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Microplastics and anthropogenic debris in rainwater from Bahia Blanca, Argentina

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ABSTRACT

Concern about atmospheric microplastic (MP) contamination has increased in recent years. This study assessed the abundance of airborne anthropogenic particles, including MPs, deposited in rainfall in Bahia Blanca, southwest Buenos Aires, Argentina. Rainwater samples were collected monthly from March to December 2021 using an active wet-only collector consisting of a glass funnel and a PVC pipe that is only open during rain events. Results obtained show that all rain samples contained anthropogenic debris. The term "anthropogenic debris" is used to refer to the total number of particles as not all the particles found could be determined as plastic. Among all the samples, an average deposition of 77 ± 29 items (anthropogenic debris) $m^{-2}d^{-1}$ was found. The highest deposition was observed in November (148 items $m^{-2}d^{-1}$) while the lowest was found in March (46 items $m^{-2}d^{-1}$). Anthropogenic debris ranged in size from 0.1 mm to 3.87 mm with the most abundant particles being smaller than 1 mm (77.8%). The dominant form of particles found were fibers (95%), followed by fragments (3.1%). Blue color predominated (37.2%) in the total number of samples, followed by light blue (23.3%) and black (21.7%). Further, small particles (<2 mm), apparently composed of mineral material and plastic fibers, were recognized. The chemical composition of suspected MPs was examined by Raman microscopy. The analysis of μ-Raman spectra confirmed the presence of polystyrene, polyethylene terephthalate, and polyethylene vinyl acetate fibers and provided evidence of fibers containing industrial additives such as indigo dye. This is the first assessment of MP pollution in rain in Argentina.

1. Introduction

Due to their physicochemical properties and low production costs, plastics processing has grown exponentially from 1950 to 2019 [1]. While the production of plastics in 2020 decreased by 0.3% - relative to the 368 million tons produced in 2019 - due to the

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COVID-19 pandemic [2], demand for single-use plastic items increased for the same reason [3]. The most commonly produced plastic consumer products include packaging made from LDPE, containers made from HDPE and PET bottles for water and other drinks [4]. The properties that make plastics useful, such as strength, flexibility and durability, also make, their disposal difficult. Due to their resistance to degradation, added to low recycling rates worldwide and the impossibility of being recycled in some cases, these plastic materials end up being transported by wind and rainfall through different matrices, introducing persistent and complex materials to the environment [5]. When plastics reach the environment they are susceptible to fragmentation into smaller particles by different processes such as photodegradation, physical abrasion, hydrolysis and biodegradation, producing particles smaller than 5 mm known as secondary microplastics [6]. In addition, primary MPs can be manufactured at the industrial level for cosmetic and cleaning uses, which are mainly discharged as domestic effluents [7].

The environmental fate of MPs has been studied extensively in inland water [8], coastal zones [9], deep ocean [10], polar waters [11], soils and sediment [12], and even in birds, mammals, and fish [13]. Most of the studies have focused on marine pollution, the origin of which derives from terrestrial activities. The main focus of research on the transport of MP routes has been through rivers to the oceans; however, terrestrial MPs could also be transported through atmospheric circulation and then undergo dry and wet atmospheric deposition [14]. At present, attention to the atmosphere as a transport route for MPs is still considered incipient. MPs are easily transported by wind and can persist in the atmosphere for extended periods of time due to their small size and relatively low density [15]. The sources of MPs in the atmosphere are multiple and were evidenced from road dust, sea spray, and agricultural soil dust [16]. Wind erosion and transport of MPs may not only redistribute particles in the terrestrial environment, as atmospheric fallout is also likely to contribute to marine pollution [17]. An estimated 1.21 tons of suspended atmospheric MPs are thought to be transported from terrestrial sources to the marine environment each year [18]. Even though the occurrence of MP atmospheric transport has been generally closely related to anthropogenic activities, MPs have also been found in remote areas, characterized as a pristine region far from anthropogenic sources, demonstrating the importance of long-range transport from large urban and industrial centers. The distance of these remote locations from urban areas suggests that airborne transports is a likely source of at least some of the MPs found there [16]. In general, it is estimated that MPs found in remote areas are transported by wind and rain. In addition, there is evidence from the open ocean, that suggests that MPs are accumulated in the ocean surface microlayer, where they can be removed by rising air bubbles. The bursting of the bubbles injects the MPs into the atmosphere in a process associated with sea spray aerosol formation [19].

Recent studies have showed the presence of MPs in the atmosphere of densely populated cities, such as Paris [17], Dongguan [20] and Shanghai [18]. However, to the best of our knowledge, there are only two studies in Latin American of evidence of MPs in the atmosphere [21,22] and no studies have been carried out in Argentina. Concern over MPs is also a public health issue, in particular, plastic fibers could have a potential impact on the respiratory system of humans depending on the particle size, as only MPs smaller than 10 μm can be inhaled. Moreover, airborne MPs could be vectors for other pollutants circulating in the atmosphere and adsorbed on their surfaces.

In particular, in Bahia Blanca MPs have been recorded in coastal sediments [23], inland waters [24], estuarine waters [25] and even in organisms [26]. In recent years, MP atmospheric transport has been considered an important vector that could lead to MP deposition on land or in aquatic environments [27]. It is known that 80% of the fibers found in marine environments come from the

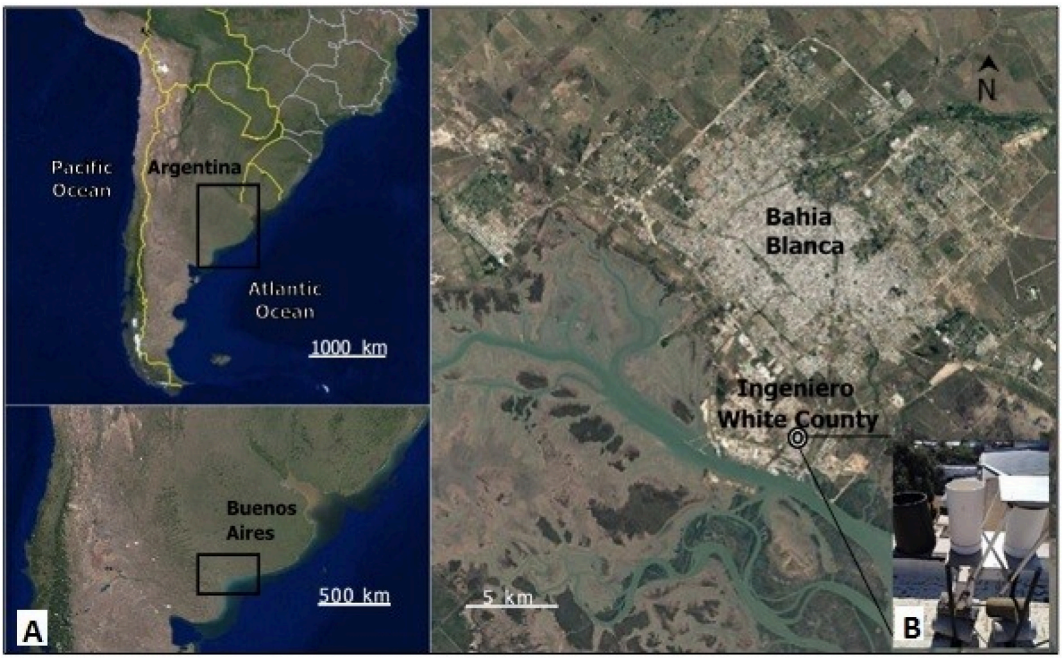

Fig. 1. A: Location of the sampling site. B. Sampling device used in this study.

continent but it has not yet been determined what percentage corresponds to the atmospheric contribution. The aim of this study was to perform a preliminary assessment of the occurrence and characteristics of MPs and other anthropogenic debris deposited in rainfall in Bahia Blanca, province of Buenos Aires, Argentina. The results obtained herein contribute new information related to MP transport and deposition in rainfall in Argentina, reinforcing the knowledge about atmospheric MP pollution in South America and filling an information gap for Argentina [28].

2. Materials and methods

2.1. Study area

Ingeniero White (38°46′37″ S; 62°16′1″ W) is located in the district of Bahía Blanca, 10 km from the city of Bahía Blanca (population of 335.190) in the province of Buenos Aires, Argentina, a few kilometers from the Atlantic Ocean and in contact with the Bahía Blanca estuary. Bahia Blanca is the most important city in the region because one of the most important ports in Argentina is located there (Fig. 1. A). The region is under the influence of semi-permanent anticyclonic centers located in the Atlantic and Pacific oceans that generate typical air masses and determine the dominant synoptic conditions in the area. The resulting circulation induces strong NW and N winds with a mean velocity of 24 km h^{-1} during 40% of the year with gusts of over 100 km h^{-1} [29]. The city has an average annual temperature of 15.6 °C and average annual rainfall of 651.4 mm.

2.2. Sampling

Rainwater was collected monthly from March to December 2021, only during the months with rainfall, i.e., March, August, September, October, November, and December.

The rain collector was an active wet-only sampler, consisting of a glass funnel and a white PVC pipe which only opened during rain events. Before sampling, the collector was preconditioned by washing and rinsing it with filtered distilled water and 70% alcohol to ensure that there was no contamination from the collector. In addition, special attention was paid during the visual inspection of the samples and no white particles were found, confirming there was no contamination from the PVC collector.

The sampling surface of the collector was 0.0254 m^2 allowing rainfall to enter through the glass funnel into the PVC pipe that receives the water with a device designed to collect the rainfall (Fig. 1. B). The sampling collector was placed on a two-story-high roof (~8 m above ground level) at Ingeniero White City Hall, located approximately 1000 m from the harbor complex and 850 m from the industrial area. The sampler was placed in an open area facing the prevailing wind, away from trees, buildings and other obstacles that could give rise to updrafts or downdrafts. Samples were stored in amber bottles that were kept in a refrigerator until they were processed in the laboratory. Each time a sample was collected, the funnel was rinsed with filtered distilled water to remove any particles that may have adhered to it.

2.3. Rain sample processing

A level of consensus regarding the effective methodology is growing in MP research in general, using a form of H_2O_2 digestion in a controlled temperature environment for a selected period in order to remove organic matter present in the environmental samples [30]. So, a digestion process was performed with 30% H_2O_2 solution at 55 °C until complete digestion which varied from 3 to 7 days according to the concentration of organic matter present in each sample. Subsequently, the samples were vacuum-filtered onto 0.45 μm pore-size glass fiber filters. The filters were transferred to Petri dishes for storage and for the detection of the MPs.

2.4. Controls

Prior to use, the glass filters and all glassware used were heated at 450 °C for 4h to eliminate any possible adsorbed organic compounds. To avoid MP contamination, cotton laboratory clothes and nitrile gloves were worn during the sample collection, pretreatment and analysis. In addition, the distilled water used was filtered onto 0.45 μm pore size glass fiber filters to ensure that no MPs were being incorporated into the sample which could lead to overestimation. With the same intention, Petri dishes with blank control filters were air-exposed during the proceedings to discard any airborne contamination. All the laboratory glassware used during digesting and filtering was covered with aluminum foil to prevent airborne contamination. According to these controls, 0 or 1 particles were found, so air contamination was considered to be negligible.

2.5. Visual observation

Filters were initially inspected with a Nikon SM-Z1500 stereomicroscope and the presence of anthropogenic particles was estimated. They were initially identified by physical characteristics, such as size, shape, color, and gloss. Previous studies have classified all particles as MPs, while others have chosen to use the more general term “anthropogenic debris”. In the current study, particles that met the criteria were considered anthropogenic debris but not necessarily plastic. The particles were counted as anthropogenic debris following morphological inclusion criteria [31]: [] homogeneous material [], unnatural shape [], shiny/glassy [], no cellular or organic structures visible and [] unnaturally colored compared to the rest of the sample. They were categorized according to their size, morphology (fragments, films, fibers, pellets, and foams; [32]) and color (blue, light blue, yellow, black, red, transparent and others).

Photographs of all the anthropogenic debris were taken and used to measure the maximum length (mm) taken along with the maximum length (mm) and the color. A hot needle test was conducted on potential plastic particles [33].

2.6. μ-Raman analysis

A random subsample of 7% of the particles (32 items) was manually separated using antistatic tweezers and transferred to a glass slide for Raman spectroscopy analysis. Raman spectroscopy provides information on the small fibers with a high spatial resolution of ~1 μm. The analysis of the results and their comparison with reference material allowed us to identify the chemical composition of a number of fibers. Furthermore, Raman spectroscopy also provided information about the presence of chemical additives in the fibers.

The μ-Raman spectra were collected using a Horiba Jobin Yvon T64000 confocal microscope Raman spectrometer in subtractive mode and cryogenic CCD detection. The samples were excited with a red line of 647.1 nm wavelength provided by a coherent Kr multiline laser. Samples were also excited with a green line of 514.5 nm wavelength provided by a coherent Ar multiline laser in order to improve the spectra. The spectra were recorded by focusing the laser beam on the surface of the particles or fibers using a 50× objective (0.75 NA). The Raman spectra were analyzed using the LabSpect 5.45.09 software program. The chemical identification of the measured fibers or particles was performed by a rigorous comparison of their Raman spectra with reference spectra. In each case, all bands of the proposed substance must be present in the expected wavenumbers and relative intensity. The reference spectra were taken from a spectra library provided by previous studies [34–36] and from our collected reference materials spectra.

2.7. Data analysis

The average, standard deviation, and range of particles (by number) per day were calculated. Graphics and data processing was carried out using R Studio (2022.12.0 version). Deposition (items m^{-2}) was estimated using the number of particles and the surface of the collector. For consistency with previous studies, anthropogenic particles and MP deposition were expressed as items per square meter per day (items $m^{-2}d^{-1}$). The concentration of particles per liter of rainwater was also estimated from the volume sampled each month (items L^{-1}).

2.8. Results comparison

A bibliographic review was carried out by searching for the following keywords in Google Scholar: "airborne microplastics", "deposition microplastics", and "atmospheric microplastics". A map of MP atmospheric concentrations was produced from the studies found. Previous studies were only taken into account when results were expressed as MPs $m^{-2}d^{-1}$ which corresponded to studies carried out with passive samplers. Results from studies based on estimates or that measured MPs indirectly from sediment, street dust and melted snow were excluded.

3. Results

3.1. Abundance

Anthropogenic particles were counted in all the atmospheric fallout samples. Typical particles observed are shown in Fig. 2. Total anthropogenic debris in the atmospheric deposition samples ranged from 35 to 113 particles per sample, with an average of 77 ± 29 particles per sample. In all the samples 461 particles in total were found. The deposition fluxes of anthropogenic debris ranged from 46

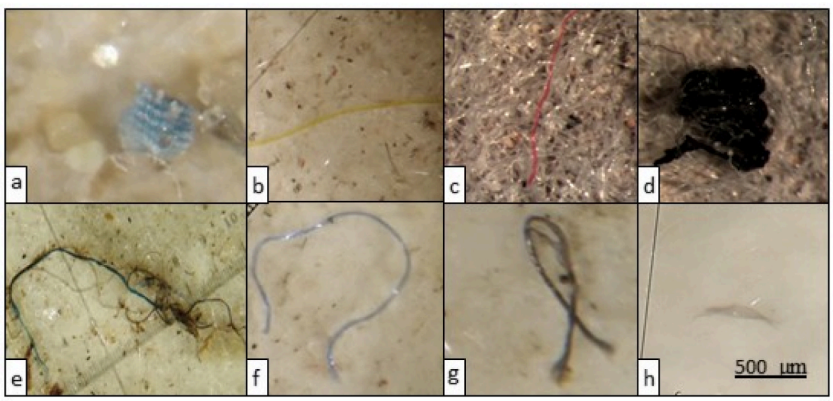

Fig. 2. Typical anthropogenic debris images of selected particles observed (fragments, fibers and film) a. light blue fragment b. yellow fiber c. red fiber d. black fragment e. blue fiber tangle f. light blue fiber g. black fiber. h. black film. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

to 148 items $m^{-2}d^{-1}$, with an average of 101 ± 38 items $m^{-2}d^{-1}$. The highest deposition was observed in November rain water (148 items $m^{-2}d^{-1}$) while the lowest deposition was found in March (45 items $m^{-2}d^{-1}$) (Fig. 3). The number of particles per liter averaged across all samples was 191 particles L^{-1} (ST1). March was the month with the highest volume of rainwater (0.62 L) and presented the lowest concentration (56 particles L^{-1}), while December presented the lowest volume of rainwater (0.215 L) and the highest concentration (260 particles L^{-1}). In comparison to other worldwide locations, anthropogenic debris deposition occurred in the middle range in rainfall of Bahia Blanca, Argentina (Fig. 4).

3.2. Shape

Deposition of anthropogenic debris was grouped by fiber, fragment, or film. Considering all the samples, fibers were the dominant form found representing 95% of the total, followed by fragments (3.1%) and films (2%). In particular, the same situation was observed in March, August, October, and December. However, during September and November the second dominant form was represented by films (3.4% on average) and the third by fragments, 1.5% on average (Fig. 3). It is worth mentioning that particles classified as foam or pellets could not be identified. The presence of small particles (<2 mm), apparently composed of mineral material and multiple-colored fibers, was recognized in the August and October samples, but they were not identified (Fig. 5).

3.3. Size

The particle sizes observed ranged between 0.1 mm and 3.87 mm with an average of 0.71 ± 0.75 mm. Approximately 57% of the total particles were in the 0.1–0.5 mm range, 22% in the 1.00–5.00 range and the remaining 21% were in the 0.5–1.00 mm range (Fig. 6. A). On average, the size of the fibers, fragments and films was 0.73 mm, 0.23 mm and 0.40 mm, respectively. Fiber length was between 0.1 mm and 3.87 mm, fragment diameter was from 0.1 mm to 0.46 mm, and that of the films was from 0.1 mm to 0.8 mm. The most frequent range size was smaller than 1 mm (77.8%) while particles larger than 1 mm represented 22.2% of the total samples (Fig. 6. B). Two exceptional particles larger than 5 mm were also found in the September rainfall depositions.

3.4. Color

The color of the particles is qualitative and the results could be influenced by the treatment of the sample with H_2O_2. Blue color predominated (37.2%) in the total number of samples, followed by light blue (23.3%), black (21.7%), yellow (12%), and red (5.9%) (Fig. 7. A). In particular, the same situation was observed in March, August, September, and December. However, during October light blue color predominated (30.9%) followed by black (25%), blue (23.5%), yellow (11.8%), and red (8.8%). During November blue color predominated (37.5%) followed by black (22.3%), light blue (20.5%), yellow (12.5%), and red (7.1%). (Fig. 7. B).

3.5. Chemical composition

A subsample of 32 items was examined using μ -Raman spectroscopy for chemical identification, all of the fibers ranged from 0.15 to 3.30 mm, which were by far the dominant form of particles found. A total of 20 measured particles presented a Raman spectrum (ST2; ST3), and 12 presented strong fluorescence or no Raman signal when using an excitation laser. Of those 20 particles that a spectrum was obtained, 10% were identified as Cotton black and 5% for Viscose. 40% of the particles generated spectra characteristic of an artificial dye known as Indigo Blue which was associated with blue fibers. From the 8 plastic particles, 50% were identified as Polyethylene vinyl acetate (PEVA), and 12.5% each for polyethylene terephthalate (PET), Polyester, Polystyrene (PS) and polypropylene (PP) material that underwent a strong degradation process. The main band regions for PP are indicated in the figure together the region where spectral changes are expected when degradation processes have taken place (SF1). From the results obtained by

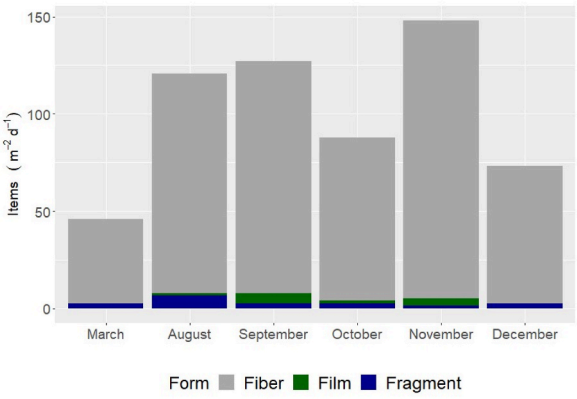

Fig. 3. Abundances in samplings grouped by form.

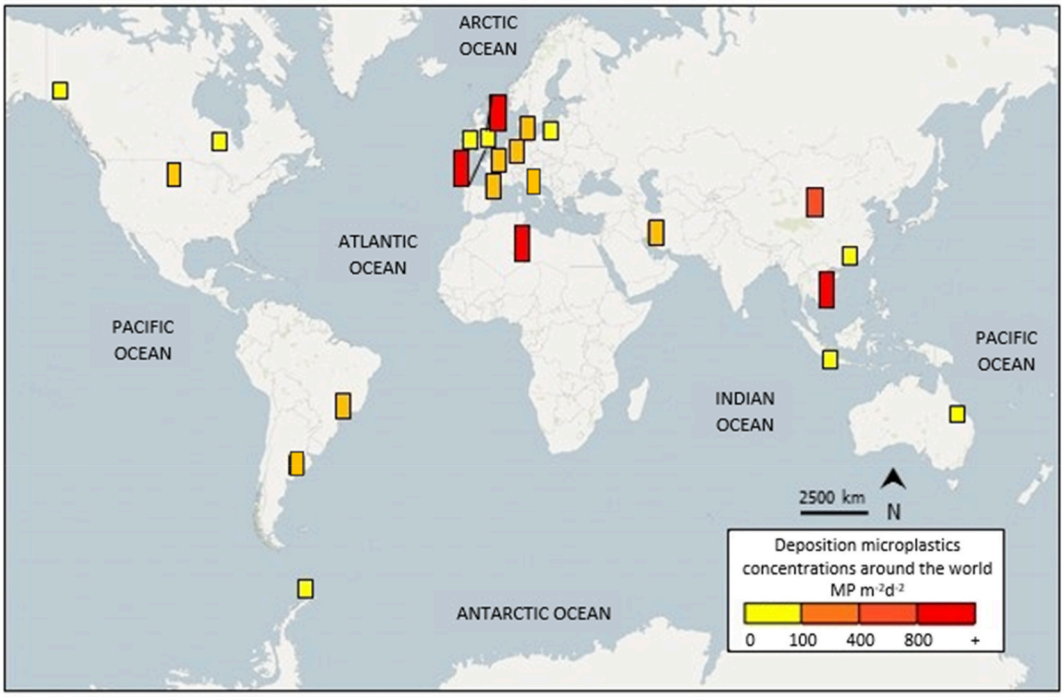

Fig. 4. Atmospheric MP deposition around the world, including the present study.

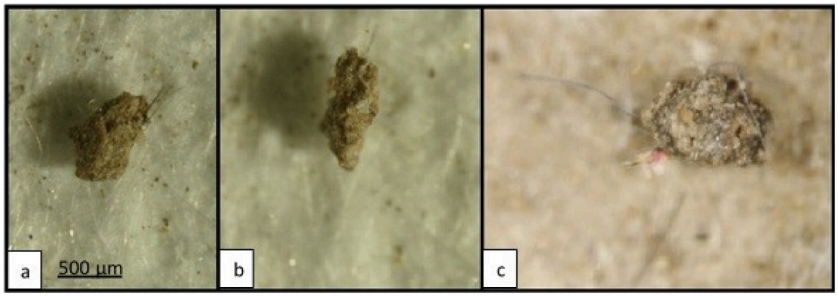

Fig. 5. Plastiglomerates from the rain samples collected in August (a and b) and October (c).

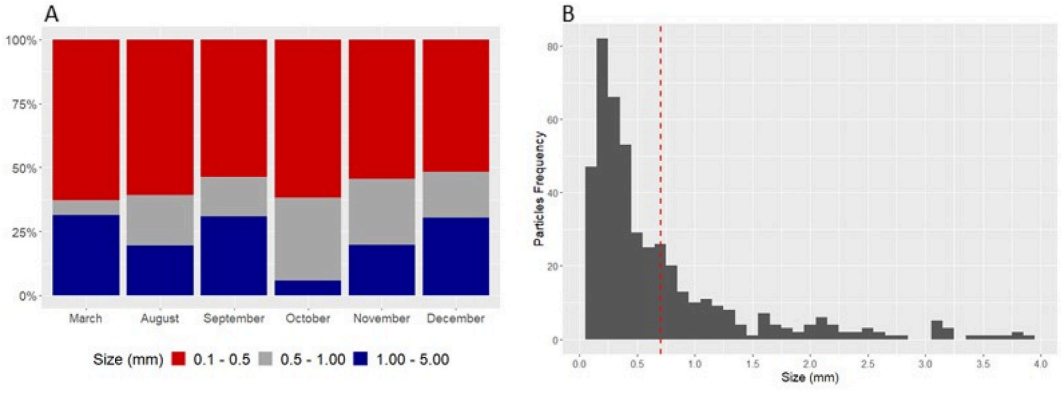

Fig. 6. **A**. Percentage of particles grouped by size and sample. **B.** Frequency distribution of particle size pooled in 0.1 mm.

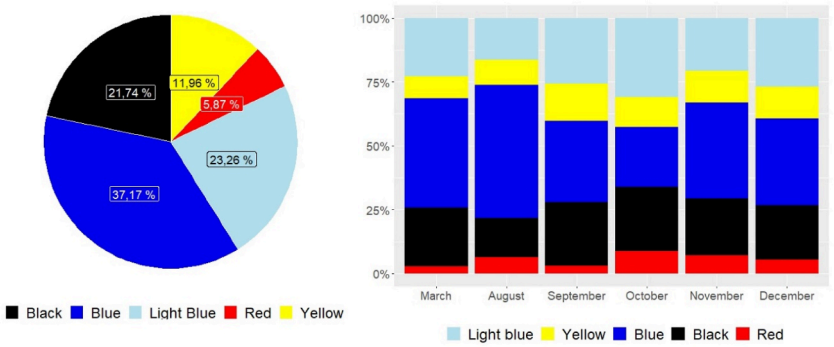

Fig. 7. A. Color distribution in the total samples. B. Color distribution per sample. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

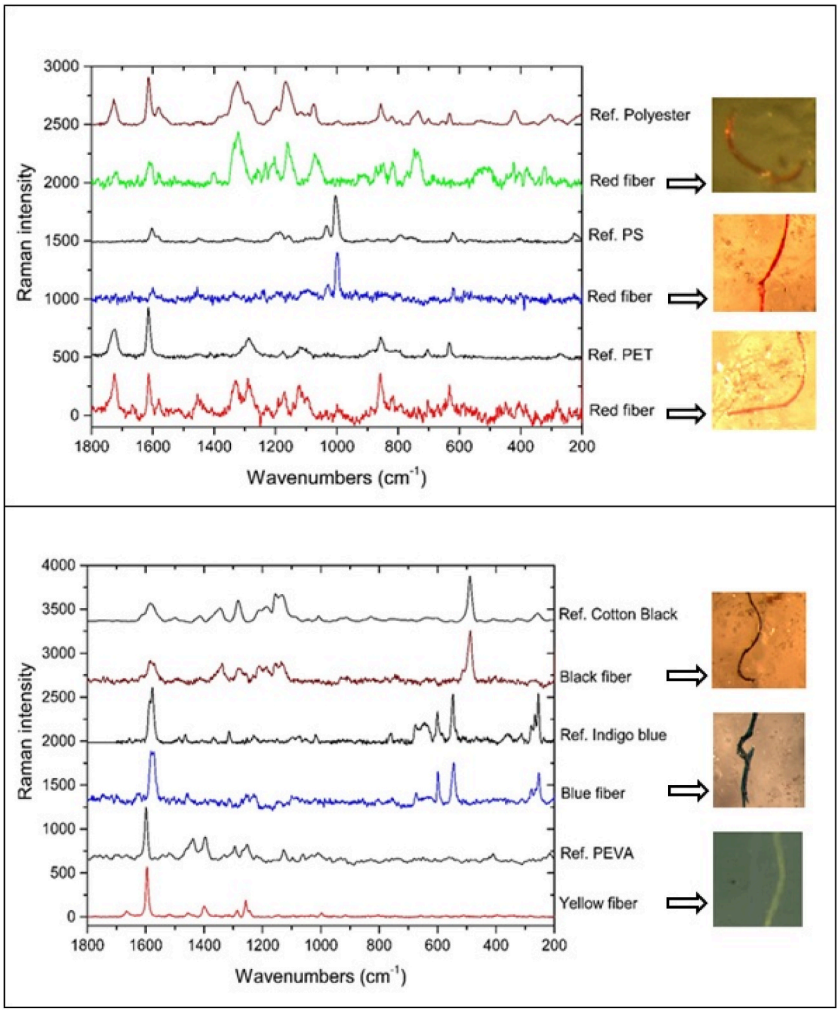

Fig. 8. Raman spectra of selected fibers found in the rainwater: red fibers (March, September, and December samples); black fibers (December sample), blue fibers (March, August, September, October, November, and December samples) and yellow fibers (September, October, and November samples). Excitation wavelength 647.1 nm, laser power: 100 mW, 50× objective (0.75 NA). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Raman, it is estimated that at least 25% of the particles found are plastic (115 particles in total). Mps concentration in a liter of rainfall water ranged from 14.11 (March) to 65.11 (December), with an average of 47.75 MP/L. The deposition fluxes of MPs ranged from 11.46 (March) to 37.02 (November) MPs $m^{-2}d^{-1}$, with an average of 25.25 MP $m^{-2}d^{-1}$. Fig. 8 shows the spectra of selected fibers found in the rainfall water together with the reference spectra.

4. Discussion

In this study we estimated the presence of anthropogenic debris, including MPs, that circulates in the atmosphere of Bahia Blanca and is deposited in rainfall. MP deposition observed worldwide varies significantly from 0 m^{-2} d^{-1} in rural and remote areas of Europe and the USA to more than 1000 particles m^2 d^{-1} in highly urbanized cities of Europe and Asia (details given in ST4). Compared to worldwide locations, the deposition obtained in Bahia Blanca was in the middle range (>100 Mps/day), similar to other urban and peripheral environments such as in China [20] and Ireland [37], respectively. However, it is difficult to make comparisons in studies where sampling methods, polymer characterization criteria and the limit of detection differ. The sampling method probably has a great impact on the MP deposition results [38], but to date, there is no unified method for sample collection. Furthermore, the issue of overestimating the quantity of MPs is emerging when they are mistaken for other anthropogenic particles. For instance, cellulose fibers can originate from natural textiles like cotton or synthetic like rayon [39], but they are generally counted as microplastics. While both rayon and cotton do not pose a risk by themselves, they can contain and release toxic additives such as phthalates and dyes.

At the regional level, the plastic particles found, as well as the predominance of fibers, coincide with the results found in other matrices, such as fish, seabirds and coastal sediments [26,40,41], suggesting that atmospheric transport and deposition are key pathways to understanding the sources of contamination in other compartments and which complete the cycle of MPs in the environment.

The results showed a dominance of small fibers (77.8%) presenting sizes smaller than 1 mm and 95% corresponded to fibers, which matched recent urban reports (e.g. Paris, Dongguan, Shanghai and Yantai) where a dominance of fibers had been found [14,18,20,42], with the exception of Hamburg, which had a predominance represented by fragments [38]. During atmospheric transport, larger fragments can degrade into smaller particles through mechanical processes and reactivity, while fibers can stay longer in the atmosphere and travel farther from their source. In urbanized areas, potential initial sources of plastics, both recently emitted MPs and those persisting in the environment for a long time may circulate between the atmosphere and the ground [43]. The high abundance of fibers present in the samples could be due to their high production rate which results in high waste generation. It is estimated that one of the main sources of fibers comes from the degradation of textiles present in clothing that may be shed and released as clothing wears out or during washing and drying [44]. In contrast, the fragments and films are usually the product of the degradation of larger plastic fragments and present smaller sizes than the limits in this study, which could explain the low proportion of these particles found.

The high abundance of smaller-sized particles may be attributed to their low weight which allows them to remain suspended in the atmosphere for longer and then they are removed during a precipitation event. According to the results, it is observed that the month with the highest volume of rainwater has a lower concentration of particles per liter, indicating that the greater frequency of rains prevents the particles from being suspended and therefore cannot be washed away by the rains. On the contrary, the month of December presented the lowest volume of rainwater and the highest concentration of particles per liter. Although the data must be correlated with other variables such as the direction and intensity of the winds, it could be hypothesized that the particles accumulate in higher concentrations in the atmosphere in the absence or little presence of rain. This conclusion is supported by Loppi et al. [33] who concluded that the dominant dry deposition is likely to accumulate a greater amount of microplastics in the air.

Nearly 15% of plastics production is destined to the elaboration of synthetic fibers, which is highly dominated by the production of polyester, and to a lesser extent Vinyon and polyethylene [45], polymers found in the samples analyzed. The main uses of both natural and synthetic fibers are clothing and apparel [45]. The detachment of fabric materials, wear and tear, and increased consumption have led to an accumulation of these fibers in the natural environment. μ- Raman analysis showed that synthetic polymers only account for a small part of the fibers extracted from rainwater samples. Our characterization revealed that most fibers were dyed cellulose. In the spectra of fibers with a lower concentration of dye, bands originating from cotton and viscose were usually predominant (SF2), while in the case of higher concentrations of dye, the majority of the bands originated from the dye [36]. The occurrence of indigo dye in blue fibers (ST2) is highly indicative of textile sources. Blue jeans microfibers are a form of “natural” microfiber, however, they are chemically processed and are sufficiently persistent to undergo long-range transport and accumulate in environment compartments being often more abundant than synthetic microfibers in environmental samples [46]. Besides, the blue color predominated as brilliant colors are more visible, whereas white, transparent, or translucent particles may be underrepresented during visual inspection [47]. Some studies claim that man-made cellulosic fibers would be expected to be synthetic and they have been included in the MPs count, making an error that results in overestimating the results. In addition, it is interesting to note that the separation of a representative sample, considering the colors and shapes, to analyze with Raman can lead to errors in the characterization since particles of the same shape and color can result in a different polymer composition (as demonstrated in the analysis of different red fibers).

Furthermore, our results show for the first time the occurrence of mineral particles fused with fibers in the atmosphere. In this sense, Corcoran et al. [48] described "plastiglomerates” as multi-composite materials hardened by the agglutination of rock and other materials with melted plastic. The source of these particles is attributed to informal and open burning of plastic trash. This type of plastic has only been described in marine environments where the melted polymeric matrix of unknown origin encapsulates materials such as sand, rock, shell fragments, and wood [48]. Moreover, Turner et al. [49] also described the occurrence of particles similar in appearance to the plastiglomerates described by Corcoran et al. [48], but these plastics, which they called pyroplastics, were embedded in rocky outcrops on the beach and cliffs. Pyroplastics are distinctly different from manufactured plastics, they are

geological in nature and are defined by an amorphous matrix that is formed by burning or melting plastic [49]. It is estimated that where there is abundant debris and a heat source, conditions exist for the formation of plastiglomerates. They can even form with persistent sun and tidal action [48]. Although these descriptions resemble the particles found in this work, the possible source is unknown.

5. Conclusions

While a dominance of small microfibers was found, considering the shape and colors, textile was pointed as the probable major source for the area. The characterization of a subsample of microfibers performed by Raman microscopy led us to confirm the presence of PP, PET, PEVA, polyester and anthropogenic fibers containing dyes (indigo-dyed fibers, cotton black and dyed viscose fiber) in the rainfall water. In urban environments, MPs can coexist with pollutants coming from vehicular and industrial emissions, as in the case study, due to the proximity to the industrial area of the city. For the first time in Argentina we showed the occurrence of MPs in the rainfall. Future studies on the health effects of both MPs and their associated contaminants should be carried out in order to propose efficient plastic waste management measures, with health as the main focus of attention. Further, it would be interesting to be able to observe differences between wet and dry deposition as the latter is influenced by different processes, such as wind speed and direction.

Author contribution statement

Villafañe Belen: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Ronda Ana, PhD: Contributed reagents, materials, analysis tools or data.
Lucas Rodríguez-Pirani, PhD; Lorena Picone; Rosana M Romano; Marcelo Pereyra: Performed the experiments.
Leandro Lucchi: Performed the experiments; Contributed reagents, materials, analysis tools or data.
Andres Arias, Ph.D.: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Data availability statement

Data will be made available on request.

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.

Acknowledgments

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Appendix A. Supplementary data

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