Environmental Research 307 (2026) 125428

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

A first inventory of plastic litter and some associated total metal contents at the coastline of the Bay of Asunción (Paraguay)

Diana Diez-Pérez Núñez [a,b], Deyanira Peralta [a], Dahiana Serafini [a], Derlysa Colmán [a], José M. Andrade [b,*], Adrián López-Rosales [b], Soledad Muniategui-Lorenzo [b,**]

[a] National University of Asunción, Faculty of Chemical Sciences, Department of Physical Chemistry, Ruta Nacional PY02 'Mariscal José Félix Estigarribia' Km. 14, San Lorenzo, 111421, Paraguay

[b] University of A Coruña, Faculty of Sciences, Group of Applied Analytical Chemistry, Campus da Zapateira, A Coruña, 15008, Spain

ARTICLE INFO

Keywords:
Metal pollution
Adsorbed metals
Atomic absorption spectrometry
Infrared spectrometry
Macroplastics
Mesoplastics

ABSTRACT

Global plastic production increased remarkably through the last decades. A drawback of this fact is that many tons of new and used plastics end up in waterways worldwide, where they can adsorb other pollutants, as heavy metals. This study is one of the very first dealing with both topics (plastic inventory and major associated metals) in South America. Its aim was twofold: to perform a first inventory of plastic litter at the Bay of Asunción (Paraguay), and to evaluate the quantity of specific metals in selected plastic items. Four sampling areas were established in a period when a serious drought was occurring, and litter was sorted as plastics, metals, rubber, ceramics/glass, natural materials, and miscellaneous. Further, plastic litter was classified by size, original use, type of polymer, and characterized by infrared spectrometry. Microwave-assisted digestion with HNO_3 and flame atomic absorption spectrometry was applied to quantify Cd, Cu, Fe, Mn, and Zn. Highest percentages of litter (60 – 82%) corresponded to plastics at all points and their abundances were: PP, 42% > PE, 31% > PET, 12% > PS, 10% > PVC, 3% > PMMA, 2%. The highest total metal concentrations were for Fe (3526 μg g^{-1}) and Mn (1163 μg g^{-1}), followed by Zn (330.2 μg g^{-1}), Cu (94.90 μg g^{-1}), and Cd (18.70 μg g^{-1}). Multivariate studies revealed that Fe and Mn became associated to PS whereas Cd was more related to PP.

1. Introduction

Global plastic production increased significantly in the last years and is expected to continue growing (Fred-Ahmadu et al., 2022; PlasticsEurope, 2024). Unfortunately, many plastics are single-use and end up in landfills (Pilapitiya and Ratnayake, 2024) while others are disposed unduly in the environment because of bad habits and inefficient solid waste collection systems, as observed in informal settlements in the city of Asunción, Paraguay (Canese de Estigarribia et al., 2019).

Plastics of all sizes are found in a range of environmental compartments including sediments, beaches, ice, and living organisms (Cera et al., 2020; Hayes et al., 2021; Li et al., 2018; Park and Park, 2021; Rodríguez et al., 2019). Typically, they reach coastal ecosystems after their direct discharge, wind- or water-transport, and persist there for many years thanks to their durability (Correa-Araneda et al., 2022; Fred-Ahmadu et al., 2022; Pilapitiya and Ratnayake, 2024; Palmas et al., 2022). In addition, plastics evolve as they undergo structural changes through photo-oxidative processes, hydrolysis, and physical and mechanical degradation induced by wind and wave erosion, which promote their degradation and fragmentation (Correa-Araneda et al., 2022; Yousafzai et al., 2025). This leads to the generation of nano- (<1000 nm), micro- (<5 mm), meso- (5 mm to 2.5 cm), and macroplastics (>2.5 cm) (Blettler et al., 2017; Huang et al., 2021).

Furthermore, plastics exposure to environmental conditions, particularly when in surface water, causes not only their physico-chemical aging but the adsorption of other contaminants; most notably metals (Rasool et al., 2026), polycyclic aromatic hydrocarbons (Traverso-Soto et al., 2025) and pharmaceuticals (Patrício Silva et al., 2024). This, along with evidences on the accumulation of the smallest particles throughout the trophic chain (Huang et al., 2021) may lead to eventual

* Corresponding author.
** Corresponding author.
E-mail addresses: ddiezperez@qui.una.py, d.diezperez@udc.es (D. Diez-Pérez Núñez), deyaniraperaltapy@gmail.com (D. Peralta), dahiser96@gmail.com (D. Serafini), dcolman@qui.una.py (D. Colmán), andrade@udc.es (J.M. Andrade), adrian.lopez.rosales@udc.es (A. López-Rosales), soledad.muniategui@udc.es (S. Muniategui-Lorenzo).

https://doi.org/10.1016/j.envres.2026.125428
Received 19 February 2026; Received in revised form 13 July 2026; Accepted 7 August 2026
Available online 7 August 2026

toxic effects on aquatic biota, the subsequent intake through the food chain and, ultimately, affect human health (Kye et al., 2023; Rasool et al., 2026).

Nevertheless, reports on the accumulation of pollutants in plastic litter are still quite limited for the marine, freshwater, and transitional water ecosystems. Therefore, dedicated studies are needed to assess and understand their distribution in plastic waste (Li et al., 2021). Likewise, it is important to measure the metals associated with macro-, meso- and microplastics due to their potential toxicity to the environment and ultimately animals and humans, since both metals and plastics are usually non-biodegradable and can accumulate throughout the food chain.

This justifies recent research on the presence of metals and metalloids in meso- and macroplastics (Awe et al., 2025; Fred-Ahmadu et al., 2022; Jachimowicz et al., 2024; Klöckner et al., 2021; Munier and Bendell, 2018). Higher concentrations of these pollutants were found in foam plastics (Polystyrene, PS; Polyurethane, PUR; Poly(ethylene vinyl acetate), PEVA), than on hard plastics (Polyethylene, PE; Polypropylene, PP; Poly(ethylene terephthalate), PET). In addition, Susanto Barus et al. (2023) studied the adsorption and desorption of heavy metals at/from microplastics (MPs).

Several metals and metalloids were investigated so far. Munier and Bendell (2018) quantified Cd, Cu, Pb, and Zn in polymers from field samples; Fred-Ahmadu et al. (2022) found significant concentrations of Al, Fe, Mn, and Zn in plastics, suggesting environmental sorption and potential sources of additives; Nakashima et al. (2012) detected mainly Cr, Cd, Sn, Sb, and Pb in plastic waste; Jachimowicz et al. (2024) measured concentrations of potentially toxic elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, and Fe) in plastic litter.

Following, the objectives of this study are twofold: first, to make an inventory of litter floating or stranded along the coastline of the Bay of Asunción, Paraguay, an internationally protected area because of its biological importance; and second, to evaluate and quantify the presence of some exemplary metals in plastic litter. It is worth noting that the presence of metals in plastic waste has not yet been studied in Paraguay, and there are still scarce reports for South America.

2. Materials and methods

2.1. Sampling

The study area was the Bay of Asunción, Paraguay (57° 49' - 57° 30' W; 25° 15' - 25° 20' S), awarded as an Ecological Reserve in 2005. To identify the most interesting sampling locations for this study (a target-oriented one) a preliminary boat cruise was made along the borderline of the Bay, and several litter hotspots were identified. Four sites were sampled in September 2022 (Fig. 1), a month characteristic of the dominant drought conditions in the area that were lasting for three consecutive years. This affected dramatically much of the Plata River basin and impacted the main waterways within the country, primarily the Paraguay River basin (DINAC, 2023). This season was selected to evaluate a worst-scenario environmental situation and to unravel macroplastics that were stranded into (or partially buried by) the superficial

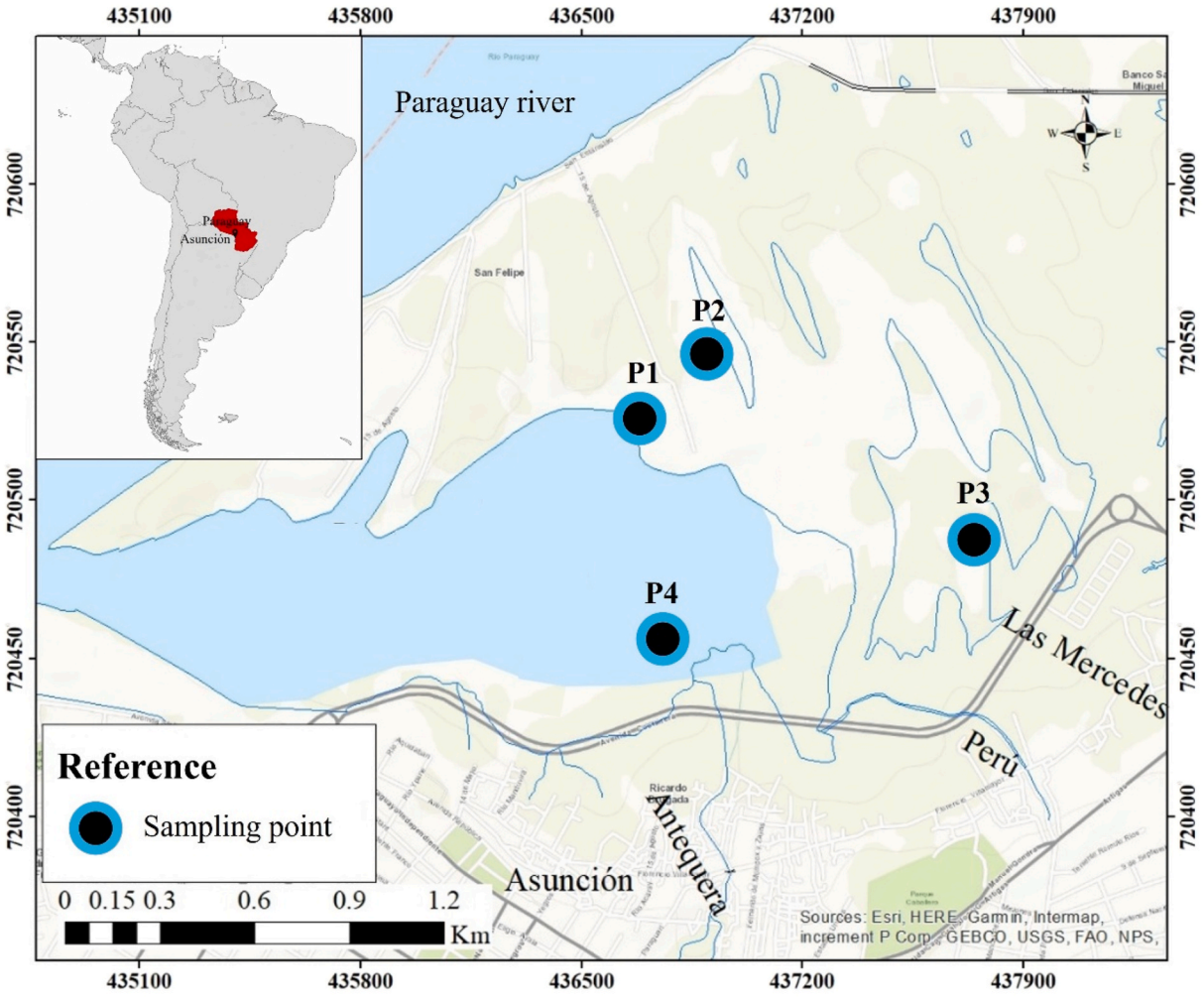

Fig. 1. Area under study. Four locations were selected according to the presence of total litter. Note that the overall map does not precisely delineate the full extent of the Bay of Asunción as the water level varies depending on the time of year (dry and flooding seasons).

sediments which, otherwise, might be unnoticed at higher water levels. Indeed litter buried on a beach has often been underestimated (Asensio-Montesinos et al., 2021; Palmas et al., 2022). The starting and final coordinates of the collection areas were recorded, using a Global Positioning System (GARMIN, GPSMAP 78S, USA), and the sampled surfaces calculated (see Table S1, Supplementary Information). Maps were created using ArcGIS 10.8 software, for which maps from the Military Geographic Institute and base maps from different sources such as Esri, HERE, and Garmin were obtained (Diez-Pérez et al., 2023).

Sampling followed the River-OSPAR protocol (Schone Rivieren, 2017) based on the OSPAR methodology (OSPAR, 2010). At each sampling location, a trajectory ranging from 40 to 100 m in length was set (according to the presence or absence of vegetation), 3 m away from the shoreline, and signaled using a measuring tape (Fig. S1). All types of litter were counted and classified as plastics, metals, rubber, ceramics/glass, natural materials, and miscellaneous (wood, paper, cardboard). EU guidelines for monitoring marine litter were followed (JRC, 2013) and, specifically, the definition of plastic litter and size categories. Items whose size were between 2.5*2.5 cm and 30*30 cm were collected, while larger ones (30*30 cm < plastics <100*100 cm) were counted but not collected. Big (>30 cm long) plastic pieces partially buried, bags with litter inside, or unsafe litter such as diapers (biological hazard) were counted but not collected. Fifty eight percent of the total inventoried items were selected randomly for subsequent laboratory studies (but for the exceptions just mentioned). No specific selection criterion was set although the number of items per category was a function of their abundance at the sampling sites (more abundant items got more representatives) (Ormeci et al., 2023). They were transported to the laboratory at room temperature. The litter categories set in the present work (bottles, food wrappers, cleaning wrappers, cups, bags, styrofoam, bottle caps, film, toys, syringes, straws and others –like domestic and electronic articles-) agree with common practice (Asensio-Montesinos et al., 2021; Palmas et al., 2022; Van Emmerik et al., 2020), being all categories represented in subsequent studies. Fig. 2a details the overall number of items per category and Fig. S2 (Supplementary Information) depicts how the distribution of the items was done.

2.2. Reagents and instrumentation

Commercial stock solutions (1000 mg L^{-1}) of Cd, Cu, Mn, and Zn were from Carlo Erba, Italy; and Sigma-Aldrich, Switzerland, for Fe. Nitric acid (65%, Ph. Eur, ISO) for microwave assisted digestion was from EMSURE (Germany). Daily metal working solutions were prepared from stock solutions, including those for calibration.

Pure water was obtained from a Direct Q-UV system from Millipore (resistivity 18 MΩ cm), in the following it is referred to as Milli-Q water.

A furnace (QUIMIS, Q317M-53, Brazil), an analytical balance (KERND ALJ, 0.1 mg, China), a Microwave-Assisted Digestion Mars2 system (CEM, USA), and an AA-6300 Flame Atomic Absorption Spectrometer (FAAS) from Shimadzu (USA) were used throughout. The instrumental and operating conditions are shown in Table S2. The system is not equipped with an automatic fast sequential mode, and the metals were measured sequentially and independently.

The infrared characterization of polymers in the mid-IR range was done with a single-bound, horizontal, diamond-based Attenuated Total Reflectance module (Pike MIRacle, Harrick) coupled to a Spectrum400 Fourier-transform infrared spectrometer (PerkinElmer, USA). A background scan was recorded (600 to 4000 cm^{-1}) before obtaining the spectrum of each potential plastic piece, 50 scans (600 to 4000 cm^{-1}) were collected and averaged, nominal resolution was 8 cm^{-1}. ATR correction to account for wavenumber penetration was applied before comparing each spectrum to a commercial spectral library (PerkinElmer) and an in-house database containing spectra of aged typical polymers. Spectral treatments were done using the 'Spectrum' software from PerkinElmer (v.10.6). IR measurements were done directly on the pieces after a gentle washing with Milli-Q water and after drying at 30 °C.

2.3. Analytical protocols

Plastic litter pieces were washed gently with Milli-Q water to remove solid residues and dried at 30 ± 1 °C in a furnace. Then, they were measured and classified by size (ranges: 2.5 – 10 cm; 10 – 20 cm; and 20 – 30 cm) and by 9 types of goods or categories of intended original use; i.e.; bottle, food wrapper, cleaning wrapper, cup, bag, styrofoam, bottle cap, film and toys (see Tables S3 and S4, Supplementary Information). Next, the items collected during sampling were cut to get a laboratory-prepared fraction of plastics whose size was <5 mm at their largest dimension (see Fig. S2, Supplementary Information), this procedure was not done for three categories: domestic goods, electronic articles, and syringes, which were counted and grouped under 'other', but were not considered for metal analysis due to the risk when handling them. In order to assure representativeness as far as possible, all items within a sample category were grinded and mixed to obtain a unique composite laboratory sample. It is acknowledged that with this approach items with different residence times in the environment (and, so, eventual different adsorption levels of metals) will be considered jointly. Hence, this approach yields a sort of 'average' picture of the metallic contents in the different plastic categories. Fig. S2, Supplementary Information, shows that the total number of items grinded for metal analysis was 29% of the items counted during sampling. As all item selections were random and all sample categories are considered through the workflow (and all items within a category grinded to yield a composite sample) it is expected that the final results are representative of the environmental situation of the Bay of Asunción at the sampling time. In total, 31 samples (sampling locations x 9 categories –when retrieved-), each one grinded and analized in duplicate were considered, and results are reported here as mean ± standard deviation.

To analyze metals 0.1000 g of each sample (fragments < 5 mm) were weighed and 10 mL of 65% HNO_3 added (Teflon vessels, TFM ®, CEM, USA). Microwave-assisted digestion was carried out setting the power between 1030 and 1640 W, ramp time 20 min, hold time 15 min, target temperature 210 °C. After finishing the digestions no remains were observed and the solutions were transferred to 25 mL flasks and diluted to their final volume using Milli-Q water, and the target metals were quantified by FAAS. This procedure does not discriminate inherent *versus* sorbed forms of metals and, accordingly, all the concentrations reported here will be considered as 'total'. The corresponding calibration curves and some figures of merit are depicted in Section S3 and in Fig. S3 (Supplementary Information). The metals (Cd, Cu, Fe, Mn, and Zn) were selected based on the sensitivity capabilities of the FAAS device available in our facilities, their potential impact on the aquatic ecosystem, their use as additives in polymers and their reported adsorption from the environment.

2.4. Validation and quality control

With regard to quality control and validation, the following studies/considerations were undergone. The IR system was validated before measurements following standard procedures (ASTM, 2021) and certified NIST polystyrene films.

For the FAAS measurements, the system was qualified by an external technician before the present study. Procedural blanks and spiked samples were prepared using HDPE and PP 'without metals' as supplied by a local plastics industry. Note that due to the fact that the aging of plastic pieces in nature is not uniform across all surfaces, field samples were not considered for recovery assay to reduce bias. They were grinded to get small laboratory-prepared fragments (<5 mm). The procedural blanks and spiked samples underwent the whole analytical procedure, under the same conditions as the samples. In all cases the metal spikes were left in contact with the laboratory-prepared fragments

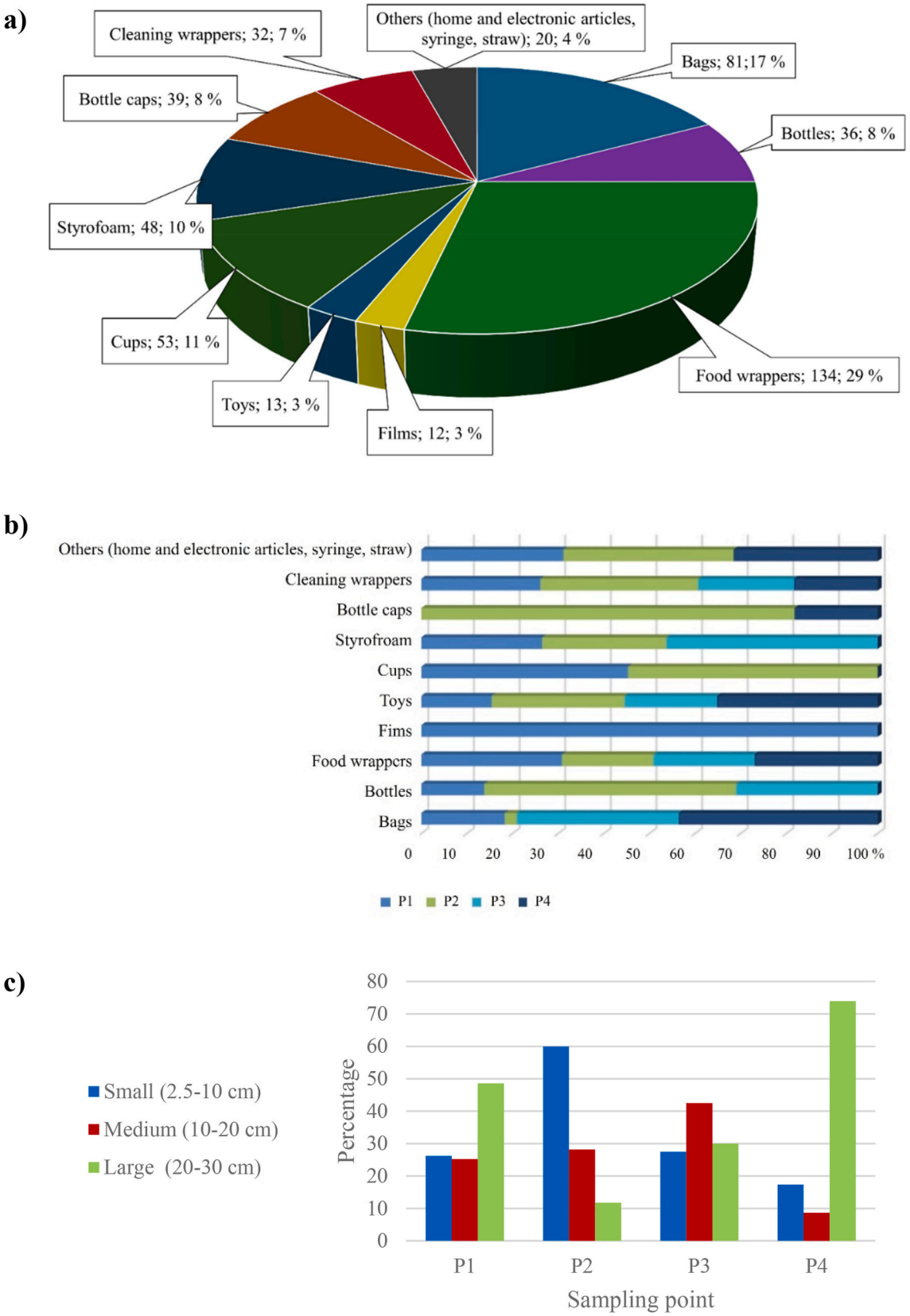

Fig. 2. Classification of plastic litter according to: overall quantities of macro- and mesoplastic items (all sites), the numbers indicate the number of items and their percentage (a); estimated original use of the plastic piece per sampling point (b); and size (c).

overnight to reach a metal adsorption equilibrium before analysis, following previous studies from Turner and Holmes (2015). The levels of the spikes shown in Table 2 and Section S1 fit concentrations from reports for field samples in this geographical region (Kutralam-Muniasamy et al., 2021). Table S5, Supplementary Information, depicts the absorbance for the procedural blanks (as defined above) and the net signals for 1 mg L^{-1} calibration standards, as well as their recoveries. It was hypothesized that the higher values for the blanks associated to Zn might be due to its presence in the plastics (despite the provider claimed they were 'metal free', it might had been included in some additive). This seems supported by the fact that the blanks yielded very low signals (Fig. S3). To validate the metal analyses several studies were done. First, precision was evaluated as repeatability (within day, single laboratory) and reported as relative standard deviation, RSD. Analytical recoveries were assessed considering six replicates of five-metal spikes (see details in section S1, Supplementary Information), at three concentration levels (see Table S6). Further, before measuring each batch of samples, a procedural blank and the slope of the batch-related calibration lines were compared against historical ranges so that obvious biases can be discarded (see section S1, Supplementary Information, for details).

CRM for Trace Metals 1-WS (metals in solution, QC1488, from Sigma-Aldrich) was used to verify the whole procedure (including instrumental conditions and the digestion step, although the plastic matrix was not present). The experimental concentrations for all metals were in good agreement with the certified ones.

2.5. Statistical treatment

Calibrations are a cornerstone of the analytical methodology and they were studied carefully. Duplicated five-points calibrations (plus a reagents blank) were done and regression statistics evaluated (see Sections S1 and S2, Supplementary Information and Fig. S3) following international guidelines (Eurachem and Barwick, 2019; Eurolab España, 2016). ANOVA was used to study their statistical significance. Residual plots were evaluated and the working linear range assessed using traditional criteria (Kateman and Pijpers, 1981). The statistical significance of the intercept was assessed by means of a Student's *t*-test. Further, different ways of calculating the LOD and LOQ were compared, namely: the classical (IUPAC) (Eurolab España, 2016; Long and Winefordner, 1983), the ISO/IUPAC/EU updated definitions (Commission Implementing Regulation, 2021; ISO, 2019; IUPAC, 2014), and a simplification posed by Eurachem. Note that the updated definitions are of most relevance because they take account of the false negative and false positive errors (Andrade-Garda and Gómez-Carracedo, 2017). Technical details and equations to perform calculations can be found in section S2 of the Supplementary Information.

The Shapiro-Wilk's test was used to determine whether the concentration of a metal throughout all the collected items in a sampling location followed a normal distribution, and the p-value for all metals was <0.05, revealing distributions not compatible with normality. Therefore, non parametric tests were employed to compare the concentrations of the metals throughout the 9 categories of plastics (according to their intended use). In particular, the U Mann-Whitney's test was used to compare two categories; the Kruskal-Wallis' test is an extension of the former for situations involving more than two groups (Fiel Peres, 2026); further, multiple pairwise comparisons were done. The p-values were adjusted using the Bonferroni correction (see Table S7, Supplementary Information). In addition, to take account of the different (and reduced) number of values in some categories the size effect in the U Mann-Whitney's test was considered by means of the Cliff's delta (Fiel Peres, 2026).

Finally, to get a general overview of the samples and to evaluate their distribution and potential similarities in accordance to their metallic contents a traditional multivariate unsupervised exploratory tool –principal component analysis, PCA-was applied. PCA will identify relationships between metals and polymers and how they determine the patterns of the sampling sites. The raw data were columwise autoscaled to take account of the different scales of the variables (concentration of the metals and polymer abundance –measured as number of items of a polymer in a site, given as %). Varimax rotation was applied to maximize the interpretability of the principal components that explain most of the sample variance (Klöckner et al., 2021). To account for the presence of <LOD experimental values (which occurred mainly for Cd) random values around them were imputed (Gómez-Carracedo et al., 2014; Lee et al., 2021). The LODs considered there corresponded to those calculated using the classical IUPAC approach in order to facilitate comparability with other works as they are used still by most researchers. The output of a PCA consists of loadings (coefficients of the principal components) that define to which extent the metals and the polymers participate in the principal components and show their internal relationships, and scores (which define the position of the sampling sites in the principal components subspace and, therefore, allow visualization of their closeness or patterns).

All statistical studies were done using Excel spreadsheets and SPSS (v. 25.0, IBMCorp., 2017; USA).

3. Results and discussion

3.1. Classification of litter

The sampled areas of the Bay of Asunción exhibited 0.4 to 2.0 items of litter m^{-2}; with sample locations # 4 and # 2 showing the lowest and the highest values, respectively (Table 1). These quantities are smaller than those reported for Isla Arena (Colombia), where 2.87 items of litter m^{-2} were found (Rangel-Buitrago et al., 2019), and similar to those from beaches of Samar, Philippines (0.12 – 2.24 items m^{-2}, Lagumbay et al., 2025).

The most abundant type of litter corresponded to plastics, from 60 to 82% of the total counted items. This finding is comparable to reports from other researchers who reported from 70.4% (in rivers of Sardinia, Italy, Palmas et al., 2022), to 88.6% (Colombian Caribbean sea, Rangel-Buitrago et al., 2019) and 93.5% (Nederrijn River, Netherlands, Van Emmerik et al., 2020) of plastic waste. Further, the abundance of plastics (0.3 to 1.2 items m^{-2}) was lower than those reported by Pinto et al. (2024), 2.3 to 17.5 items m^{-2} on the riverbank of Odaw, Ghana; Andrade-Garda and Gómez-Carracedo (2017) for beaches of Malta, 53.9 ± 4.3 items m^{-2} in Golden Bay and 29.7 ± 4.0 items m^{-2} in Rivera Beach.

It is worth noting that certain types of plastic were not found at all locations; for instance, only a film was collected in P1, and hard cleaning wrappers were only found in P2. In contrast, bags, hard and soft food

Table 1
Classification of the litter found at the four sampling locations along the coastline of the Bay of Asunción. P = Plastic; Me = Metal; R = Rubber; C/G = Ceramic/Glass; NM = natural materials; M = Miscellaneous (wood/paper/cardboard).

Sampling site (area, m^2)	P	Me	R	C/G	NM	M	Total items of litter per site	Items of litter m^{-2}
1 (300)	343 (77%)	3 (1%)	6 (1%)	18 (4%)	19 (4%)	59 (13%)	448	1.5
2 (300)	365 (60%)	22 (4%)	25 (4%)	32 (5%)	12 (2%)	150 (25%)	606	2.0
3 (120)	77 (79%)	3 (3%)	1 (1%)	8 (8%)	3 (3%)	5 (5%)	97	0.8
4 (120)	36 (82%)	3 (7%)	0 (0%)	0 (0%)	3 (7%)	2 (5%)	44	0.4

Table 2
Performance parameters obtained for the metals studied in this work (n = 6). Sensitivity calculated as the average of the slope of four calibration lines. CC_α = critical value; CC_β=Capability of detection; LOD = Classical limit of detection; LOQ = classical limit of quantification; repeatability, calculated as relative standard deviation (RSD_r), see text for details, (uA = absorbance units). Additional details can be found in Table S5 and Table S6 (Supporting Information). Four significant figures are given for the performance characteristics.

Metal	Linear range mg L^{-1}	Sensitivity uA/mg L^{-1}	Spiked Concentrations µg g^{-1}	Repeatability	Overall Recovery (%)			
				RSD_r,%	min	max	$\overline{X}$	SD
Fe	1 – 25	0.0301	300, 800, 2500	8.9	100	121	110	8
Mn	0.05 – 2.0	0.1181	20, 100, 800	1.1	68	110	90	10
Cu	0.1 – 1.0	0.1388	12, 40, 200	2.7	84	120	96	11
Zn	0.01 – 1.0	0.4159	40, 100, 250	2.0	91	107	101	4
Cd	0.005 – 0.1	0.4060	2.5, 4, 7.5	2.4	84	120	96	11

Metal (µg g^{-1})	Modern definitions			Classical definitions			
				Using intercept		Using blanks	
	CC_α	CC_β	LOQ (IUPAC)	LOD	LOQ	LOD	LOQ
Fe	780.8	1442	3047	709.0	1936	8.947	29.82
Mn	14.95	27.60	61.03	12.49	35.93	1.597	5.323
Cu	6.822	12.60	27.65	7.990	19.89	0.8956	2.985
Zn	4.585	8.468	19.14	0.656	6.803	5.045	16.82
Cd	1.231	2.272	4.888	0.390	2.422	0.3224	1.075

wrappers, and toys were present at all four locations. Other items, such as bottles, styrofoam, and soft cleaning wrappers were found at three locations, while cups, soft food wrappers, and bottle caps, were identified at two locations (see details in Table S3, Supplementary Information). A reflection on the 'accuracy' of environmental inventories in general is in order here as their results depend on many factors, including sampling season, extent of the sampled surface, litter accumulation in some places of the water bodies (due to ship traffic, waves, wind, etc.; Harris et al., 2021; Schwarz et al., 2019), etc. No doubt, the inventories reflect what was found in the sites, so they are correct in absolute terms. Whether the number of items per sampled surface represent the environmental situation of the whole water body is an insidious question and alternatives are not obvious at all. Hence, following general practice in scientific literature, the philosophy of the EU precautionary principle, and for the sake of environmental protection, we think that reporting number of items of litter per surface can be accepted, even though that area may be a hotspot. This would, likely, correspond to a worst-case scenario and foster environmental prevention.

In total, 468 plastic litter fragments were classified according to their intended original use and size. It was seen that food wrappers accounted for the major percentage of items (29%), Fig. 2a, similar to reports from Canada (27%) (Barone et al., 2025). Noteworthy, if cleaning wrappers (7%) are added to this result, the total amount of wrappers is higher than that reported by Munier and Bendell (2018), who found that plastic packaging accounted for 22% of litter (mostly personnel hygiene items and food packaging). Note that in the present study wrappers from either personal hygiene items (like soap packaging), and home cleaning products (like detergent and laundry soap packaging) were included in the category of cleaning wrappers. The quantity of wrapper litter requires special attention as it currently accounts for 53% of single-use plastics (Barone et al., 2025).

On the other hand, if the percentage of plastic cups (11%) is added to food wrappers, the overall quantity is higher than that reported by Munier and Bendell (2018), 21% in the food-associated category. Anyway, it is worth noting that plastics associated with typical wrappers and food commodities are predominantly found in coastal rivers.

In the present study, the predominant collected plastic litter size ranged 20 - 30 cm (sampling points # 1 and # 4), while at point # 2 smaller plastics (2.5 to 10 cm, with many bottle caps) were more abundant (see Fig. 2b and c), similar to what was found in Morocco (Nachite et al., 2019). It is worth noting that even though sampling sites # 1 and # 2 are relatively distant from the coastline, 1-1.2 km; and, so, from the urban area with the highest anthropogenic impact, they presented not only the largest amount of total litter (see Table 1) but relevant quantities of large-to-medium plastics (roughly 74 and 40%, respectively; see Fig. 2c). This might be a consequence of an intense drought that led to a general affection of the Plata River basin (DINAC, 2023).

3.2. Classification of plastics according to polymer type

In total, 234 meso- and macroplastics (50% of the total collected items, see Fig. S2) were analyzed by ATR-FTIR spectrometry and categorized as PE, PP, PS, PET, PVC and PMMA. Noteworthy, some fragments were found to consist of several adjacent layers that could be separated and characterized individually. This is exemplified in Fig. S4, where PP was identified in the outer parts of a mesoplastic piece, while PE was found in the middle.

Up to 73% of the plastic fragments analyzed were either PP (42%) or PE (31%) (Fig. 3a, Table S4). This happened also when studying microplastics in the Bay of Asunción and its freshwater tributaries (Diez-Pérez et al., 2023) where the most common polymers were PP (40.2%) and PE (38.0%). This fact suggests that the main source of microplastics in the Bay can be the meso- and macroplastics that fragment in the freshwater and coastal river environments. This agrees also with the worldwide production and consumption of polymers, being PP (19%), PE (26%) and PVC (13%) the outstanding worldwide players (PlasticsEurope, 2024).

Fig. 3b and Table S4 show that PP was present mostly in food wrappers (hard 28.9%, soft 13.4%), toys (13.4%), cups (11.3%), films (10.3%), and bottle caps (9.3%) whereas PE was identified in bags (39.7%), soft wrappers (food: 21.9%, cleaning-related items: 13.7%), bottle caps (9.6%), and hard wrappers (cleaning: 8.2%, food: 2.7%).

Comparing with other studies, soft PE and PP (bags, foils) were the main plastics identified in the Meuse, Waal and Nederrijn rivers (Netherlands) (Van Emmerik et al., 2020). Despite in Paraguay, since 2015, a law limits the consumption of single-use polyethylene bags (Ley No 5414, 2015) many bags were found thrown away in the aquatic system of the Bay of Asunción. A possibility to reduce their environmental impact may be to substitute them by biobased and biodegradable compostable bags of PLA (polylactic acid), PBAT (poly (butylene adipate-co-terephthalate), or PCL (poly-caprolactone), although these biopolymers may be more susceptible to aging and can also adsorb metals (Shi et al., 2023). At present, the Ministry of Industry and Commerce of Paraguay established that businesses such as supermarkets and general stores must offer biodegradable packaging alternatives as a way to reduce the plastic impact on the national and international

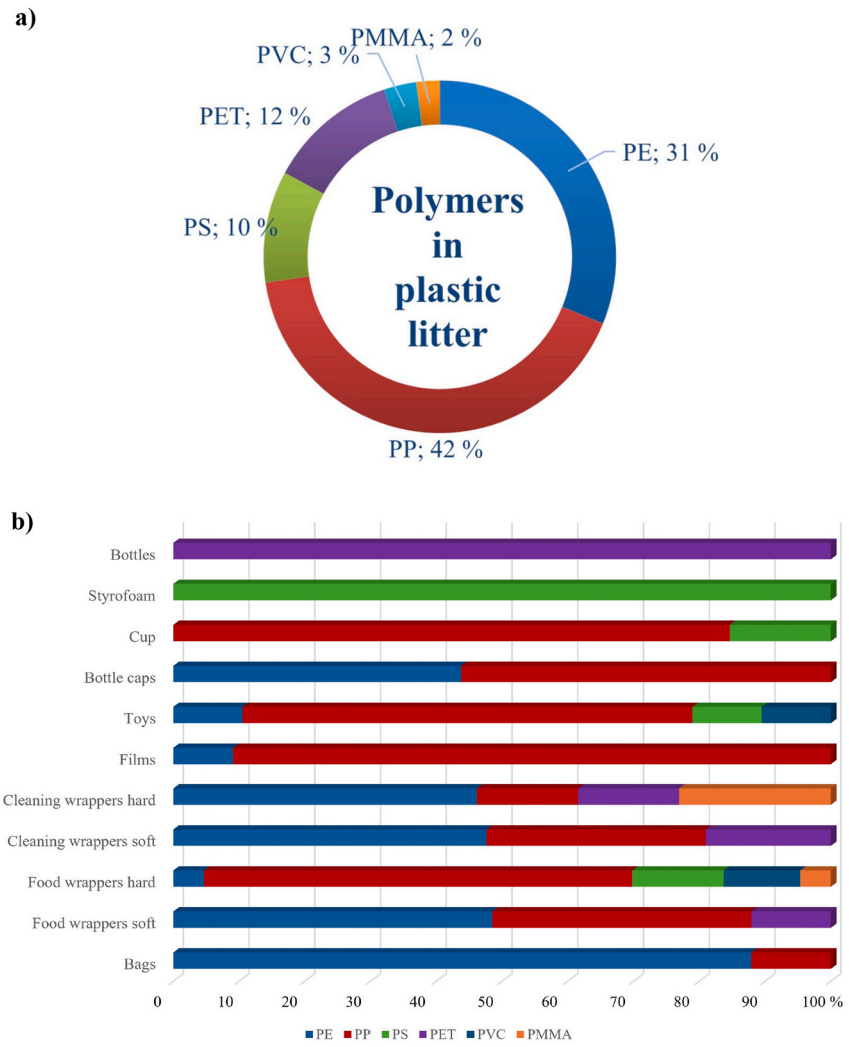

Fig. 3. Polymers identified in plastic litter found in the Bay of Asunción: percentage calculated based on 234 identified polymers (a); percentage of polymers when litter was classified per intended original use (b).

environment(Resolución No 757, 2024). It would be of most interest to repeat the present study in the future to evaluate whether legislation reduced plastics in the Bay.

The remaining 27% of the plastic pieces found in the Bay of Asunción were PET (12%, with 64.3% present in bottles and 35.7% in wrappers), PS (10%, with 58.3% as Styrofoam, 25% of food wrappers, 8.33% of cups, and 8.33% of toys, Tables S3 and S4). PMMA was found only in wrappers (cleaning: 60%, food: 40%) especially as a cover of the packaging labels (Fig. S5), whereas PVC was found in food wrappers (71.4%) and toys (28.6%), see Fig. 3b and Table S4. The percentage of PVC items (3%) was lower than that reported by Munier and Bendell (2018), although they did not specify the origin of this polymer. On the contrary, the value found here was higher than that reported by Asensio-Montesinos et al. (2020), who found 0.3% of PVC, mostly associated with pieces of hard plastic and hard films.

3.3. Analysis of metals in the plastic litter

3.3.1. Analytical performance parameters

The main performance parameters of the analytical methodology described in section 2.4 are shown in Table 2. Precision (measured as repeatability) was satisfactory, with relative standard deviations <10% for all metals. Recoveries calculated at three levels through the calibration working ranges (see Table 2, Table S5 and Table S6) were in good agreement with some previous reports (Ottander, 2022; Hildebrandt et al., 2020), as it happened for the linear ranges and sensitivities (Lee et al., 2021; Nakashima et al., 2012).

The detection and quantitation limits (Table 2) were higher than those obtained for MS-ICP and AAS-graphite furnace, as expected because of their higher sensitivity (a comparison is shown in Table S8, Supplementary Information). Nevertheless, they are adequate to measure field samples, considering previous reports (Duarte et al., 2010; Kutralam-Muniasamy et al., 2021; Martins et al., 2020; Munari et al., 2021; Vedolin et al., 2017). More details are given in Section S3, Supplementary Information.

As expected, CC_β (modern 'LOD') values are higher than LODs calculated by the classical procedure and this is relevant for those involved in reporting data for policy makers, due to EU legislation (Commission Decision/657/CE, 2002; Commission Implementing Regulation, 2021; Hildebrandt et al., 2020; Maršić-Lučić et al., 2018). Extended discussions are given in section S3 of the Supplementary Information.

3.3.2. Concentration of metals in plastic litter

In general, the metal concentrations varied quite markedly among the samples (Table 3), as expected. As a matter of example, the highest total metal concentrations were for Fe (3526 μg g^{-1}) and Mn (1163 μg g^{-1}), followed by Zn (330.2 μg g^{-1}), Cu (94.92 μg g^{-1}), and Cd

Table 3
Metal concentrations (μg g^{-1}) considering the category of 'intended original use' of the plastic fragments (Mean ± Standard Deviation). LOQ (Mn: 5.32; Cu: 2.98; Cd: 1.08) calculated using the classical IUPAC definition.

Category (n[a])	Fe	Mn	Zn	Cu	Cd
Bags (33)	1524 ± 1016	209.5 ± 246.7	70.99 ± 18.50	21.13 ± 13.56	< LOQ
Bottles (18)	76.25 ± 43.31	< LOQ	25.38 ± 31.63	6.310 ± 8.373	< LOQ
Food wrappers (76)	352.6 ± 267.5	26.22 ± 37.96	96.88 ± 107.0[b]	14.28 ± 9.685	3.538 ± 5.661
Films (11)	827.0 ± 130.0	15.50 ± 0.8485	134.2 ± 52.11	< LOQ	< LOQ
Toys (13)[d]	751.1 ± 284.6	30.50 ± 16.27	96.05 ± 74.42	7.422 ± 12.11	< LOQ
Styrofoam (14)	1835 ± 1095	397.8 ± 569.9[b]	115.0 ± 45.48	6.680 ± 8.997	< LOQ
Cleaning wrappers (32)[d]	369.0 ± 158.6	7.962 ± 11.81[b]	65.05 ± 34.52	40.07 ± 36.63	< LOQ
Bottle caps (16)	1055 ± 112.4	34.90 ± 27.77	73.58 ± 16.79	10.94 ± 11.61	< LOQ
Cups (13)	511.1 ± 97.00	< LOQ	24.62 ± 24.08	< LOQ	< LOQ
Overall mean ± SD	744.9 ± 746.8	80.59 ± 221.7	79.20 ± 69.50	14.58 ± 19.08	1.300 ± 3.122
Range found in South America([c])	n/s	0.3 – 9	0.3 – 8	0.2 – 1	< 0.22

[a] Number of items employed to get the grinded sample where from aliquots were drawn for analysis.
[b] Statistical significant difference between sampling points (Kruskal-Wallis, $p < 0.05$). Detailed statistical comparisons among plastics classified by their original use can be seen in Table S6, Supplementary Information.
[c] As reported by Kutralam-Muniasamy et al. (2021) for different types of microplastics, n/s: not specified.
[d] Table S4, Supplementary Information, reports more items for these categories because some fragments were composed of several layers (see Figure S4).

(18.72 μg g^{-1}) –see Fig. S6, Supplementary Information. Likewise, the highest average concentration was for Fe (744.9 ± 746.8 μg g^{-1}) whereas the lowest average was for Cd (1.300 ± 3.122 μg g^{-1}). For all metals, significant differences (Kruskal-Wallis, $p < 0.05$) were observed between plastics classified by their original use (Table S9). Besides, Dunn-Bonferroni's tests demonstrated significant pairwise differences (Table S7) among various metals and categories. The variability in metal concentrations may proceed from various factors, including type of polymer and its usage, the production process, environmental exposure and aging, among others (Awe et al., 2025).

The average metal concentrations per category of original use revealed (Table 3) that Fe was high in PS (Styrofoam): 1835 ± 1095 μg g^{-1}. The highest concentration occurred at sampling point #3 (Fig. S6a), although it was not statistically different from the other sampling points (Kruskal-Wallis, $p = 0.102$), likely due to the large standard deviations. As Styrofoam consists of 100% PS it seems quite likely that Fe got adsorbed preferentially in this plastic, although its concentrations might not be solely due to the medium from which the samples were collected. Indeed, Fred-Ahmadu et al. (2022) reported that foam plastic had the highest accumulation ratios of Al, As, Cd, Cr, Cu, Fe, and Mn. Taking into account the adsorption capacity of Fe reported for plastics elsewhere (PS > PP > PE > PET) (Liu et al., 2021), that order was observed also in our study here. For instance, the average concentration of Fe for the three sampling locations in PET was almost twenty-five times smaller (76.25 ± 43.31 μg g^{-1}) than the corresponding one in PS (1835 ± 1095 μg g^{-1}), a statistically significant difference (U-Mann Whitney, $p < 0.05$, $U = 0.000$, $\delta = 1$), with an extremely large size effect (denoted by the Cliff's delta); further, all values for Styrofoam are greater than those for the bottles.

As it happened for Fe, Mn presented its highest concentration in plastic fragments classified as PS (1.133 ± 41.88 μg g^{-1}) at sampling point #3 (Fig. S6b). The levels found at the other sampling points (P1 = 23.91 ± 5.042 μg g^{-1}; P2 = 36.39 ± 6.674 μg g^{-1}) became different (Kruskal-Wallis, $p < 0.05$). Similarly, the cleaning wrappers category presented significant differences for Mn among the sampling sites (Table 3, Kruskal-Wallis, $p < 0.05$). The results obtained at the Bay of Asunción are similar to those reported for China (microplastics collected in beach sand from the Pearl River estuary, 730 ± 797 μg g^{-1}, with predominance of PS, PE and PP) and the Persian Gulf (with concentrations around 32.2 ± 12.4 μg g^{-1}, Liu et al., 2021), despite the ranges under consideration were broad. Similarly, Jachimowicz et al. (2024) reported concentration of 309.0 μg g^{-1} in Golden Bay and 63.1 μg g^{-1} in Rivera Beach, two beaches in Malta.

Regarding Zn, its concentrations were highly variable throughout the various categories of original use and the sampling locations, as observed in Fig. S6c. The category for which significant difference among the sampling points was found corresponded to food wrappers (Table 3, Kruskal-Wallis, $p < 0.05$). For plastic bottles collected at sampling points #1 and #2 the concentrations were <LOQ (16.82 μg g^{-1}), while at sampling point #3 the average concentration was 66.2 ± 4.0 μg g^{-1}. With respect to bags, it was observed that the concentrations of Zn in the sampling locations were very close, P1 = 97.70 ± 5.501 μg g^{-1}; P2 = 69.00 ± 14.40 μg g^{-1}; P3 = 56.05 ± 3.606 μg g^{-1}; P4 = 61.21 ± 8.491 μg g^{-1} (Kruskal Wallis, $p = 0.139$). Nhanga et al. (2025) reported higher Zn concentration in bags, which even exceeded the permissible limits established for plastic supermarket bags. Meanwhile, a hypothesis that might explain the similar contents of Zn in the plastics is its use as a heat stabilizer, flame retardant and smoke suppressor (ECHA, 2024; Jachimowicz et al., 2024; Liu et al., 2021) –see Table S10 (Supplementary Information). Therefore, its concentrations might not be solely due to adsorption from the medium from which the samples were collected (note that in sites #2, #3 and #4 up to 100% of the bags were made of PE, Table S3).

With respect to Cu (Table 3, Fig. S6d), the metal was detected in 55% of the samples, which is comparable to 54% reported by Awe et al. (2025). The highest concentrations were found for cleaning wrappers (40.07 ± 36.63 μg g^{-1}), without statistically significant differences between the sampling points (Kruskal-Wallis, $p = 0.05$). This level is similar to reports from Woodbridge beach, South Africa, 33.04 μg g^{-1} (Awe et al., 2025). The concentrations of Cu in our samples were very similar, 14.58 ± 19.08 μg g^{-1}. As for Zn, the similarity on the levels might be caused by its use in plastic pigments (see Table S10) (Charvat and Road, 2004; ECHA, 2024). Cu was found in most colored plastics collected at sampling point #2, including blue bottles (PET). However, adsorption is a complex process regulated by many factors (pH, salinity, temperature, desorption, etc.) that we could not evaluate in this work.

Cd presented the overall lowest concentrations when compared to the other metals (Table 3, Fig. S6e). In seven out of nine categories of intended original use concentrations were <LOQ (1.075 μg g^{-1}). The highest concentration was 3.538 ± 5.661 μg g^{-1} in food wrappers (P1: < LOQ; P2: 8.559 ± 9.623 μg g^{-1}; P3: 1.245 ± 0.1 μg g^{-1}; P4: 4.069 ± 3.633 μg g^{-1}). It is worth noting that although some Cd compounds may be added to the polymers to yield plastics with high heat resistance and stabilize PVC (ECHA, 2024), they are of low commercial value for food-related uses due to the toxicity of this metal (Awe et al., 2025; Charvat and Road, 2004).

When comparing our results with reports from other countries, lower concentrations of Cd have been found there (Liu et al., 2021; Rodrigues et al., 2023). Hence, it appears that this metal requires special attention in our region in order to evaluate working hypotheses and associate it to either the environment where the plastics are (and, so, it would became adsorbed after their improper disposal) or to the plastics themselves (as

per fabrication), especially considering that it presented the highest concentrations on food wrappings. Besides, more sensitive analytical techniques would also need to be applied to ascertain this issue. Right now, the total levels measured in this study do not allow us to draw sound conclusions.

3.4. Multivariate analysis of the samples

The scores and loadings of the PCA study were studied (Table 4 and Fig. 4). Three PCs were considered as they explained 56.3% of the variance (PC1: 22.6%, PC2: 19.5%, and PC3: 14.2%). Recall that some < LOD values for Cd were imputed, as indicated in section 2.5.

The first factor is defined mostly by PS and Fe and Mn, with positive correlation. Those two metals are very frequently associated as they are main components of the soils and might be attributed to a natural origin. This finding is coherent with the results and discussions presented in the previous section. PS is a very porous plastic and, so, its correlation with Fe and Mn can be attributed to the interaction between those abundant metals and biofilms (Liu et al., 2021; Stabnikova et al., 2022) and/or the PS porous surface. Our working conditions were similar to those reported in the referred papers and these are potential reasons for the observed relations; however, they could not be addressed fully in this study. The scores plot (Fig. 4) reveals that sampling point #3 outstands in PC1 because the sample aliquots labelled as 59, 60, 61 and 62 contain the highest overall concentrations of these two metals and 100% of the plastic fragments were identified as PS. In Fig. S7 the macroscopic characteristics of three samples of Styrofoam collected at sample point #3 can be seen.

PC2 is clearly linked to PVC, PMMA and Zn. Opposed to Fe and Mn (for which a natural origin is mostly considered), Zn and Cu may be present in the polymers as typical additives, primarily associated to pigments (as noted in Table S10) (ECHA, 2024). Further, they can be considered also as road traffic tracers (Järlskog et al., 2021). Besides, it is well-known that PVC contains many additives usually (Campisi et al., 2025; Santos et al., 2023; Vikhareva et al., 2021). Interestingly, the two sample aliquots with the highest numbers of PVC and PMMA fragments (coming from food wrappers) show also very high Zn contents (although not the overall maxima) and, so, they outstand in PC2, they are numbered as 5 and 8 in Fig. 4.

Regarding PC3, it is clearly associated to PP and to Cd. This metal is a rather typical tracer for road traffic (Järlskog et al., 2021) and might be an indication of anthropogenic inputs to the area. However, as explained in section 3.3 above, it is also a typical metal contained in pigments used to colour plastics. Therefore, both situations can be occurring here. Two sample aliquots get very high scores, and they are associated to sampling point # 2, which is not too close to the buildings and roads (samples labelled as 7 and 9, Fig. 4). They have the overall maximum values of Cd but also a mixture of PP, PE and PS (ca. 67% of the plastic items were identified as PP). As stated above additional studies are needed to ascertain its origin in more detail.

Table 4
Loadings of the Varimax-rotated principal components and amount of explained variance.

Rotated factors	PC1	PC2	PC3
Explained variance	22.6%	19.5%	14.2%
PE	0.10	−0.15	−0.45
PP	−0.16	0.09	0.89
PS	0.63	0.13	0.01
PET	−0.48	−0.37	−0.45
PVC	−0.16	0.80	0.01
PMMA	−0.16	0.81	−0.24
Fe	0.93	−0.09	−0.13
Mn	0.86	−0.09	−0.17
Cu	−0.15	−0.10	0.05
Zn	0.30	0.67	0.19
Cd	−0.06	−0.15	0.58

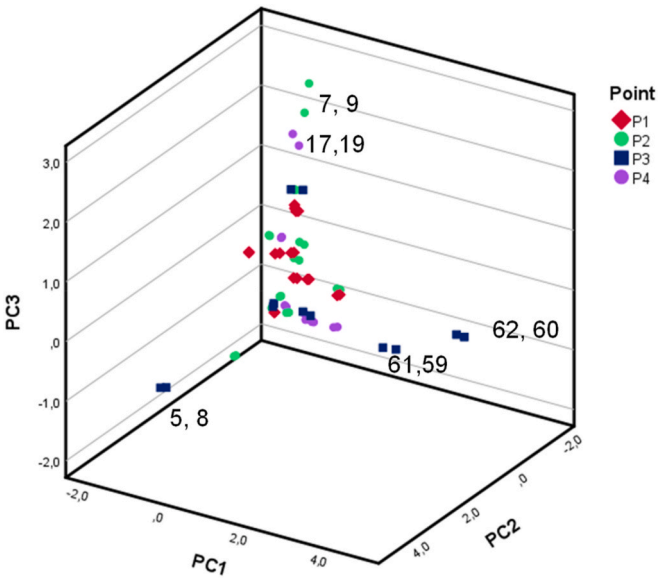

Fig. 4. Scoreplot obtained for the sampling sites on the Varimax-rotated PC1-PC2-PC3 subspace. The labels displayed in the plot correspond to the serial number of the sample aliquots discussed into the text.

4. Conclusions

Out of the overall litter items identified at the Bay of Asunción (Paraguay) plastics accounted for the majority of them (60 to 82% of the total items), particularly food and cleaning wrappers (36% of the plastic items), including soft food wrappers (for example, rice and cookies packaging), hard food wrappers (like yogurt cups), personal hygiene items (like soap packaging) and home cleaning products (like detergent and laundry soap packaging).

The main types of plastics identified by ATR-FTIR were PP (42%), PE (31%), PET (12%), PS (10%), PVC (3%), and PMMA (2%). The first four accounting for ca. 95% of the plastic items.

The macroplastic litter retrieved for further anaysis was mainly in the size range from 2.5 to 30 cm, with relevant quantities of large-to-medium plastics, constituting approximately 40 to 85% of the plastic items. The metals studied in this work (Cd, Cu, Fe, Mn and Zn) were found in diverse concentrations depending on the sampling points, the assumed original use of the plastic item, and the type of polymer. In particular, when the sampling sites are considered, differences were found for Mn in Styrofoam and cleaning wrappers and for Zn in food wrappers; regarding the categories, differences were observed for example for cups and bottles across four categories, depending on the metal under study. The concentrations of Fe and Mn were higher than those of the other studied metals, likely due to a natural crustal origin. The overall order for the metallic concentrations was Fe > Mn > Zn > Cu > Cd. Regarding the association of these metals with the polymers, the strongest relationship was observed between Fe, Mn and PS; presumably as the result of adsorption in porous PS. Zn was associated mostly with PVC and PMMA; and Cd with PP. In this study total metals were analyzed but additional studies are required to differentiate between inherent (to the plastics) and adsorbed metals, and being able to address outstanding questions that remain open, like evaluating the possible origin of adsorbed metals. This, will likely require the use of different digestion acid media to extract total and adsorbed metals from polymers.

CRediT authorship contribution statement

Diana Diez-Pérez Núñez: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources,

Validation, Writing – original draft, Writing – review & editing. **Deyanira Peralta:** Formal analysis, Investigation, Writing – original draft. **Dahiana Serafini:** Formal analysis, Investigation, Writing – original draft. **Derlysa Colmán:** Formal analysis, Investigation, Resources, Writing – original draft. **José M. Andrade:** Conceptualization, Formal analysis, Investigation, Validation, Writing – original draft, Writing – review & editing. **Adrián López-Rosales:** Conceptualization, Formal analysis, Investigation, Writing – original draft. **Soledad Muniategui-Lorenzo:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The work was supported by the National University of Asuncion (UNA) from Paraguay (project N° FCQ/09/2022), and the National Incentive Program for Researchers of Paraguay (PRONII, in its Spanish initials) from the National Council of Science and Technology (CONACYT). The Program 'Consolidación e Estructuración de Unidades de Investigación Competitivas' of the Galician Government, Spain (Xunta de Galicia) is also acknowledged (Grant ED431C-2025/57). Funding for open access charge: Universidade da Coruña/CISUG.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2026.125428.

Data availability

Data will be made available on request.

References

Andrade-Garda, J.M., Gómez-Carracedo, M.P., 2017. Basic data analysis. Problems of Instrumental Analytical Chemistry. A Hads-On Guide, pp. 43–108. A Coruña.

Asensio-Montesinos, F., Anfuso, G., Williams, A.T., Sanz-Lázaro, C., 2021. Litter behaviour on Mediterranean cobble beaches, SE Spain. Mar. Pollut. Bull. 173. https://doi.org/10.1016/j.marpolbul.2021.113106.

Asensio-Montesinos, F., Oliva Ramírez, M., González-Leal, J.M., Carrizo, D., Anfuso, G., 2020. Characterization of plastic beach litter by Raman spectroscopy in Southwestern Spain. Sci. Total Environ. 744, 140890. https://doi.org/10.1016/j.scitotenv.2020.140890.

ASTM, 2021. E1421-99: ASTM standard practice for describing and measuring performance of fourier transform Mid-Infrared (FT-MIR) spectrometers: level zero and level one tests. https://www.astm.org/e1421-99r21.html.

Awe, A., Oputu, O., Aigbe, U.O., Sparks, C., 2025. Metals associated with Beach plastic litter at Woodbridge Island and Derdesteen in Table Bay, South Africa. Microplastics and Nanoplastics 5 (1). https://doi.org/10.1186/s43591-025-00117-w.

Barone, A.S., Maragoni-Santos, C., Farias, P. M. de, Cortat, C.M.G., Maniglia, B.C., Ongaratto, R.S., Ferreira, S., Fai, A.E.C., 2025. Rethinking single-use plastics: innovations, polices, consumer awareness and market shaping biodegradable solutions in the packaging industry. Trends Food Sci. Technol. 158, 104906. https://doi.org/10.1016/j.tifs.2025.104906.

Blettler, M.C.M., Ulla, M.A., Rabuffetti, A.P., Garello, N., 2017. Plastic pollution in freshwater ecosystems: macro-, meso-, and microplastic debris in a floodplain lake. Environ. Monit. Assess. 189, 581. https://doi.org/10.1007/s10661-017-6305-8.

Campisi, L., La Motta, C., Napierska, D., 2025. Polyvinyl chloride (PVC), its additives, microplastic and human health: unresolved and emerging issues. Sci. Total Environ. 960, 178276. https://doi.org/10.1016/j.scitotenv.2024.178276.

Canese de Estigarribia, M.I., Vuyk, C., Sagüi, N., Ibarra, G., Marcelino, R., Velázquez, N., Villalba, G., Laterra, D., Chamorro, J., Godoy, P., Duré, V., 2019. Urbanización popular en la ciudad de Asunción, Paraguay. Rev. INVI 34 (95), 9–42. https://doi.org/10.4067/S0718-83582019000100009.

Cera, A., Cesarini, G., Scalici, M., 2020. Microplastics in freshwater: what is the news from the world? Diversity 12 (7). https://doi.org/10.3390/d12070276.

Charvat, R.A., Road, B., 2004. Introduction to Colorants. Coloring of Plastics. Fundamentals. United State of America, pp. 85–99.

Commission Decision/657/CE, 2002. Commission Decision, of 12 August 2002, implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Official Journal L 221, 17/08/2002. http://data.europa.eu/eli/dec/2002/657/oj.

Commission Implementing Regulation (EU), 2021. Commission Implementing Regulation (EU) 2021/810 of 20 May 2021 amending Implementing Regulation (EU) 2021/2021/808 as regards transitional provisions for certain substances listed in Annex II to decision 2002/657/EC. Off. J. Eur. Union.

Correa-Araneda, F., Pérez, J., Tonin, A.M., Esse, C., Boyero, L., Díaz, E., Figueroa, R., Santander-Massa, R., Cornejo, A., Link, O., Jorquera, E., Urbina, M.A., 2022. Microplastic concentration, distribution and dynamics along one of the largest Mediterranean-climate rivers: a whole watershed approach. Environ. Res. 209, 112808. https://doi.org/10.1016/j.envres.2022.112808.

Diez-Pérez, D.B., Arenas, I., Maidana, E., López-Rosales, A., Andrade, J.M., Muniategui-Lorenzo, S., 2023. Microplastics in surface water of the Bay of Asunción, Paraguay. Mar. Pollut. Bull. 192, 115075. https://doi.org/10.1016/j.marpolbul.2023.115075.

DINAC, 2023. Anuario hidrológico 2022. https://www.meteorologia.gov.py/wp-content/uploads/2023/05/ANUARIO-_HIDRO7_2023_V2.pdf. (Accessed 13 August 2025).

Duarte, A.T., Dessuy, M.B., Silva, M.M., Vale, M.G.R., Welz, B., 2010. Determination of cadmium and lead in plastic material from waste electronic equipment using solid sampling graphite furnace atomic absorption spectrometry. Microchem. J. 96 (1), 102–107. https://doi.org/10.1016/j.microc.2010.02.008.

ECHA, 2024. Mapping exercise - plastic additives initiative. https://echa.europa.eu/plastic-additives-initiative. (Accessed 7 August 2024).

Eurachem, 2019. In: Barwick, V. (Ed.), Planning and Reporting Method Validation Studies - Supplement to Eurachem Guide on the Fitness for Purpose of Analytical Methods, 1o. www.eurachem.org. (Accessed 14 June 2020).

Eurolab España, 2016. Guía Eurachem: La adecuación al uso de los métodos analíticos – una Guía de laboratorio para la validación de métodos y temas relacionados (1°). www.eurachem.org. (Accessed 14 June 2020).

Fiel Peres, F., 2026. Effect sizes for nonparametric tests. Biochem. Med. 36 (1), 010101. https://doi.org/10.11613/BM.2026.010101.

Fred-Ahmadu, O.H., Ayejuyo, O.O., Tenebe, I.T., Benson, N.U., 2022. Occurrence and distribution of micro(meso)plastic-sorbed heavy metals and metalloids in sediments, Gulf of Guinea coast (SE Atlantic). Sci. Total Environ. 813, 152650. https://doi.org/10.1016/j.scitotenv.2021.152650.

Gómez-Carracedo, M.P., Andrade, J.M., López-Mahía, P., Muniategui, S., Prada, D., 2014. A practical comparison of single and multiple imputation methods to handle complex missing data in air quality datasets. Chemometr. Intell. Lab. Syst. 134, 23–33. https://doi.org/10.1016/j.chemolab.2014.02.007.

Harris, P.T., Westerveld, L., Nyberg, B., Maes, T., Macmillan-Lawler, M., Appelquist, L.R., 2021. Exposure of coastal environments to river-sourced plastic pollution. Sci. Total Environ. 769. https://doi.org/10.1016/j.scitotenv.2021.145222.

Hayes, A., Kirkbride, P., Leterme, S.C., 2021. Variation in polymer types and abundance of microplastics from two rivers and beaches in Adelaide, South Australia. Mar. Pollut. Bull. 172, 112842. https://doi.org/10.1016/j.marpolbul.2021.112842.

Hildebrandt, L., von der Au, M., Zimmermann, T., Reese, A., Ludwig, J., Pröfrock, D., 2020. A metrologically traceable protocol for the quantification of trace metals in different types of microplastic. PLoS One 15 (7), 1–18. https://doi.org/10.1371/journal.pone.0236120.

Huang, D., Tao, J., Cheng, M., Deng, R., Chen, S., Yin, L., Li, R., 2021. Microplastics and nanoplastics in the environment: macroscopic transport and effects on creatures. J. Hazard. Mater. 407, 124399. https://doi.org/10.1016/j.jhazmat.2020.124399.

ISO, 2019. ISO 11843-6 Capability of Detection - Part 6: Methodology for the Determination of the Critical Value in Poisson Distributed Measurements by Normal Approximation, 2o Ed.

IUPAC, 2014. Compendium of chemical terminology. Gold Book. https://doi.org/10.1002/9783527626854.ch7.

Jachimowicz, P., Klik, B., Osińska, A.D., 2024. Plastic pollution in paradise: analyzing plastic litter on Malta's beaches and assessing the release of potentially toxic elements. Toxics 12 (8). https://doi.org/10.3390/toxics12080568.

Järlskog, I., Strömvall, A.M., Magnusson, K., Galfi, H., Björklund, K., Polukarova, M., Garção, R., Markiewicz, A., Aronsson, M., Gustafsson, M., Norin, M., Blom, L., Andersson-Sköld, Y., 2021. Traffic-related microplastic particles, metals, and organic pollutants in an urban area under reconstruction. Sci. Total Environ. 774, 145503. https://doi.org/10.1016/j.scitotenv.2021.145503.

JRC, 2013. Joint Research Centre. Guidance on Monitoring of Marine Litter in European Seas. https://doi.org/10.2788/99475.

Kateman, G., Pijpers, F.W., 1981. Quality Control in Analytical Chemistry. John Wiley & Sons, New York, Chichester.

Klöckner, P., Reemtsma, T., Wagner, S., 2021. The diverse metal composition of plastic items and its implications. Sci. Total Environ. 764, 142870. https://doi.org/10.1016/j.scitotenv.2020.142870.

Kutralam-Muniasamy, G., Pérez-Guevara, F., Martínez, I.E., Shruti, V.C., 2021. Overview of microplastics pollution with heavy metals: analytical methods, occurrence, transfer risks and call for standardization. J.Hazard. Mater. 415, 125755. https://doi.org/10.1016/j.jhazmat.2021.125755.

Kye, H., Kim, J., Ju, S., Lee, J., Lim, C., Yoon, Y., 2023. Microplastics in water systems: a review of their impacts on the environment and their potential hazards. Heliyon 9 (3), e14359. https://doi.org/10.1016/j.heliyon.2023.e14359.

Lagumbay, I.J., Adona, J., Brillantes, S.G., Balindo, D.S., 2025. Abundance, characterization, and distribution of marine litter in Samar, Philippines: a comparison between mainland and Island beaches. J. Mar. Island Cultures 14 (3). https://doi.org/10.21463/jmic.2025.14.3.11.

Lee, A., Mondon, J., Merenda, A., Dumée, L.F., Callahan, D.L., 2021. Surface adsorption of metallic species onto microplastics with long-term exposure to the natural marine environment. Sci. Total Environ. 780, 146613. https://doi.org/10.1016/j.scitotenv.2021.146613.

Ley N° 5414, 2015. Law of Paraguay. Promoción De La Disminución Del Uso De Plástico Polietileno. https://www.bacn.gov.py/leyes-paraguayas/4407/ley-n-5414-promocion-de-la-disminucion-del-uso-de-plastico-polietileno. (Accessed 11 March 2024).

Li, J., Liu, H., Paul Chen, J., 2018. Microplastics in freshwater systems: a review on occurrence, environmental effects, and methods for microplastics detection. Water Res. 137, 362–374. https://doi.org/10.1016/j.watres.2017.12.056.

Li, L., Zuo, J., Duan, X., Wang, S., Hu, K., Chang, R., 2021. Impacts and mitigation measures of plastic waste: a critical review. Environ. Impact Assess. Rev. 90, 106642. https://doi.org/10.1016/j.eiar.2021.106642.

Liu, K., Zhang, Z., Wu, H., Wang, J., Wang, R., Zhang, T., Feng, Z., Li, D., 2021. Accumulation of microplastics in a downstream area of a semi-enclosed bay: implications of input from coastal currents. Sci. Total Environ. 791, 148280. https://doi.org/10.1016/j.scitotenv.2021.148280.

Long, G.L., Winefordner, J.D., 1983. Limit of detection. A closer look at the IUPAC definition. Anal. Chem. 55, 712 A–722 A.

Maršić-Lučić, J., Lušić, J., Tutman, P., Bojanić Varezić, D., Šiljić, J., Pribudić, J., 2018. Levels of trace metals on microplastic particles in beach sediments of the island of Vis, Adriatic Sea, Croatia. Mar. Pollut. Bull. 137, 231–236. https://doi.org/10.1016/j.marpolbul.2018.10.027.

Martins, I., Rodríguez, Y., Pham, C.K., 2020. Trace elements in microplastics stranded on beaches of remote islands in the NE Atlantic. Mar. Pollut. Bull. 156, 111270. https://doi.org/10.1016/j.marpolbul.2020.111270.

Munari, C., Scoponi, M., Sfriso, A.A., Sfriso, A., Aiello, J., Casoni, E., Mistri, M., 2021. Temporal variation of floatable plastic particles in the largest Italian river, the Po. Mar. Pollut. Bull. 171, 112805. https://doi.org/10.1016/j.marpolbul.2021.112805.

Munier, B., Bendell, L.I., 2018. Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. PLoS One 13 (2), 1–13. https://doi.org/10.1371/journal.pone.0191759.

Nachite, D., Maziane, F., Anfuso, G., Williams, A.T., 2019. Spatial and temporal variations of litter at the Mediterranean beaches of Morocco mainly due to beach users. Ocean Coast Manag. 179. https://doi.org/10.1016/j.ocecoaman.2019.104846.

Nakashima, E., Isobe, A., Kako, S., Itai, T., Takahashi, S., 2012. Quantification of toxic metals derived from macroplastic litter on Ookushi Beach, Japan. Environ.l Scic Tech. 46 (18), 10099–10105. https://doi.org/10.1021/es301362g.

Nhanga, M.C., Geraldo, D., Nhapulo, S.L., João, A.F., Carneiro, J., Costa, M.F.M., 2025. Evaluation of heavy metal content in plastic bags used as improvised food cooking covers: a case Study from the Mozambican community. Sustainability 17 (3). https://doi.org/10.3390/su17030964.

Ormeci, B., Senapathi, V., Francesco, G., Lama, C., De Lange, S.I., Mellink, Y., Vriend, P., Tasseron, P.F., Begemann, F., Hauk, R., Aalderink, H., Hamers, E., Jansson, P., Joosse, N., Löhr, A.J., Lotcheris, R., Schreyers, L., Vos, V., Van Emmerik, T.H.M., 2023. Sample size requirements for riverbank macrolitter characterization. Front. Water. https://doi.org/10.3389/frwa.2022.1085285.

OSPAR, 2010. Guideline for monitoring marine litter on the beachs in the OSPAR Maritime Area. OSPAR Commission 1, 84.

Ottander, N., 2022. Distribution and Transport of Microplastics and Metals in Sewage sludge-amended Agricultural Soil - a Comparative Study Between Microplastics. Swedish University of Agricultural Sciences.

Palmas, F., Cau, A., Podda, C., Musu, A., Serra, M., Pusceddu, A., Sabatini, A., 2022. Rivers of waste: anthropogenic litter in intermittent Sardinian rivers, Italy (Central Mediterranean). Environ. Pollut. 302, 119073. https://doi.org/10.1016/j.envpol.2022.119073.

Park, H., Park, B.S., 2021. Review of microplastic distribution, toxicity, analysis methods, and removal technologies. Water 13 (19). https://doi.org/10.3390/w13192736.

Patrício Silva, A.L., Barceló, D., Rocha-Santos, T., 2024. Pharmaceuticals and micro (nano)plastics in the environment: sorption and analytical challenges. TrEAC 44, e00243. https://doi.org/10.1016/j.teac.2024.e00243.

Pilapitiya, P.N.T., Ratnayake, A.S., 2024. The world of plastic waste: a review. Clean. Mater. 11, 100220. https://doi.org/10.1016/j.clema.2024.100220. Elsevier Ltd.

Pinto, R.B., Bogerd, L., van der Ploeg, M., Duah, K., Uijlenhoet, R., van Emmerik, T.H.M., 2024. Catchment scale assessment of macroplastic pollution in the Odaw river, Ghana. Mar. Pollut. Bull. 198, 115813. https://doi.org/10.1016/j.marpolbul.2023.115813.

PlasticsEurope, 2024. Plastics – the fast facts 2024. https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2024/. (Accessed 11 February 2025).

Rangel-Buitrago, N., Gracia, C.A., Velez-Mendoza, A., Carvajal-Florián, A., Mojica-Martinez, L., Neal, W.J., 2019. Where did this refuse come from? Marine anthropogenic litter on a remote island of the Colombian Caribbean sea. Mar. Pollut. Bull. 149, 110611. https://doi.org/10.1016/j.marpolbul.2019.110611.

Rasool, A., Halfar, J., Brožová, K., Čabanová, K., Chromíková, J., Malíková, P., Motyka, O., Pertile, E., Drabinová, S., Heviánková, S., 2026. Interactions of microplastics with heavy metals in the aquatic environment: mechanisms and mitigation. J. Hazard. Mater. Adv. 21, 100984. https://doi.org/10.1016/j.hazadv.2025.100984.

Resolución N° 757, 2024. Ministerio de Industria y Comercio (MIC) de Paraguay. https://www.mic.gov.py/wp-content/uploads/2024/09/Resolucion_N.%C2%B0_757_2024_Cronograma_de_reemplazo_de_bolsas_modifica_articulo_4%C2%B0_8%C2%B0_29%C2%B0_y_Anexo_I_Resolucion_N.%C2%B0_353-1.pdf. (Accessed 22 January 2025).

Rodrigues, J.P., Rivera-Hernández, J.R., Bernárdez, P., Rocha-Santos, T., Duarte, A.C., Santos-Echeandía, J., 2023. Metal(oid)s in plastic debris, with distinct features, from Spanish Mediterranean beaches with different anthropogenic pressure: are these particles potential monitors for metal pollution? Mar. Pollut. Bull. 193, 115107. https://doi.org/10.1016/j.marpolbul.2023.115107.

Rodríguez, L., Yubero, F., Díez Pérez, D., 2019. Presencia De Microplásticos En La Arena De Playa De La Bahía De Asunción, Paraguay. Universidad Nacional de Asunción.

Santos, A., Oliveira, M., Venâncio, C., 2023. Concomitant presence of nanosized plastics and metal(loid)s: is there cause for alarm? State-of-the-art and recommendations for future studies. TrAC. 164, 117110. https://doi.org/10.1016/j.trac.2023.117110.

Schone Rivieren, 2017. Handleiding voor monitoring. www.schonerivieren.org. (Accessed 7 March 2024).

Schwarz, A.E., Ligthart, T.N., Boukris, E., van Harmelen, T., 2019. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study. Mar. Pollut. Bull. 143, 92–100. https://doi.org/10.1016/j.marpolbul.2019.04.029.

Shi, M., Xie, Q., Li, Z.L., Pan, Y.F., Yuan, Z., Lin, L., Xu, X.R., Li, H.X., 2023. Adsorption of heavy metals on biodegradable and conventional microplastics in the Pearl River Estuary, China. Environ. Pollut. 322, 121158. https://doi.org/10.1016/j.envpol.2023.121158.

Stabnikova, O., Stabnikov, V., Marinin, A., Klavins, M., Vaseashta, A., 2022. The role of microplastics biofilm in accumulation of trace metals in aquatic environments. World J. Microbiol. Biotechnol. 38 (7), 1–16. https://doi.org/10.1007/s11274-022-03293-6.

Susanto Barus, B., Ida Sunaryo Purwiyanto, A., Suteja, Y., 2023. Microplastic and heavy metal interactions (adsorption and desorption) at different salinities. BIO Web of Conferences 74. https://doi.org/10.1051/bioconf/20237405004.

Traverso-Soto, J.M., Figueredo, M., Punta-Sánchez, I., Campana, O., Ciufegni, E., Hampel, M., Buoninsegni, J., Manzano Quiñones, M.A., Anfuso, G., 2025. Assessment of organic pollutants desorbed from plastic litter items stranded on Cadiz beaches (SW Spain). Toxics 13 (8). https://doi.org/10.3390/toxics13080673.

Turner, A., Holmes, L.A., 2015. Adsorption of trace metals by microplastic pellets in fresh water. Environ. Chem. 12 (5), 600–610. https://doi.org/10.1071/EN14143.

Van Emmerik, T., Roebroek, C., De Winter, W., Vriend, P., Boonstra, M., Hougee, M., 2020. Riverbank macrolitter in the Dutch Rhine-Meuse delta. Environ. Res. Lett. 15 (10), 104087. https://doi.org/10.1088/1748-9326/abb2c6.

Vedolin, M.C., Teophilo, C.Y.S., Turra, A., Figueira, R.C.L., 2017. Spatial variability in the concentrations of metals in beached microplastics. Mar. Pollut. Bull. 129 (2), 487–493. https://doi.org/10.1016/j.marpolbul.2017.10.019.

Vikhareva, I.N., Aminova, G.K., Moguchev, A.I., Mazitova, A.K., 2021. The effect of a zinc-containing additive on the properties of PVC compounds. Adv. Polym. Technol. 2021, 593184. https://doi.org/10.1155/2021/5593184.

Yousafzai, S., Farid, M., Zubair, M., Naeem, N., Zafar, W., Zaman, Asam, ul, Z., Farid, S., Ali, S., 2025. Detection and degradation of microplastics in the environment: a review. Environ. Sci. Adv. 4, 1142. https://doi.org/10.1039/d5va00064e.