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Monitoring and Size Fractionation of Micro-Nanoplastics in Porto's Atmosphere: Quantification over a Five-Month Period†

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Abstract: Airborne micro-nanoplastics (MNPs) have become one of the important and emergent constituents of atmospheric aerosols, garnering significant attention in recent times. However, the absence of any standard methods for collecting, sample preparation, and analysis, as well as an open database for comparison and compilation of results, has given rise to numerous questions and challenges. Between August 2022 and January 2023, air samples were collected in Porto, Portugal, using two types of passive collectors: the NILU Precipitation Collector for collecting wet atmospheric particulate fallout and the Atmospheric Microplastic Collector for capturing microplastics in wet and dry deposition. As passive deposition does not provide size-resolving particle sampling, a size-fractioning filtration process was adopted after collecting the samples from the air. Different types of sieves and filters, with various porosities, were used to separate particles of different sizes. Sieves with mesh sizes of 125, 63, and 25 μm were employed to retain larger particles, while filters with pore sizes of 12, 0.45, and 0.22 μm were used to retain smaller particles. These smaller particles include the respirable fraction of microplastics, making part of the respirable matter PM_{10} and $PM_{2.5}$. Optical microscopy was used to quantify microplastics after the filtration process. To ensure accuracy in quantification, recovery and blank tests were conducted. The analysis revealed that the respirable fraction size accounted for 25% of the total MNPs, and the number of microplastics with sizes ranging from 12 to 0.45 μm in the atmosphere of Porto was more than 500 microplastics per square meter per day (MP / m² / day).

Keywords: Airborne micro-nanoplastics; atmosphere; aerosols; monitoring; quantification; size fractionation.

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1. Introduction

From the first scientific reports of the existence of microplastic (MPs) in the atmosphere in 2015 in Paris and 2017 in China, several questions and doubts began to be raised [1, 2], such as danger to human health, transport routes, degradation speed and lifetime in the atmosphere, size distribution. Many scientific articles reported the number of airborne microplastics investigated in various parts of the world [3-13]. But on the other hand, among the scientific literature, there are mostly reviews, which try to summarize the existing information in this area [14-15]. This is because, for now, there is no legislation or standardized protocols and methods that can obtain results for comprehending, comparison or compilation in a database.

The scientific community adopted that particles of synthetic polymers smaller than 5 mm are considered microplastics (MPs), and the inferior fractions are named micro-

nanoplastics (MNPs). Although the types of polymers that constitute MNPs can vary, the most common are: polyethylene (PE), polypropylene (PP), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polystyrene (PS) [16]

The persistence of MNPs in the air, coupled with long-distance transport, makes them ubiquitous and, recently, MNPs detection in the human body, including the heart, lungs, breast milk, or placenta, has been reported [17-19].

To improve the understanding of airborne MNPs dynamics, in this work it was performed a five-month monitoring and size-fractionation quantification of MNPs in the atmosphere.

2. Materials and Methods

In order to quantify airborne MNPs, the air samples were collected from August 2022 to January 2023 in Porto, Portugal (41º15'N, -8º63'W). Two types of passive collectors were utilized: the Precipitation Collector for collecting wet atmospheric particulate fallout (*A*) and the Atmospheric Microplastic Collector for capturing microplastics in wet and dry deposition (*B*) of the Norwegian Institute of Air Research – NILU. These collectors were placed at 2.3 meters above ground level in the green yard of the Faculty of Sciences of the University of Porto. Every 14 days, the inside of the collectors was washed with deionized water and transferred to a dark glass vial for future size fractionation. All samples were identified by the month's name, indicating the associated collector: Sep/A, Oct/A, Nov/A, Dec/A, Jan/A and Sep/B, Oct/B, Nov/B, Dec/ B, Jan/B.

After bulk sampling, an optimized size fractionation procedure was adopted to obtain samples into several homogeneous sub-fractions based on a sequence of sieving and filtration unitary operations [20]. A cascade of metallic sieves (125, 63, and 25 μm) was used to remove large organic matter, minimize clogging and separate the biggest sizes of microplastics. After sieving, cellulose nitrate (CN) and cellulose acetate (CA) membrane filters with a pore size of 12, 0.45 and 0.22 μm were used to separate the smallest MNPs size fractions. These membrane filters were chosen to quantify the number of microplastics that fall within the respirable fraction of the particulate matter (PM_{10} and $PM_{2.5}$).

After sieving the samples, the sieves and their content were placed in beakers with 200 mL of H_2O_2 (15%) for 12 hours (overnight) at 50 C° for organic matter digestion. The material retained on the sieve is previously detached by sonication for 30 seconds. After this step, to recover the micro-nanoplastics glued to the bigger non-organic/organic particle matter, the samples were dispersed by sonification for 30 seconds and went again through the cascade of sieves and filters. From this size-fractionation filtration procedure, we obtained the following MNPs fractions: > 125 μm; 125 – 63 μm; 63 – 25 μm; 25 – 12 μm; 12 – 0.45 μm; 0.45 – 0.22 μm.

To ensure the accuracy of all procedures, three blank-size fractionations were concluded using just deionized water. Two more tests, using samples from the Febrary and March, because of complex matrix, were performed to calculate the percentage recovery of microplastics. Bright purple plastic was ground, and the amount of one spoon was suspended in 500 ml of deionized water. The suspension was then filtered through a 125 micrometer pore size sieve and suspension after sieving was filtered again through a 0.45 micrometer pore size CA filter. The amount of microplastics retained on the filter was confirmed by the optical microscope (about one hundred particles). The filter with the plastic microparticles for recovery was placed in the collector and the protocol described above for the size-fractionation was carried out. After washing the collector with the sample and the filter with the microplastics destined for the recovery calculation, the filter was removed. It was again subjected to analysis by optical microscopy to verify the amount of microplastics that did not enter in the analysis. The recovery rate of MNPs (RR_{MNPs}) was calculated where RR_{MNPs} result from the number of MNPs in the filter before placing it in the collector, minus the number of MNPs in the filter after removal from the

collector, divided by the number of MNPs quantified by optical microscopy and multiply by hundred.

In each filtration step, three times water-throw-washing were applied to obtain reliable values.

Optical microscopy was used to quantify MNPs and fibres from the filter membranes. Taking into account the limitations of the optical microscopy technique, that refers to the identification of microplastics, where it is impossible with certainty to identify some cases due to the color shown, which could be confused with other materials, bright colors were considered for counting microplastics that is non-existent in nature of this size: blue, green, red, yellow, orange, pink. Synthetic fibres were also considered for analysis.

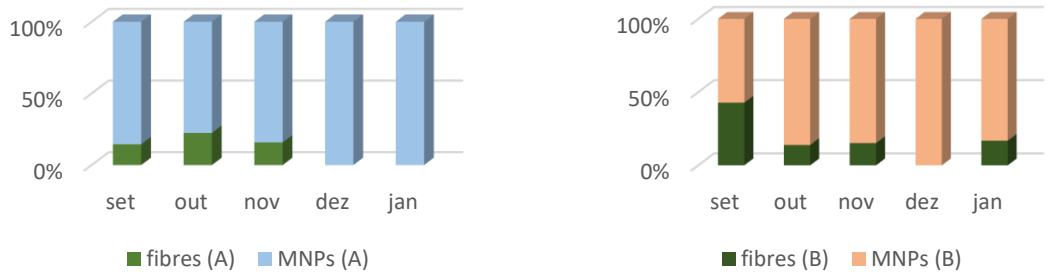
3. Results

According to the results obtained for the blank tests, there is evidence of contamination, although all the tests were carried out carefully and inside the laboratory hotte. The recovery tests showed different values for the recovery rates of the MNPs of polyethylene and present values of 5.4% for collector *A* and 21.7% for collector *B*. Due to the 0.45 - 0.22 micrometers small size fraction and optical microscopy capacity, it was impossible to quantify this fraction.

Quantification of MNPs and fibers by optical microscopy in the samples revealed the dominant amount of MNPs in each month and in both collectors (Figure 1).

Figure 1. Percentage of fibres and MNPs from collectors *A* and *B* in each month.

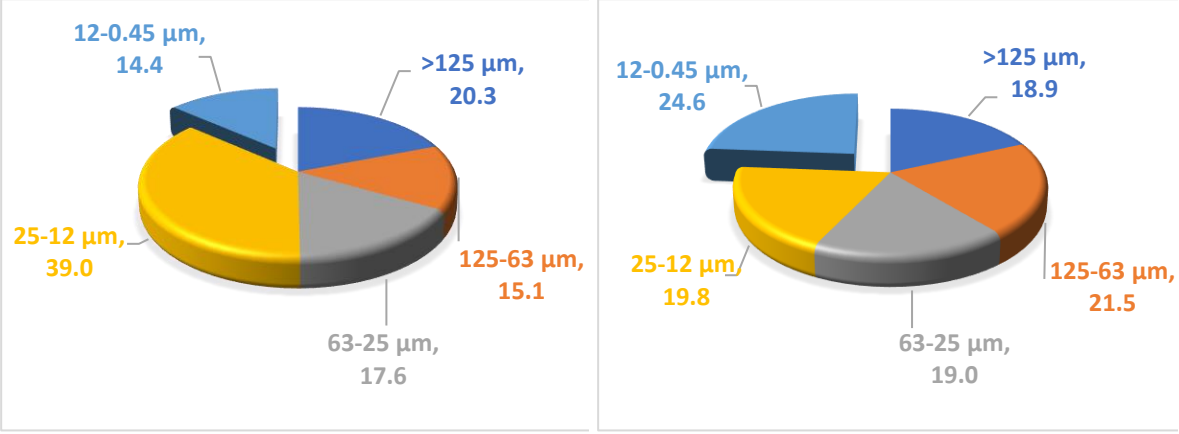
However, there is no trend or obvious relation in the monthly total amount of MNPs and fibres between the two collector types, but a decrease in fibres is observed in December and January in both samplers (Figure 2a, 2b).



(**a**) (**b**)

Figure 2. Percentage of fibres and MNPs in each month: (**a**) Collector *A*; (**b**) Collector *B*.

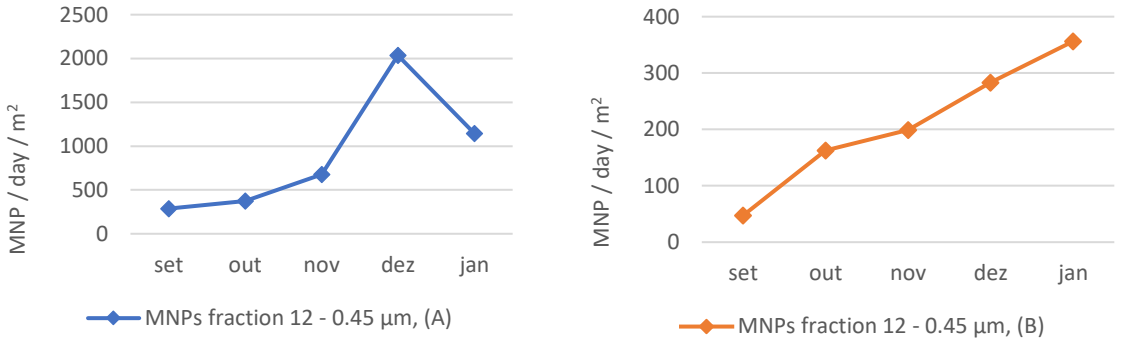
Analyzing the percentage of MNPs in each size fraction per month, the largest amount referred to the fractions 25 - 12 and 12 - 0.45 micrometers. When considering the average value of the sampling period for each fraction, in collector *A*, the fraction 25 - 12 micrometers attained the highest MNPs number, while for collector *B* it was the 12 - 0.45 micrometers size (Figure 3).



(**a**) (**b**)

Figure 3. Average percentage of MNPs for fractions: (**a**) Collector *A*; (**b**) Collector *B*.

The average amount of MNPs detected each month and converted into number of MNP per day and per square meter (MNP / day / m2) was 8387 for collector A and 839 for collector B. Considering the sum of MNPs from the fractions between 12 – 0.45 micrometers detected each month reveals an increase during the study months in both collectors (Figure 4). A sudden increase in the number of microplastics in December from collector A was observed. Noted that the quantity of MNPs is higher for collector A.



(**a**) (**b**)

Figure 4. Number of MNPs in the size fraction between 12 – 0.45 micrometers by day and by meter square in each month. (**a**) Collector *A*; (**b**) Collector *B*.

4. Discussion

The results obtained from the quantification of MNPs in size fractioned atmospheric samples, where two passive collectors were used, show different values for the average numbers of MNPs per day and per square meter (MNP / day / m²): 8387 for the Precipitation Collector for collecting wet atmospheric particulate fallout (*A*) and 839 for the Atmospheric Microplastic Collector for capturing microplastics in wet and dry deposition (*B*). The samplers were located next to each other, and further investigation needs to be conducted to ascertain if there is a difference in the sampling efficiency. In the recovery tests performed with polyethylene plastic, recovery rates were 5.4% for collector *A* and 21.7% for collector *B*, being also observed differences between the collectors for the same period. As for the average percentages of MNPs in the fractions, the values are similar. When focusing on the percentage of MNPs per size fraction, the average values per day and per square meter (MNP / day / m²) for the fraction 12 - 0.45 micrometres, that correspond to

particles with greatest danger to human health due to their size that can enter the respiratory tract, were 4.3 times higher in collector *A*.

5. Conclusions

For more knowledge about the levels of MNPs and the behaviour of their change over time, seasonal periods and atmospheric conditions, more monitoring time is needed, including identification studies.

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