (Dris et al., 2017) or even ten-fold more (Liu et al., 2019a, 2019b). This is specifically so whenever there is more human activity in the room (Song et al., 2021).

In our work, although we followed most recommendations of Prata et al. (2021), a number of PET, PE and PP particles were found in the procedural blanks (of various sizes, mostly at the 50–20 μm range; see Fig. SM3). Although those values were lower (3- to 4-fold) than those observed for the samples, they were subtracted from the raw counts. The final results are those discussed in the next sections. Here we stress the importance of washing the glassware with 15 % HCl (for 24 h) and rinsing it with 1:1 ethanol:water and, next, abundant Milli-Q water just before use (instead of using it from the storage), to reduce any possible contamination. Fig. SM3 (supplementary material) shows the influence of this practice on the number of particles of the procedural blanks.

Analytical recoveries were calculated spiking samples with 20 particles of each studied polymer (PP, PS, PE, PET, PA, PVC) plus 20 PET fibres; accordingly, recovery (%) was calculated as (100 × (number of particles of polymers encountered in the spiked sample/number of particles of polymers encountered in the unspiked sample)). The average of 3 experiments was calculated.

Table 1
Analytical recoveries (as %) obtained for the studied digestion protocols (20 items of each polymer were spiked in Milli-Q water and all the protocols repeated three times) ($n = 3$).

	PP	PS	PE	PET	PA	PVC	All particles	PET Fibres
Alkaline-oxidative ($KOH + H_2O_2$)	83 ± 6	80 ± 5	85 ± 5	77 ± 3	86 ± 8	83 ± 3	82 ± 5	62 ± 5
Alkaline-oxidative (NaClO)	87 ± 3	82 ± 6	87 ± 3	78 ± 3	88 ± 6	87 ± 3	85 ± 5	68 ± 7
Oxidative (H_2O_2)	87 ± 3	88 ± 3	88 ± 3	85 ± 5	88 ± 3	90 ± 5	88 ± 3	73 ± 7

3. Results and discussion

3.1. Sample digestion

Despite, so far, many authors did not digest atmospheric samples there is really a need for eliminating the organic matrix present in most samples in order to characterize correctly the MPs using spectrometric techniques (dos Santos Galvão et al., 2022). Most reported digestions applied oxidative procedures with H_2O_2, although under different conditions. For example, Allen et al. (2020, 2019) used 30 % H_2O_2 and incubation at 55 °C for 7 days, Abbasi et al. (2019) took 8 days at room temperature, Zhou et al. (2017) used 70 °C for 6 h and Tunahan Kaya et al. (2018) used 35 % H_2O_2 but did not specify other conditions. Liu et al. (2020) used the Fenton's reaction with 30 % H_2O_2 and 0.04 M $FeSO_4$ at a 1:1 ratio. Other authors employed mild oxidations, such as 15 % H_2O_2 at room temperature for 8 days (Prata et al., 2020a), or 13 % total volume of NaClO; i.e., 6–14 % active chloride, Klein and Fischer (2019).

It is worth noting that strong oxidative digestions (ca. 30 % H_2O_2) can destroy some synthetic polymers and/or induce physical degradation in PA6.6, PP, PS, PET, PA and tyre (Hurley et al., 2018; Karami et al., 2017; Pfohl et al., 2021; Treilles et al., 2020). After an inter-laboratory comparison, Tsangaris et al. (2021) established that 15 % H_2O_2 was adequate to preserve MPs. However, it was reported recently that further verification that the recoveries are satisfactory is still necessary (Munyaneza et al., 2022). Finally, enzymes are more respectful with MPs. For example, Thinh et al. (2020) used an enzymatic digestion with SDS, protease, amylase, lipase (48 h), and H_2O_2 oxidation (48 h). The main problem being that enzymes involve very large operating times and high expenses.

In this study three digestion protocols (described in Section 2.2) were compared. They three destroyed the organic matter satisfactorily (as per visual observation) and yielded satisfactory analytical recoveries (Table 1); ranging from 82 to 90 %. Worse recoveries were obtained for fibres (62–73 %), but in good agreement with previous studies (López-Rosales et al., 2022a; Yuan et al., 2022). Recovery for PS was a bit lower when the alkaline treatment was used but not statistically significant (95 % confidence level). Note that several previous reports found also problems to recover PET fibres and PS particles after alkaline treatments, although they used higher temperatures (Hurley et al., 2018; Karami et al., 2017; López-Rosales et al., 2021; Treilles et al., 2020). In our view, the alkaline mild oxidation protocol (KOH + NaClO) is the most convenient and simple one because it avoids foam problems and the need for adding H_2O_2 aliquots at different steps.

On the other hand, the oxidative digestion (H_2O_2 alone) can be particularly useful whenever the amount of organic matter is low, while $KOH + H_2O_2$ would be required when (very) large quantities of organic matter are present (e.g., a sample taken in spring close to a forest).

Table 2
Comparison of polymer identifications obtained when different match thresholds are used (0.85 and 0.9). N is the total number of particles added to the samples (despite the spiked polymers were reported in the interlaboratory exercise, the number of particles was not; particles were in the 299–50 μm range). Sample 10 W was spiked only with PE, PET and PS, and sample 11 W with PP, PVC, PC. (*) indicates false positives and/or overestimations.

	Sample 10 W $N = 45$		Sample 11 W $N = 49$		Sample 12 W (blank) $N = 0$	
Match threshold	0.85	0.9	0.85	0.9	0.85	0.9
PE	15	12	*16	*2	0	0
PET	8	7	*5	*1	0	0
PS	15	11	*5	*1	*1	0
PP	*6	*1	9	8	0	0
PVC	*10	0	21	11	*2	*1
PC	*27	*2	14	12	*1	0
Total MPs detected	81	33	70	35	–	–
Overall MPs recovery (%)	180	73	143	71	–	–
Other polymers	*8	*5	*10	*7	*5	*1

3.2. Spectral identification

As commented in Section 2.3, the selection of too low thresholds to match an unknown spectrum to those of the library will lead to too many false positives, as we experienced in a recent EUROQCHARM interlaboratory study (Van der Veen et al., 2022), some results from it are shown in Table 2. The total recoveries are overestimated when the matching threshold is set at 0.85 while most of the problem is avoided when that is increased to 0.90.

In theory, the safest way to assign a particle to a polymer is to evaluate visually the IR spectrum of each and every 'high index' match but due to the very large number of particles present in usual samples this is impractical. Therefore, we need a sort of 'automated assignment criterion' or 'automatic threshold match index' (that nonetheless has to be checked from time to time). To set it, we studied carefully many spectra of pristine and weathered polymers and different degrees of match indexes. The spectra of the unknowns and 'automated' assignations were overlaid and checked for reliability. Hence, we suggest establishing a tiered classification of the matches and setting three levels of confidence: low (0.85–0.9 match index), medium (0.9–0.95 match index) and high confidence (>0.95 match), as seen in Fig. 3.

Nevertheless, we keep a special assignation threshold for tyre, because the spectra of the tyres show so many peaks that they tend to yield very high correlations with many different spectra, which are not tyres (as we knew their composition). Therefore, we suggest to accept only a tyre assignation whenever the match index is higher than 0.95 (Fig. 3).

No doubt, a relevant cornerstone of any identification process is the reference spectral database or spectral library. We combined an in-house database created with aged and pristine polymers, different chemicals, types of particles and polymers, the Agilent Microplastics Starter library (v.1) and a collection of typical pollens of the area under study (*Pinus* sp., *Eucalyptus* sp.), the latter are used to take account of natural polyamide (Kerstan and Robey, 2021).

3.3. Fibre or particle classification

When AMPs are reported it is good practice to differentiate fibres and particles (or, best, fragments). Whiting et al. (2022) differentiated between fibres and particles using the aspect ratio (width/height ratio) alone, and this might be because the European Chemical Agency established an aspect ratio > 3 to define a fibre (ECHA, 2019). It is worth noting that the particular location of the filament in the optical field makes the ideas of 'width' and 'height' interchangeable and, so an aspect ratio < 1/3 (0.33) would also be a fibre (Whiting et al., 2022) (see Fig. 4, the different orientation in coarse fibres).

However, the aspect ratio should not be the unique criterion to determine whether an item is a fibre or a particle (fragment). Curved thin fibres have moderate aspect ratios (see Fig. 4, b), so the solidity (particle area/convex hull area ratio) is relevant to detect thin fibres and reduce erroneous assignations. Circularity is important to differentiate rounded particles from irregular fragments or coarse fibres. Aspect ratio can help differentiate between the latter two. After different studies, we set a tiered approach that can be deployed easily and will assign an item to a particle or to a fibre (Fig. 4). Such a workflow yields 'particles' (fragments) in two stages and 'fibres' in three stages. It was tested on a collection of 500 items (100 items of each 'type'), and all assignations were validated visually, and they can be organized in a contingency table. Thus, up to 94 % of the real fibres were identified as such (7 % of them were considered as particles) and up to 93 % of the real particles were identified as such (6 % were identified wrongly as fibres); $n = 500$ particles.

3.4. Comparison among the two samplers

AMPs obtained for the two types of samplers during the same sampling periods and the same location were classified according to the fibres and particles they contained, as a function of their size ranges (i.e., the main diameter for particles, the length for fibres) and polymer type. Recall that the procedural blanks were subtracted from the overall counting. The AMPs deposition is given as MP/m^2/day, and that should be called deposition rate, taking into account the number of MPs, the area of the funnel and the number of sampling days.

For the Depobulk® sampler the total number of collected particles ranged from 9219 to 20,802 (out of which only 0.7 % ± 0.6 % ($n = 6$) were identified as MPs). For the EnviroPlaNet sampler a range of 4254–7696 particles was registered (of which 1.62 % ± 0.84 % (n = 6) were considered MPs). The immense majority of particles had not an HQI high enough (<0,85) to assign them to a polymeric material when they are compared to the database (see Fig. 3), or were identified as non-polymeric but soil-related (silica, clay, dust). Many particles were identified as natural polyamide (3–4 %) and cellulosic particles (6.5 %).

When the results are compared considering 95 % confidence intervals (average ± 2SD) the samplers yielded statistically comparable results for two sampling campaigns (although not for November), see Fig. 5. However, when only the average ± SD (i.e., 68 % confidence level) is considered, only results for July were comparable (Fig. 5).

This can be explained by several circumstances. First, the low number of samples that arguably affect any statistical comparison (few degrees of freedom). Second, the obvious natural variability and inhomogeneous distribution of the particles in the air masses. Third, in literature many papers report averages ± standard deviation (SD) but this is a too strict interval due to the inherent natural variability (through days, hours, local events, rain, etc.). In our view, it should be preferable to consider -at least- ±2·SD confidence intervals. The effect this consideration has on the comparability of the samples is shown in Fig. 5. The confidence intervals overlap at 95 % confidence, as it seems logical in this experiment (but they do not at the 68 % level). A fourth aspect to take into account is the extrapolation factors required to convert the number of MP to MP/m^2, which are 26.3 (Depobulk®, 0.038 m^2) and 105.2 (EnviroPlaNet, 0.009 m^2). This involves huge extrapolations, which may be unreliable as any minor error in the raw data gets magnified hugely. This is a general problem for all researchers because unless some standard sampling conditions are developed to evaluate the trueness of the sampling collection, no objective sound conclusions can be drawn.

A hypothesis to explain why November behaved so differently might be that it was a very rainy month (116,559 mL/m^2), with strong gust of wind, as opposed to July (18,647 mL/m^2) or January (27,449 mL/m^2). Perhaps very strong atmospheric instability might yield different results in different collectors.

Table 3 considers different options to present the results, an

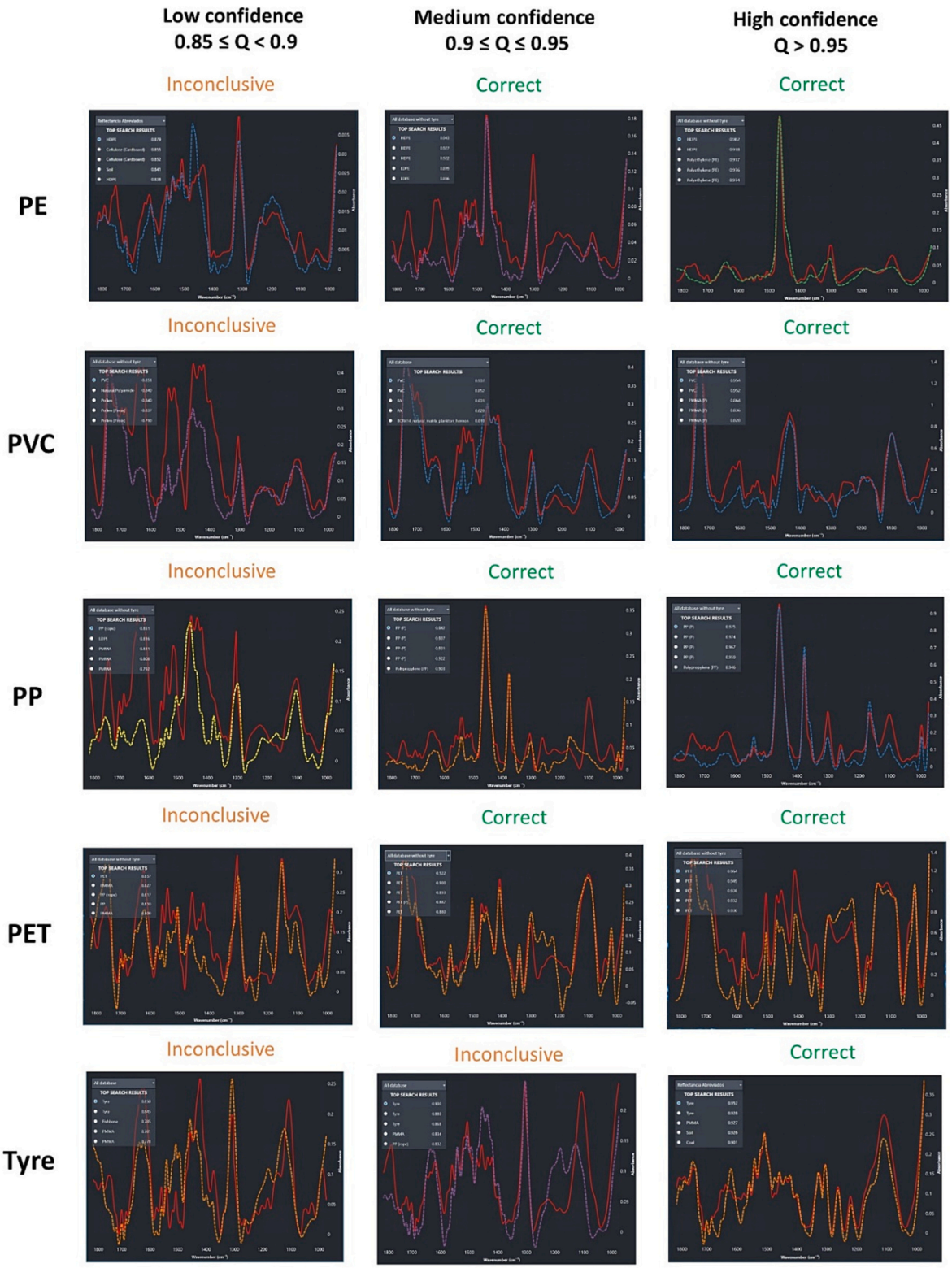

Fig. 3. Examples of high, medium and low confidence assignations according to the threshold selected for the match index after LDIR characterization.

interesting issue suggested by a referee. Plain raw data, normalization to 1 m^2, normalization of the raw data among the EnviroPlaNet and Depobulk® systems (the collection area of the latter is 4.2 times that of the former) were considered. The first option yields results which are more comparable. Quoting a referee's suggestion, that might indicate that the size of the sampler might not be as important. However, the relevance of normalization is also clear as it is useful to set a common reference for all samplers. However, common normalization to 1 m^2 seems a too large extrapolation and needs further consideration as it could yield statistically significant differences. Something similar occurs when the results of the EnviroPlaNet device are normalized to the Depobulk® ones (extrapolation). On the contrary, normalizing the Depobulk® system to the EnviroPlaNet one still retains comparability at the two confidence levels (a kind of interpolation). Nevertheless, we

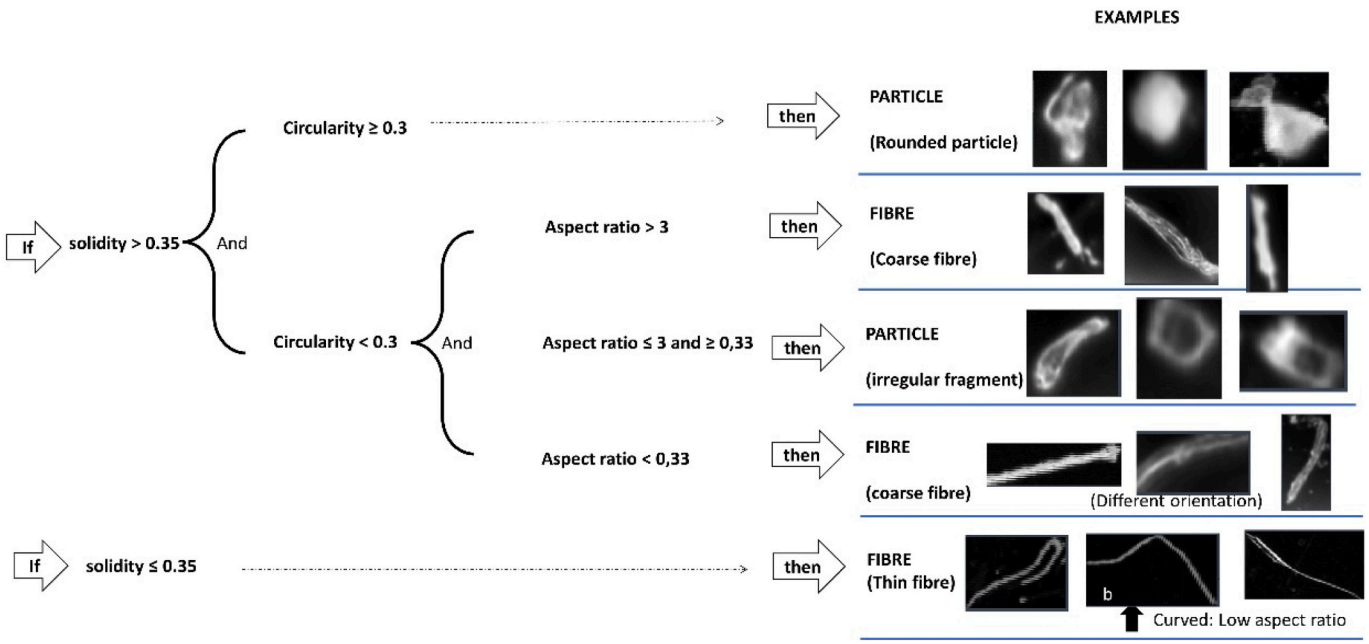

Fig. 4. Tiered approach to classify an item as a fibre or a particle (fragment) after its LDIR measurement.

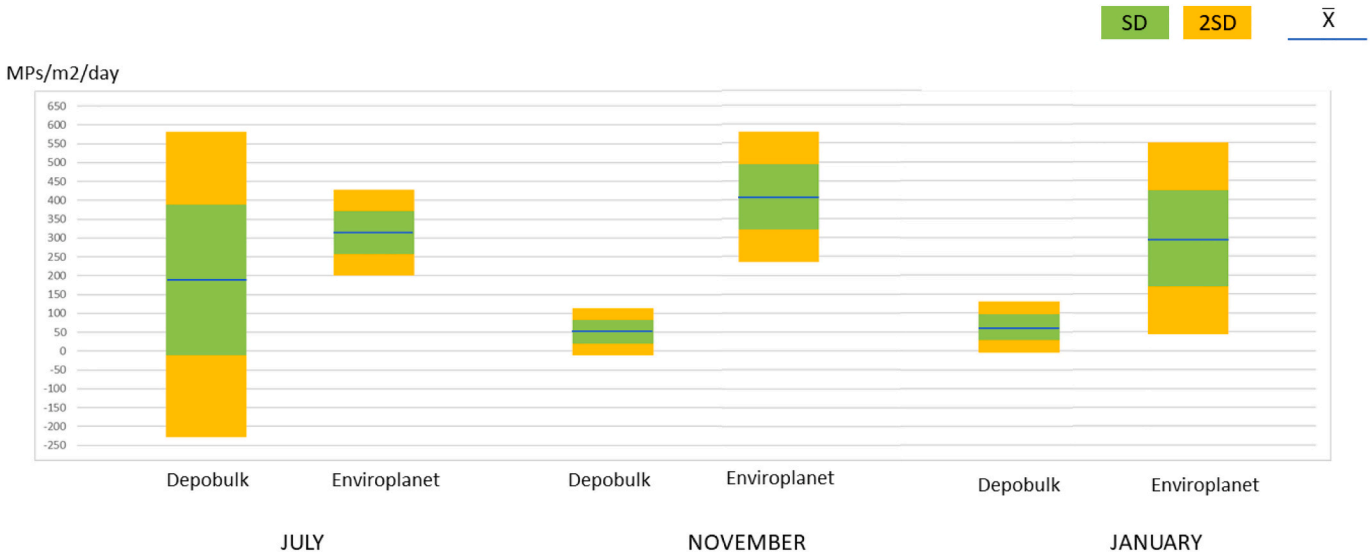

Fig. 5. Average ± SD (green) and average ± 2·SD (yellow) of total MPs deposition (MP/m^2/day) encountered for each sampling device in each sampling month (n = 2).

Table 3
Comparison of the average data generated by the two types of samplers considering different confidence intervals (68 % confidence level, ± SD, and 95 % confidence level, ±2·SD) and normalization options (n = 2 for each type of sampler).

Sampler	Normalization	July	November	January	July	November	January	
		Average ± SD			Average ± 2·SD			
Depobulk®	None	7.0 ± 7.4	2.0 ± 1.2	2.4 ± 1.3	7.0 ± 14.8	2.0 ± 2.5	2.4 ± 2.6	MP/day
EnviroPlaNet	None	3.0 ± 0.5	4.0 ± 0.9	2.8 ± 1.2	3.0 ± 1.0	4.0 ± 1.7	2.8 ± 2.4	MP/day
EnviroPlaNet	To Depobulk® area	11,9 ± 2.2	15.9 ± 3.5	11.3 ± 3,3	11,9 ± 4,3	15.9 ± 7,0	11.3 ± 9,7	MP/day
Depobulk®	To EnviroPlaNet area	1.7 ± 1.8	0.5 ± 0.3	0.6 ± 0.3	1.7 ± 3.7	0.5 ± 0.6	0.6 ± 0.6	MP/day
Depobulk®	To area = 1 m^2	182.8 ± 194.1	50.9 ± 31.2	62.8 ± 33.6	182.8 ± 388.2	50.9 ± 62.4	62.8 ± 67.2	MP/m^2/day
EnviroPlaNet	To area = 1 m^2	313.9 ± 57.1	407.3 ± 86.4	297.0 ± 127.2	313.9 ± 114.1	407.3 ± 172.8	297.0 ± 254.4	MP/m^2/day

cannot set a definite conclusion with the data generated in this study alone. In our view, this issue merits more attention and studies, including aerodynamic evaluations to ascertain whether the size of a sampler might affect its collection properties.

Next, and positively enough, it can be observed that the profiles for the number of particles and fibres for the different sizes ranges (i.e., the

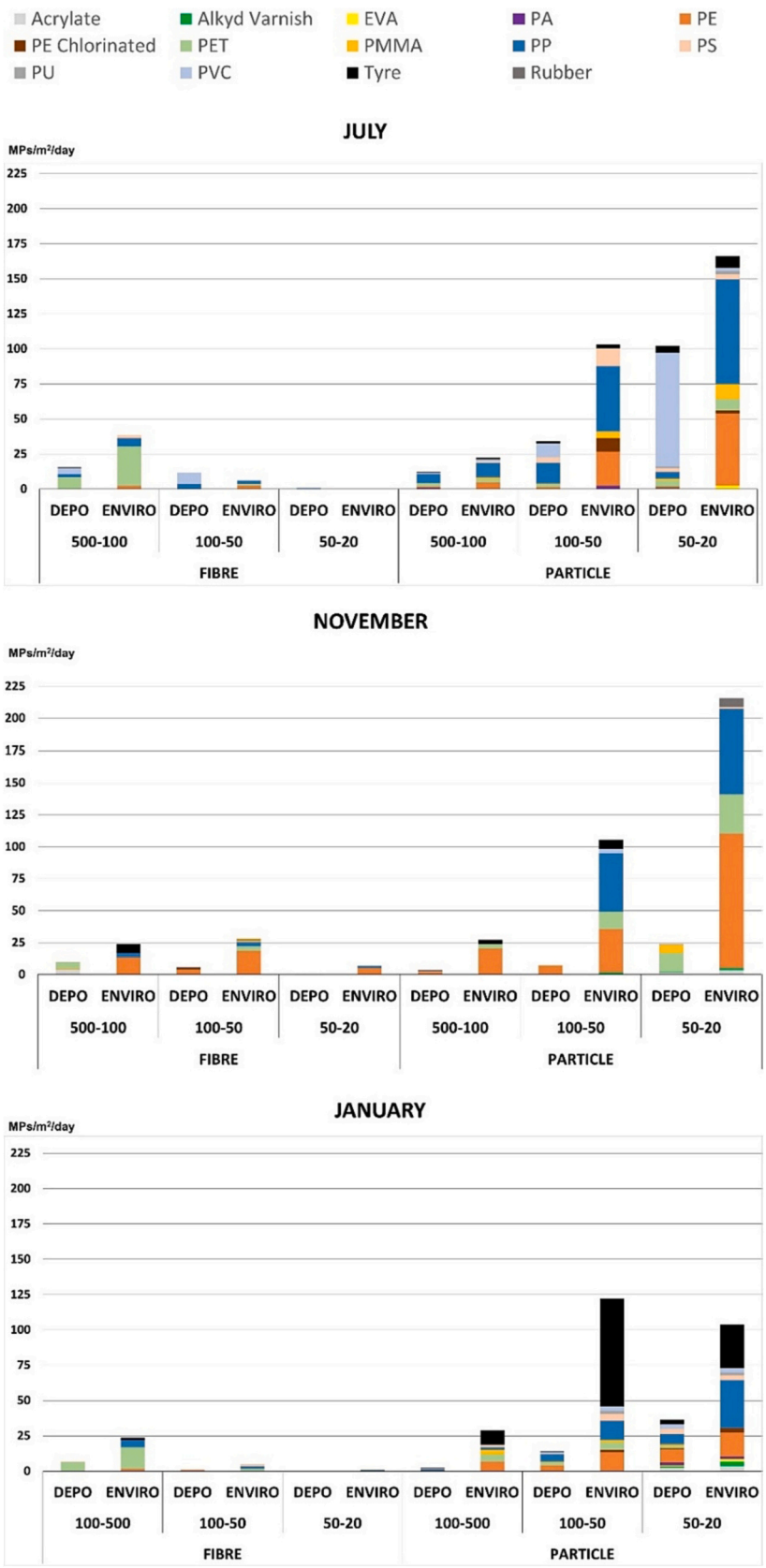

Fig. 6. Average deposition rates (MP/m^2/day) of airborne microplastics (n = 2) using the two sampling devices, classified by shape (fibre or fragment), size (μm) and polymer type. 'Depo' stands for the Depobulk® systems, whereas 'Enviro' denotes the prototype of the Spanish Network of Plastics in the Environment ('EnviroPlaNet'). Sampling time: 1 month.

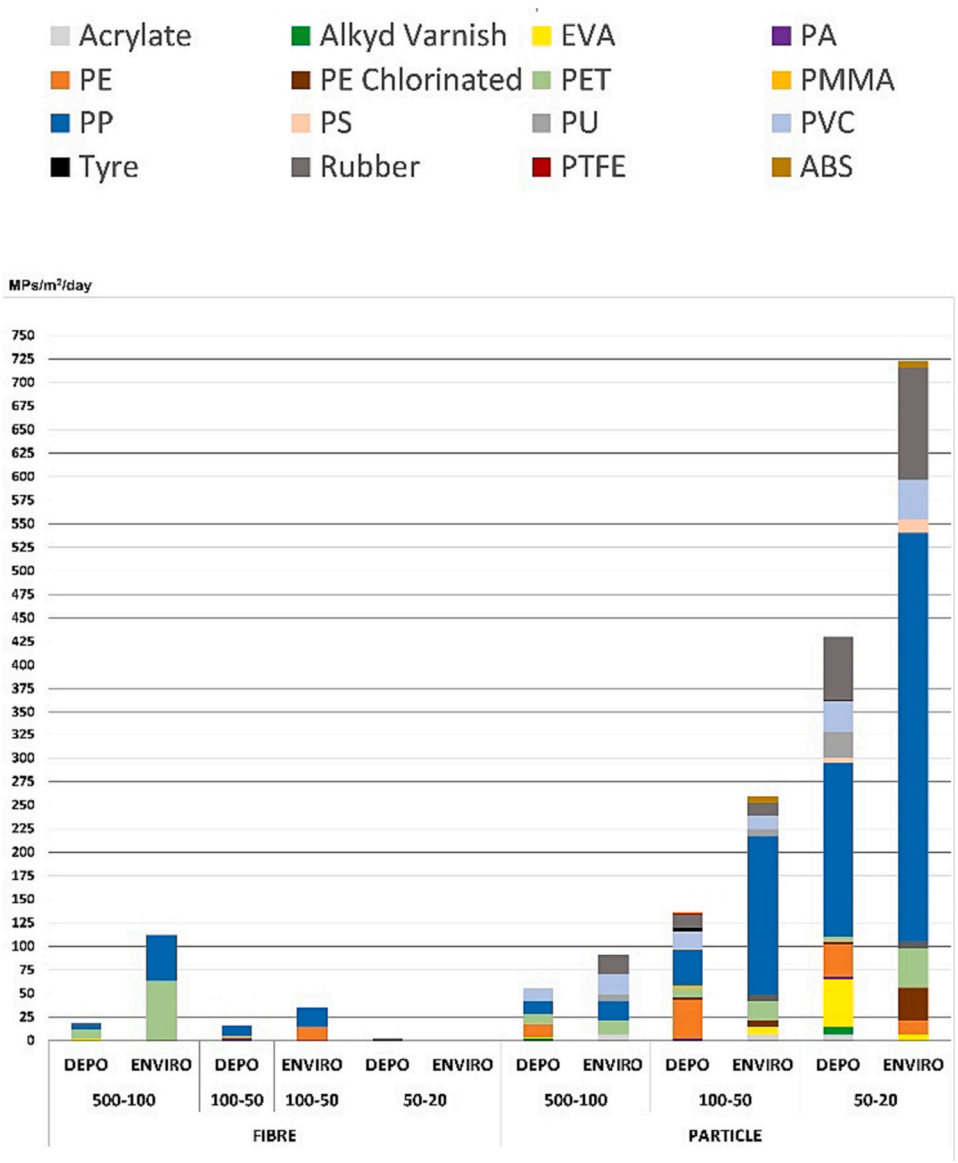

Fig. 7. Deposition rates of airborne microplastics (MP/m^2/day) when sampling lasted for 15 days, January 2023.

'relative abundance') are the same for both sampling devices. Our results agree with the general statement that the overall abundance of MPs increases when they decrease in size. In our case, that was particularly so for the items identified as particles. Thus, the 20–50 μm fraction is the main contributor to the total content of MPs (Fig. 6); in particular, around 49.9 % ± 10.2 % of the total MPs was in this size fraction ($n = 12$ samples). It is clearly seen that in this fraction particles were more abundant than fibres. On the contrary, more fibres were in the 50–500 μm size range.

Despite this being an interesting finding, it has to be considered with some caution as it is worth noting that it might be a consequence of the limitations of the measurement system. In effect, although the LDIR device has a pragmatic, routine, limit of detection around 10 μm, in this particular study we set the minimum size to be detected at 20 μm. Recalling the ECHA criterion by which a particle is considered as a fibre when its aspect ratio >3, the maximum width of a 50 μm-length particle should be 16.7 μm. This value is too close to the working limit set here and, so, some particles would remain undetected. The situation is even more complicated for smaller particles (very close to the practical limit of detection of the system, which is 10 μm), for example it is impossible to detect fibres under 30 μm of length (aspect ratio 30 μm/10 μm = 3). Furthermore, fibres with low solidity are very difficult to identify. Furthermore, some particles <50 μm may be secondary microplastics from fragmented fibres.

All this facts may explain that most fibres were detected in the 500–50 μm range and not in the <50 μm range, where the total number of particles increase exponentially (Schymanski et al., 2021).

An additional study was undergone, although considering only 15 days of collection, in January 2023 and the same general behaviour was obtained (663 MP/m^2/day for the Depobulk® system vs. 1214 MP/m^2/day for the EnviroPlaNet one). Details on the distribution of the particles and fibres can be seen in Fig. 7, and they reinforce the findings above.

The truth is that huge natural variability in air sampling is a general fact in almost all reported studies, as it is shown in Table 4. There, confidence intervals amounting ca. 50 % of the average value and huge MP ranges (>200 % when only number of particles were reported) are seen. Our levels of MPs agree quite well with those from Hamburg, Pyrenees, Donnguan and Paris. A relevant issue when comparing results with literature is the minimum size of the items detected in this study (in most studies, the instrumental limit of detection is not stated) because in general the number of particles increases a lot under 50 μm.

Finally, the most abundant polymers found in our samples agree with

Table 4
Comparison of reported deposition rates for passive bulk sampling systems in urban, suburban and natural environments.

Place	MP/m^2/day	Funnel diameter (cm) and its area (m^2)	Minimum size of MPs (μm)	Reference
Quzhou (China)	86–75.421	30 (0.071)	>3,23	Li et al. (2023)
London (urban)	771 ± 167	20 (0.031)	>75	Wright et al. (2020).
Ho Chi Minh City, Vietnam	2–913	25 (0.049)	>100	Thinh et al. (2020).
Yantai, China	382 (unreported range)	11 (0.0095)	>50	Zhou et al. (2017)
Hamburg, Germany (rural)	395 ± 82	12 (0.011)	>63	Klein and Fischer (2019)
Oleiros (suburban), Spain	388 ± 152	11 (0.0095) (EnviroPlaNet)	>20	This study
Pyrenees, France	365 ± 69	13,5 (0.014) 20 (0.03)	>5	Allen et al. (2019).
Hamburg, Germany (Urban)	215 ± 55	12 (0.011)	>63	Klein and Fischer (2019)
Donnguan, China	175–313	15 (0,018)	>200	Cai et al. (2017)
Paris, France (Urban)	29–280	unreported (0.325)		Dris et al. (2015)
Paris, France (Urban)	110 ± 96	65 (0.332)	>100	Dris et al. (2016)
Oleiros (suburban), Spain	98 ± 110	22 (0.038) Depobulk®	>20	This Study
Guangzhou, China	66 ± 7	20 (0.031)	>10	Yuan et al. (2023)
Paris, France (suburban)	53 ± 38	65 (0.332)	>50	Dris et al. (2016)
Nottingham, UK	3–128 (fibres)	12 cm (0.011)	>38	Stanton et al. (2019)
Gdyna, Poland	10 ± 8	65 (0.332)	>5	Szewc et al. (2021)

other previous studies (Allen et al., 2019; Cai et al., 2017; Can-Güven, 2021; Klein and Fischer, 2019) and they were PE, PP and PET. However, the variability between months is very large, as somewhat expected due to the different rain events, predominant winds, traffic density, etc. The commonest polymers for the particles in the 20–50 μm fraction were PP and PE. However, in July an abnormal number of PVC particles in the Depobulk® system appeared, without a clear explanation. The relative abundance of tyres was higher in January (Fig. 5) than in the other months and this was explained by the higher traffic density during winter, strong rains and winds, which might create a sort of 'aerosol' that can be transported by wind.

To decide on the 'best' passive airborne sampler we took into account several pragmatic considerations (recall that since there is no recognized airborne MP sampling standard conditions we cannot make a statistically-based final decision). Considering, first, the number of total particles from the samples to be characterized chemically, the QCL-LDIR system characterizes about 8000 particles/24 h. As the Depobulk® and EnvironPlaNet devices collected 9219 to 20,802 and 4254 to 7696 particles, respectively, the EnviroPlaNet system seems more suited for routine monitoring using the QCL-LDIR instrument in order to be able to characterize 1 sample/day. Second, from an operative viewpoint, the volume of solution to clean thoroughly the funnel and, mostly, the glass container are clearly smaller for the EnviroPlaNet device, which reduces the working times. Finally, the EnviroPlaNet prototype is far more simple to manipulate (reduced size and weight). Its drawback is that the big extrapolation factor (to normalize data to a 1 m^2 surface) might be too high and lead to overestimations. On the contrary, Depobulk® systems may be more representative but they are less practical for routine use than the EnviroPlaNet device.

4. Conclusions

It was seen that there is huge variability in the results obtained using different sampling systems. Of the two sampling devices studied here, the so-called EnviroPlaNet sampler is more adequate for monitoring purposes because it can be handled easily and leads to smaller numbers of particles to be processed later by the QCL-LDIR in a working day. Its main disadvantage might be that it could involve overrepresentations on the number of AMPs; at least when compared to the commercial Depobulk® system, or when the results have to be extrapolated to a 1 m^2 area. Both sampler types yield comparable results as far as a 95 % confidence level is considered. Since no sampling standards exist yet, it is not possible to assess this issue in more detail. With regards to the sample treatment, the alkaline-oxidative method based on KOH and NaClO can be recommended as the most suitable one for a mild organic matrix digestion, due to its operational simplicity and good recoveries (82–90 % for particles and 62–73 % for fibres). Three additional methodological points can be of interest. First, we suggest cleaning the glassware with 15 % HCl just before using it (not from the storage shelves) to reduce the presence of MPs in blanks. Second, a high quality index (HQI) numerical value >0.9 is suggested to consider a match as positive when comparing an unknown spectrum against the spectral database. In any case it is highly recommended to check visually at least some matches to assure that the assignations are reasonable. Third, we propose a fast and reliable tiered approach to determine and classify AMPs as fibres or particles (fragments) using the outputs of the LDIR device; in particular, circularity, aspect ratio and solidity. Finally, in a very preliminary study of AMPs in atmospheric deposition, the levels of AMPs found in our location (NW of Spain) are similar to those from other locations with deposition rates ranged 98–1220 MP/m^2/day, being most of the identified microplastics <50 μm.

CRediT authorship contribution statement

Adrián López-Rosales: Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Borja Ferreiro:** Formal analysis, Validation, Writing – review & editing. **José Andrade:** Conceptualization, Data curation, Investigation, Supervision, Writing – review & editing. **María Fernández-Amado:** Formal analysis, Methodology, Writing – review & editing. **Miguel González-Pleiter:** Investigation, Methodology, Writing – review & editing. **Purificación López-Mahía:** Conceptualization, Investigation, Resources, Writing – review & editing. **Roberto Rosal:** Conceptualization, Investigation, Resources, Writing – review & editing. **Soledad Muniategui-Lorenzo:** Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgements

This work constitutes a part of the LABPLAS project (Grant Agreement No. 101003954), supported by the EU H2020 program. The Program 'Consolidación e Estructuración de Unidades de Investigación Competitivas' of the Galician Government (Xunta de Galicia) is acknowledged (Grant ED431C 2021/56). Ministerio de Ciencia,

Innovación y Universidades is also acknowledged (PTA2017-13607-MFA and PTA 2018-016005-MPEP). The authors acknowledge the support provided by the Spanish Network of Plastics in the Environment, EnviroPlaNet (www.enviroplanet.net, RED2018-102345-T Ministerio de Ciencia, Innovación y Universidades). Funding for open access charge: Universidade da Coruña/CISUG.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.169678.

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