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Pilot study on microplastics in the Suquía River basin: Impact of city run-off and wastewater treatment plant discharges in the mid-2010s

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ABSTRACT

The presence of microplastics (MPs) in both water and sediment has been extensively reported in marine environments, with fewer works on their presence in rivers, particularly in rivers affected by semi-arid conditions. It is likely to expect a different behavior of MPs in the sea with respect to a river, mainly because of differences in the hydrology, salinity, etc. Thus, our main goal was evaluating the presence and behavior of MPs in a river belonging to a semi-arid region (Suquía River, Province of Córdoba, Argentina), looking to assess the main sources of MPs and verifying their changes along a river section that includes a big city and its wastewater treatment plant (WWTP). Sampling was performed in October 2016, with the river at its lower flow. Results show that MPs are present in high amount throughout the studied river basin, even upstream from the main city. The WWTP was identified as one of the main sources of MPs to the stream, but the city run-off was the responsible for the higher amount of MPs in sediments. Our results show qualitative and quantitative differences with other reports on MPs in water and sediment of rivers, having a range of MPs that exceeds most previous reports in rivers. Furthermore, among MPs found, fibers were more abundant than plastic fragments, triggering the need for a deep evaluation of probable negative effects of fibers on the aquatic biota.

1. Introduction

Worldwide plastic pollution has become a growing issue since the first reports of small plastic particles found in surface sea water in the earlier 1970’s (Bergmann et al., 2015; Carpenter and Smith, 1972), also known as microplastics (MPs). Since then, the global annual plastic production expanded dramatically, exceeding 368 million tons in 2019 (PlasticsEurope, 2020). As a result, the concentration of MPs in the marine surface water increased over the last decades, raising the public interest, fed by scientific reports about the potential impacts of MPs in the aquatic environment (Auta et al., 2017). So far, there is no a universally accepted definition of MPs, although most reports consider plastic particles with a size < 5 mm as MPs. The lower bound can vary according to the author but in this study the size of 1 µm will be considered. Nanoplastics are defined as those particles with a size ranging from 1 to 1000 nm. A size threshold of 500 micrometres (µm) is often applied to differentiate between large and small MPs (Brander et al., 2020; UNEP, 2020).

MPs can result from the so called primary microplastics (*e.g.* microbeads in cosmetic peeling products), or secondary microplastics (*e.g.* breakdown products from larger plastic pieces (Cole et al., 2011; Dris et al., 2015). According to their shape, MPs can be classified in fibers (length >> diameter) and fragments (diameter >> thickness) (Dris et al., 2018). The biggest concern with MPs in the environment is due to its potential bioaccumulation in the aquatic food web (Lusher et al., 2017), increasing the risk to reach humans through the ingestion of marine organism having MPs. Furthermore, MPs can function as vectors for different organic pollutants (*e.g.* PCB or PBDE), adsorbed on their surface (Pozo et al., 2020; Tan et al., 2019). The accumulation of MPs in the aquatic biota can lead to biodiversity loss and increased risks for human health as stated above (Wang et al., 2021). A big part of the research on MPs has been performed in marine envi-

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ronments (Auta et al., 2017; Bergmann et al., 2015; Cole et al., 2011; Hidalgo-Ruz and Thiel, 2013), with fewer studies on MPs in freshwater systems (Eerkes-Medrano et al., 2015; Wang et al., 2021), and much fewer on MPs in river basins (Dris et al., 2015; Horton et al., 2017). Thus, an emerging need to study the fate and accumulation of MPs in rivers facing diverse pollution scenarios is observed from the reviewed literature on MPs. Waste management practices, including wastewater treatment plant (WWTP) and solid residues disposal, were reported to have a significant impact over MPs release on the environment (Wagner and Lambert, 2018). The need to increase field data bases about plastics in freshwater environments has been recently highlighted, especially in rivers from developing countries where poor waste management occur (Blettler et al., 2018).

Even if during the last years a huge number of studies about environmental MPs distribution were published, evidencing a strong predominance towards marine reports, database about South America MPs pollution is poorly represented compared with other world regions. Following worldwide tendency, reports from Brazil are mostly focused in marine environments and estuaries impacted by river discharges (Lima et al., 2014; Lins-Silva et al., 2021; Olivatto et al., 2019) while, very scarce studies evaluated MPs concentrations in water and sediments from freshwater ecosystems. According to previous publications, only five studies quantified MPs in freshwater habitats: three analyzed river and lagoon sediments (Bueno et al., 2021; Gerolin et al., 2020; Toyama et al., 2021) and two water samples, one from a lake and one from a river (Bertoldi et al., 2021; Ferraz et al., 2020, respectively). Several studies reported MPs in marine environments from Chile, Uruguay and Argentina (Castillo et al., 2020; Hidalgo-Ruz and Thiel, 2013; Lozoya et al., 2016; Ríos et al., 2020; Rodríguez et al., 2020; Ronda et al., 2019). While eight studies informed MPs levels in water and sediments of freshwater environments from Argentina (Alfonso et al., 2020a, 2020b; Blettler et al., 2019, 2017; Mitchell et al., 2021; Montecinos et al., 2021; Pazos et al., 2021, 2018), no data were found for the other two mentioned countries at this time. Moreover, MPs concentrations in river waters for the three mentioned countries were not reported at this time. Thus, also in South America, there is an emerging need of studying MPs in freshwater and river basins, considering both water and sediment, in addition to identify potential MPs sources, namely WWTPs, cities runoff, among others.

According to previous studies, MPs sources in urban area can be associated with atmospheric fallout, urban runoff, wastewater discharges (with different grade of treatment), automobile traffic, etc. Fibers have been reported as the more frequent shape in atmospheric fallout (Cai et al., 2017). The level of MPs in urban runoff was strongly associated with previous rain events. However, predominant shape varied according to the city while differential pattern in transport was observed depending on their shape. Treilles et al. (2021) reported concentrations of fragments higher than fibers in urban stormwater. While no relationship or trends were observed for fibers, the highest fragments concentrations were observed before the flow rate peak of the rain events. Otherwise, Dris et al. (2018) mention a strong predominance of fibers in urban runoff compared to fragments. Regarding urban wastewater, washing machine effluents have been reported as a significant source of fibers and the percentages of their removal was strongly variable according to the efficiency of the WWTP (Cai et al., 2017; Dris et al., 2018).

The Suquía River basin (Province of Córdoba, Argentina) has been extensively studied, showing an increasing pollution gradient from the upper basin (mountain area), through the middle basin (impacted by Córdoba city with 1.4 mill. inhabitants), with the worse water quality at the beginning of the lower basin, coincident with the release of wastewater treatment plant (WWTP) effluents from Córdoba city to the river. Thus, pollution sources in this river go from point like sewage discharges (including clandestine ones), industrial effluents and emissions; and disperse or nonpoint sources such as urban run-off, automobile traffic and non-point agricultural pollution downstream from the WWTP (Wunderlin et al., 2001; Corcoran et al., 2019; Valdés et al., 2021). The WWTP was identified to have a significant impact over the water quality of the river although the city runoff contribution has been mentioned to not be negligible (Merlo et al., 2011).

Until now, pollutants found in the Suquía River basin range from nutrients to pharmaceuticals, including heavy metals, agrochemicals, petroleum derivatives and antibiotics (Ballesteros et al., 2014; Bonansea et al., 2013; Monferrán et al., 2011; Nimptsch et al., 2005; Pesce and Wunderlin, 2000; Valdés et al., 2014; 2021; Wunderlin et al., 2001). Thus, considering the above-mentioned facts, we are now interested in assess the presence of MPs along the Suquía River basin, looking to identify the relative importance of tentative anthropogenic sources (e.g. urban run-off, domestic activities, etc.) on the release of MPs to a river basin, including the load of MPs from the WWTP. We hypothesize that: (1) MPs partition differentially from river water into sediments depending on their shape; (2) Levels of MPs fragments and fibers vary as the river runs through different urban sections with point and diffuse sources of pollution. To our knowledge, this is the first study seeking to understand the dynamic of MPs in a river catchment, belonging to a semi-arid area, impacted by city run-off and WWTP discharge in South America.

2. Material and methods

2.1. Sampling sites

The five sampling sites are placed along the Suquía River basin (Fig. 1): Site 1 includes mountainous areas upstream from Córdoba City with low urban density and native vegetation, considered the reference site in the present study; Sites 2 and 3 are located within the city but upstream from its WWTP, both receiving urban run-off from the city. Site 2 is located in a sector with open dumps on river banks while Site 3 is located downstream of a rain drainage channel runoff, next to the ringway of the city. Sites 4 and 5 are located 6.6 and 10 km downstream the WWTP, respectively both receive sewage pollution not retained at the WWTP. Geographical localizations of monitoring sites are reported in Table 1. The basin has a high flow period during the wet season (December to April) with an average flow of 15 m^3s^{-1}, whereas during the dry season (May to November) its estimated average flow is 2.7 m^3s^{-1} (Amé and Pesce, 2018).

2.2. Sampling

The sampling took place during the dry season (October 2016), with the river at its lower flow (Pesce and Wunderlin, 2000). Two water samples and two sediment samples were collected from each site. Water samples ($n = 2$ at each site) were taken the middle of the river channel, 20 cm below the river surface and a river depth up to 1 m, using a sieve-array consisting of four sequential sieves (4.75; 2; 0.6, and 0.075 mm, respectively), having a diameter of 20 cm (Masura et al., 2015; Qiu et al., 2016). Thus, microplastics were retained in last sieves, avoiding clogging by elements dispersed in the water flow (fragments of plants, paper, etc.). The sampling time was of 5 min. The water velocity was registered on the surface, measuring the time used by a floating device to cover a given distance ($n = 3$ for each sampling site). Thus, the amount of water filtered at each point was calculated (Table 1). After sampling, sieves were thoroughly cleaned using RO (reverse osmosis) water (ca. 200 mL), collecting the material retained in filters (2 to 0.075 mm) into labeled glass jars with metallic caps. The material from the first sieve (4.75 mm) was discarded (large MPs were not observed in the discarded material). All used glass jars and equipment were pre-cleaned beforehand with RO water before taking each sample.

Sediment samples ($n = 2$ at each site) were taken from the first 15 cm of benthic zone of the river, using a stainless-steel shovel (Masura et al., 2015; Qiu et al., 2016). Samples were stored into glass jars (250 mL) with metal caps.

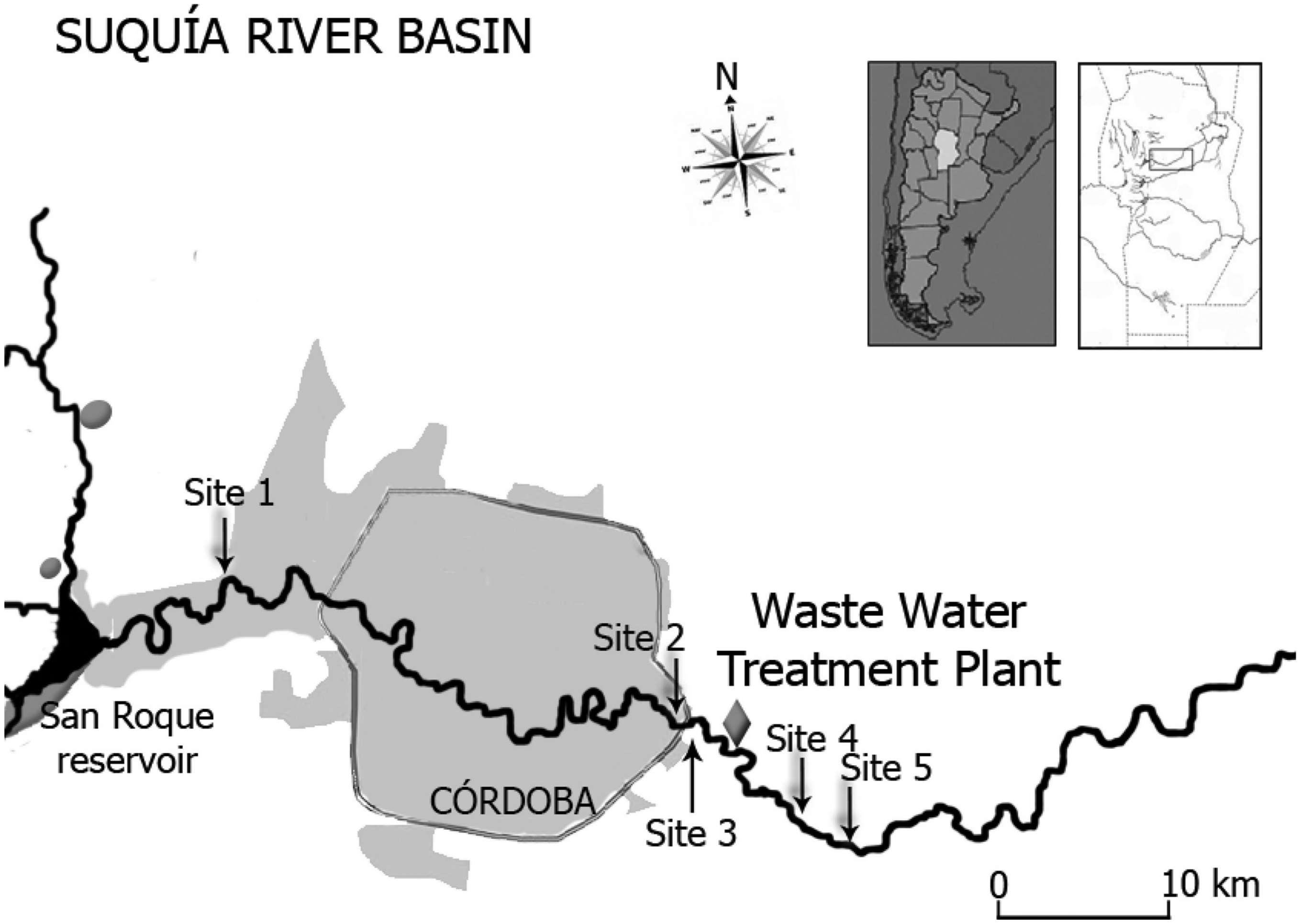

Fig. 1. Sampling sites along the middle and low Suquía River Basin (Córdoba, Argentina). ◆ Waste Water Treatment Plant.

Table 1
Sampling areas at the Suquía River basin (Córdoba, Argentina), showing few physical-chemical parameters and filtered volume.

	Sampling Site (Name)	coordinate SOUTH	coordinate WEST	pH	Conductivity (µS cm^{-1})	T (°C)	Dissolved Oxygen (mg L^{-1})	Superficial Water Speed (m s^{-1})	Filtered Water (m^3)
1	El Diquecito - La Calera	31° 21′ 24.90"	64° 23′ 19.20"	8.9	272	18.2	9.4	0.98	0.09
2	Campo de la Ribera	31° 24′ 32.19"	64° 7′ 40.62"	7.6	566	18.4	6.8	1.39	0.13
3	Circunvalación	31° 24′ 23.25"	64° 7′ 21.45"	7.5	531	18.8	7.6	0.83	0.08
4	Chacra de la Merced	31° 25′ 21.86"	64° 3′ 14.95"	7.6	673	19.6	3.1	0.96	0.09
5	Puente Negro	31° 25′ 50.09"	64° 1′ 51.63"	7.7	628	19.9	2.5	2.23	0.21

Both water and sediment samples were ice cooled and transported to the laboratory within 4-5 h.

2.3. Sample pre-treatment

Primarily, all the samples were oven dried (50 °C for sediments and 75 °C for water; until constant weight, 3-5 days). Temperatures ≤ 80 °C are considered to be below the melting point of the most common plastic types (Horton et al., 2017). Dried sediment samples were then sieved using a mesh size of 4.75 mm to discard materials with a higher granulometry. H_2O_2 (30%, analytical grade, ca. 20 mL) was carefully added to sieved sediment (ca. 20 g) contained in a glass flask, within a good ventilated hood, stirred with a metallic bar until obtaining a slurry, which were kept overnight at 60°C (until evaporation of added H_2O_2). This procedure was repeated during 5 days until complete digestion of the organic material present in sieved sediments. Total solids arising from evaporated water samples were carefully treated with 7 mL H_2O_2 into a laboratory hood, kept overnight at 60°C, repeating these steps during 5 days until digestion of organic material contained in the solid residue (Nuelle et al., 2014).

2.4. Flotation

To extract MPs from digested samples a flotation density separation was carried on. Briefly, 3 g of sediments were weighted in a glass vial, 10 mL of filtered $ZnCl_2$ solution with a density of 1.7 g mL^{-1} were added and left for 3 days to settle. The flotation procedure is based on the specific densities of different plastics, ranging from 0.8 to 1.4 g cm^{-3},whereas sand or other sediments have densities of about 2.65 g cm^{-3}; thus, plastic particles were separated by an overflow method (Hidalgo-Ruz et al., 2012).

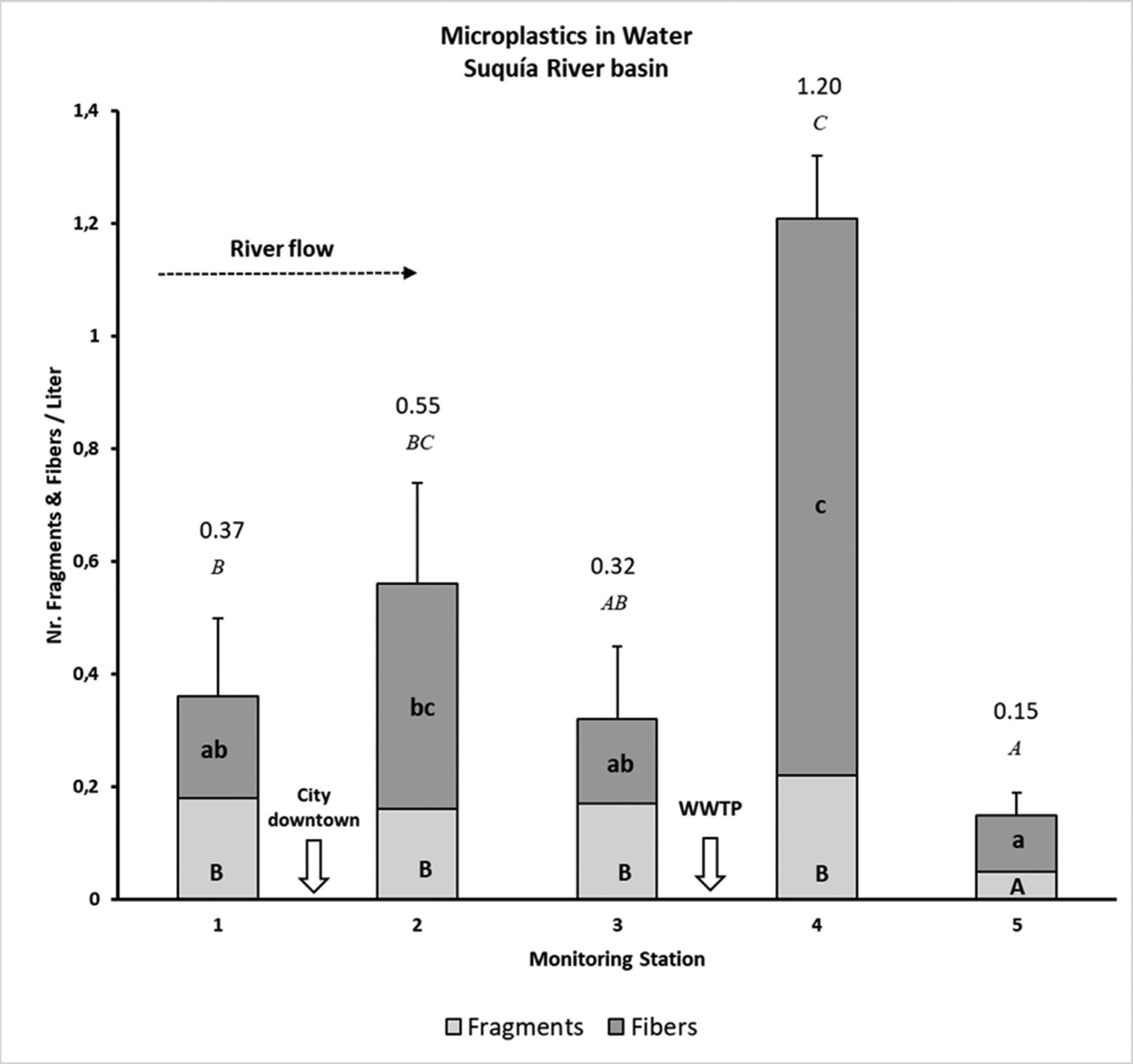

Fig. 2. Distribution of microplastics in the water of the Suquía River.
Fig. 2 (footnote): Results from ANOVA (Log10 transformed) correspond to: Fragments(uppercase); Fibers (lowercase); the sum of Fragments + Fibers (uppercase italics). Error bars correspond to one SD of the sum of Fragments+ Fibers. The sum of Fragments+ Fibers per liter, corresponding to each monitoring site, is indicated in the upper part of each column.

2.5. *Filtration and microscopically analysis*

Supernatants resulting from the flotation procedure were filtrated using a Büchner funnel, 0.45 μm nitrocellulose filters (Sartorius Stedim Biotech, Germany) and vacuum. The visual inspection of the filters was performed using a Leica CTR5000 microscope (Leica Microsystems, Hong Kong, China) at 4x, 10x, 20x, and 40x magnifications. The criteria applied for defining microplastics were based on the work of Norén (2007):

- No cellular or organic structures visible in the plastic particle or fiber.
- Equally thick fibers, no tapers towards the ends.
- Three-dimensional bending of the fibers.
- Clear and homogeneously colored particles.

After visual inspection the detected MPs were categorized into the two most abundant shapes - fibers and fragments. The average numbers of MPs (considering separately fibers and fragments) for the water samples are reported by liter, considering the total volume of water filtered at each monitoring site (Table 1, Fig. 2). On the other hand, MPs in sediments are reported by kg dry weight (d.w.), considering the amount of starting dry sediment used (before sieving) (Fig. 3).

2.6. *Spectroscopic analyses*

Vibrational spectroscopy was used to delve into the chemical composition of selected plastic-like items. A sub sample ($n = 21$) of randomly selected items larger than 0.5 mm were analyzed by attenuated total reflection infrared spectroscopy (ATR-FTIR), using a Nicolet iN10 MX Ultrafast spectrometer equipped with a SlideOn MicroTip Ge-ATR crystal and analyzed with Omnic 8 software. Spectra recorded in the range of 500 to 3500 cm^{-1} with a resolution of 4 cm^{-1} and digital subtraction of blank spectrum were made until the complete disappearance of signals corresponding to nitrocellulose of filters, based on NO_2 peaks at 1647 and 1280 cm^{-1}. The obtained patterns were compared with reference spectra. In this regard, the HR Nicolet and Hummel Polymer

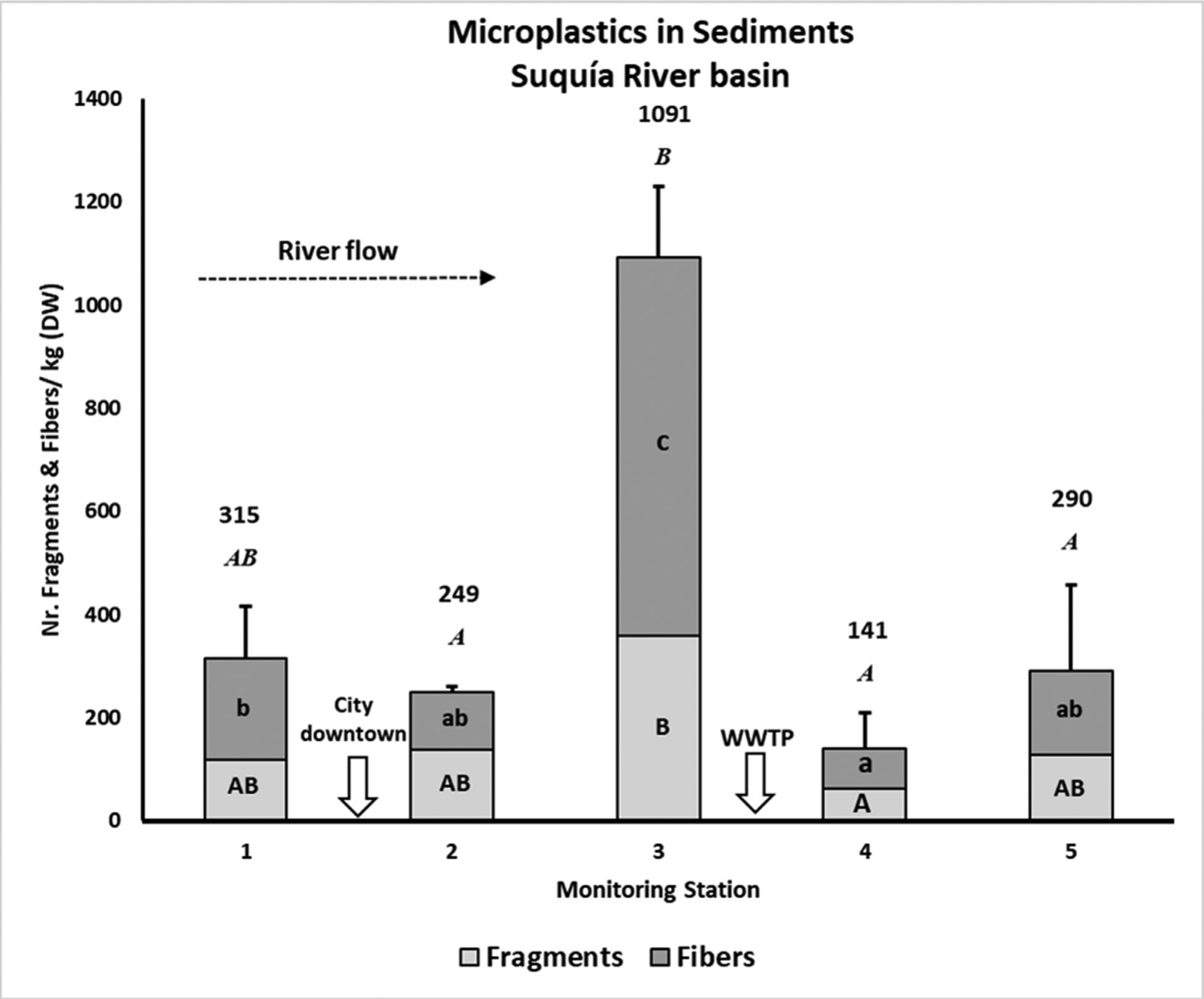

Fig. 3. Distribution of microplastics in the sediment of the Suquía River.

Fig. 3 (footnote): Results from ANOVA (Log10 transformed) correspond to: Fragments (uppercase); Fibers (lowercase); the sum of Fragments + Fibers (uppercase italics). Error bars correspond to one SD of the sum of Fragments + Fibers. The sum of Fragments + Fibers per kg, corresponding to each monitoring site, is indicated in the upper part of each column.

sample libraries were used, in addition to a personal library of pure polymeric materials recorded with the same acquisition parameters mentioned above.

2.7. Quality assurance and quality control

Strict measures for contamination control, which are essential for quality control and quality assurance, were applied (Grillo et al., 2022). All working surfaces and materials were cleaned with acidified ultrapure water (0.2% HCl) and 70% alcohol. Water and sediment samples were collected using metallic material (sieves and stainless-steel shovel) pre-cleaned beforehand with RO water. Samples were immediately transferred to pre-cleaned glass jars. In the laboratory, samples were processed in fume hood to avoid atmospheric deposition. Also, laboratory coats and nitrile gloves were worn for all procedures to reduce cross contamination. All solution (H_2O_2, $ZnCl_2$, RO water) used in the MPs extraction procedure were filtered using a 0.45 μm nitrocellulose filters previous their use. Plastic materials were avoided as much as possible and metal or glass laboratory materials were used for the manipulation of the samples. Samples and materials used during the extraction protocols were kept covered with aluminum foil as much as possible. All samples were collected and analyzed by duplicate for each site. Blanks were processed at the same time than samples using the same protocol previously described and MPs counted following the described criteria. Plastic fragments were not identified in blanks while an average of 3.5 fibers was found (n= 4).

2.8. Statistics

All values are expressed as mean and standard deviation. Analysis of variance (ANOVA) was used to assess significant differences among log-transformed MPs concentrations. The normality (Shapiro Wilks test) and the homogeneity (Levene's test) of the data were previously checked and a posteriori test, LSD Fisher test with Bonferroni errors correction, was applied ($P< 0.05$). Infostat (Version 2013p, Di Rienzo et al., 2016) were used for all statistical analysis.

3. Results and discussion

3.1. Water samples

Decay in water quality parameters was observed along the Suquía River with an increase in conductivity and a decrease in dissolved oxygen while the pH and temperature remained constant in studied sites

(Table 1). Previous studies reported a similar pattern and described a significant impact of Córdoba city on water quality compared to the river areas located upstream (Site 1 of the present study). The WWTP, but also the urban runoff and discharges from La Cañada Brook, were identified as the main responsible for the negative impact on the river (Merlo et al., 2011; Wunderlin et al., 2001).

The levels of MPs pollution along the Suquía River can be seen in Fig. 2. The highest number of microplastics per liter (1.21 MPs L^{-1}), was found at Site 4, which is located close downstream from the WWTP (ca. 6.6 km). The number of MPs in this station is about eight times higher than the one detected at site 5 (ca. 10 km downstream the WWTP), which had the lowest MPs numbers (0.15 MP L^{-1}). The second highest level of MPs in water (0.55 MPs L^{-1}) was found at Site 2, located downstream from the city downtown but upstream from the WWTP. Regarding the shape of quantified MPs, fibers were predominant over fragments in all the mentioned sites with an 82%, 66% and 72% in Sites 4, 5 and 2, respectively. This result is in agreement with previous studies where fibers have been reported as the more frequent shape in atmospheric fallout, wastewater discharges and urban runoff (Dris et al., 2018; Treilles et al., 2021). Moreover, during the previous three months of the MPs monitoring, precipitations in the city ranged from 0 to 2 mm with absence of city runoff. Instead, during October 2016 precipitations reached 100 mm with streets flood and runoff (BCCBA, 2016).

Among recognized colors, red, blue, transparent, orange, pink and black were observed for fibers while blue, red, green and black were identified for fragments.

Looking at Fig. 2, it is evident that MPs show a different behavior, depending on their shape. In effect, fragments did not show significant differences along the river, with the exception of Site 5 that shows a significant drop of fragments per liter (Fig. 2). It is worth mentioning that neither the city nor its WWTP are increasing the number of fragments per liter in the Suquía River, which means that these are not evident sources for this kind of pollutants. On the other hand, it is also obvious that the WWTP is releasing a big number of fibers to the river (Fig. 2, site 4). Also, the city seems to be contributing to the increase of fibers in the river (Fig. 2, site 2), although this was not statistically significant. During the last years, strongly variable charges of MPs in WWTP' effluents have been reported including average concentrations of 2.02 ± 0.40 particles L^{-1} in Bandar Abbas City (Irán), 12.8 ± 6.3 particles L^{-1} in Madrid (Spain) and 276.3 ± 137.3 particles L^{-1} in different WWTP from Mauritius (Legan et al., 2020; Naji et al., 2021; Ragoobur et al., 2021).

Concentrations of MPs in WWTP effluents is strongly related with the treatment efficiency but also with the charge of plastic particles in the WWTP' influents (range from 1 to 675 MP L^{-1}; Ngo et al., 2019; Xu et al., 2021). Even whit a high efficiency of the WWTP (>90%), the load of microplastics can represented an approximate of 350 particles m^{-3} in the receiving river (Legan et al., 2020). Considering particles shape, fiber, fragment, and film are the main microplastic types found in the influent but fibers are the shape most frequently found (Ngo et al., 2019; Zhang et al., 2021). In the present study, the access to WWTP for MPs quantification in sewage effluents was not possible. Even so, the WWTP can be considered as one of the main sources of fibers to the river water, particularly for Site 4. This WWTP is a secondary treatment plant that has been working incorrectly because of lack of facility maintenance and increased population (Valdés et al., 2021). When overloading occurs, urban sewage is by-passed without treatment with a high negative impact in the river water quality, particularly in the dry season. Therefore, present results should be compared to rivers receiving poorly treated sewage effluents. Regarding the Site 2, levels of MPs quantified can be attributed to city runoff and clandestine domestic discharges.

So far, the amount of MP detected in water samples of the Suquía River are among the highest reported in rivers from different world regions including South America (Wang et al., 2021). Namely, the Suquía River showed an average of 0.52 MPs L^{-1}, ranging from 0.15 to 1.2 MPs L^{-1} at stations 5 and 4, respectively (Table 1S). Previous reports on MPs in rivers have shown a huge variability of concentrations, mainly due to employed methodology, ranging from 0.00004 to 3622 particles L^{-1} (Wang et al., 2021). Even so, concentrations > 0.3 MPs L^{-1} are usually less frequent. Among those rivers showing an important load of MPs, an alarmingly high numbers of MPs were reported for the Kinnickinnic River in USA, ranging from 545 to 3622 particles L^{-1} (Simmerman and Coleman Wasik, 2020). Rodrigues et al. (2018) reported MPs water concentrations in the Antuã River (Portugal), known to present intensive anthropogenic activities, similar than those from Suquía River (Table 2). It is worth to remark that most MPs detected were fragments and fibers associated with urban point sources (storm water outfalls and WWTP), which reached levels up to three times higher downstream of the city, compared with upstream locations, being a similar case than the observed in the Suquía River during this work. Further, in the Wei River from China the concentration varied from 3.67 to 10.7 particles L^{-1}, with a clear predominance of fibers (50.1%) associated, among others, with domestic sewage discharge (Ding et al., 2019), which is the case in the Suquía River. In concordance, Han et al. (2020) reported fibers as the principal MPs shape (more than 90%) in the Yellow River in China, pointing out domestic sewages as one of the major sources of them, mainly due to the inefficiency of WWTPs filtration systems to remove these particles. The huge impact of WWTPs on MPs concentrations was reported by Leslie et al. (2017), who found high MPs concentrations in the influents (68–910 particles L^{-1}) as well as in the effluents (51–81 particles L^{-1}) of seven WWTPs in the Amsterdam region. Moreover, Liu et al. (2020) reported concentrations of MPs in water significantly lower in sites located upper reaches of WWTPs than downstream of the WWTPs. This shows that even the effluents of WWTPs can carry high concentrations of MPs, which is in agreement with our current results at site 4, downstream from the WWTP (Fig. 2). There are only few reports regarding levels of MPs in South America, evidencing a lack of information from countries as Chile and Uruguay (Table 2). Surprisingly, only two reports of MPs were found for Brazilian freshwaters, which reported concentrations ranged from 0 to 940 particles L^{-1}. The most frequent shapes found were fibers in the Sinos River (Ferraz et al., 2020), and fragments in the Guaíba Lake (Bertoldi et al., 2021). Domestic sewages were mentioned as the principal source of fibers in the river catchment, considering that less than 10% of discharges receive treatment before to reach the watercourse (Ferraz et al., 2020). In Argentina, six reports informed MPs in freshwater with variable concentrations (from 0.0003 to 23,600 particles L^{-1}) although only one study (Montecinos et al., 2021) informed levels surpassing the level of MPs found in the Suquía River. In all the cases, fiber was the predominant shape.

To our best knowledge, this study is the first in the region to describe MPs contamination gradient along a stretch of river containing diverse MPs sources, including WWTP, urban run-off, clandestine domestic discharges among others, considering both water and sediment. Even when Montecinos et al. (2021) mentioned the occurrence of a WWTP discharge upstream of the monitored site, their work did not report data upstream from the WWTP, which preclude a clear conclusion on the amount of MPs arising from the WWTP, comparing MPs concentrations detected before and after the wastewater discharge.

It is difficult to make a straight comparison of our results with previous reports, mainly because of differences in the minimal sieve used during sampling (Table 2). All the other South American studies used smaller sieve pore which probably imply an underestimation of MPs concentrations in the studied sites. Moreover, our results show concentrations of MPs that are above the average reported for most freshwater systems from other world regions (Wang et al., 2021), but also from Argentina and Brazil, except those informed by Montecinos et al. (2021) and Ferraz et al. (2020). Taking into account maximal concentrations, the Suquía River surpassed between 3.5 and 636-times levels reported by all the other South American authors (Table 2). These results point out the need for future studies about MPs levels in the studied freshwater systems, delve into the contribution of the different sources reaching the Suquía River as well as to evaluate the possible risks for both the environment and human health.

Table 2

Microplastics reported in water and sediments of freshwater ecosystems in South American countries and other world regions. Mean, minimum and maximum concentrations, predominant shape/s, identified polymer, percentage (%) of the predominant shape and minimal sieve used are informed when information was available. Polymers references:polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyurethane (PU), polystyrene (PS), low-density PE (LDPE), polytetrafluoroethylene (PTFE), polyamide (PA), poly(ethylene-propylene)(EPC), polyvinyl chloride (PVC). *Data obtained from plots in Pazos et al. (2018).

	Freshwater						
	Country	Site	Water concentration (particles L^{-1})	Predominant shape	Identified polymer	Minimal sieve used	Reference
South America	Argentina	La Salada Lake	Min: 0.14 – Max: 0.18 Mean: 0.14	Fibers (70%)	Not informed	47 μm	Alfonso et al., 2020
	Argentina	Irrigation channel (main affluent of La Salada Lake)	Min: 0.04 – Max: 0.14 Mean: 0.06				
	Argentina	Patagonians lakes	Min: 0.0003 – Max: 0.0019 Mean: 0.0009	Fibers (≥ 60%)	PET, PU, PP, PS	38 μm	Alfonso et al., 2020b
	Argentina	Langueyú Stream	23600 (without digestion) 8700 (with digestion)	Fibers (56 %), fragments (44%)	PET, PA-based and polyacrilic-based fibers	44 µm	Montecinos et al., 2021
	Argentina	Estuarine (freshwater zone)	Min: aprox 0.025* -Max: aprox. 0.35* Mean: 0.139	Fibers (most frequent)	Not informed	36 μm	Pazos et al., 2018
	Argentina	Estuarine (freshwater zone)	Min: 0.005 - Max: 0.110 Mean: 0.024	Fibers (most frequent)	PE, PP	36 μm	Pazos et al., 2021
	Argentina	Suquía River	Min: 0.15 - Max: 1.21 Mean: 0.52	Fibers (up to 82%)	Cellulosic and cellulosic mixed with polyester fibers	75 μm	This study
	Brazil	Sinos River	Min: 0 – Max: 940 Mean: 330.2	Fibers (89.4 %)	Not informed	37 μm	Ferraz et al., 2020
	Brazil	Guaíba Lake	Min:0.012 - Max: 0.061	Fragments (82%)	PP, LDPE, PTFE, PA, PU, PS	60 μm	Bertoldi et al., 2021
Other world regions	India	Netravathi River	Min: 0.056 - Max: 2.328 Mean: 0.288	Fibers (51.59%), Films (34.92%)	PE, PET, PP, PVC	300 μm	Amrutha and Warrier, 2020
	Portugal	Antuã River	Min: 0.058 - Max: 1.265	Fragments (up to 49.6 %), foams (up to 42.2%), fibers (up to 37.8%), films (up to 27,6%)	PE, PP, PS, PET	55 μm	Rodrigues et al., 2018
	USA	Los Angeles River / San Gabriel River	Min: < 0.001 / 0 - Max: 0.123 / 12.652	Foam, pellets, fragments	Not informed	333 μm	Moore et al., 2011Moore et al. (2011)
	Canada	Ottawa River	Min: 0.05 - Max: 0.24 - Mean: 0.1	Fibers (95 %), microbeads	Not informed	100 μm	Vermaire et al., 2017
	China	Haihe River	Min: 0.00069- Max: 0.07495 Mean: 0.01417 ± 0.01464	Fibers (17.4- 86.7%), fragments (6.5 - 50.2%), films (5.3- 41.8%), pellets (1.2 - 62.5%), foams (0.0 - 34.7%	PE, EPC, PA, PP, PS, PU	333 μm	Liu et al.,2020

	River Sediments						
	Country	Site	Sediment concentration	Predominant shape	Identified polymer	Minimal sieve used	Reference
South America	Argentina	Paraná River (shoreline sediments)	Mean: 704 microplastic m-2	Fragments (40.9%), fibers (20%)	Not informed	350 μm	Blettler et al., 2017
	Argentina	Paraná River (shoreline sediments)	Min: 131. Max: 12687 Mean: 4654 particles m-2	Films (48.2 %), fibers (33.1 %)	Not informed	350 μm	Blettler et al., 2019
	Argentina	Paraná River (shoreline sediments)	Min: 2864 -Max: 88224 Mean: 18578 particles m-2	Fibers (93.4%)	PE	350 μm	Mitchell et al., 2021
	Argentina	Suquía River	Min: 141 -Max: 1091 -Mean: 417 particles kg dried sediment-1	Fibers (45% - 67%), fragments (55% - 33%)	Not informed	75 μm	This study
	Brazil	Negro River and Amazon River	Min: 417 - Max: 8178 particles kg dried sediment-1	Fibers (100%)	Not informed	63 μm	Gerolin et al., 2020
	Brazil	ÁguaBranca basin	Min: 0 - Max: 5160 particles kg dried sediment-1	Fibers and fragments	Not informed	75 μm	Toyama et al., 2021
Other world regions	India	Netravathi River	Min:9.44 -Max:253.27 Mean: 96 particles kg dried sediment-1	Fibers, films and fragments	PE, PET, PP	300 μm	Amrutha and Warrier, 2020
	Australia	Brisbane River	Min: 10 - Max: 520 particles kg dried sediment-1	Films, fragments and fibers	PE, PA, PP	0.45 μm	He et al. 2020
	China	Shajinggang River	Mean: 765 ± 276 particles kg dried sediment-1	Spheres (88.98%), fibers (7.55 %) and fragments (3.47 %)	PP, PE, rayon	1 μm	Peng et al., 2018
	Portugal	Antuã River	Min: 18 - Max: 629 particles kg dried sediment-1	Foams (up to 65.4 %), fragments (up to 46.5%), fibers (up to 38%), films (up to 28,6%)	PE, PP, PS, PET	55 μm	Rodrigues et al., 2018
	South Africa	Bloukrans River	Min: 1.0 - Max: 563.8 - Mean: 160.1 ± 139.5 particles kg dried sediment-1	Not informed	Not informed	63 μm	Nel et al., 2018

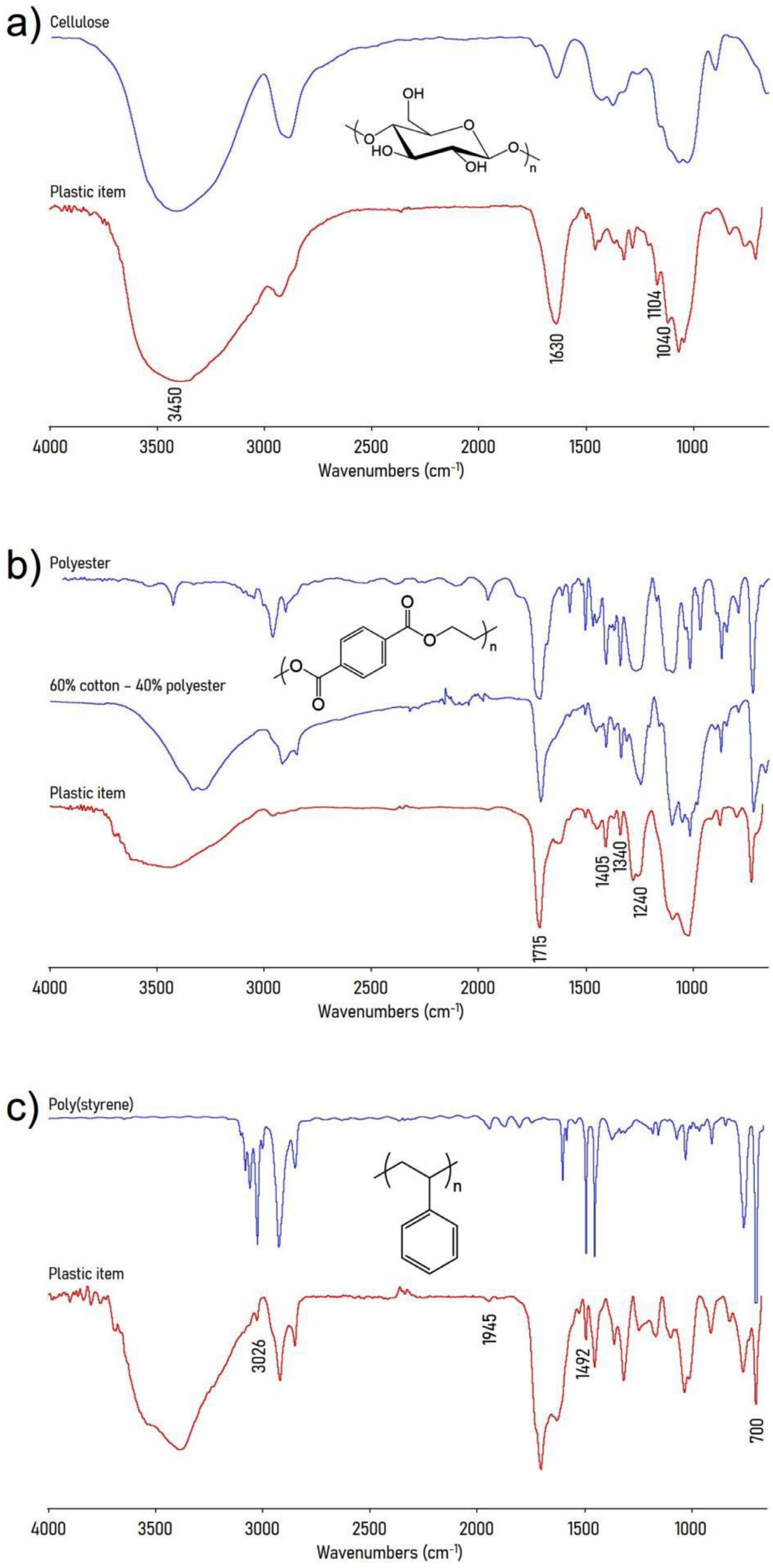

Fig. 4. Infrared patterns/signature of analyzed particles: Samples infrared pattern (blue line) in comparison with a reference of plastic item (red line). **a-** cellulosic fiber, **b-** cellulosic mixed with polyester fiber, **c-** poly (styrene) fragment.

3.2. Sediment samples

From Fig. 3 we can see that the highest amount of MPs in the studied basin section correspond to the Site 3, located downstream from the city downtown but upstream from the WWTP. This site showed significant differences ($p < 0.05$) with all the other points monitored, with 1091 MPs kg^{-1} sediment (d.w.) (358 fragments and 734 fibers per kg; Table 1S). Fig. 3 shows a behavior of MPs in sediments similar to that observed in the water (Fig. 2). That is, fragments are present in fewer amounts than fibers, showing less variation throughout the studied river section. However, it is worth to mention that sediments had the highest amount of MPs (both fragments and fibers) downstream the city downtown, and upstream the WWTP. This site is located in a wide area with the presence of open-air dumps on the banks of the river, which may contribute to the presence of fragments in the sediment. In this section the river has also received the runoff from the entire city.

Additional explanation for the MPs behavior can be attempted by looking at the water velocity and MPs shapes. Frequently, fibers are comprised of polymers that are denser than water and fibrous shapes exhibit a slower settling velocity than other shapes (Bagaev et al., 2017). The Site 3 registered the lowest water velocity along the studied section (Table 1), favoring fibers deposition added to the sandy characteristic of the river sediment in this section (Valdés et al., 2021). Both characteristics can contribute to the deposition in the river bottom of MPs released by the city, which are accumulated in a place with lower turbulence. Moreover, discharges from the ringway could be also contributing to the MPs levels in sediments at this site.

On the other hand, considering MPs introduced in the stream by the WWTP (Fig. 2) the concentration in sediments from the Site 4 was not the expected. However, it is noticeable that effluents are usually strategically dumped in river sections with fast-flowing, which could enable the rapid downstream transport of microplastics. Particles from WWTP are probably filtrated between sites 4 and 5, in a river section that is also characterized by the high amount of sand in the sediment (Valdés et al., 2021). Identified colors of fibers and fragments were the same as reported in water samples.

According to recent studies, average concentrations of MPs in river sediments range from 30.3 ± 15.9 to 832 ± 150 items kg^{-1} (d.w.) for Ciwalendke River (Indonesia) and St Lawrence River (Canada), respectively; and from 87.5 to 1010 items kg^{-1}d.w. for surface sediments from Lakes Mead and Mohave, US (Wang et al., 2021). Average concentrations from St Lawrence River, with a range from 65 to 7562 plastic particles per kg d.w., were reported among the highest recorded (in the top 25%) for the world's freshwater and marine systems (Crew et al., 2020). Although data about MPs levels in freshwater sediments in South America is very scarce, maximal concentrations reached 8178 particles kg^{-1}d.w. in the Amazon River (Brazil) and 4654 particles m^{-2} in shoreline sediments from the Paraná River (Argentina) (Table 2). Once more, the high diversity of methodologies used for MPs, added to results expressed in different units, make comparisons between different studies difficult. As it can be observed in the Table 2, minimal sieve used for sediment samples ranged from 0.45 to 350 μm modifying significantly the obtained size fractions in each case. Nevertheless, it becomes clear that our current findings cannot be considered outlier results in comparison with previous reports. Gerolin et al. (2020) associated the highest MPs concentrations with shallow water and lower water velocity of the Negro River (Brazil) sections, which is the case of the Suquía River. Moreover, our findings of MPs in all samples along the Suquía River basin highlight the ubiquity of microplastics in aquatic systems, pointing out their role as emergent environmental pollutants. According to our knowledge this is the first report of MPs levels in sediments from river bed in Argentina. Future studies are necessary for a better understanding of MPs deposition and to evaluate their potential impact over ecosystem species.

3.3. Spectroscopic analyses

The great majority of the fibers (73% of the total) exhibited the typical pyranose carbohydrates infrared pattern (O-H stretching at 3450 cm^{-1}; O-H bending at 1630 cm^{-1}; and C-O-C stretching at 1040 cm^{-1}; Fig. 4a) (Cai et al., 2019). This fact allows us to assign all these fibers to cellulosic materials. Semi-artificial fibers made from regenerated cellulose, such as viscose or Rayon, and natural fibers like cotton, have very similar spectral patterns, thus no differentiation were made here. Additionally, instead cellulose is a natural and renewable polymer, its processing into fibers involves the addition of chemical additives such as dyes, antistatic agents, or flame retardants, which can be dangerous components potentially released into the environment or transferred to the biota (Remy et al., 2015). Cellulosic materials were the most abundant fiber items recovered from diverse Argentinean aquatic environments (Fernández Severini et al., 2020; Forero López et al., 2021; Ojeda et al., 2021; Pérez et al., 2020). One fiber presented the typical signals correspondent to cellulosic material plus the peaks of poly(ethylene terephthalate) (C=O stretching at 1715 cm^{-1}; C-H bending at 1405 and 1340 cm^{-1}; and C-O ester stretching 1240 cm^{-1}; Fig. 4b) (Peets et al., 2017). This is in fully agreement to fabrics like Jersey, which combines natural fibers whit polyester ones. Both materials, cellulosic and cellulosic mixed with polyester, are widely employed in textile fabrics and clothing, which can be mechanically degraded during domestic washing cycles and enter to the river water as a consequence of poor waste waters treatment (Henry et al., 2019).

Finally, in the analyzed sub samples, one fragment exhibited the signals correspondent to poly(styrene) (aromatic C-H stretching at 3026 cm^{-1}; aromatic overtones comprised between 2010 and 1750 cm^{-1}; ring stretching at 1492 cm^{-1}; aromatic C-H out of plane bending at 700 cm^{-1}; Fig. 4c) (Veerasingam et al., 2020). The spectrum showed other signal, demonstrating a copolymeric composition of the fragment. Poly(styrene) copolymers are one of the most widely used plastic material, employed in packaging, food containers and tableware, tanks, among others (Li et al., 2016).

4. Conclusion

This pilot study is the first report of MP in Suquía River basin, a low-flow river located in a semi-arid region of South America. Considering the presence of MPs in both water and sediment of this river, it is evident that the amount of fibers is much more important than the one corresponding to fragments. On the other hand, the WWTP was the main responsible for the fate of MPs to the water, while the city run-off also released MPs which were retained by the sediment within a few kilometers downstream. Thus, in this case, deposition or retention of plastic particles in sediment would be an efficient mechanism for removing MPs from the river water, probably due to the water turbulence and sandy characteristics of the sediment in the studied river section.

Our current results open the need for a deep study on the effects caused by fibers on the aquatic native biota, proved that they are more abundant than fragments in this type of streams. It is also worth to remark the need of further studies on the dynamics of MPs in rivers with different hydrology, as many reports on MPs are from marine environment, with few works corresponding to big rivers, but fewer studies on small rivers. Studies focusing on the role of riverbed as MPs reservoir and their possible resuspension and transport during river flood should be also contribute to the comprehension on MPs dynamics and distribution in environmental compartments. Local, national and regional MPs monitoring programs based on updated standardized methodology are urgently needed in most countries of the region.

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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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2022.100185.

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