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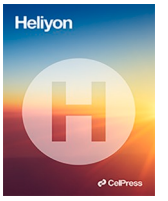

Research article

Temporal and spatial distribution of microplastics in the freshwater Atibaia river basin, Campinas-SP, Brazil

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ABSTRACT

The contamination of surface waters by microplastics (MPs) is an emerging concern, due to their environmental impact and negative effects on biota. However, in recent years, although the occurrence of these pollutants has been widely reported in marine systems, studies on MPs in freshwater are still scarce in the literature, particularly in Southeastern Brazil. In this context, the current study aimed to provide unprecedented information on the abundance and spatial and temporal distribution of MPs in three sites located in the Atibaia river basin (Southeastern Brazil) - the main river, a tributary, and the discharge of effluent from a sewage treatment plant. Surface water was sampled in four sampling campaigns, two in wet season and two in dry season, between 2019 and 2020, at three sampling points. At each point, 200 L of water were collected with the aid of an aluminium bucket, followed by sieving in the field to isolate the particles between 100 μm and 5000 μm, using stainless steel sieves. Chemical identification of the polymer was performed by ATR-FTIR micro spectroscopy. The abundance of MPs in the water ranged from 188 to 533 items/m^3. The water samples with the greatest MPs abundance corresponded to the sampling point that includes the receipt of domestic effluent treated by the local Sewage Treatment Station. The chemical identification of the polymers highlights polyester polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), and polypropylene (PP) as the most frequent, respectively. This study emphasizes the importance of discharged domestic effluents and rivers as MPs transport systems. Therefore, further studies should be carried out to identify the main sources and contribute to the gathering of information, aiming to mitigate the emission of this pollutant in aquatic systems.

1. Introduction

In recent decades, plastics have become widely used by society in a wide variety of sectors, which has contributed to quality of life and provided great convenience. However, due to the exacerbated use, improper handling, and stable chemical properties of these

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materials, a large amount is accumulating in the environment [1,2]. With exposure time, plastics degrade and fragment into small particles that, when less than 5 mm, are classified as microplastics (MPs) of secondary origin [3]. The entry of MPs particles into the environment can also occur through the disposal of plastic materials already produced in reduced sizes, these being classified as primary source MPs [4–6].

Environmental contamination by MPs is enhanced by anthropogenic factors, such as the presence of urban centres, low efficiency of wastewater treatments, and the use of plastic mulch in agriculture, among others [7]. The textile industry, for example, also employs plastic fibers for the production of synthetic fabrics and the process of washing clothes made of these fabrics releases this material, which also makes up domestic effluents and contaminates the environment. This type of MPs is frequently reported in environmental samples by the scientific community [8–10].

The distribution and transport of MPs in the environment are related to particle properties, such as polymer density, size, and shape and also by natural factors, such as wind, rain events, topography of the watercourse [7], and the presence of microorganisms that influence biofouling or descaling on the surface of the particles, which interferes with vertical transport in the aquatic matrix [11,12]. All these factors combined are directly related to the dynamics of MPs in the environment, which leads to the occurrence of these anthropogenic residues in different geographical locations and environmental compartments [13–15], including remote areas [16].

Considering their wide persistence, small size, and difficult removal from the environment, MPs can be considered as persistent pollutants with the potential to cause negative impacts on ecosystems [17]. Growing evidence indicates that plastics interact with freshwater biodiversity, from plants to animals. Plastic ingestion by animals has been reported for over two hundred species, ranging from invertebrates to mammals. Many studies, particularly conducted in laboratory conditions, show negative effects (lethal and sublethal) associated with the ingestion of MPs, which can cause deleterious effects by physical or physiological mechanisms for organisms from the lower trophic levels [13,18,19].

In the aquatic matrix, many studies have reported the scenario of contamination by plastics and MPs in the marine environment. However, knowing that most of the plastic waste that reaches the oceans comes from freshwater ecosystems and that these are also used for the population's water supply, it is extremely important to understand the composition and distribution of MPs in these environments. Studies on this theme are still scarce, especially in Brazil.

In Brazil, the few studies carried out on MPs contamination in the freshwater environment were carried out in the north [20,21], south [22–25], and central west [26], with only three in the southeast region, two in the state of Rio de Janeiro and only one in the state of São Paulo [27]. [28,29]. Knowing that the purchasing power of the population is directly associated with the high consumption and, consequently, disposal of plastic litter and MPs [30], the need is highlighted for research on the contribution of MPs in freshwater in the metropolitan regions of the state of São Paulo, southeastern Brazil, where the cities with the highest gross domestic product indices are concentrated [31], that is, where the consumption pattern resembles developed countries, despite Brazil being classified as an underdeveloped country with poor sanitation conditions [32].

Thus, the objective of the current study was to provide unprecedented information on the physical and chemical characteristics of

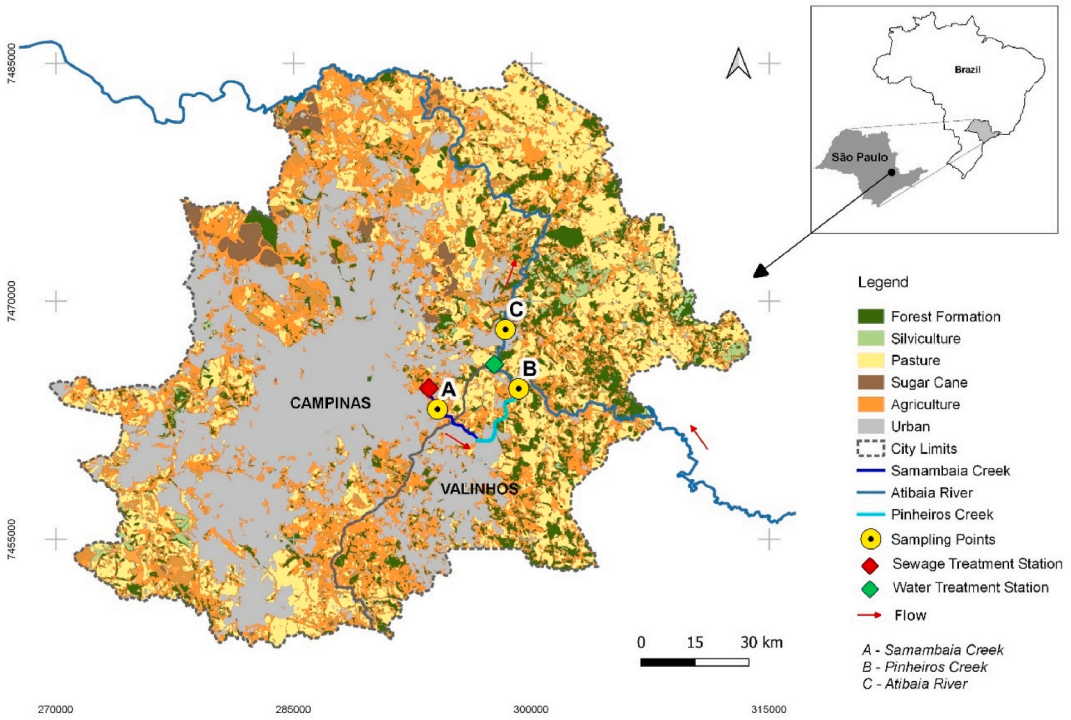

Fig. 1. Map of the Atibaia river basin, SP, Brazil, with the sampling points.

the MPs found at three strategic points in the surface waters of the Atibaia river basin, in the metropolitan region of the city of Campinas, São Paulo, Brazil, as this is a lotic environment that receives domestic and industrial effluents, in addition to having a high population density in the surrounding area and the use of its waters for public supply. This assessment was focused on understanding whether there is a spatial correlation between the types of MPs found, and their respective stages of degradation, with human activities in the surrounding areas, as well as the influence of seasonality on the abundance of MPs, in order to assist in the implementation of effective mitigation strategies for the preservation of this environment.

2. Materials and methods

2.1. Study area and sampling

The study area is located in the Atibaia river basin, metropolitan region of Campinas, municipality of the state of São Paulo (SP), Brazil (S 22° 88' - 22° 93′, W 46° 95' - 47° 01′). With an area of 2837.3 km^2, this catchment comprises municipalities in the state of São Paulo and also in Minas Gerais, with an altitude of 509 m in the west to 2029 m in the east. The main river, Atibaia, is formed by the confluence of the Atibainha and Cachoeira Rivers, between the municipalities of Atibaia-SP and Bom Jesus dos Perdões-SP, and has an average flow of 12 $m^3 s^{-1}$, length of 180 km, average annual temperature of 19.7 °C, and total average accumulated rainfall of 1509.5 mm, with a rainy summer and dry winter [33].

The collection points selected for the investigation of MPs represent strategic locations with regard to the assessment of different types of anthropogenic impacts, due to the characteristics of the surroundings, with an extensive urban infrastructure, high population density, agricultural areas, and pastures (Fig. 1). Therefore, it is justifiable to be concerned about the water quality of this environment and the potential risks to aquatic life, due to the receipt of domestic sewage, industrial effluents, and other contaminants from agricultural activities, such as MPs and pesticides that also reach its surface waters by runoff or leaching. In addition, this same basin is also used to supply drinking water to more than one million inhabitants in Campinas-SP alone [33,34].

All collection points are located in the municipality of Campinas-SP. Point A is located in Samambaia Creek, at the outlet of the treated effluent from the Samambaia Sewage Treatment Plant, point B is located in Pinheiros Creek, approximately 100 m before its entry into the Atibaia River, and point C is located in the Atibaia River, near the raw water intake of the Campinas-SP Water Treatment Plant.

Four sampling campaigns were carried out, between October 2019 and August 2020, two during the wet period and two during the dry season. In each sampling campaign, 200 L (0.2 m^3) of surface water were collected at each of the points (A, B, and C) of the study area, totalling 12 samples and a volume of 2400 L (2.4 m^3) (2 replicates x 3 sampling points x 2 seasonal periods). The surface water samples from each point, first 40 cm from the surface of the watercourse for points B and C and discharge of treated domestic effluent from point A, were collected with the aid of a pre-sanitized 10 L aluminium bucket. The bucket was positioned in the centre of the watercourses, on top of a bridge, as the sampling site does not allow the use of a boat, and this is the methodology adopted in similar studies for these types of environments [35]. Sieving was then carried out in the field, in a stacked system of 3 granulometric sieves in the following order: 5000 μm mesh sieve above, 1000 μm mesh sieve in the middle, and finally 100 μm mesh sieve. Three sieves of different mesh sizes were then assigned to each point and pre-identified with the sampling point [36]. Immediately after sampling, each sieve was washed with distilled water, covered with aluminium foil, and stored in a cardboard box to avoid sample loss or contamination through atmospheric air [35]. The size range of the microplastics investigated here was 100 μm–5000 μm.

2.2. Sample preparation

In the laboratory, the sieves covered with aluminium foil were kept at room temperature for 24 h, until the solid material dried. Afterwards, all the solids contained in the sieves were transferred to pre-identified beakers, with the aid of a minimum amount of distilled water, and treated with 20 mL of 0.05 M Fe (II) sulphate aqueous solution and 20 mL of 30 % hydrogen peroxide, under stirring on a heating plate at approximately 70 °C, for 30 min, to remove organic matter, according to the NOAA (National Oceanic and Atmospheric Administration) procedure [5]. This method has been applied in many other studies because it shows that the plastic material is resistant to oxidation by hydrogen peroxide in humid conditions. However, it is possible that heating the peroxide close to 70 °C can contribute to the degradation of some types of polymer, such as polyamide [37]. Therefore, as a disadvantage, our results may have underestimated this type of plastic polymer.

After this process, the entire contents of the beaker were transferred to a size 100 μm mesh stainless steel sieve to remove the liquid solution, semi-covered with aluminium foil, and dried at room temperature for 24 h. The solids retained in the 100 μm mesh were then manually transferred to Petri dishes, under optical magnification and using stainless steel tweezers, for quantification and categorization [35,38].

2.3. Observation, categorization and quantification of microplastics

All the solids stored in the Petri dishes were manually examined with the aid of a binocular stereoscopic magnifier with up to 35× magnification (Leica, EZ4E), and the MPs particles were then separated from the non-plastic waste, and quantified and classified according to the shape and colour parameters.

According to shape, the isolated MPs were classified into five categories: fibers, fragments, films, microbeads, and styrofoam [38,39]. The criteria adopted for these classifications were the shape, lightness, and thickness of the particles [38]. In the colour criterion,

the MPs were classified into four categories: coloured, white, transparent, and aged for those particles that showed loss of colour and cracks and porosity on the surface [12,39–41].

The MPs identified from this visual screening were counted for the quantitative analysis. For each sample stored in the Petri dish, there was a description of the sampling campaign, the collection point, and the particle size range, according to the mesh of the sieve where the particles were retained, and classified into three size ranges: ≥100 μm < 1000 μm, ≥1000 μm < 5000 μm, and = 5000 μm.

2.4. Chemical identification and oxidation of microplastics

Chemical identification of the MPs particles was performed by ATR-FTIR micro spectroscopy (Bruker). Spectra were recorded in Ge-tipped attenuated total reflectance mode (Hyperion coupled to a Vertex 80v, Bruker), at a fixed resolution of 4 cm^{-1}, with 64 scans, and in the wavenumber range 4000 to 400 cm^{-1}. The spectra were measured in a temperature and humidity controlled environment, and converted to absorption mode by Bruker OPUS 8.0 software, providing absorbance values for each respective wavenumber. The analysis was performed proportionally on the particles considered most representative, including all the categories of MPs found in this study (fiber, fragment, film, microbead and styrofoam), chosen randomly for each sampling site (n = 75 spectra, particle sizes ≥100 μm and <1000 μm).

In addition to the identification of the polymers, the spectra obtained by micro FTIR were also used to characterize the oxidation stage of the surface of the MPs particles of the polymers polyethylene (PE) and polypropylene (PP), by calculating the carbonyl index (CI), according to equation (1):

$$CI = \frac{A}{B} \quad \text{(Eq. 1)}$$

where A corresponds to the carbonyl band stretching mode between 1735 and 1715 cm^{-1} and B to the reference band between 1471 cm^{-1} and 1460 cm^{-1} due to CH_2 scissor vibrations for PE and PP polymers, respectively [41]. To remove the errors caused by baseline fluctuations, the absorbance values used in the IC calculation were normalized according to the baseline of each band.

The carbonyl stretching band presents a strong intensity in the infrared spectrum, being characteristic in compounds that present the functional groups carboxylic acids, aldehydes, amides, ketones, and esters (between 1630 and 1750 cm^{-1}) [23]. While PE presents characteristic bands at 2915, 2849, 1471, and 717 cm^{-1}, PP presents bands at 2950, 2916, 2850, 2839, 1460, and 1376 cm^{-1} [41]. These polymers, classified as polyolefins, have saturated carbon-carbon bonds, and the carbonyl band is not characteristic in their compositions. Therefore, when the spectra of these polymers present a band, it is evident that the surface of the material has undergone photo-oxidative degradation, that is, oxygen has been introduced into its polymer chain, by exposure to UV radiation [42,43].

2.5. Quality assurance and quality control

To avoid contamination from external sources during sampling and sample processing, stainless steel and glass materials were used. All materials were properly washed before use, with filtered water followed by deionized water, three times. After collection and during each procedure in the laboratory, samples were immediately covered with aluminium foil to avoid airborne contamination. Samples were handled in a clean environment, with all surfaces pre-sanitized with alcohol and paper three times, free of external air current, with a reduced number of people working in the same laboratory, and researchers properly prepared wearing cotton lab coats, masks, and free of plastic utensils during the whole process. Contamination-free Petri dishes were exposed near the samples during sampling campaigns and all procedures performed in the laboratory to assess MPs contamination. The plates were visually inspected under optical magnification, so that the MPs particles present could be discounted from the MPs count of the samples, in order to avoid overestimation, i.e., negative control. However, no MPs particles were found in the corresponding contamination control at any time during the process [35].

2.6. MPs risk assessment

The potential risk of the MPs collected in the surface waters of the study area was calculated based on two indicators, the concentration and chemical composition of the particles analyzed. According to Lithner et al. [44], each type of synthetic polymer presents different levels of risk to the ecology of ecosystems. Therefore, the risk assessment was calculated based on the score assigned by Lithner et al. [44] for each type of polymer identified, according to the following formula:

$$PI = \sum Pn \; x \; Sn \quad \text{(Eq. 2)}$$

where P*n* corresponds to the percentage of polymers found and S*n* corresponds to the score assigned by Lithner et al. [44] for the identity of the polymer. The risk level of the MPs found can be classified from low to high [39]: i) < 10, ii) 10–100, iii) 100–1000 and iv) > 1000.

2.7. Statistical analysis

The abundance of MPs was measured by the amount of particles per volume of water collected, being expressed in items per m^3, for comparison purposes, as this is the quantitative unit considered in most studies. Microsoft Excel 2019 was used to process the

quantitative data of each sampling point, as well as graphs, and calculated values for the carbonyl index of the particles identified as PE and PP. The Origin 2020 program was used to make the polymer spectra. Finally, the relationship between types of MPs, collection locations and seasonality was explored through principal components analysis (PCA), and the PCA was plotted in R Core team version 4.0.

3. Results and discussion

3.1. Abundance: spatial-temporal distribution of MPs

The results showed that all surface water samples collected in this study presented MPs contamination. A total of 739 MPs particles were counted in the sum of all 4 sampling campaigns from the 3 different sampling points, i.e., a total of 12 samples. The abundance of MPs ranged from 188 ± 95 to 533 ± 60 items/m^3, as shown in Fig. 2. In general, the highest concentrations of MPs were obtained at point A, during the dry season, a collection point referring to the direct discharge of treated domestic effluent from the WWTP, and the lowest concentration was at point C, a collection point located downstream of the Atibaia River.

The abundance and distribution of MPs in the freshwater environment is influenced by several factors, including anthropogenic factors, such as land occupation, high population density in the surrounding area, discharge of effluents from wastewater treatment plants, and industrial and agricultural activities, and also due to natural factors, such as rainfall levels and the physical characteristics of the watershed, which can favour the transport of MPs to the watercourse through rainwater runoff, for example, and their accumulation [30,45,46].

Thus, the result obtained for point A was already predicted, since previous studies have shown that among the types of aquatic matrices, WWTP effluent or surface waters of rivers or streams, the WWTP effluent matrix has the highest concentrations of MPs [35]. It is also known that this WWTP has conventional sewage treatment (screening, aerated lagoons with complete mixing, and secondary decantation), which does not include the complete removal of impurities from its final effluent. However, it is supposed that this treatment significantly reduces the direct release of MPs into the adjacent creek, because, according to Murphy [47], who evaluated the efficiency of MP removal from a WWTP located in Scotland, although these anthropogenic particles occur in the final effluent of the WWTP, the treatment is responsible for the removal of 98.41 % of these particles.

The lowest concentrations of MPs were obtained at point C, which can be justified by the fact that these samples were collected from the central channel of a river, which has greater depth, water volume, and water flow velocity compared to point B, Pinheiros Creek, for example. As found in previous studies, watercourses with lower flow rates and weakened hydrological conditions favour the accumulation of MPs, while the opposite conditions contribute to a negative correlation, which can be explained by the dilution effect of the rivers [30,48].

Regarding seasonal variability, this study included a sample from each season of the year. In southeastern Brazil, the spring and summer seasons typically have rain events with greater frequency, which is even more intense in the summer (from December to March), commonly known as the flood period of the watercourses, while the fall and winter seasons typically have low rainfall, commonly known as the drought period. Our results indicate that the highest MPs concentrations at sites B and C, Pinheiros Creek and Atibaia River, occurred at the peak of the flood period, in March, while the lowest MPs concentrations at these same sites occurred at the peak of the drought, in June. As expected, despite the increase in the flow velocity of the watercourse in the flood period, this variability between the flood and drought periods is justified by the increased input of MPs into the aquatic environment, through the transport of these terrestrial particles by rainwater runoff. The same positive correlation, higher rates of MPs in the period of higher rainfall, was also observed in other studies [46,49].

For point A there was no positive correlation between rainfall and an increased abundance of MPs, as the highest concentrations of MPs at this point were those of the drought period. In the drought period of 2020 in Brazil, social isolation occurred due to the high transmission rate of the SARS-CoV-2 virus, responsible for the Covid-19 disease. This fact may have contributed to the increase in the generation of plastic waste in households and, consequently, an increase in the concentration of MPs at this point in this period, since the population served by this WWTP comprises approximately 50,000 people, who at that time, carried out all their daily activities only in their homes.

In general, the comparison of the quantitative results of this study with other similar aquatic environments is quite complex, due to

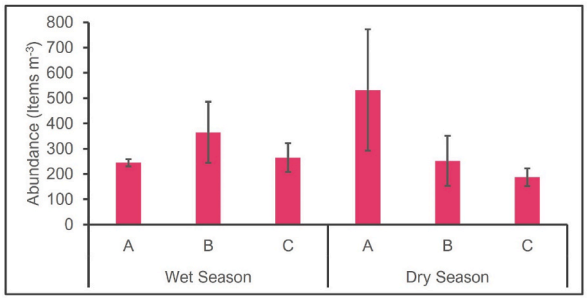

Fig. 2. Temporal and spatial abundance of microplastics.

the differences between the environmental compartments with their peculiar topographic, hydrological, and meteorological characteristics, the differences between the land occupation in the vicinity of the watercourse, and also to the numerous differences involved during the sampling methodology, such as collection equipment (bucket, bottle, net, or pump), minimum mesh during sampling and/or sample preparation, and the volume of water collected.

However, when comparing the mean concentration of MPs found in this study (308 ± 126) with those reported by similar studies also carried out in freshwater, in different locations in the world (Table 1), it is possible to conclude that the Atibaia river basin presents a relatively high concentration regarding MPs pollution, with values within the concentration ranges found by other studies that also evaluated lotic environments that suffer from the same anthropogenic impacts of high population density and the receipt of effluents from WWTP. These factors are directly proportional to the results obtained [29,41].

In addition, despite the widespread contamination by MPs even in remote locations, it is worth mentioning that the discrepancy between the reported abundances may also be associated with the use of a higher sampling mesh, as many studies reported that in the aquatic environment smaller particles are the most abundant, as well as the lower volume of water collected, since, according to Koelmans et al. [35], these factors compromise the representativeness of the study and increase the margin of error.

3.2. Morphological characterization of the microplastics and their relationship to location and seasonality

The MPs found in this study were classified into 5 groups: fibre, fragment, film, microbead, and styrofoam (Fig. 3). Fig. 4 (A) shows the abundance and spatial and seasonal distributions of these groups for all 12 samples, where it is possible to observe that fibers were the predominant category in all samples, representing 61 % of the total, with the highest concentrations, in general, being in those from point C. This is directly related to the greater input of domestic effluent received in this catchment area, since this area corresponds to the main river in the catchment area, which receives many tributaries carrying treated and untreated domestic sewage; this category of MPs corresponds to the mechanical breakdown of synthetic fabric during the washing machine cycle. The fragments correspond to 19 % of the total, with point A having the highest concentrations in all samplings. Films accounted for 16 % of the total, with the highest concentrations found at point B. The Styrofoam category presented 3 % of the total and was found in only four samples located at points A and C, with the highest concentration obtained at point C. Microbeads were the least frequent and abundant in this study, representing only 1 % of the total, being found in three samples, two located at point A and one at point C, with the highest concentration obtained at point A.

In line with previous studies conducted in all parts of the globe, these results corroborate with what has been reported for water samples from freshwater ecosystems, with, overall, the most frequent major categories being fragment, fibre, film, and styrofoam, respectively [35]. Fibers were also predominant in the study by Mao et al. [55], in the surface water samples in Lake Wuliangsuhai, a lentic environment, in China. Fibers and fragments, respectively, were also the predominant categories in the study by Sutton et al. [60], who investigated the occurrence of MPs in the discharge of treated effluents from eight wastewater treatment plants discharging their effluents into San Francisco Bay, California. In addition, other lotic environments have also reported the predominance of the fibre and fragment categories in their results [20,41].

Regarding the variability of the categories as a function of seasonality, no variations or trends associated with meteorological conditions were observed, with the same categories always being predominant; fibre, fragment, and film, for the four sampling campaigns, regardless of the time of year, and styrofoam and microbeads the least frequent, however, still reported in both scenarios, in the flood period and in the drought period.

The high concentration of fibre-type MPs in all samples of this study may be associated with the receipt of domestic effluents at all sampling points, since during the washing machine process, mechanical and chemical stresses occur that drive the detachment of microfibers from the threads that constitute the fabric and, due to their small dimensions, these fibers are not fully retained in the WWTPs and reach aquatic environments [9]. It is estimated that this practice contributes to the release of 640,000 to 1,500,000 fibers per kg of washed fabric into the effluents [61].

Microbeads, like fibers, can also contribute to the aquatic environment, associated primarily with the discharge of domestic effluents, since the use of cosmetics containing these particles in their formulation, in order to produce an abrasive effect, for example, can contribute to their release into this environment [62,63]. The fact that this class of MPs was the least abundant is consistent with previous studies [35], which may be associated with the low consumption of these cosmetics by the population, as well as the limitation of the sampling mesh of this study (100 μm), since according to reports of previous studies [63,64], the majority of microbeads have particle diameters <100 μm.

Thus, the morphological characterization of MPs is extremely important, since aspects related to the shape of the particles can provide information regarding their possible polluting sources; for example, fragments, films, and styrofoam may be associated with the improper disposal of solid waste into the environment (household items and/or packaging), which, over time, due to exposure to stressors, suffer degradation and fragment into MP particles, commonly classified in the scientific literature as secondary MPs [65,66]. The high concentrations and frequency of these categories in our study, with the exception of the styrofoam category, demonstrate a lack of proper solid waste management in the study area investigated.

Coloured and transparent MPs were predominant, being found in all samples and representing 63 % and 21 %, respectively, of the total (Fig. 4 - B). Similar results were also described in other studies carried out in freshwater environments [23,29]. The coloured MPs demonstrate a great cause for concern regarding the possibility of ingestion by aquatic biota when compared, for example, with transparent MPs, as these MPs stand out visibly in the water column and are more easily confused with natural prey, indicating a greater influence of colour on bioavailability. In addition, coloured MPs indicate the presence of chemical additives, such as dyes in the manufacture of plastic during its processing, which may also favour the leaching of the additives during ingestion [67,68]. The colour

Table 1
Abundance of microplastics in wastewater effluent and surface waters across the world.

Region	Location	Sample	Sampling method	Volume sampled per sample (m^3)	Minimum mesh (μm)	Abundance (Items. m^{-3})	References
South America	Atibaia river basin, SP, Brazil	River water (surface) and Wastewater effluent	Aluminium bucket followed by sieves	0.2	100	188–533	This study
South America	Guaíba Lake, RS, Brazil	Lake water (surface)	Manta net	35	60	11.9–61.2	Bertoldi et al., 2021 [23]
South America	Guapimirim, Macacu and Maracanã Rivers, Brazil	River water (surface)	Neuston net	0.045–51.42	300	3.6–51,166.5	Drabinski et al., 2023 [29]
South America	Amazonas River, AM, Brazil	River water (surface)	Aluminium bucket	0.06	64	2672–4772	Queiroz et al., 2022 [20]
South America	La Salada Lake, Argentina	Lake water (surface)	Bucket and plankton net	0.1	47	100–180	Alfonso et al., 2020 [50]
North America	Lake Simcoe, Canada	Lake water (surface)	Bottle and manta trawls	0.004 and 48–51	335	$0.7\ 10^{-3}$ and 0.4–1.3	Felismino et al., 2021 [51]
North America	North Saskatchewan River, Canada	River water (surface)	Nylon plankton net	5.5	53	4.6–88.3	Bujaczek et al., 2021 [52]
North America	City of Saskatoon WWTP, Canada	Wastewater effluent	Plankton nets	0,10	20	$0.22\ 10^{-3}$- $1.49\ 10^{-3}$	Prajapati et al., 2021 [53]
Africa	Plankenburg River, South Africa	River water (surface)	Steel bucket	0,030	250	$1.52\ 10^{-3}$ – $5.13\ 10^{-3}$	Apetogbor et al., 2023 [54]
Europe	Sewage treatment station, Scotland	Wastewater effluent	Steel bucket	0.050	11	$2.5\ 10^{-5}$	Murphy et al., 2016 [47]
Europe	Antuã River, Portugal	River water (surface)	Pump with nylon net	0.012	55	58–1265	Rodrigues et al., 2018 [41]
Europe	Garonne River, France	River water (surface)	Manta trawls	4.25–259.10	500	0.00–3.4	De Carvalho et al., 2021 [48]
Asia	Wuliangsuhai Lake, China	Lake water (surface)	Steel bucket	0.020	75	$3.12\ 10^{-3}$ – $11.25\ 10^{-3}$	Mao et al., 2020 [55]
Asia	Hanjiang River and Yangtze River, China	River water (surface)	Teflon pump	0.020	50	2516.7–2933	Wang et al., 2017 [56]
Asia	Municipal wastewater treatment plant, China	Wastewater effluent	Steel bucket	0,010	47	$28.4\ 10^{-3}$ - $79.9\ 10^{-3}$	Liu et al., 2019 [57]
Asia	Tamsui River and its tributaries, Taiwan	River water (surface)	Manta net	13.730–61.898	300	2.8–83.7	Wong et al., 2020 [49]
Antarctica	Byers Peninsula, Antarctica	Peninsula water (surface)	Nylon drifting nets	4.200	100	$0.47\ 10^{-3}$ – $1.43\ 10^{-3}$	González-Pleiter et al., 2020 [58]
Oceania	Freshwater streams, Adelaide, Australia	River water (surface)	Composite sample by pump	0.005	20	$6.4\ 10^{-3}$	Leterme et al., 2023 [59]

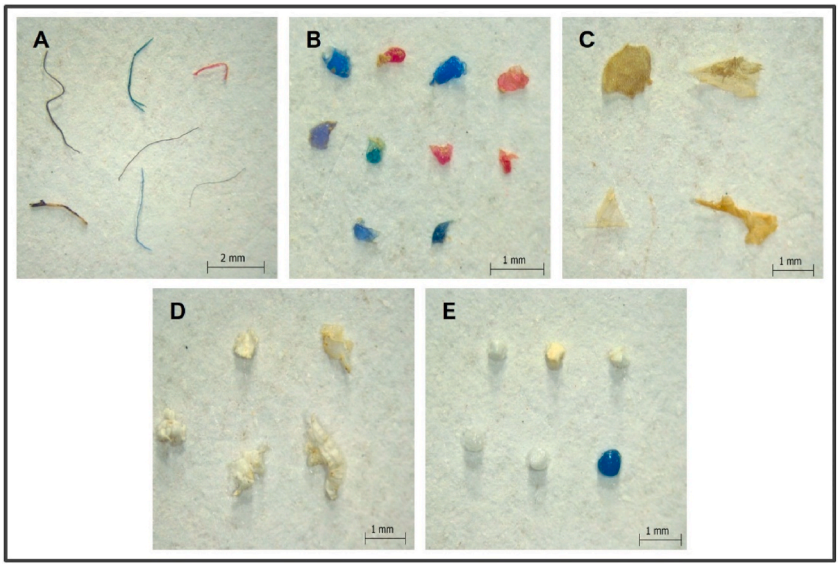

Fig. 3. Examples of microplastics found in the samples. A) Fibre, B) Fragment, C) Film, D) Microbead, and E) Styrofoam. Photographs taken with the ZEISS Axio Scope 7 attached to the microscope.

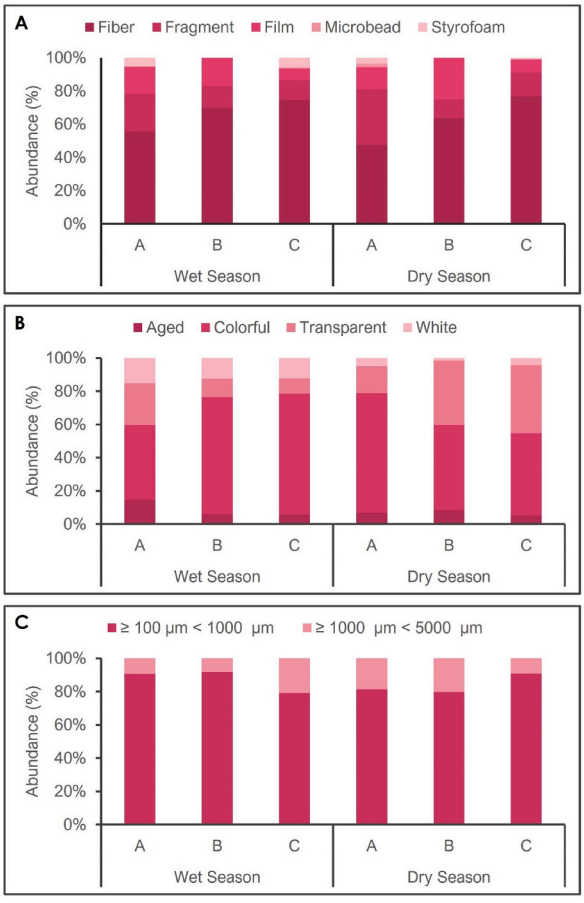

Fig. 4. Quantitative results of the morphological characteristics of microplastics in terms of shape A), colour B), and size C).

also suggests the estimated time that the material has been exposed to weathering in the environment, where the aged colour may be associated with the longer residence time of the particle in the environment; in this study the aged MPs were also present in all samples and made up 7 % of the total [65].

The size classes considered here were ≥100 μm to ≤1000 μm and ≥1000 μm to ≤5000 μm. The predominant result for all collection points and regardless of the time of year was MPs of size ≥100 μm to ≤1000 μm, making up 83.90 % of the total (Fig. 4 - C), which was already expected according to reports from previous studies in similar environments [23,55]. This size range suggests that MPs of secondary origin, for example, have been intensely degraded, which favours fragmentation to progressively smaller particles. This fact compromises the maintenance of water quality and preservation of aquatic life, due to the difficulty of removing particles with such reduced sizes. In addition, this size range is compatible with meso and microplankton, which suggests that aquatic organisms from the lower trophic levels of the food chain are susceptible to ingestion of MPs, which can cause physical impacts, such as blockage of the digestive tract, lacerations, a false sense of satiety, and, consequently, impairment in reproduction and growth rate [68].

Fig. 5 presents the principal component analysis (PCA) of the data collected, including the correlation of the abundance data and morphological characteristics of the MPs with the collection sites (Fig. 5A) and the collection seasons (Figure B). The distribution of the data within the highlighted fields indicates that location A demonstrates the greatest variability in shape, colour, and size, followed by regions B and C, in that order. This corroborates the information described in Fig. 2, ie., point A shows the greatest abundance of MPs and, consequently, the greatest variability of components in the samples. In addition, location C has the highest abundance of smaller fibre particles, which can also be seen in the analysis of Fig. 4A. Fig. 5B highlights the data by the dry and wet seasons. We can observe that the projection is well represented by the content of transparent particles as well as an increased variability of shape. In the dry season, there is an increase in the abundance of particles of greater size and also films. In terms of colour, the dry season is well represented by both transparent and colourful particles, while the wet season also presents larger variance in the abundance of white particles.

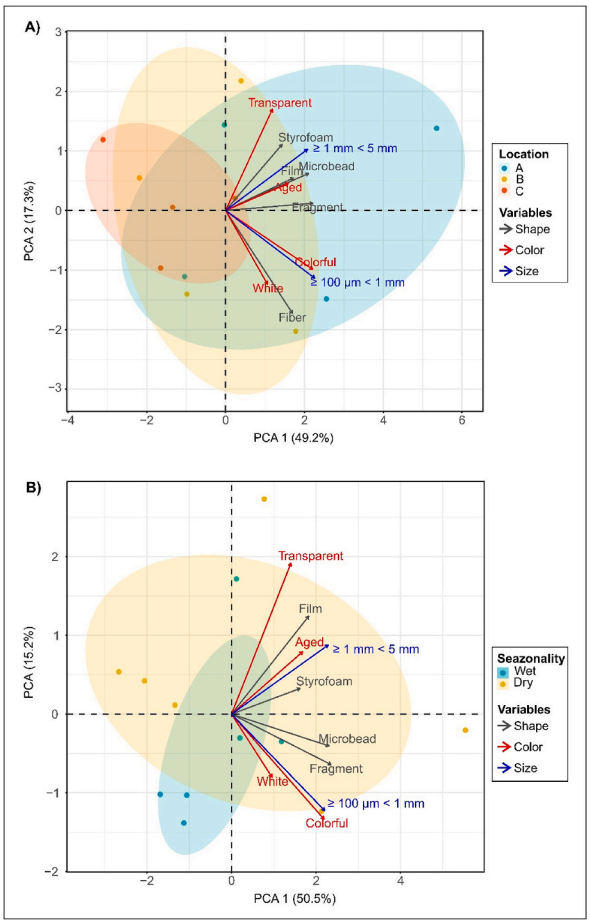

Fig. 5. Principal component analysis (PCA) of the data in terms of the relationship between types of MPs collected and A) locations and B) seasonality.

3.3. Chemical identification and oxidation stage

A total of 75 spectra were analyzed by micro-FTIR-ATR, of these 67 were positively identified as synthetic polymers and 8 were identified as non-plastic. Typical bands of different polymer types were identified for all types of MPs found, with the polyester polymer polyethylene terephthalate (PET) (31 %) being the most frequent, followed by PE (30 %), polyvinyl chloride (PVC) (24 %), PP (12 %), and expanded polystyrene (PS) (3 %) (Fig. 6). These 5 types of polymers found in the current study are also the most commonly reported in the literature in water samples in similar environments [35]. The abundance and frequency of these polymers in all samples can be justified by the worldwide consumption of such materials, as well as the type of sampling used in this study, which included the water courses (points B and C), and collection from the water column (40 cm deep) to the surface, that is, covering the polymers of higher (PVC and PET >1.3 g cm^{-3}) and similar density to the water (PS $= 1.0$ g cm^{-3}), and also the floating MPs, of lower density (PE and PP < 1 g cm^{-3}).

Identification of the polyester polymer PET occurred only for fibre-type MPs. This chemical identity reinforces the point that such MPs come from the wearing or washing of synthetic fabrics, which are transported to the aquatic matrix through atmospheric deposition, rainfall runoff, or domestic effluent discharge [15,69]. Currently, synthetic fibers represent 60 % of the annual world consumption of fibers in the textile industry, with the most frequent chemical composition being polyester, polyamide, acrylic, and polyolefin, respectively [9]. The results indicated that of all the fibers subjected to chemical analysis (n = 23), 87 % were identified as PET, 9 % as PP, and 4 % as non-plastic, probably classified as natural cellulose fibre. These results are in accordance with what has been reported in the scientific literature regarding the chemical identification of fiber-type MPs, the most frequent chemical composition being polyester (70 %), followed by acrylic, polyamide, and polypropylene [1,8].

The PE polymer was identified in 3 categories of MPs: fragments (85 %), films (10 %), and microbeads (5 %). Fragment-type MPs may come from various packaging (food, beverages, cleaning, and/or cosmetics) and/or plastic utensils discarded in the environment, while film-type MPs, according to thickness and physical characteristics, may be more likely to come from plastic bags, as it is known that this polymer is the predominant one in the production of bags [70,71], and/or plastic films used in agriculture [72], as well as that these materials have, primarily, the respective chemical identity and the surroundings of the study area include this practice. Finally, the microbeads identified as PE also confirm reports in the literature, since Napper and collaborators [64], who investigated several cosmetic products containing microbeads in their composition, reported the predominance of this polymer for this type of primary source of MPs.

The PP polymer was identified in samples of MPs of the types fibers (25 %) and fragments (75 %), and the PVC polymer was identified in samples of MPs of the types fragments (44 %) and films (56 %). PE, PP, and PVC polymers are classified as the three most consumed types of polymer resins in the world, with production percentages of 36 %, 21 %, and 12 %, respectively [73]. The main consumer sectors of these materials are civil construction, followed by food packaging, beverages, perfumery, hygiene, cleaning, cosmetics, commercial and household utensils, disposables and textiles [1,73]. Resins composed of expanded PS, the least frequent polymer found in this study, are the least consumed in the global market, representing only about 2.1 % [73].

The classification of MPs with respect to their origin, whether primary or secondary, is considered quite complex if only the visual analysis of the particles is explored, for example, microbeads, primary MPs, although they most often present the morphology of regular pearls, can also be found in cosmetics in the form of fragments [63,74], which could lead to their erroneous classification as secondary MPs. Thus, accurate analysis of the chemical changes that occurred on the surface of the polymer, through the spectra obtained by FTIR, can assist in the classification of MPs regarding their residence time in the environment and origin, since the generation of secondary MPs results from the fragmentation of larger plastic waste that, with the time of exposure, have undergone physical changes (discoloration, porosities, and cracks) and chemical changes, that induced their degradation [65].

Polyolefin polymers, PE and PP, are the most susceptible to photo-oxidative degradation in the aquatic environment, due to the degradation mechanism of these polymers and also because, as a result of their low density, they are arranged on the surface of the water column, where they receive ultraviolet radiation more strongly, which thus initiates the chemical reactions of oxidation, with

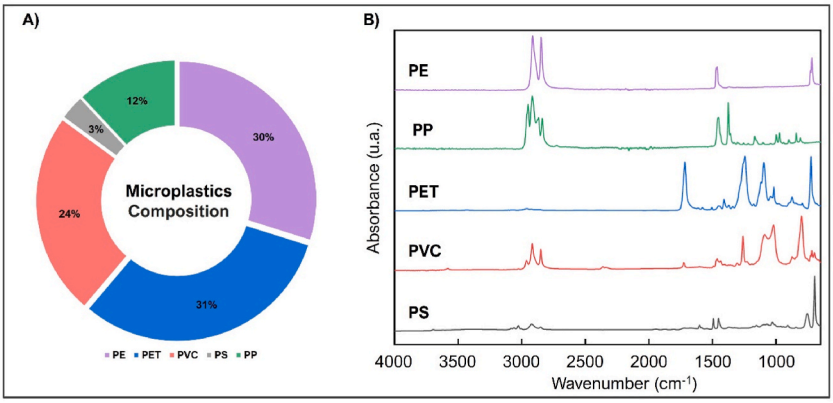

Fig. 6. Chemical characterization: A) Abundance of polymers identified by types of microplastics. B) FTIR spectra of typical microplastics.

the introduction of oxygen in the polymer chain and formation of carbonyl groups [65,75]. These same polymers are also often used in both the manufacture of plastic objects that originate secondary MPs and in the manufacture of primary MPs of the microsphere type, for example. Therefore, it is useful to adopt the carbonyl index to measure the oxidation levels in such polymers and to perform a more assertive classification as to the origin of the particle, which increases proportionally with the aging time of the MPs [65].

The presence of the characteristic carbonyl band in the spectra of PE and PP polymers for some fragment and film-type MPs reinforces their classification as being of secondary origin (Fig. 7). The values of the carbonyl index calculation were in the range of 0.13–1.97, which demonstrates that 67.86 % of the MPs identified as PE and PP were highly oxidized (Carbonyl index >0.30). As in other similar studies, this fact can be attributed to the long residence time of these particles in the environment [23,41].

The longer aging stage of the particle is also directly associated with a greater possibility of sorption of pollutants in the environment when compared to non-aged MPs. Although this fact was not investigated in the current study, the characteristics of the MPs analyzed herein may indicate an additional problem with regard to the possibility of ingestion of such particles by biota, with probable desorption of pollutants [40,76].

3.4. MPs risk assessment

Although synthetic polymers are biochemically inert, MPs distributed in the aquatic environment pose potential risks to the biota present there, which is directly related to the chemical identity of the polymer, particle size, stage of degradation, among other factors [39,50,77]. The chemical identification of the MPs particles found in this study highlights PET (28 %), PE (27 %), PVC (21 %), PP (11 %) and expanded PS (3 %) as the most frequent, respectively and, according to Lithner et al. [44], the risk assessment scores for these polymers are 4, 11, 10,551, 1 and 4, respectively. Thus, the risk assessment value calculated in this study, based on the polymer index, was 2,221, which indicates that the study area investigated can be classified as level IV, i.e. a high-risk site, according to the concentration of MPs obtained and the types of synthetic polymers identified [39].

The scoring criteria for each type of polymer was based on the chemical identity of the monomers in the polymer chain, their mass percentage in the structure and the mass percentage of possible chemical additives applied, as well as the potential toxicological risks of these monomers and their respective chemical additives used. PVC, common polymer in this study, received the highest score, due to the high percentage by mass of chemical additives in its composition, some of which are classified as phthalate chemical compounds,

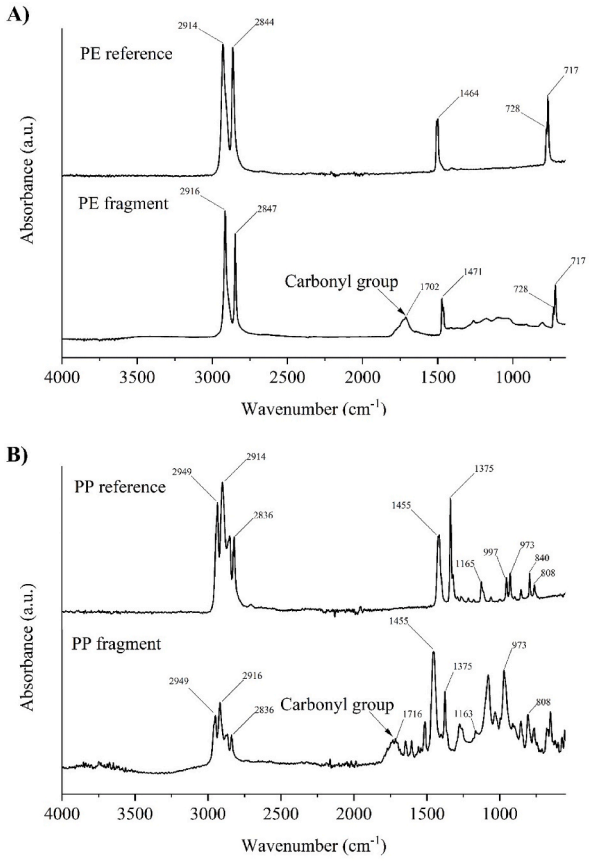

Fig. 7. FTIR-ATR spectra for polyethylene A) and polypropylene B) from references and microplastics collected in the Atibaia river basin, SP, Brazil. The peaks around 1715 and 1735 cm^{-1} indicate the presence of carbonyl groups formed by oxidation.

which have been identified as endocrine disruptors, toxic and carcinogenic [77,78].

When comparing our results with other similar studies, it can be seen that the Atibaia River basin can be classified as an area of high environmental risk for MPs pollution [39].

4. Conclusion

This study indicated for the first time the contamination by MPs in the aquatic matrices discharged from treated domestic effluent and surface waters in the Atibaia river basin, Campinas-SP. MPs were found in all samples, with chemically identified synthetic PET fibers being the most frequent and abundant, followed by highly oxidized PE fragments. Regarding size and colour, the predominant results were MPs in the size range $\geq$100 μm $<$ 1000 μm and coloured. Anthropogenic factors, such as a high population density and domestic effluent discharge at this site can be pointed out, according to the results obtained, as the major contributing pollutant sources. Climatic factors, such as a higher rainfall can be pointed out a contributing factor to the increased concentration of MPs in this environment. The abundance found here and high level indicated in the risk assessment demonstrates that MP contamination in the Atibaia river basin is among the highest reported in the literature at other lotic environments, indicating an ecological and public health concern, considering that the water from this watershed is used for the public supply of a considerable population. Therefore, further studies are needed on the efficiency of the Water Treatment Plant (WTP) located in the study area regarding the removal of microplastics from its processes, as well as investigation of the ingestion of these anthropogenic particles by aquatic biota, in order to mitigate the emission of these pollutants into this environment and contribute to its preservation.

CRediT authorship contribution statement

Glaucia Peregrina Olivatto: Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Romulo Augusto Ando:** Validation, Software, Methodology, Data curation, Conceptualization. **Rafaella Ferreira Fernandes:** Validation, Formal analysis, Conceptualization. **Ana Laura Athayde Lourenço:** Writing – review & editing, Methodology, Formal analysis. **Adijailton José de Souza:** Writing – review & editing, Conceptualization. **Valdemar Luiz Tornisielo:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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.

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