

# 1 Distribution and characteristics of microplastic deposits on sandy beaches: integrating 2 GNSS positioning, $\mu$ -Raman spectroscopy, and unsupervised models

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4 **Abstract:** This study conducts a comprehensive investigation of microplastic (MP) pollution along  
5 the São Paulo State coastline (Brazil). The primary sources of MPs are identified as inadequate  
6 plastic waste management and containment system failures in port and industrial areas. These  
7 pollutants not only compromise the natural beauty of the beaches but also negatively impact marine  
8 life by altering the physical and chemical characteristics of the beaches and impacting dependent  
9 ecosystems. The research utilized a five-step methodology comprising a geodetic survey, analysis  
10 of beach morphometric parameters, collection of beach sediments,  $\mu$ -RAMAN spectrometry for  
11 polymer identification, and the application of multivariate statistical models. For MP sample  
12 collection, the coastline was divided into six segments (C1 to C6). The results indicated higher MP  
13 concentrations in C3 and C2, suggesting the influence of industrial and port activities. Various MP  
14 types, such as pellets, fragments, and fibers, exhibited distinct distribution patterns, likely due to  
15 their different sources, intrinsic properties like shape and density, and emission and deposition  
16 processes. The analysis for the entire São Paulo coast revealed that beaches with characteristics  
17 (intermediate profile and facing the southern quadrant) tend to accumulate more MPs. The  
18 predominance of polymers such as polyethylene and polypropylene reflect the influence of  
19 industrial products on marine pollution. This study highlights the complexity of MP dynamics in  
20 the coastal environment and underscores the importance of considering the physical characteristics  
21 of the beaches, the diversity of MP types, and local human activities. Identifying areas more prone  
22 to the accumulation of this emerging pollutant is critical for developing targeted environmental  
23 monitoring and remediation strategies, which align with the peculiarities of each coastal region  
24 and contribute to the Sustainable Development Goals related to ocean health (SDG – 14).

25 **Keywords:** Marine litter, plastic particles, coastal deposition, extreme events.

## 26 27 1. Introduction

28 The Santos estuary, encompassing the city and the Port of Santos, along with the industrial  
29 region of Cubatão, represents a critical area for microplastic (MP) pollution, especially pellets,  
30 along the São Paulo coast (Ferreira et al., 2021). Inadequate plastic waste management and failures  
31 in containment systems are the leading causes of the entry of this pollutant into the environment,  
32 particularly during production, transport, and transshipment processes in factories and port  
33 terminals (Balthazar-Silva et al., 2020; Moreira et al., 2016; Turra et al., 2014).

34 The intense port activity, combined with high population density and industrial  
35 concentration, makes this region a hub for the dispersion of MP (Jong et al., 2022). Ivar do Sul &  
36 Costa (2014) pointed out that on Brazilian beaches, a high concentration of MPs is correlated with  
37 the intensity of port and industrial activities, especially in the Southeast region. The impacts caused  
38 by this pollutant affect not only the aesthetics of the beaches but also marine life due to the  
39 ingestion of these particles by marine organisms, causing physical and chemical damage, reflecting  
40 the severity of the situation (Rochman et al., 2013).

41 The presence of this emergent pollutant on coastal beaches has been observed to detract  
42 from their intrinsic aesthetic value, thereby impacting the visual appeal and recreational quality of  
43 these environments (Borriello, 2023; Corbau et al., 2023). Its diminutive size and the challenge in  
44 detection contribute to a gradual yet significant visual deterioration of beach landscapes. This  
45 degradation is frequently attributed by non-expert observers to ineffective environmental  
46 management and a general decline in ecosystem health (Hartley et al., 2015). Furthermore, this  
47 phenomenon not only reduces the attractiveness of these areas to tourists but also raises concerns  
48 regarding the health and well-being of both visitors and the local wildlife (Botero et al., 2021;  
49 Costa et al., 2022; da Silva et al., 2022; Göktuğ, 2021).

50 From a physical perspective, MP alter the composition and physical characteristics of beach  
51 environments, with potential repercussions for coastal ecosystems and the organisms reliant on  
52 these habitats for survival (Fries et al., 2013). The presence of MPs modifies sediment porosity,  
53 thereby impacting the drainage and moisture retention capabilities of beach substrates. This change  
54 in the physical environment can influence temperature-dependent sex determination in certain  
55 species, such as crustaceans and marine turtles (Carson et al., 2011; Nelms et al., 2016).

56 Chemically, MP can absorb and concentrate organochlorine contaminants, which include  
57 polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), Polycyclic Aromatic  
58 Hydrocarbons (PAHs) and MEHP (Mono-ethyl-hexylphthalate, degraded from Diethyl-hexyl-  
59 phthalate or DEHP) (Brighty et al., 2015; Hartley et al., 2015; Ogata et al., 2009; Teuten et al.,  
60 2009) residual plastic from the action of Ultraviolet (UV) rays and/or the process of mechanical  
61 abrasion (Harris, 2020) begins to release greenhouse gases such as methane and ethylene (Royer  
62 et al., 2018). These chemical compounds can concentrate and transport chemical contaminants to  
63 marine biota and, by extension, humans through the food chain (Chelsea M Rochman et al., 2013;  
64 Rochman et al., 2014; Smith et al., 2018).

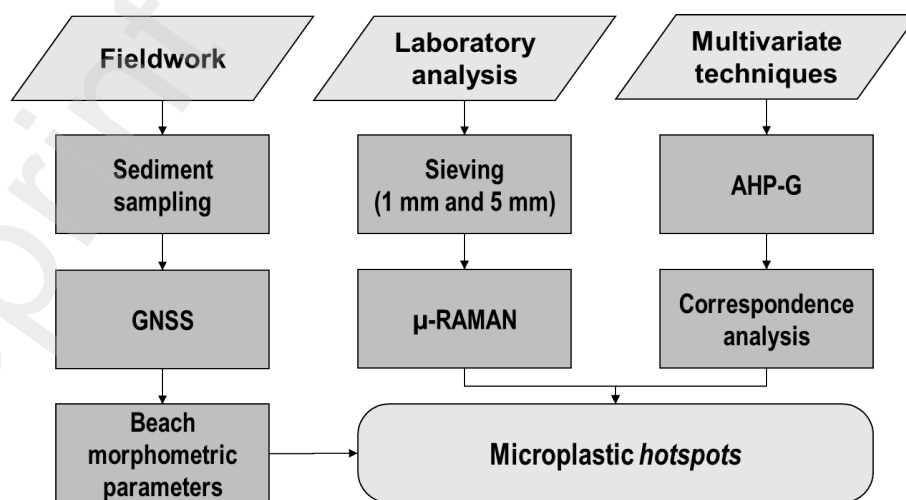
65 Through the combined analysis of geodetic, geomorphometric, and meteoceanographic  
66 factors at a beach along the São Paulo coastline, Ferreira et al. (2021) demonstrated that factors  
67 such as coastal currents and storm events can influence the deposition patterns of MP. Therefore,  
68 identifying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

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## 77 2. Methods

78 To indicate locations susceptible to MP deposition (MP hotspots), the data collection and  
79 analysis can be divided into three stages: 1) fieldwork – sediments sampling and beach  
80 morphometric parameters (aspect, slope, and altitude) using GNSS positioning; 2) laboratory  
81 analysis – sieving (1 – 5 mm mesh) and  $\mu$ -RAMAN spectrometry for the confirmation of polymeric  
82 properties; 3) exploratory multivariate techniques – analytical hierarchy process-gaussian (AHP-  
83 G) and correspondence analysis (CA) (Figure 1).

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85 **Figure 1.** Flowchart summarizing the methods used in this research. GNSS: global navigation  
86 satellite system; AHP-G: analytical hierarchy process-gaussian.  
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## 2.1. Fieldwork

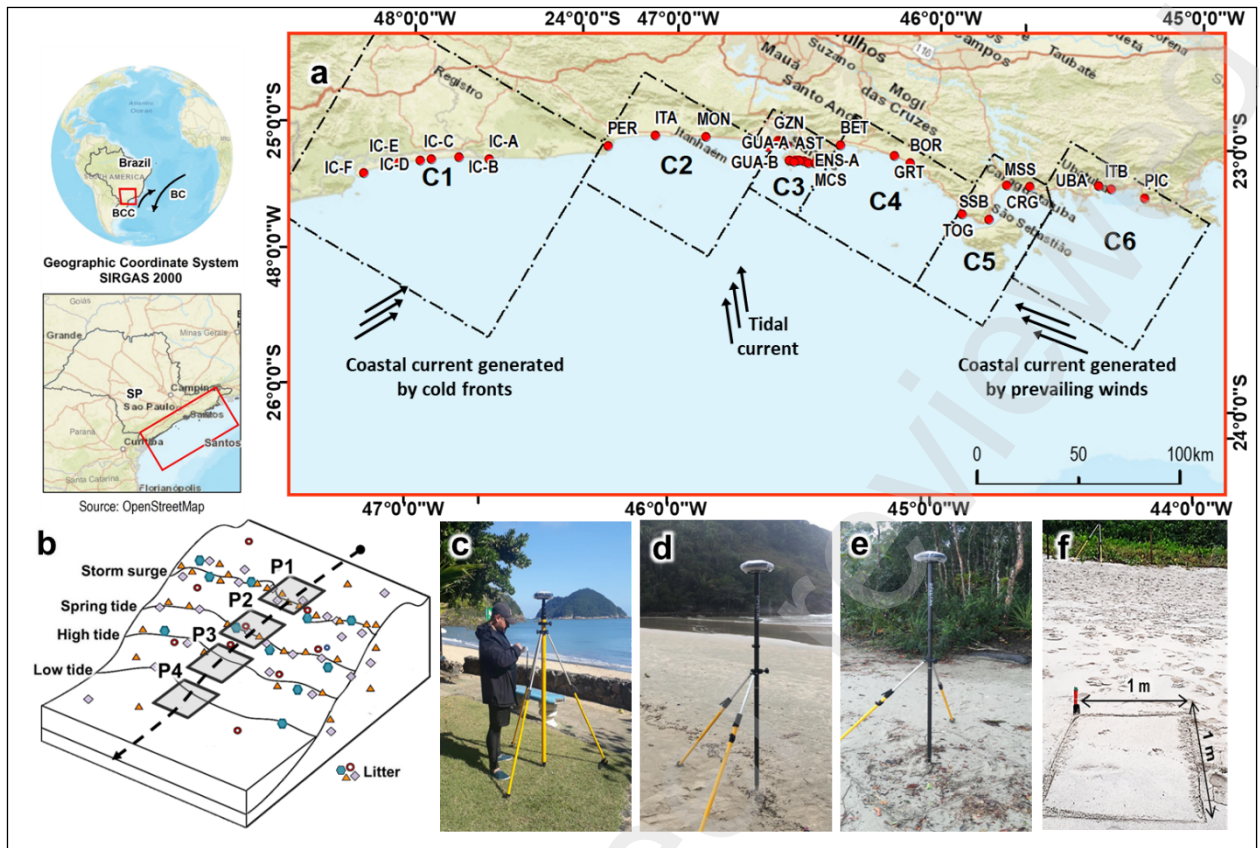
A complex interaction between geology, climate, and anthropic settings results in the varied coastal landscapes found in the state of São Paulo. The southern coast is dominantly low-lying, characterized by a wide coastal plain with extensive sandy beaches, lagoons and mangroves, including the Juréia-Itatins Ecological Station and Itinguçu State Park. Along the central and northern coasts, urbanization intensifies, and the Serra do Mar escarpment gradually approaches the coast, forming rocky headlands, pocket beaches and small islands (Souza, 2012; Tessler et al., 2018). This coast includes the city of Santos, where the largest port in Latin America is located. Ocean circulation is influenced by the warm Brazil Current flowing southward and the Brazil Coastal Current (Figure 2a), with coastal dynamics affected by the prevailing east-northeast winds and the stronger south-southeast winds, particularly during the winter (Campos et al., 1995; De Souza and Robinson, 2004; Möller Jr et al., 2008).

Sediment samples and beach morphology parameters were obtained along beach profiles distributed across all six compartments of the São Paulo coastline (Tessler et al., 2018), as shown in Table 1 and Figure 1a. 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. Sediment samples were obtained at four water levels (Figure 2b): storm strandline (P1), spring high tide (P2), neap high tide (P3), and low tide (P4). Each sample consisted of 500 g collected from the top layer of sediment within from 1 m<sup>2</sup> area (Figure 2f) at each of the 128 sampling points, yielding 1026 items identified as MP between 1 – 5 mm.

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

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

## 118 2.2. Morphometric parameters (GNSS)

119 The altimetry of the sampling points (P1, P2, P3, and P4) was obtained using the Global  
 120 Navigation Satellite System (GNSS), following the method described in Ferreira et al. (2021).  
 121 Reference stations were established within less than 5 km of markers distributed along the beach  
 122 and positions were received from the nearest active stations of the Brazilian Network for  
 123 Continuous Monitoring using the SIRGAS2000 coordinates system. Coordinates and altitudes of  
 124 sampling points recorded by the mobile station were post-processed relative to the reference station  
 125 (Monico, 2008; Monico et al., 2009) using the Survey Office software. The orthometric altitude  
 126 ( $H$ ) relative to the mean sea level of the Imbituba/SC datum of the Brazilian Geodetic System was  
 127 obtained through Eq. 1 (Blitzkow et al., 2016):  
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$$129 \quad H = h - N \quad (1)$$

130 where  $h$  is the geometric altitude obtained with GNSS referenced to the SIRGAS2000 ellipsoid,  
 131 and  $N$  is the geoidal height determined by the IBGE geoidal model - MAPGEO2015. The altitudes  
 132 ( $H$ ) of the sampling points were classified according to Ferreira et al. (2021), as: Very Low (VL;  
 133 < 1.42 m); Low (L; 1.42 – 1.57m); Mean (M; 1.58 – 1.89m); High (H; 1.90 – 2.06m); and Very  
 134 High (VH; >2.06 m). The beach slope ( $\tan\beta$ ) was derived from Eq. 2:  
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$$137 \quad \tan\beta = \text{atan}(VD/HD) \quad (2)$$

140 where VD and HD are the vertical and horizontal distances, respectively, between sampling points  
141 P1 and P4 (Figure 2b). The slope can be used as a proxy of the beach morphodynamic stage (Bujan  
142 et al., 2019), and can be categorized into steep ( $\tan\beta > 0.12$ ); intermediate ( $0.05 < \tan\beta < 0.12$ ); and  
143 sloping ( $\tan\beta < 0.05$ ) (Ferreira et al., 2023).

144 The aspect of the beach face is determined by the direction of the beach transect relative to  
145 the geographic north as follows (Burrough et al., 1998): North – N ( $0^\circ - 22.5^\circ$ ); Northeast – NE  
146 ( $22.5^\circ - 67.5^\circ$ ); East – E ( $67.5^\circ - 112.5^\circ$ ); Southeast – SE ( $112.5^\circ - 157.5^\circ$ ); South – S ( $157.5^\circ -$   
147  $202.5^\circ$ ); Southwest – SW ( $202.5^\circ - 247.5^\circ$ ); West – W ( $247.5^\circ - 292.5^\circ$ ); Northwest – NW ( $292.5^\circ$   
148  $- 337.5^\circ$ ); North – N ( $337.5^\circ - 360^\circ$ ).

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## 150 **2.3. Microplastic analysis**

### 151 **2.3.1. Sieving (surface samples)**

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

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### 157 **2.3.2. Polymeric characterization ( $\mu$ -RAMAN spectrometry)**

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

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## 171 **2.4. Unsupervised models**

172 Given the heterogeneous nature of the data (quantitative and qualitative variables),  
173 exploratory multivariate techniques such as analytical hierarchy process-gaussian (AHP-G) and  
174 correspondence analysis (CA) were employed (dos Santos et al., 2023; Fávero and Belfiore, 2017).

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

181 The CA examines associations between variables of interest using the chi-square test ( $X^2$ ;  
182  $p\text{-value} < 0.05$ ). In it, the Adjusted Standardized Residuals (ASR) check for dependence  
183 relationships between each variable based on the reference critical value ( $+1.96 \leq$ ) of the standard  
184 normal curve for a 5% significance level. Thus, if the value of the ASR in a cell is greater than or  
185 equal to 1.96, it is interpreted that significant dependence relationships exist (Fávero and Belfiore,  
186 2017; Haberman, 1978; Johnson and Wichern, 1992). All statistical analyses were performed in  
187 Anaconda/Spyder software using Python.

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$$189 \text{ Standardization} = \frac{(\text{observed value}) - (\text{minimum value})}{(\text{maximum value}) - (\text{minimum value})}$$

190 (3)  
 191  
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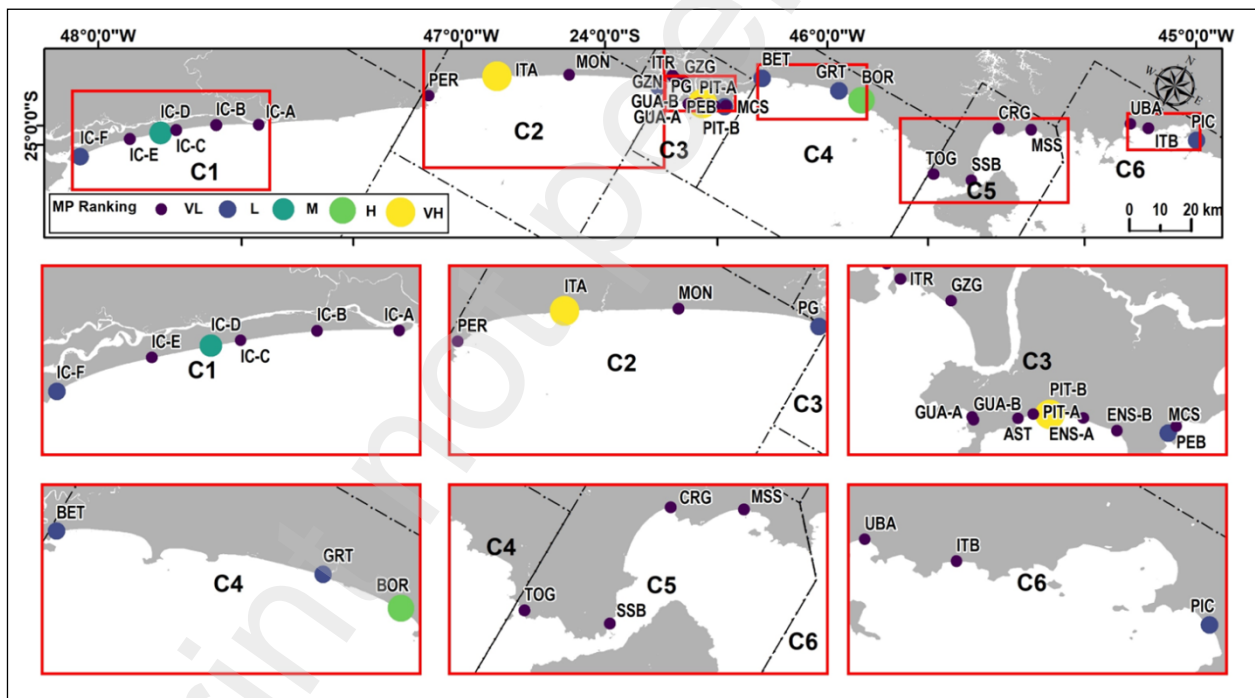
Table 2 – Standardized qualitative data based on the total count of polymers.

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)

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 194 **3. Results**

195 **3.1. Geographic distribution of microplastic**

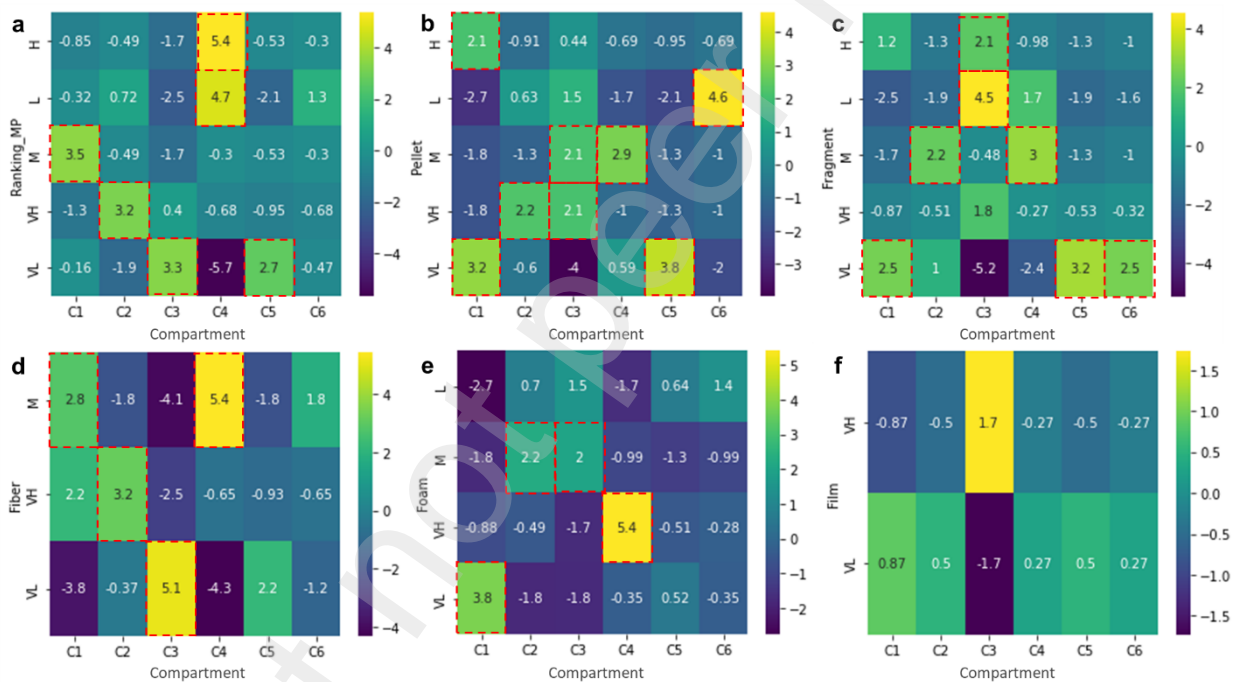
196 The majority of the 1,026 MP found consisted of fragments (42%) and foams (35%), with  
 197 pellets, fibers, and films accounting for 20%, 3%, and 0.3%, respectively. Figure 3 shows the  
 198 distribution of the standardized MP ranking across the study area. Low (L) and very low (VL) MP  
 199 concentrations were found on beaches across all coastal compartments. In contrast, very high (VH)  
 200 concentrations were predominantly found on beaches located in compartments C2 and C3 (PIT-B  
 201 and ITA), with high (H) and moderate (M) concentrations identified in C4 and C1 (BOR and IC-  
 202 D), respectively.  
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204  
 205 Figure 3 – MP ranking generated by the AHP-G method for the entire São Paulo coastline,  
 206 highlighting compartments C1, C2, C3, C4, C5, and C6.  
 207

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

215 The concentration of pellets exhibited significant variations between compartments. Very  
 216 high (VH) concentrations of pellets were significantly associated with beaches in C2 and C3  
 217 (Figure 4b). Significant associations were found between high (H) and very low (VL)  
 218 concentrations of pellets in C1 beaches, with VL also found in C5. Moderate (M) concentrations  
 219 were associated with beaches in C3 and C4, while low concentrations were significantly associated  
 220 only with beaches in C6 (Figure 4b). Considering fragments, no significant association was found  
 221 for VH concentrations, while H concentrations showed a significant relationship only with beaches  
 222 in C3 (Figure 4c). Moderate concentrations of fragments were found to be significantly related to  
 223 beaches in C2 and C4, with low concentrations associated with C3. Very low (VL) concentrations  
 224 were significantly related to C1, C5, and C6. The presence of fibers showed no significant  
 225 relationships with beaches in C5 and C6, while VH and VL concentrations were associated with  
 226 beaches in C2 and C3, respectively, and moderate (M) concentrations with beaches in C1 and C4  
 227 (Figure 4d). Similar to fibers, the presence of foam showed no significant relationships with C5  
 228 and C6. Significant associations were found between VH concentration of foam in C4, M in C2  
 229 and C3, and VL in C1 (Figure 4e). Films did not display significant dependency relationships with  
 230 any compartment, although C3 exhibited the highest ARS values (Figure 4f).  
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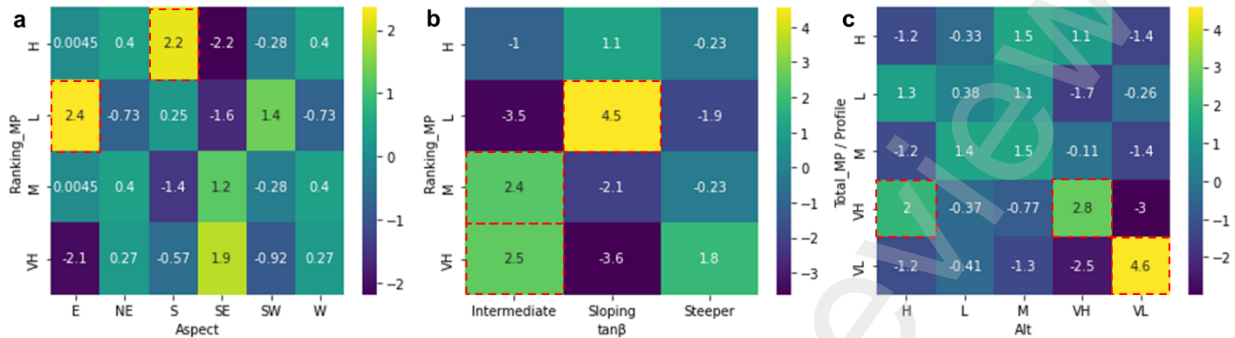


232  
 233 Figure 4 – Matrices showing the Adjusted Standardized Residual (ARS) values between the  
 234 concentration rankings for MP (a), pellets (b), fragments (c), fibers (d), foam (e), and film (f) for  
 235 each compartment (C1, C2, C3, C4, C5, and C6). Dashed red contours indicate variables  
 236 exhibiting significant dependency relationships (ARS ≥ 1.96).  
 237

### 238 3.2. Associations between morphometric variables and microplastics

239 The  $X^2$  test showed statistically significant associations between beach slope ( $\tan\beta$   
 240  $p=2.2239E-07$ ), aspect ( $p=1.1805E-06$ ), and altitude ( $p=0.0016$ ) and MP concentrations.  
 241 Dependency relationships were identified between high MP concentrations and a southerly beach  
 242 aspect (the slope faces the S quadrant), while low MP concentrations (L) were associated with an  
 243 easterly beach aspect (Figure 5a). Very high and moderate MP concentrations showed a significant  
 244 relationship with beach slopes classified as intermediate ( $0.05 < \tan\beta < 0.12$ ) with low  
 245 concentrations associated with gentler beach slopes ( $\tan\beta < 0.05$ ), as illustrated in Figure 5b.

246 The analysis of ASR values indicated that very high MP counts along the beach profile are  
 247 significantly related to high and very high altitudes (Figure 5c), reflecting strandlines along the  
 248 upper parts of the beach profile (2.06 m to 2.62 m, above mean sea level). Conversely, very low  
 249 MP concentrations were associated with very low altitudes (<1.90 m), suggesting strandlines along  
 250 the lower part of the beach profile.  
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252  
 253 Figure 5 –Matrices showing the Adjusted Standardized Residual (ASR) values between MP  
 254 rankings and the orientation of the beach face (Aspect) (a); beach slope (tanβ) (b), the total MP  
 255 count per profile and the altitude (Alt) (c). Dashed red contours indicate significant relationships  
 256 (ASR ≥ 1.96).  
 257

258 Results from the X<sup>2</sup> tests reveal that different MP types are more likely to be found at  
 259 certain beach elevations, with significant associations (p < 0.05) found between altitude levels and  
 260 pellets (p=1.6604E-10), fragments (p=0.0003), fibers (p=0.03677), foam (p=5.69E-08), and film  
 261 (p=0.04353). Very high pellet concentrations were associated with very high altitudes (the upper  
 262 beach), while low and moderate concentrations were significantly more prevalent in low and  
 263 moderate altitudes, (Figure 6a). For fragments, high and very high concentrations were  
 264 significantly associated with moderate altitudes (Figure 6b), with concentrations reducing in  
 265 higher and lower beach elevations. Concentrations of fragments were very low at the lowest beach  
 266 elevations, low at both high and low beach levels, and moderate at high and very high altitudes  
 267 (Figure 6b). The accumulation of fibers showed a significant relationship only between moderate  
 268 concentrations and very low altitudes (Figure 6c). Similar to fragments, very low concentrations  
 269 of foam were significantly associated with very low altitudes and low concentrations were  
 270 associated with high altitudes (Figure 6d). However, high and very high foam concentrations were  
 271 found at the highest parts of the beach rather than at moderate altitudes as shown for fragments.  
 272 Finally, very high film concentrations were associated with low altitudes, the only significant  
 273 relationship found between this type of MP and altitude (Figure 6e).  
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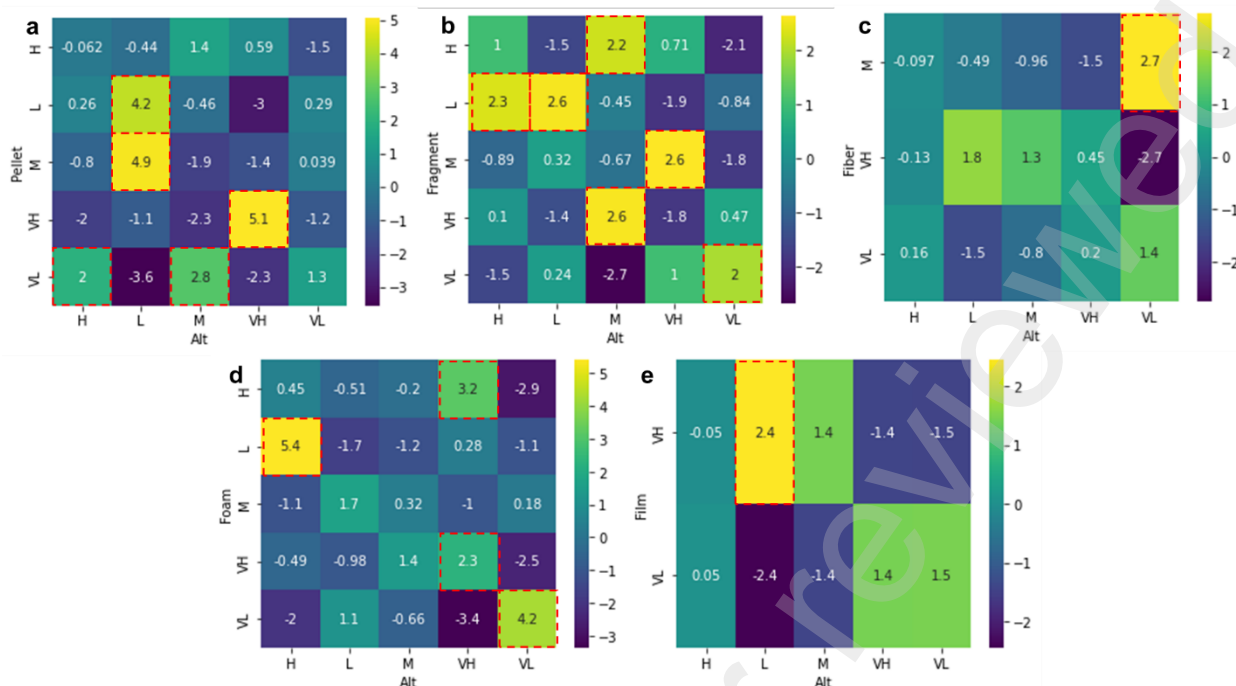


Figure 6 –Matrices of the Adjusted Standardized Residual (ASR) values between altitude (Alt) and the total count of pellets (a), fragments (b), fibers (c), foams (d), and films (e) per profile. Dashed red contours indicate significant relationships (ASR ≥ 1.96).

### 3.3. $\mu$ -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  $\mu$ -Raman analyses (Figure 7) 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 3). They were typically found in the form of small spherical or cylindrical granules, with HDPE exhibiting significant Raman peaks around  $1130\text{ cm}^{-1}$ ,  $1295\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$ , and a density range between  $0.941$  and  $0.965\text{ g/cm}^3$ . LDPE showed Raman peaks similar to those of HDPE, maintaining the same characteristic peaks at  $1130\text{ cm}^{-1}$ ,  $1295\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$ , but with subtle differences in the spectral profile and a lower density range ( $0.910$  to  $0.940\text{ g/cm}^3$ ).

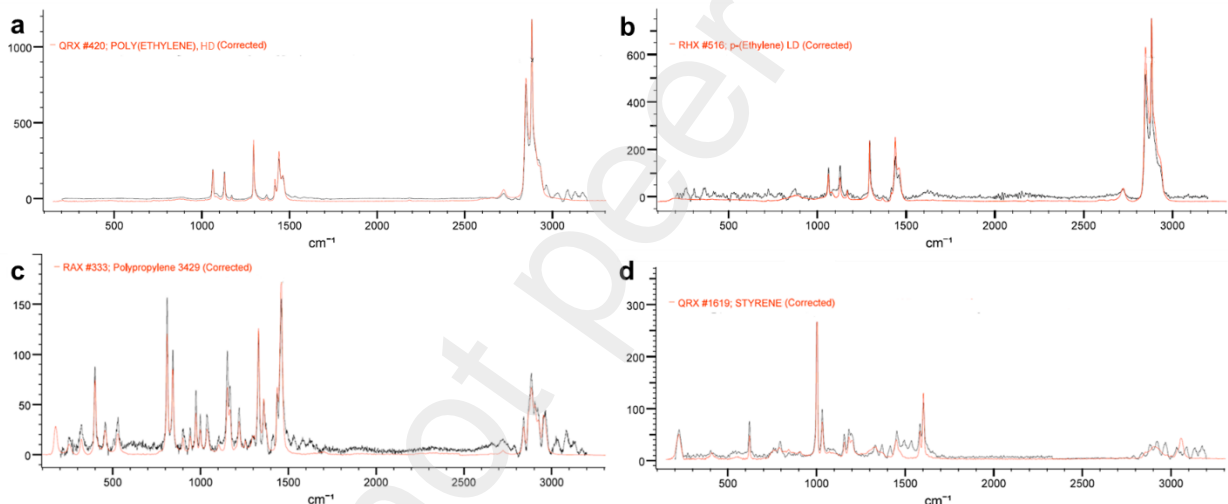
The fragments and the fibers predominantly found at moderate altitudes in the beach profile exhibited the greatest diversity of polymeric material encountered. As they are derived from already industrialized products, these are commonly found in the form of polymers such as high and low-density Polyethylenes (HDPE and LDPE, respectively), identical to the pellets in Figures 7a and b, as well as Polypropylene (PP) (Figure 7c), 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  $841\text{ cm}^{-1}$ ,  $973\text{ cm}^{-1}$ , and  $1160\text{ cm}^{-1}$ , with a density ranging between  $0.855$  and  $0.946\text{ g/cm}^3$ .

Similarly to the fragments, foams also stood out for the diversity of their compounds. These polymers were predominantly identified and classified as Styrene (Figure 7d), including Polystyrene, Polyurethane, and Styrene/Allyl Alcohol Copolymer 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  $1000\text{ cm}^{-1}$ ,  $1030\text{ cm}^{-1}$ , and  $1600\text{ cm}^{-1}$ . The density of polystyrene, a styrene derivative, is approximately  $0.91\text{ g/cm}^3$ .

307 Table 3 – Main Polymers Identified by  $\mu$ -Raman Spectrometry at different beach elevations (IC-  
 308 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-Acrylic-Acid)	Polypropylene		Polystyrene	
	Ethylene-Polypropylene		Polyurethane	
	Poly(Ethylene-co-Vinyl Acetate)		Styrene/Allyl Alcohol Copolymer Low Molecular Weight	
	Poly(Propylene-Ethylene-Acrylic Acids)			

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310 Figure 7 – Polymeric characterization by  $\mu$ -Raman of the main polymers found in different  
 311 sections of the beach profile: (a and b) High-Density and Low-Density Polyethylene (HDPE and  
 312 LDPE, respectively); (c) Polypropylene; and (d) Styrene.  
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 314

#### 315 4. Discussion

316 The MP Ranking observed a distribution starting from the Santos Estuary and Mar Pequeno  
 317 (São Vicente), initially depositing on beaches near these channels (e.g., sectors C3 and C2) and  
 318 progressively accumulating as it moves toward the SSW, the same direction as the predominant  
 319 coastal current in the region (NE-SW) (Tessler et al., 2018) on beaches such as Itanhaém (ITA)  
 320 and those located on Ilha Comprida (IC-D), in sectors C2 and C1 of Figure 3, respectively.  
 321 Conversely, beaches in sectors C4, C5, and C6 showed the lowest values in the Ranking. This  
 322 suggests that beaches near Santos Bay are the first to be impacted due to their proximity to the  
 323 primary sources of this pollutant, resulting from cities with higher population densities like Santos  
 324 and São Vicente, in addition to the Port of Santos and the petrochemical industries in Cubatão. The  
 325 latter two are responsible for the reception and processing of this material (Balthazar-Silva et al.,  
 326 2020; Ferreira et al., 2021; Turra et al., 2014).

327 The analysis of the results on the distribution of MP across different compartments of the  
 328 São Paulo coast provides a comprehensive overview of the environmental impact of this pollutant.

329 The applications of AHP-G, the  $\chi^2$  test, and AC have provided a robust statistical understanding of  
330 the distribution of these materials (Ferreira et al., 2023; Pereira et al., 2023; Santos et al., 2021).

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

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

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

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

354 The relationship between the beach slope ( $\tan\beta$ ) and the concentration of MP suggests that  
355 beaches with intermediate slope profiles are more prone to accumulate higher concentrations of  
356 MP, in general. This may be due to sediment and debris transport and deposition dynamics on  
357 these profiles (Andrady, 2011; Ferreira et al., 2021). Beaches with a dissipative trend ( $\tan\beta < 0.05$ )  
358 show lower concentrations. The flatter and lower profiles favor beach washing during high tides  
359 and, consequently, the fluctuation of MPs back into the coastal current (Cooper and McLaughlin,  
360 1998; Ferreira et al., 2021). The orientation of the beaches (Aspect) also shows a significant  
361 relationship with the concentration of MP (Vito et al., 2022). Beaches facing the South quadrant  
362 exhibit higher concentrations in the same direction as the higher energy storm waves (Ferreira et  
363 al., 2021; Young and Elliott, 2018) come from this direction. According to Ferreira et al. (2023),  
364 beaches on the São Paulo coast with this orientation naturally accumulate sediments and marine  
365 litter.

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

373 The chemical identification of MPs through the  $\mu$ -Raman technique has provided a robust  
374 approach to characterizing these materials, as evidenced in similar studies (Löder et al., 2015;  
375 Löder and Gerdt, 2015; Silva et al., 2018). Beach profiles IC-D, ITA, PIT-B, and BOR showed  
376 the highest values in the MP Ranking, indicating a significant concentration of MP in these areas.  
377 The predominance of polyethylene pellets (PE), both high-density (HDPE) and low-density  
378 (LDPE), reflects a typical pattern in coastal pollution of the São Paulo coast. These polymers are

379 widely used for their versatility and low cost, commonly found in consumer products and  
380 packaging (Chen et al., 2022; Zeng, 2023; Ziani et al., 2023).

381 HDPE, LDPE, PP, and Styrene exhibit distinct characteristics crucial for their identification  
382 and analysis in the Raman spectrum. Due to its resistance and durability, HDPE, a widely used  
383 polymer, displays significant Raman peaks around  $1130\text{ cm}^{-1}$ ,  $1295\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$ ,  
384 associated with C-C and CH oscillations and  $\text{CH}_2$  bending. The density of HDPE varies between  
385  $0.941$  and  $0.965\text{ g/cm}^3$ , reflecting its high crystallinity. On the other hand, LDPE, characterized by  
386 its flexibility, shows Raman peaks similar to those of HDPE but with subtle differences in the  
387 spectral profile due to its more branched structure, maintaining the same characteristic peaks at  
388  $1130\text{ cm}^{-1}$ ,  $1295\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$ . Its density, influenced by lower crystallinity, is in the range  
389 of  $0.910$  to  $0.940\text{ g/cm}^3$  (Brandrup et al., 1999; Katsara et al., 2022; Tarani et al., 2023).

390 The diversity of polymers found in fragments and fibers, including PE, PP, and various  
391 copolymers, suggests a variety of pollution sources. These materials are often derived from already  
392 industrialized and discarded products, reflecting the widespread use of plastics in modern society  
393 and the inadequacy of waste management systems (Gao et al., 2022; Geyer et al., 2017). The  
394 identified foams and films, mainly composed of styrene and other polymers such as polystyrene  
395 and polyurethane, are consistent with literature highlighting the presence of these materials in  
396 marine environments. The former (styrene and polystyrene) are commonly used in packaging and  
397 thermal insulation applications due to their lightness and resistance. Polyethylene, widely used as  
398 the primary material in the manufacture of plastic bags and packaging, represents one of the most  
399 significant sources of MP pollution in the marine environment (Gao et al., 2023; Gunawan et al.,  
400 2022; Katsara et al., 2022).

401 The accumulation of pellets in the higher portions of beach profiles is a phenomenon that  
402 can be attributed to a combination of physical and geomorphological factors (Ferreira et al., 2021).  
403 These pellets' spherical or cylindrical shape, along with their relatively low density ( $0.910$  and  
404  $0.965\text{ g/cm}^3$ ), plays a crucial role in their deposition and distribution on beaches. This enhances  
405 the transportation of these microplastics by ocean currents and, specifically, their mobilization by  
406 high-energy waves and winds. When high-energy waves strike the beaches, particularly during  
407 high tides and storm events, these microplastics are driven to the upper sections of the beach  
408 profiles. Moreover, the spherical or cylindrical shape of the pellets reduces friction with the sand  
409 and other beach materials, facilitating wind transport through rolling and/or saltation. Once in the  
410 higher areas of the beach profile, these MPs tend to be retained due to the decreased energy of  
411 these factors (waves, winds, and tides), where they end up depositing and accumulating (Alvarez-  
412 Zeferino et al., 2020; Ferreira et al., 2021; Ryan et al., 2009).

413 In contrast to pellets, fragments and fibers often exhibit faceted or irregular shapes,  
414 influencing their transport dynamics and deposition on beaches. These irregular shapes increase  
415 resistance to movement in this environment, limiting their ability to be transported to higher beach  
416 areas, especially under the influence of less intense winds and waves (Oliveira et al., 2023;  
417 Lefebvre et al., 2023; Zhang et al., 2022). Furthermore, the density of these MP, generally higher  
418 than that of pellets, also contributes to their accumulation in the mid-regions (P2 and P3) of the  
419 beach profile. Fragments and fibers tend to settle where wave and current energy diminish, but it  
420 is still sufficient to mobilize them. This intermediate zone of the beach profile typically  
421 corresponds to a balance between areas reached by high tides and the extent of significant aeolian  
422 transport (Andrady, 2011; Ferreira et al., 2021; Jambeck et al., 2015).

423 The accumulation of expanded foams and plastic films in higher concentrations in the lower  
424 parts of beach profiles (P4, primarily, and P3) can be attributed to specific characteristics of these  
425 materials and the environmental dynamics of beaches. Foam, commonly composed of polystyrene  
426 and polyurethane, has a cellular structure that endows low density and high buoyancy (Auta et al.,  
427 2017; Gao et al., 2023). This low density allows foam to be easily transported by water, particularly  
428 by waves. However, its voluminous structure and lightness contribute to these materials being

429 deposited in the lower parts of beach profiles, where wave energy is insufficient to carry them to  
430 higher areas. In contrast, plastic films are generally thin and flexible, facilitating their movement  
431 by wind and wave action. Nevertheless, their flat shape and larger surface area relative to weight  
432 mean they are easily trapped in the lower beach areas (P4), where wind and wave energy is lower.  
433 Additionally, plastic films can become entangled with natural debris or adhere to moist sand,  
434 reducing mobility. (Andrady, 2011; Barnes et al., 2009; Browne et al., 2011; Martin et al., 2017;  
435 Rochman et al., 2013; Thompson et al., 2004).

436 This way, based on the aspects raised (Aspect,  $\tan\beta$ , and Altitude), it is possible to state  
437 that the locations with greater susceptibility to MP accumulation or potential hotspots depend on  
438 intermediate beach profiles facing the South quadrant and locations with excellent coastline  
439 stability and/or accretion. This is due to the  $\sim 90^\circ$  angle between storm waves formed by cold fronts  
440 coming from the same quadrant, resulting in the near cessation of sediment transport on these  
441 beaches, favoring the accumulation of sediments and anthropogenic debris, including MP (Ferreira  
442 et al., 2023, 2021; Harris, 2020; Jong et al., 2022; Laurino et al., 2023; Stein and Siegle, 2019).  
443 This is because relative stability at some beaches can favor such deposition (Veerasingam et al.,  
444 2020), as seen in those associated with slow accretion processes, such as sandy spits and areas  
445 protected by tombolos, respectively, in compartments C1 and C3 (Ferreira et al., 2023; Mahiques  
446 et al., 2016; Mascagni et al., 2018; Silva et al., 2021).

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

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

461

## 462 5. Conclusions

463 This study presented a comprehensive examination of the distribution of various types of  
464 MP (categories: pellet, fragment, fiber, foam, and film) along the São Paulo coastline, taking into  
465 account morphometric characteristics (i.e., beach face orientation - aspect; slope -  $\tan\beta$ ; and  
466 altitude) and meteo-oceanographic conditions, uncovering complex and significant patterns in the  
467 dispersion and accumulation of this pollutant. The findings, grounded in robust statistical analyses  
468 such as AHP-G, the  $X^2$  test, and CA, ranked and indicated statistically significant associations  
469 between the presence of MP and specific geographic compartments and with the morphometric  
470 variables of the beaches. Notably, the highest concentrations of MP are predominantly found on  
471 compartments C3 and C2 beaches, suggesting a direct influence of proximity to urban and  
472 industrial sources, like the Santos Estuary and Mar Pequeno. The types of MP, including pellets,  
473 fragments, fibers, and foams, exhibit distinct patterns of dependency on these compartments,  
474 reflecting potential differences in emission sources and transport and deposition processes.

475 The observed relationship between the environmental characteristics utilized and MP  
476 provides a comprehensive understanding of these pollutants' accumulation dynamics. The  
477 association of higher altitudes with elevated MP concentrations suggests a significant role of high  
478 tide processes and storm surges in depositing debris in higher beach areas.

479  $\mu$ -Raman spectroscopy revealed the predominance of polymers such as polyethylene (PE)  
480 in high and low-density forms, polypropylene (PP), and styrene, highlighting the significant  
481 contribution of industrialized and consumer products to MP pollution. Identifying susceptible  
482 locations for MP accumulation or hotspots along the coastline, using remote sensing data and  
483 morphometric analyses, observed that certain areas are particularly prone to MP concentration.  
484 These hotspots are often associated with intermediate beach profiles facing the South quadrant and  
485 locations with greater stability or accretion of the shoreline, where aggradation processes favor the  
486 accumulation of anthropogenic debris, including MP.

487 The study further highlights the complexity of MP dynamics in the coastal environment,  
488 emphasizing the importance of considering both the physical characteristics of the beaches and  
489 local human activities to understand and manage this type of pollution. Moreover, the variability  
490 in MP types and their relationships with different beach environments points to the need for  
491 differentiated management approaches tailored to the specific characteristics of each coastal  
492 compartment and pollutant type. Therefore, future studies linking the results found here with  
493 information derived from orbital remote sensing could generate models capable of predicting and  
494 synoptically expanding all these aspects.

495 Understanding these distribution patterns is crucial for developing effective monitoring and  
496 environmental remediation strategies in the São Paulo coast and other similar coastal regions. This  
497 contributes to achieving Sustainable Development Goal 14 (Life Below Water), explicitly  
498 targeting goal 14.1 —to prevent and significantly reduce marine pollution, particularly from land-  
499 based activities, including marine debris (indicator 14.1.1 — density of plastic debris) by 2025 —  
500 and 14. a, which seeks, among other objectives, to enhance scientific knowledge, develop research  
501 capacities, and transfer technology to improve ocean health (<https://sdgs.un.org/goals/goal14>).

502

## 503 **6. Acknowledgment**

504

## 505 **7. References**

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