Journal of Applied Phycology
https://doi.org/10.1007/s10811-023-03146-1

RESEARCH

From a heavy metal perspective, is macroalgal biomass from Madeira Archipelago and Gran Canaria Island of eastern Atlantic safe for the development of blue bioeconomy products?

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Received: 10 April 2023 / Revised: 9 November 2023 / Accepted: 14 November 2023

Abstract
Macroalgae are considered a valuable source of several compounds with nutritional, nutraceutical, cosmeceutical, and pharmaceutical applications. They are also used for crop fertilization and biofortification by introducing important minerals into the soil essential for crop productivity. At the same time, however, they are known bio-accumulators of some heavy metals. In this work, we assessed the content of 7 minerals considered as heavy metals in 25 macroalgae samples, comprising 4 greens, 9 reds and 12 browns, from Madeira Archipelago, Portugal, for their potential use as blue bioeconomy products. These heavy metals included zinc (Zn) with concentrations that ranged from 1.95 – 242.65 mg kg^{-1} dw, nickel (Ni, 0.6 – 34.78 mg kg^{-1} dw), copper (Cu, 0.42 – 7.98 mg kg^{-1} dw), chromium (Cr, 0.47 – 45.74 mg kg^{-1} dw), cadmium (Cd, 0.1 – 2.58 mg kg^{-1} dw), lead (Pb, 0.05 – 2.79 mg kg^{-1} dw) and mercury (Hg, 0.03 – 8.49 µg kg^{-1} dw). We also analysed 22 samples of beach-cast macroalgae from Gran Canaria Island, Spain, collected from November 2016 to November 2019. The same heavy metals were assessed with their concentrations that ranged as follows: Zn (11.41 – 42.20 mg kg^{-1} dw), Ni (3.17 – 17.78 mg kg^{-1} dw), Cu (1.85 – 4.20 mg kg^{-1} dw), Cr (6.08 – 37.98 mg kg^{-1} dw), Cd (0.02 – 0.11 g kg^{-1} dw), Pb (0.16 –5.42 mg kg^{-1} dw) and Hg (3.59 – 31.00 µg kg^{-1} dw). These concentrations are all within the normal ranges reported in earlier studies in low industrialized areas, except for the brown algae *Gongolaria abies-marina* and *Sargassum vulgare* with high mean ($\pm$SD) Cd concentration (1.91 ± 0.36 and 1.75 ± 0.07 g kg^{-1} dw respectively). Our results suggest that most of the biomass prospected in these localities covered in the present study would be a viable source of materials for the development of a blue economy industry with emerging products following the European Union directives.

Keywords Beach wrack · Heavy Metals · Chromium · Cadmium · Lead · Mercury

Introduction

Macroalgae are macroscopic photosynthetic organisms differentiated into three main groups as green (Chlorophyta), red (Rhodophyta) or brown (Phaeophyceae) based on the prevalence of their photosynthetic pigments (Belghit et al. 2017). Their occurrence in a locality depends on their preference for sheltered bays or exposure to strong waves and currents. Additionally, some species thrive in the intertidal and others in the subtidal, down to depths where light becomes a limiting factor for photosynthesis (Lähteenmäki-Uutela et al. 2021). Macroalgae are often envisioned as an additional biomass that could help in the effort of developing new feed and food products to overcome serious concerns regarding the future of mankind food security. The global human population, which is expected to reach 9.735 billion in 2050 and 10.875 billion in 2100, will certainly reach an unsustainable

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Published online: 11 December 2023

level (United Nations 2019), exerting an extreme pressure on the already scarce natural resources including food. The threat from climate change and ultimately the protection of the ecosystems and life on earth are other serious concerns, driving the need for an energetic shift from fossil fuels to more sustainable and eco-friendly sources (del Río et al. 2020). Macroalgae could play an increasingly significant role in addressing these challenges with more and more macroalgae being screened for multiple applications, including as novel foods (Lähteenmäki-Uutela et al. 2021), feeds (Maia et al. 2019), cosmetics (Ariede et al. 2017), bioplastics (Lim et al. 2021), plant protection and crop improvement (Hamed et al. 2018), biofuels (Chen et al. 2015) and pharmaceuticals (Nunes et al. 2020a).

Sources of macroalgal biomass include harvesting of natural populations, harvesting of beach-cast macroalgae and cultivation of macroalgae. Macroalgae harvest contributed 1.1 million tonnes while cultivation reached up to 34.7 million tonnes, or about 97% of the worldwide macroalgal biomass production in 2019 (Cai et al. 2021). More than 221 macroalgae species are known to be used worldwide, with 145 species for food and 101 species for the extraction of phycocolloids (Zemke-White and Ohno 1999). The production of macroalgal biomass is economically and sustainably appealing in the sense that it does not compete for arable land or freshwater resources (Hughes et al. 2012). Harvesting of natural populations is an attractive possibility, but it needs to be strictly regulated to prevent environmental impacts thus setting a quantitative constraint on its extensive development (European Commission 2022). On the other hand, beach-cast biomass is a natural resource that is mainly composed of macroalgae detached naturally from the sea bottom and/or drifting macroalgae which cast ashore (Mossbauer et al. 2012). Location where biomass is deposited as beach-cast depends on the characteristics of the beach shore and wrack buoyancy and hydrodynamics, enabling the detachment, transport, and accumulation of the macroalgae (Chubarenko et al. 2021). The biomasses generated through these natural phenomena have crucial environmental roles in protecting the coasts from erosion, providing organic matter to the local plants that work as sand immobilizers, trapping sand and maintaining the sand dunes (Portillo 2008). Therefore, the exploitation of beach-cast macroalgae should be limited to cases in which the beach-cast macroalgae are systematically being removed by the local authorities for sanitary or tourism-related reasons, to be dumped in landfills. Then again, climate change, pollution and other anthropogenic disturbances are known to be major drivers, modifying and/or intensifying the accumulation of beach cast macroalgae (Wade et al. 2020). It is the case, for instance, of the extensive proliferation of *Ulva prolifera* O.F. Müller "green tide" in Yellow Sea, China, due to the systematic removal of this species from large scale *Porphyra* aquaculture along the Jiangsu coast (Liu et al. 2013), as well as of the "green tide", i.e. thick green macroalgae mats of *Ulva intestinalis* L. (formerly *Enteromorpha intestinalis* (L.) Nees), that occurs along the shore of the Finnish Baltic Sea coast (Bäck et al. 2000). Likewise, the *Sargassum* spp. "golden tides", represented by *Sargassum natans* (L.) Gallion and *Sargassum fluitans* (Børgesen) Børgesen, have their biomasses increased regularly along the Gulf of Mexico during the summer months that accumulate in nearby beaches and into the Sargasso Sea, reaching even the west African coast (Smetacek and Zingone 2013). These macroalgal beach-casts of various origins can have enormous economic impacts as they tend to cover large expanses of the coastline, thus inevitably damage traditional fishery, affect local tourism and disturb aquaculture production (Oyesiku and Egunyomi 2014). In 2018, a substantial accumulation of pelagic *Sargassum* sp. biomass occurred in the Mexican Caribbean coast. Decomposition of the biomass produced high amounts of ammonium and hydrogen sulphide, causing hypoxic conditions in the water and increased water turbidity that resulted in the death of 78 animal species, including demersal neritic fish and crustaceans (Rodríguez-Martínez et al. 2019). To mitigate the negative local impact of this phenomenon, there is a need to develop new uses of this biomass to avoid its wastage. An alternative could be the possible integration of this biomass into a feedstock to supply the future demands for animal feeds, as well as for food, fuels, materials, and fertilizers (Chubarenko et al. 2021). The economical use of this biomass greatly depends on its cleaning process. For example, German regulation specifies that the agricultural use of eelgrass and macroalgae wrack should satisfy the following technical features, i.e., the wrack should contain less than 5% of stones, 0.5% of garbage in dry weight, minimal quantities of nitrogen, phosphorus, potassium, and trace values of heavy metals. Macroalgal biomass should be previously composted or fermented to get approval for its use as fertilizer or soil conditioner (Mossbauer et al. 2012). Nevertheless, this biomass is continuously being studied as a biofertilizer due to its favourable features such as the presence of biological compounds that can act as growth factors, and of mineral nutrients which improve soil organic matter and humus content, and ultimately its structure (Greger et al. 2007).

The amount and composition of mineral contents, which can reach up to 87% of dry matter, is a valuable information when evaluating macroalgae for their targeted application (Nunes et al. 2017, 2019, 2020b). The mineral fraction is composed of major elements such as P, Na, K, Mg and Ca which are present in mg g^{-1} dry weight (dw) and of trace elements such as Fe, Mn, Zn, Cu, Ni, Co, Cr, Pb and Cd present in µg g^{-1} dw. These composition changes depend on the macroalgal groups, their physiology, seasonality, environmental factors, and geography (Mabeau and Fleurence 1993; Ortega-Calvo et al. 1993). Macroalgae are a known source of essential minerals such as Fe, Mn, Cu, Zn, Co, Mo, Se and I whose concentrations could be much higher than those in higher plants (Mabeau and Fleurence 1993; Ortega-Calvo et al. 1993; Circuncisão et al. 2018). Several authors already recommended the use of edible macroalgae as a food supplement (Rupérez 2002; Rao et al. 2007; Astorga-España et al. 2015) and nutraceuticals (Mišurcová et al. 2011) due to their high mineral composition. Conversely, however, macroalgae efficiently accumulate heavy metals, which could limit their use as food, feed, or for other commercial purposes (Bonanno and Orlando-Bonaca 2018; Franzén et al. 2019). This efficiency of accumulation depends on the macroalgae species, the heavy metal concentration in their surrounding environment and its bioavailability, which is inversely proportional to seawater salinity (Greger et al. 2007).

Apparently, there is no agreement on a common criterion to classify any particular chemical elements as heavy metals. Nonetheless, in this present work, a heavy metal is interpreted to include minerals with high density (> 5 g cm^{-3}) and with an atomic weight higher than 40.04, being five times denser than water (Velusamy et al. 2022). Based on this interpretation, a chemical classification of heavy metals is further proposed, taking into consideration their functional role and toxicity that can be differentiated. Heavy metals such as Cu, Ni, Mn, Fe and Zn are essential micronutrients for animals and plants but can become toxic at high concentrations (Corales-Ultra et al. 2019). A different set of heavy metals has no (As, Hg, Pb) or limited (Cr, Cd) biological functionality and has high toxicity to human metabolism, even at low concentrations (Khan et al. 2015; Paz et al. 2019). Although these heavy metals are ubiquitous, their concentration in the marine environment is increased by anthropogenic activities, including release of significant quantities of hazardous waste that contaminates the marine environment and causes ecosystem degradation (Akcali and Kucuksezgin 2011; Sá Monteiro et al. 2019). To develop a safe and economical use of macroalgal biomass for specific applications, e.g. as food, animal feed, fertilizers or biostimulants, their concentration of heavy metals should be assessed. Depending on its specific application, different standards on the allowable concentration of heavy metals in the macroalgal biomass may be set with legal implications following European directives, FAO and WHO guidelines. Nonetheless, only a restricted number of biological toxins have been described from edible and medicinal macroalgae (Higa and Kuniyoshi 2000). Very few cases of poisoning are known and even fewer of these are fatal, which have not been clearly attributed to the consumption of the macroalga itself but rather to epiphytic cyanobacteria contamination (Cheney 2016).

This present work explored the potentials of macroalgal biomass from Madeira Archipelago, Portugal, and macroalgal beach cast from Canary Islands, Spain, both in eastern Atlantic, for developing into downstream products. Madeira Archipelago has a total land area of 801 km^2. Its urbanization level is 313 inhabitants km^{-2}, higher than the average value of Portugal at 1122 inhabitants km^{-2} (DREM 2021). The archipelago of the Canary Islands has a total area of 7447 km^2 with 2,118,519 inhabitants, or a population density of 28,448 inhabitants km^{-2}. The largest island Gran Canaria has an area of 1 560 km^2 with 845,676 inhabitants or a population density of 542 inhabitants km^{-2} (La Guia de Gran Canaria 2023). Both these island groups have a low level of industrialization with no known proliferative source of heavy metal emission. While heavy metal pollution is not suspected, domestic sewage pollution from its high population density, including its high number of visitors during winter, could potentially be a problem. Heavy air traffic with potential contamination from aviation fuel could also be a source of heavy metals. Macroalgae being efficient in accumulating heavy metals, the focus of the present study is therefore on screening the concentration of heavy metals such as Zn, Ni, Cu, Cr, Cd, Pb and Hg in 25 macroalgal species collected in Madeira Archipelago and 22 samples of macroalgae beach-cast from Gran Canaria Island, to determine if any of these heavy metals might have accumulated in these biomasses thus limiting their potential use for the development of downstream products. Direct comparison of macroalgae beach-cast between the two archipelagos was not possible because there is no significant and consistent accumulation of macroalgae beach-cast in the Madeira Archipelago, mainly because it does not have a continental shelf. This study also provided baseline information on possible heavy metal contamination of the local macroalgae from the surrounding waters. To date, no information is available on the accumulation of heavy metals in these macroalgal biomasses from this region. Results from this work will help other researchers or companies in evaluating the potential of these biomasses for integration into a blue biotechnology industry, producing valuable and safe products.

Materials and methods

Macroalgae sampling

Macroalgae were collected in Madeira Archipelago, during the spring of 2017, to a maximum 10 m depth by free diving. A total of 25 samples were collected, 14 from Madeira and 11 from Porto Santo Island (Fig. 1A). In spring, sea surface temperature ranges between 18.5 and 22.5ºC, salinity from 32 to 39 psu, conductivity from 54.8 to 55.4 mS cm^{-1}, pH from 8.1 to 8.2 and the dissolved oxygen from 8.7

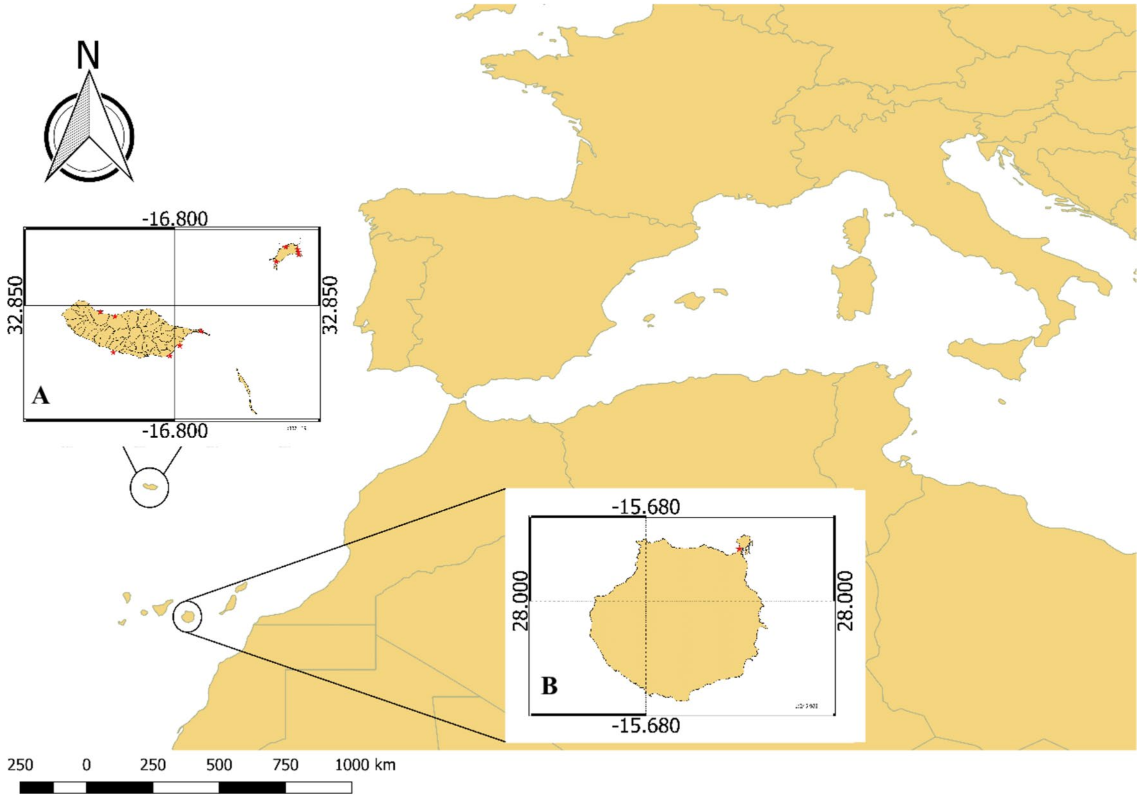


Fig. 1 Map showing north Africa and western Europe with locations of Madeira Archipelago and Gran Canaria Island. More details of the location sites in Madeira Archipelago and Gran Canaria Island are shown in the insert maps **(A)** and **(B)** respectively

to 9.2 mg L^{-1}. (Determined using a seawater multiparameter device; Multi 3430 Set G, WTW, Germany). The seawater is oligotrophic, showing a range of 0 – 0.8 µM phosphate, 0.2 – 9.2 µM silicic acid, 0 – 0.6 µM nitrite and 0 – 34 µM nitrate, present in low concentrations throughout the whole year (Kaufmann and Maranhão 2017).

Macroalgae beach-cast was collected in Playa de Las Canteras, along the northern shore of Gran Canaria, Canary Islands (Fig. 1B). A total of 22 events were sampled between November 2016 and November 2019. At this site the sea surface temperature shows an average of 23ºC and salinity of 36 psu (Pelegrí et al. 2005), with an average pH of 8.0 (Pérez et al. 2001). The seawater in this area is also oligotrophic, with 0.4 µM nitrate, 0.3 µM silicon dioxide and 0.01 µM phosphate (Pérez et al. 2001).

Attached macroalgae from Madeira Archipelago

The sampled macroalgae comprised 4 green, 9 red and 12 brown species. After harvesting, samples were transported to the laboratory with local seawater in individual propylene bags, where they were gently rinsed with filtered freshwater. Thereafter the macroalgae were frozen at -35 °C and freeze-dried under reduced pressure (4×10^{-4} mbar) with a cooling trap (Scanvac Coolsafe Model 55–4, Labogene, Denmark) set at -56 °C for 5 days. Lyophilized samples were milled to 200 mesh particle size in an electric mill (IKA Werke Model M20, Germany), vacuum-packed with a vacuum sealer and stored at -35 °C until further use.

Beach-cast macroalgae

Beach-cast macroalgae are regularly collected from Playa de las Canteras by local authorities and sent to a local landfill. During this study, samples of this biomass were sent to Instituto Tecnológico de Canarias (ITC) where they were sieved and cleaned of sand, stones and anthropogenic litter and rinsed with fresh water. The remaining macroalgae were identified and their biomass accounted for. Samples were then dried and sent to the University of Madeira, ISOPlexis Centre, where they were milled to 200 mesh particle size in an electric mill (IKA Werke Model M20, Germany), vacuum-packed with a vacuum sealer and stored at -35 °C until further use.

Heavy metals analysis

The content of Zn, Ni, Cu, Cr, Cd and Pb in the macroalgae biomass was assessed according to Hansen et al. (2012). Algal biomass was digested in a macroscale with nitric acid (HNO_3) and hydrogen peroxide (H_2O_2), microwave treated (Speedwave two, Berghof Instruments, Germany) and their content quantified with an ICP-OES with a dual mode of acquisition (iCAP 7000, Thermo Scientific, UK). Mercury was assessed using thermal decomposition, followed by a silver amalgamation, and quantified using an atomic absorption spectrophotometer in a direct mercury analyser (DMA-80, Milestones Srl, Italy). In each series of analysed samples, a control sample was used (internal standard) and quality control was performed using the Z-score. If a parameter in each series has a result outside the range + 2/-2* standard deviation, the results were repeated.

Metal Pollution Index (MPI)

The metal pollution index (MPI, Peng et al. 2022) was calculated for the four toxic heavy metals, Cr, Cd, Pb and Hg, determined in this work. The MPI is calculated based on the average values of each heavy metal detected in each species with the following equation:

$$\mathbf{MPI} = \frac{[\mathrm{Cr}] \times [\mathrm{Cd}] \times [\mathrm{Pb}] \times [\mathrm{Hg}]}{4}$$

Statistical analysis

Data are expressed as the average of three replicates ± standard deviation (SD), using the SPSS 26 software. One-way ANOVA was performed to compare the contents of individual heavy metals (Zn, Ni, Cu, Cr, Cd, Pb and Hg) in different species, taxonomic groups (green vs. brown vs. red), sampling sites in Madeira Archipelago and between Madeira and Porto Santo islands. One-way ANOVA was used to compare the contents of the same individual heavy metals in 22 samples of beach-cast macroalgae from Gran Canaria Island collected at different dates, of attached and beach-cast algae from different islands (Madeira vs Porto Santo vs Gran Canaria), and between attached macroalgae from Madeira Archipelago and beach-cast algae from Gran Canaria. Spearman correlation was used to evaluate the relation between individual heavy metal contents in the different attached algal samples from Madeira Archipelago. The beach-cast macroalgae species from Gran Canaria were also assessed to identify possible correlations in their biomass, between the contents of individual heavy metals, and between the individual heavy metal and the relative % of individual algal species found in each macroalgae beach-cast. This analysis was performed with the goal to comprehend if changes in the biomass of a specific macroalga were statistically related with fluctuation in the biomass of another macroalga over time. A principal component analysis (PCA) was performed using MVSP 3.2 software to visualize the variability observed in heavy metal content of Madeira macroalgae and beach-cast macroalgae from Gran Canaria. Cluster analysis was also performed to generate a dendrogram separately for individual macroalgae (Figure S1A) and beach-cast macroalgae (Figure S1B), based on Euclidean distances of their heavy metal contents, to determine the linkage distance between different samples.

Results

On average, heavy metals were detected in the macroalgal samples from Madeira Archipelago in the following order of concentration: Zn > Cr > Ni > Cu > Pb > Cd > Hg (Table 1). Zn content varied from 1.95 mg kg^{-1} dw in *Corallina officinalis* to 242.65 mg kg^{-1} dw in *Laurencia obtusa*. The average value of zinc is 27.74 mg kg^{-1} dw of which red macroalgae exhibited the highest values, 35.86 mg kg^{-1} dw. Zn content in samples from Madeira was lower than those from Porto Santo, 24.20 and 32.32 mg kg^{-1} dw, respectively. Ni content varied from 0.6 mg kg^{-1} in *Ericaria selaginoides* to 34.78 mg kg^{-1} in *Dasycladus vermicularis*. Average values were 7.25 mg kg^{-1}, in which green macroalgae showed the highest value at 10.53 mg kg^{-1}. Ni content in both locations was dissimilar, with the lowest value in Madeira (5.27 mg kg^{-1} dw) and highest in Porto Santo (9.82 mg kg^{-1}). Cu content varied from 0.42 mg kg^{-1} dw in *Padina pavonica* to 7.98 mg kg^{-1} dw in *Lobophora variegata*. Average values of Cu were 3.35 mg kg^{-1}, with green macroalgae showing the highest value, 4.73 mg kg^{-1}. Comparison of Madeira and Porto Santo Island macroalgae showed that samples from both locations had a comparable content of Cu, 3.22 and 3.51 mg kg^{-1} dw respectively. Cr content varied from 0.47 mg kg^{-1} dw in *U. intestinalis* to 45.74 mg kg^{-1} dw in *D. vermicularis*. Average value was 12.84 mg kg^{-1} dw, where green macroalgae exhibited the highest concentration of 17.56 mg kg^{-1} dw. Furthermore, Madeiran macroalgae had a significantly lower value of Cr (7.74 mg kg^{-1} dw) than at Porto Santo (19.45 mg kg^{-1} dw). Cd concentration varied from 0.10 mg kg^{-1} dw in *Ulva* sp. to 2.58 mg kg^{-1} dw in *E. selaginoides*. Average content was 0.51 mg kg^{-1} dw, with brown macroalgae having the highest value, 0.85 mg kg^{-1} dw. Madeiran macroalgae showed the lowest value of Cd, 0.48 mg kg^{-1} dw, and Porto Santo the highest, 0.56 mg kg^{-1} dw. Pb concentration varied from 0.05 mg kg^{-1} dw in *Ulva lactuca* to 2.79 mg kg^{-1} dw in *Asparagopsis armata*. Average value of Pb was

Table 1 Mean (±SD) concentration of heavy metals in macroalgae from Madeira Archipelago examined in the present study

Species	Zn (mg kg^{-1} dw)	Ni (mg kg^{-1} dw)	Cu (mg kg^{-1} dw)	Cr (mg kg^{-1} dw)	Cd (mg kg^{-1} dw)	Pb (mg kg^{-1} dw)	Hg (μg kg^{-1} dw)
Chlorophyta							
Dasycladus vermicularis (Scopoli) Krasser	49.68 ± 7.29	34.78 ± 8.68	5.89 ± 1.03	45.74 ± 8.46	0.16 ± 0.03	0.14 ± 0.04	0.06 ± 0.01
Ulva intestinalis Linnaeus	15.23 ± 1.51	2.51 ± 0.23	6.13 ± 0.6	0.47 ± 0.47	0.22 ± 0.01	0.34 ± 0.03	0.14 ± 0.01
Ulva lactuca Linnaeus	14.55 ± 0.44	1.05 ± 0.01	1.94 ± 0.11	0.82 ± 0.08	0.25 ± 0.03	0.05 ± 0.01	2.94 ± 0.03
Ulva sp. Linnaeus	6.12 ± 1.23	4.80 ± 0.72	4.90 ± 1.07	8.69 ± 0.72	0.10 ± 0.01	0.09 ± 0.02	0.22 ± 0.01
Average	20.22 ± 17.53	10.53 ± 14.39	4.73 ± 1.82	17.56 ± 26.94	0.19 ± 0.06	0.15 ± 0.11	1.05 ± 1.43
Rhodophyta							
Asparagopsis armata Harvey	53.65 ± 9.68	7.81 ± 1.66	4.71 ± 0.7	12.09 ± 2.58	0.14 ± 0	2.79 ± 0.21	0.39 ± 0.24
Asparagopsis taxiformis (Delile) Trevisan	13.89 ± 1.36	10.64 ± 2.44	3.99 ± 0.36	15.77 ± 2.45	0.15 ± 0.03	0.95 ± 0.04	0.09 ± 0.03
Coralina officinalis Linnaeus	1.95 ± 0.12	1.00 ± 0.04	1.20 ± 0.09	1.06 ± 0.12	0.25 ± 0.02	0.31 ± 0.07	0.03 ± 0.01
Chondrus crispus Stackhouse	29.23 ± 5.61	3.73 ± 0.14	1.84 ± 0.23	7.10 ± 0.29	0.17 ± 0.01	0.41 ± 0.09	0.69 ± 0.23
Galaxaura rugosa (J.Ellis & Solander) J.V.Lamouroux	2.81 ± 0.45	2.45 ± 0.59	1.56 ± 0.09	2.38 ± 0.4	0.22 ± 0.02	0.38 ± 0.04	3.98 ± 0.51
Grateloupia lanceola (J.Agardh) J.Agardh	20.66 ± 3.77	0.99 ± 0.06	2.06 ± 0.41	0.57 ± 0.01	0.18 ± 0.03	0.56 ± 0.06	0.10 ± 0.02
Halopithys incurva (Hudson) Batters	18.99 ± 2.25	12.16 ± 0.9	5.94 ± 0.3	18.10 ± 2.45	0.35 ± 0	0.31 ± 0.05	0.09 ± 0.03
Laurencia obtusa (Hudson) J.V.Lamouroux	242.65 ± 20.60	3.59 ± 0.8	2.18 ± 0.36	4.22 ± 0.5	0.20 ± 0	0.69 ± 0.13	0.13 ± 0.01
Nemalion elminthoides (Velley) Batters	26.57 ± 3.68	1.48 ± 0.28	3.85 ± 0.31	5.09 ± 0.76	0.23 ± 0.02	0.91 ± 0.19	0.06 ± 0.01
Average	35.86 ± 59.49	5.08 ± 4.56	2.93 ± 1.59	7.16 ± 6.34	0.24 ± 0.08	0.83 ± 0.94	0.71 ± 1.35
Phaeophyceae							
Cystoseira humilis Schousboe ex Kützing	16.02 ± 3.24	1.56 ± 0.21	1.58 ± 0.28	1.45 ± 0.29	0.33 ± 0	0.29 ± 0.05	0.18 ± 0.12
Dictyota dichotoma (Hudson) J.V. Lamouroux	5.73 ± 0.71	2.85 ± 0.09	1.90 ± 0.07	3.97 ± 0.19	0.49 ± 0.11	0.07 ± 0	0.19 ± 0.02
Dictyopteris polypodioides (A.P.De Candolle) J.V.Lamouroux	49.52 ± 8.25	20.19 ± 0.91	4.28 ± 0.85	24.70 ± 4.88	0.55 ± 0.11	0.83 ± 0.09	0.22 ± 0.04
Ericaria selaginoides (Linnaeus) Molinari & Guiry	8.60 ± 0	0.60 ± 0	1.07 ± 0	0.59 ± 0	2.58 ± 0	0.65 ± 0	0.23 ± 0
Gongolaria abies-marina (S.G.Gmelin) Kuntze	25.57 ± 3.53	0.91 ± 0.13	0.83 ± 0.06	0.78 ± 0.37	1.91 ± 0.36	0.33 ± 0.06	0.07 ± 0.01
Gongolaria usneoides (Linnaeus) Molinari & Guiry	6.61 ± 1.39	2.01 ± 0.13	1.27 ± 0.12	1.67 ± 0.13	0.70 ± 0.15	0.27 ± 0.02	0.11 ± 0.01
Halopteris filicina (Grateloup) Kützing	17.27 ± 1.33	17.67 ± 1.4	5.14 ± 0.02	37.62 ± 0.97	0.54 ± 0.04	0.31 ± 0.05	0.05 ± 0
Halopteris scoparia (Linnaeus) Sauvageau	29.41 ± 0.79	15.81 ± 2.4	5.89 ± 1.14	19.34 ± 2.57	0.12 ± 0	1.22 ± 0.01	0.19 ± 0.03

Table 1 (Continued)

Species	Zn (mg kg^{-1} dw)	Ni (mg kg^{-1} dw)	Cu (mg kg^{-1} dw)	Cr (mg kg^{-1} dw)	Cd (mg kg^{-1} dw)	Pb (mg kg^{-1} dw)	Hg (μg kg^{-1} dw)
Lobophora variegata (J.V. Lamouroux) Womersley ex E.C. Oliveira	25.71 ± 3.69	15.08 ± 0.8	7.98 ± 1.18	35.93 ± 6.06	0.59 ± 0.14	0.32 ± 0.07	1.96 ± 0.04
Padina pavonica (Linnaeus) Thivy	27.76 ± 0.82	15.48 ± 2.63	0.42 ± 0.10	36.76 ± 5.38	0.13 ± 0.03	0.28 ± 0.01	0.55 ± 0.09
Sargassum vulgare C. Agardh	25.20 ± 4.97	1.37 ± 0.08	1.37 ± 0.04	1.19 ± 0.3	1.75 ± 0.07	0.40 ± 0.04	0.04 ± 0.01
Stypopodium zonale (J.V.Lamouroux) Papenfuss	22.40 ± 1.51	5.23 ± 0.23	4.63 ± 0.21	13.30 ± 0.34	0.40 ± 0.02	0.20 ± 0.02	8.49 ± 0.51
Average	23.91 ± 12.37	7.83 ± 7.50	3.18 ± 2.41	15.72 ± 16.41	0.85 ± 0.77	0.47 ± 0.37	0.96 ± 2.35
Madeira average content	24.2 ± 14.42	5.27 ± 5.77	3.22 ± 1.78	7.74 ± 8.30	0.48 ± 0.56	0.71 ± 0.83	1.28 ± 2.35
Porto Santo average content	32.32 ± 55.35	9.82 ± 10.29	3.51 ± 2.50	19.45 ± 21.45	0.56 ± 0.67	0.35 ± 0.22	0.36 ± 0.72
Madeira archipelago average content	27.74 ± 38.02	7.25 ± 8.32	3.35 ± 2.12	12.84 ± 16.43	0.51 ± 0.61	0.55 ± 0.66	0.88 ± 1.87

0.55 mg kg^{-1} dw, with red macroalgae showing the higher content, 0.83 mg kg^{-1} dw. Macroalgae sampled in Porto Santo Island showed the lowest content, 0.35 mg kg^{-1} dw and Madeiran the highest value, 0.71 mg kg^{-1} dw. Mercury content varied from 0.03 μg kg^{-1} dw in *C. officinalis* to 8.49 μg kg^{-1} dw in *Stypopodium zonale*. Average content was 0.88 μg kg^{-1} dw, where green macroalgae presented the highest value, 1.05 μg kg^{-1} dw. The average Hg in macroalgae was lower in Porto Santo, 0.36 μg kg^{-1} dw than in Madeiran ones, 1.28 μg kg^{-1} dw. The MPI in the macroalgae species collected from Madeira archipelago were very low, all ≤ 0.002.

One-way ANOVA indicates that the sampled species were significantly different from each other in terms of their heavy metal contents (Table S1, $p \leq 0.05$). Contents of three (Cd, Pb and Cu) of the seven heavy metals are significantly different between taxonomic groups, contents of four (Cr, Ni, Hg and Pb) of these are also significantly different between collection sites in Madeira Archipelago. This indicates that for these heavy metals, their contents in group of macroalgae collected at each site are significantly different from each other. The variation of Cr, Ni, Hg and Pb contents is also statistically significantly different with respect to the geographic origin (Madeira or Porto Santo islands) of the macroalgae.

Spearman correlation (Table S2) showed significant ($p \leq 0.05$) positive correlations between several heavy metals, the most prominent ones being Zn vs Pb ($r = 0.52$), Cu vs Cr ($r = 0.56$), Ni vs Cu ($r = 0.61$) and the highest of all was Ni vs Cr ($r = 0.90$). The only significant negative correlation was detected between Cd vs Ni ($r = -0.34$). Axes 1 and 2 from the PCA analysis explained 88.78% and 10.64% of the observed variations, respectively (Fig. 2A). Three distinct groups were separated, including 1, 3 and 21 macroalgal species. Zn, Cr and Ni were the major heavy metals influencing samples separation. This pattern was further confirmed by the dendrogram (Figure S1A) which showed *L. obtusa* to be clearly separated from all the other macroalgae, suggesting that *L. obtusa* has a distinct concentration of heavy metals.

The 22 samples of beach-cast macroalgae collected from Playa de las Canteras, Gran Canaria, over the 3-year period had an average weight of 39.72 kg dw ranging from 16.70 to 74.30 kg dw (Fig. 3A). The average macroalgae content in these samples was 17.12%, varying from 6.88 to 31.68%. Sand was the main composition of the samples, with an average of 81.67% ranging between 61.73 and 93.12%. Also, trash was sometimes part of the samples, about 1.2% on average that fluctuated from 0 to 13.58%. The remaining macroalgae included *Cymopolia barbata* (Linnaeus) J.V.Lamouroux (green alga); *Asparagopsis taxiformis*, *Hypnea* sp., *Halopithys incurva*, *Jania* sp., *Laurencia* sp., *Liagora* sp. (red algae); *Dictyota* sp., *Lobophora variegata*, *Halopteris scoparia* and *Taonia* sp. (brown algae). Additionally, the seagrass *Cymodocea* sp. was also present. On average, samples were composed of green algae (9.59%), red (23.69%), brown (60.31%), marine plants (0.64%) and indistinct biomass (5.90%) (Fig. 3B). *Lobophora variegata* and *Dictyota* sp. were the most common brown macroalgae in the beach-cast samples, averaging 32.14% and 27.83% respectively. Contents of the same heavy metals were also assessed in these samples, showing the same order of variation as those detected in the attached macroalgal samples: Zn > Cr > Ni > Cu > Pb > Cd > Hg (Table 2). Zn content varied from 12.33 to 45 mg kg^{-1} dw with an average value of 28.7 mg kg^{-1} dw. Ni content varied from 3.55 to 18.67 mg kg^{-1} dw with an average value of 8.86 mg kg^{-1}

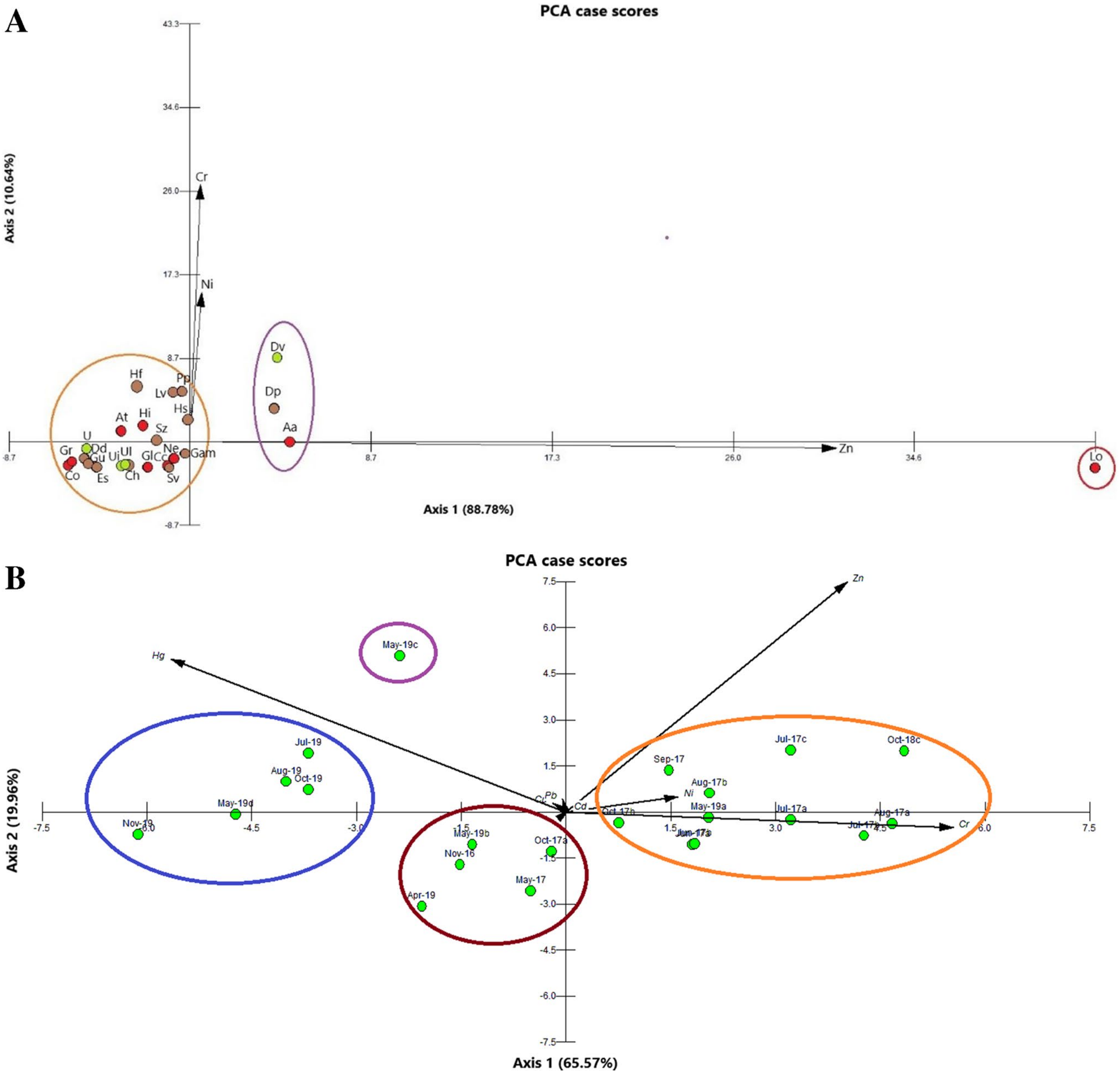


Fig. 2 **A** Principal component analysis (PCA) plot, using the data of seven heavy metals, including Zn, Ni, Cu, Cr, Cd, Pb and Hg, for 25 samples of attached macroalgae from Madeira archipelago. Each dot represents a macroalgal sample and the color of the dot, its taxonomic group. Axis 1 explains 88.78% of the observed variability and distribution of samples and axis 2 explains 10.64% of this variability. Arrows indicate the contribution of the metals for the separation of macroalgae samples in the plot. Samples are labelled by species as follows: Chlorophyta—*Dasycladus vermicularis* (Dv), *Ulva intestinalis* (Ui), *Ulva lactuca* (Ul), *Ulva* sp. (U); Rhodophyta—*Asparagopsis taxiformis* (At), *Asparagopsis armata* (Aa), *Coralina officinalis* (Co), *Chondrus crispus* (Cc), *Galaxaura rugosa* (Gr), *Grateloupia lanceola* (Gl), *Halopithys incurva* (Hi), *Laurencia obtusa* (Lo), *Nemalion elminthoides* (Ne); Phaeophyceae—*Gongolaria abies-marina* (Gam), *Cystoseira humilis* (Ch), *Ericaria selaginoides* (Es), *Gongolaria usneoides* (Gu), *Dictyota dichotoma* (Dd), *Dictyopteris polypodioides* (Dp), *Halopteris filicina* (Hf), *Halopteris scoparia* (Hs), *Lobophora variegata* (Lv), *Padina pavonica* (Pp), *Sargassum vulgare* (Sv) and *Stypopodium zonale* (Sz). **B** Principal component analysis (PCA) plot, using data of the same seven heavy metals as in A) for 22 samples of beach-cast macroalgae from Gran Canaria island. Each dot represents a sample with the corresponding date of collection. Axis 1 explains 65.57% of the observed variability and distribution of the samples and axis 2 explains 19.96% of the variability. Arrows indicate the contribution of the metals for the separation of macroalgae samples in the plot

dw. Cu content varied from 1.98 to 4.64 mg kg^{-1} dw with an average value of 3.02 mg kg^{-1} dw. Cr content varied from 5.44 to 40.32 mg kg^{-1} dw with an average value of 19.74 mg kg^{-1} dw. Cd content varied from 0.25 mg kg^{-1} dw and 1.09 mg kg^{-1} dw, with an average concentration of 0.48 mg kg^{-1} dw. Pb concentration varied from 0.17 to 2.48 mg kg^{-1} dw with an average value of 1.33 mg kg^{-1} dw. Hg content varied from 3.59 to 31 µg kg^{-1} dw with an average concentration of 13.36 µg kg^{-1} dw. The MPI's of the beach-cast macroalgae were also found to be very low, ≤ 0.11.

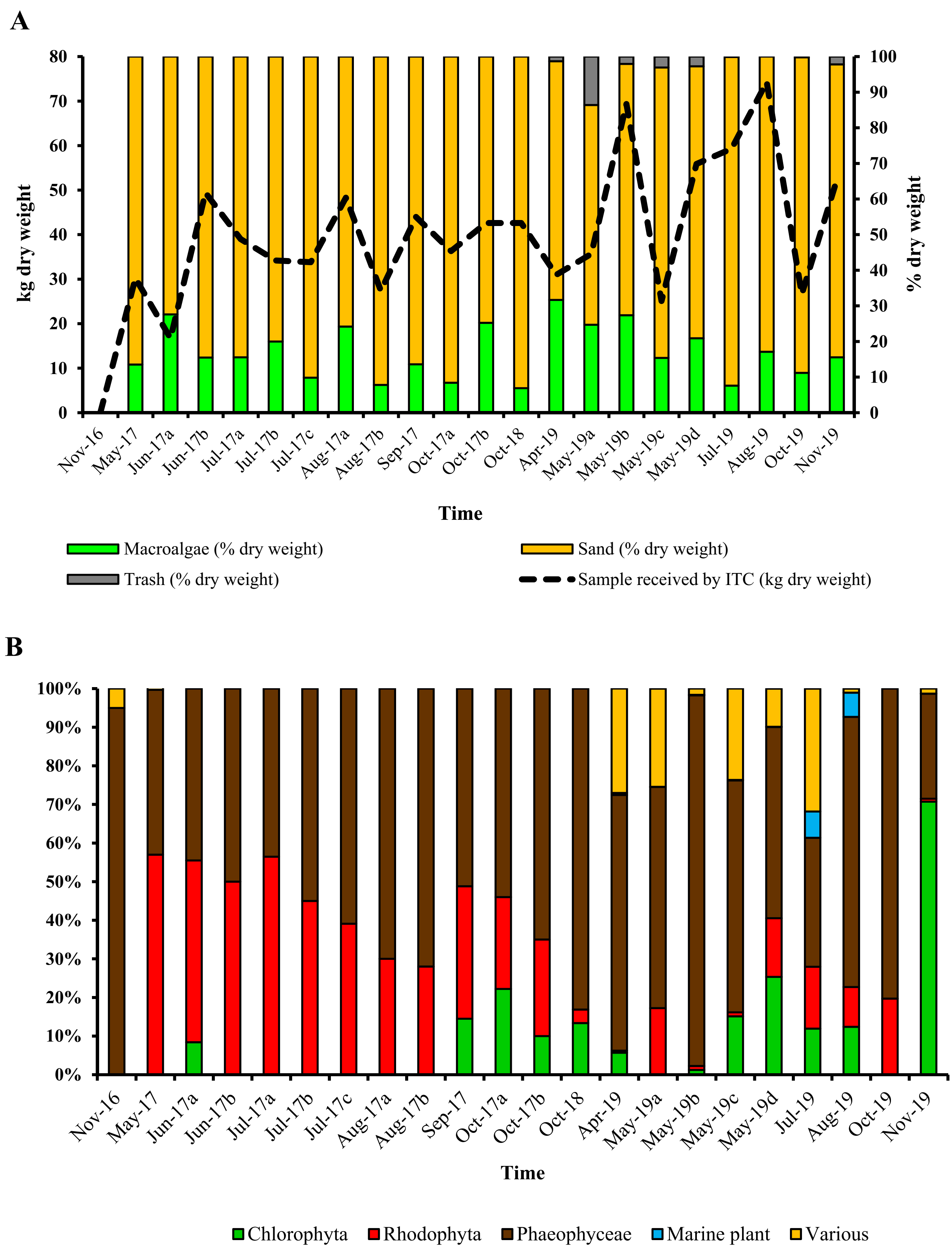
The contents of six heavy metals, except for Pb, in the beach-cast macroalgae were significantly different between beach-cast macroalgae samples ($p \leq 0.05$, One-Way ANOVA, Table S3). Variations in the content of four of these heavy metals, Ni, Cr, Pb and Hg, were also statistically significantly different among algal samples (both attached and beach-cast) of different geographical origins (Gran Canaria, Madeira and Porto Santo). Hg, Pb and Cr contents in attached macroalgae from Madeira archipelago were significantly different from those found in the beach-cast macroalgae from Gran Canaria. Cr average content in beach-cast macroalgae is 35%, higher than in attached macroalgae. The same is also observed for Pb and Hg, which are 59% and 83% higher in beach-cast macroalgae, respectively (Table 1 vs. Table 2). Spearman correlation (Table S4) showed numerous significant correlations ($p \leq 0.05$) among individual macroalgal species in beach-cast samples, the most notable of which are as follows. Significant positive correlations were found between *Cymodocea* sp. and various indistinct macroalgae ($r = 0.81$), *Hypnea* sp. ($r = 0.68$), and *Taonia* sp. ($r = 0.58$). At the same time, *Hypnea* sp. shows positive correlations with *C. barbata* ($r = 0.63$), *Taonia* sp. ($r = 0.61$), and various indistinct macroalgae ($r = 0.54$). Significant negative correlations were detected between *Dictyota* sp. and *L. variegata* ($r = -0.63$), and *A. taxiformis* and various indistinct macroalgae ($r = -0.54$). With respect to the heavy metal content, significant positive correlations were found between *Cymodocea* sp. and Hg ($r = 0.71$), and Cu ($r = 0.59$); *Halopteris scoparia*, with Ni ($r = 0.61$), and Cr ($r = 0.57$); *Hypnea* sp. and Hg ($r = 0.69$); various indistinct macroalgae with Hg ($r = 0.58$); *A. taxiformis* with Ni ($r = 0.58$) and *C. barbata* with Hg ($r = 0.51$). Negative correlations were found between various indistinct macroalgae and Cr ($r = -0.54$), and Zn ($r = -0.50$); *C. barbata* with Cr ($r = -0.50$) and *Hypnea* sp. also with Cr ($r = -0.50$). Between heavy metals, significant correlations were detected as follows, Ni vs Cr ($r = 0.79$), Cu vs Hg ($r = 0.61$), Zn vs Cr ($r = 0.59$), Zn vs Ni ($r = 0.57$), Pb vs Hg ($r = 0.52$) and Cr vs Hg ($r = -0.51$).

PCA analysis of heavy metals in the beach-cast macroalgae showed 65.57% of the observed variance to be explained by the 1st axis, and 19.96% by the 2nd axis (Fig. 2B). In the scatter plot, four separations are evident which include 1, 5, 5 and 11 samples. Heavy metals responsible for the major spatial distribution on the plot were Zn, Cr, Hg, and Ni. The first separation is attributed to the concentration of Ni, Cr and Zn, but the 2nd separation is not well defined by these elements. The 3rd separation appears to be influenced by Hg and the 4th, constituted only by one event, is being influenced partly by Zn and Hg. Separation of sampling dates into four main groups is further supported by the dendrogram generated from the cluster analysis (Figure S1B). It should be meaningful to note that samples collected close to one another could differ very distinctly (e.g., May 19c vs May 19d), yet some samples collected at different times far apart could be well related (e.g., May 19b vs. Nov 17).

Discussion

The attached macroalgae collected in Madeira archipelago demonstrated a broad range of values for heavy metal bioaccumulation. Comparison with published data allowed us to gain some insights on the possible bioaccumulation behaviour of these algae, which may be influenced by several factors, such as hydrodynamics, grazing and the presence of epiphytes. Water pollution, e.g., from urbanization, industrial effluents, outfall from wastewater treatment plant and mining operations, affects heavy metal accumulation in local macroalgae.

Zn was detected in high concentration (242.65 ± 20.60 mg kg^{-1} dw) in *L. obtusa* collected in the north shore of Porto Santo. This accumulation appears to be specific to this species since this location is characterized by low density of human population and lack of industrialization, thus is unlikely to be contaminated with heavy metals (although no testing was done on the water). Other species of macroalgae collected in this same site did not demonstrate this concentration value. The accumulation of Zn by six different macroalgal species in Rio de Janeiro (Brazil) indicates that Zn bioaccumulation is species specific, varying from low to high, depending on species tolerance (Amado Filho et al. 1997). In the present study, red macroalgae had higher Zn content compared to green and brown ones. This phenomenon already has been observed in 19 species of macroalgae collected in western Ireland (Stengel et al. 2004). However, Irish macroalgae that contained the lowest Zn were from the high intertidal, in contrast with the present study where the highest Zn content was recorded


A
kg dry weight
% dry weight
Time
Nov-16
May-17
Jun-17a
Jun-17b
Jul-17a
Jul-17b
Jul-17c
Aug-17a
Aug-17b
Sep-17
Oct-17a
Oct-17b
Oct-18
Apr-19
May-19a
May-19b
May-19c
May-19d
Jul-19
Aug-19
Oct-19
Nov-19
Macroalgae (% dry weight)
Sand (% dry weight)
Trash (% dry weight)
Sample received by ITC (kg dry weight)
B
Time
Chlorophyta
Rhodophyta
Phaeophyceae
Marine plant
Various

◂**Fig. 3** Composition of the untreated beach-cast macroalgae samples indicating (**A**) the total kg received in dry weight (broken line), mean percentage dry weight of macroalgae, sand and trash in the samples collected; and **(B)** the mean percentage of each algal group (Chlorophyta, Rhodophyta and Phaeophyceae), marine plants and other unidentified macroalgae (Others) in the beach-cast macroalgae samples collected along the timeline. Letters after the date indicate collection sequence within a particular month

in the high intertidal *L. obtusa*. On the other hand, the lowest concentration of Zn was found in red alga *C. officinalis*, which agrees well with data of the same species in western Ireland (Stengel et al. 2004). Table 3 lists the heavy metal data in macroalgal species collected from earlier studies and allows comparison with those from the present study. Cross analysis of these data shows that *L. obtusa* collected in Marsa-Matrouh beaches (Egypt) had a lower Zn content (11.11—111.7 mg kg^{-1} dw) (Khaled et al. 2014) than in the present study (242.65 ± 20.60 mg kg^{-1} dw). The same species from other localities, including Northern Adriatic (Munda and Hudnik 1991) or Aegean Sea (Sawidis et al. 2001), presented even lower values. Similar finding was observed for the green alga *D. vermicularis* collected from the same site, with a value (49.68 ± 7.29 mg kg^{-1} dw) much higher than that for the same species collected in Antikyra Gulf, Greece (28.6—61.9 mg kg^{-1} dw) (Malea et al. 1995). Heavy metal accumulations have also been more extensively studied in several other algal species such as *U. lactuca*. In the present work, this species recorded a zinc content of 14.55 ± 0.44 mg kg^{-1} dw which is comparable to the published values that range from 2.35 to 340 mg kg^{-1} dw (Buo-Olayan and Subrahmanyam 1996; Sawidis et al. 2001; Storelli et al. 2001; Al-Homaidan 2007; Chakraborty et al. 2014; Allam et al. 2016; Arisekar et al. 2021). Other well studied macroalgae are *C. officinalis* (Munda and Hudnik 1991; Sawidis et al. 2001; Allam et al. 2016), *Dictyota dichotoma* (Munda and Hudnik 1991; Malea et al. 1995; Chakraborty et al. 2014; Arisekar et al. 2021) and *P. pavonica* (Munda and Hudnik 1991; Malea et al. 1995; Sawidis et al. 2001; Al-Masri et al. 2003; Akcali and Kucuksezgin 2011; Dadolahi-Sohrab et al. 2011; Alahverdi and Savabieasfahani 2012a). This present work recorded Zn values for these macroalgae close to the minimum values described by these earlier studies.

Interestingly, *L. obtusa* had a low content of Ni but *D. vermicularis*, collected in the same area, exhibited the highest content of this heavy metal (34.78 ± 8.68 mg kg^{-1} dw). This trend could be intrinsically connected with differences in the macroalgal physiology, since they could selectively bioaccumulate specific minerals, as described for *Sargassum oligocystum* Montagne, collected in the Bay of Bengal, Cox's Bazar (Bangladesh) which bioaccumulated Pb (Rakib et al. 2021), or *A. taxiformis* collected in the south shore of Madeira Island that accumulated iodine (Nunes et al. 2019). Ni content in Madeiran macroalgae agrees well with the values determined in different locations worldwide, as is the case for *U. lactuca* (Buo-Olayan and Subrahmanyam 1996; Sawidis et al. 2001; Al-Homaidan 2007; Chakraborty et al. 2014; Allam et al. 2016; Arisekar et al. 2021), *C. officinalis* (Munda and Hudnik 1991; Sawidis et al. 2001; Allam et al. 2016) and *P. pavonica* (Sawidis et al. 2001; Dadolahi-Sohrab et al. 2011; Alahverdi and Savabieasfahani 2012b). Cu content in the algae from Madeira Archipelago was lower than any published values. Cu content in the green alga *D. vermicularis* collected in the Antikyra Gulf, Greece, had between 12.8 and 253 mg kg^{-1} dw, far more than that of the same species collected in north Porto Santo Island (5.89 ± 1.03 mg kg^{-1}) in the present study. Although Porto Santo has a higher population density than Antikyra municipality, this latter locality has an aluminium factory known to produce effluents containing Mg, Fe, Ca, K, Fe, Na and Cu (Malea et al. 1995) that can be bioaccumulated by the surrounding macroalgae and other organisms. In comparison, *U. intestinalis* in the present work showed Cu values to be in the range interval reported for the same species collected in the Persian Gulf, Iran (Alahverdi and Savabieasfahani 2012b); and *U. lactuca* showed Cu values within the range published by Buo-Olayan and Subrahmanyam (1996), Sawidis et al. (2001), Storelli et al. (2001), Al-Homaidan (2007), Chakraborty et al. (2014), Allam et al. (2016) and Arisekar et al. 2021. The red macroalgae, *A. taxiformis, Chondrus crispus, C. officinalis* and *L. obtusa* also had values of Cu within the published ranges (Munda and Hudnik 1991; Sawidis et al. 2001; Besada et al. 2009; Khaled et al. 2014; Allam et al. 2016; Peng et al. 2022). This is also the case for brown macroalgal samples, including *Dictyopteris polypodioides* (Munda and Hudnik 1991), *D. dichotoma* (Munda and Hudnik 1991; Malea et al. 1995; Chakraborty et al. 2014; Arisekar et al. 2021), *P. pavonica* (Munda and Hudnik 1991; Malea et al. 1995; Sawidis et al. 2001; Al-Masri et al. 2003; Akcali and Kucuksezgin 2011; Dadolahi-Sohrab et al. 2011; Alahverdi and Savabieasfahani 2012b), *S. vulgare* and *S. zonale* (Al-Masri et al. 2003). All the information regarding Zn, Ni and Cu contents for Madeira's macroalgae is consistent with those for a locality with no mining industry, no industrialization and with low population density.

Regarding toxic metals, Cr is a naturally occurring element considered carcinogenic, especially in its high soluble form, Cr(VI), used in several industrial applications. It contaminates ground water and is eventually transferred to the food chain (Sharma et al. 2020). Its daily consumption limit in a human adult should not surpass 120 µg per day (Balali-Mood et al. 2021). The green alga *D. vermicularis* tends to bioaccumulate a lot of Cr, compared with other algae such as *Ulva* sp. collected in the same location that shows a Cr content that is less than ¼ of that of *D. vermicularis*.

Table 2 Mean (±SD) concentration of heavy metals in beach-cast macroalgae samples collected in Gran Canaria examined in the present study

Collection date	Code	Zn (mg kg^{-1} dw)	Ni (mg kg^{-1} dw)	Cu (mg kg^{-1} dw)	Cr (mg kg^{-1} dw)	Cd (mg kg^{-1} dw)	Pb (mg kg^{-1} dw)	Hg (µg kg^{-1} dw)
14/11/2016	Nov-16	19.99 ± 0.87	4.77 ± 0.46	3.19 ± 0.14	14.62 ± 1.58	0.26 ± 0.01	1.12 ± 0.03	12.07 ± 0.61
29/05/2017	May-17	20.88 ± 0.55	5.15 ± 0.26	2.32 ± 0.07	12.74 ± 2.00	0.40 ± 0.03	0.17 ± 0.02	3.59 ± 0.11
23/06/2017	Jun-17a	28.47 ± 2.10	10.2 ± 1.03	2.55 ± 0.08	24.73 ± 1.53	0.32 ± 0.02	1.13 ± 0.14	5.23 ± 0.11
26/06/2017	Jun-17b	28.60 ± 1.88	10.25 ± 0.96	2.56 ± 0.11	24.86 ± 1.85	0.33 ± 0.01	1.13 ± 0.12	5.26 ± 0.13
05/07/2017	Jul-17a	32.87 ± 1.26	13.75 ± 0.73	2.58 ± 0.08	31.34 ± 0.35	0.25 ± 0.02	1.57 ± 0.16	5.55 ± 0.17
12/07/2017	Jul-17b	30.90 ± 2.82	18.67 ± 1.42	2.72 ± 0.22	38.05 ± 1.92	0.36 ± 0.03	1.09 ± 0.07	4.49 ± 0.17
20/07/2017	Jul-17c	45 ± 1.60	10.49 ± 0.70	2.70 ± 0.07	23.60 ± 1.60	0.64 ± 0.02	2.13 ± 0.15	5.67 ± 0.14
08/08/2017	Aug-17a	33.28 ± 1.70	15.95 ± 0.57	3.32 ± 0.12	40.32 ± 1.75	1.09 ± 0.03	1.07 ± 0.54	4.64 ± 0.08
21/08/2017	Aug-17b	37.51 ± 4.35	8.77 ± 0.46	2.68 ± 0.02	20.42 ± 2.07	1.07 ± 0.07	0.77 ± 0.07	5.26 ± 0.21
18/09/2017	Sep-17	41.50 ± 1.65	5.48 ± 0.14	2.83 ± 0.09	13.93 ± 0.66	0.97 ± 0.04	1.09 ± 0.04	5.07 ± 0.24
06/10/2017	Oct-17a	25.32 ± 1.57	6.56 ± 0.21	1.98 ± 0.14	15.41 ± 0.47	0.57 ± 0.03	0.9 ± 0.16	7.63 ± 0.17
10/10/2017	Oct-17b	30.64 ± 1.26	7.9 ± 0.25	2.51 ± 0.59	18.07 ± 0.45	0.55 ± 0.04	1.16 ± 0.14	7.33 ± 0.67
22/10/2018	Oct-18	44.24 ± 6.98	10.51 ± 0.45	2.74 ± 0.12	38.7 ± 1.56	0.27 ± 0.02	1.51 ± 0.25	8.10 ± 0.51
25/04/2019	Apr-19	13.50 ± 0.52	3.55 ± 0.58	3.47 ± 0.18	14.07 ± 0.70	0.25 ± 0.01	0.96 ± 0.07	10.54 ± 0.37
06/05/2019	May-19a	30.47 ± 1.38	13.09 ± 0.71	2.73 ± 0.15	28.66 ± 2.45	0.25 ± 0.02	1.81 ± 0.22	9.66 ± 0.63
13/05/2019	May-19b	23.64 ± 0.98	5.75 ± 0.69	3.98 ± 0.20	12.54 ± 1.09	0.29 ± 0	1.22 ± 0.06	11.60 ± 0.80
15/05/2019	May-19c	44.95 ± 16.88	6.42 ± 0.43	4.64 ± 1.04	7.98 ± 0.75	0.25 ± 0.04	2.48 ± 0.47	30.00 ± 1.73
20/05/2019	May-19d	16.55 ± 1.36	8.11 ± 1.96	3.84 ± 0.11	10.57 ± 0.54	0.31 ± 0	2.25 ± 0.46	30.00 ± 1
22/07/2019	Jul-19	27.16 ± 5.81	8.54 ± 1.00	3.2 ± 0.37	11.18 ± 1.89	0.72 ± 0.01	1.57 ± 0.27	30.67 ± 0.58
01/08/2019	Aug-19	22 ± 1.18	8.64 ± 0.57	3.51 ± 0.68	12.83 ± 0.14	0.62 ± 0.02	1.39 ± 0.18	31.00 ± 1
17/10/2019	Oct-19	21.51 ± 3.69	8.57 ± 3.47	3.59 ± 0.27	14.27 ± 4.18	0.6 ± 0.14	1.71 ± 0.30	29.67 ± 1.15
11/11/2019	Nov-19	12.33 ± 2.43	3.87 ± 0.23	2.91 ± 0.05	5.44 ± 0.44	0.29 ± 0	1.01 ± 0.22	31.00 ± 0
	Average	28.7 ± 9.72	8.86 ± 3.87	3.02 ± 0.62	19.74 ± 10.21	0.48 ± 0.27	1.33 ± 0.52	13.36 ± 10.91

Cd is also extensively used by the industrialized countries and its concentration in the water is intensified near mining operations (Gutiérrez et al. 2015). Several human medical syndromes are attributed to high consumption of Cd, including hypertension, lung damage, renal dysfunction, hepatic injury and teratogenic effects (Sari and Tuzen 2008). The daily consumption limit of Cd in an adult is 55 µg per day (Balali-Mood et al. 2021). All the attached macroalgae in Madeira showed a low concentration Cd below or within the range of previous published data (Table 3), except for specific brown algae such as *S. vulgare, G. abies-marina* and *E. selaginoides* which showed the highest Cd contents ranging from 1.75 to 2.58 mg kg^{-1} dw (Table 1). These brown algae are intertidal species collected near the Madeira airport. Cd has been shown to be the second most prevailing element in the general aircraft emission originating from the use of aviation oil and aircraft fuel (Turgut et al. 2019). Phaeophyceaen macroalgae accumulate more Cd than members of the other two taxonomic groups (Table 1). Based on Cd absorption kinetics in five different brown macroalgae from Galicia (Spain), the bioaccumulation rate was shown to be extremely fast (Lodeiro et al. 2005). This intrinsic characteristic allows the higher accumulation of Cd by brown macroalgae when this element is available in the environment. However, Pb and not Cd, is the prevailing pollutant from aircraft emissions and this element is more readily accumulated by rhodophytes (Table 1) than by phaeophycean species, resulting in the discrepancy in its contents between the two groups. The presence of Pb in marine water can also be linked with abandoned boat paint particles that included lead-based formulations (Turner 2022). Chronic exposure to Pb by human through food consumption has a negative impact on nervous system structures, kidneys, and blood circulation, with children, infants, and foetuses being more sensitive to this element (Guo et al. 2018). The daily consumption limit of Pb in an adult is 250 µg per day (Balali-Mood et al. 2021). Pb contents found in the attached macroalgae collected from the Madeira archipelago (Table 1) were all lower than those in previously published data (Table 3) and are comparable with those reported in sites with minimal heavy metal contamination.

There are only few studies regarding Hg content in macroalgae, limiting the comparison with published data. Still, Hg values in most attached algae collected in the present study are generally low (< 1 µg kg^{-1} dw) (Table 1) except for four species, *L. variegata*, *U. lactuca*, *Galaxaura rugosa* and *S. zonale*. Nonetheless, *U. lactuca* collected from Santa Cruz, Madeira. has a lower Hg content (Table 1) than the same species from other locations (Table 3). Similarly, Hg content in *U. intestinalis* from Madeira (0.14 ± 0.01 μg kg^{-1} dw, Table 1) is much lower than that in the same species (2100 μg kg^{-1} dw) collected in Ria de Aveiro, Portugal (Coelho et al. 2005). This reinforces the assumption that low Hg content can generally be associated with sites with minimal industrialization impact. Since this species is an edible macroalga permitted in the EU, it is important to pay attention to its Hg content as Hg toxicity impairs cellular function, modifying tertiary and quaternary protein structures, damaging organs and subcellular structures in human (Carocci et al. 2016). The daily consumption limit of Hg in an adult is 50 μg per day (Balali-Mood et al. 2021).

Zn average content (28.7 ± 9.72 mg kg^{-1} dw) in the beach-cast macroalgae collected in Gran Canaria Island from November 2016 to November 2019 was much lower than that from the beach-cast collected in the Gulf of Gdansk, Poland (39.4 – 223 mg kg^{-1} dw) (Table S5) (Filipkowska et al. 2008). This could be attributed to several factors but the most prominent one seems to be the complete difference in the species composition of beach-cast from these two sites (Table S6). Portillo (2008) published a technical report which characterized beach-cast biomasses in several locations in the Island of Gran Canaria, including Playa de Las Canteras, the same location assessed in the present study. Zn concentration in these biomasses had a broader range, having its higher concentration being more than twice the highest value reported in the present work (Table S5). The total wet weight of beach-cast biomass retrieved from this beach in 2005 was estimated to be more than 1000 t in which macroalgae composition of individual cleanups varied from 5 to 37%, and the species composition being slightly different from that reported from the present work (Table S6). Also, beach-cast macroalgae in Galicia, Spain, gathered from November 2004 till October 2005 (Villares et al. 2016), had a higher average content of Zn at 54.7 mg kg^{-1} dw (Table S5). The beach-cast macroalgae from Galicia, once again, have a different species composition (Table S6). Furthermore, a single collection of beach-cast in Ondo State, Nigeria composed only of two species, *Sargassum fluitans* and *S. natans* drift from the Sargasso Sea, had a much lower Zn content at 0.5 mg kg^{-1} dw (Oyesiku and Egunyomi 2014, Table S5). It appears that different beach-cast macroalgae contained different Zn concentrations, but it is not possible to infer if this variability is due specifically to differences in the collecting location, species composition, and/or collection time.

Ni content in the beach-cast macroalgae (Table 2) examined in the present study showed a lower value than that in the beach-cast macroalgae collected in Galicia, Spain, (Table S5) (Villares et al. 2016), but a higher value than that from the Gulf of Gdansk, Poland (Filipkowska et al. 2008). Ni content from beach-cast biomass collected earlier from Gran Canaria in 2005 (Portillo 2008) had more than twice the highest value determined in the present work (Table S5). In contrast, Gran Canaria beach-cast macroalgae had a low Cu content (Table 2) compared to samples collected in the Gulf of Gdansk (Filipkowska et al. 2008) and Oland, Sweden (Greger et al. 2007). However, Cu content in beach-cast collected from Gran Canaria in 2005 (Portillo 2008) was more than tenfold higher than that recorded in the present work (Table S5). Similarly, biomass collected in Galicia, Spain showed a higher Cu content, which may be a result of anthropogenic pollution as the collection site in Galicia is highly industrialized, with contaminants entering from the farthest sites of the Ría de Vigo and with daily tidal fluxes enhancing the extent of contamination (Villares et al. 2016). Beach-cast macroalgae collected in the Gulf of Gdansk (Poland) showed a much lower Cr content (Filipkowska et al. 2008), than that of the Gran Canaria beach-casts (Table 2). Interestingly, the maximum value of Cr found in Gran Canaria in 2005 (Portillo 2008) is much lower than that reported in the present work (Table S5). The Sopot Pier in the Gulf of Gdansk, although a touristic place similar to the Gran Canaria Island, has seawater with a much lower salinity (6.652 psu) and a higher pH (8.71) (Zakowski et al. 2014) which could influence heavy metal bioaccumulation. Galician beach-cast macroalgae had four times more Cr (Villares et al. 2016) than Gran Canaria beach-casts. But as mentioned earlier, Galicia is a highly industrialized area. Heavy metals in contaminated coastal seawater would inevitably be bioaccumulated by the marine organisms.

Cd content in beach-cast macroalgae of Gran Canaria was lower than most of those reported in the literature (Table S5), except that of Portillo (2008) in which the present work recorded only half the highest Cd content of that reported in this previous study on beach-cast biomass from the same locality. Nonetheless, none of the highest values reported in the assessed literature exceeded 4.7 mg kg^{-1} dw detected in Oland, Sweden (Greger et al. 2007). The same is true with Pb content where Gran Canaria beach-casts generally showed lower values than those reported elsewhere (Table S5) except for Portillo (2008), where the higher concentration of Pb (32.73 mg kg^{-1} dw) was much higher than the values described in the present work (Table S5). In the Gulf of Gdansk (Poland) these values fluctuated between 0.95—10.50 mg kg^{-1} dw (Filipkowska et al. 2008) whereas in Galicia, Spain, the value was highest at 12.75 mg kg^{-1} dw. For Hg content, only two reports were found in the literature. However, of greater concern is that the average Hg content in Gran Canaria beach-casts is close to the highest level of around 14 μg kg^{-1} dw reported in the same location in 2005 (Portillo 2008) and in Gulf of Gdansk (Filipkowska et al. 2008) (Table S5). More in-depth analysis shows that from mid-May till November 2019, Hg content in Gran Canaria beach-casts increased to around 30 μg kg^{-1} dw, which is two

Table 3 Mean (± SD) and range concentration of heavy metals recorded from other studies in macroalgal species that are also reported in the present study

Macroalgae	Zn (mg kg^{-1} dw)	Ni (mg kg^{-1} dw)	Cu (mg kg^{-1} dw)	Cr (mg kg^{-1} dw)	Cd (mg kg^{-1} dw)	Pb (mg kg^{-1} dw)	Hg (µg kg^{-1} dw)	References
Chlorophyta								
Dasycladus vermicularis	28.6—61.9	-	12.8—253	-	0.9—12.5	71.7—737	-	Malea et al. 1995
Ulva intestinalis	-	16—50.33	4.89—9.56	-	2.89—5.33	11.0—51.0	-	Alahverdi and Savabieasfahani 2012b
Ulva lactuca	115—275	2.9—12.8	85—445	-	-	0.7—4.5	-	Buo-Olayan and Subrahmanyam 1996
	16.4—88	5.1—52.6	7—14.5	-	0.24—1.1	0.02—2.8	-	Sawidis et al. 2001
	127.27 ± 60.15	-	12.07 ± 7.12	-	0.2 ± 0.23	0.84 ± 0.34	120 ± 50	Storelli et al. 2001
	35.46—48.17	26.31—32.37	8.41—18.5	-	0.81—0.95	13.9—17.67	-	Al-Homaidan 2007
	146—340	0.5—2.6	14.2—21.5	4.09—5.65	2.76—3.6	0.8—3.5	-	Chakraborty et al. 2014
	2.81—3.54	0.58—0.82	0.45—0.46	-	0.15—0.16	1.44—2.2	-	Allam et al. 2016
	2.35 ± 0.23	0.59 ± 0.16	3.15 ± 0.62	0.62 ± 0.21	0.11 ± 0.09	0.31 ± 0.14	360 ± 300	Arisekar et al. 2021
Rhodophyta								
Asparagopsis taxiformis	21.72 ± 3.61	5.78 ± 0.97	3.37 ± 0.29	7 ± 0.37	0.46 ± 0.03	4.85 ± 0.48	-	Peng et al. 2022
Chondrus crispus	51.8—53.3	-	1.55—2.21	-	0.72—0.74	0.40—0.73	6—7	Besada et al. 2009
Coralina officinalis	30—44	-	2—3	-	0.1—0.3	4.0—7.0	-	Munda and Hudnik 1991
	37.5	18.3	0.85	-	2.9	0.02	-	Sawidis et al. 2001
	4.16—5.31	1.86—2.44	0.35—0.45	-	0.35—0.45	3.29—3.96	-	Allam et al. 2016
Laurencia obtusa	17	-	2	-	0.3	6	-	Munda and Hudnik 1991
	25.4	17.5	7.1	-	1.2	0.02	-	Sawidis et al. 2001
	11.11—111.70	4.27—52.56	4.53—7.73	-	0.21—0.49	41.26—41.55	-	Khaled et al. 2014
Phaeophyceae								
Dictyopteris polypodioides	83	-	3	-	0.4	11	-	Munda and Hudnik 1991

Table 3 (continued)

Macroalgae	Zn (mg kg^{-1} dw)	Ni (mg kg^{-1} dw)	Cu (mg kg^{-1} dw)	Cr (mg kg^{-1} dw)	Cd (mg kg^{-1} dw)	Pb (mg kg^{-1} dw)	Hg (µg kg^{-1} dw)	References
Dictyota dichotoma	45.0—85.0	-	3—5	-	0.4—0.9	5.0—11.0	-	Munda and Hudnik 1991
	21.9—86.9	-	11.0—23.0	-	3.1—3.3	43.3—375	-	Malea et al. 1995
	28 ± 4.0	0.6 ± 0.1	5.4 ± 1.4	4.1 ± 0.8	2.2 ± 0.5	1.3 ± 0.2	-	Chakraborty et al. 2014
	0.40 ± 0.34	0.31 ± 0.15	0.54 ± 0.33	0.31 ± 0.14	0.19 ± 0.07	0.15 ± 0.08	60 ± 40	Arisekar et al. 2021
Padina pavonica	52.0—105.0	-	2—8	-	0.4—1.1	3.0—11.0	-	Munda and Hudnik 1991
	17.1—71.1	-	4.6—103	-	7.3—24.5	13.2—525	-	Malea et al. 1995
	19.3—26.3	18.3—32.3	3—3.7	-	1.2—1.6	0.002—2.1	-	Sawidis et al. 2001
	32.66—37.11	-	3.88—5.15	33.3—72	0.50—0.78	0.77—1.20	-	Al-Masri et al. 2003
	26.3—75.1	-	3.73—8.22	0.73—3.19	0.02—0.15	0.001—0.005	43—47	Akcali and Kucuksezgin 2011
	48.7 ± 14.6	46.5 ± 28.2	16.9 ± 13.6	-	5 ± 2.1	18.4 ± 11.8	-	Dadolahi-Sohrab et al. 2011
	-	10.58—27.92	4.33—10.03	-	3.22—7.02	9.33—22.11	-	Alahverdi and Savabieasfahani 2012b
Sargassum vulgare	13.17—23.74	-	1.71—4.75	9.86—23.1	0.14—0.16	0.27—1.04	-	Al-Masri et al. 2003
Stypopodium zonale	15.24—18.77	-	4.8—6.5	9.26—13.1	< 0.1—0.13	0.35—0.74	-	Al-Masri et al. 2003

times that of the average. This pattern is quite unlike those of the other heavy metals examined in the present study so further investigation is needed to explain this pattern and the apparent pattern of having consistently high contents of Hg in beach-cast macroalgae from this site.

Comparing beach-cast algal biomass collected in the same location reported by Portillo (2008) and that in the present study, higher maximum contents of Zn, Ni, Cu and Pb and lower contents of Cr, Cd, and Hg were reported in Portillo (2008) (Table S5). The species composition is slightly different (Table S6), wherein Portillo (2008) included macroalgae not reported in the present work, such as *Cladophora* sp., *Lophocladia trichoclados*, *Jania virgata* and *Sargassum vulgare*. Variability in the different heavy metal concentrations reported between these two works may be attributable to differences in their species compositions, since individual species of macroalgae tends to bioaccumulate heavy metals differently. Wild-harvest brown macroalgae, *H. scoparia* and *P. pavonica,* collected in the island of Tenerife (Canary Islands), were detected to have higher concentrations of Pb (Paz et al. 2018). Additionally, two red macroalgae, *Asparagopsis* spp. and *Liagora* spp., collected on the same island, were also assessed to have higher Cu and Pb concentration (Paz et al. 2022), compared with that detected in the beach-casts in the present study. As Tenerife is the most populated island of the Canary Archipelago, it is expected to experience more prominent anthropogenic effects than in Gran Canaria Island. Presence of cleaner, uncontaminated seawater around Gran Canaria could explain the generally lower concentrations of heavy metals in its beach-cast macroalgae.

Comparing the two sources of algal biomass, i.e., the attached algae from Madeira and the beach-cast algae from Gran Canaria, average Cr content in beach-cast algae is 35% higher than that in attached algae. The same was also observed for Pb and Hg, which are 59% and 83% higher in beach-cast algae, respectively. The strong positive correlations between the biomass of certain macroalgae that were part of the beach cast, e.g. *Hypnea* sp. with *Cymodocea* sp. and *C. barbata*, or between *Taonia* sp. and *Cymodocea* sp., *Hypnea* sp; or negative correlations such as between *L.*

variegata and *Dictyota* sp., demonstrates that some macroalgae are expected to be present in high quantity in the beach-cast together or in opposite patterns, i.e. when some are present in higher quantities, other species would be present in lower quantities. This may reflect similar or opposite responses of these algae to certain conditions, including hydrodynamics, currents and nutrients, and potentially their bioaccumulation of heavy metals that are responsible for these variations in their heavy metal contents.

Some heavy metal contents are positively correlated with different algal species, suggesting that some affinity or preferential ability to bioaccumulate certain heavy metals by these algae. Given that beach-casts differ in their composition of algae over time, heavy metal contents in the beach-cast are likely to be influenced by differences in their algal compositions. This is statistically relevant, for example in the case of the positive correlation of Hg with *Cymodocea* sp. and *Hypnea* sp., indicating that the quantity of these algae directly influenced Hg concentration within the beach-cast. There are also several cases of negative correlations, for example between *Hypnea* sp. and Cr. Statistically significant correlations were also observed between several metals present in beach-cast algae with strong positive correlations between Ni and Cr, Cu and Hg and negative correlations between Cr and Hg. This information will be useful to help predict the heavy metals that may be present in the algal biomass, and hence the potential usage of this biomass. However, PCA and Cluster analysis results pointed to some important implication about the use of beach-cast macroalgae. Variability of their heavy metal content is very high and this variability is not only attributed to the type of heavy metals of concern but also to the high variability in the algal compositions and biomass such that beach cast samples collected in dates close to one another could differ much from one another, and yet samples collected from different times far apart could be quite similar. This adds another level of unpredictability to the potential usefulness of beach cast macroalgae as a long-term supply of biomass for algal product development.

Guidelines for the safe utilization of macroalgae and their products are continuously being updated in the European Union legislation. These include guidelines on their heavy metal contents. There are numerous EU directives referring to macroalgae and describing them as herbal medicines, novel or not novel foods, food and food additives, feed and feed additives, cosmetics, packaging materials, fertilizers, biostimulants and biofuels (Lähteenmäki-Uutela et al. 2021). The herbal medicines are regulated under Directive 2001/83/EC, which states that these formulations must undergo regular toxic metal assessments, although no specific concentration limits are stated. Four samples of algae included in this work are considered as food by the EU, including *U. intestinalis*, *U. lactuca, Ulva* sp. and *C. crispus*. However, due to the low popularity of these food products in the EU, they are not included in the Commission Regulation (EC) No 1881/2006, which regulates the maximum level of contaminants in foods. Directive 2002/32/EC determines the maximum use of 40 mg kg^{-1} of macroalgae in feed formulations. These formulations should also show a moisture content of 12%, but only As is regulated and must be maintained under 2 mg kg^{-1}. This regulation is not an impediment to developing new feed formulations as only the concentration of As in algal biomass needs to be assessed. Cosmetic products and packaging materials must comply with Regulations 1223/2009/EC and EC/1935/2004, respectively, which do not limit the use of macroalgae. Macroalgae can possibly be used as a fertilizer and amendment product, which is regulated under EU 2019/1009. The limits for heavy metals differ in organic fertilizers, organo-mineral fertilizers, inorganic fertilizers, soil improvers, plant biostimulants or fertilizing product blend and are described in this regulation as follows: 1.5 mg kg^{-1} dw of Cd, 2 mg kg^{-1} dw of hexavalent Cr, 1 mg kg^{-1} dw of Hg, 50 mg kg^{-1} dw of Ni, 120 mg kg^{-1} dw of Pb, 40 mg kg^{-1} dw of inorganic As, 300 mg kg^{-1} dw of Cu and 800 mg kg^{-1} dw of Zn. Additionally, the Joint FAO/WHO Expert Committee of Food Additives (JECFA) limits Pb general content by 2 mg kg^{-1} or by 1 mg kg^{-1} or less if high consumption is expected, and Cd and Hg by 1 mg kg^{-1} (FAO 2002). In Codex Alimentarius (2014), values for Cd are permitted within the range of 0.05—2 mg kg^{-1}, Pb 0.01—2 mg kg^{-1} and Hg 0.001 – 0.1 mg kg^{-1} for food applications.

Other than hexavalent Cr and inorganic As, which were not assessed in this present work, the heavy metal contents in most attached macroalgae from Madeira archipelago are all within the limits prescribed under different EU regulations or directives and in JECFA for different products. The MPI values for toxic metals were all very low, ≤ 0.002, suggesting that these metals are not posing any environmental health risk. These algae should therefore be able to serve as a good source of useful biomass for use in developing any of the products described above. Some exceptions are to be noted. The brown algae *E. selaginoides, G. abies-marina* and *S. vulgare* may be limited in their applications due to their higher Cd content that is > 1 mg kg^{-1}. The red alga *A. armata* has a Pb content that is > 2 mg kg^{-1}.

Beach-cast macroalgae tended to have higher heavy metal contents with samples collected in three events (dates) having Pb content, and in two events demonstrating Cd content higher than the permissible values described in FAO (2002) and Codex Alimentarius (2014). Nonetheless, these higher values are very close to the limiting values, indicating that this source of biomass still exhibits a generally low level of heavy metal contamination. Beach-cast macroalgae assessed in this present work from Gran Canaria Island would therefore be suitable for fertilizer development, pending further investigation on their hexavalent Cr and inorganic As contents. Nonetheless, as indicated earlier, attention should be paid on the high variability in the heavy metal contents of beach cast samples collected at different times if these samples are to serve as a long-term supply of biomass for algal product development.

Conclusions

The study of heavy metal contents in 25 species of attached macroalgae from Madeira archipelago and 22 samples of beach-cast macroalgae, collected in Gran Canaria Island, was relevant to assess the potential use of these biomasses in product development and in the promotion of blue economy in these localities.

This study showed that contents of heavy metals occur in the same order of Zn > Cr > Ni > Cu > Pb > Cd > Hg in attached macroalgae and beach-cast macroalgae. Heavy metal levels in most of the samples analyzed in this work were within the safe EU limits, allowing further development of these algae into downstream products. There are, however, a few exceptions. The red alga *L. obtusa* was found to selectively bioaccumulate Zn and the green alga *D. vermicularis*, Zn, Ni, Cu and Cr. Other macroalgae, such as *G. abies-marina*, *E. selaginoides* and *S. vulgare,* contained high Cd content. This phenomenon could be explained by the proximity of these algae from the Madeira airport, with Cd being the 2nd major pollutant released from aviation fuel. Four macroalgae collected from different sites, including *L. variegata*, *U. lactuca*, *G. rugosa* and *S. zonale*, selectively accumulated Hg. The taxonomic grouping of macroalgae was shown to influence the bioaccumulation of Cu, Cd and Pb. Additionally, Hg, Pb and Cr contents differed significantly between attached and beach-cast macroalgae, with the latter having higher heavy metal contents. In beach-cast macroalgae, Pb content was not statistically significantly different among samples collected at different dates. This is, however, not the case with the other heavy metals thus demonstrating that collection date is relevant in reference to these other heavy metal contents and should be considered when planning the use of beach-cast biomass. Proximity of the collection dates was found not to be a good predictor of heavy metal contents, i.e. beach-cast collected in dates close to each other could be similar or very dissimilar in their heavy metal contents. It was apparent that the presence of specific genera of macroalgae, i.e. *Cymodocea* sp. and *Hypnea* sp, was significantly correlated with the concentration of Hg within the beach-cast biomass. Thus, species composition in the beach-cast macroalgae could give some indication of the possible heavy metal contents of the beach-cast. This implies that the use of beach-cast macroalgae for further development into other downstream products may not be so straight-forward.

Inorganic As and hexavalent Cr were not assessed in the present study. They should be considered in future works to comply with EU directives and regulations, if macroalgae from Madeira or beach cast from Gran Canaria are to be considered for use in future product development. Nonetheless, except for *G. abies-marina* and *S. vulgare* with their higher Cd concentrations, most other macroalgae examined in the present study remain a viable source of biomasses for developing into novel products within the legal limits imposed by several EU directives. While a stronger effort should be exerted to clarify certain EU legislations, increasing the popularity of these algal biomasses among EU citizens is a more important challenge to be overcome.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10811-023-03146-1.

Author's contributions 1)Nuno Nunes contribution included conception and design of the study, performed the statistics, and wrote the article.2)Sónia Ferraz provided the study materials, obtained funding, and revised it critically.3)Marianna Venuleo provided the study materials, obtained funding, and revised it critically.4)Ana I. R. N. A. Barros obtained funding and revised it critically.5)M.A.A. Pinheiro de Carvalho helped with the conception and design of the study, obtained funding, revised it critically and provided the final approval.

Funding Open access funding provided by FCT|FCCN (b-on). Thanks to ARDITI—Regional Agency for the Development of Research, Technology and Innovation for the support granted under Project M1420-09–5369-FSE-000002- Post-Doctoral Scholarship, co-financed by the Madeira 14–20 Program—European Social Fund. This work is supported by National Funds from FCT—Portuguese Foundation for Science and Technology, under the project UIDB/04033/2020. The Programa Operacional Madeira 14–20, Portugal 2020, and the European Union through the European Regional Development Fund, grant number M1420-01–0145- FEDER-000011 [CASBio]. Also, we acknowledge the support of the project MACBIOBLUE (MAC/1.1b/086), program Interreg MAC 2014–2020. Finally, we are thankful for the support of the INTERREG V España- Portugal program within the European Regional Development Fund (FEDER) MAC2/1.1b/279 [Ahidagro].

Data availability All data generated or analysed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests The authors declare no competing interests.

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