Recognizing microplastic deposits on sandy beaches by altimetric positioning, μ-Raman spectroscopy, and multivariate statistical models

Abstract: This study investigates microplastic (MP) pollution along the coast of São Paulo State, southeastern Brazil. We utilized a five-step methodology: geodetic survey, analysis of beach morphometric parameters, beach sediment collection, μ-RAMAN spectrometry for polymer identification, and multivariate statistical models. The coastline was divided into six compartments (C1 to C6) for MP sample collection. Higher MP concentrations were found in C3 and C2, likely influenced by industrial and port activities. Various types of MP, such as pellets, fragments, and fibers, showed distinct distribution patterns due to their sources, intrinsic properties like shape and density, and emission and deposition processes. Fragments and foams were the most common, representing 42% and 35% of the 1,026 MP items found. Statistical tests revealed significant associations between MP types and beach morphometric characteristics, with higher elevations correlating with higher MP concentrations, particularly for pellets and foams. Beaches with intermediate profiles and those facing the southern quadrant tended to accumulate more MPs. The study highlights the complexity of MP dynamics in coastal environments, emphasizing the importance of considering beach physical characteristics, MP type diversity, and local human activities. Identifying areas prone to MP accumulation is crucial for developing specific monitoring and environmental remediation strategies. These strategies align with the peculiarities of each coastal region and contribute to Sustainable Development Goal 14 (Life Below Water) related to ocean health. The practical applications of this research contribute to the development of more effective plastic waste management and containment systems, and the design of specific monitoring and environmental remediation strategies that consider the unique characteristics of each coastal region.

1. Introduction

According to GESAMP (2019), microplastics (MP) are defined as plastic particles less than 5 mm in diameter. This definition aims to harmonize monitoring methods and reduce ambiguities, as it is widely used in national and regional programs. As emerging pollutants on sandy beaches, MPs reduce their aesthetic value, affecting their visual appeal and the recreational quality of these environments (Borriello, 2023; Corbau et al., 2023; Ghosh et al., 2023). Studies indicate that the presence of microplastics on beaches not only harms the physical beauty and tourist appeal but also reflects issues in waste management and public perception of marine ecosystem health (Amelia et al., 2021; Ghosh et al., 2023; Hartley et al., 2015; Oliveira et al., 2020). Furthermore, this phenomenon not only reduces the attractiveness of these areas to visitant travelers but also raises concerns regarding the health and well-being of both the local wildlife (Botero et al., 2021; Costa et al., 2022; da Silva et al., 2022; Göktuğ, 2021).

From a physical perspective, MPs alter the composition and characteristics of beach environments, with potential repercussions for coastal ecosystems and the organisms reliant on these habitats for survival (Fries et al., 2013). MPs modify sediment porosity, thereby impacting beach substrates' drainage and moisture retention capabilities. These changes in the physical environment can influence temperature-dependent sex determination in certain species, such as crustaceans and marine turtles (Carson et al., 2011; Nelms et al., 2016).

Chemically, MPs can absorb and concentrate organochlorine contaminants, which include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), Polycyclic Aromatic Hydrocarbons (PAHs) and MEHP (Mono-ethyl-hexylphthalate, degraded from Diethyl-hexyl-phthalate or DEHP) (Brighty et al., 2015; Hartley et al., 2015; Ogata et al., 2009; Teuten et al., 2009). Residual plastic from the action of UV rays and/or the process of mechanical abrasion (Harris, 2020) begins to release greenhouse gases such as methane and ethylene (Royer et al., 2018). These chemical compounds can concentrate and transport contaminants to marine biota

and, by extension, humans through the food chain (Rochman et al., 2013; Rochman et al., 2014; Smith et al., 2018).

The Santos estuary, encompassing the city of Santos, its Port, and the industrial region of Cubatão, represents a critical area for MP pollution, especially pellets, along the São Paulo coast (Ferreira et al., 2021). Inadequate plastic waste management and failures in containment systems are the leading causes of the entry of this pollutant into the environment, particularly during production, transport, and transshipment processes in factories and port terminals (Geyer et al., 2017; Jambeck et al., 2015).

The intense port activity, combined with high population density and industrial concentration, makes this region a hub for the dispersion of MP (Jong et al., 2022). Ivar do Sul & Costa (2014) pointed out that on Brazilian beaches, a high concentration of MP is correlated with the intensity of port and industrial activities, especially in the Southeast region. The impacts caused by this pollutant affect, among others, marine life due to the ingestion of these particles by marine organisms, causing physical and chemical damage, reflecting the severity of the situation (Rochman et al., 2013).

Through the combined analysis of geodetic, geomorphometric, and meteoceanographic factors at a beach along the São Paulo coastline, Ferreira et al. (2021) demonstrated that factors such as coastal currents and storm events can influence the deposition patterns of MP. Therefore, identifying the most suitable zones for their accumulation and systematizing potential MP accumulation areas are critical considerations (Avio et al., 2017; Hidalgo-Ruz et al., 2012a; Kim et al., 2015; Van Cauwenberghe et al., 2015). This study aims to conduct a novel and extensive evaluation of the correlations and interdependencies between various parameters, including the abundance and characteristics of MP, such as their shape and polymer type, and morphometric variables like elevation, slope, and orientation of beach facades. The focus is on identifying and understanding the distribution of these deposits across approximately 880 kilometers of beaches along the São Paulo coast in São Paulo, Brazil.

The primary research questions aim to identify critical accumulation points of MPs to better direct remediation efforts. Understanding these aspects can help trace potential sources and comprehend their behavior in the coastal and marine environment, linking geomorphological aspects with pollution patterns. Finally, the study considers the implications of MP pollution for marine life due to the ingestion of these materials and for the aesthetic and recreational experience of beach visitors, emphasizing the importance of effective environmental monitoring and remediation strategies.

2. Methods

To indicate locations susceptible to MP deposition (MP hotspots), the data collection and analysis can be divided into three stages: 1) fieldwork – sediments sampling and beach morphometric parameters (aspect, slope, and altitude) using altimetry from the Global Navigation Satellite System (GNSS); 2) laboratory analysis – sieving (1 – 5 mm mesh) and μ-RAMAN spectrometry for the confirmation of polymeric properties; 3) exploratory multivariate techniques – analytical hierarchy process-gaussian (AHP-G) and correspondence analysis (CA) (Figure 1).

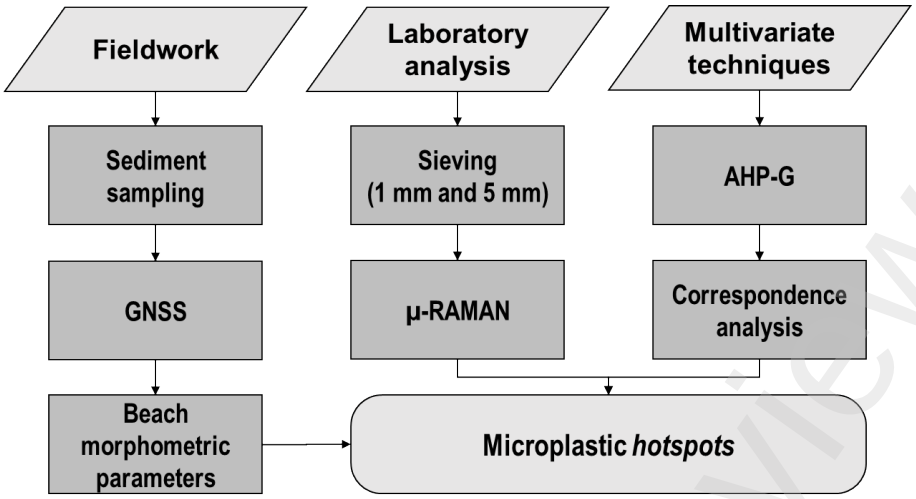

Figure 1. Flowchart summarizing the methods used in this research. GNSS: Global Navigation Satellite System; AHP-G: analytical hierarchy process-gaussian.

2.1. Study area

The almost 880 km coastline of São Paulo State in southeastern Brazil is segmented into six distinct compartments: (C1) Ilha do Cardoso to Serra do Itatins; (C2) Peruíbe to Praia Grande; (C3) Santos to Bertioga; (C4) Bertioga to Toque-Toque; (C5) Toque-Toque to Tabatinga; and (C6) Tabatinga to Picinguaba (Figure 2**a**), as outlined by Tessler et al. (2018). This coastline features diverse geomorphological characteristics such as beaches, rocky shores, sandbars, and mangroves, shaped by a combination of geological, geomorphological, climatic, and human factors (Ferreira et al., 2023).

A flatter topography characterizes the southern part of the coastline and includes critical ecological zones like the Juréia-Itatins and Itinguçu State Park (Suguio and Tessler, 1984; Tessler et al., 2018). Here, the Serra do Mar escarpment is situated further from the shore (10 km to 70 km), allowing for a wide coastal plain that features long, uninterrupted beaches and several islands (Souza, 2012; Tessler et al., 2018).

Moving northward from the central to the northernmost section, the Serra do Mar mountain range narrows the coastal plain. It reduces the size of hydrographic basins compared to the southern region. The northern coastline is more topographically diverse, with smaller, secluded beaches shaped into coves and bordered by pre-Cambrian rocky promontories found at locations like Itaguaré, Massaguaçu, and Praia Vermelha do Norte (Souza, 2012; Tessler et al., 2018). Significant urban centers such as Santos, which hosts the largest port in Latin America, are located in this region (Reid et al., 2022). The northern coastal area is characterized by sandy beaches interspersed with rocky outcrops and a rugged landscape, featuring the presence of the Serra do Mar and numerous nearby islands (Suguio et al., 1985).

The hydrodynamics along the Brazilian continental margin are governed primarily by the southward-flowing Brazil Current (BC) in deep waters and the Brazil Coastal Current (BCC), which travels from the south-southeast to the northeast along the continental shelf during spring and winter (Campos et al., 1995; De Souza and Robinson, 2004; Möller Jr et al., 2008). Predominant east-northeast winds create currents that run parallel to the northeast-southwest direction of the coastline. In winter, however, cold fronts influence the region, producing more intense south-southeast winds that generate stronger currents and waves from the southern quadrant (Andrade et al., 2019; Castro Filho et al., 1987; Ferreira et al., 2021; Harari et al., 2006; Pianca et al., 2010). Additionally, the urban development and coastal infrastructure significantly alter the coastal physiography and dynamics, potentially leading to erosion and progradation (Corrêa et al., 2021; Franzen et al., 2021).

2.2. Fieldwork samples and morphometric parameters

The field trips were conducted from April to September 2023, when the cold fronts produced waves of up to 4 m and approached the coast from the south and southeast quadrants. Favoring maximum sediment transport capacity, beach morphological changes, and microplastic deposition and/or remobilization (Ferreira et al., 2021). We opted for several varied beach profiles (32) that would proportionally cover the entire coast of São Paulo for each compartment, encompassing urban and rural beaches. Additionally, these locations were selected for their relatively easy accessibility by road, optimizing financial costs and time. Sediment samples and beach morphology parameters were obtained along beach profiles distributed across all six compartments of the São Paulo coastline, as shown in Table 1 and Figure 2**a**.

The locations of sediment collection along each beach profile were selected based on environmental factors influencing litter dynamics on sandy beaches (GESAMP, 2019), particularly water levels (strandline altitudes) pointed out by Ferreira et al. (2021). Approximately 1500 g of sediment were collected at each of the four water levels (Figure 2**b**): storm strandline (P1), spring high tide (P2), neap high tide (P3), and low tide (P4). The collected sediments were subsequently homogenized and separated into aliquots of 500 g to ensure consistency and repeatability of the sampling process, if necessary. This approach allowed for collecting samples from the top layer of sediment within a 1 m² area (Figure 2**f**) at each of the 128 sampling points, yielding 1026 items/pieces identified as large MP, between 1 – 5 mm (GESAMP, 2019).

Table 1 – List of beach profiles per coastal compartment.

Compartment	Profiles ID	Number of profiles
C1 Ilha do Cardoso – Serra do Itatins	IC-A, IC-B, IC-C, IC-D, IC-E, IC-F	6
C2 Peruíbe – Praia Grande	PER, ITA, MON, PG	4
C3 Santos – Bertioga	GZN, ITR, GZG, GUA-A, GUA-B, TMB, AST, PIT-A, PIT-B, ENS-A, ENS-B, MCS, PEB	14
C4 Bertioga – Toque-Toque	BET, GRT, BOR	3
C5 Toque-Toque – Tabatinga	TOG, SSB, CRG, MSS	4
C6 Tabatinga – Picinguaba	UBA, ITB, PIC	3

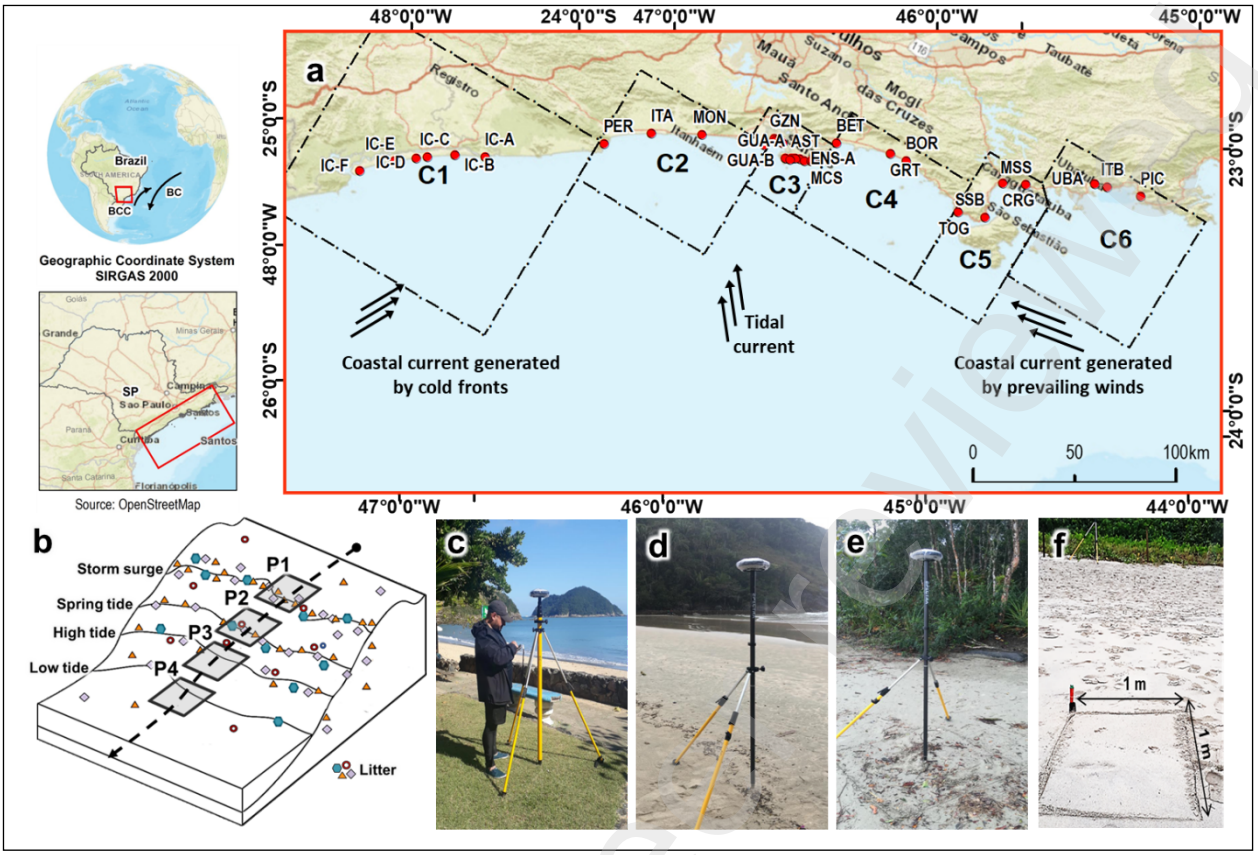

Figure 2 – (**a**) Sampling location distributed within the six compartments on the São Paulo coast. (BCC = Brazil Coastal Current, BC = Brazil Current), modified from Pianca et al. (2010); Tessler et al. (2018). (**b**) Sampling points by beach profile (P1, P2, P3, and P4), modified from GESAMP (2019); (**c**, **d**, and **e**) base and GNSS Rovers; (**f**) area (1 m^2) of superficial sediment collection.

The morphometric parameters are divided into aspect, beach slope, and altitude. The first (aspect) is the beach face orientation determined by the direction of the beach transect relative to the geographic north as follows (Burrough et al., 1998): North – N (0º - 22.5º); Northeast – NE (22.5º - 67.5º); East – E (67.5º - 112.5º); Southeast – SE (112.5º - 157.5º); South – S (157.5º - 202.5º); Southwest – SW (202.5º - 247.5º); West – W (247.5º - 292.5º); Northwest – NW (292.5º - 337.5º); North – N (337.5º - 360º). The beach slope (tanβ) was derived from Eq. 2:

$$\tan\beta = \operatorname{atan}(VD/HD) \quad (2)$$

VD and HD are the vertical and horizontal distances between sampling points P1 and P4 (Figure 2b). The slope can be used as a proxy of the beach morphodynamic stage (Bujan et al., 2019), and can be categorized into steep ($\tan\beta > 0.12$); intermediate ($0.05 < \tan\beta < 0.12$); and sloping ($\tan\beta < 0.05$) (Ferreira et al., 2023). The altitudes (*H*) of the sampling points were classified according to Ferreira et al. (2021), as: Very Low (VL; < 1.42 m); Low (L; 1.42 – 1.57m); Mean (M; 1.58 – 1.89m); High (H; 1.90 – 2.06m); and Very High (VH; >2.06 m).

The altimetry of the sampling points (P1, P2, P3, and P4) was obtained using the GNSS, following the method described in Ferreira et al. (2021). Reference stations were established within less than 5 km of markers distributed along the beach, and positions were received from the nearest active stations of the Brazilian Network for Continuous Monitoring using the SIRGAS2000 coordinates system. Coordinates and altitudes of sampling points recorded by the mobile station were post-processed relative to the reference station (Monico, 2008; Monico et al., 2009) using the

Survey Office software. The orthometric altitude (H) relative to the mean sea level of the Imbituba/SC datum of the Brazilian Geodetic System was obtained through Eq. 1 (Blitzkow et al., 2016):

$$H = h - N \quad (1)$$

Where *h* is the geometric altitude obtained with GNSS referenced to the SIRGAS2000 ellipsoid, and *N* is the geoidal height determined by the IBGE geoidal model - MAPGEO2015.

2.3. Microplastic analysis

2.3.1. Polymeric characterization

The MP was extracted by sieving the samples using 1 – 5 mm mesh. The retained MP were visually separated from biological materials, such as shells, algae, and vegetation debris, and subsequently identified, counted, and categorized according to shape (Löder and Gerdts, 2015): pellets (spherical or smooth), granular (foam), lines (fibers and filaments), and films (plastic film).

The polymeric characterization of MP was undertaken using μ-Raman spectroscopy (McCreery, 2005), using lasers with wavelengths of 473 nm, 532 nm, 633 nm, and 785 nm and a long-range 50x objective numerical aperture (NA = 0.55). First, the laser's power is calibrated to obtain ideal spectra in the polymer identification region (around 1600 cm^{-1}) to prevent damage to the materials. Subsequently, the analysis extends to the spectral region from 200 cm^{-1} to 3200 cm^{-1}, focusing on identifying hydrocarbons (Araujo et al., 2018; Ferraro, 2003; Smith and Dent, 2019). Additionally, adjustments in integration time, number of accumulations, and slit diameter are made to enhance the signal-to-noise ratio and avoid sensor saturation. A baseline is established for the acquired spectra, with subsequent noise filtering via a computational routine in Matlab®. Finally, the spectra are compared with the Knowitall® software database to identify polymer types. Concurrently, images of the MP are captured by the Raman system microscope, complementing the database.

2.4. Unsupervised models

Given the heterogeneous nature of the data, which includes both quantitative and qualitative variables, we employed exploratory multivariate techniques such as the Analytical Hierarchy Process-Gaussian (AHP-G) and Correspondence Analysis (CA). These algorithms were chosen based on their simplicity and effectiveness for exploratory analyses. Specifically, the AHP-G was utilized to analyze quantitative data and perform rankings, as it effectively represents these types of data. Conversely, Correspondence Analysis was selected to examine qualitative variables, also known as latent or categorical variables, which cannot be directly measured but can only be categorized or counted (dos Santos et al., 2023; Fávero and Belfiore, 2017).

The AHP-G incorporates the Gaussian distribution to quantify and assess, through distributions, uncertainties in evaluations and probabilistic decision-making while maintaining the classic hierarchical structure of Saaty`s AHP (2008), without arbitrary weighting (Dos Santos et al., 2021; dos Santos et al., 2023). The result generates a ranking of MP abundance, subsequently standardized (Eq. 3) and transformed into a Likert scale (Table 2), allowing an assessment of the association between this ranking and beach morphometric parameters through CA.

The CA examines associations between variables of interest using the chi-square test (X^2; p-value < 0.05). In it, the Adjusted Standardized Residuals (ASR) check for dependence relationships between each variable based on the reference critical value ($+1.96 \leq$) of the standard normal curve for a 5% significance level. Thus, if the value of the ASR in a cell is greater than or equal to 1.96, it is interpreted that significant dependence relationships exist (Fávero and Belfiore, 2017; Haberman, 1978; Johnson and Wichern, 1992). All statistical analyses were performed using Python in Anaconda/Spyder software.

$$Standardization = \frac{(observed\ value)\ -\ (minimum\ value)}{(maximum\ value)\ -\ (minimum\ value)} \quad (3)$$

Table 2 – Standardized qualitative data based on the total count of polymers.

Ranking	Qualitative data
0.80 – 1.00	Very High (VH)
0.60 – 0.79	High (H)
0.40 – 0.59	Moderate (M)
0.20 – 0.39	Low (L)
0.00 – 0.19	Very Low (VL)

3. Results

3.1. Geographic distribution of microplastic

The 34 transects perpendicular to the coastline had an average width of 37.57 m, with minimum and maximum values of 5.52 m and 182.48 m, respectively. The beach faces had an average direction of 158◦ (SE), with values varying from 43◦ (N) to 259◦ (W). The slope of these faces was predominantly intermediate. In Table 3, it is possible to observe that fragments, Foams, and Pellets appeared in more significant quantities when compared to Fibers and Films. The same table also shows that the highest proportions of this material are found mainly in P1 (highest points of the beach profile), gradually decreasing to P4 (close to the waterline) (Table 3).

Most of the 1,026 MP items found consisted of fragments (42%) and foams (35%), with pellets, fibers, and films accounting for 20%, 3%, and 0.3%, respectively. Figure 3 shows the distribution of the standardized MP ranking across the study area. Low (L) and very low (VL) MP concentrations were found on beaches across all coastal compartments. In contrast, very high (VH) concentrations were predominantly found on beaches located in compartments C2 and C3 (PIT-B and ITA), with high (H) and moderate (M) concentrations identified in C4 and C1 (BOR and IC-D), respectively.

Table 3 – Absolute and percentage values of items sampled collectively for each corresponding position across all collection points.

Point	Pellet	Fragment	Fiber	Foam	Film	Total	%
P1	70	105	9	167	0	351	34
P2	59	133	7	69	2	270	26
P3	51	86	3	80	0	220	22
P4	26	103	7	48	1	185	18

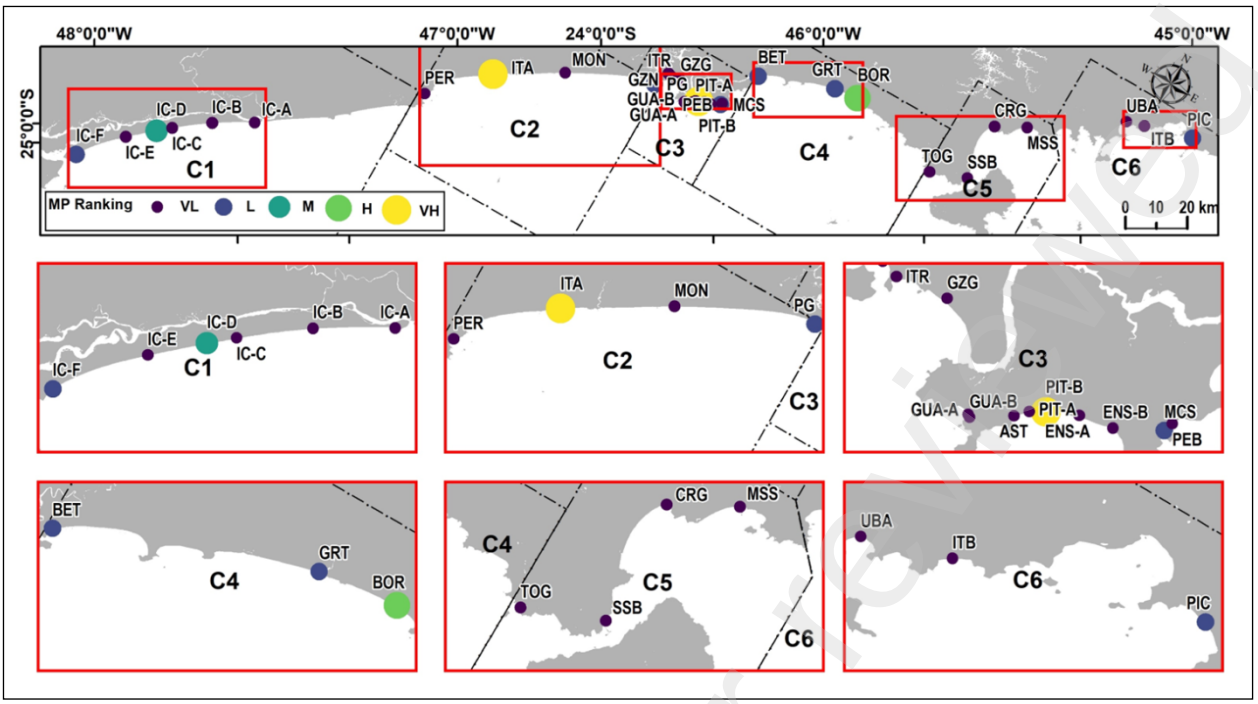

Figure 3 – The AHP-G method generated an MP ranking for the entire coast of São Paulo, emphasizing compartments C1, C2, C3, C4, C5, and C6. The map features circles of varying sizes that represent Very High (VH), High (H), Moderate (M), Low (L), and Very Low (VL), respectively.

The X^2 statistical test indicated statistically significant associations ($p<0.05$) between the presence of all types of MP and the specific compartments in which they were found, except for films ($p=0.6885$). The CA identified a clear dependency relationship (ASR ≥1.96) between high (H) and very high (VH) MP concentrations and compartments C2 and C4, respectively. On the other hand, moderate (M), low (L), and very low (VL) concentrations were observed in compartments C1, C4, C3, and C5, in this order (Figure 4a). No significant relationship was found between MP concentrations and C6.

The concentration of pellets exhibited significant variations between compartments. Very high (VH) concentrations of pellets were significantly associated with beaches in C2 and C3 (Figure 4b). Significant associations were found between high (H) and very low (VL) concentrations of pellets in C1 beaches, with VL also found in C5. Moderate (M) concentrations were associated with beaches in C3 and C4, while low concentrations were significantly associated only with beaches in C6 (Figure 4b). Considering fragments, no significant association was found for VH concentrations, while H concentrations showed a significant relationship only with beaches in C3 (Figure 4c). Moderate concentration of fragments was significantly related to beaches in C2 and C4, with low concentrations associated with C3. Very low (VL) concentrations were significantly related to C1, C5, and C6. The presence of fibers showed no significant relationships with beaches in C5 and C6. At the same time, VH and VL concentrations were associated with beaches in C2 and C3, respectively, and moderate (M) concentrations with beaches in C1 and C4 (Figure 4d). Similar to fibers, the presence of foam showed no significant relationships with C5 and C6. Significant associations were found between VH foam concentration in C4, M in C2 and C3, and VL in C1 (Figure 4e). Films did not display significant dependency relationships with any compartment, although C3 exhibited the highest ARS values (Figure 4f).

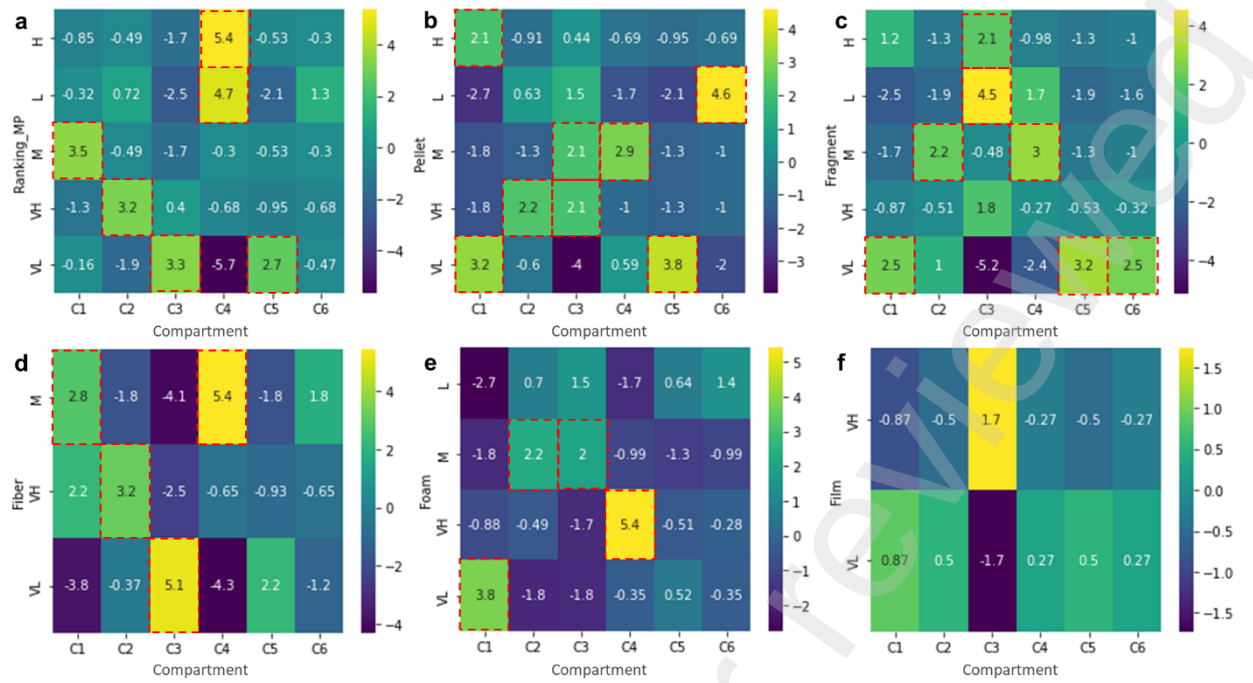

Figure 4 – Matrices showing the Adjusted Standardized Residual (ASR) values between the concentration rankings for MP (a), pellets (b), fragments (c), fibers (d), foam (e), and film (f) for each compartment (C1, C2, C3, C4, C5, and C6). Dashed red contours indicate variables exhibiting significant dependency relationships (ASR ≥ 1.96).

3.2. Associations between morphometric variables and microplastics

The X^2 test showed statistically significant associations between beach slope (tanβ p=2.2239E-07), aspect (p=1.1805E-06), altitude (p=0.0016), and MP concentrations. Dependency relationships were identified between high MP concentrations and a southerly beach aspect (the slope faces the S quadrant). In contrast, low MP concentrations (L) were associated with an easterly beach aspect (Figure 5**a**). Very high and moderate MP concentrations showed a significant relationship with beach slopes classified as intermediate (0.05 < tanβ < 0.12), with low concentrations associated with gentler beach slopes (tanβ < 0.05), as illustrated in Figure 5**b**.

The analysis of ASR values indicated that very high MP counts along the beach profile are significantly related to high and very high altitudes (Figure 5**c**), reflecting strandlines along the upper parts of the beach profile (2.06 m to 2.62 m above mean sea level). Conversely, very low MP concentrations were associated with very low altitudes (<1.90 m), suggesting strandlines along the lower part of the beach profile.

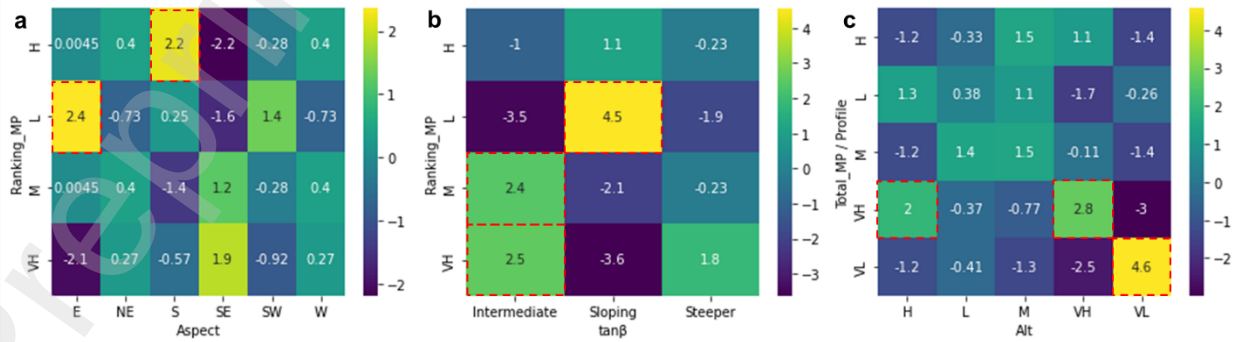

Figure 5 –Matrices showing the Adjusted Standardized Residual (ASR) values between MP rankings and the orientation of the beach face (Aspect) (**a**); beach slope (tanβ) (**b**), the total MP

count per profile and the altitude (Alt) (**c**). Dashed red contours indicate significant relationships (ASR ≥ 1.96).

Results from the X^2 tests reveal that different MP types are more likely to be found at specific beach elevations, with significant associations ($p < 0.05$) found between altitude levels and pellets (p=1.6604E-10), fragments (p=0.0003), fibers (p=0.03677), foam (p=5.69E-08), and film (p=0.04353). Very high pellet concentrations were associated with very high altitudes (the upper beach), while low and moderate concentrations were significantly more prevalent in low and moderate altitudes (Figure 6**a**). High and very high concentrations for fragments were significantly associated with moderate altitudes (Figure 6**b**), with concentrations reducing in higher and lower beach elevations. Concentrations of fragments were very low at the lowest beach elevations, low at both high and low beach levels, and moderate at high and very high altitudes (Figure 6b). The accumulation of fibers showed a significant relationship only between moderate concentrations and very low altitudes (Figure 6**c**). Similar to fragments, very low concentrations of foam were significantly associated with very low altitudes and low concentrations were associated with high altitudes (Figure 6**d**). However, high and very high foam concentrations were found at the highest parts of the beach rather than at moderate altitudes as shown for fragments. Finally, very high film concentrations were associated with low altitudes, the only significant relationship found between this type of MP and altitude (Figure 6**e**).

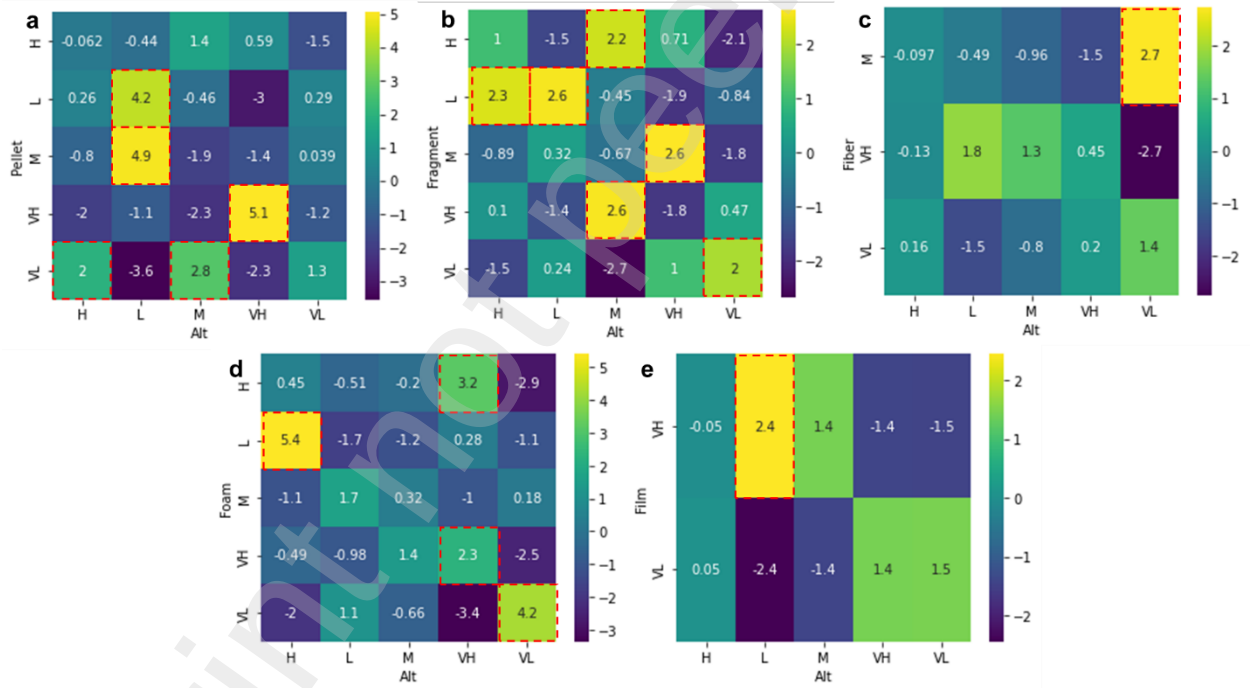

Figure 6 –Matrices of the Adjusted Standardized Residual (ASR) values between altitude (Alt) and the total count of pellets (**a**), fragments (**b**), fibers (c), foams (**d**), and films (**e**) per profile. Dashed red contours indicate significant relationships (ASR ≥ 1.96).

3.3. µ-Raman analysis

At the sites where the highest MP concentrations were observed (beach profiles IC-D in C1, ITA in C2, PIT-B in C3, and BOR in C4, Figure 3), the µ-Raman analyses indicated that most pellets found on the upper beach were primarily polymers derived from high (HDPE) and low-density Polyethylenes (LDPE), along with other copolymers (Table 4). They were typically found in the form of small spherical or cylindrical granules, with HDPE exhibiting significant Raman peaks around 1130 cm^{-1}, 1295 cm^{-1}, and 1460 cm^{-1}, and a density range between 0.941 and 0.965

g/cm³. LDPE showed Raman peaks similar to those of HDPE, maintaining the same characteristic peaks at 1130 cm^{-1}, 1295 cm^{-1}, and 1460 cm^{-1}, but with subtle differences in the spectral profile and a lower density range (0.910 to 0.940 g/cm³).

The fragments and the fibers predominantly found at moderate altitudes in the beach profile exhibited the greatest diversity of polymeric material. As they are derived from already industrialized products, these are commonly found in the form of polymers such as high and low-density Polyethylenes (HDPE and LDPE, respectively), identical to the pellets in Figures 7a and b, as well as Polypropylene (PP), and other copolymers including Ethylene-Polypropylene, Poly(Ethylene-co-Vinyl Acetate), Poly(Propylene-Ethylene-Acrylic Acids), and High Ethylene Random Copolymer (RCP) (Table 1). PP is identified in the Raman spectrum by its distinct peaks at 841 cm^{-1}, 973 cm^{-1}, and 1160 cm^{-1}, with a density ranging between 0.855 and 0.946 g/cm³.

Similarly to the fragments, foams also stood out for the diversity of their compounds. These polymers were predominantly identified and classified as Polystyrene, Polyurethane, and Styrene/Allyl Alcohol Copolymers with Low Molecular Weight (Table 2). Meanwhile, films primarily featured materials derived from polyethylene (Table 2). Styrene, a base monomer for polystyrene production, exhibits peaks in the Raman spectrum at 1000 cm^{-1}, 1030 cm^{-1}, and 1600 cm^{-1}. The density of polystyrene, a styrene derivative, is approximately 0.91 g/cm³.

Table 4 – Main Polymers Identified by μ-Raman Spectrometry at different beach elevations (IC-D, ITA, PIT-B, and BOR).

Pellet	Fragment	Fiber	Foam	Film
High and Low Density Polyethylene	High and Low Density Polyethylene	High and Low Density Polyethylene	Styrene	Polyethylene
Poly(Ethylene), p-(Ethylene-co-Acrilyc-Acid)	Polypropylene		Polystyrene	
	Ethylene-Polypropylene		Polyurethane	
	Poly(Ethylene-co-Vinyl Acetate)		Styrene/Allyl Alcohol Copolymer Low Molecular Weight	
	Poly(Propylene-Ethylene-Acrylic Acids)			

4. Discussion

4.1. Factors responsible for the MP distribution and accumulation along the coast

The MP Ranking observed a distribution starting from the Santos Estuary and Mar Pequeno (São Vicente), initially depositing on beaches near these channels (e.g., sectors C3 and C2) and progressively accumulating as it moves toward the SSW, the same direction as the predominant coastal current in the region (NE-SW) (Tessler et al., 2018) on beaches such as Itanhaém (ITA) and those located on Ilha Comprida (IC-D), in sectors C2 and C1 of Figure 3, respectively. Conversely, beaches in sectors C4, C5, and C6 showed the lowest values in the Ranking. This suggests that beaches near Santos Bay are the first to be impacted due to their proximity to the primary sources of this pollutant, resulting from cities with higher population densities like Santos and São Vicente, in addition to the Port of Santos and the petrochemical industries in Cubatão. The latter two are responsible for the reception and processing of this material (Balthazar-Silva et al., 2020; Ferreira et al., 2021; Turra et al., 2014).

The analysis of the results on the distribution of MP across different compartments of the São Paulo coast provides a comprehensive overview of the environmental impact of this pollutant. The applications of AHP-G, the χ^2 test, and CA have provided a robust statistical understanding of the distribution of these materials (Ferreira et al., 2023; Pereira et al., 2023; Santos et al., 2021).

Regarding different types of MP, the lack of a significant relationship for films suggests a distinct distribution dynamic or emission sources compared to other types of MP. This observation aligns with research indicating variations in sources and their environmental persistence (Tiwari et al., 2023).

The analysis of pellets and fragments shows significant dependence on specific compartments, indicating potential point sources of pollution or specific transport and deposition processes for these materials (Barnes et al., 2009; Lebreton et al., 2017). The high concentration of these materials in specific compartments (C3 and C2) underscores the need for more competent handling, transport, and manufacturing management (Tian et al., 2023). For fibers, the observed distribution suggests wide dispersion across different compartments, aligning with studies indicating their release from various sources, including the wear of synthetic fabrics and fishing nets (Oliveira et al., 2023; Zhang et al., 2022).

The results for foam are exciting, given the high dependency relation with compartment C4. This observation may be attributed to this material's specific characteristics or sources near this compartment. On beaches, foam is commonly associated with waste from fishing materials or insulated containers for storing beverages and/or food, typically used by merchants and/or beachgoers (Chen et al., 2022; Zeng, 2023; Ziani et al., 2023).

The analysis of results regarding morphometric variables and their relationship with MP concentrations on beaches provides a relevant understanding of the distribution of this pollutant on the São Paulo coast and in the coastal environment. The χ^2 test and the analysis of RPA reveal statistically significant associations between the physical characteristics of the beaches and the presence of MP, aligning with previous studies that highlight the influence of geomorphological factors on the accumulation of marine debris (Ferreira et al., 2021; Hidalgo-Ruz and Thiel, 2013).

The relationship between the beach slope ($\tan\beta$) and the concentration of MP suggests that beaches with intermediate slope profiles are more prone to accumulate higher concentrations of MP, in general. This may be due to sediment and debris transport and deposition dynamics on these profiles (Andrady, 2011; Ferreira et al., 2021). Beaches with a dissipative trend ($\tan\beta < 0.05$) show lower concentrations. The flatter and lower profiles favor beach washing during high tides and, consequently, the fluctuation of MP back into the coastal current (Cooper and McLaughlin, 1998; Ferreira et al., 2021). The orientation of the beaches (Aspect) also shows a significant relationship with the concentration of MP (Vito et al., 2022). Beaches facing the South quadrant exhibit higher concentrations in the same direction as the higher energy storm waves (Ferreira et al., 2021; Young and Elliott, 2018) come from this direction. According to Ferreira et al. (2023)With this orientation, beaches on the São Paulo coast naturally accumulate sediments and marine litter.

Regarding altitude, the observed association between higher altitudes and higher MP concentrations can be attributed to the deposition of debris brought by high tide processes combined with storm events, which deposit material in higher areas of the beach (Álvarez-Hernández et al., 2019; Ferreira et al., 2021; Lavers and Bond, 2017; Schmuck et al., 2017; Young and Elliott, 2018). The distribution of pellets, fragments, fibers, foams, and films about altitude reinforces the idea that different types of MP have distinct distribution dynamics, possibly influenced by their physical characteristics and sources of origin (Hidalgo-Ruz et al., 2012b).

This way, based on the aspects raised (Aspect, $\tan\beta$, and Altitude), it is possible to state that the locations with greater susceptibility to MP accumulation or potential hotspots depend on intermediate beach profiles facing the South quadrant and locations with excellent coastline stability and/or accretion. This is due to the ~90° angle between storm waves formed by cold fronts

coming from the same quadrant, resulting in the near cessation of sediment transport on these beaches, favoring the accumulation of sediments and anthropogenic debris, including MP (Ferreira et al., 2023, 2021; Harris, 2020; Jong et al., 2022; Laurino et al., 2023; Stein and Siegle, 2019). This is because relative stability at some beaches can favor such deposition (Veerasingam et al., 2020), as seen in those associated with slow accretion processes, such as sandy spits and areas protected by tombolos, respectively, in compartments C1 and C3 (Ferreira et al., 2023; Mahiques et al., 2016; Mascagni et al., 2018; Silva et al., 2021).

Due to the configuration of the São Paulo coastline (SW-NE), beaches facing SE are more susceptible to erosive processes, as the acute angle (~45°) of incidence of storm waves (South) can reach up to 4.0 m (Andrade et al., 2019; Ferreira et al., 2023, 2021; Stein and Siegle, 2020, 2019) during the austral autumn and winter (April to September), favoring maximum sediment transport capacity (Lavenère-Wanderley and Siegle, 2019; Pianca et al., 2010; Sousa et al., 2013; Stein and Siegle, 2020, 2019). On erosive beaches, sand removal can expose buried layers containing MP, increasing their availability to the marine environment (Ranjani et al., 2022; Sun et al., 2021; Wang et al., 2021).

In this context, the seasonal incidence of storms and extreme events (increasingly frequent) on the São Paulo coast (Gramcianinov et al., 2023; Nunes et al., 2018) may alter the MP dynamics. During storms, the resuspension and redistribution of sediments can increase the mobility of this pollutant (Cheung and Not, 2023). Harris et al. (2021) and Lebreton et al. (2017) emphasize that estuaries are significant vectors for transporting MP to the sea, influenced by urbanization and human activities. Thus, areas near river mouths and estuarine channels, such as those in Santos, São Vicente, and Bertioga, are critical points for the entry of MP into the ocean.

4.2. Polymer Diversity and microplastic accumulation

The diversity of polymers found in fragments and fibers, including PE, PP, and various copolymers, suggests a variety of pollution sources. These materials are often derived from already industrialized and discarded products, reflecting the widespread use of plastics in modern society and the inadequacy of waste management systems (Gao et al., 2022; Geyer et al., 2017). The identified foams and films, mainly composed of styrene and other polymers such as polystyrene and polyurethane, are consistent with literature highlighting the presence of these materials in marine environments. The former (styrene and polystyrene) are commonly used in packaging and thermal insulation applications due to their lightness and resistance. Polyethylene, widely used as the primary material in the manufacture of plastic bags and packaging, represents one of the most significant sources of MP pollution in the marine environment (Gao et al., 2023; Gunawan et al., 2022; Katsara et al., 2022).

The accumulation of pellets in the higher portions of beach profiles is a phenomenon that can be attributed to a combination of physical and geomorphological factors (Ferreira et al., 2021). These pellets' spherical or cylindrical shape and relatively low density (0.910 and 0.965 g/cm³) play a crucial role in their deposition and distribution on beaches. This enhances the transport of these microplastics by ocean currents and, specifically, their mobilization by high-energy waves and winds. When high-energy waves strike the beaches, particularly during high tides and storm events, these microplastics are driven to the upper sections of the beach profiles. Moreover, the spherical or cylindrical shape of the pellets reduces friction with the sand and other beach materials, facilitating wind transport through rolling and/or saltation. Once in the higher areas of the beach profile, these MP tend to be retained due to the decreased energy of these factors (waves, winds, and tides), where they end up depositing and accumulating (Alvarez-Zeferino et al., 2020; Ferreira et al., 2021; Ryan et al., 2009).

In contrast to pellets, fragments, and fibers often exhibit faceted or irregular shapes, influencing their transport dynamics and deposition on beaches. These irregular shapes increase resistance to movement in this environment, limiting their ability to be transported to higher beach

areas, especially under the influence of less intense winds and waves (Oliveira et al., 2023; Lefebvre et al., 2023; Zhang et al., 2022). Furthermore, the density of these MP, generally higher than that of pellets, also contributes to their accumulation in the mid-regions (P2 and P3) of the beach profile. Fragments and fibers tend to settle where wave and current energy diminish, but it is still sufficient to mobilize them. This intermediate zone of the beach profile typically corresponds to a balance between areas reached by high tides and the extent of significant aeolian transport (Andrady, 2011; Ferreira et al., 2021; Jambeck et al., 2015).

The accumulation of expanded foams and plastic films in higher concentrations in the lower parts of beach profiles (P4, primarily, and P3) can be attributed to specific characteristics of these materials and the environmental dynamics of beaches. Foam, commonly composed of polystyrene and polyurethane, has a cellular structure that endows low-density and high buoyancy (Auta et al., 2017; Gao et al., 2023). This low density allows foam easily transported by water, particularly by waves. However, its voluminous structure and lightness contribute to these materials being deposited in the lower parts of beach profiles, where wave energy is insufficient to carry them to higher areas. In contrast, plastic films are generally thin and flexible, facilitating their movement by wind and wave action. Nevertheless, their flat shape and larger surface area relative to weight mean they are easily trapped in the lower beach areas (P4), where wind and wave energy is lower. Additionally, plastic films can become entangled with natural debris or adhere to moist sand, reducing mobility (Andrady, 2011; Barnes et al., 2009; Browne et al., 2011; Martin et al., 2017; Rochman et al., 2013; Thompson et al., 2004).

5. Conclusions, limitations, and future perspectives

This study provided a comprehensive examination of the distribution of various types of MP (categories: pellet, fragment, fiber, foam, and film) along the São Paulo coastline, considering morphometric characteristics (beach face orientation - aspect; slope - tanβ; and altitude) and meteo-oceanographic conditions. It revealed complex and significant patterns in the dispersion and accumulation of MPs. Robust statistical analyses, including AHP-G, the X^2 test, and Correspondence Analysis (CA), identified statistically significant associations between MP presence and specific geographic compartments and morphometric variables of the beaches. Notably, the highest concentrations of MPs were found predominantly on beaches in compartments C3 and C2, suggesting a direct influence of proximity to urban and industrial sources, such as the Santos Estuary and Mar Pequeno. Different types of MPs, including pellets, fragments, fibers, and foams, exhibited distinct patterns of dependency on these compartments, reflecting potential differences in emission sources, transport, and deposition processes. The relationship between environmental characteristics MP accumulation accumulation dynamics was comprehensively understood. Higher altitudes were associated with elevated MP concentrations, indicating a significant role of high tide processes and storm surges in depositing debris in higher beach areas.

μ-Raman spectroscopy revealed a predominance of polymers such as polyethylene (PE) in high and low-density forms, polypropylene (PP), and styrene, underscoring the significant contribution of industrialized and consumer products to MP pollution. The study identified susceptible locations for MP accumulation (hotspots) along the coastline, using remote sensing data and morphometric analyses. These hotspots were often associated with intermediate beach profiles facing the Southern quadrant and areas with greater stability or shoreline accretion, where aggradation processes favored the accumulation of anthropogenic debris, including MPs.

The findings highlight the complexity of MP dynamics in the coastal environment and emphasize the importance of considering both the physical characteristics of beaches and local human activities to understand and manage this type of pollution. The variability in MP types and their relationships with different beach environments points to the need for differentiated

management approaches tailored to the specific characteristics of each coastal compartment and pollutant type.

However, the study has some limitations. The samples were collected only once over six months during the cold front period, not accounting for temporal variability due to seasonal changes, sediment composition, sedimentary processes, or human activities, which could provide new interpretations of the data. Additionally, the sampling depth limited to the top 4-5 centimeters of a 1 m² area, potentially not reflecting the entire topographic profile of the beach and the more stable, deeper sediment layers. The absence of detailed information on human activities, urbanization, and industrialization also limits the understanding of the direct impact on MP distribution.

Future studies linking these results with data derived from orbital remote sensing could generate models capable of predicting and synoptically expanding all these aspects. Understanding these distribution patterns is crucial for developing effective monitoring and environmental remediation strategies along the São Paulo coast and other similar coastal regions. This contributes to achieving Sustainable Development Goal 14 (Life Below Water), specifically targeting goal 14.1 — to prevent and significantly reduce marine pollution, particularly from land-based activities, including marine debris (indicator 14.1.1 — density of plastic debris) by 2025 — and goal 14.a, which seeks to enhance scientific knowledge, develop research capacities, and transfer technology to improve ocean health (https://sdgs.un.org/goals/goal14).

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7. Data Availability Statement

- Data table < https://doi.org/10.5281/zenodo.12193104>
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