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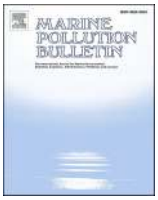

Metal(oid)s in plastic debris, with distinct features, from Spanish Mediterranean beaches with different anthropogenic pressure: Are these particles potential monitors for metal pollution?

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ABSTRACT

Metal(oid)s concentrations have been quantified in plastic pieces collected from four beaches located in the Mediterranean coast of Spain with different characteristics (i.e. anthropogenic pressure, zone). Metal(oid)s content was also related to selected plastic criteria (i.e. color, degradation status, polymer). The selected elements were quantified with mean concentrations in the sampled plastics with the following order: Fe > Mg > Zn > Mn > Pb > Sr > As > Cu > Cr > Ni > Cd > Co. Moreover, black, brown, PUR, PS, and coastal line plastics concentrated the higher metal(oid)s levels. Local of sampling (influence of mining exploitation) and severe degradation were key factors for uptake of metal(oid)s from water by plastics as modification of surfaces strengths their adsorption capacity. Determined high levels of Fe, Pb and Zn in plastics reflected the pollution degree of the marine areas. Therefore, this study is a contribution for the potential use of plastics as pollution monitors.

1. Introduction

Plastic usage in land is considered of major concern for marine pollution, contributing to >80 % of the marine litter as a result of released plastic debris (GESAMP, 2019; Plastics Europe, 2017). Literature on studies reporting the presence of metal(oid)s in plastics has grown in the recent years. Metals were firstly related to plastics with their inclusion as additives (i.e. catalysts, fillers, plasticizers) from their production to confer them resistance properties (Castro et al., 2018; GESAMP, 2015). However, in the last decades, research studies revealed that metal(oid)s can be present in polymers after being adsorbed from the environment (i.e. water) (Ashton et al., 2010; Cobelo-Garcia et al., 2007; Giusti et al., 1994; Robertson, 1968; Struempler, 1973; Weijuan et al., 2001). Features of polymers may be indicative of the associated metal(oid)s, as they interfere in their uptake capacity (Rodrigues et al., 2022). Furthermore, properties of polymers can be naturally (degradation in the environment) or artificially (oxidized plastics) modified, conferring them a new more reactive surface (Wang et al., 2020). Frequently, high metal load is found in beached plastics (Acosta-Coley et al., 2019; Maršić-Lučić et al., 2018; Santos-Echeandía et al., 2020). These coastal regions receive and accumulate plastic debris from macro to micro and nanoplastics both from land and sea origin (Garcés-Ordóñez et al., 2020; Turner and Holmes, 2011). As matter of fact, these marine areas are suitable for polymer surface degradation as physical (erosion and wave action) and chemical (direct UV exposure), helped by the deposition of plastics which remain in the sand (Nakashima et al., 2016). Moreover, industrial activity is highly present in coastal areas, reuniting the ideal conditions for interaction of polymers and metal (oids)s and potentially giving indication of the local contamination status.

Color is a feature associated with specific metal addition over plastic production (e.g. copper (Cu) to blue color and chromium (Cr) to green color) (Carbery et al., 2020). Moreover, color of environmental plastics is frequently responsible for visual identification of aged polymers (Acosta-Coley et al., 2019; Fisner et al., 2017). The main polymers that constitute plastics are polyethylene (PE), polypropylene (PP), polyvinyl

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chloride (PVC), polystyrene (PS), and polyurethane (PUR), with values for their production of 9.3–14.7 %, 16.6 %, 11.4 %, 6.1 %, and 5.5 %, respectively (Plastics Europe, 2022). Polymers are manufactured with the inclusion of several metals and/or metalloids to give or reinforce plastic characteristics. Due to structural differences among polymers, the specific functional groups of each polymer are responsible for affinity towards certain metal ions (Rodrigues et al., 2022). Furthermore, this affinity can be altered or magnified through degradation from environmental exposure, which is driven by other physico-chemical parameters. Coatings on polymer surfaces, as biofilms and mineral silts, and association with organic matter, form complexes which allow the uptake of metal(oid)s. For those reasons, it is expected to find a higher load of metal(oid)s in plastics from marine environments, especially concerning more degraded pieces. The influence of the deposition area of plastics and associated metal(oid)s is also worth of investigation, as these conditions may conduct to changes in metal(oid)s content.

The monitoring and control of plastics are included in environmental protection agencies, as in the European Water Framework Directive (2000/60/CE) and Marine Strategy Framework Directive (2008/56/CE), along with the reduction of metal concentrations in the environment. As far as we know, no studies have been previously reported in literature concerning comprehensive metal(oid)s content (quantification of 12 elements was performed in this study) characterization from local plastics collected in the SE Spain beaches as the ones selected for this study, highlighting the important contribution of this work. This study also provides baseline information of the profile of plastic debris (according to their characteristics) deposited in this coastal region.

The present study is aimed to determine the metal(oid)s content in plastics sampled from the sediment of marine areas to investigate their contribution to assessment of local contamination degree. To achieve this, quantification of metal(oid)s was related to influence of: 1) anthropogenic pressure and beach zone considering different sampling areas, 2) plastic features as color, polymer and residence time on environment as confirmed by the degradation status. In this way, the present work will contribute for establishing important and uniform conclusions concerning the environmental risk of (micro)plastics and associated contaminants.

2. Materials and methods

2.1. Study area

The beaches selected for this study are located in the Mediterranean coast, Murcia region, SE Spain. Portman and Calblanque are situated facing the Mediterranean Sea, and Islas Menores and Beal are part of the Mar Menor lagoon which is a semi-enclosed coastal system (Fig. 1). Those beaches were chosen mainly for their differences concerning anthropogenic pressure but also for other characteristics as geology, area, and related human activities. Among the beaches with low human disturbance are included Calblanque, which takes part of a regional natural park, and Islas Menores, representing a remote area with tourism activity restricted to the summer season (Bayo et al., 2019). On the contrary, Portman and Beal are recognized for being adjacent beaches from a former mining exploitation area reach in metallic sulphide (i.e. Fe, Pb, Zn) (Martínez-López et al., 2021), the Sierra Minera of Cartagena-La Unión (cessation of activity in 1990), thus having anthropogenic influence. This coastal area embracing a Mining District (50 km^2) is described to be not high in altitude but having pronounced slopes towards the coast, being mostly parallel to the Mediterranean Sea (Conesa and Schulin, 2010; Martínez-López et al., 2020). It is a semi-arid region highly affected by strong rainfalls (especially on spring and autumn) promoting surface runoff of minerals and chemicals from the mine exploitation and agriculture as well. Also, intensive agriculture and tourism are activities highly practiced in this region, since populations are installed in the surroundings. This also contribute a lot to the input of plastics in beaches of Mar Menor Lagoon and Mediterranean Sea. Furthermore, the complete environment existing here with vegetation, agricultural lands, semi/salty waters, and more enclosed/open water lands is ideal for observation, studying and comprehension of alterations in biogeochemical cycles of trace metal(oid)s coming from mine exploitation (Conesa and Schulin, 2010) and the role of plastics on this phenomenon. Moreover, due to the old and also long duration of the mining exploration in this region, new ecological communities were originated there, especially plant species adapted to the extreme new conditions of the ecosystems reached in metals as a result of mine wastes

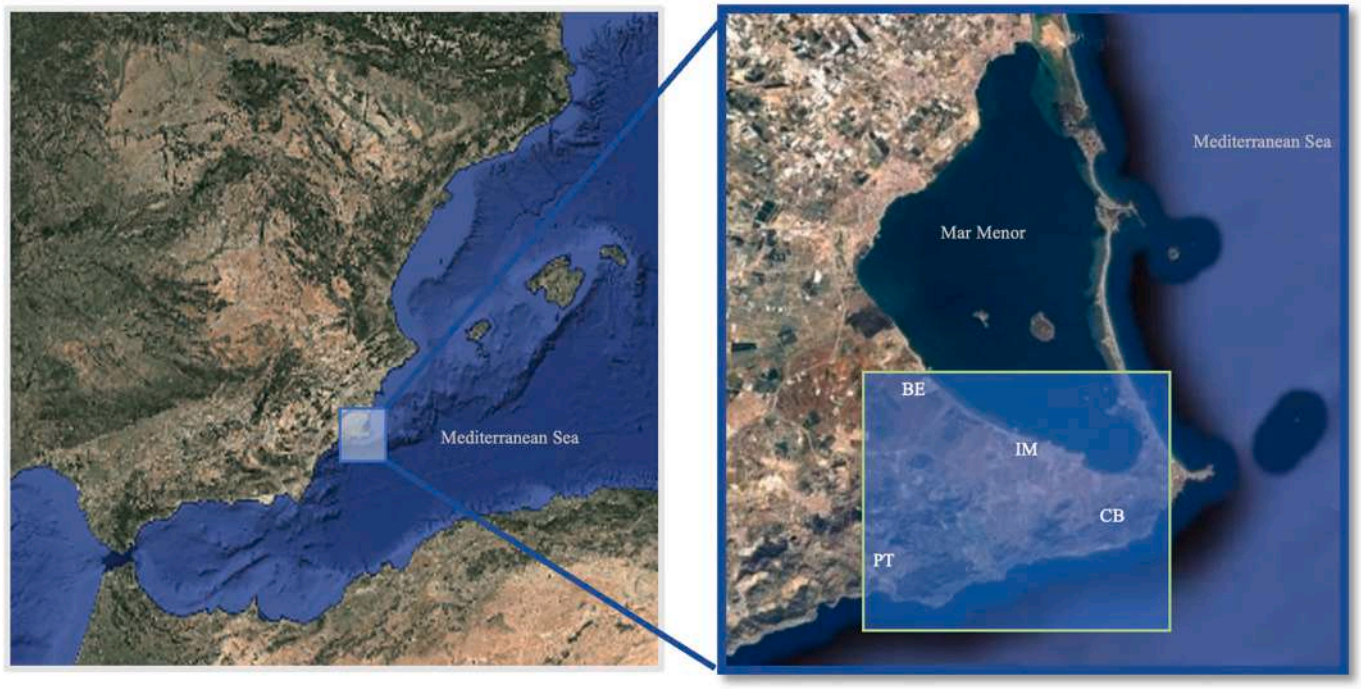

Fig. 1. Map illustrating the sampling area for this study, where Portman (PT), Calblanque (CB), Islas Menores (IM) and Beal (BE) beaches are located, in SE coast of Spain.

and saline soils (in Portman Bay). Thus, the mine dumping products ending up in Mar Menor Lagoon and Mediterranean sea affected biological communities (e.g. macrophytes and mussels) (Conesa and Schulin, 2010). This can be a problem since the closeness of the study area to the exploitation mine area leads to threatening of these adjacent zones with high ecological value (i.e. Martínez-López et al., 2021).

2.2. Plastics collection

Sampling took place between March and May of 2018 with manual collection of plastic items (<10 cm size) detected by naked eye, as described elsewhere (Santos-Echeandía et al., 2020) and following the Guideline for Monitoring Marine Litter on the Beaches from OSPAR Maritime Area (OSPAR, 2010). The collection of plastic items was divided in 3 zones: i) Costal line along 100 m (representing recent plastics deposited from the sea) to collect superficial plastics; ii) middle beach using density squares (50 × 50 cm area) placed randomly in the sand (×3) to collect all visible superficial sand layer plastics at maximum 1 cm depth sand; iii) upper zones with random collection of visible plastics over the higher beach area reinforcing a higher diversity in the plastics collected (i.e. color, material, and use). Additionally, new commercial plastics (bought in a local shop) composed by different polymers (PP, PS, PE, PUR and PVC) and different uses were included in this study for further metal determination and comparison with environmental samples. All plastic samples were manipulated with metal free plastic material to avoid contamination.

2.3. Screening and classification of plastics

Once in the laboratory, all collected samples were firstly cleaned with a brush before further manipulation, to eliminate residual organic matter and sediment particles, as much as possible, and rinsed with deionized water. All plastic pieces were screened (Figs. 2, S1) and classified to be grouped according to the following criteria: beach and zone, polymer type and degradation appearance (later confirmed by ATR-FTIR analysis), and color. Age, color, and polymer were features selected as they may influence adsorption capacity of polymers towards metal(oid)s in water. In addition, each sample was photographed (CANON SX 410 IS). In a brief description of the plastics items found, they were diverse with different colors, sizes and shapes, and also related to different usages. The more collected items (the whole piece or part of them) were bottle caps, pellets, bio-beds, clothespins, cotton buds, spoons, fishnets, bottles, PUR or PS foams, and other fragments not possible to identify.

2.4. Polymer and degradation status identification

A portion of each plastic piece was used to be analyzed by Attenuated Total Reflection Fourier-transform Infrared Spectroscopy (ATR-FTIR) (Spectrum 400 FT-IR/FT-NIR Spectrometer and horizontal ATR PIKE Miracle with a Perkin Elmer diamond/Zn Se crystal plate) to identify the main structural polymer (i.e. PE, PP, PS, PVC or PUR) of each sample. The methodology was described in the work of Santos-Echeandía et al. (2020). In addition, the degradation status of the observed plastics, previously characterized by naked eye, was confirmed with the FTIR technique, following Santos-Echeandía et al. (2020). Plastic samples were then classified qualitatively by degradation status level from (1) low, (2) medium, to (3) moderate, and high (4), according to their % of transmittance wavelength of 3300 cm^{-1} for each polymer (Fig. S2 and Table S1).

2.5. Determination of trace metals by ICP-MS

Trace-element content in the plastic samples was measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) using an Agilent 8900 Triple Quad with Integrated Sample Introduction System (ISIS). The following elements were analyzed: Magnesium (Mg), Cr, manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), Cu, zinc (Zn), arsenic (As), strontium (Sr), cadmium (Cd), and lead (Pb). Preliminary digestion of the plastic samples (around 200 mg) with acidic extraction was performed, as Aqua Regia with 1:3 HNO_3 (20 %) + HCl (20 %) (2 mL:8 mL) using Suprapur acids and ultrapure water. For the ICP-MS analysis, a dilution factor of 4 was applied for the samples, obtaining final sample solutions at 5 % acidic mixture. The standards for the calibration curves were prepared from ICP-MS mix stock solution and Aqua Regia stock solution (5 %). The detection limits of the ICP-MS for trace elements were between 0.001 and 0.500 μg/g and the analytical precision (RSD, n = 3) for trace elements was <10 %. In order to have a good quality control of the analysis, blanks and sediment Certified Reference Material (MESS-3) was used. Percent recoveries of CRM were within 93–104 % for all the elements analyzed. The analyses of the Internal Standards (ISTD solution) containing beryllium (Be), germanium (Ge), scandium (Se), iridium (Ir), and rhodium (Rh) for recovery of all elements agreed with the recommended values and patterns as quality controls were analyzed when necessary for validation of the method, together with daily checking of the Tunning solution.

Fig. 2. Screening and identification of characteristics of plastics collected from Portman beach.

2.6. Data analysis

The values for metal(oid)s content in plastic samples are represented as μg/g. Pie chart graphs were obtained using Microsoft Excel (v. 16.69). Box plot graphs with data transformed by logarithm transformation were designed using R studio (v. 4.2.1). For representation of the total metal(oid)s content by each plastic sample classification criteria, the sum of all values of elements for each sample was estimated. Statistical analysis was performed with IBM SPSS statistics (v. 27) software and a significance level of $p \leq 0.05$ was considered for testing all the significant differences. Normality of the data was verified with the Shapiro-Wilk test. As the data was not normal distributed, non-parametric tests were applied to check for significant differences. Kruskal-Wallis test was used to find the significant factors (plastic classification criteria) influencing the metal(oid)s content followed by pairwise Mann-Whitney test to identify the differences among the levels (categories) of each significant factor. Principal Component Analysis (PCA) was conducted in R studio (v. 4.2.1) to investigate for any grouping relations concerning metal(oid)s concentrations (by plastic classification criteria).

3. Results and discussion

3.1. Plastic items

In total, 216 plastic items were considered for this study, with 201 representing beached sampled plastics, and extra 15 new commercial (Table 1). Portman beach had the highest number of plastics collected followed by Calblanque, particularly in the middle beach zone. The location of both beaches in the open sea of the Mediterranean coast could explain a high input of plastic debris (Faure et al., 2015) and exemplifies the ubiquitousness of plastics found even in protected areas. On the other hand, Islas Menores and Beal, in Mar Menor lagoon, presented a lower number of plastic items, which were mainly concentrated in the upper dunes (potentially coming directly from land due to higher populational frequency location). Beal and Islas Menores are mainly seasonal activity recreation beaches, which may explain the low plastic waste in low seasons, combined with regular cleaning of these two beaches all year long (Santos-Echeandía et al., 2020).

Concerning the number of plastic items by polymer, the following sequence was identified: PE > PP > PS > PUR > PVC (Fig. 3a). PE and PP represented around 90 % of all the plastics which is in line with PE and PP being the two most globally produced polymers and, therefore, the most abundant in environment, as reported in other field studies (Acosta-Coley et al., 2019; Carbery et al., 2020), and specifically in the Mediterranean Sea (Suaria et al., 2016). Moreover, the low density of these two polymers (<1 g/cm^3) comparing to fresh- and seawater allows them to float in the superficial waters, thus, they are easily and constantly transported by wave currents to end up in beach sediments.

Table 1
Number of plastic items collected by beach and zone and the number of new commercial plastics considered for the study.

Origin	Zone	Number of items
Portman	Coastal line	14
	Middle beach	42
	Upper dunes	27
Calblanque	Coastal line	3
	Middle beach	35
	Upper dunes	15
Islas Menores	Coastal line	3
	Middle beach	2
	Upper dunes	21
Beal	Coastal line	13
	Middle beach	2
	Upper dunes	24
New commercial		15
Total		216

On the contrary, PVC tends to sink, due to its high density (1.38 g/cm^3) to be accumulated in the sediments underwater (Andrady, 2011).

White, blue, and colorless plastics were the predominant colors of the plastic items (14.4–18.9 %), while the presence of purple, orange, red, grey, black, pink, and yellow plastics (2.0–6.0 %) was lower (Fig. 3b). Brown and green plastics represented 9.0–11.9 % of the plastics. White and colorless plastics presence in beaches is frequent (Maršić-Lučić et al., 2018; Souza et al., 2022), either with evidence of age or not, having various derived tones (Acosta-Coley et al., 2019). Interestingly, a high number of blue and white colored plastics found in the present study was also verified in the Carbery et al. (2020) work which was performed in a very distant geographical marine area (Australian coast). Additionally, Li et al. (2023) and Turner (2017) also found a higher number of blue plastics, in a lake in China and in an English beach, respectively. From one hand, this suggests a common frequency for colored plastics most found. Conversely to our study, in the work of Li et al. (2023) black plastics (along with blue) were among the most collected ones. Thus, on the other hand, the high diversity that plastics have is demonstrated, either in the same or distinct environment locations. As matter of fact, Mar Menor lagoon was characterized for having a high diversity of plastics, mainly regarding polymer and color (Bayo et al., 2019). In addition, the predominant degradation status of plastics for all the sampling areas was 3 (Fig. 3c).

3.2. Metal(oid)s content in plastics

Mean metal(oid)s concentrations on the environmental plastic samples were sequenced as follows: Fe > Mg > Zn > Mn > Pb > Sr > As > Cu > Cr > Ni > Cd > Co (Table 2). Overall, Co was the metal presenting the lowest concentrations (only 1.15 ± 7.95 μg/g mean) among the samples (most of them bellow the detection limit), while Fe was found with the highest values ($6.50 * 10^3 \pm 4.69 * 10^3$ μg/g mean concentration). Higher content of Fe on environmental plastic particles from beach sediment is in agreement with Maršić-Lučić et al. (2018), Vedolin et al. (2017), and Souza et al. (2022). Also, the fact that Fe was extensively explored in the old mining area near Portman and Beal (Martínez-López et al., 2021) supports the highest maximum and mean levels found for this metal in the sampled plastics. Detectable levels of the following elements were determined in all the plastics collected: Mg, Fe, Zn, Sr, Pb, and Mn. It is important to highlight from our results that Pb, listed as a priority pollutant (US EPA, 2014), represent the hazardous substance with the highest content ($4.06 * 10^3$ μg/g maximum and $5.64 * 10^2 \pm 4.05 * 10^3$ mean concentration, respectively) estimated concerning the sampled plastics (Table 2), despite its restriction laws in European plastic manufacturing (Hahladakis et al., 2018). Considering that maximum allowable levels for Pb in plastic production is nowadays $1.00 * 10^3$ μg/g (Turner and Filella, 2021) that helps to protect water quality (Directive 2008/56/EC European Parliament and Council, 2008; Napierska et al., 2018), the plastics in study hold higher levels, exceeding the safe limits for Pb by far (in other samples this value was also exceeded). This observation emphasizes the fact that environmental plastics with increasing widespread in water environments can storage unsafe levels of hazardous pollutants, higher than their trace levels in water (Maršić-Lučić et al., 2018), with a potential release to the environment. Turner (2016) reported a high value of total Pb concentrations (analyzed by field-portable-x-ray fluorescence spectrometry) in the 209 beached plastics they sampled ($1.7 * 10^4$ μg/g), while in our study the sum of all Pb levels in the 201 plastic samples was even higher ($5.7 * 10^4$ μg/g total concentration). This can be worrying, particularly if we look at the restrictions of Pb levels in plastic production. Although, the presence of Pb in sampled plastics could be justified, in a minor part, by the presence of this element (used as additive) in legacy plastics found in environment (Filella and Turner, 2018). Additionally, legacy plastics reflect the long time periods that plastics can remain in the environment, potentially carrying their intentionally added metal(oid)s plus the ones adsorbed from water after plastics were discarded. As matter of fact,

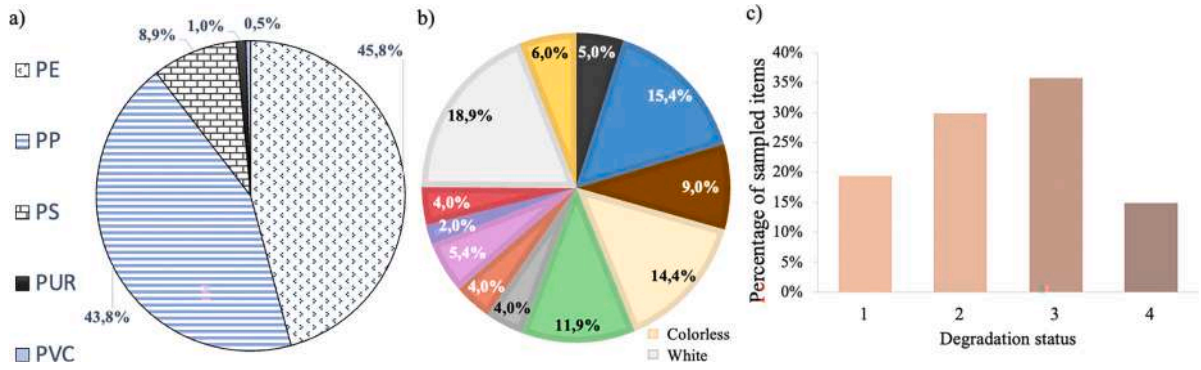

Fig. 3. Physico-chemical characterization of plastics from the Mediterranean beaches considering the number of items collected (%) for this study. Percentage of plastic items by criteria is represented concerning a) polymer type; b) color; c) degradation status.

Table 2
Metal(oid)s concentrations (μg/g) (minimum, mean ± SD, maximum) for selected elements determined in the beached plastics collected, and maximum levels determined in the new commercial plastics considered for this study. The elements are ordered according to descending mean levels quantified in the environmental samples of this study.

Element	Determined min, mean, andmax values in sampled plastics (μg/g)			Determined max values in new commercial plastics (μg/g)
	Min	Mean	Max	
Fe	1.09 * 10^1	6.50 * 10^3 ± 4.69 * 10^3	1.11 * 10^5	1.27 * 10^1
Mg	8.89	2.65 * 10^3 ± 1.89 * 10^4	1.46 * 10^4	1.22 * 10^1
Zn	1.14	7.37 * 10^2 ± 5.29 * 10^3	5.67 * 10^3	4.08 * 10^1
Mn	6.11^{-1}	5.91 * 10^2 ± 4.26 * 10^3	7.29 * 10^3	1.56
Pb	1.24 * 10^{-1}	5.64 * 10^2 ± 4.05 * 10^3	4.06 * 10^3	5.00 * 10^{-1}
Sr	2.00 * 10^{-1}	7.25 * 10^1 ± 5.25 * 10^2	1.33 * 10^3	5.33 * 10^{-1}
As	BDL	3.95 * 10^1 ± 2.78 * 10^2	6.75 * 10^2	1.51 * 10^{-1}
Cu	BDL	1.83 * 10^1 ± 1.36 * 10^2	5.25 * 10^2	4.07 * 10^{-1}
Cr	BDL	2.30 ± 1.62 * 10^1	2.78 * 10^1	4.06 * 10^{-1}
Ni	2.00 * 10^{-3}	1.79 ± 1.22 * 10^1	1.09 * 10^1	9.43 * 10^{-1}
Cd	BDL	1.21 ± 8.69	2.07 * 10^1	3.00 * 10^{-3}
Co	BDL	1.15 ± 7.95	1.09 * 10^1	BDL

adsorption was most probably the responsible for the high levels observed for Pb in the plastics from our study, as the sampling areas were contaminated from old mining exploitation. Pb has been quantified with considerable levels in surface waters from Portman (600 μg/L) and Beal (9500 μg/L) (García-Cortés et al., 2019) and also in water courses (stream sediments) from those regions (1.95 * 10^3 and 1.97 * 10^3 μg/g, respectively) (García-Lorenzo et al., 2012; Martínez-López et al., 2021). Furthermore, after a rainfall, concentrations of Pb in flowing water from adjacent areas can reach 1.80 * 10^3 μg/L and around 7.00 * 10^3 μg/g in the sediment (which is in the same order of magnitude as our maximum value for Pb) (Conesa and Schulin, 2010). Additionally, pollutants adsorption by plastics on environment could likely occur for other metal (oid)s listed as priority pollutants (i.e., Pb, As, Cr, Cd, Co, Ni) by environmental agencies (US EPA, 2014). As matter of fact, other metal(oid)s were quantified with also high concentrations (and some similar to our levels quantified in plastics) in surface waters in Portman and Beal, as Zn (4.30 * 10^2, 9.88 * 10^3 mg/L), Cd (1.60 * 10^1, 7.00 mg/L), Fe (1.86 * 10^3, 7.00 mg/L), As (1.53 * 10^4, 1.40 * 10^1 μg/L), Cu (7.60 * 10^1, 1.40 * 10^1 mg/L), and Mn (2.70 * 10^2, 2.10 * 10^3 mg/L) (García-Cortés et al., 2019;; Martínez-López et al., 2021) and in sediments of Portman as Zn (7.80 * 10^3 μg/g), Pb (6.00 * 10^3 μg/g), and As (1.70 * 10^3 μg/g) (Martínez-Sánchez et al., 2008). In the most polluted stream of Beal were quantified 5.00 * 10^2 μg/g for As, 1.20 * 10^4 μg/g for Pb and 7.0 * 10^3 for Zn (Conesa and Schulin, 2010; María-Cervantes et al., 2009). One can observe that contamination of metals and metalloids is particularly higher in this study area. Therefore, those hazardous substances could be further bioavailable to marine organisms eventually bioaccumulating on them, who could suffer effects from their toxicity. Accordingly, Pb was already identified in aquatic biota (e.g. bivalve shells) and to be accumulated in high levels in the region of Beal (Auernheimer et al., 1996). Additionally, it was found that MPs had high influence on transferring metals to zooplankton in the Mediterranean sea (Squadrone et al., 2022), thus, with potential impacts to higher level species of the trophic chain, as zooplankton represents organisms from the first levels of the food webs (Squadrone et al., 2022). Other environmental changes coming from the input of metals and metalloids through MPs is the potential higher mobilization of the chemicals present in the study region to water and inducing acidification, oxidation and reduction (Martínez-López et al., 2021).

In turn, regarding Cd as another priority pollutant with level restrictions for its use as a plastic additive, this metal was determined not exceeding the limit levels (1.00 * 10^2 μg/g) (European Commission, 2011) in any of the collected plastics. Even more, the sum of Cd quantified in all the samples (1.2 * 10^2 μg/g) was near the stablished limit for this metal (and with mean levels of 1.21 ± 8.69 μg/g), conversely to, for example, the sum of Cd levels (1.46 * 10^3 μg/g) on plastic samples in the Turner (2017) study that exceeded it by far. In addition, no samples or the mean of all of them transcended the levels allowable for Cr [1.00 * 10^3 μg/g CR(VI)] (Horn, 2016) in our study (2.30 ± 1.62 * 10^1 μg/g mean of Cr levels in all beached samples).

Concerning the new commercial samples, levels of metal(oid)s were much lower (Table 2), and Co was below the detection limit. On the other hand, Zn, a metal widely used as an additive (Deanin, 1975), presented the highest concentration (4.08 * 10^1 μg/g) observed for the new commercial plastics. On the other hand, As was quantified with low maximum levels in the new commercial samples (comparing to the levels found for the sampled plastics), driving to initial thoughts that the high concentrations of As on the beached plastics was due to their adsorption from environment. As matter of fact, all metals presented higher concentrations in the sampled plastics, confirming this observation. One would expect to find higher metal content in the environmental (micro)plastics when compared to non-exposed new plastic particles as it was reported in consulted studies (Li et al., 2023; Prunier et al., 2019; Santos-Echeandía et al., 2020; Vedolin et al., 2017), agreeing with our study. Although, Prunier et al. (2019) reported levels for elements used as additives in new packaging plastics that they considered high, despite to be higher in the exposed ones. As an

example, they obtained a maximum value for Pb of 2.25 μg/g in the non-exposed plastics while our new commercial plastics shown a maximum level for Pb of 5.00 * 10^{-1} μg/g.

The metal(oid)s concentrations in the plastic material from the present study were compared to literature of similar studies on beached plastics (Table 3). It is important to highlight that our study is the one reporting the higher number of different metal(oid)s quantified in plastics, concerning the similar studies of metal contamination in plastics collected from the sediment of marine areas published so far. The mean levels for Pb, Cr, Co, and Cd in our samples were 1 order of magnitude higher than for Acosta-Coley et al. (2019) (4.34 * 10^1, 9.83 μg/g 0.34, and 0.22 μg/g, respectively) and 2 orders for the metalloid As (0.35 μg/g) concerning their microplastics (MPs) (quantification by ICP-MS with preliminary sample digestion with 8 mL HF + 3 mL HNO_3 solution; followed by 3 mL HNO_3, and 3 mL HCl) collected from an industrial influenced marine area. Although, if we look at our maximum concentrations, our levels were higher. Thus, apparently our samples presented higher levels for the metal(oid)s estimated, but not neglecting the different extraction method used to quantify the metal(oid)s levels present in the plastics in both studies and inherent different conditions of the sampling areas. Furthermore, Carbery et al. (2020) information of quantified similar maximum levels for Cu and Cr on sampled coastal MPs is given, as 1.43 * 10^2 and 2.77 μg/g, respectively, but higher for Cr in our samples. However, mean measured concentrations for Cd and Cu in our plastic samples were lower. Accordingly, the priority pollutant Cd revealed approximated levels (1.15 * 10^1 μg/g) on plastics with ours (1.21 μg/g mean concentration), concerning the studies of Table 3. In turn, levels of Pb (1.84 * 10^1 μg/g) and As (1.53 μg/g) were lower than the maximum and mean levels quantified in our samples. It is important to highlight that in the mentioned study a total of 3559 environmental MPs were analyzed, compared to our 201 total plastic items. The authors highlighted the highest levels found in their study for Mn, Cr, Cu, As and Pb on environmental plastics debris to be related to the influence of industrial site, giving initial insight that content of metal(oid)s in plastics is essentially location dependent. This observation was supported by Fernandes et al. (2020) who found maximum levels for Pb (1.51 * 10^2 μg/g) and Cd (5.43 * 10^1 μg/g) quantified in bigger plastic samples (levels for Cd were even higher than in the samples from our study) higher in industrial pressured beaches but also high levels for Zn (6.57 * 10^2 μg/g) were determined (by Atomic Adsorption Spectrometry with prior acid extraction with 10 % solution of 73 % analytical grade nitric) in recreational beaches. Therefore, the high metal(oid)s content concerning maximum concentrations and taking into account the distinct total number of plastic samples analyzed for Carbery et al. (2020) work and our study (both studies had the same extraction method) might be indicative that our study area was more polluted concerning metal(oid)s contamination. Moreover, their few higher levels reported comparing to our mean levels were found in polluted regions as well. This could support plastic particles as being potential monitoring tools for metal pollution assessment on beaches. Following the Table 3 studies, mean levels in our data for the measured elements in common with Vedolin et al. (2017) study on beached MPs [quantified by ICP-OES with prior partial acid digestion with 10 mL HNO_3 (1:1), 5 mL HNO_3, 3 mL H_2O_2 (30 % V/V), and 10 mL of HC] were much higher comparing to their mean levels, particularly for Zn and Mn with 2 orders of magnitude lower in their study (8.00 and 9.00 μg/g, respectively) and also one magnitude lower for Cu (1.00 μg/g). Only Fe had high levels 2.28 * 10^2, as reported in other studies. Another study performed with beached microplastic samples (pellets) reported lower metal content when compared to our results (Maršić-Lučić et al., 2018). Accordingly, for Fe, Mn, Zn, Sr, and Cu and metals, the maximum levels quantified were 2 or more orders of magnitude lower in the samples of Maršić-Lučić et al. (2018) work and 3 orders for Cd (5.4 * 10^{-3} μg/g). For Cr and Ni, the difference was 2 orders of magnitude lower (0.74 and 0.27 μg/g, respectively) than for mean levels of our samples, altough both studies presenting low levels quantified for these metals. Souza et al. (2022) determined Pb also in pellets [through ICP-MS with prior microwave acid digestion with 2 mL HNO_3, 2 mL HCl, and 2 mL H_2O_2, 30 % (V/V)] in the range of 0.57 to 1.10 μg/g which is much lower than the levels found here for the same metal. Thereby, this might suggest that pellets have not a strong sorption capacity or maybe those pellets represented recent plastics in the sampled beaches and so with low degradation and thus lower metal and/or metalloid adsorption capacity, compared to the diversity of plastics that we sampled (e.g. shape, size, age). For the literature that we have collected considering similar works and with the same acid extraction, i.e. Carbery et al. (2020) Maršić-Lučić et al.

Table 3
Mean ± SD metal(oid)s levels measured in our study and levels reported in other studies on coastal (micro)plastics collected from sediment.

Samples	Maximum concentration values (μg/g)												
	Fe	Mg	Mn	Zn	Pb	Sr	As	Cu	Cr	Cd	Ni	Co	Ref
Beached plastics and MPs	6.50 * 10^3 ± 4.69 * 10^3	2.65 * 10^3 ± 1.89 * 10^4	5.91 * 10^2 ± 4.26 * 10^3	7.37 * 10^2 ± 5.29 * 10^3	5.64 * 10^2 ± 4.05 * 10^3	7.25 * 10^1 ± 5.25 * 10^2	3.95 * 10^1 ± 2.78 * 10^2	1.83 * 10^1 ± 1.36 * 10^2	2.30 ± 1.62 * 10^1	1.21 ± 8.69	1.79 ± 1.22 * 10^1	1.15 ± 7.95	This study
Beached MPs	NA	NA	NA	NA	4.34 * 10^1	4.07 * 10^1	0.35	NA	9.83	0.22	NA	0.34	(Acosta-Coley et al., 2019)[a]
Coastal MPs (i.e. beach, bay, river sediment)	NA	NA	1.75 * 10^2	9.52 * 10^1	1.84 * 10^1	NA	1.53	1.43 * 10^2	2.77	1.15 * 10^1	NA	NA	(Carbery et al., 2020)[b]
Beached MPs	2.28 * 10^2	NA	9.00	8.00	NA	NA	NA	1.00	NA	NA	NA	NA	(Vedolin et al., 2017)[c]
Beached MPs	8.85 * 10^1	NA	8.25	3.61	NA	0.85	NA	0.61	0.74	5.4 * 10^{-3}	0.27	NA	(Maršić-Lučić et al., 2018)[b]
Beached plastic pellets	3.25 * 10^2	NA	NA	38	1.10	NA	NA	7.00	NA	0.59	2.22	NA	(Souza et al., 2022)[d]

NA not available.
[a] HF and HNO3 (8 mL:3 mL) followed by HNO3 (3 mL) and HCl (3 mL).
[b] 20 % Aqua Regia with HNO_3 and HCl (1:3).
[c] HNO_3 (10 mL, 1:1), HNO_3 (5 mL), H_2O_2 (3 mL), 30 % (V/V), followed by HC (10 mL).
[d] HNO_3 (2 mL), HCl (2 mL), and H_2O_2 (2 mL), 30 % (V/V).

(2018), our study is the one reporting the highest maximum values of metal(oid)s content and general high mean levels, for most of the studied metal(oid)s, found in plastics collected from beaches. At last, in the several similar studies consulted, the elements studied (at least for the ones in common) follows roughly the same order from their maximum levels to lower ones quantified in beached plastics (Table 3). For instance, Fe, Mn, Zn and Pb concentrations were frequently found among the highest in the environmental plastics.

Frequently, the identification of some elements is reported to be related to others, used together as additives to confer a determined characteristic to polymers, namely pigmentation. For instance, Turner (2017) related the levels quantified for Pb ($3.77 * 10^3$ μg/g maximum concentration) to the presence of lead-chromate ($9.09 * 10^2$ μg/g Cr maximum concentration) as pigment additives in the analyzed samples. As matter of fact, their measured maximum concentration of Cr in all samples was higher than the one maximum found in our study ($2.78 * 10^1$ μg/g), but not for Pb, as mentioned before. This could support even more that the high levels of Pb in our plastic samples are more due to adsorption from the contaminated environment. As matter of fact, among the twelve selected elements that were analyzed in this study, Fe, Zn, and Pb were among the five elements with the highest maximum concentrations reported in the plastics collected, reflecting the tendency for adsorption of local metal(oid)s by plastics, as it will be discussed in the next section. Therefore, through analysis of metal(oid)s content in the plastic debris from sediment beaches, relevant information on the pollution status of marine areas might be reported.

3.3. Metal(oid)s content by plastic classification criteria

3.3.1. Beach

Substantial lower levels of metal(oid)s were measured in the new commercial plastics with significant differences comparing to the environmentally exposed plastics (Mann-Whitney, $p < 0.05$). Total metal (oid)s content in plastics in the selected beaches resulted as follows: Beal > Portman > Islas Menores > Calblanque (Fig. 4), with the highest metal (oid)s quantification identified in the most anthropogenic influenced marine areas (with significantly higher levels) (Pairwise comparisons, $p < 0.05$). Overall, Beal had the highest content in metal(oid)s in the sampled plastics (with significant differences from all remaining beaches), while Islas Menores had samples concentrating the lowest metal (oid)s levels determined. Nevertheless, in Portman, the two highest contaminated samples were found, as represented by the two high outlier values for metal(oid)s concentrations, resulting in significant differences with all the other beaches as well. The significant differences between the metal(oid)s content of the most contaminated beaches emphasizes the high and higher metal contamination observed for Beal, justified by its close Mar Menor geographical position to the former mining exploitation, concentrating more trace metals there. Moreover, the outliers observed for Calblanque, which was, overall, the lowest contaminated beach in this study, evidence the high diversity of plastics and associated elements they carry. The high heterogeneity of plastics in the Mediterranean water was reported in the survey Suaria et al. (2016), particularly their different status of degradation. Once Islas Menores and Calblanque had lower and similar levels of metal(oid)s content between each other, no significant differences (Pairwise comparisons, $p > 0.05$) were observed only between these two less human disturbed beaches.

Beal and Portman are adjacent zones for the mountains of the mining exploitation area (La Unión). Ergo, the residuals and accumulated metal (oid)s on sediment particles from the old mining have been transported through surface waters, mainly originated by strong rainfalls and floods, containing the dissolved metal(oid)s (leached) and also carrying sediments associated with them, arriving the coastal waters of Mar Menor and Mediterranean sea (Bayo et al., 2019; Robles-Arenas et al., 2006). Hence, water allows both transportation and higher interaction of the pollutants with other particles, as plastics, in this case, which end up deposited on the beach sediment. Pb, Fe and Zn were formerly metals exploited in the mine (Martínez-López et al., 2021), which activity stopped from >25 years ago. Yet, this area was extensively exploited over around 2500 years (Oen et al., 1975). These three metals were found with higher levels in the plastics collected from the referred most anthropogenic pressured beaches (Fig. S3). The outlier high values of As for Portman samples also reflect the presence of this metalloid in the sediment (Martínez-López et al., 2020), which could explain the dark-colored sediment there, justified by the mining activity. Soil samples from adjacent areas of the mine region ,including Portman, area were found with $7.52 * 10^2$ μg/g (Martínez-López et al., 2020), which is similar to the maximum level reported for As in the plastics from this study ($6.75 * 10^2$ μg/g, Table 2), reflecting the highest adsorption capacity of plastics towards metal(oid)s from contaminated marine areas (Fig. S3). In turn, Sr, for example, was not exploited in those areas, which is demonstrated by its poor content in plastics from Portman and with higher levels in samples from Islas Menores and Calblanque (Fig. S3).

From the PCA analysis (Fig. 5) two-component model biplot was obtained to group the elements and relating them to the beaches, obtaining a cumulative variance of PC1 and PC2 of 68.56 % that

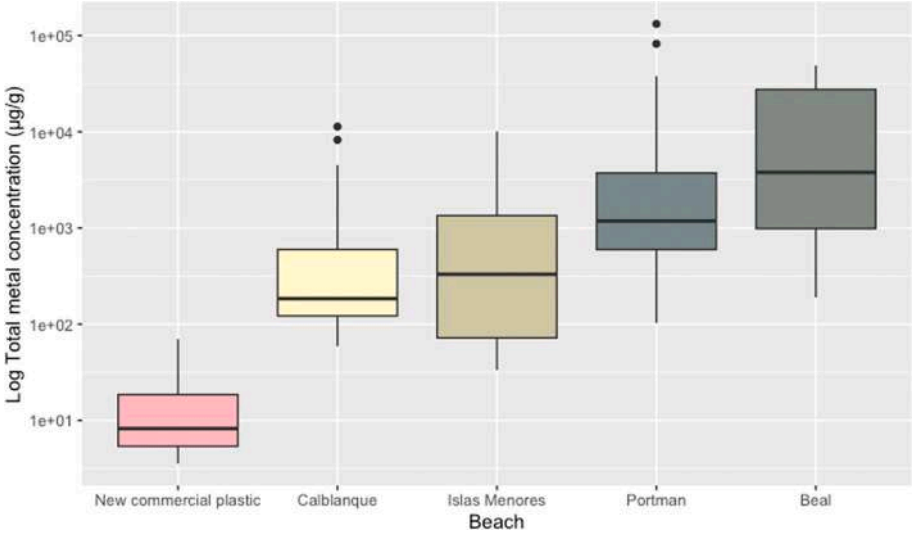

Fig. 4. Box plots representing the metal(oid)s content (μg/g) determined in all the plastic items by beach. Levels of metal(oid)s determined in the new commercial plastics were also included here.

explains the variation of the dataset. One first grouping can be observed for Cd, Co, Ni, Pb and Zn concentrated in the samples from Portman beach and also related to the highest more dispersed levels found for Beal. Exploitation of lead-zinc in the mine explains the close correlation observed for Pb and Zn. In addition, As, Cu, Fe and Mn also seemed to form a second group and more associated to samples from Portman beach. On the contrary, Sr was isolated from other elements, being the element more related with PC2 contrary to the other, and its different behavior regarding its levels in plastics according to criteria was observed before in the box plots (Fig. S3), explaining its association with more samples from the less anthropogenic influenced beaches. All elements in the PC1 were positively correlated; this plot explains 58.17 % of the data variation, the majority, thus the metal(oid)s are potentially related to their adsorption by plastics in common from the beach environment. The 10.39 % of explanation of the data variation of PC2 that correlated negatively 2 groups of elements might be indicative that the second group (in the negative axis) was more influenced for Portman beach, whereas the other elements were most found in Beal plastics. Moreover, the most distant elements were As and Sr, and we said before that Sr was found in low concentrations in Portman and that quantification of As in plastics was strongly related with its presence in sediment of Portman beach, reflecting this in the PCA. From one hand, elements could be unlikely correlated due to its co-presence as additives, as no relation in the biplot was found, for example, for lead-chromate or iron-cobalt (Klöckner et al., 2021). On the other hand, the strong contamination of the more anthropogenic areas with respect to the before mentioned metal(oid)s could explain why some typically additive related metal(oid)s were not grouped together. In other words, the high anthropogenic pressure masked, at some extent, the other cause-relations of metal(oid)s regarding their presence in plastics. This evidence demonstrates the strong influence of anthropogenic pressure of marine areas concerning metal(oid)s content in the local plastics.

Carbery et al. (2020) and Vedolin et al. (2017) also demonstrated higher metal(oid)s content in plastics collected from anthropogenic/industrial influenced marine areas. Our previous survey, conducted in the same beaches of this work, confirmed a higher Hg (the only metal studied) content in plastic debris from Portman and Beal beaches with higher anthropogenic influence (Santos-Echeandía et al., 2020). Furthermore, Souza et al. (2022) found higher metal load in beaches with river input more than with ocean input. These findings can be related to our study as we found lower metal(oid)s content in the beaches with ocean input (Portman and Calblanque) if we neglect the anthropogenic influence. In other words, for the anthropogenic beaches Portman and Beal, the one containing lower metal(oid)s levels in plastics was Portman, as the renewing of water (carrying higher or lower trace dissolved metal(oid)s in open water) is usually higher, thus metal(oid)s flow with currents in a greater extent. Onrubia et al. (2021) found higher concentration of metal(oid)s in MPs (measured in the biofilm covering their surfaces) collected from other Mediterranean beaches (NW Italy) than in their surrounding water (2 orders of magnitude). Moreover, their average levels found for hazardous substances Pb and As sand were lower than the ones reported in this study (4.8 and 4.79 * 10^{-1} μg/g, respectively). This reflects that different areas have different metal pollution and that is reflected in the plastics collected from the respective sites.

3.3.2. Zone

The analysis of metal(oid)s content by zone was conducted using Portman and Calblanque samples as they presented a higher number of plastic items, and with less discrepancy between zones in the case of Portman (Table 1). For most of the elements identified in the plastic samples, their highest content was observed in the coastal line region (Fig. 6), representing the recently deposited plastics in the sediment from sea. This observation might be explained due to high adsorption interactions between metal(oid)s and polymers occurring in the surface water layer, as dissolved metals are more concentrated there (Tovar-Sánchez et al., 2014) as well as buoyant polymers. On the other hand, in the middle and upper regions of the beach, degradation action is more severe due to erosion (mechanical) and UV exposure (chemical), thus, some metal(oid)s can be dissociated from the plastics. Also, the upper plastics could be present there because they were thrown away directly from land to the sediment, avoiding contact with water where interaction with metal(oid)s essentially occurs. Calblanque was the only beach presenting significant differences concerning metal(oid)s content among zones (Pairwise comparisons, $p < 0.05$), as trace-element levels in the middle beach were different (and lower) from those in upper and coastal lines. Although no significant differences between beach zones were estimated for Portman (Pairwise comparisons, $p > 0.05$), coastal lines containing the highest meta(oid)s content (Fig. 6a) in plastics supports this tendency, also observed for Hg in the study of Santos-Echeandía et al. (2020). In addition, Souza et al. (2022) determined that metal content is intertidal region dependent, reinforcing the influence of coastal sediment to metal content in plastic debris. The fact that Calblanque allowed to collect only 3 samples in the coastal line however having the highest metal(oid)s content in the plastics from this zone (Fig. 6b) supports coastal surficial waters as the principal locations where metal(oid)s and plastics interact. Moreover, the weathering from strong UV action and high erosion occurring in the upper beach zones could lead to dissociation of the previously adsorbed/added pollutants from plastic surfaces. This may suggest that the more recently deposited plastics debris from water hold the metal(oid)s for a while.

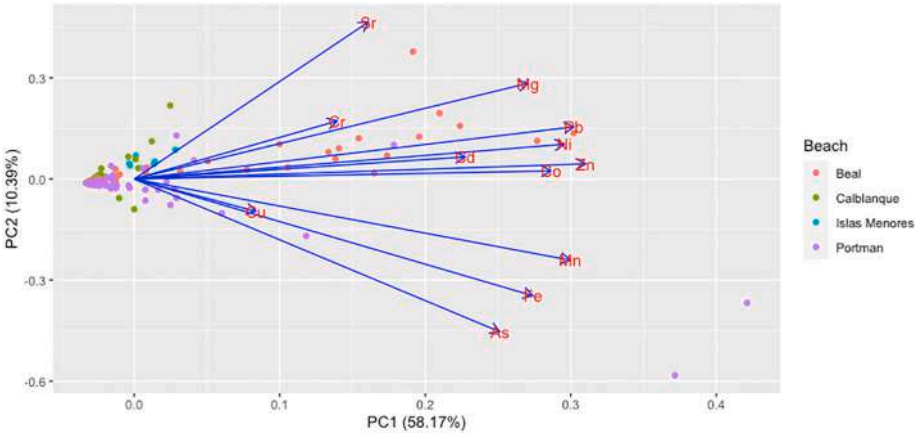

Fig. 5. Biplot from PCA analysis representing the metal(oid)s concentrations in plastics according to the sampled beaches. Vectors represent the elements, and the colored points show the beaches.

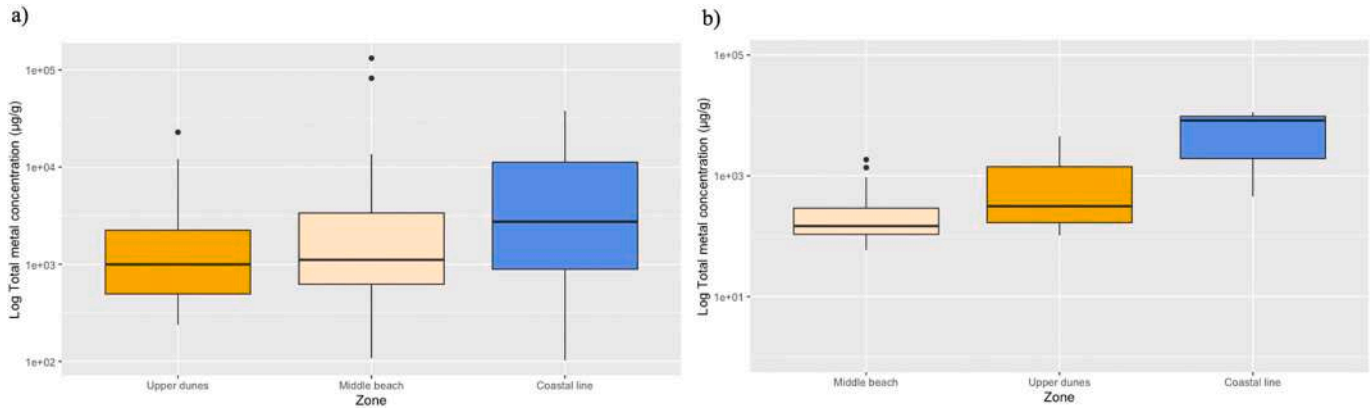

Fig. 6. Box plots representing the Total metal(oid)s content (µg/g) determined in all the plastic items by zone for (a) Portman and (b) Calblanque beach.

3.3.3. Polymer

PPUR and PVC based plastics concentrated high levels of metal(oid)s in this study (Fig. 7), despite only 0.5 and 1 %, respectively, of the plastic samples corresponded to these polymers. Overall, metal(oid)s content in plastics by polymers followed the order from more concentrated to less: PS > PUR > PP > PVC > PE. Even so, no statistical differences on metal (oid)s content were found between polymers (Pairwise comparisons, $p > 0.05$), maybe due to the differences in the number of samples by category and to the high scattering values for PP and PS. The priority pollutants Pb and Cd showed their higher concentrations in PVC plastic (Fig. S4). This observation is in line with other works, who reported high association of PVC polymer with metals, namely Pb (Salvaggio et al., 2019) and Cd, used mainly as stabilizers (Turner, 2018). This can be justified either with intentional addition of these and other elements to PVC or to its natural adsorption capacity, which could be improved due to degradation and chemical transformation, as formation of new functional groups able to bind available metal ions in water. Moreover, PUR is a porous polymer which is a common feature proven to enhance surface rugosity (Turner and Lau, 2016) and PVC has chlorine-based groups in its composition, so these polymers reunite ideal traits for uptake of metal and metalloid ions from water (Rodrigues et al., 2022). On the other hand, floating plastics as PE and PP are more subject to UV action which can, at the same time, remove weakly bonded metal(oid)s from their surfaces (Acosta-Coley et al., 2019).

3.3.4. Color

The metal(oid)s load in plastics by color followed this order: colorless > black > brown > white > green > yellow > blue > red > purple > orange > pink > grey (Fig. 8). From these results it is clear that grey plastics contained lower metal(oid)s concentrations, presenting significant differences from black and brown plastics (Pairwise comparisons, $p < 0.05$), which were the colors that accumulated higher levels of metal (oid)s. The low levels observed for blue color (despite the high number of blue plastics found in this study) plastics concerning total metal(oid)s content also resulted in differences from black and brown plastics. In general, dark colored as brown and black plastics concentrated the highest levels of metal(oid)s (Fig. 8), with brown presenting significant differences from pink, white and yellow plastics (Pairwise comparisons, $p < 0.05$), apart from the significant differences of both brown and black plastics to blue and grey ones, as mentioned. The tendency of metal(oid)s to be associated with darker plastics had a few exceptions, as Co for red plastics (Fig. S5), and Cr who presented the highest levels in red and orange plastics (Fig. S5), apart from brown. This is in agreement with Filella and Turner (2018) who attributed Cr content to brown-, red-, yellow- and orange-colored plastics. However, a few peak values concerning metal(oid)s concentrations were observed for individual colorless and white/yellow-colored plastics. Visual characteristics as abrasion of plastics may represent aged polymers which suffered from higher weathering, grinded down the original color (Endo et al., 2005; Fisner et al., 2017). Thus, sorption capacity of plastics with these colors may be enhanced to favoring the metal binding from the surrounding water. One thing to note for our study is that no distinct color tone was solely attributed to aged plastics. However, we assumed colorless to be related to mainly aged ones (our data had colorless plastics from degradation status 1 to 4, but mainly with degradation level of 3 and 4), as discoloration is a sign of degradation. As matter of fact, transparent/colorless plastics can have lighter or darker tones, and some literature associate the yellowing/darkening (Acosta-Coley et al., 2019) of initially clear colorless plastics with oxidation over UV exposure of the pieces. This reaction over polymers can increase of the carbonyl index of contained elements as thermal stabilizers (Turner and Holmes, 2011), explaining the initial color change. Therefore, color might be related to identification of aged polymers (due to mainly oxidation effect) and its higher metal(oid)s load estimated reflects the higher adsorption capacity of environmentally exposed plastics. Intentional high metal(oid)s load in plastics for other reason than uptake from environment is highlighted by the high metal(oid)s content measured in the black plastics of this study, as only 5.0 % of the plastics collected were black. Some of them probably came from wasted electric and electronic equipment known to contain a higher number of metals (Haarman and Gasser, 2016; Shaw and Turner, 2019). Therefore, one would expect darker plastic showing high variety of elements, from additives to adsorbed ones.

From our knowledge, field studies on quantification of metal(oid)s content in plastic samples from marine or aquatic environments taking into account the color to relate and analyzing their data by this plastic feature is limited (Carbery et al., 2020; Fernandes et al., 2020; Li et al., 2023; Santos-Echeandía et al., 2020). Souza et al. (2022) found higher Total metal content in white plastics, followed by the black ones which contained the highest concentrations for Zn and Pb. Conversely to the previous mentioned study and to the present one, Turner (2017) obtained the highest maximum values of the hazardous substances (Cr and Pb) for orange colored plastics. This reveals the diversity of plastics in nature (concerning their characteristics and local of sampling) and in their metal(oid)s load. Overall, in this study Pb was represented with high values in all plastic colors (Fig. S5), being in agreement with its former wide application as a pigment in plastic manufacturing (Turner and Filella, 2021). Even so, Pb levels were more concentrated in black and red plastics. The frequent association of hazardous substances with plastics as pigments demonstrates their wide application and ongoing presence of them on colored plastics that storage the metal(oid)s and carry them to long distances and to several environments. For instance, high outlier levels and also more scattered observed for Co on blue colored plastics (Fig. S5) might be explained by its use as a pigment for blue pieces. As matter of fact, Prunier et al. (2019) found significantly higher levels for Co on colored new packaging plastics than in the white ones. Moreover, Cu that is also associated with blue plastic pigmentation

(i.e. phthalocyanine blue pigment) (Carbery et al., 2020) showed one of its highest values in a blue plastic sample (BL18_LC4) among all sampled plastics in our study. Carbery et al. (2020) attributed the high levels found for Cu in their data to the high number of blue plastics found (most frequent color they sampled) on the coastal study area and to be justified to its potential use as a pigment. Nonetheless, overall, blue color plastics in our study contained low metal(oid)s concentrations for elements, which may suggest that Cu was not adsorbed in a great extent from environment (but it is present as an additive). Furthermore, the high number of blue plastics collected reunited a high diversity of characteristics, ones being effective to enhance metal(oid)s adsorption and others not, justifying the scattered values observed for some metal (oid)s concerning blue color (Fig. S5). Therefore, the different adsorption behaviors observed may be justified by the stronger influence of other plastic or environmental characteristics apart from color. Some elements are included together as pigments in plastics to apply a variation for some colors, as, for example, the addition of Zn to cadmium sulphite (CdS) that is used to color plastics with yellow to obtain a more green variation color of yellow (Fernandes et al., 2020; Turner, 2019). In our samples, Zn outlier high values were observed for green colored plastics (Fig. S5). Overall, Cr was observed with high values in green plastics, and despite being concentrated in yellow plastics with high levels, showing their association, did not presented the highest levels for yellow color (Fig. S5). Thus, environmental colored plastic will always have metal(oid)s as pigments initially added, which some of them could be removed through intensive weathering. At last, the association of some elements as pigments in plastics with determined colors, which was observed for our samples, do not explain, or bias the high total metal (oid)s levels found. In the present study, substantial low levels were also determined for new commercial plastics which presence is attributed to additive application, as they were not exposed before. Therefore, from these results we suggest that metal(oid)s content observed in the plastics collected are, in most of the cases, better justified by adsorption from environment than for intentional addition.

3.3.5. *Degradation status*

From our analysis, higher metal(oid)s content was found in the most degraded (stage 3 and 4) beached plastics (Fig. 9). Significant differences in total metal(oid)s content of plastics were found between the less degraded 1 and more degraded 3 and 4, as well as significant differences (Pairwise comparisons, $p < 0.05$) were observed between plastics with degradation level 2 and the most degraded plastics stage 4. Therefore, evidenced aged plastics (degradation level 4) contained significant higher metal(oid)s content than the less degraded plastics, despite the smaller number of items exhibiting stage 4 of degradation that was found in the sampling areas. This is the main evidence for the strong adsorption capacity of aged plastics towards metal ions in marine environments. Moreover, these results support our prior assumptions that the elements determined in the plastic samples were acquired essentially from adsorption on environment. Higher metal(oid)s load in more degraded plastics is in agreement with several other authors (Acosta-Coley et al., 2019; Santos-Echeandía et al., 2020; Wang et al., 2020). Nonetheless, despite longer time on environment means more time of plastics to interact with metals and metalloids, weathering can also remove the initial additive plastics and also the adsorbed ones (Andrady, 2017), apart from surface modification favoring the metal(oid)s binding. On environment, plastics are subject to several conditions (erosion, UV, ionic strength, pH changes, biofouling), which some promote changes in polymer characteristics to modification of their surfaces (e.g. fragmentation, cracks, porosity, microbial activity, organic matter complexes, oxidation, formation of new functional groups) that become more reactive through degradation, and so adsorption capacities towards metal ions is strengthened. Thus, those observations illustrate the strong adsorption capacity of aged plastics and support degradation as a key role for the uptake and storage of metal(oid)s from water, more than other characteristics (e.g. polymer, color) or more than due to additives.

Overall, in the samples of the present study, metal(oid)s load was proportional to the increasing of degradation status of plastics (Fig. 9) as well illustrated by Fe and Pb boxplots (Fig. S6). However, some fluctuations were observed for Sr and Cr with several outlier values in plastics with status degradation 2 (Fig. S6). This observation could mean that the presence of Sr and Cr was less to do with low availability of those metals in environment, and more, in the case of Cr, to its presence as additive. Once again, Sr demonstrated a slightly different behavior in plastics concerning the remaining elements analyzed by criteria in this study, as exemplified in the biplot (Fig. S7) where Sr is not correlated with other elements, and it is distant from sample points representing the more degraded samples. Concerning the metal(oid)s content by degradation status of plastics from the PCA analysis, grouping of As, Cu, Fe and Mn is suggested to be associated with the degraded pieces (yet with lower concentrations) and the correlation of Co, Cd, Ni, Pb, and Zn is associated more with their high levels in most part of 3 and 4 level degraded plastics. Prunier et al. (2019) also related As to Fe in their PCA analyses, justifying affinity of As for Fe oxides which helps their concentration in soils (Martínez-López et al., 2020). The PCA also showed correlation of Fe with Mn, that could be explained by the Mn—Fe oxides which are frequent in this mined zone (Conesa and Schulin, 2010). This supports plastic metal(oid)s content as being greatly influence by the local pollution and their potential use as pollution monitors. In addition, Cr and Mg were also correlated with each other, yet Mg presented much higher levels. From the biplot is also possible to observe Pb to be highly associated with 3 and 4 degradation status plastics (Fig. S7), also

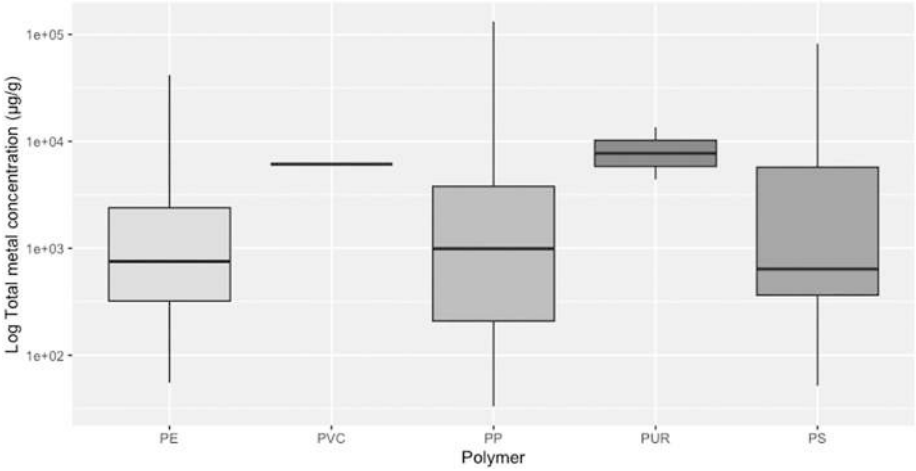

Fig. 7. Box plots showing the metal(oid)s load (µg/g) determined in the plastic samples by polymer type.

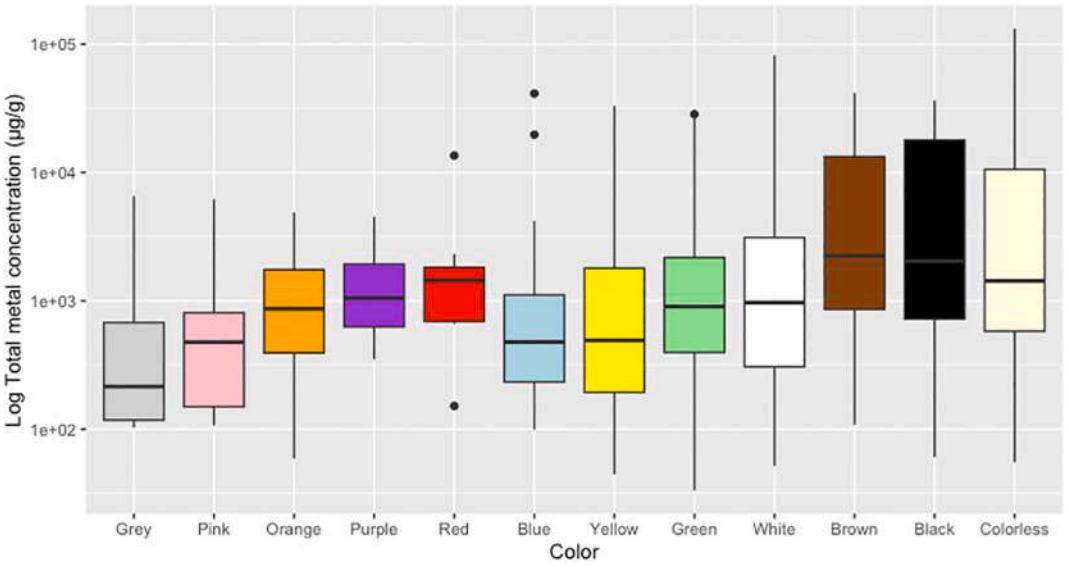

Fig. 8. Box plots illustrating the metal(oid)s concentrations (µg/g) for all the plastic items by color.

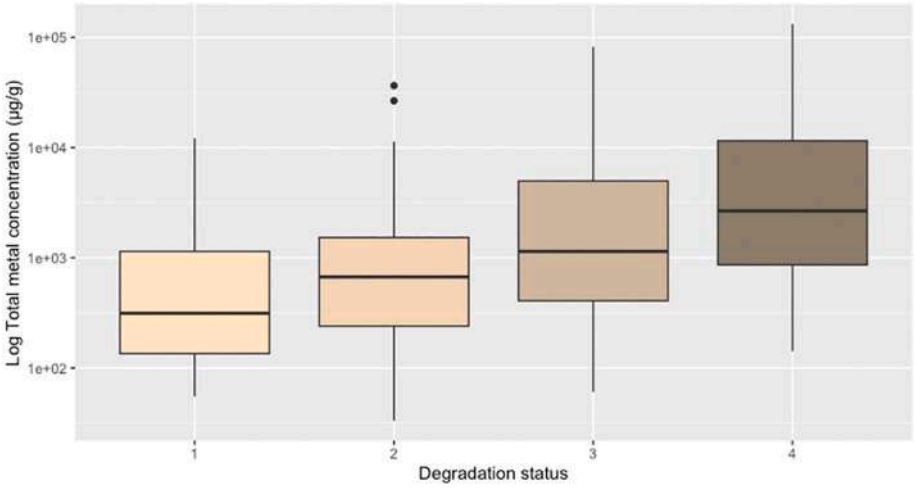

Fig. 9. Box plots representing the metal(oid)s concentrations (µg/g) for all the plastic items by degradation degree.

representing the high values for Beal and Portman, as demonstrated before. Nonetheless, Pb was also represented in the less aged plastics, showing its relation to additive inclusion in plastics.

PVC polymer, known to have Pb on its composition and to be an efficient adsorbent (Rodrigues et al., 2022), as observed before, was only represented by 0.5 % of the collected samples. As matter of fact, Pb was quantified with low levels in the new commercial plastics used in this study (Table 2), suggesting, once more, that its presence in the environmental plastics is indeed more due to their uptake from environment. Moreover, this metal was found in all the collected samples (especially in the beaches with higher anthropogenic pressure) with a high diversity, namely different polymer composition, and its highest levels were determined in the more degraded plastics. Therefore, those observation represent another finding supporting the strong influence of plastic age and also polymer type in the sorption of metal and metalloid ions from polluted environments.

3.4. Environmental implication of plastic associated metal(oid)s and contribution of (micro)plastics to metal pollution monitoring

In order to associate the levels of metal(oid)s with the different characteristics of plastics, the 10 samples with the highest Total concentrations (sum of metal(oid)s concentrations) measured (Table S2) considering all plastic samples have been selected ($3.3 * 10^4 - 1.32 * 10^5$ µg/g total content). The piece containing the highest sum value had the highest maximum concentration of As and overall high levels for the other metals measured. More important to highlight, is that these samples either had degradation status of 3 or 4 (with one exception of a black colored plastic) and were collected from Beal and Portman beaches. This confirms aging and local as the factors most influencing content of metal(oid)s in beached plastics. Accordingly, the plastic pieces concentrating the higher levels for all the selected elements have very different plastic criteria (according to our classification), which suggests local being a factor of the most importance concerning influence of metal(oid)s accumulation on plastics, as they have adsorption capacities by themselves. Therefore, this is another contributive argument that plastics can identify locals of high pollution related to anthropogenic influence there, even ancient, supporting role of beached plastics as pollution monitors.

Moreover, we suggest the use of selected more degraded polymers to be used as monitors as they were potentially longer deposited in the study area with higher capacity to adsorb the local pollutants. In turn,

new plastics have more metal(oid)s content related to the additives included, despite their unmodified surfaces can also form bonds with pollutants on environment. Among the previously consulted literature of similar studies, our study is the one reporting higher maximum values of metal(oid)s content found in plastics collected from beaches, considering the higher number of elements we analyzed, to the best of our knowledge. The anthropogenic influence in Beal and Portman is the main responsible for this. Local (human disturbance) and degradation status were undeniably the factors most impacting metal(oid)s content of plastics in our study, related to their adsorption capacity towards metal(oid)s in marine areas Therefore, we propose the use of sampled (micro)plastics from beach sediment as potential efficient monitors for metal pollution, especially the ones with aging characteristics.

Managements tools were previously developed to attenuate the metal pollution as a result from mine exploration over so many years with consequent spreading of contaminated sediment to surrounding beaches. This is the example of sediment removal proposal for Portman beach due to aggravation of sediment reached in hazardous substances (Conesa and Schulin, 2010). Since sediment is a major contributor to contamination of water, this could be avoided, and, thus, plastics present in surface water would not adsorb, carry, and concentrate high levels of hazardous substances, as interactions mainly occur in the surface layer. Additionally, plastics, especially the small ones, would be more effectively removed from sediment. However, this can bring even worse effects as resuspension of contaminated particles release chemicals which promote toxicity effects on local biota, threatening the ecosystems. Martínez-López et al. (2021) reunited studies investigating the health risk of this mine region and mentioned the mixture of sediments with limestone filling potentially capable to remediation of contaminated sediments. Furthermore, some studies have been contributing to the development of the use of phytoremediation solutions using plants with low or neglected translocation rate of metals, particularly to the soil, preventing from transfer to biota and potentially to humans by bioaccumulation (Conesa and Schulin, 2010; Martínez-López et al., 2021). Therefore, this work can be an important contribution to pollution dispersion models, despite the ones created for only dispersion of metals by water and sediments, since new and increasing introduction of emergent MPs can change biogeochemical cycles, that can add insights for the development of management tools for dealing with this environmental problem.

4. Conclusion

Considering the environmental plastic samples collected from SE Spanish beaches and all the selected elements quantified on them, the mean levels determined were sequenced as follows: Fe > Mg > Zn > Mn > Pb > Sr > As > Cu > Cr > Ni > Cd > Co. The major conclusions regarding our classification criteria of the items collected (by beach, zone, polymer, color, and degradation status) concerning metal(oid)s concentrations is related to plastics: 1) from beaches with high anthropogenic influence, 2) recently deposited in the coastal lines, 3) composed by PUR and PS polymers, 4) darker (black and brown) and colorless (discolored with signs of degradation) - indicators of aged polymers with longer residence time in environment, and 5) with moderated to severe degradation degree – suffering from more chemical and physical changes as oxidation, enhancing adsorption capacity of plastics towards metals and metalloids. The high diversity of plastics found (concerning their different characteristics) explains the variation observed for the metal(oid)s content. Location (i.e. old mining exploring area) and age (degradation) were found in this study to be the main responsible for the high content in metal(oid)s found in our plastic debris.

In addition, laboratory studies are frequently performed resorting to high metal(oid)s concentrations, even when exposure to organisms is involved to investigate the effects of plastic vectorization. Considering the trace metal and metalloid levels existing in seawater, the exposure to more environmentally realistic concentrations is recommended in a study on ecological risk assessment.

Therefore, the present work is of major importance to help and advice other researchers in the planning of their experiments under the metal(oid)s-plastics interaction investigation. Moreover, the high variety of elements and the diversity of plastics found in this study may reflect the capacity of plastics to storage (potentially adsorbed) metal (oid)s (i.e. priority pollutants) and transport them over long-distances to become bioavailable to organisms. From our results, marine deposited plastics are suggested to reflect the local metal(oid)s content of the sampled areas, thus, this work supports plastics as potential monitors of metal environmental pollution.

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CRediT authorship contribution statement

Contribution of the authors: Joana Patrício Rodrigues: investigation, methodology, writing - original draft, review and editing. José Rivera-Hernández: investigation, methodology, review. Patrícia Bernárdez: ICP-MS analysis. Teresa Rocha-Santos and Armando Costa Duarte: resources, supervision, review. Juan Santos-Echeandía: conceptualization, methodology, ICP-MS analysis, resources, supervision, review and editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Juan Santos Echeandia reports financial support was provided by Spanish State Research Agency (AEI) and the Ministry of Science, Innovation and Universities (MICIU). Teresa Rocha-Santos reports financial support was provided by Portuguese Science Foundation (FCT). Armando Costa Duarte reports financial support was provided by Portuguese Science Foundation (FCT). Joana Patricio Rodrigues reports financial support was provided by Portuguese Science Foundation (FCT).

Data availability

Data will be made available on request.

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