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Review

Environmental Impact of Cadmium in a Volcanic Archipelago: Research Challenges Related to a Natural Pollution Source

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Abstract: Cadmium (Cd) is a highly toxic heavy metal particularly susceptible to mobilization by anthropogenic and natural processes. The volcanic nature of oceanic islands in the Macaronesia geographical region such as the Azores archipelago, located near the Mid-Atlantic Ridge, is reflected in deep-sea and shallow-water hydrothermal activities that release heavy metals such as Cd to seawater, affecting marine organisms and integrating food webs. In this paper, a thorough systematic review of all studies performed on coastal marine species in Macaronesia focusing on Cd was conducted, specifically considering the Azorean geological setting and socioeconomic context. Present results are compared and discussed with data from the Mediterranean, a region with apparent strong anthropogenic pollution. The Azorean marine species seem to be particularly strong Cd accumulators, displaying high levels that should be closely monitored, reflecting an important local natural source that should not be underestimated; especially considering the high consumption rates of some of these organisms, which may lead to a potential seafood safety issue. In light of these findings, the potential effects, impacts, and future research challenges are discussed, from an ecological and public health perspective.

Keywords: cadmium; bioaccumulation; volcanism; Azores

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1. Introduction

Heavy metals are natural constituents of the Earth's crust, released into the marine environment through human activities such as industrial waste discharges, agricultural practices, coastal construction, and dredging. These elements are classified as either essential, with known biological roles and only toxic above threshold concentrations, or non-essential, when lacking any known biological role and exhibiting a high degree of toxicity. They are non-biodegradable, persistent, and toxic to biota, thus causing serious ecotoxicological problems [1–4]. The extent of their bioaccumulation and subsequent toxicity depends on the total levels, the availability in the environment, and uptake route, storage, and excretion mechanisms [4].

Metal pollution occurs naturally through volcanic eruptions and associated phenomena, either released in gaseous form during the eruption itself and disseminated in the atmosphere and oceans [5,6], or from the release to the ground from the erosion and weathering of pyroclastic or ashes [7]. These emitted materials are rich in trace elements and plant nutrients but also contain toxic or potentially harmful elements and minerals [8–11]. Several studies indicate that leachable elements from this material easily enter the biological cycle and, in the long term, enrich the soil by adding nutrients such as Ca, Mg, K, Na, P, Si, and S [12]; however, in the short term, this potential transfer of bioavailable elements may have toxicological implications for the environment, which is of concern to producers and consumers [13–15]. In addition, episodic or continuous outgassing inputs into the water at mid-ocean ridges also help to explain the high concentrations of metals found in the water column and some marine fauna [5,16]. The presence or detection of metals and metalloid elements are also indicators of significant degassing of magmatic vapors during submarine eruptions, playing an important role in the net transfer of chemical elements from erupting volcanoes to seawater in addition to that arising from hydrothermal systems [5].

Metals play an important role in human nutrition through micronutrients [11,17]. Their deficiency can cause diseases, for example, iodine deficiency (thyroid hormone production), which affects 241 million children worldwide [18], and their excess can also affect human health (e.g., fluoride in oceanic islands [19]). However, diet is also the main uptake route for non-essential heavy metals, harmful even in very low concentrations. Seafood is an important food source for humans, which currently exceeds the consumption of meat from all other animal-protein foods combined [20] and is also the primary pathway of heavy metal uptake.

Cadmium (Cd) is a relatively mobile and acutely toxic heavy metal to almost all forms of life, widely found in terrestrial and aquatic environments but in relatively low concentrations [21,22]. Its high volatility, large ionic radius, and chemical speciation in the aquatic system make it particularly susceptible to mobilization by anthropogenic and natural processes. This element usually occurs in the Earth's crust at an abundance of 0.1–0.5 ppm and is also a natural constituent of ocean water, with values between <5 and 110 ng L^{-1} [23]. It is known to accumulate in spawners tissue and gonads (e.g., [24]), impair gametes quality and fertilization (e.g., [25]), and embryo and larval development (e.g., [26]). Regarding humans, it is classified as a human carcinogen, group I [27], hence a very dangerous toxicant. Moreover, its consumption can cause many health problems, such as kidney dysfunction, bone damage via oxidative stress (osteomalacia, osteoporosis, and fractures), nephrotoxicity and can induce the disruption of DNA repair, leading to mutations that together with increased cell proliferation can result in tumor formation [28,29].

As a recently formed volcanic archipelago within the Macaronesia region, the Azores are surrounded by deep seafloor with a complex geotectonic setting where seismic–volcanic phenomena occur, reflected by lava emissions, diffuse degassing from soils, and hydrothermal activity [30,31]. Although important anthropogenic sources of heavy metal pollution are not known in the Azores, owing to the frequent seismic and volcanic activity, high inputs of heavy metals can be leached to seawater surrounding these islands, affecting marine organisms and being integrated into food webs, also reaching edible species [32–34]. High levels of heavy metals have been reported for several local species from thermal hot springs and volcanic littoral, more specifically Cd was detected at values higher than the maximum levels (MLs) set out in Regulation (EC) no. 1881/2006 for the EU [33,34].

In this paper, a thorough systematic review of all studies on marine coastal species sampled in the Macaronesia focusing on Cd was conducted, analyzing its potential impacts and future research challenges, particularly considering the geological setting and socio-economic context of the Azores region from ecological and public health perspectives. Data is also compared and discussed with studies performed in the Mediterranean with apparent strong anthropogenic pollution.

2. Methodological Approach

2.1. Geographic and Geotectonic Setting

The Azores Archipelago is located in the middle of the North Atlantic Ocean, approximately 1400 km west of Europe's mainland and 1900 km east of North America and between latitudes 36° and 40° N and longitudes 24° and 32° W, is (Figure 1). With the oldest subaerial ages ranging from ~6 My (Santa Maria [35]) to 0.186 My (Pico [36]), the archipelago straddles an area where three major tectonic plates interact—North American, Eurasian, and Nubian plates—known as the Azores Triple Junction (Figure 1; [37]). The islands rise from a prominent bathymetric anomaly broadly defined by the 2000 m isobath, termed the Azores Plateau [38]. The plateau is, in general terms, delimited by the Mid-Atlantic Ridge to the west, the Terceira's Rift to the north, and the inactive East Azores Fracture Zone to the south [39].

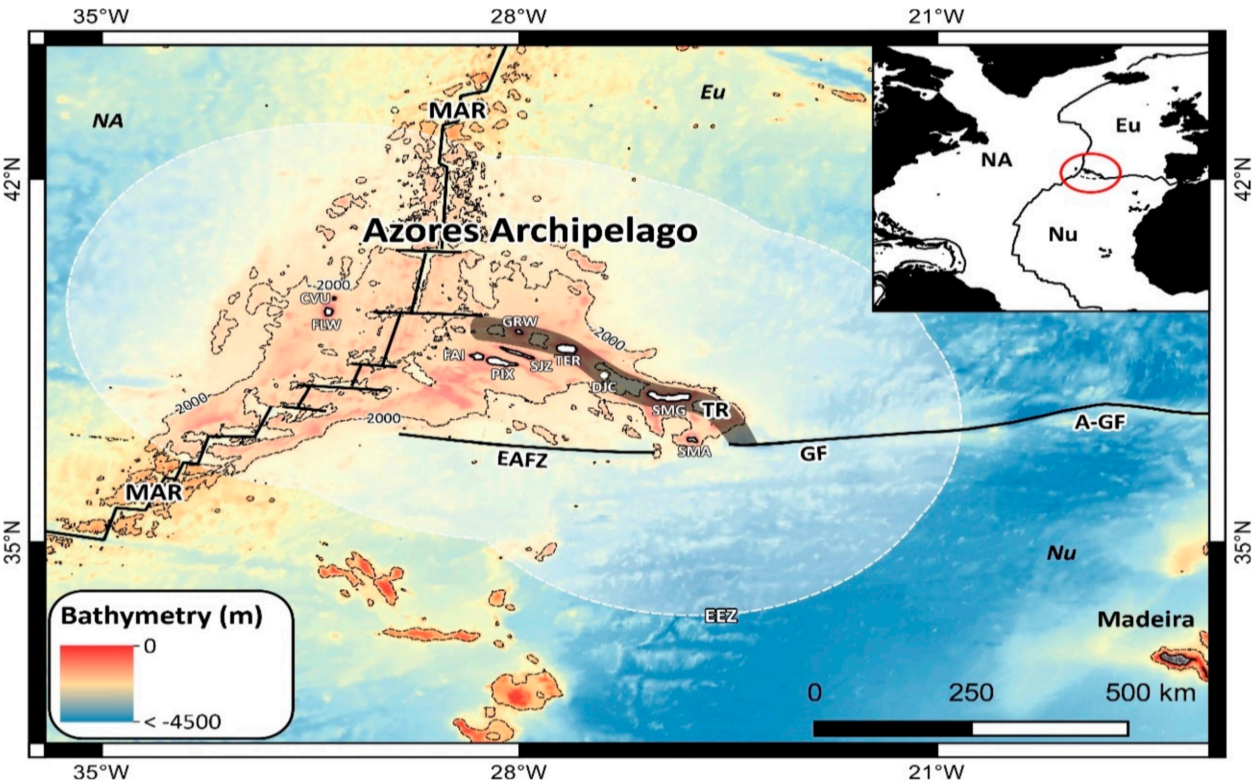

Figure 1. Geographic and geotectonic setting of the Azores Archipelago. NA: North American Plate; Eu: Eurasian Plate; Nu: Nubian Plate; MAR: Mid-Atlantic Ridge; TR: Terceira Rift; EAFZ: East Azores Fracture Zone; GF: Glória Fault; A-GF: Azores-Gibraltar Fault; SMA: Santa Maria: SMG: São Miguel; DJC: Dom João do Castro seamount; TER: Terceira; GRW: Graciosa; SJZ: São Jorge; PIX: Pico; FAI: Faial; FLW: Flores; CVU: Corvo. Geotectonic structures modified from Miranda et al. (2018). Coastline from the Portuguese Hydrographic Institute "https://www.hidrografico.pt/op/33 (accessed on 20 September 2022)" and bathymetry derived from GEBCO "https://www.gebco.net (accessed on 20 September 2022)".

As a result of the complex volcanic setting in where the Azores Archipelago is found, volcanic active systems are present in most of the islands, with common seismic events and, more rarely, volcanic eruptions [40]. Deep-water hydrothermal vents also occur within the Azores Economic Exclusive Zone (EEZ) [41]. Although less common than reports of shallow-water hydrothermal vents, in the archipelago, such structures are known to occur at least in 10 different locations, mostly around islands (São Miguel, Graciosa, Faial, and Flores islands) and at D. João de Castro seamount [31]. Although the Azores include an EEZ of about one million km^2, this is largely deep-sea (avg. depth of 3000 m [42]). The islands' narrow contiguous shelf represents a mere 0.4% of the EEZ, reaching 200 m depth at distances from the coastline between 1 and 10 km [43], while seamounts <500 m account for 37% of the EEZ, although most of their summits are deeper than 1000 m [44]. Hence, bottom fishing grounds are limited and concentrated on the island slopes and the seamounts within the region [44,45].

2.2. Selection of Publications

To conduct the systematic literature review, the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-analysis) method was used as a guide [46], Figure 2. Web of Science (WoS) (https://webofknowledge.com (accessed on 20 September 2022)) database was used to perform the bibliographic search on all of the peer-reviewed literature published until September 2022. In these databases, using title, abstract, and keywords, the following combined terms were searched: (Azores OR Canary OR Canarias OR Cape Verde OR Cabo Verde OR Madeira) AND (heavy metals OR cadmium OR trace metals) AND (coast* OR marine OR ocean). Only publications in English, Portuguese, and Spanish were considered. This search resulted in 146 in WoS and 3 more were added by the authors resulting in a combined first list of 149 publications (see Supplementary Material-Table S1).

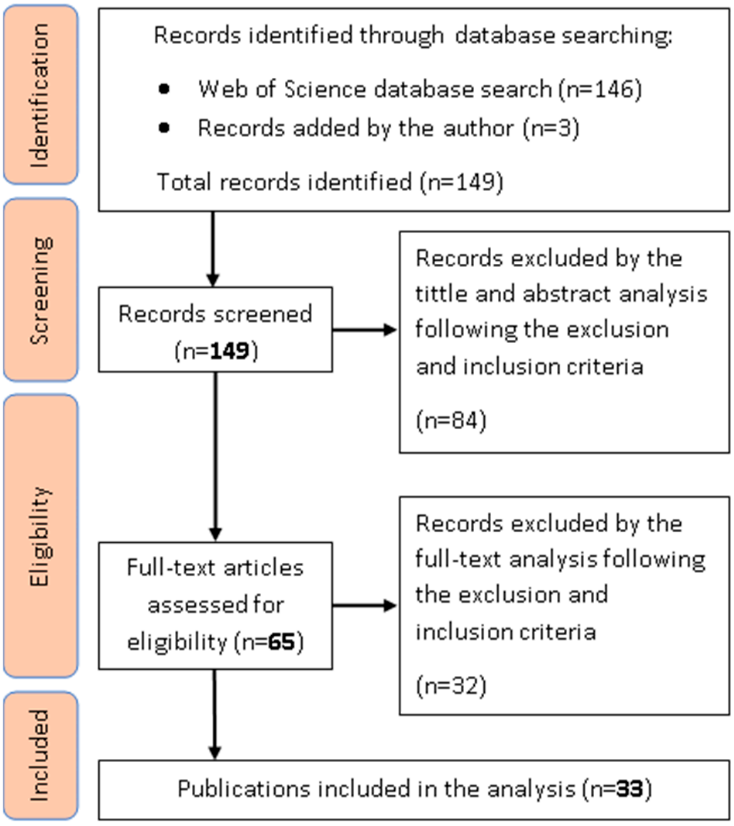

Figure 2. Flow diagram of selection and eligibility criteria of the methodology. The PRISMA rules are followed to filter publications obtained from the databases according to the eligibility criteria.

The screening process started with the analysis of the title and abstract of these 149 publications. Using the inclusion and exclusion criteria (Table 1), a total of 84 were removed (see Supplementary Material-Table S2). For the 65 remaining publications, the full text of each eligible article was then reviewed for relevance using the same inclusion and exclusion criteria as in the screening process. A total of 32 articles were removed, living a remaining total of 33 for further analysis.

A highly mobile species is usually subjected to different parts or aspects of an impacted environment and will thus provide information on a wider region than if it were restricted to a single area. In addition, a small home range allows researchers to pinpoint the location of pollution or disturbance with greater accuracy. Indicators of environmental quality might usually be resident species because they are subject to sustained environmental stress. Hence, this study focused on coastal resident species, with small home ranges and low mobility. Herein, coastal area is defined as what lies from the seashore to a depth of 200 m from the coastal zone. In this study, "coastal" species are defined as those that inhabit exclusively or mostly island shelves with maximum abundance in the first 200 m [47,48].

Offshore, deep-sea, or migratory species were therefore excluded (Table 1). To compare the Macaronesian archipelagos with an anthropogenic polluted marine area, a list of Cd studies was compiled focusing on similar species of algae, invertebrates, and fishes, whenever possible and available.

Table 1. Inclusion and exclusion criteria used to select the publications for the final analysis, including Cd studies, location, and coastal species.

Inclusion Criteria	Exclusion Criteria
Cadmium (Cd) concentration studies	Metal concentration in water or sediment studies
Macaronesia region study area (the Azores, Canaries, Cape Verde, and Madeira)	Studies outside the Macaronesia region
Coastal algae, invertebrates, and fish (sea-line to 200 m depth)	Deep-sea (more than 200 m depth), offshore, or non-coastal species without a link to the coast
Offshore islets, shallow seamounts, and banks	Studies where the origin of samples is unknown (e.g., samples obtained in markets)
Articles in English, Portuguese, or Spanish	Migratory species (e.g., mammals, turtles, pelagic sharks, dolphins, or seabirds)

2.3. Data Analysis

For 33 publications included in the study, the following data and information was extracted: (i) whether the study in question was carried out in the Azores, Canaries, Cape Verde, or Madeira archipelagos, trying to be as specific as possible about the location of the study, arriving whenever possible at coordinates; (ii) the group of organisms on which the study is focused (algae, invertebrates, or fish), species, tissue, publication year, number of samples, sex, minimum and maximum range, and concentration of Cd in dry and wet weight (mg kg^{-1}). When a study gave the Cd concentration of a group of different species, they were treated in the graphs as a single unit (bulk). Relative dissimilarities among locations, grouping species in algae, invertebrates, and fishes were determined using non-metric multidimensional scaling (NMDS) and tested under ANOSIM. PRIMER 7 (PRIMER Ltd., Plymouth, UK) was used for the statistical analyses.

3. Results and Discussion

3.1. Systematic Review

In the supplementary material (Table S3), all the details of each of these studies can be consulted, including species, habitat, site, number of samples, size, tissue, sex, Cd content, and reference. Only the Azores and Canaries presented studies focusing on Cd in coastal species, in Madeira and Cape Verde they are absent, and the Canaries are leading mainly due to their work on fishes, while in the Azores, invertebrates are, by far, the most studied group (Figures 3 and 4). The Canaries show a constant evolution in the number of studies over the years while the Azores seem to stabilize since 2016, reflecting a working group specifically focused on this topic. The University of the Azores has a research group (IVAR: Institute of Vulcanology and Risk Assessment) that focuses on ecotoxicology and human health issues linked to volcanism but from a more inland perspective. The marine and coastal realms are therefore subject to more spontaneous or circumstantial projects or other student works and theses.

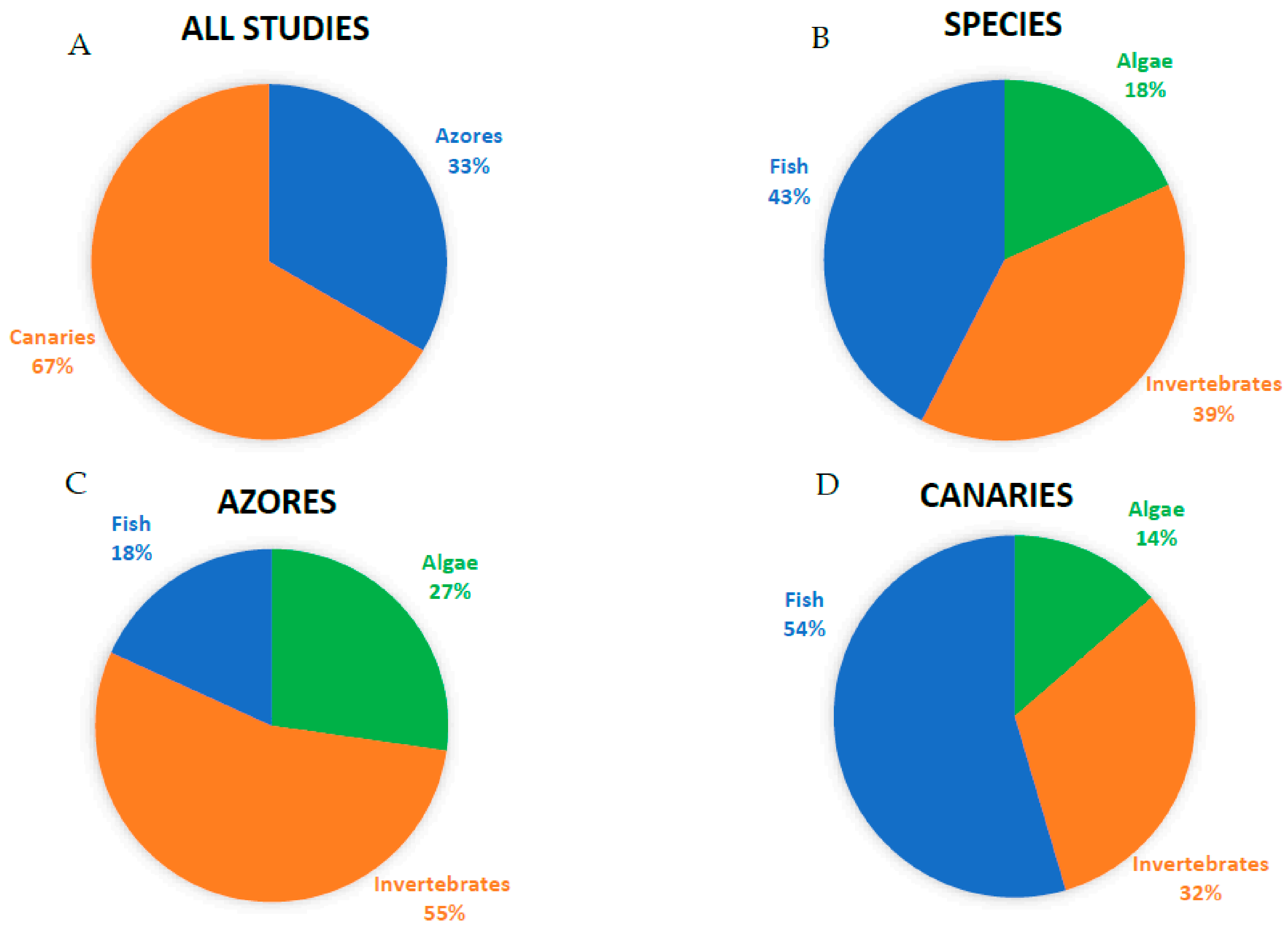

Figure 3. The proportion of groups/taxa recorded in the articles included in the Azores and Canaries systematic review: (**A**) Proportion of studies for each archipelago; (**B**) Proportion of groups/taxa studies among archipelagos; (**C**) Proportion of groups/taxa studies in the Azores; (**D**) Proportion of groups/taxa studies in the Canaries.

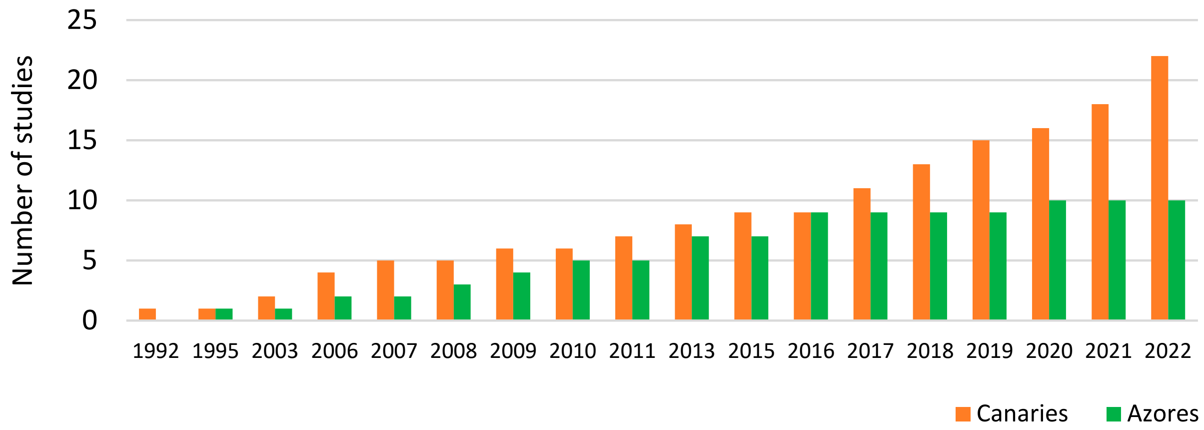

Figure 4. Number of published studies for the Azores and the Canaries over time.

3.2. Shallow Hydrothermal Vents

Seafloor hydrothermal vents emanate hot fluids with high heavy metal contents due to the seawater–rock interaction at elevated temperatures [49,50]. Although most are precipitated onto the sub-seafloor due to cooling when the hot fluids encounter seawater [51], the remaining content is still bioavailable to the surrounding ecosystem. Shallow-water vents

(<200 m) are usually located close to the coastline and in zones of high primary production, posing a higher potential impact on the local environment and ecosystem (e.g., [52]).

Degassing areas in the Azores are related to hydrothermal systems and active shallow-water hydrothermal vent fields are found on the islands of Flores, Faial, Graciosa, São Miguel, and at D. João de Castro Bank [31]; except for the last, most of the other known vents are located near or on the island's shores and are variable in their shore height, depth, substratum composition, and exposition, even vents on the same island [31]. While some are known for their thermal baths (e.g., Ferraria, Varadouro, Lajedo, and Carapacho), on São Miguel Island, the vent sites Mosteiros, Ferraria, Ribeira Quente, and Porto Formoso are in intertidal areas used by locals for leisure. Data on the gas is only available for D. João de Castro Bank [53].

Most data obtained for the Azores are concentrated in São Miguel Island (see Supplementary Material). In [54], the authors evaluated the bioavailability of metals in *Patella candei* d'Orbigny, 1839, living close to shallow-water hydrothermal vents, reported modifications in the organism's morphometry, and higher metal concentrations (Cs, Co Cu, Mn, Rb, and Zn) but not for Cd. However, trace metal assessment on barnacles *Chthamalus stellatus* (Poli, 1791) by [55] and *Megabalanus azoricus* (Pilsbry, 1916) by [56] revealed high levels of Cd in the organisms near the Ferraria and Mosteiros vents, several times higher than MLs. In [16], the study aimed at evaluating trace metal concentrations in algae and invertebrates and concluded they were well adapted to the metal-enriched waters of the study site with high Cd content, especially invertebrates (D. João de Castro Bank). In [32], the authors showed that algae in the vicinity of vents had higher concentrations of Mn, Rb, and Zn, although not Cd. The studies [57,58] looked at metal content in the crab *Pachygrapsus marmoratus* (Fabricius, 1787) and the ray *Raja clavata* Linnaeus, 1758, and detected some Cd, although not at high levels. Recently, a study focusing on the abalone *Haliotis tuberculata* Linnaeus, 1758, detected levels of Cd several times higher than the MLs [34].

Figure 5 shows the location of shallow hydrothermal vents around São Miguel and the Cd content detected in the various sites where biota was collected. In addition, the Cd content of *M. azoricus* did not show significant differences between populations from S. Miguel and Santa Maria, the oldest island, where there are no vents. Some studies have argued that, although the submarine discharges of heavy metals affect marine organisms [59–61], the measurable influence of hydrothermal activity is quite localized and limited to an area of <1 km^2 [50,62]. Hence, an influence beyond the vicinity of the vents is probably negligible given the huge dilution in seawater. Present results attest to this hypothesis, considering that it is not possible to ascertain a clear relationship between the Cd content and vents' proximity.

The Canaries have two shallow water vents, one in El Hierro [63], although not so shallow, and another recently discovered in La Palma [62]. However, the Cd values detected in the few studies performed were low in the gastropod species tested (see Supplementary Material). Similar to the Azores, there is no obvious link between vent proximity and Cd content in the few studied species.

Considering these results, it would be important to focus on other variables. In [64], the authors reported high concentrations of Cd in samples of basalt from the mid-ocean ridge, in basalt from submarine and subaerial oceanic volcanic islands, and submarine arc lavas; this would be in line with the higher Cd content detected in more sessile species (e.g., barnacles), usually occurring closer to the coast (intertidal), hence closer to vents. Cd in the water column may not be the problem according to [65], nor in the sediments [66]. More studies are thus crucial to understanding this phenomenon. Species with different habitats and life traits should be sampled at various distances from vents and the coastline, in different islands, and among other geographical locations, while considering each species' distribution to allow reasonable comparisons between and within populations and ecosystems over time and space. At the same time, vent fluids should be analyzed and monitored, and the substrate where these species occur should also be investigated.

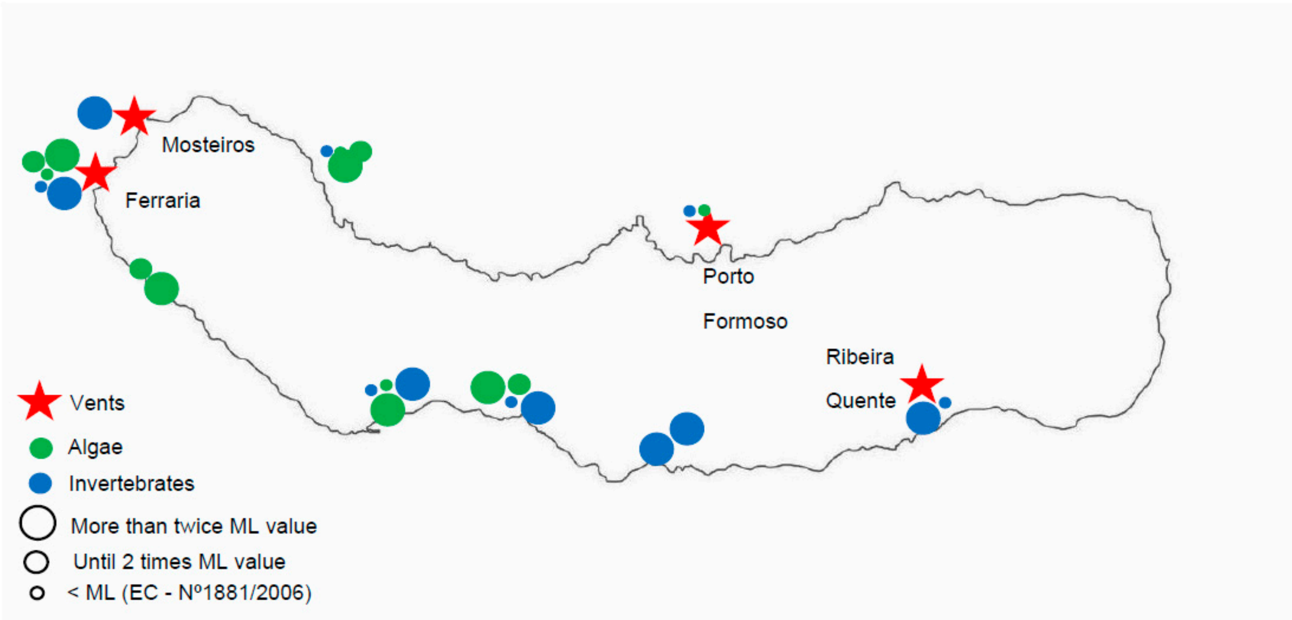

Figure 5. Location of studies on Cd content in São Miguel Island in algae (green color dots) and invertebrates (blue color dots). Stars represent the location of shallow water hydrothermal vents based on Couto et al. (2015) and the size of the dots represents the amount of Cd detected according to maximum legislated limits (ML); Regulation (EC) No 1881/2006: 0.05 (algae), 0.5 (crustaceans), 1 (mollusks) in mg kg^{-1} wet weight.

3.3. Natural vs. Anthropogenic

There was considerable variability in the detected concentrations between and within species and populations, reflecting the influence of ecological features in the concentration of metals accumulation in fish species, such as habitat use and feeding habits. Age, size, and feeding habits of fish, as well as the amount of time spent in habitats with polluted waters during their life cycle, are also known to influence metal contents in these organisms [67–69].

Figure 6 shows the Cd content of the various coastal species studied in Macaronesia. According to available studies, it should be noted that Cd concentration was found to increase significantly with size, although further biomagnification in higher trophic levels appeared unlikely (Figure 6, invertebrates and fish). There are no obvious biomagnification or biodilution trends in global marine food webs [70]. Prey specificity, which affects metal assimilation efficiency (AE), ingestion rate (IR), and metal efflux rate constant (ke), influences metal magnification throughout trophic levels [71]. Gender has been also reported to influence metal concentration, which can be attributed to prey preference, diet seasonal shifts, or maturity stage; some species can even transfer heavy metals from the female body to the eggs, or directly to the embryo, however, no significant differences were found between genders in the selected studies (see Supplementary Material).

Macroalgae bioaccumulate trace metals from the surrounding water column [72,73]. Rocky subtidal habitats of these oceanic islands are dominated by macroalgae and other temperate algal beds, which are particularly sensitive accumulators as their cell walls contain many sulfated polysaccharides for which metals display a high affinity for Zn, Cu, and Pb [72] but not Cd, which appears relatively low in both archipelagos and not exceeding the MLs (Figure 6).

Overall, invertebrates seem to accumulate more Cd, particularly the Azorean coastal species, and especially the most sessile (Figure 6). Azorean barnacles seem to accumulate high levels of Cd, together with some gastropods and polychaetes. Consistently, numerous studies indicated the potential biomagnification of Cd in crustaceans, as they could effectively sequester dietary Cd and store it in a detoxified form, whereas fish had very low assimilation efficiencies in this process [71,74]. However, this does not explain the huge differences between archipelagos.

Fish species, as expected, accumulate Cd in the liver [58,75,76], although the number of studies performed on Azorean species is still too low to allow reasonable conclusions or even comparisons. One of the most common detoxification strategies observed in marine vertebrates is the binding of metals to metallothioneins [77], which are mainly present in liver and kidney tissues [78,79], thus protecting against the toxic effects of certain metals, Cd in particular [80]. Hence, the liver has an important role in contaminant storage, redistribution, detoxification, or transformation acting as an active site of pathological effects induced by contaminants, mainly in fish [81,82]. Benthic coastal species (e.g., *Diplodus* sp. Rafinesque 1810, *Sparisoma cretense* (Linnaeus, 1758), and *Sarpa salpa* (Linnaeus, 1758)) feeding near the substrate should be more carefully focused and monitored, allowing more reasonable comparisons between and within populations of the same species across different geographical locations.

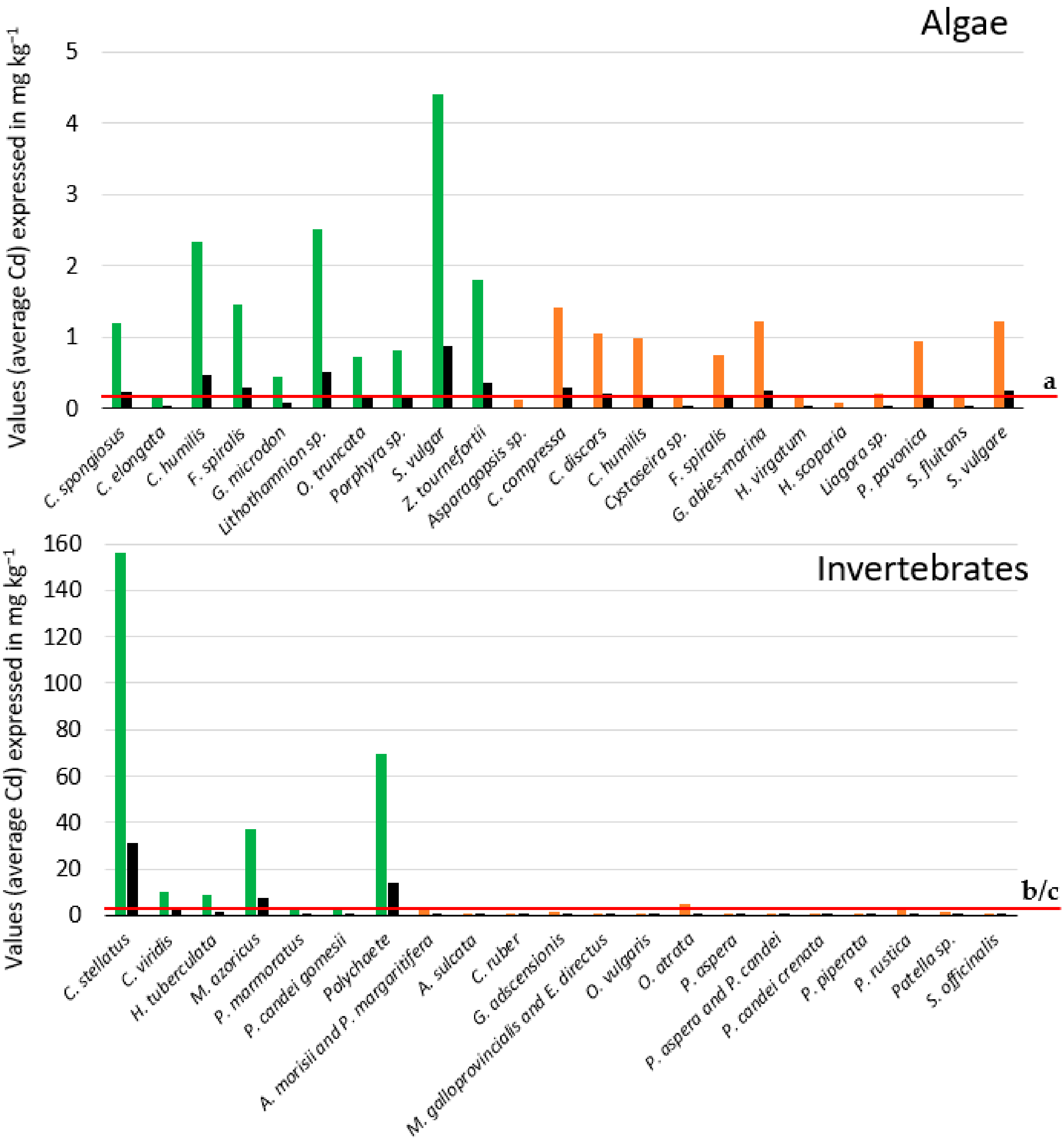

Figure 6. *Cont.*

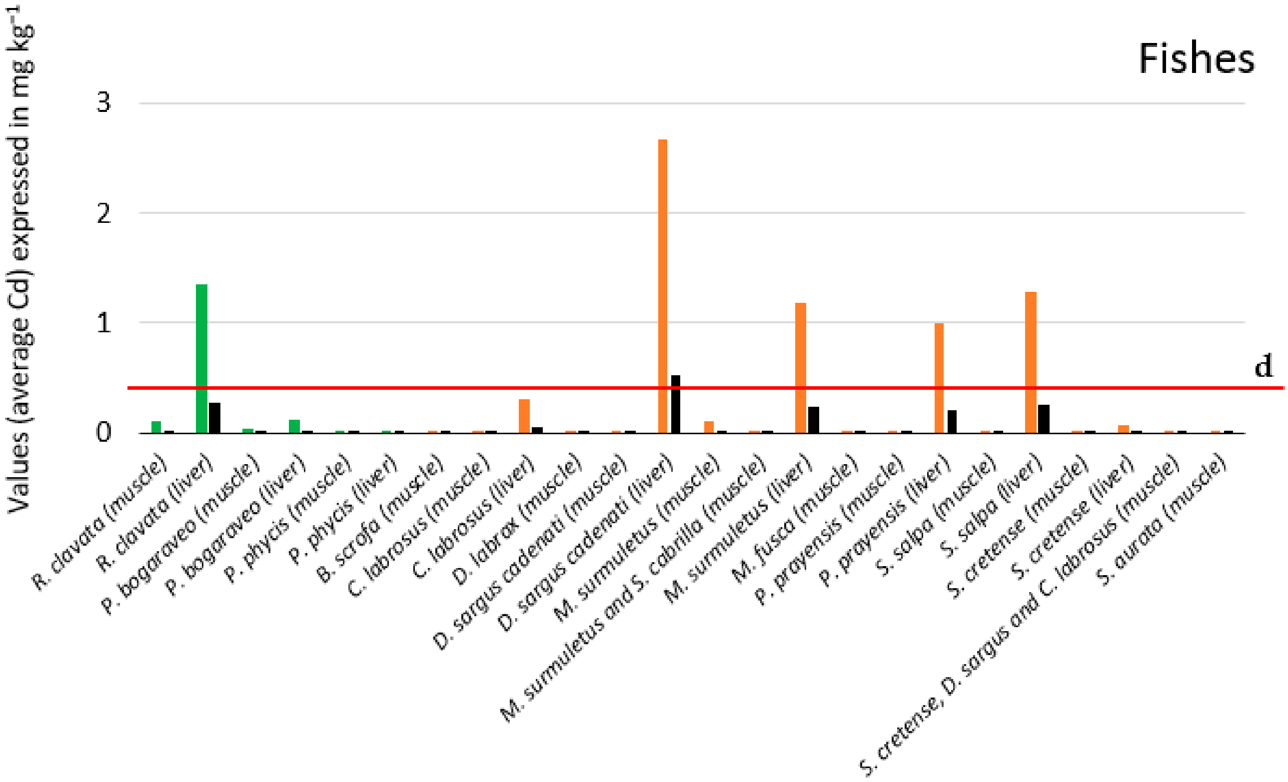

Figure 6. Cadmium content (mean mg kg^{-1} dry weight) according to several taxa. Green columns represent Azores studies, orange columns represent studies performed in the Canaries, and black columns represent values in wet weight. Red lines represent maximum levels of cadmium, in wet weight, according to Regulation (EC) No 1881/2006: (a) 0.05 (seaweeds), (b) 0.5 (crustaceans), (c) 1 (mollusks), and (d) 0.05 (fishes).

Data from both archipelagos were compared with the Cd concentrations reported for other species, including edible ones, from different localities with known anthropogenic impact (Mediterranean Sea), sharing the same trophic niche for algae, invertebrates, and fishes (see Supplementary Material-Table S4). From this large survey, it is possible to observe that Cd concentrations are generally lower than the ones obtained for Macaronesia. Results from NMDS and subsequent ANOSIM analysis (Figure 7) clearly show significant dissimilarities between regions, attesting to the presence of strong, apparently natural, Cd coastal sources that should be carefully studied and monitored. These results should always be looked at with some care considering the reasons stated above regarding variability between and within species (different species were grouped into algae, invertebrates, and fishes) and the number of selected studies of the Mediterranean that, while thorough, does not include all the works performed in that region.

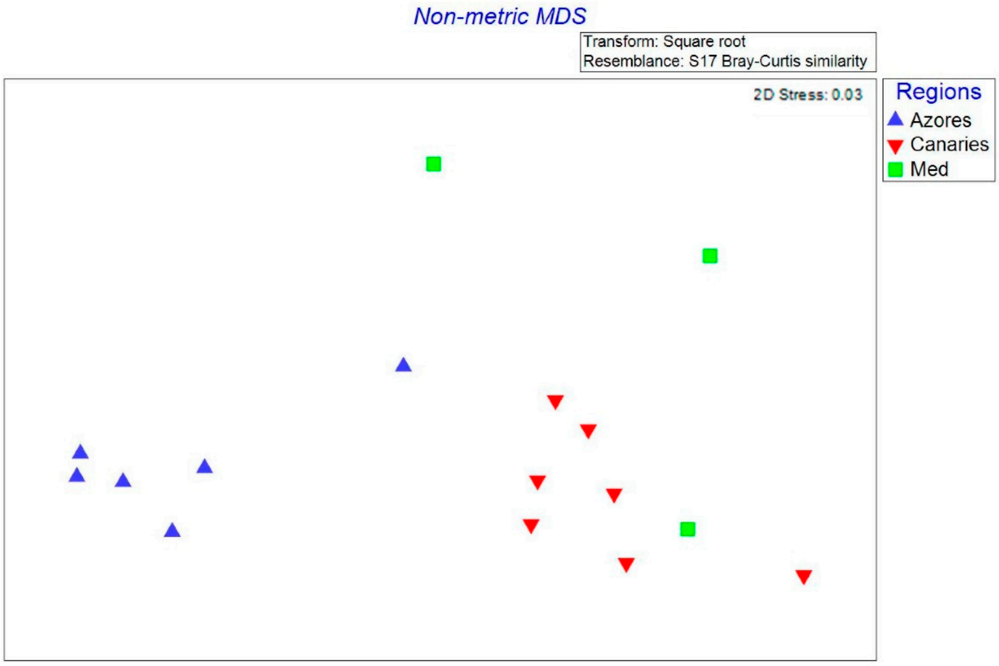

Figure 7. Non-mMDS, based on Bray–Curtis similarity of square root transformed data of the Cd content among algae, invertebrates, and fishes compared between regions (Azores, Canaries, and Mediterranean). Tests for differences between unordered regions groups (ANOSIM): Global Test Sample statistic I: 0.789; Significance level of sample statistic: 0.1%; Number of permutations: 999.

3.4. Risk Assessment

According to Eurostat, Portugal has the highest annual seafood per capita consumption in the EU (60 kg/capita) and mollusks are an important component in consumers' diets. In addition, as tourism grows in the Azores, many edible marine resources are rapidly becoming a local delicacy with increasing demand, which makes it important to ensure a healthy and sustainable supply, especially considering the high Cd levels reported.

A health-based guidance value for Cd of 7 μg kg^{-1} body weight (bw)/wk (provisional tolerable weekly intake-PTWI) was established previously by the Joint FAO/World Health Organization (WHO) Expert Committee on Food Additives and endorsed by the Scientific Committee for Food [83]. Hence it is important not only to establish Cd content in the several edible tissues of different species but also to estimate the corresponding PTWI based on the average daily metal exposure EDI (mg/kg/day body weight), according to the target population diet and consumption rate. The Joint FAO expert Committee of Food Additives has also suggested provisional tolerable daily intakes (PTDI) for Cd (JEFCA, 2015) for an average adult (70 kg body weight). Another important parameter to estimate is the target hazard quotient (THQ), a ratio of the determined dose of a pollutant to a reference dose level. If the ratio is less than 1, the exposed population is unlikely to experience obvious adverse effects [34,84].

As stocks of some coastal resources diminish, there is increasing pressure to find alternatives. Apart from the gathering of stranded seaweed for traditional agricultural use, there are currently 11 'algae' legally regulated and allowed to be collected in the Region of the Azores (Portaria n°69/2018), and, in the future, others might arise. Some of these species show Cd content higher than respective MLs, although Regulation (EC) No 1881/2006 uses the general term "seaweed".

The barnacle *M. azoricus* [33] and abalone *H. tuberculata* [34] are important socioeconomic resources, both are already proven to contain Cd concentrations much higher than MLs. In addition, more studies and monitoring are required for the limpets (*Patella* sp.), another locally prized delicacy sought by foreigners like octopuses, lobsters, and crabs [48]. Additionally important, although often neglected, are other potential invertebrate species such as holothurians, sea urchins, or even other gastropods that should be subject to heavy metal assessment, especially considering their life traits. These species face growing worldwide pressure as food resources, especially for the gourmet market. It is therefore not surprising that local demand has started to rise, also taking advantage of an unregulated open-access regime and lack of scientific advice [48].

Fishes are very poorly studied, especially in the Azores. Although Cd preferentially accumulates in the liver, it is still essential to monitor these resources, which are very important at a socioeconomic level and part of the local diet; these include mostly benthic species with small home ranges: morays, groupers, parrotfish, seabreams, hogfishes, and even wrasses [48].

4. Future Research Challenges

4.1. Stable Isotopes

Cadmium is a non-essential metal for living organisms and natural sources include weathering of rock and volcanic activity, while anthropogenic activity also contributes to its inputs, although this distinction may not be so obvious when dealing with marine ecosystems. Recently, new tools became available to study geochemical and ecotoxicological aspects of marine metal contamination, pushing the frontiers of present knowledge.

The development of the Multicollector ICP-MS in the middle 1990s, together with improvements in field sampling, chemical purification, and automatization increased throughput, allowing access to several “new” metal isotope systems (e.g., Li, Mg, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, Sr, Ag, Cd, Sn, Pt, and Hg) referred to as “non-traditional” isotopes (see [85] for a review). These isotopes can be a valuable tool to detect human-induced changes across time-space involving metals and their interaction with marine ecosystems, trophic transfers, and intracellular interactions of trace metal contaminants, up to physiological effects.

Source identification is critical to effectively improving the control and treatment of heavy metal contamination and isotope technology can assist in tracing the sources of heavy metal pollution. Despite its infancy, Cd isotopes have already proven to be effective source tracers successfully applied to the studies of river sediments, water, aquatic organisms, aerosols, plants, and soil pollution, characterizing metal transfer from contamination sources [86–103]. Cadmium isotopic compositions in non-contaminated systems and anthropogenic sources generally have different isotopic signatures, allowing fingerprinting of the original sources.

The Macaronesia region would indeed greatly benefit from this new field of study and perhaps many questions could be finally answered, especially considering the apparent low anthropogenic activity when compared to regions in the mainland.

4.2. Biomarkers

Organisms such as fish and other marine species are used as bioindicators of environmental pollution (Okay et al., 2016). Recently, the use of biological markers or biomarkers, at the molecular or cellular level, has been proposed as sensitive ‘early warning’ tools in environmental quality assessment, anticipating changes at higher levels of biological organization, i.e., population, community, or ecosystem [104–106].

The most studied biomarkers used to evaluate exposure to and the effect of differentcontaminants, such as metals, organic xenobiotics, and organometallic compounds are: metallothionein induction, acetylcholinesterase inhibition, cytochrome P450 system induction, imposex, lysosomal enlargement, lysosomal membrane destabilization, and peroxisome proliferation [105]. In addition, when in contact with metals, the cells generate specific reactive oxygen species (ROS), a major precursor of oxidative stress [107,108]. To counter these effects, the body activates a series of antioxidant defense systems such as superoxide dismutase (SOD), catalase (CAT), and the glutathione triad: reduced glutathione (GSH), glutathione s-transferase (GST), and glutathione peroxidase (GPx). These specific functions in detoxifying the ROS species generated by aquatic pollutants are a major focus of research nowadays, serving as early warning signals for higher-level organismal responses so that health-compromising functional disorders can be anticipated.

Besides oxidative stress, one of the sub-cellular responses to Cd exposure is modified metallothionein levels (MT), low molecular weight proteins commonly found in detoxifying organs such as the liver and kidney [106,109]. Cholinesterase activity (ChE) is another widely used biomarker of Cd exposure, since it tends to be inhibited by neurotoxic insecticides, hence used as an early-warning and specific response biomarker for neurotoxic effects [110].

Biomarkers have been incorporated into several pollution monitoring programs in Europe and the USA. The United Nations Environment Program has funded a biomonitoring program in the Mediterranean Sea including a variety of biomarkers. More recently, biomarkers have also been included in the Joint Monitoring Program of the OSPAR convention where Portugal and Spain are members, justifying its research in the Macaronesia context, especially considering its geological setting, reflected in the Cd levels detected so far, particularly in the Azores.

5. Conclusions

This study presents a detailed description of the current situation or state of research on Cd in coastal species of the Macaronesia archipelagos, looking at the strengths and weaknesses that need to be addressed. The literature used for this review corresponds to that which is published and available in the database used; therefore, it is possible that these databases or even the keyword search used may not contain all the studies carried out on the coast of both archipelagos. The studies for each region depend very much on the allocation of resources and the different strategies of the research teams or regional governments.

Regarding Cd, the Azorean studied species seem to be strong accumulators and important bioindicators according to each species' biological and ecological traits, particularly the less mobile and sessile, displaying high and potentially toxic levels that should be closely monitored. Available data reveals an important local natural source of Cd given the volcanic nature and geological setting of the Azores that should not be underestimated, although the available studies do not seem to reflect the influence of shallow water hydrothermal vents on the reported Cd contents.

Future studies should assess this issue in more detail, focusing on the development of a set of key biomarkers to easily assess the status and trends within an ecosystem both at the population and community levels, together with studies focused on vent fluids, sediments, petrology, and mineralogy. Several species from different taxonomic and trophic levels should be sampled to measure heavy metal content and determine baseline levels in several areas and different islands, according to each species' traits, home range, and distribution (to allow reliable and reasonable geographical comparisons). Sampling should also be conducted several times during the year to understand oceanographic and seasonal constraints, providing a temporal perspective and helping to determine the main accumulation and detoxification pathways. Regarding edible species, it is also vital to ascertain and monitor whether the concentrations of these pollutants are below the maximum legal levels established by the EU from a public health perspective, also considering the increasing number of tourists that consume many of these local delicacies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jmse11010100/s1, Table S1: Systematic review screening process; Table S2: Full-text articles assessed for eligibility; Table S3: Data extracted from the final publications included in the analysis; Table S4: Cadmium concentrations reported for Mediterranean species.

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