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Metal Concentration in *Palaemon elegans* along the Coastal Areas of Gran Canaria (Canary Islands): Potential Bioindicator of Pollution

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Abstract: Ocean pollution poses a significant issue in the marine ecosystem. Coastal areas are particularly impacted by this pollution, and consequently, organisms associated with these coasts bear the brunt of its effects. Therefore, the presence of robust bioindicators, such as the shrimp species *Palaemon elegans*, is critically important. In this study, 20 *P. elegans* specimens were examined in each of the five areas on Gran Canaria Island. Water samples were collected to assess the potential existence of elevated concentrations. Significant discrepancies were observed in the levels of Al and Li across all zones, except those previously mentioned. The highest concentrations were recorded in Arguineguín (Southern sector), reaching 49.14 ± 4.51 mg/kg (Al) and 47.64 ± 2.86 mg/kg (Li). The authors contend that *P. elegans* proves to be a reliable bioindicator for tourist and port-related pollution, specifically for the metals Al, Zn, Cd, Pb, Ni, Fe, B, and Li analyzed in this research.

Keywords: biomonitor; shrimp; ICO-OES; trace elements

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1. Introduction

Crustaceans play a vital role as a significant fishing resource in numerous countries, serving as a key source of sustenance and a well-established industry contributing to economies worldwide. Diverse methods are utilized to capture these resources, including trawling, gill nets, pots, traps, traditional shellfishing, and spearfishing. Ensuring the sustainable management of this resource is imperative, taking into account the varied interests of stakeholders residing in coastal areas or relying on marine and coastal resources. These stakeholders encompass fishermen, fishing industries, aquaculturists, handling and trade companies, educators, local authorities, and consumers [1–6]. The management of marine resources revolves around the principles of conservation and sustainable utilization. This involves the implementation of conservation strategies, regulation of fishing activities, and addressing pollution. Furthermore, it entails the preservation of biological diversity and wildlife, controlling overfishing, protecting marine ecosystems, and preventing anthropogenic pollution [7–12].

Marine pollution arises from the infiltration of toxic substances and waste into oceans, leading to various adverse effects on the health of marine organisms, human communities relying on them for sustenance, and various adverse effects on overall environment. These harmful substances stem from a variety of sources, including agriculture, industry, sewage discharge, shipping activities, atmospheric debris, oil extraction, and fishing operations [13–19]. The repercussions of marine pollution are extensive, encompassing a range of issues such as habitat destruction, alterations in the oceans' chemical composition, depletion of wildlife populations, and contamination of food sources. Additionally, marine pollution can pose health risks to humans, including poisoning from mercury, lead, and cadmium, as well as foodborne illnesses [20–22]. Given these concerns, it is crucial to conduct periodic monitoring of coastal and pelagic fishing resources to assess the levels of metals and trace elements. The present study examined a sample of the pool shrimp *Palaemon elegans* Rathke, 1836, obtained from coastal waters surrounding the island of Gran Canaria (Canary Islands), and aimed to evaluate its potential as a bioindicator of coastal pollution.

2. Material and Methods

For the monitoring study, a total of 20 *Palaemon elegans* samples were collected from each designated zone along the coastal periphery of Gran Canaria, and the areas have been chosen based on the topography of the island of Gran Canaria, taking into account pollution sources as well. Bañaderos and El Confital were selected because they are the two areas with the lowest tourist density, resulting in significantly lower pollution levels. Arguineguín was chosen because it is the most touristic area among the selected ones, leading to higher pollution due to tourist pressure. El Confital was chosen due to its proximity to the island's capital and, therefore, its exposure to strong tourist pressure. Agaete was chosen because it is located in a port with high maritime traffic. Moreover, we gathered 10 water samples from the identical puddles where we retrieved the shrimp (n = 50) in February 2022 (Figure 1).The choice of these zones was deliberate, comprising Confital, recognized as a legislatively protected area; Agaete with a bustling ferry port; Bañaderos situated on the less anthropogenically pressured northern slope; Arinaga positioned on the southwestern slope abundant with factories; and Arguineguín on the southern slope known for its high tourist population. The total length of each specimen was measured in millimeters (mm) using a digital caliper.

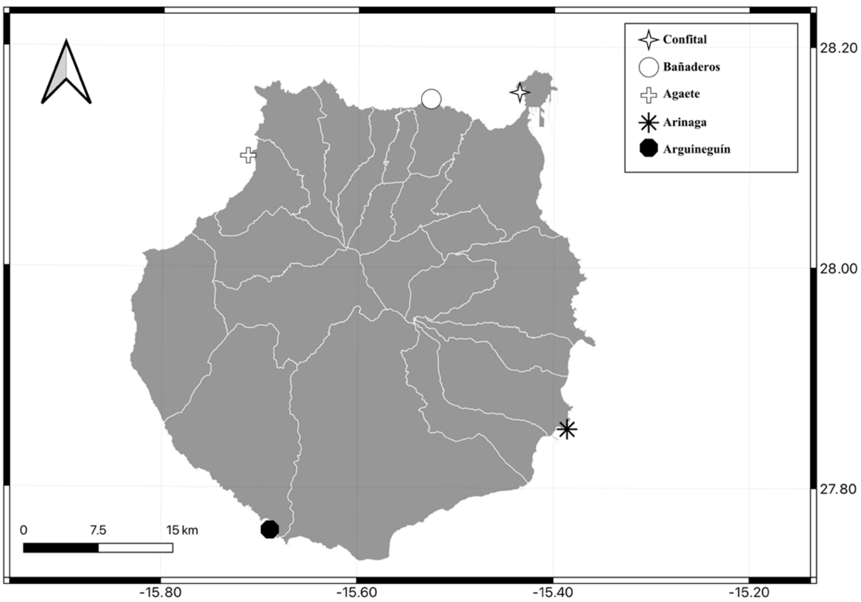

Figure 1. Map of Gran Canaria showing study areas.

2.1. Sample Preparation

For analytical procedures, a 0.5 g sample of the abdomen was extracted from each shrimp specimen. Concurrently, water samples were collected from the same intertidal pools where the study specimens were captured, utilizing 25 mL of water for the sampling process. The sample preparation entailed initial drying in an oven at 70 °C, followed by ashing in a muffle furnace at 450 ± 25 °C. Subsequently, a solution comprising 10 mL of 1.5% HNO_3 was introduced to each sample. The subsequent analysis of the samples was performed utilizing inductively coupled plasma-optical emission spectrophotometry (ICP-OES) employing a Thermo Scientific ICAP 6300 Duo model (Waltham, MA, USA) equipped with an Auto Sampler (CETAX model ASX-520). Al, Zn, Cd, Pb, Ni, Fe, B, and Li were analyzed because they are anthropogenic metals when found in high concentrations [23]. Table 1 contains details regarding the limits of detection. To ensure the precision and accuracy of the analytical measurements, quality control measures were rigorously enforced. This encompassed the use of blank samples as controls and the incorporation of reference materials like ERM-CE278 mussel tissue and SRM1566b oyster tissue in the analysis. Notably, the recovery rate achieved using these reference materials exceeded 98%.

Table 1. Limits of detection and quantification of the analyzed elements.

Metal	Wavelength (nm)	Limit of Detection (mg/L)	Limit of Quantification (mg/L)
Al	167.0	0.004	0.012
B	249.7	0.003	0.012
Cd	226.5	0.0003	0.001
Fe	259.9	0.002	0.005
Li	670.8	0.005	0.013
Ni	231.6	0.0007	0.003
Pb	220.3	0.0003	0.001
Zn	206.2	0.002	0.007

2.2. Statistical Analysis

To investigate the potential differences in heavy metals and trace metals content and relative composition among the analyzed tissue samples, a permutational multivariate analysis of variance (PERMANOVA) was conducted. Euclidean distances were utilized for the analysis. The study employed a one-way design with the fixed factor "zone", which consisted of five variation levels (Confital, Bañaderos, Agaete, Arinaga, and Arguineguín). The analysis incorporated the following variables: Al, Zn, Cd, Pb, Ni, Fe, B, and Li. To examine the dissimilarities between the zones, a principal coordinate analysis (PCoA) was employed. This analysis represented the metals that best accounted for the data variability as vectors. Additionally, one-way permutational analyses of variance were performed using Euclidean distances based on the raw data. A total of 9999 permutations of interchangeable units were employed in the analyses. Pairwise post hoc comparisons were conducted to assess differences between significant factors at a p-value threshold of <0.05. The statistical packages PRIMER 7 and PERMANOVA þ v.1.0.1 were used for the statistical analyses [24,25].

3. Results

Table 2 presents the mean total length and descriptive statistics for the metal content of the shrimp samples. Shrimp specimens from Bañaderos exhibited the longest mean length. In terms of metal and trace element concentrations, Arguineguín had the highest levels, followed by Agaete. Table 3 displays the outcomes of the PERMANOVA analyses. No noteworthy disparities were observed in the total length among the sampling areas. Consequently, the total length of the specimens will not be factored into the analysis of metals and trace elements. Moreover, in the statistical examination of each metal and trace element, no significant differences emerged for any of the elements between Bañaderos

(Northern sector) and Arinaga (Eastern sector), nor between Confital (NE sector) and Agaete (NW sector). Al and Li presented significant differences between all the zones, except for those already mentioned, with the highest concentrations being registered in Arguineguín (Southern sector) with 49.141 ± 4.511 mg/kg (Al) and 47.640 ± 2.865 mg/kg (Li). The samples from Arguineguín had higher concentrations of all metals than the other four zones, followed by those from Agaete.

Table 2. Descriptive statistics of all the elements analyzed in each sampling zone (Mean, standard deviation, minimum, and maximum). Total length (TL, cm) and metal content (mg/kg).

		Confital	Bañaderos	Agaete	Arinaga	Arguineguín
TL	**Mean**	3.72	3.78	3.76	3.72	3.72
	Sd	0.16	0.28	0.27	0.16	0.21
	Min	3.5	3.4	3.4	3.5	3.4
	Max	4.0	4.2	4.2	4.0	4.0
Al	**Mean**	40.70	36.30	42.23	36.52	49.14
	Sd	2.27	2.57	4.12	3.58	4.51
	Min	36.68	32.04	34.86	31.39	42.25
	Max	43.27	39.34	47.08	41.94	56.43
Zn	**Mean**	19.23	17.14	19.92	17.18	22.82
	Sd	2.22	2.07	2.63	1.81	1.53
	Min	16.26	14.78	17.15	15.17	20.78
	Max	23.68	21.53	25.77	21.10	25.70
Cd	**Mean**	0.073	0.065	0.075	0.065	0.084
	Sd	0.016	0.014	0.017	0.013	0.014
	Min	0.058	0.052	0.057	0.051	0.070
	Max	0.096	0.088	0.105	0.086	0.109
Pb	**Mean**	0.132	0.118	0.137	0.118	0.152
	Sd	0.028	0.026	0.033	0.026	0.016
	Min	0.107	0.098	0.109	0.096	0.132
	Max	0.201	0.182	0.218	0.179	0.184
Ni	**Mean**	0.590	0.525	0.609	0.523	0.695
	Sd	0.186	0.164	0.188	0.152	0.222
	Min	0.376	0.342	0.409	0.369	0.496
	Max	0.903	0.789	0.928	0.773	1.094
Fe	**Mean**	20.21	18.01	20.98	18.0	22.974
	Sd	3.27	2.98	3.94	2.641	0.92
	Min	16.29	14.81	17.73	15.97	21.49
	Max	27.75	25.22	30.19	24.72	24.62
B	**Mean**	4.128	3.681	4.265	3.687	5.04
	Sd	0.840	0.768	0.890	0.721	0.442
	Min	2.839	2.479	3.089	2.430	4.451
	Max	5.789	5.263	6.299	5.158	5.657
Li	**Mean**	38.59	34.39	39.95	34.56	47.64
	Sd	2.51	2.34	3.23	2.93	2.86
	Min	34.93	31.75	36.24	31.11	43.92
	Max	42.17	38.33	45.88	40.28	54.20

Table 3. Results of pairwise tests examining the significant factor "Zone" obtained in a one-way ANOVA analyzing the metal content variation and Total length (TL). * $p < 0.05$.

Groups	TL	Al	Zn	Cd	Pb	Ni	Fe	B	Li
Bañaderos, Confital	0.688	0.009 *	0.088	0.306	0.348	0.483	0.203	0.327	0.009 *
Bañaderos. Agaete	0.882	0.007 *	0.034 *	0.237	0.235	0.352	0.131	0.215	0.001 *
Bañaderos, Arinaga	0.706	0.923	0.967	0.973	0.956	0.997	0.974	0.985	0.912
Bañaderos, Arguineguín	0.696	0.001 *	0.002 *	0.015 *	0.007 *	0.127	0.003 *	0.003 *	0.001 *
Confital, Agaete	0.839	0.424	0.609	0.725	0.721	0.832	0.706	0.760	0.399
Confital, Arinaga	0.986	0.020 *	0.077	0.273	0.321	0.484	0.184	0.320	0.022 *
Confital, Arguineguín	0.955	0.002 *	0.009 *	0.115	0.079	0.311	0.048 *	0.029 *	0.001 *
Agaete, Arinaga	0.857	0.019 *	0.036 *	0.200	0.267	0.342	0.119	0.212	0.002 *
Agaete, Arguineguín	0.842	0.007 *	0.031 *	0.276	0.217	0.446	0.156	0.041 *	0.003 *
Arinaga, Arguineguín	0.963	0.001 *	0.002 *	0.016 *	0.009 *	0.042 *	0.002 *	0.001 *	0.001 *

These findings were prominently evident in the PCoA analysis, elucidating approximately 89.1% of the overall data variability (Figure 2). The sample distribution distinctly showcased a notable disparity in heavy metal content within the Arguineguín area in comparison to the other four zones. While these groups exhibited some overlap, indicating a resemblance in heavy metal levels among them, the Arguineguín area stood out. The metals delineating the observed data variability were visually represented as vectors in the PCoA plot. Particularly, aluminum (Al), iron (Fe), lithium (Li), and zinc (Zn) demonstrated a discernible ascending trend in the Arguineguín area in contrast to the other locations, despite considerable variation observed within the samples.

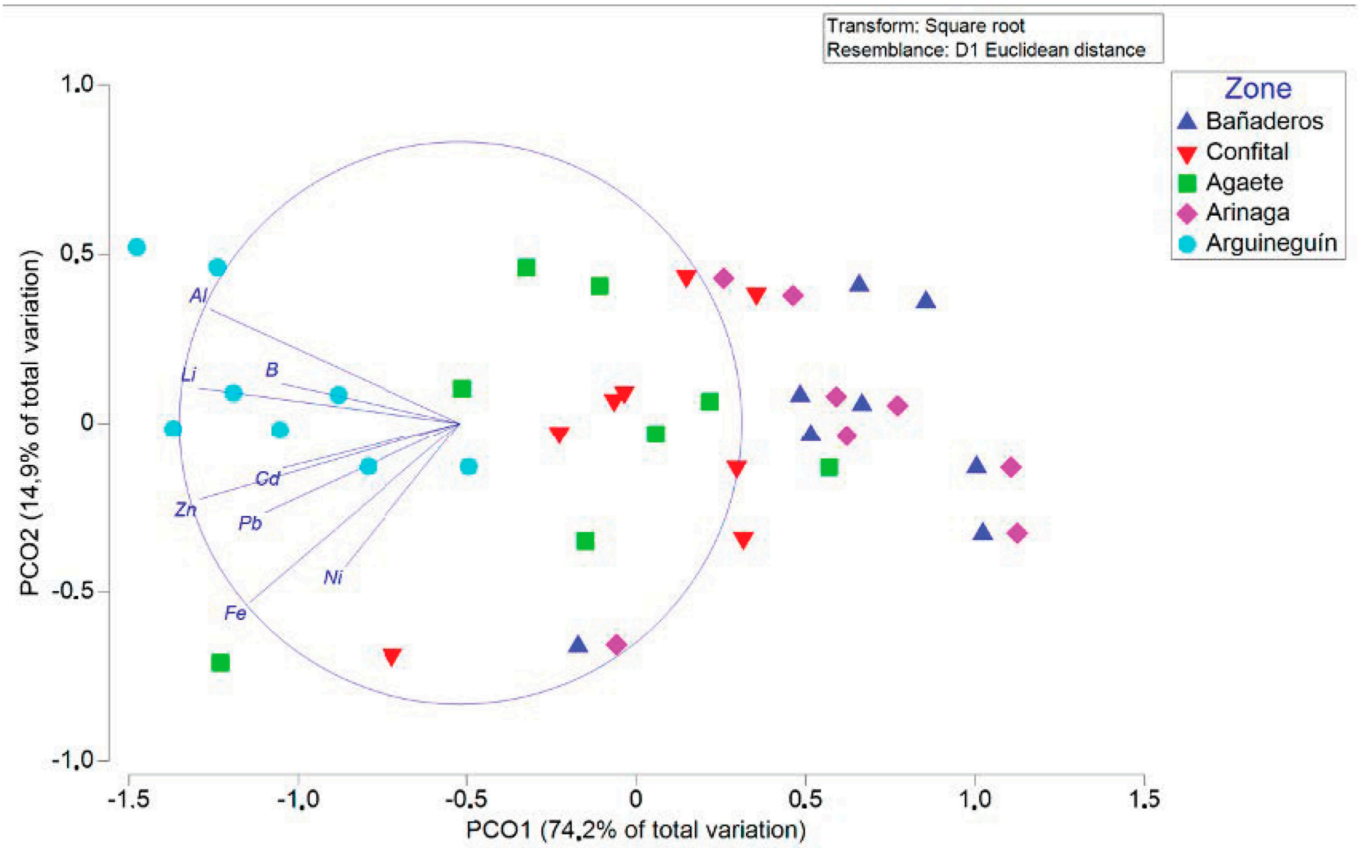

Figure 2. Principal coordinate analysis (PCoA) showing the first two axes (89.1% of variability), based on Euclidean distances of square-root-transformed data of heavy metal and trace element content in the five areas.

4. Discussion and Conclusions

The obtained results revealed that *Palaemon elegans* specimens from the Arguineguín zone exhibited elevated concentrations of metals and trace elements compared to the other areas. This disparity may stem from the fact that the southern sector of the island, being the most touristic, experiences heightened anthropic activity in comparison to the other designated stations. Pollution in tourist-oriented regions is a burgeoning concern affecting numerous parts of the globe. This surge is primarily attributed to the escalating number of tourists visiting these locations, consequently driving up the demand for fossil fuels, waste production, and pollution of air, water, and soil [26–30]. Agaete represented the zone where *P. elegans* demonstrated the second-highest concentrations of heavy metals and trace elements. Notably, this area is characterized by the presence of both a commercial and fishing port. Pollution from ports poses a significant environmental challenge for coastal communities worldwide [31–34]. While ports are vital sources of employment, they can also become sources of pollution if adequate preventative measures are not implemented. Pollution from ports can stem from various origins, including the release of industrial waste, fuel disposal, usage of pesticides and herbicides, sewage discharge, and rainwater runoff. These sources can have detrimental impacts on human health, the environment, and marine ecosystems [35–39]. The authors posit that *P. elegans* serves as a reliable bioindicator of both tourist and port-related pollution, particularly for metals like Al, Zn, Cd, Pb, Ni, Fe, B, and Li, as examined in this study. Shrimps have been widely employed as bioindicators of pollution across various regions globally. This is attributed to their capacity to absorb and metabolize contaminants present in the water, including heavy metals, pesticides, and other toxic substances. Shrimps also function as environmental sentinels, reflecting contamination levels in the water [1,40–42]. Table 4 displays the concentrations noted in water samples analyzed at diverse locations, all sourced from the identical pools where the shrimp specimens were gathered, while Table 5 delineates the significant differences within each zone concerning specific metals, presenting a consistent trend in the shrimp samples. The existence of contamination by heavy metals in intertidal zones can have profound implications for both the organisms inhabiting these ecosystems and the overall environmental balance. Heavy metals, characterized by their high density, encompass elements such as lead, cadmium, zinc, copper, and others. These metals have the propensity to accumulate within intertidal organisms along the food chain, resulting in an increasing concentration as one ascends the chain. Such accumulation can adversely impact apex predators and, ultimately, individuals who consume contaminated organisms.

Table 4. Descriptive statistics of all the elements analyzed in each water sampling zone (Mean, standard deviation) and metal content (mg/kg).

	Confital	Bañaderos	Agaete	Arinaga	Arguineguín
Al	0.400 ± 0.112	0.383 ± 0.150	0.481 ± 0.178	0.388 ± 0.119	0.502 ± 0.186
Zn	0.067 ± 0.040	0.063 ± 0.027	0.075 ± 0.051	0.069 ± 0.034	0.078 ± 0.060
Cd	0.001 ± 0.000	0.001 ± 0.000	0.002 ± 0.001	0.001 ± 0.000	0.001 ± 0.001
Pb	0.003 ± 0.002	0.003 ± 0.001	0.005 ± 0.003	0.003 ± 0.002	0.004 ± 0.003
Ni	0.060 ± 0.040	0.059 ± 0.042	0.072 ± 0.042	0.062 ± 0.041	0.073 ± 0.051
Fe	0.521 ± 0.251	0.519 ± 0.241	0.561 ± 0.273	0.520 ± 0.244	0.566 ± 0.271
B	1.861 ± 0.620	1.851 ± 0.614	1.900 ± 0.714	1.854 ± 0.624	1.915 ± 0.661
Li	0.052 ± 0.003	0.050 ± 0.003	0.060 ± 0.004	0.051 ± 0.004	0.062 ± 0.005

Table 5. Results of pairwise tests examining the significant factor "Zone" obtained in a one-way ANOVA analyzing the metal content variation in water sample. * $p < 0.05$.

Groups	Al	Zn	Cd	Pb	Ni	Fe	B	Li
Bañaderos, Confital	0.005 *	0.988	0.321	0.357	0.235	0.210	0.427	0.008 *
Bañaderos. Agaete	0.005 *	0.024 *	0.257	0.214	0.450	0.141	0.235	0.002 *
Bañaderos, Arinaga	0.532	0.857	0.943	0.958	0.985	0.920	0.915	0.922
Bañaderos, Arguineguín	0.001 *	0.002 *	0.005 *	0.006 *	0.110	0.001 *	0.005 *	0.002 *
Confital, Agaete	0.317	0.655	0.521	0.472	0.252	0.758	0.760	0.772
Confital, Arinaga	0.009 *	0.085	0.241	0.358	0.417	0.178	0.620	0.012 *
Confital, Arguineguín	0.003 *	0.007 *	0.215	0.087	0.320	0.038 *	0.019 *	0.002 *
Agaete, Arinaga	0.009 *	0.046 *	0.218	0.350	0.471	0.222	0.522	0.001 *
Agaete, Arguineguín	0.007 *	0.022 *	0.242	0.310	0.358	0.165	0.011 *	0.004 *
Arinaga, Arguineguín	0.001 *	0.001 *	0.011 *	0.005 *	0.032 *	0.001 *	0.001 *	0.002 *

Table 6 presents findings from various studies on different *Palaemon* species. Notably, two of these studies were conducted in the Canary Islands on Tenerife, showcasing considerable variability both within those studies and in comparison, to the results of the current study. Lozano et al.'s (2010) concentrations, being determined twelve years ago in an area of Tenerife's capital, suggest a significant source of contamination, particularly considering *P. elegans's* efficacy as a bioindicator. Conversely, Lozano et al. (2016) reported lower values compared to our study, which were attributed to the smaller, juvenile specimens analyzed. In the study by Adebiyi et al. (2020), notably high concentrations of Cd and Pb were reported, potentially linked to the lax pollution control regulations in Nigeria [43–47], and metal values were higher than those obtained in our study, possibly due to the Sea of Marmara being surrounded by countries with extensive maritime traffic. This resulted in concentrated contaminants incorporated into organisms due to slow water renewal rates [48–52]. A study in Scotland (Nugegoda and Rainbow, 1995) reported higher Zn and Cd concentrations than our study, which were potentially linked to shrimp collection near a river mouth, and lad to the sedimentation of nutrients enriching the ocean with metals and trace elements [53–57]. The concentration of heavy metals and trace elements in *P. elegans* muscle is notably higher in the Arguineguín area, which experiences the most significant contamination due to human activities, and is particularly heightened by tourist density. Hence, a more extensive monitoring initiative should be undertaken in this area to assess the ecosystem's condition.

The selection of *P. elegans* as a bioindicator for heavy metal contamination, as opposed to other species like fish, mollusks, jellyfish, seabirds, and marine reptiles, is based on a series of key factors that establish this shrimp as an exceptionally valuable choice for assessing water quality and the well-being of aquatic ecosystems. First and foremost, *P. elegans* boasts a short life cycle and a high reproductive rate, allowing it to swiftly respond to alterations in water conditions and the presence of heavy metals. This rapid response is vital for early pollution detection, ensuring effective monitoring of fluctuations in metal concentrations in water and their impact on aquatic organisms. In contrast to many fish species with longer life cycles and lower reproductive rates, *P. elegans* offers a more concise timeframe for assessing pollution effects, rendering it a more sensitive indicator [58–61]. Moreover, these shrimp are comparatively easy to maintain in laboratory settings, streamlining the execution of long-term studies and controlled experiments. This advantage holds particular significance in scientific research as it facilitates the replication of consistent and comparable experimental conditions across various studies. In comparison, many fish and seabird species pose challenges in terms of captivity, making controlled research more cumbersome. Another advantage of *P. elegans* is its position within the aquatic food chain. As a benthic organism and a part of the diet of numerous fish and seabirds, these shrimp tend to accumulate heavy metals through their dietary intake, effectively reflecting the exposure of other organisms to pollution. This positions them as a valuable indicator for gauging the bioavailability of metals in the environment and their transfer through the food web, which can have significant implications for the health of fish and seabird populations. Additionally, *P. elegans* exhibits a wide geographical distribution and inhabits a variety of aquatic environments, permitting its use as a bioindicator in diverse regions and ecosystems, ranging from estuaries to coastal lagoons. This geographical versatility is especially pertinent for pollution monitoring across varying scenarios where other species may be absent or less representative [62–67].

Table 6. Comparison with other studies on different species of Palaemon (mg/kg).

	Canary Islands			**Nigeria**	**Turkey**	**Scotland**
	P. elegans	*P. elegans*	*P. elegans*	*P. hastatus*	*P. serratus*	*P. elegans*
Zn	19.92	76.9			21.9	86.4
Fe	20.98	62.8		18.8	38.4	
Ni	0.61	8.3	0.03		6.7	
Cd	0.075		0.011	1.3	0.7	0.576
Pb	0.137		0.315	0.91	2.9	
B	4.26		0.177			
	Este estudio	[68]	[69]	[70]	[71]	[72]

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Informed Consent Statement: We confirmed that this manuscript has not been published elsewhere and is not under consideration by another journal. Ethical approval and informed consent are not applicable for this study.

Data Availability Statement: Data will be made available on request.

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