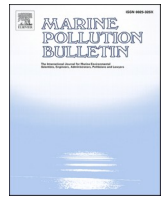




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Microplastics in Santos São Vicente estuarine – Hotspot in sediments caused by low energy hydrodynamic events in strongly populated areas

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ABSTRACT

Microplastics (MPs) have emerged as a significant class of contaminants due to their widespread presence in various environmental compartments. The ingestion of these particles poses a risk to both human health and the local biota. The investigation of the Santos estuary reveals the abundance of microplastics in the mangrove sediment. The highest concentration was 62,850–93,050 MPs·kg⁻¹dw, never seen before in Latin America coast. The region investigated is characterized for silting sites and low energy events, notably Rio dos Bugres, influenced by anthropic aspects, while the São Vicente e Santos channels prevail the high energy hydrodynamic regime. In consequence, the MPs are entrapped in the interior of the estuary, affecting drastically the biota of mangrove. Spectroscopic investigation identified: polymers, pigments, herbicide and additives. The hypothesis is that densely populated siltation areas combined with low-energy events serve along the estuary for MPs accumulation and hotspots formation.

1. Introduction

Estuaries are important sources of ecological sedimentation for the oceans and, at the same time, economically strategic transition areas between rivers and oceans incorporating port facilities (da Cunha Lana et al., 2018; Neto et al., 2019; Conte, 2016). Estuaries environments have little or scarce microplastic pollution information (Picó and Barceló, 2019) even though are considered microplastics hotspots in some countries (Fok and Cheung, 2015; Haddout et al., 2021).

The world's estuaries are considered important for filtering microplastics from coastal waters to avoid integrating pollution into the ocean. However, this consideration fails if we observe that the contaminants can be entrapped in places with dense populations, where they damage biota and human life.

The present work investigates sediments from an important and greatly impacted mangrove area, both from an ecological and economic point of view. The Santos-São Vicente Estuarine System (SESS) is considered a study model for presenting a permanent preservation under the domain of port and industrial facilities. The SESS is in the Santos

basin in a sedimentary area that extends over approximately 352 thousand km², covering the northern portion of the coast of the state of Santa Catarina, the southern portion of the state of Rio de Janeiro, and the entire coast of Paraná and São Paulo (Viana and Marum, 2020). In addition to the characteristic and dynamic conditions of the estuary, settlements of irregular dwellings lacking basic sanitation system are present in that coastal region.

The Santos-São Vicente estuary, home to the Port of Santos and the Cubatão Industrial Complex, despite its designation as a permanent preservation area, faces substantial challenges stemming from human activities, irregular occupation, and the presence of municipal sanitary landfills and dumps (Moschetto et al., 2021; Abessa et al., 2011; CETESB, 2019; Lamparelli et al., 2001). The estuarine channels and river sections within the SESS directly experience the influence of the tidal patterns and harbor a vital mangrove ecosystem, Fig. 1.

Microplastics (MPs) are vectors of microorganisms and plastic additives present in their composition, as well as chemical contaminants carried or adsorbed from the environment, being leached, or desorbed to organisms or in the internal region of organs and tissues (Picó and

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Barceló, 2019). Microplastics can be transferred along the food chain and when ingested, accumulate in the digestive tract, and reach points in the body such as the circulatory system, placenta and breastmilk (Browne et al., 2008; Nobre et al., 2015; Van Cauwenberghe and Janssen, 2014; Ragusa et al., 2021, 2022).

Microplastics from polluted rivers can accumulate in the sediment and remain available to the consumers entering the food chain, affecting biota and health through the consumption of contaminated fish (Queiroz et al., 2022).

Microplastics have become ubiquitous in the human food supply, raising concerns for potential health risks. The assessment of MP in food is vital for food security (FAO, 2009). Fish and marine organisms of commercial interest serve as major pathways for human exposure of microplastics. Ingestion of microplastics causes physical effects, compromising the ability of organisms to feed, as well as the toxic effects at cellular and biochemical levels (Osman et al., 2023).

Among the techniques used to identify and characterize

microplastics, micro-Raman is commonly regarded as the gold standard for characterizing the morphological features of the microparticles and identification of multicomponent structures, including polymer matrices, pigments and contaminants, with ease of use for particles down to the micrometer range but allowing the characterization of nanoplastics in the submicron range down to dimensions of 30 nm. Another important technique capable of identifying polymeric composition in microplastics is the infrared spectroscopy with the limitations in terms of spatial resolution, especially when analyzing heterogeneous samples or small particles (<20 μm) (Ragusa et al., 2022; Sobhani et al., 2019). Investigation of microplastics in highly populated areas can have considerable implication with the quality of life of the people.

Slums on stilts represent one of the most worrying issues from an environmental point of view in the region. In addition, they are characterized as one of the main polluting sources of illegal disposal of solid waste and sanitary sewage that daily pollute the sources in the ecosystem. However important factors influence the deposition or



Fig. 1. Localization of the sites in the SESS complex, São Paulo, Brazil. Geographic map of investigated sites includes urban area in the center, interior of the estuary (at top) and the Channels of Santos (at right) and São Vicente (at left). The dept. at which the sediment surface was found were approximately: (P1) 6.0 m; (P2) 4.0 m; (P3) 2.0 m; (P4) 1.5 m; (P5) 1.0 m; (P6) 2.0 m; (P7) 4.0 m; (P8) 2.0 m; (P9) 3 m; (P10) 2.0 m.

fixation of MPs in sediments.

Would the abundance of microplastics in different sedimentary zones of the estuary have the strong influence of water hydrodynamics and consequently the presence of potential microplastic hotspots? In this case, would the local population be held hostage to the damage caused by the pollution of MPs?

Given this geographical space, the present research made it possible to know several sites integrating the possible causes of environmental impact. It was then intended to show in which parameters to act for the remediation of environmental damage.

2. Methodology

2.1. Sampling and collection site

The collections were carried out in partnership with the Instituto EcoFaxina, a Non-Governmental Organization (NGO) that works on marine pollution mitigation and restoration of degraded mangrove areas in regions occupied by stilt shanty towns. The purpose was to obtain PMs samples from highly populated sites, sites of strong hydrodynamic events and site of sedimentation in siltation area, of the large mangrove region of estuarine between Santos and São Vicente (from Port of Santos Channel to Canal de São Vicente, close to México 70 stilt shanty town. Sites considered as sources of irregular waste disposal were highlighted in the contamination gradient between regions occupied by shanty-towns on stilts and port terminals. The collection of sediments was carried out at ten different sites of the geographic coordinates reported in Table 1 and illustrated at Fig. 1, during the period April–July 2018. The tool used was one Van Veen grab sampler, (Gimiliani et al., 2020), area of 680 cm², and volume of 5.12 L, collecting sediment from 1 to 10 cm of the surface of sediment. Three times the van Veen dredged a volume of sediment in the same site, to collect a total of about 8 kg of sediment transferred to stainless steel container and identified for each site.

2.2. Preparation of collected samples of the sediment in lab and size separation

It was not used high density solutions for separate the MPs because higher density polymers such as polyvinyl chloride and polyethylene terephthalate may have been excluded (Leads et al., 2023). Sample preparation and microplastic quantification were performed according to the methodology established by Frias et al. (2019).

The size-frequency distribution of microplastics was analyzed with the using a series of stacked sieve meshes. First, each previously stored sediment sample was homogenized, followed by drying 500 g in an oven at 50 °C for maximum 48 h. Next, samples of dried 20 g were selected for wet sieve separation, using water type 1, and the system of sieves mesh: 2.0, 1.0, 0.5 and 0.25 mm. After the sieving process, the wet samples, removed from each sieve, were transferred to previously weighed Petri dishes and dried once again, in an oven at 50 °C for 12 h. and weighted

Table 1
Geographic coordinates of the sampled local position.

Point	Region	Geographic coordinates	
		Latitude	Longitude
P1	Canal de São Vicente	23°58'22,60"S	46°24'53,35"O
P2	Lagoa da Pompeba	23°56'11,89"S	46°24'51,05"O
P3	Rio dos Bugres I	23°56'50,15"S	46°22'57,26"O
P4	Rio dos Bugres II	23°56'40,62"S	46°23'6,66"O
P5	Rio dos Bugres III	23°56'26,85"S	46°23'30,09"O
P6	Rio São Jorge	23°55'55,86"S	46°22'48,15"O
P7	Rio Casqueiro	23°55'20,00"S	46°24'7,56"O
P8	Foz do Canal de Piaçaguera	23°54'44,61"S	46°22'44,14"O
P9	Ilha do Barnabé	23°55'5,57"S	46°20'7,72"O
P10	Canal de Santos	23°56'59,94"S	46°18'20,37"O

on an analytical balance to determine the mass of MPs in each sieve. During the processes of drying, wet sieving and redrying of the sediment samples, “blanks” samples were used in Petri dishes with filter membrane (0.45 µm). The use of these “blanks” permitted to identify and control contamination of samples by synthetic fibers and other microplastics present in the laboratory environment, avoiding false positive results (Masura et al., 2015).

Visual identification of extracted microplastics from estuarine sediments were classified using stereomicroscope (Olympus SZX16) equipped with a camera (Olympus DP73) and connected to the PC with a software image analysis (Olympus cellSens Version 1.5). Visual classification of microplastics was based on the selection criteria proposed by Imhof et al. (2012) and Crawford and Quinn (2017) in terms of a size range and standardized size. In terms of shape, they were classified as fibers, fragments, foams, and films. The colors remained in the MPs were only observed on the capted images.

2.3. Microplastic quantification

The Petri dishes containing the dry material removed from each sieve were examined under a stereomicroscope at 0.7 to 15× magnification to count the number of microplastics present in the sediment samples obtained from the sieves with sieve meshes of 2.0, 1.0, 0.5 and 0.25 mm. As part of the quantification method, the total average count of the five replicates of each sample was calculated and is presented as plastic particles per 20 g of sediment.

A recognition pattern was used based on the descriptions made by Masura et al. (2015), Nor and Obbard (2014) and visual count by magnifying glass of plastic materials. Stainless steel tweezers were used to assist in the active search for microplastics and their separation from the fragments, to facilitate their visualization. Plastic fragments observed were ones colored, opaque, transparent, and with irregular shapes. Colored and transparent lines with uniform thickness, including that in agglomerates with other residues, were also identified. To confirm the constitution of the plastic particles during the stereoscopic examination, the fragment was macerated with the aid of tweezers. If the particles retained their shape, they would be separated and correctly identified as plastic.

The number of MPs counted in the Petri dishes after transfer from the sieves means the quantity by size of microplastics in the sediment sample and represents the size distribution of each site. Particles retained in the 0.25 mm mesh could not be removed due to their small size and invisibility to the naked eye. After that, MP by MP were transferred, using inox tweezers, to a glass sample holder (2 mL) and named according to the original site (P_x site MP_y N°MP) for characterization of its polymer type through FTIR spectroscopy and micro-Raman spectroscopy techniques. Details of the methodology are described in Supplement S1.

2.4. Quality control and prevention of cross-contamination

MP samples are separated after care with appropriate measures to reduce microplastic contamination in the field and laboratory by using stainless steel and glass equipment and no plastic tools, when processing the collected material, according to Wesch et al. (2017) and Torre et al. (2016). The following precautions were taken:

1. Sample storage and preparation: The collected sediment samples were stored in metal or glass containers. Milli-Q type 1 water was used in the laboratory washing processes to avoid contamination of PM in water. The sieves system used was covered with aluminum foil during the tests and the glass dishes with the separated MP samples were also covered to avoid possible deposition of any MP from the laboratory environment.

- Equipment cleaning: The sample holders of the stereomicroscope and the FT-IR spectrometer were thoroughly cleaned with ethanol and inspected before use.
- Blank tests: Blank tests were conducted to check for potential contamination from the laboratory environment. During the preparation of selected sediment samples, blanks consisting of a filtration membrane (0.45 μm) on a glass dish were evaluated for MP deposition from air, water or the environment (Frias et al., 2019). No microplastics or fibers were detected on these membranes, following the same procedure used of washing the sample under sieving and drying the glass dishes, indicating negligible contamination.
- Laboratory precautions: cotton lab coats and gloves, metal tweezers were used and the samples were kept in closed spaces to minimize plastic pollution in the air.

2.5. Polymer identification using micro-Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR)

The FTIR identification of the samples was processed in spectrophotometer Lumos model from Bruker using a Vetex 70v ATR accessory. It has a microscope attached for imaging register. The identification was made by the attribution of the reported peaks according to literature references of polymers, % of match >85. This technique allows characterization of smallest medium size (1 < 5 mm). The use of the FTIR technique with ATR (Attenuated Total Reflectance) mode allows analysis of smaller particles and high precision due to the reflectance mode of the infrared light that passes through the ATR crystal and the sample. The resulting attenuated radiation is measured in wavelength by the spectrometer, generating the spectral characteristics of the sample's absorption. Spectra of the MPs are reported in the Supplement 1, Fig. SF1.1 to SF1.10.

The characterization of MPs fractions by micro-Raman, based on the attribution by Hit Quality Index (HQI) using the software KnowItAll provided the composition of MPs by spectroscopy techniques. The MPs samples were mounted on a glass slide for Raman spectral analysis which was carried out on a micro-Raman spectrometer (LabRam, Horiba) utilizing a long-range objective (50 \times , 0.55 N.A.) that allowed focusing through the cover slide. The Raman spectrum of the MPs is reported in Supplement 1, Fig. SF1.11, with technical details. The morphology of the particles and Identification of additives by micro-Raman are reported in the Supplement Table S1.2. The relative abundance of particles distinguished by the ratio of lines/fibers: fragments per 20 g of sediment, is reported in F51.12.

2.6. Sites investigated for the study

The Estuarine System of Santos and São Vicente (SESS) is in the Metropolitan Region of Baixada Santista (RMBS), central portion of the coast of the State of São Paulo. This area is influenced by multiple polluting anthropic activities that alter its ecological processes. In the 60s and 70s, the expansion of the Port of Santos and the Industrial Pole of Cubatão, as well as the increase in tourism on the coast of São Paulo, generated a growing demand for labor, resulting in a large migratory flow to the RMBS. As a result, mangrove swamps and hillsides became places of illegal construction and housing.

The hydrodynamic events analysis for the present study considered the Marine currents reported by methodology of collected data on sea level, current velocity, and direction using instruments like Acoustic Doppler Current Profilers (ADCPs) and tide gauges. And use Numerical Modeling Delft3D-FLOW to simulate the behavior of water currents. This model considers various factors like tides, wind, and bathymetry (the underwater topography) to predict current patterns (Baptistelli, 2015). The sampling station setup was designed to capture data from various locations within the SESS, considering both ecological impacts and hydrodynamic processes. These stations provide information for assessing sediment contamination, and overall ecosystem health. The

choice of sampling sites was based on previous information associated with plastics waste deposition around the mangrove region. The criteria for site selection included proximity to slums, the number of inhabitants or houses, and water distribution patterns in the estuary which aimed to investigate the influence of water hydrodynamics on the abundance of MPs and to identify potential microplastic hotspots showing in which parameters to act for the remediation of environmental damage.

3. Results

3.1. Microplastics (MPs) in the sediments of SESS

The collection of samples for investigation was done with the support of a non-governmental organization. The Ecofaxina NGO, organism that works in the estuary region, collected sediments samples of ten different, from Santos to São Vicente through the interior of the estuary.

The quantitative determination of microplastics (MPs) in ten investigated sites listed in Table 1, reported the high contamination in the area, Table 2.

MPs ranged from 6.150 to 93.050 microplastic items $\cdot\text{kg}^{-1}\text{dw}$ (dry weight), Among the studied sites, MPs count was inversely proportional to the mesh used.

As the MPs count increased, the standard deviation values increased considerably. According to the literature (Van Cauwenberghe et al., 2015), the result implies great variability of the MPs dimensions.

The MPs identified in the ten sites of the estuarine region presented the polymeric distribution in quantity of MPs according to Fig. 2A. Association of particles of different dimensions with the hydrodynamic of site, Fig. 2B and distribution of typical plastics Fig. 2C are also reported.

The microplastics reached were Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Poly(ethylene terephthalate) (PET), Polyurethane (PU), Poly(methyl) methacrylate (PMMA), Polyamide (PA), Ethylene Vinyl Acetate Copolymer (EVA), Polyvinyl Chloride (PVC), Polycarbonate/Acrylonitrile butadiene styrene blend (PC/ABS) and Polyvinyl chloride acetate (PVCAC). The distribution in sediments is strongly dependent on hydrodynamic of the sites and is quantitatively intensified for lower strength events.

The map in Fig. 3 presents the intensity of water hydrodynamic events in the estuary and supported the analysis of Fig. 2B. In evidence, the inset reports the detail of Rio dos Bugres.

Supported by the results in Fig. 3, the Rio dos Bugres and Ilha de Barnabé presented a greater abundance of MPs in the sediment samples in relation to all the collected sites between Canal de Santos and São Vicente. It ranged in an extensive distribution and high quantity from 36.300 in Ilha de Barnabé and 93.050 microplastic items $\cdot\text{kg}^{-1}\text{dw}$ in Rio dos Bugres. A high count like that of Rio dos Bugres (in MP > 250 μm) has never been reported before, and is among the most contaminated sites in the world (Nawar et al., 2023).

Table 2
MPs quantification in 20 g of sediment in total mean.

Site	Total mean \pm DP 20 g	PM kg^{-1} dw
Canal de SV (P1)	356 \pm 95	17,800
Largo da Pompeba (P2)	424 \pm 149	21,200
Rio dos Bugres I (P3)	1257 \pm 431	62,850
Rio dos Bugres II (P4)	864 \pm 388	43,200
Rio dos Bugres III (P5)	1861 \pm 844	93,050
Rio São Jorge (P6)	349 \pm 159	17,450
Rio Casqueiro (P7)	339 \pm 185	16,950
F. C. de Piaçaguera (P8)	123 \pm 62	6150
Ilha do Barnabé (P9)	726 \pm 283	36,300
Canal de Santos (P10)	134 \pm 12	6700

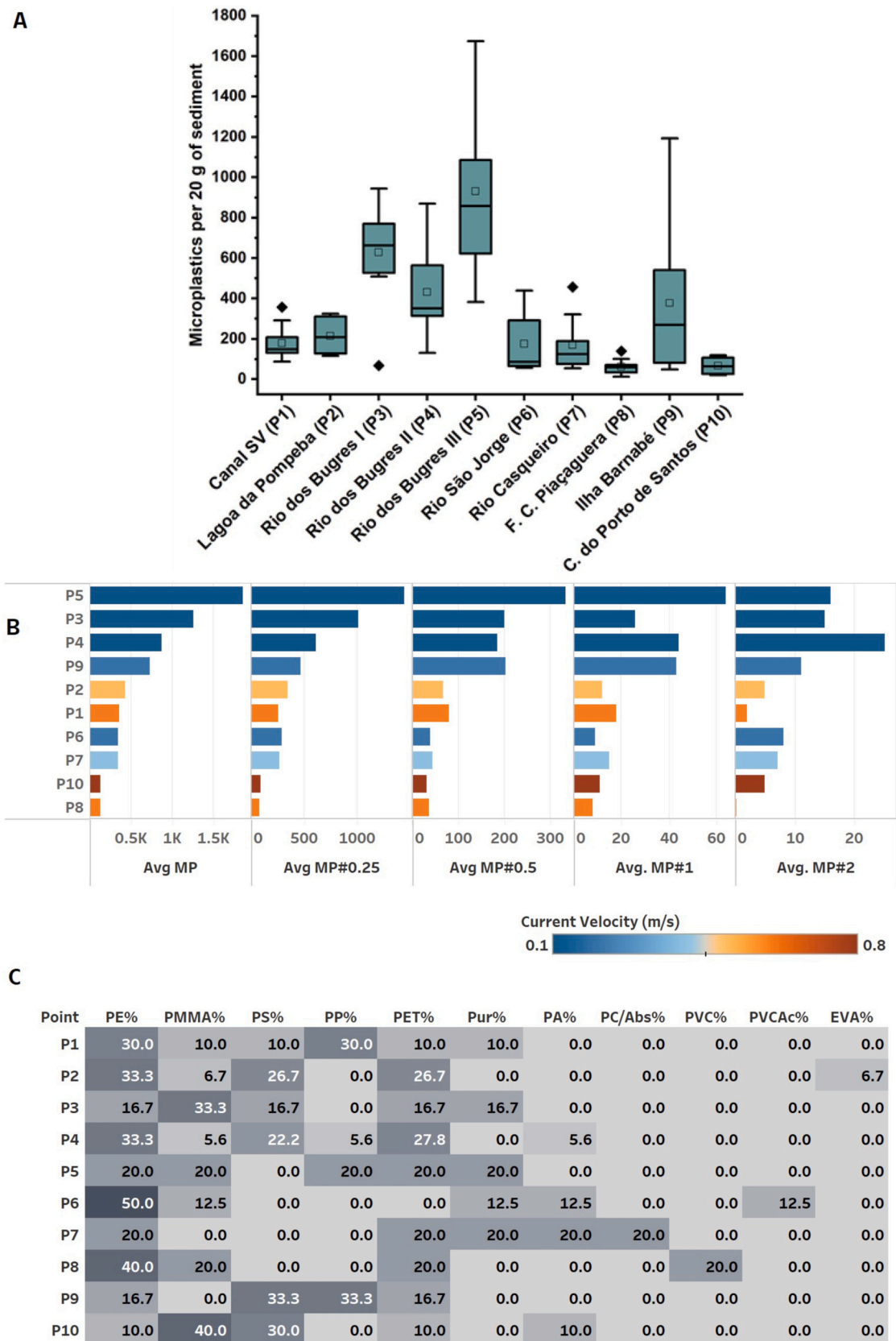


Fig. 2. Distribution of MPs abundance per 20 g of sediment collected in each site (A); average of particles in different mesh (0.25; 0.5; 1.0; and 2.0) associated to the current velocity scale of the hydrodynamic of sites (B); and types and content of the different polymers identified in the sites (C).

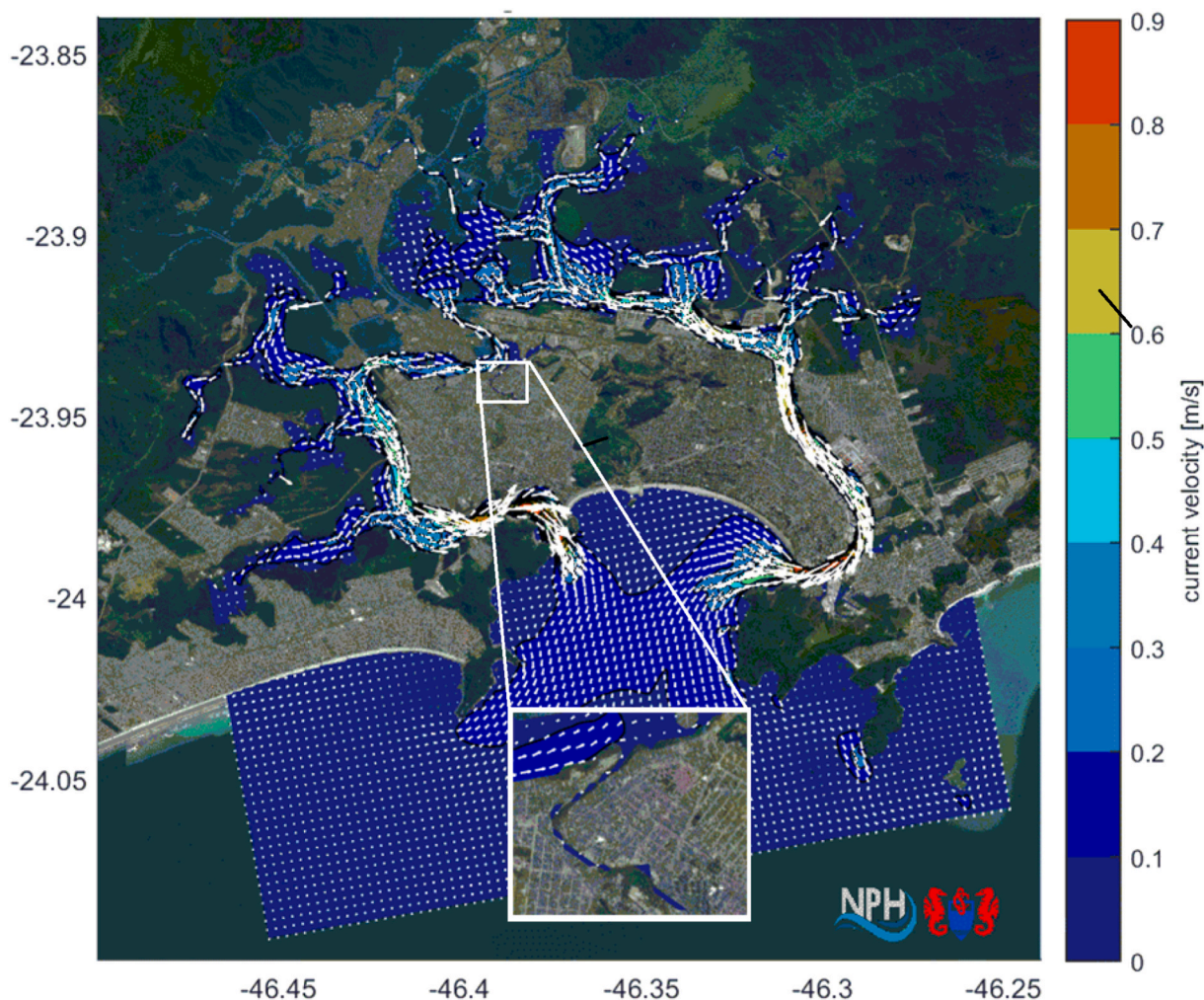


Fig. 3. Maritime currents map indicates the strong events in both channels and events of low intensity in the interior of the estuarine, in rivers and small channels. Based on the current velocity m/s values, the scale on color intensity reported in Fig. 2B. In the detail is represented relative intensity of events found in the Rio dos Bugres.

Source: NGO EcoFaxina (Instituto Ecofaxina, 2023).

3.2. FTIR and RAMAN images and multicomponent identification of microplastics

The particles of MPs have different forms between fibers, fragments, fragments foams, and lines. Fig. 4 illustrates the MPs images obtained by microscopy-FTIR from particles identified by FTIR.

FTIR spectra are reported in the Supplement S1, Fig. FS1.1 a FS1.10. Some features were obtained through the micro-Raman technique spectra as the identification of multicomponent of a single sample. The images captured simultaneously to the Raman spectrum showed details of the MPs surfaces. The difference expected for HDPE and LDPE, in FTIR spectra, would be observed at wavelength of 718 cm^{-1} for LDPE, and at the split in 720 and 730 cm^{-1} for HDPE instead. However, that split many times is not observed. That difference was clearly observed in the micro-Raman spectra concerning the $-\text{CH}_2$ bending of crystalline at 1297 and 1418 cm^{-1} as observed in P3MP1, and absent in P1MP1 and P2MP15 (Strobl and Hagedorn, 1978).

Identification by Micro-Raman spectroscopy is convenient for multiple components analysis in which additives are combined with MPs (Furukawa et al., 2006; Hendra and Agbenyega, 1993). Other than spectra identification, the punctual images of particles were captured by RAMAN and reported for illustration, in Fig. 5 and Supplement S1, Fig. FS1.11.

Fig. 5 displays the images of the MPs particles, with each Mosaic

image capture associated to the respective sample name. The scale bar in all images represents a length of 1 mm. Insets within the images show pictures taken using a $50\times$ objective, with a scale bar of $50\text{ }\mu\text{m}$ for reference.

MPs particles, $>250\text{ }\mu\text{m}$, are composed by fibers/lines, foams, and fragmented pieces. Detailed of FTIR and micro-Raman spectra are reported in the Supplement, Fig. FS1.1 to FS1.10, and Fig. FS1.11, (Dias et al., 2010; Hummel, 2002; Silverstein et al., 2005). See also rapport of fragments and fibers in Fig. FS1.12.

Raman technique showed multicomponent spectra in some cases as reported in Table S1.2. Their identification integrated information about the composition in additives as environmental pollutants such as dyestuff, pigment, among others impregnated in MPs (Song et al., 2015).

One sample of particular importance was the P1MP8, in which were detected butyl acrylate-methyl methacrylate graft copolymer associated to herbicide (Trifluoromethyl)phenylhydrazine and additive 2,2-Diethoxyacetophenone used in the acrylate-based composition.

In Rio dos Bugres was found the highest diversity of MPs. This area holds the largest SESS stilt shantytown. This makes clear the apparent pollution by plastic waste over mangrove regions in its incessant disposal by residents without basic sanitation conditions and home garbage collection.

The Lagoa da Pompeba count is attributed to garbage deposition that comes from the populated area (P1) but also, and probably mainly,

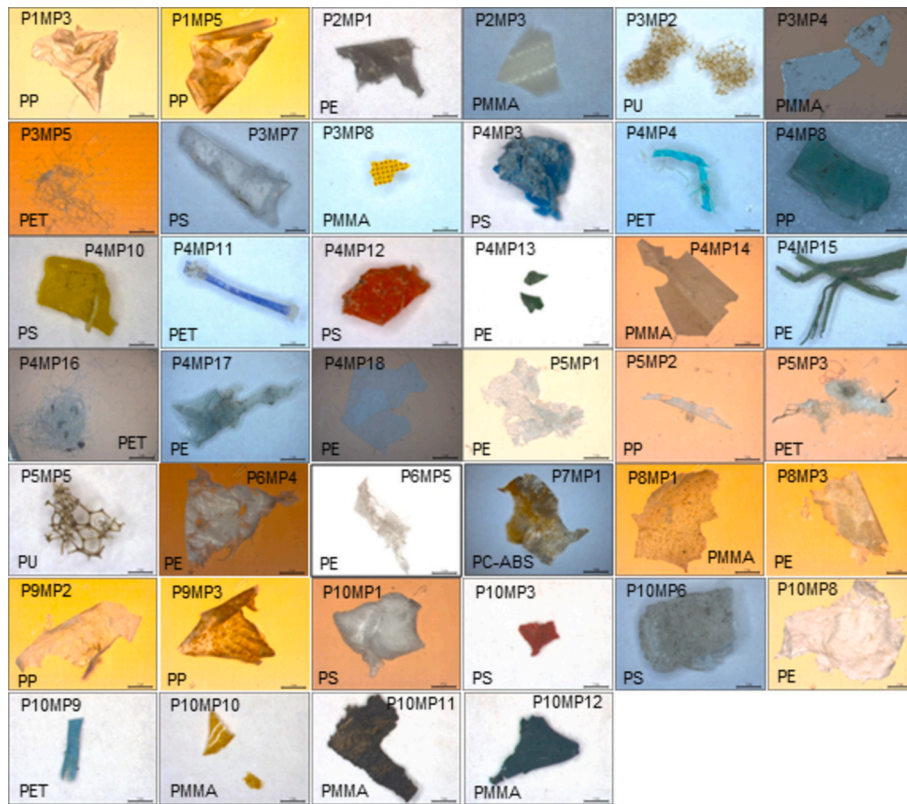


Fig. 4. Images of MPs identified by FTIR characterization. Different forms of fiber, foams and fragments.

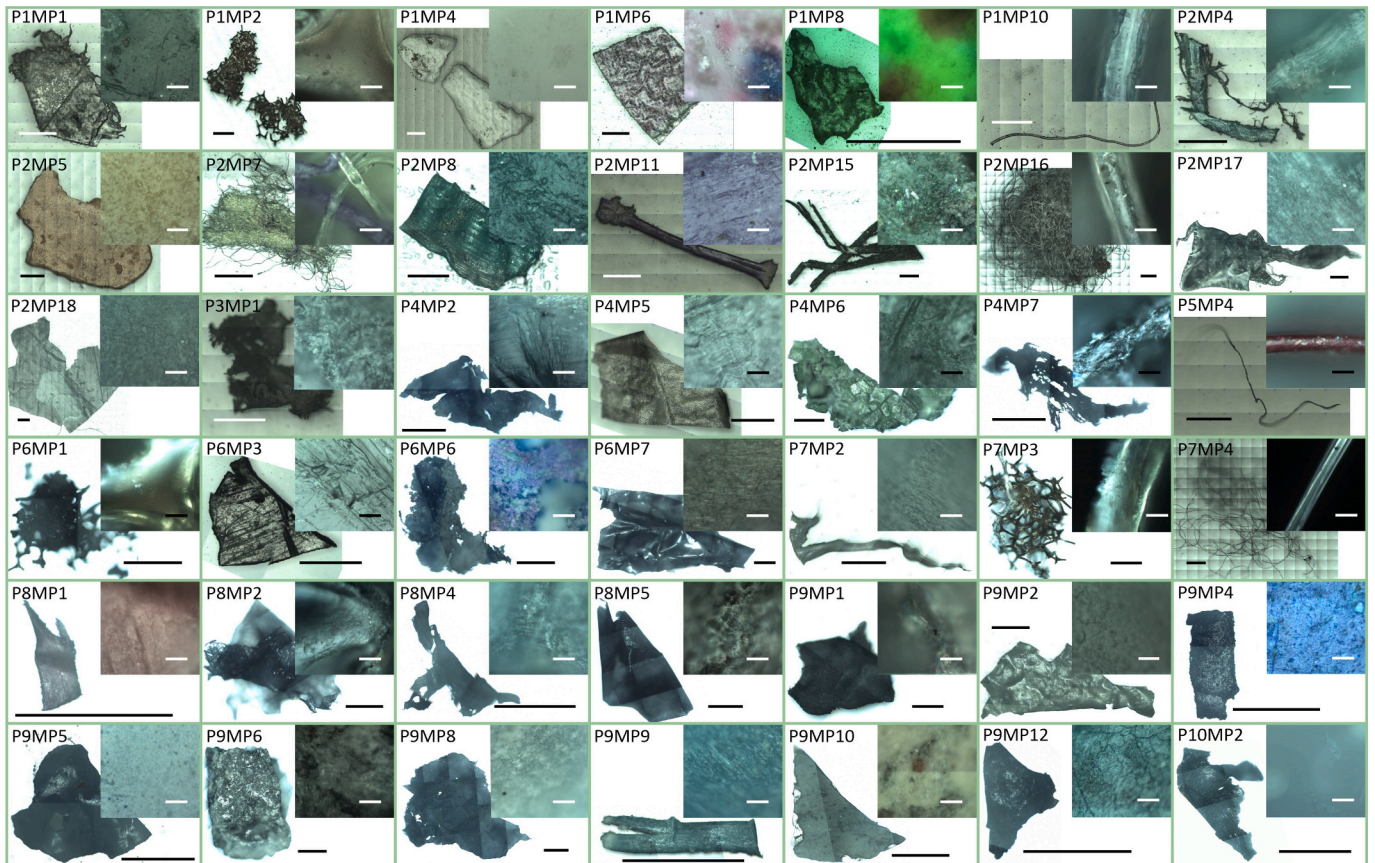


Fig. 5. Illustration of MPs investigated by micro-RAMAN spectroscopy based on Mosaico image capture.

owing to the sedimentation on siltation area.

The plastic lines and fibers presence are probably influenced by the proximity of some sources, as well as raw sewage and effluents from washing clothes, waste disposal sites and stilt shantytowns, fishing materials lost in SESS. According to the literature (Van Cauwenberghe et al., 2013) residues of those sources are commonly present in the sediment. Fibers are preferably removed from the suspension as they are trapped between the sediment grains that settle. Due to the elongated shape and the large surface area to volume ratio, the fibers tend to be dragged and deposited along with the sediment grains, which explains the fiber enrichment in sediment samples. According to Pohl the fragment deposition is inversely controlled by its low density, making the fragments prone to suspension and therefore, less prone to deposition (Pohl et al., 2020). But the question remains: why Rio dos Bugres presents sediments with high MPs count? Are anthropogenic aspects the more important parameter to be considered and addressed?

4. Discussion

4.1. General considerations

What are the differences between estuaries in Santos, Brazil, and highly contaminated estuaries in China or India are attributed to: 1) Local sources of pollution: Estuaries in Santos, India and China may have different sources of pollution, such as industrial activities, sewage discharge, and littering. These sources affect the local levels of MPs and other pollutants. 2) Waste management practices: Santos, India and China have different waste management practices, which can impact the amount of plastic waste entering estuaries and the ocean. Effective waste management practices, including waste reduction, recycling, and proper disposal, can help reduce plastic pollution in estuaries. 3) Environmental conditions: The specific environmental conditions, such as water temperature, salinity, and tidal patterns, influence the distribution of pollutants and the local ecosystem. 4) There are many industrial areas near estuaries in China, one of the world's largest producers of goods and a growing economy, which has led to the development of numerous industrial areas along the coast (Chen et al., 2023).

Industrial activities release pollutants and waste into the nearby waterways, rivers, and channels. These include pellets and MPs, which can have negative effects on the local ecosystem and biota life. Contamination found in the Pearl River Estuary, the East China Sea, and the Yellow Sea, where MPs have also been detected in sediments, surface water, and marine biota, suggests that the contamination has entered the food chain. The main source of MPs in China's estuaries from wastewater treatment plants, land-based litter, and shipping activities (Chen et al., 2023; Duan et al., 2021).

The abundance in the studied estuaries in China and India varies depending on the location and the methodology. However, in general, MPs have been found to be present in high concentrations in their estuaries. Mean concentration of MPs in mangrove sediments between five regions of Southern China, was the highest in Futian mangrove with 2249 items·kg⁻¹ dw in the region composed by fiber, white-transparent MPs (Fan et al., 2019).

It was reported in the Bay of Bengal, India, 180 items·kg⁻¹ dw (Chen et al., 2023); Sanggou Bay, China 2178 items·kg⁻¹ dw; South Yellow Sea, China 560–4205 items·kg⁻¹ dw; Eastern Guangdong, the South China Sea, China, 0–444 items·kg⁻¹ dw; Changjiang Estuary, China 20–340 items·kg⁻¹ dw. Shenzhen was especially impacted, owing to industrial development in this city which has brought about tremendous pressure on the coastal ecosystem (Ding et al., 2022). And even higher concentration of 10.0×10³ items·kg⁻¹ dw MPs was found in specific site of the sediments.

In the Ganges River Delta, studies have found that the abundance of microplastics in sediments 1200 items·kg⁻¹ dw, range similar levels of the Pearl River estuary in China. In the Krishna River Estuary, the abundance in surface water has been found to be in the range of

hundreds to thousands of particles per cubic meter (Neelavannan et al., 2023). In seven different sampled rivers of the Indian estuarine – Ganga-Brahmaputra delta, in area of intense industrial activity, abundancies of 15–120 up to 80–9597 items·kg⁻¹ dw were reported and considered as the more contaminated estuarine of India.

In SESS minimum and maximum amounts of MPs ranged in a large distribution and high quantity from 6.150 to 93.050 items·kg⁻¹ dw between the studied sites. Storm water run-off from urban areas, construction areas and landfills are the major land based source of debris. If is true that the amount of MPs in the marine environment is increasing (Andrady, 2011; Horton and Barnes, 2020), and considering that about 80 % of marine MPs are of land-based origins such as wastewater treatment plants, coastal landfills, and touristic activities (Neelavannan et al., 2023; Sadri and Thompson, 2014; Sousa et al., 2021), the influx of contaminated water from plateau or plain ending in the estuaries are determinant in the MPs abundance (Kane et al., 2020). Emphasized that microplastics are strongly controlled by near-bed thermohaline currents, characterized by saline density and temperature differences, in which deep sea benthos are fed and consequently exposed to MPs, a kind of “hotspot” for both benthos and pollutants.

Describing the dynamic of currents in the Tyrrhenian Sea, (Kane et al., 2020) affirms its influence in the transfer of MPs along shelf currents. Powerful gravity flows effectively flush them to the deep-sea, while thermohaline-drive bottom currents segregate MPs into localized hotspots of high concentration. The sedimentation as result of their long-term sequestration depends upon the intensity of subsequent bottom current activity and rate of burial. All of MPs buried would be exhumed as leaching stresses exceed the critical shear to be transferred by water suspension (Pohl et al., 2020).

Similar dynamics may be associated with the port bed dredging cycle for different impacts. On the negative side, the dredging process can disturb the sediment bed, releasing pollutants, such as MPs accumulated in bottom sediments and rising pollution levels in the ocean increasing marine life risks. However, dredging is economically advantageous for accessing larger vessels.

In general, dredged material is often disposed of in designated areas such as offshore disposal sites. Containment prevents contamination of the oceans, but it also requires a clear disposal policy avoiding being thrown back into the ocean.

4.2. Transport and deposition of MPs, pellets, and plastic debris

Microplastics, pellets and plastic debris are spread across the coastal environments of beaches, rivers, and mangroves, as an effect of various transport and deposition mechanisms that occur over time. Plastic waste is associated with intense anthropogenic practices; pellets are frequent industrial products in port loading and unloading zones, especially in areas of the petrochemical industry, while microplastics derive from the environmental degradation of both plastic residues from which they are formed, along the way per years, due to weathering, photodegradation, constant impact on dynamic processes, leaching, among others.

Turra et al. (2014) demonstrated that plastic pellets are consistently found distributed at depth, rather than just floating along the seacoast. As a result, using the vertical distribution data of pellets taken and collected at the Santos seafront, it was demonstrated that when the abundance in deep sediments is included, analyzing along the sediment column, the estimates are much higher. As reported by Magini et al., (2007), the high sedimentation rates in the of the seafront Santos Bay, at around +1.6 m/year is due to the influence of local oceanographic parameters coastal currents, waves and tides. It was highlighted the deposition of marine litter on west beaches of the estuary. Thus, the transport of pellets, litter and debris occurs from east to west, as pointed out by Turra et al. (2014) and Gorman et al. (2020). Do MPs behave the same way?

Hydrodynamic of waters in Santos Bay drives the transport of residues from east to west owing to low energy refraction current combined

with estuarine flows (Harari and Camargo, 1998). A similar trend of Marine litter (specially floating debris) distribution was observed for pellets (Ribeiro et al., 2021). In this context, the hydrodynamics of water bodies also interferes strongly in the MPs transport.

4.3. The case of SESS

Considering the possibility of contamination movement from the São Paulo plateau towards Santos's estuary, the following discussion should be made: the Guarapiranga reservoir flows into the Pinheiros River as well as the water of the Billings reservoir. Therefore, this contamination does not reach the ocean but other directions. The wind moves prominently from Santos towards São Paulo. Only the cleanest and least contaminated branch of Billings reservoir flows to Santos. Therefore, the MPs pollution does not come from reservoirs, as they undergo continuous water treatment before reaching the SESS estuary. However, hydrodynamic dispersion associated with high and low tides can explain the MP contamination of the Santos-São Vicente estuary.

SESS and Santos Bay region have complex water circulation comprising fresh continental waters that come from the Serra do Mar and salty waters from the Atlantic Ocean. The tide regime, winds, and oscillations in sea level oscillations associated with cold fronts incursions contribute to the hydrodynamics of the region (Harari and Camargo, 1998; Harari and Gordon, 2001). In the floods and ebbs of spring tides, there is convergence and divergence of surface currents in the Bertioiga and São Vicente Channels (area where the tides meet) and single direction currents in the Santos Channel.

During the syzygy (period with large intensity currents, the ebb flood tides can favor the solid waste dispersion within the SESS and in Santos Bay. During the flood tides, it is expected that residue transport from Santos Bay to the interior of SESS occurs from west to northwest direction. The intensity of the ebb currents is greater than the flood currents in periods of syzygy, providing greater transport of waste from the interior of the estuary to Santos Bay.

In the Canal of São Vicente, the presence of convergence and divergence in relatively weak flood and ebb currents is in opposite directions while in the Canal do Porto de Santos, the currents have a single direction with greater intensity, which leads to a more intense transport of waste through the Canal do Porto de Santos.

On the coast of São Paulo there are influences of currents generated by the tides (perpendicular to the coast), prevailing winds (NE-S direction) and cold fronts. The most intense currents are those coming from the cold fronts, being parallel to the coast and flowing in the S-NE direction (Moreira et al., 2016).

All these considerations were applied in the analysis of materials collected in bottom sediments of ten different sites within the Santos-São Vicente estuary.

At sites P1, P8 and P10, the lower abundances of MPs found coincide with tidal currents with higher energy and intense boat traffic (P1, P10), making the deposition of plastic particles slower at these points, especially at site P10 where it is influenced by dredging of Santos Port.

On the other hand, at the P9 site (Ilha do Barnabé), as it is a port area and without the presence of slums on stilts, it was not expected to find high abundance compared to the other collection sites. The P9 site presents the formation of a water gyre influenced by the junction between the unidirectional fluvial flow with the brackish water tides, providing an area of siltation (Sartoretto, 2014), that is, of accumulation of sediments, which justifies the abundance of microplastics in this location.

Considering Rio dos Bugres as a MPs hotspot, some features are important. The Rio Bugres, that gained notoriety for the irregular occupation of its banks by stilt houses, called Dique da Vila Gilda, receives water from an extensive network of small channels in the neighborhood. These urban drainage channels are a land-based source of pollution and contribute to the pollution of the Rio Bugres on rainy days, when there is surface runoff, with the solid waste that reaches

these channels through the stormwater galleries. Surrounding the Rio Bugres is the largest community of stilt houses in Brazil. This subnormal settlement, located on the banks of the Rio Bugres, borders the municipality of São Vicente for 2.7 linear kilometers. It contains >3500 houses and a population of >12.000 people. Despite being inserted in neighborhoods with regular garbage collection services, its irregular and disorderly distribution does not allow for door-to-door collection, requiring residents of these areas to walk to the public cleaning containers if are available. As many do not do so, due to different physical and socioeconomic conditions, irregular disposal is favored by the tidal regime under which these communities are submitted, Fig. 6. In this way, the tides are considered by residents of the stilt houses to be the "garbage collector of the slum" but is not sufficient to collect MPs or clean them from the areas of low energy events.

Rio dos Bugres with the lowest energy and having therefore the lowest influence of the tidal flow, is signed in the Fig. 3 by almost zero arrows, in the inset. This indicates that the accumulation of MPs which, in fact, is the largest in the Rio dos Bugres, despite being highly influenced by the anthropogenic aspect, does not have flow favored by the hydrodynamic regime of the interior of the estuary. Thus, while a considerable amount does not flow into the ocean, it is deposited in such a way as to harm the local population and the river's biota. Considering the evidence that there is leakage of solid waste into the marine environment from areas with low coverage of regular urban cleaning services inside the estuary, this leakage, as demonstrated by hydrodynamic modeling (USEPA, 2001), is subject to a minimal influence of the regime of active tide, in sites with low energy events. The dispersion and transport of MPs derived from the solid waste generated is hampered. Over time, the MPs generated there are deposited in the sediment. Therefore, hotspots for microplastics can be created in places of siltation and low energy events (hydrodynamic dependent) in which slums are also installed, see also the values reached in our study at Supplement 1, Table S1.2. MPs remain trapped inside the estuary increasing the contamination over time. Pohl reported the obtained value of 1.9 M/m² (million fragments per square meter) in the Tyrrhenian Sea as "the highest value yet recorded from the deep seafloor". The highest value found in the Rio dos Bugres, if calculated in the same unit, reaches 47 M/m² (million fragments per square meter) MPs in the SESS estuary. Fig. 7 compares the abundance of microplastics in which the Santos estuary is highly contaminated in the current world context.

5. Conclusion

In conclusion, this study investigated the presence of MPs in ten different sites within the estuarine region of Canal de São Vicente and Canal do Porto de Santos, located on the southeastern coast of São Paulo, Brazil.

The identified MPs were Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Poly(ethylene terephthalate) (PET), Polyurethane (PU), Poly(methyl) methacrylate (PMMA), Polyamide (PA), Ethylene Vinyl Acetate Copolymer (EVA), Polyvinyl Chloride (PVC), Polycarbonate/Acrylonitrile butadiene styrene blend (PC/ABS) and Polyvinyl chloride acetate (PVCAc). These MPs were present in different forms, including fibers, lines, and fragment particles from films and foams. Additionally, polymer dyestuffs, pigments and herbicides impregnated in the MPs were identified by micro-Raman spectroscopy.

The identification of processing additives, pigments, dyestuffs, and herbicides within the MPs suggests that they originate from various sources such as packaging materials, bottles, electronic parts, textile fibers, and numerous other discarded materials. Notably, the association of MPs with herbicides was verified in a sample collected from the Canal de São Vicente, likely originating from a fragment of an herbicide container. These findings underscore the effectiveness of micro spectroscopy methodologies as valuable tools for environmental monitoring programs.

The contamination level in the Santos estuary (>250 µm) is among



Fig. 6. Stilt houses at Rio dos Bugres highly impacted by plastics debris. Source: William R. Schepis, NGO EcoFaxina (Instituto Ecofaxina, 2023).

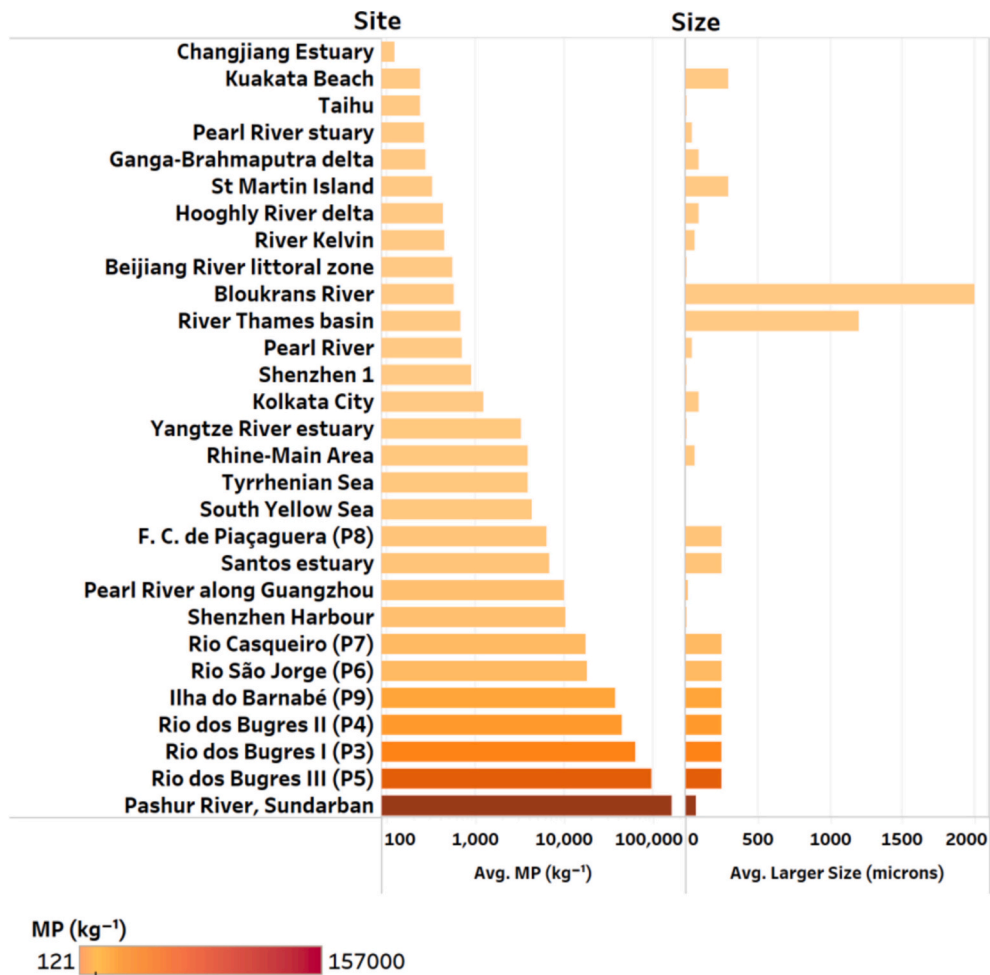


Fig. 7. MP abundance comparison between Santos's estuary and other sites of the world. (Source: the author).

the highest reported globally. Regarding MPs in the SESS sediment samples, their abundance was higher in densely populated stilt house areas. Evidence suggests that siltation regions allow the deposition of

MPs in sediments, and low-energy events significantly influence the deposition of MPs in rivers and mangroves of urban areas. However, natural geographic conditions are unchangeable. Consequently, MP

hotspots will form in populated areas where plastic waste accumulates, and geographical constraints contribute to their persistence over time, harming the biota of rivers and the local human population of the SESS.

In relation to MPs distribution in the SESS sediment samples, the abundance was higher in places with a dense population on stilts, and precarious garbage collection containing plastic waste. The importance of sanitation measures for the proper disposal of plastic waste outside the mangrove areas is emphasized as a fundamental condition for damage remediation. This reality must guide public policies towards addressing the environmental consequences of growing contamination, as well as the prevention and remediation of estuary pollution.

CRedit authorship contribution statement

Duclerc Fernandes Parra: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Giovana Teixeira Gimiliani:** Methodology, Data curation. **Jacinete Lima dos Santos:** Methodology, Investigation. **Niklaus Ursus Wetter:** Data curation. **William Rodriguez Schepis:** Investigation. **Allan Berezcki:** Writing – review & editing, Investigation. **Marycel Elena Barboza Cotrim:** Supervision, Funding acquisition.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2024.117286>.

Data availability

The raw data supporting the conclusion of this article will be made available by the authors without undue reservation.

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Corrigendum



Corrigendum to “Microplastics in Santos São Vicente estuarine – Hotspot in sediments caused by low energy hydrodynamic events in strongly populated areas” [Mar. Pollut. Bull. (2024) 117286]

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The authors regret to inform readers that due to an oversight, Dr. Diego Roberto da Cunha Pascoal, who contributed significantly to the research presented in this article titled “Microplastics in Santos São Vicente estuarine – Hotspot in sediments caused by low energy hydrodynamic events in strongly populated areas” published in Marine Pollution Bulletin 117286, Volume 210, was inadvertently omitted from the author list.

We apologize for this error and acknowledge Dr. Diego Roberto da Cunha Pascoal for valuable contributions to the study. The correct author list should read as mentioned in this corrigendum article.

The CRediT authorship contribution statement should read as

follows:

Duclerc Fernandes Parra: Conceptualization, Methodology, Writing – review & editing, Writing – original draft. **Jacinete Lima dos Santos:** Methodology, Investigation. **Giovana Teixeira Gimiliani:** Methodology, Data curation. **Diego Roberto da Cunha Pascoal:** Investigation, Data curation. **Niklaus Ursus Wetter:** Data curation. **William Rodriguez Schepis:** Investigation. **Allan Berezcki:** Writing – review & editing, Investigation. **Marycel Elena Barboza Cotrim:** Supervision, Funding acquisition.

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