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Article

Airborne Microplastic in the Atmospheric Deposition, How to Identify and Quantify the Threat? Novel Semi-quantitative Approach based on Kraków Case Study

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Abstract: Airborne microplastic (MP) is an emerging pollutant, still under-characterised and insufficiently understood. Detailed description of MP air pollution is crucial as it has been identified in human lungs and remote locations, highlighting atmosphere as medium of MP dispersion and transportation. The lack of standardization of methods for measuring and further monitoring of the MP pollution is an obstacle towards the assessment of health risks. Since the first recognition of MP presence in the atmosphere of Krakow in 2019, this research was conducted to further characterise and develop the methods for qualitative and quantitative analysis of airborne MP (ATR-FTIR, Pyr-GC-MS, SEM-EDS) and pre-treatment of samples.The data was gathered in seven cycles, from June 2019 to February 2020. Methods used in the study allowed the identification and analysis of the changing ratio of the different types of synthetic polymers identified in the atmospheric fallout (LDPE, Nyl-66, PE, PET, PP, PUR). Observations of interactions between MP particles and environment were made with analyses of surface changes due to the degradation. Mineral phases attached to the MPs' surfaces, with some of the inorganic contaminants transported on these surfaces, determined to also be of anthropogenic origin.Methodology proposed in this study, allows further characterisation of MP from multiple locations to provide highly comparable data, leading to the identification of the sources of this phenomenon, as well as seasonal changes.

Keywords: airborne microplastics; urban pollution; microplastic pollution monitoring

1. Introduction

Airborne microplastic (MP) is one of the most concerning, and least described pollutant of recent years. It has been detected in human lung tissue [1], making research on MP even more urgent.

MPs are defined as particles composed of synthetic polymers of primary or secondary origin [2] that are small enough to be easily dispersed in the environment. In most cases, the MP size range is limited from 1 µm to 5 mm [3]. However, other classification standards are in use, as well as arguments for the different size boundaries between nano-MPs and meso-MPs [4].

The mechanical proprieties of synthetic polymers are characterised by resistance and durability. Plastics are exposed to destructive processes and agents (e.g. in washing machines) or environmental factors (e.g. UV radiation) [5], causing degradation processes. Interactions between MPs and the environment take place [6], resulting in heavy metal adsorbtion [7] and pesticide absobtion into the surface of MPs [8]. Secondary MP come from improper plastic waste management [9] and use of everyday products [11]. Exposure of synthetic polymer-made products to environmental factors leads to fibres and particles entering the environment [11]. It remains challenging to identify all the major sources and assess the proportions of the different sources of MP pollution.

MP is not homogenous pollutant in terms of share of different polymers [12] and the different pathways that MP particles follow in the environment [13]. The number of studies on airborne MP is still limited [14] compared to aquatic environment. Research on MP presence is widespread [15], the main scope focused on water and soil pollution [16, 17]. Basic information about airborne MP are lacking [18]. MP presence has been confirmed in nature reserves [19], mountain ranges [20] and the Arctic [21].

MP pollution is connected to human activity. Densely populated areas account for the environment penetration of MP, MP formation, and MP presence. Cities have features that increase the release rate of MP, such as anthropopressure, specific location, microclimate and urban morphology.

The current state of MP research does not reflect MP abundance in the environment [22]. There are studies regarding the negative impact of MP pollution on human health [23,24]. To assess health risks, complex and accurate data on airborne MP abundance is needed. Majority of studies on health impact are focused on extremes, like workers in textile plant [25; 26].

Data acquisition, development of standardised research procedures, will allow monitoring of MP abundance in atmosphere and determination of related risks with new standards for monitoring and understanding MP.

There are many methods in use, in terms of sampling and examining the MP [27], therefore the unified procedure is crucial, neither the sampling procedures nor the pre-processing and separation procedures have been standardised [28].

It is challenging to compare the airborne MP abundance, which is connected to sample type: wet or dry deposition, suspended atmospheric MP, MP settled in street dust. In some studies, no separation was carried out, in others different solutions were used, most notably ZnCl2 for density-based separation [29] and H2O2 for digestion and later density separation with NaI [30]. In some studies, the researchers used filters either made of quartz [31], glass [32], polytetrafluoroethylene [13] or nitrocellulose [33]. Different methods bring different results in terms of the MP recovery rate. Differences originate from the different sampling methodologies (e.g. considering only particles of a certain size and using the optical method for hand-picking MP) and technicalities (e.g. different collectors, their location and height). The results acquired do not objectively regard MP abundance.

Classifying MP into categories (fibrous/non-fibrous, colour) [30, 34; 35] represents the main means of quantifying. Usually, from this count, only some of the particles are later tested with Raman spectroscopy, Fourier transform–infra-red (FT-IR) or gas chromatography–mass spectrometry (GC-MS) techniques. This leads to the particle count being misleading [3] Similarly, only part of the MP particles are identified, with the others assessed based on similarities. Data concerning the overall weight ratio of the different types of polymers' ratio is high value, complementing the results and help identify sources, as MPs break down further in the environment.

The aim of this research was to recognise the major MP types and examine the changes in the chemical composition of this pollutant in the most unaltered form possible. Although the approach based on the counting of different particle types provides some useful information, the total relative mass of MP of a certain polymer type might not be only faster, but also could be even more useful for a number of reasons. Further degradation and fragmentation of MP takes place. As a consequence, the gathered data can fail the objectivity criterion as MP break down and separate over time, and one particle could easily become two or more. Decomposition, including nanoplastic emission, can be better understood and estimated by relative chemical composition data regarding the MP abundance. Enhancing and validating MP separation protocols may be the best means of establishing the total net weight of different synthetic polymers in the most comparable and reliable manner.

There is ongoing research investigating the different degrees of MP toxicity. This pollutant often appears as a mixture of different synthetic polymers present simultaneously, and should thus be examined as such [36]. More accurate research on the health risks and toxicity might be carried out based on the relative chemical composition data.

The quantification of MP particles is even more problematic, due to the limitation of the consideration of only particles of a certain size in the majority of cases in the literature [37]. Some measures have been taken to overcome this problem in comparing the results, yet a universal and reliable approach is lacking.

One of the promising techniques for fast and comparable airborne MP identification is coupled pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), which is now more frequently used to characterise MP in the environment [38], although primarily to characterise the particles individually, with the main methods used based on microscopic analysis combined with infra-red or Raman spectroscopies. According to researchers, there is considerable room for improvement in the quality of quantitative analysis with Py-GC-MS [39], whereby the procedures require further development. The selection and separation of indicator ions has proven to be challenging when MPs exist in complex mixtures of biopolymers [40]. The results from different environmental matrices and places are important to fill the existing analytical gap [41].

The present study collected data from seven sampling cycles of atmospheric wet and dry deposition in an urban area of Krakow, focusing on the identification and quantification of MP without chemically removing the naturally occurring biopolymers. Additionally, to fill the gap in the health risks of MP inhalation, the chemical analysis of the MP fibres' surfaces was performed.

2. Materials and Methods

2.1. Sample collection and processing

2.1.1. Study area

The city of Krakow lies in the South of Poland and is the second-largest city in the country with a population of 779 115 for the period of sample collection (i.e. June 2019 to February 2020). In 2019 itself, it was visited by more than 14 million tourists. In terms of MP abundance, it is worth highlighting that the city is not only a place of culture and history, but also of industry, with an increase in housing and other construction currently underway. The air quality in Krakow is one of the worst in Poland, and moreover among European countries (EEA Report No. 9/2020). Poor air quality is caused mainly by the high concentration of particulate matter [42] and nitrogen oxides [43]. The high concentration of pollutants is related, besides local and distant emissions, to meteorological conditions and topography, and in the case of Krakow its location in the Wisla valley.

2.1.2. Sampling

Passive sampling was chosen as the method for this study. Both dry and wet deposition were collected for the purpose of this research. A glass container (height: 0.21 m, collection area: 0.5675 m2) was placed on a platform on the rooftop of the five-storey-high building of the Pedagogical University in Krakow. It was situated on a platform to prevent contamination from the roof, itself at a total height of 35 m. The location for the container was chosen so that no vents would affect the collecting process. The sampling was carried out over eight months from the 2nd of June 2019 until the 2nd of February 2020, in seven sampling cycles (cf. Table 1).

Table 1. Summary table showing the sample data and implemented processing methods of samples, together with the techniques of their analysis.

SAMPLE	D68	D89	D99	D101	D1112	D0102
Period of collection	2.06-9.8.19	9.08-9.09.19	9.09-5.11.19	1.10–5.11.19	3.12.2019-3.1.2020	3.01-2.02.2020
Dry mass of total atmospheric deposition [g]	0.245	0.178	0.026	0.059	0.045	0.045
Daily average dry mass of atmospheric deposition [g/day]	0.0036	0.0057	0.0012	0.0017	0.0016	0.0015
ATR-FT-IR	X	X	X	X	X	X
Py-GC-MS	X	X	X	X	X	X
SEM-EDS	X					
Sample preparation procedure						
HF pre-treatment						X
Manual concentration	X	X	X	X	X	

The first sample was collected over a two-month period to assure sufficient material for analysis. After analysis of the D68 sample, it was decided that one month would be sufficient to gather an optimal amount of material for the analytical techniques chosen.

2.1.3. Sample processing

For manual separation after collection, the sample container was closed and transported to a cleaned laboratory, where it was successively transferred to a Petri dish placed to evaporate on a laboratory water bath. The portion of material attached to the bottom and walls of the glass container was washed carefully using deionised water. The material was then the subject of visual inspection based on the physical properties, according to the criteria described in Hidalgo-Ruz et al. [43] and using a binocular stereoscope. Fibres and particles that we had the slightest suspicion to be of synthetic polymer were picked with micro tweezers from the Petri dish with added deionised water. This allowed the smaller particles, that would not have otherwise been picked, to bind together. The initial picking of fibres and fragments was necessary as a majority (as per sample D68) or just some part of the sample contained materials of clearly biological or inorganic origin. The discarded particles were mostly atmospheric dust mineral grains, plant fragments and small insects.

Analysis of the sample prepared without this step was conducted, whereby the quality of the attenuated total reflection–Fourier transform–infra-red (ATR-FT-IR) spectra made further identification difficult, and quantification impossible.

The sample from the final described sampling cycle (marked D0102) was concentrated using hydrofluoric acid on a cellulose filter, instead of applying a visual inspection procedure.

2.1.4. Quality assurance

To assure that the samples were not contaminated with external MPs, a cotton laboratory coat and non-synthetic clothes were worn, while the equipment and laboratory surfaces were wiped and rinsed, and plastic use was avoided in the protocol where possible. The laboratory staff were present in the laboratory only for the short periods necessary to perform the experiments (e.g. to transfer a new portion of the sample to a Petri dish). When possible, the containers and Petri dishes were covered.

2.2. MP particles' identification, quantification and characteristics

2.2.1. ATR-FT-IR spectroscopy

Mid-infra-red spectra were collected in an ATR mode in the wave-number range of 400–4000 cm-1 using a Nicolet iS5 (Thermo Scientific) FT-IR spectrometer equipped with an iD7 ATR accessory (Thermo Scientific) and DTGS detector. For each sample, 32 scans were acquired at a resolution of 4 cm-1. The ATR-FT-IR analysis was performed for all samples. The obtained spectra were compared with those of the reference samples representing the six most popular synthetic polymers (i.e. polyethylene (PE), polypropylene (PP), polyurethane (PUR), nylon-66 (Nyl-66), polystyrene (PS), and poly(ethylene terephthalate) (PET)). Additionally, to verify the hypothesis of the presence of particles of rubber in the MP originating from grated tyres, the ATR-FT-IR spectra of two types of commercial rubber were added (the typical tyre materials are marked T3 and T7).

2.2.2. Py-GC-MS

Py-GC-MS was carried out using a pyrolyser unit (CDS Analytical, model 5200) coupled directly to a gas chromatograph (Agilent Technologies, model 7890B) and a mass spectrometer (Agilent Technologies, model 5977A). The Py-GC-MS runs were carried out using small amounts (ca. 1.00 mg) of weighted sample placed in a quartz tube (L=2.5 cm, ID=1.5 mm) that was double-side plugged with quartz wool. Then, the sample was placed in a dedicated platinum coil of the pyrolysis unit and the analysis procedure was commenced after the pyrolysis furnace was purged with helium (grade: 6.0) for 3 min. The pyrolysis tests were performed in a direct mode.Afterwards, the column was baked off at 260 °C for 5 min. The collected total ion chromatograms (TICs) were analysed using the deconvolution approach. The extracted ion chromatograms were extracted from the TICs using Agilent ChemStation software.

2.2.3. Electron microscope observation of the MP surfaces

A field emission scanning electron microscopy and energy depressive spectrometry (SEM-EDS) HITACHI S-4700 microscope equipped with a NORAN NSS energy dispersive spectrometer was applied to gather detailed information on the MPs in terms of the environment interaction. After visual inspection, typical synthetic polymer fibres from sample D68 were picked. Those fibres were of blue and orange colour. The selection criteria for those were colour, gloss and flexibility. MP particles were attached to the carbon holder and coated with carbon. A secondary electron signal was used for the observation of the particles' morphology. An accelerating voltage of 20 kV and beam current of 10 °A were used for spot chemical analyses.

3. Results and discussion

3.1. Atmospheric deposition

The amount of the material deposited (wet and dry) on the 0.5675 m2 surface was converted into daily deposition on 1 m2 and the major differences were observed. The dynamics of the atmospheric deposition during the sample collection period were visibly different in summer in comparison with autumn and winter. June and July resulted in 0.006 g/m2, while August saw the highest deposition of 0.01 g/m2, and autumn and winter resulted in approximately half of the amount of the daily deposition, with September, November, December and January resulting in 0.002, 0.003, 0.0025 and 0.003 g/m2, respectively. The biggest difference in weight of the daily deposited material occurred between August and September, whereby the August daily fallout weight was almost four times higher than that of September. The high amount of deposited material was observed in the June and July period. The year 2019 was a record year for tourist traffic, and the June–August period is the most popular. Additionally, those months involve high vegetation growth, and intense construction and maintenance works. Additionally, the sample mass is higher for months with higher wet deposition due to the presence of dissolved substances.

3.2. Visual characteristics of MPs

Among the six samples prepared for further analysis, the transparent, blue, black, orange and red fibres were dominant in the anthropogenic material collected (Figure 1). There were, however, fragments that resembled torn pieces of foil, foam, irregular particles and some spheres that were potentially primary MP (van Wezel et al., 2015). The material in all samples looked similar. The number of particles considered to be MPs varied between the samples.

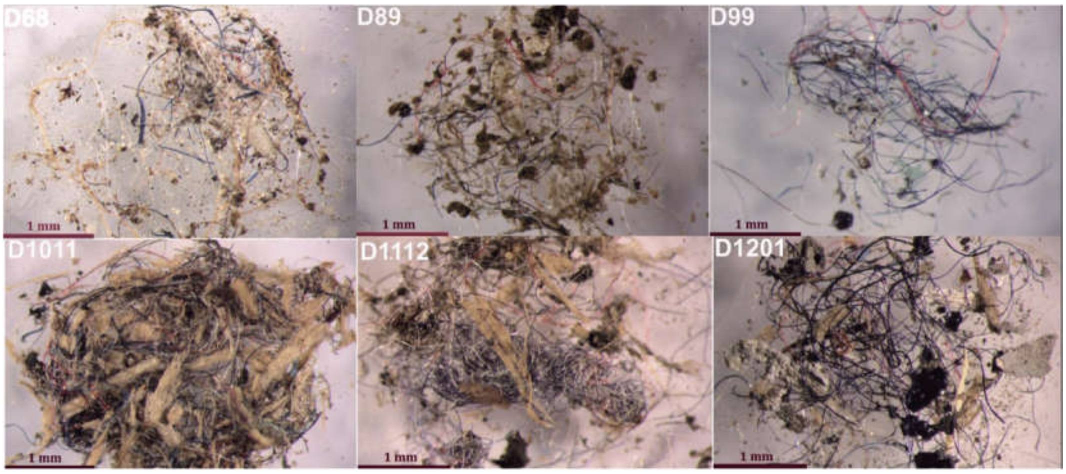

Figure 1. General view of the collected samples after visual identification and preconcentration.

It could be emphasised that based solely on the visual characteristics of the studied samples, the presence of MP could be confirmed. Some of the fibres were longer than 5 mm, but still small enough to be transported into the atmosphere, and therefore they contributed to the overall airborne MP pollution.

The length-to-diameter ratio of the majority of the material present was greater than 3:1. This could pose a health risk as the higher the ratio, the greater the likelihood of the MP entering the upper airways due to mucociliary clearance [18], while fibrous-shaped particles are generally considered more difficult to remove from the respiratory system [24].

Quantitative analysis is sometimes based only on optical inspection [45]. This approach was applied in the present study as the initial step. However, the total content of the potential MP was then assessed based on the instrumental analysis for the samples 1-6, and the final sample was prepared omitting this step. In the collected samples (Figure 1), some of the particles present were clearly made of synthetic polymers, while others were possibly of natural origin; for instance, beetle carapace pieces, or from non-synthetic-polymer anthropogenic material such a dyed natural silk, whose colourful fibres are often easier to recognise as MP, with most of the research suggesting that these are the major component of MP pollution [45].

Often, the polymer type is confirmed by instrumental methods for only a few representative MPs from the sample, and the classification is then extrapolated to the rest of the similar-looking particles. Some of the foreseen artificial-intelligence-based procedures of MP identification are based on the same principles [46]. However, data gathered in this way might be misleading or lacking of rigour. Although the samples collected had a similar appearance to the samples collected in 2018 [42] the analysis was more advanced in the current study.

3.3. Identification of MPs and analysis of the change in their relative share over time

3.3.1. ATR-FT-IR identification

ATR-FT-IR is a relatively fast technique suitable for the identification of synthetic polymers [47]. The ATR-FT-IR spectrum of the D68 sample was selected for the clarification of our approach in terms of the qualitative analysis (Figure 22). All the acquired spectra were compared with the polymer and rubber references. The presence of certain polymers in the MP samples was evidenced based on the presence of the characteristic absorption bands with regards to these references.

The ATR-FT-IR spectra were analysed in detail with regards to the plastic references (Figure 2). The chosen synthetic polymers can be identified mainly by the specific spectra of functional groups [48, 49]. In the spectrum recorded for Nyl-66, the bands at ~3300−1 and ~3200 cm−1, as well as at 1450 cm−1 and ~ 750 cm−1 can be recognised as the stretching, deformation, and wagging vibrations of N–H bonds, respectively. The stretching, asymmetric deformation and wagging modes of the NH amide groups are present at ~1550 cm-1 and ~1650 cm-1.

The spectrum for low density polyethylene (LDPE) features a characteristic doublet at 2800–3000 cm−1, ascribed to the stretching vibrations of methylene C–H bonds, bending at ~1470 cm−1 and ~1460 cm−1, and the rocking deformations of CH2 710 cm−1 as well as 1090 cm-1 bands from C–O stretches.

In the case of PS, the presence of the absorption at 3020 cm−1 may be assigned to the aromatic C–H stretch, 2850 cm−1 C–H stretch and 1600 cm-1 of C=C bonds originating from the aromatic rings' stretching vibration. The absorption at 1490 cm−1 ascribed to aromatic ring stretch, 1450 cm−1 –CH2– bend, 1027 cm−1 aromatic C–H bend and an intensive mode at ~700 cm-1 of aromatic C–H out-of-plane bend are also specific for PS.

PET can be recognised by the presence of C=O carbonyl group stretch (~1700 cm−1), C(O)–O stretching of ester groups (~1240 cm−1), and C–O stretch (~1090 cm−1), aromatic C–H out-of-plane bend (~720 cm−1), together with the –CH2– deformation band (~1410 cm−1). For the PUR, weak symmetric and asymmetric stretching vibrations of –CH2– aliphatic groups at 2970 cm−1 and 2870 cm−1 can be identified. Furthermore, stretching vibrations of the C=O carbonyl group at 1700 cm-1, the most intense peak at 1600 cm−1 from the stretching skeletal vibrations of C=C bonds present in the aromatic rings, the stretching and bending vibrations of the N–H as a strong band at 1500 cm−1, the deformation vibrations of the C–H at 1410 cm−1 and the stretching vibration of C(O)O–C groups band at 1230 cm−1 can be seen.

To identify the PP vibrations of CH bands at ~2920 cm−1, deformation vibrations of the plane methylene group in the spectral range of 1450–1480 cm−1, methyl groups' vibrations in the 1370–1400 cm−1 range, and the characteristic vibrations of the terminal unsaturated CH2 groups ~1170 cm−1 , ~1000 cm−1 and ~850 cm−1 are recognised (Noda et al., 2007).

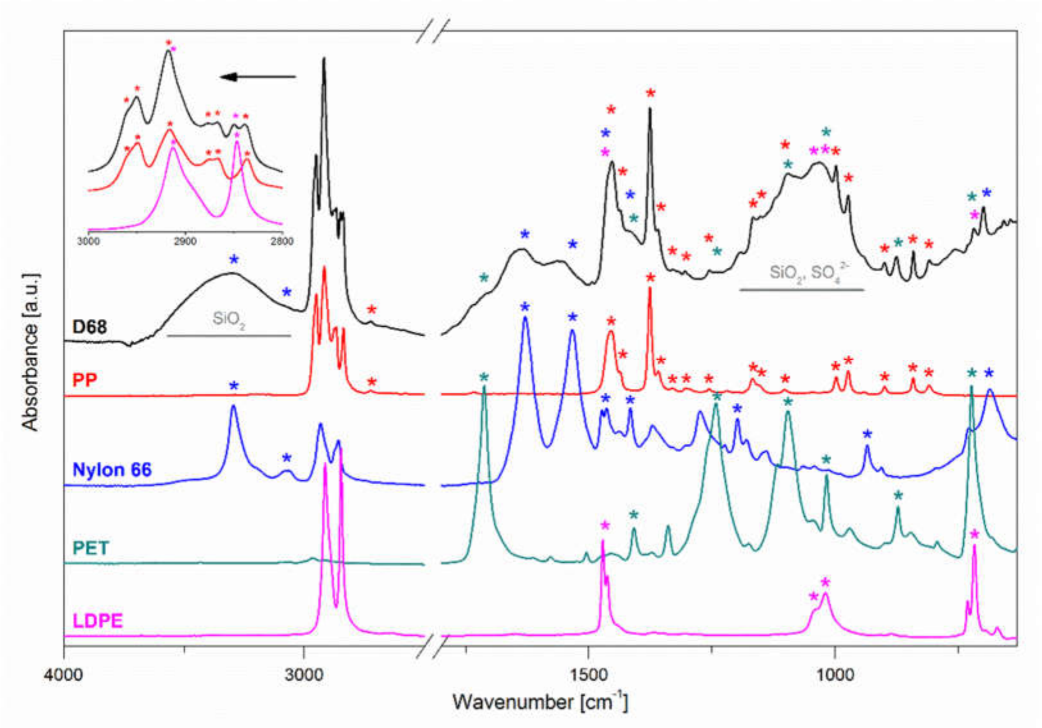

Figure 2. Methodology of the ATR-FT-IR spectra interpretation: the case of the D68 sample. The colour asterisks above the D68 spectrum refer to the characteristic bands of certain plastic components of this sample.

The ATR-FT-IR spectra collected for all the studied MP samples are depicted in Figure 3. It may be conjectured that Nyl-66 and LDPE were present in all samples. Amide bonds are also present in organic matter in the form of peptides; for example, in leaves, grasses, animals, hair or fur, and therefore omnipresent in the environment. Other examined synthetic polymers, namely, PS and PP, were recognised in samples D68 and D99. Sample D68 revealed only traces of PET. Based in the collected spectra, the presence of rubber particles in the tested MPs cannot be excluded (see the methyl and methylene bands at 3800–3000 cm-1). It should be noted that the spectra for samples D1011, D1112 and D1201, although similar to the rest of the MPs, show lower intensities, which is most likely due to a significant mineral content (silica, see the bands at 1000–1300 cm-1). For this reason, we decided to attempt to remove the mineral part by treating the MP samples with hydrofluoric acid (see section 3.3.1.1.).

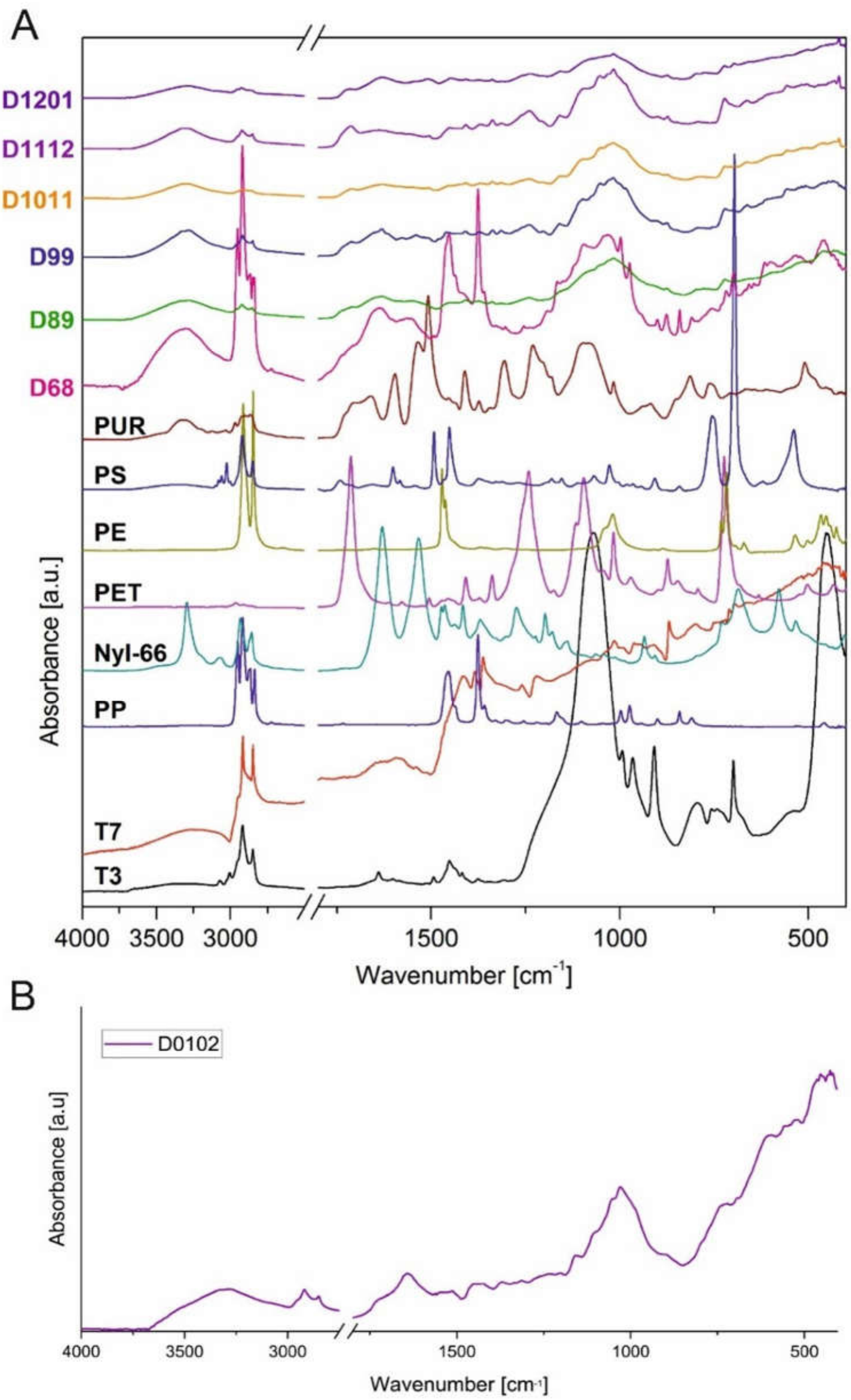

Figure 3. (A) ATR-FT-IR spectra for the samples under study and all plastic and rubber references. (B) ATR-FT-IR spectrum of the January sample; D0102 after HF (Hydrofluoric Acid) demineralisation.

The ATR-FT-IR spectrum for sample D68 was the most varied among the studied MPs. This was surprising, since the visual inspection indicated that colour or shape division provides limited or even misleading information about the MP particles' origin. The passive MP collector was placed at the height of the fifth storey, which might be the reason behind the significantly lower presence of tyre traces. Furthermore, the MP

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originating from tyres reaching this height might be small enough to be undetected. It can be also ascribed to another category, because polyamide and PE fibres are also used for tyre manufacture [50], and in this form MP pollution originating from tyres could still potentially be present as, for example, Nyl-66 fibre.

The presence of the most popular plastics of low- and medium-density MP (Plastic Europe, 2020) was observed. Identifying MP made with the most commonly produced synthetic polymers might be further expanded to other less prevalent polymers if the toxifcity or health-risks data emerged. The ratio of different polymers' total weight content might lead to improved understanding of the pathways and sources of this pollution. The presence of the main synthetic polymers produced might be a good base to develop and monitor the MP pollution index.

3.3.1.1. Sample pre-treatment with HF

An attempt was made to omit the manual concentration step after unsuccessful attempts to analyse the sample without any prior treatment due to the sediment effect on the spectra. he previous six samples provided information about the MPs' presence and characteristics, and demineralisation was performed with the final sample gathered through the use of HF solution (Tab. 1) and compared with the spectra from prior months. Therefore, a homogenic sample was obtained, for which good quality ATR-FT-IR spectrum was acquired (Figure 3).

3.3.2. Py-GC-MS study

3.3.2.1. A semi-quantitative approach with regards to the MP components

A semi-quantitative analysis of the share of the six types of plastic most commonly found in the MP samples (i.e. PE, PP, PS, PET, Nyl-66 and PUR) was feasible using the coupled techniques of Py-GC-MS. Our approach is based on the MS analysis of the volatiles that evolved during the flash pyrolysis of the MP sample. Each type of plastic yields a certain characteristic set of volatile products when pyrolysed. It should, however, be kept in mind that the pyrolytic decomposition of MP is in fact the process of co-pyrolysis. It is well documented that in such cases, the mechanisms (and products) of degradation may be mutually influenced. For this reason, we prepared a reference MP counterpart composed of the aforementioned six samples of plastic taken equimassic. Then, the known mass of the reference mixture was subjected to the Py-GC-MS analysis at identical conditions to the real MP samples. Additionally, we performed the same analyses for all the six plastics separately. Next, we analysed the collected total ion chromatograms and extracted ion chromatograms. For each plastic type, we selected one characteristic and intensive mass line (m/z) featuring the maximum number of retention times, thus being unaffected by the mass lines contributed by other polymers' decomposition. The integration of the chosen peaks with regards to the mass of the real sample taken for analysis allowed us to calculate the semi-quantitative shares of each component of MP.

The Py-GC-MS confirmed the result of the ATR- FT-IR analysis, since the same types of polymers were found. Therefore, it was decided that it would be safe to rely solely on the Py-GC-MS technique to recognise the synthetic polymers present in the atmospheric fallout. Moreover, the use of this technique was successful in providing information about the relative concentration of the different polymer types (Tab. 2).

Table 2. Composition of the MPs by polymer type, determined by means of the analysis of the evolved pyrolytic gas (Py-GC-MS technique).

Polymer	Polymer content [wt.%]					
	D68	**D89**	**D99**	**D101**	**D1112**	**D0102**
PS	13.6	–	0.8	1.6	0.2	22.2
LDPE	14.7	7.0	17.7	49.4	9.6	13.8
PUR	–	–	–	–	–	–
Nyl-66	66.9	93.0	56.9	47.5	89.7	64.0
PP	3.7	–	24.6	1.0	0.2	–
PET	1.1	–	–	0.4	0.2	–
PS	13.6	–	0.8	1.6	0.2	22.2

The results of the Py-GC-MS confirm that the samples collected in June–July (D68), October (D1011) and November (D1112) were the most varied, with the MPs composed mainly of Nyl-66, LDPE, PS, PP and PET. The sample collected through September 2019 (D99) did not contain PET, while in December no PP was present, and the only synthetic polymers detected in August were Nyl-66 and LDPE.

In five samples, Nyl-66 accounted for the majority of MPs, comprising 56.9–93% of all the synthetic polymer mass. In the sample collected in October (D1011), LDPE was more prevalent than Nyl-66, but only slightly by 1.9%.

Nyl-66 is not only used for single-use-plastics, but is also an important component in the automotive (up to 40% of total nylon usage in high-income countries), textile and construction industries [50]. Additionally, each sample contained a considerable amount of LDPE. This synthetic material is widely used in multiple industries due to its low cost of production, low weight and good flexibility [51]. LDPE is often used for packaging, carry-out and waste bags, and agricultural and contracting films. The high content of LDPE may be likely ascribed on the one hand to its widespread use, and on the other to its resistance to chemical degradation.

PS is commonly used for take-out packaging (e.g. coffee cup lids) and as expanded PS insulation foam [52. It is also a very important material for construction applications in the form of expanded PS used for many purposes, primarily decorative tiles and mouldings, insulation blocks and as an additive to construction blocks [53]. In the five samples containing PS, its share difference reached 20%. Since PS is most often used and disposed of in expanded form, its extremely low density is understandable (from 0.01 g/cm3). This, in turn, allows for the uplift and transportation of larger secondary PS particles.

From sample seven up to almost 50 wt.% of the polymer relative content is LDPE, although it is present in all samples. LDPE is one of the most popular synthetic polymers used, and it is both durable and chemically resistant. The most common items made with LDPE are plastic bags, containers, toys, gas and water pipes, and high frequency insulation.

Contrary to the fact that PET is a commonly used synthetic polymer, its amount in the samples was either very limited or none at all. One of the reasons behind this may be the fact that PET is more resistant to mechanical degradation in comparison to more durable synthetic polymer types [54]. Another reason is that PET has less chemical stability than other synthetic polymers. It is prone to some reactions including acid and alkaline hydrolysis and methanolysis, which are also used in the chemical recycling of PET [55]. Those are possible reasons behind its limited presence in the samples. MP research still tends to focus on MP particles in soil, water and sediments. Airborne MP particles may, to some extent, form in different conditions, and even if the degradation pathways are initiated in the same manner, the particles are present in a different medium. PET plastic is highly popular and used mostly as single-use plastic, but also in textile products.

The lack of PUR particles in the studied MPs may be explained similarly. Observation of PUR behaviour under the influence of UV radiation (e.g. construction foams used for the sealing of cracks and holes in buildings) indicates that PUR 'withers' fast under direct sunlight.

Moreover, both PUR and PET are of higher density than other polymer types, at 1.20–25 and 1.38–1.41 g/cm3, respectively [56]. Their decreased presence or total absence at the height of a five-storey building might be explained by their density. It cannot be ruled out, however, that apart from a clear difference between months, the main reason behind the presence of certain types of synthetic polymers and the lack of others may be caused by local levels of MP emission, as opposed to the characteristics themselves.

The MPs detected are not only the most commercially used, but are also the same as those present in the highest quantities in human lungs [1].

The main drawback of the Py-GC-MS method is the very limited amount of sample that can be subjected to analysis at any given time [57]. This, however, has little importance in the study of airborne MP [58], since those particles even in monthly periods of collection do not amount to large volumes, and thus do not pose a problem regarding the sample size.

3.4. SEM observations and microanalysis of the airborne MP fibres' surfaces

Airborne MP fibres are subject to further degradation in the atmosphere (Figure 4). It is often assumed that fibrous MPs come from fibrous materials, such as textiles. With the use of SEM, images of the fibrous fragmentation of PE bottles collected on the pavement were documented. MP identification is often based on the protocol described by Chubarenko et al. (2018) or others, where one of the criterion is that the fibres have to be equally thick throughout their entire length, and not tapered at the end. The degrading bottle example proves that this is not the case for at least some of the secondary origin fibres.

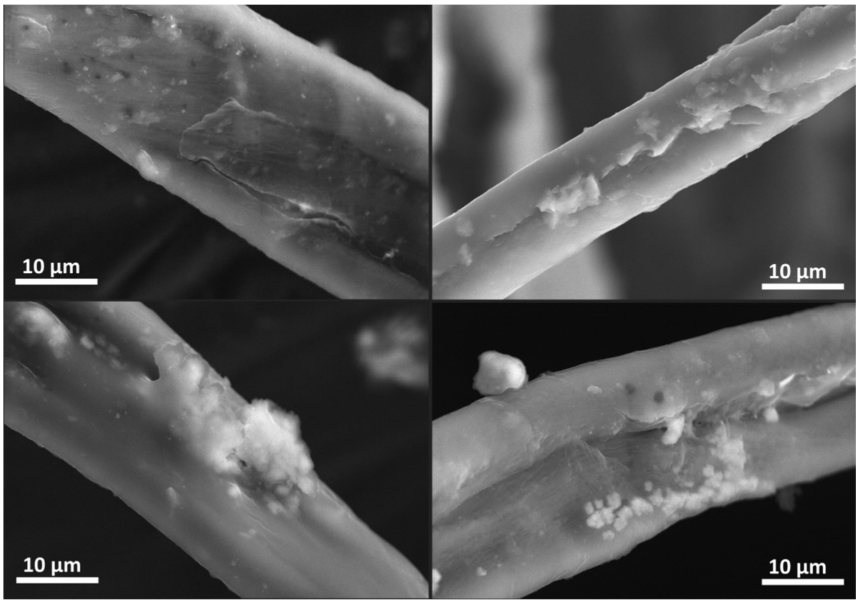

Figure 4. The SEM images of MP fibres with mineral phases attached (sample D68).

The phases identified on the surfaces vary considerably. The most prevalent elements are Al, Ca, Cl, Fe, K and Si. The presence of aluminum was noted in numerous locations. The presence of chlorine is connected to compounds with lower aluminium content. At the same time, a correlation between chlorine and sodium can be noted.

The chemical composition of the substances attached to various MP fibres' surface is depicted in Figigure 5, where SEM-EDS analysis led to the observation of aluminum salts' attachment to airborne MP, which appears to be the most interesting observation made

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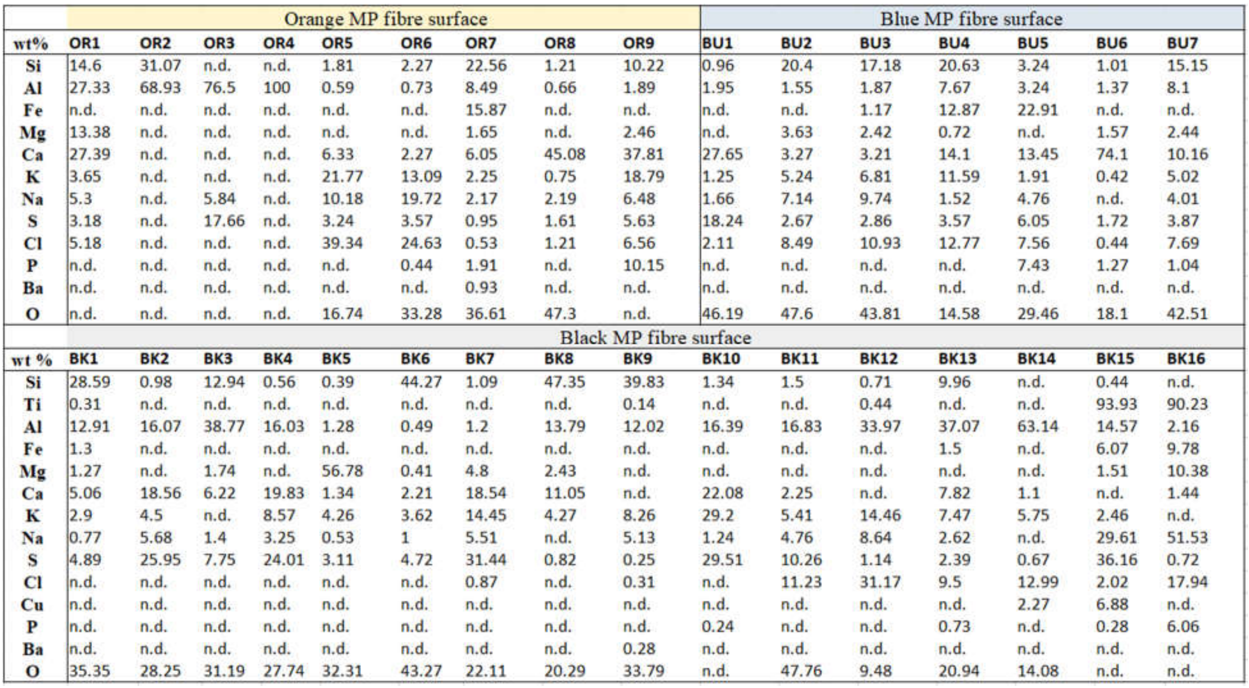
(Figure 5). The main airborne aluminum source is human industrial activity [59], and also, even though rarely in a temperate climate, wind-transported soil particles. Aluminum salts detected in the samples are rarely present among air pollutants in Krakow [60]. Aluminum salts, among others, were previously detected as present in the form of particulate matter in the so-called 'personal cloud' [61]. The possible source of that being antiperspirant-deodorant products, where aluminium chlorohydrates are often used. The comparison of EDS data from deodorants was made and confirmed to be of similar composition and form as that found in the examined MP samples. There is a possibility for this to be direct proof that some MP fibres originated from clothes. Furthermore, airborne MP can not only represent a dangerous pollutant by itself, but also a direct medium to contaminants from personal hygiene products. Other phases on the surface of MP could be mostly classified as silicates or aluminosilicates. Metals such as iron and copper are present on the surface in complex compounds. Sulphur is also present, as the only element or as a component in most of the analysed attached particles. The presence of this element might be associated generally with air pollution and wet deposition components [62].



	Orange MP fibre surface									Blue MP fibre surface						
wt%	OR1	OR2	OR3	OR4	OR5	OR6	OR7	OR8	OR9	BU1	BU2	BU3	BU4	BU5	BU6	BU7
Si	14.6	31.07	n.d.	n.d.	1.81	2.27	22.56	1.21	10.22	0.96	20.4	17.18	20.63	3.24	1.01	15.15
Al	27.33	68.93	76.5	100	0.59	0.73	8.49	0.66	1.89	1.95	1.55	1.87	7.67	3.24	1.37	8.1
Fe	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.87	n.d.	n.d.	n.d.	n.d.	1.17	12.87	22.91	n.d.	n.d.
Mg	13.38	n.d.	n.d.	n.d.	n.d.	n.d.	1.65	n.d.	2.46	n.d.	3.63	2.42	0.72	n.d.	1.57	2.44
Ca	27.39	n.d.	n.d.	n.d.	6.33	2.27	6.05	45.08	37.81	27.65	3.27	3.21	14.1	13.45	74.1	10.16
K	3.65	n.d.	n.d.	n.d.	21.77	13.09	2.25	0.75	18.79	1.25	5.24	6.81	11.59	1.91	0.42	5.02
Na	5.3	n.d.	5.84	n.d.	10.18	19.72	2.17	2.19	6.48	1.66	7.14	9.74	1.52	4.76	n.d.	4.01
S	3.18	n.d.	17.66	n.d.	3.24	3.57	0.95	1.61	5.63	18.24	2.67	2.86	3.57	6.05	1.72	3.87
Cl	5.18	n.d.	n.d.	n.d.	39.34	24.63	0.53	1.21	6.56	2.11	8.49	10.93	12.77	7.56	0.44	7.69
P	n.d.	n.d.	n.d.	n.d.	n.d.	0.44	1.91	n.d.	10.15	n.d.	n.d.	n.d.	n.d.	7.43	1.27	1.04
Ba	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
O	n.d.	n.d.	n.d.	n.d.	16.74	33.28	36.61	47.3	n.d.	46.19	47.6	43.81	14.58	29.46	18.1	42.51

	Black MP fibre surface															
wt %	BK1	BK2	BK3	BK4	BK5	BK6	BK7	BK8	BK9	BK10	BK11	BK12	BK13	BK14	BK15	BK16
Si	28.59	0.98	12.94	0.56	0.39	44.27	1.09	47.35	39.83	1.34	1.5	0.71	9.96	n.d.	0.44	n.d.
Ti	0.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	0.44	n.d.	n.d.	93.93	90.23
Al	12.91	16.07	38.77	16.03	1.28	0.49	1.2	13.79	12.02	16.39	16.83	33.97	37.07	63.14	14.57	2.16
Fe	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	n.d.	6.07	9.78
Mg	1.27	n.d.	1.74	n.d.	56.78	0.41	4.8	2.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.51	10.38
Ca	5.06	18.56	6.22	19.83	1.34	2.21	18.54	11.05	n.d.	22.08	2.25	n.d.	7.82	1.1	n.d.	1.44
K	2.9	4.5	n.d.	8.57	4.26	3.62	14.45	4.27	8.26	29.2	5.41	14.46	7.47	5.75	2.46	n.d.
Na	0.77	5.68	1.4	3.25	0.53	1	5.51	n.d.	5.13	1.24	4.76	8.64	2.62	n.d.	29.61	51.53
S	4.89	25.95	7.75	24.01	3.11	4.72	31.44	0.82	0.25	29.51	10.26	1.14	2.39	0.67	36.16	0.72
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.87	n.d.	0.31	n.d.	11.23	31.17	9.5	12.99	2.02	17.94
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.27	6.88	n.d.
P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.24	n.d.	n.d.	0.73	n.d.	0.28	6.06
Ba	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
O	35.35	28.25	31.19	27.74	32.31	43.27	22.11	20.29	33.79	n.d.	47.76	9.48	20.94	14.08	n.d.	n.d.

Figure 5. Chemical composition of substances attached to the MP fibres' surfaces.

4. Conclusions

Airborne MP pollution needs to be well recognised and addressed, especially in highly urbanised areas with significant human exposure. The proposed approach will lead to highly comparable results and therefore enable future monitoring and legislation. The presence of at least five different synthetic polymers in the atmosphere of Krakow was confirmed by means of both employed methods: ATR-FT-IR spectroscopy and Py-GC-MS. The main synthetic polymers present in the atmospheric deposition in Krakow were Nyl-66 and LDPE. Temporal changes in the MP-type share were also confirmed, giving scope for further research on possible patterns and the reasons behind this. A wide spectrum of attached mineral phases was observed on the MP fibres' surfaces. In terms of ways to identify the MP particles' source, further study of the presence on the surface of the MP particles might lead at least to the identification of the potential source thereof. Aluminium salts' presence on the surfaces might come from personal hygiene products. The inorganic pollutants on the surface of MPs potentially add to the risks associated with MPs' inhalation. Py-GC-MS was efficient in airborne MP composition determination, and the results were consistent with the ATR-FT-IR results. It might be possible to exclude the visual inspection step in future investigations, using instead the pre-concentration of MP via the demineralisation of samples using HF. However, this method still needs to be further validated.

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