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Heavy metals and trace elements in a threatened population of guanay cormorants (*Leucocarbo bougainvilliorum*) from an industrialized bay in the Humboldt Current System, Chile

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ABSTRACT

Metal contamination from industrial and mining activities threatens coastal and marine ecosystems, leading to bioaccumulation in marine organisms and biomagnification through the trophic chain. The Guanay cormorant (*Leucocarbo bougainvilliorum*), an endemic species of the Humboldt Current System, is experiencing population declines and serves as a key bioindicator of heavy metal contamination due to its high trophic position, reliance on commercially exploited pelagic fish, and capacity to accumulate contaminants over time. This study analyzed the concentrations of five heavy metals (Hg, As, Pb, Cr, Cd) and three trace elements (Cu, Zn, Se) in liver, muscle, feathers, and kidney of 10 Guanay cormorants found dead in Mejillones Bay, Chile, a highly industrialized area. Feathers exhibited the highest concentrations of Cr (2.03 ± 0.63 mg/kg), Cu (19.72 ± 3.82 mg/kg), and Zn (109.84 ± 11.95 mg/kg), emphasizing their role in detoxification. Females showed significantly higher Cu and Pb concentrations in muscle and Cr in kidneys, likely due to physiological and hormonal differences related to reproduction. Correlations between metal concentrations across tissues suggest shared bioaccumulation mechanisms, while the Hg:Se molar ratio (e.g., 0.25 ± 0.04 in liver) indicated a protective role of Se against Hg toxicity. Metal concentrations were comparable to those reported in other marine cormorants but differed from freshwater populations, highlighting the influence of habitat on metal accumulation. Although current levels do not indicate acute toxicity, the ongoing population decline of Guanay cormorants underscores the need for long-term biomonitoring. Future research incorporating biochemical and enzymatic biomarkers is essential to assess potential sublethal effects and long-term ecological risks associated with heavy metal exposure in this species.

1. Introduction

Mejillones Bay, located in northern Chile, serves as a notable example of the impacts of contamination on marine ecosystems. This region is part of the Humboldt Current System, one of the world's most productive marine systems due to its coastal upwelling dynamics, which provide essential nutrients for marine life [1,2]. The Humboldt Current System sustains exceptional biodiversity, including important commercial fisheries, but also faces intense anthropogenic pressure. In particular, Mejillones Bay is highly affected by copper (Cu) mining and other extractive industries, which generate significant emissions of heavy metals into the marine environment [1]. Studies have reported high concentrations of Cu, zinc (Zn), arsenic (As), and lead (Pb) in sediments and marine organisms from this area, demonstrating its environmental degradation [3,4].

Heavy metals such as mercury (Hg), Cd, Pb, and As stand out for their high toxicity even at low concentration. Although As is not a metal in the strict sense but a metalloid, it is included among heavy metals due to its high toxicity and similar environmental behavior [5]. These metals are particularly dangerous due to their ability to induce chronic effects in organisms, including metabolic, reproductive, and systemic alterations [6,7].

However, within the group of heavy metals, there are some trace elements such as Cu, Zn, and Se that play essential roles in living

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organisms. Although they are not strictly considered heavy metals, they are included in this group due to the physiological imbalances they can cause when present in excess. These trace elements are essential for biological processes such as enzymatic activity and antioxidant defense, yet both their deficiency and excess can be toxic [1,8,9]. For instance, insufficient levels of Se can trigger oxidative stress, whereas elevated concentrations can disrupt critical cellular functions [5]. The dual role of trace elements highlights the complexity of their management in ecosystems. While they are indispensable in small amounts, their toxicity when present in excess reinforces the need to monitor not only the most harmful heavy metals but also these essential elements. Studies have shown that both bioaccumulation and biomagnification of metals and trace elements can have critical consequences at higher trophic levels, affecting the health of top predators and entire ecosystems [8]. Understanding these dynamics and their effects is crucial for developing effective conservation and environmental management strategies that mitigate the associated risks [1,3].

The Guanay cormorant (*Leucocarbo bougainvilliorum*), is an endemic seabird species of the Humboldt Current System and one of the most representative species of this system. They are distributed from Isla Lobos de Tierra in northern Peru (ca. 6ºS) to Isla Mocha in southern Chile (ca. 38ºS) in the Southeast Pacific and a small colony appears to be ecologically extinct in the Patagonian Atlantic coast of Argentina [10,11]. Its diet is dominated by small pelagic fishes mostly exclusively of Peruvian anchovies, with some Peruvian silverside (*Odonthestes regia*) and more sculpin (*Normanichythes crockeri*) [12–14]. This was the most dominant seabird species in the Peruvian and Chilean Humboldt Current in terms of numbers with 21 million individual just found in central Peru in the 1954–1955 period [15]. However the population has decreased in a 20–29 % in the last three decades due to El Niño events, human exploitation and competition with fisheries for food [14,16,17] and currently they are catalogued as Near Threatened by the Red List of Threatened Species of the International Union for the Conservation of Nature [18]. A recent study has demonstrated that cormorants such as the red-legged cormorant (*Poikilocarbo gaimardi*) nesting in industrialized areas of Mejillones Bay exhibit significant concentrations of heavy metals such as Cadmium (Cd) and Pb, and trace elements such as Selenium (Se), in their feathers, which could be linked to sublethal effects such as metabolic and reproductive alterations [3].

In this context, it is crucial to investigate the levels of accumulation of heavy metals and trace elements and their possible toxicological implications in this species, guanay cormorant, whose high trophic position and distribution in coastal areas make it an ideal model for assessing the impact of pollution in industrialised marine ecosystems. Moreover, as previously mentioned, this species has experienced a significant decline in recent years [14,16,17] and understanding the role of environmental pollutants in this process is essential.

This study aims to analyze the concentrations of five heavy metals (Hg, As, Pb, Cd and chromium (Cr)) and three trace elements (Cu, Zn, and Se) in key tissues of dead Guanay cormorants collected in Mejillones Bay, Chile. Additionally, it seeks to identify accumulation patterns among tissues, explore differences related to biological variables such as sex and nutritional status, and evaluate the molar Hg:Se ratio to determine Se's potential protective effect against Hg toxicity. These findings

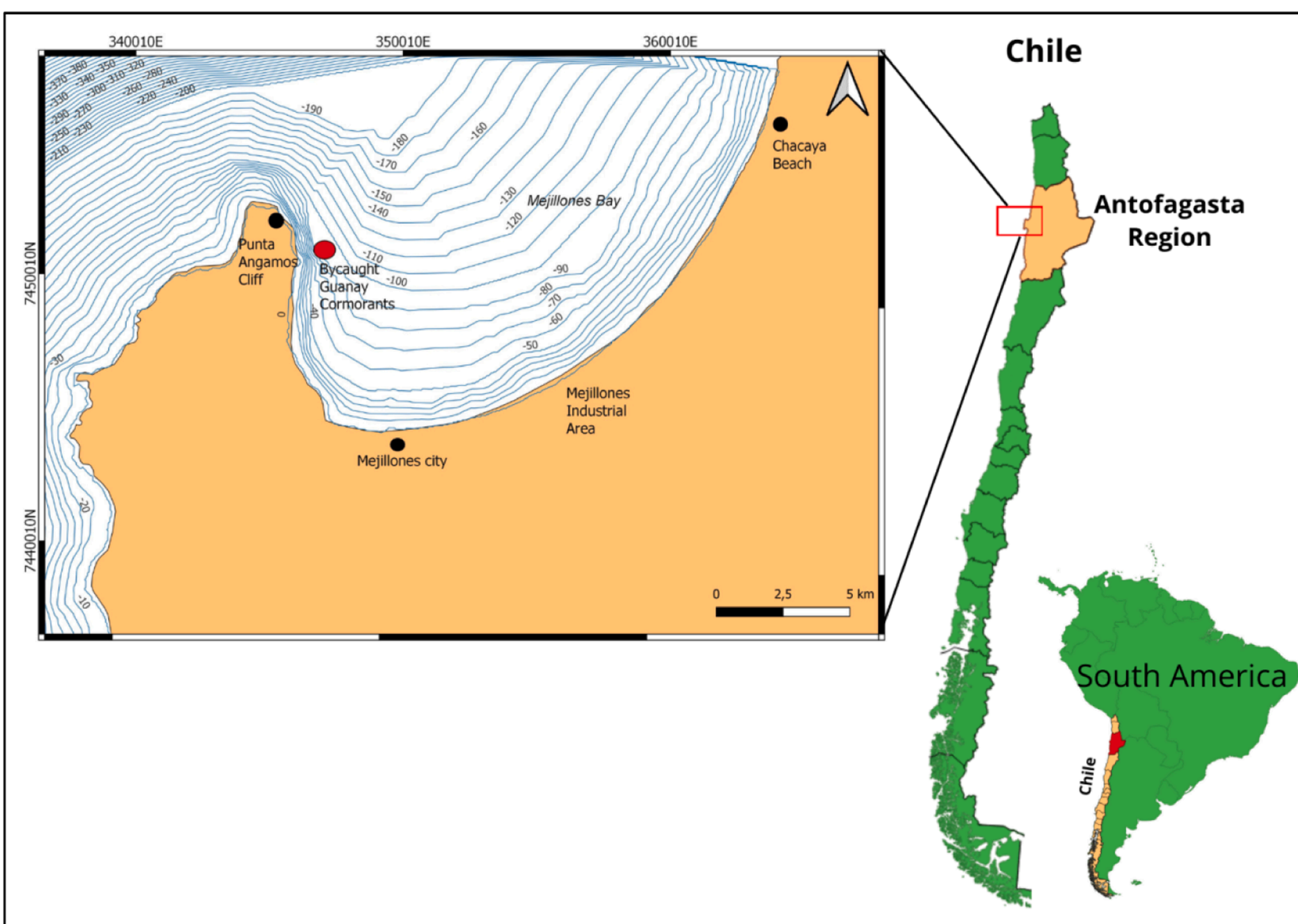

Fig. 1. Study area map of Mejillones bay in Antofagasta Región (northern Chile) and point in Mejillones bay where Guanay cormorants (*Leucocarbo bougainvilliorum*) were bycaught in coastal gillnets the 12 january 2024.

will not only contribute to the conservation of this threatened species but also provide valuable information for contaminant biomonitoring in one of the world's most productive and vulnerable marine ecosystems.

2. Materials and methods

2.1. Study area

Mejillones Bay, located in the northern region of Antofagasta, Chile, within the Atacama Desert, has a semicircular shape resembling a "J," with an approximate length of 18 km from Punta Angamos Cliff to Chacaya beach and a maximum depth of 120 m (Fig. 1) [19]. This bay is influenced by the Humboldt Current System, which is renowned for its high biological productivity. The continuous upwelling of cold, nutrient-rich waters, particularly in coastal areas such as Punta Angamos, plays a key role in biogeochemical cycles and primary productivity, further contributing to carbon exchange between the ocean and the atmosphere [20,21]. These upwelling events not only sustain significant fishing activities but are also highly sensitive to climatic variations, underscoring their importance for studies on ocean-atmosphere interactions [3,19].

The bay holds one of the most important artisanal purse seine fishing industries in the north of the country with a total of 45 artisanal purse seine fishing vessels industrial purse seine fishing vessels and 68 artisanal coastal guillnets fishing vessels registered by the National Service of Aquaculture and Fisheries [22]. Fishing activity is focused in the Peruvian anchovy fleet followed by the Pacific bonito (Sarda chilensis) fishing. In addition is characterized by the presence of sandy beaches and allocates the Mejillones city and the industrial port area of Mejillones with a total of 9 maritime terminals for the import and export of mining supplies.

2.2. Sample collection

Data for this study were obtained from ten Guanay cormorants that were bycaught the 12 January 2024 in artisanal gillnets and subsequently drowned.

The specimens were collected by SERNAPESCA and the CETALAB research team, at the University of Antofagasta, Chile. Each individual was assigned a specific identification number and underwent an *in situ* necropsy in the Wildlife Fauna Rescue and Rehabilitation Center at the University of Antofagasta. During necropsy, the following parameters were recorded: species, total length (cm), weight (g), sex (male or female), age (juvenile or adult), nutritional status (good or intermediate), beak length and development, stomach content (well digested, partially digested, or undigested), and ocular hydration. We determined nutritional status according to Franeker [23] three characters (subcutaneous fat, abdominal fat and pectoral muscle) were scored on a four-point scale (0–3) and the overall condition index was calcu lated based on the sum of scores for fat stores and breast muscles (0–9): score 0–1 = mortally emaciated; 2–3 = critically emaciated; 4–6 =moderate or intermediate body condition; and 7–9 =good body condition. We have included this information in sample collection. In our study only good or intermediate individuals were found. Additionally, morphological anomalies were inspected.

Tissue samples were collected from each individual, including muscle, kidney, liver and feathers. These samples were stored in labelled Eppendorf microtubes and kept at −20°C until further analysis. A total of 39 samples were analyzed, as kidney samples were unavailable from one specimen. Of the ten collected individuals, six were males and four were females, all classified as adults. The analyzed variables included tissue type, sex, weight, length, nutritional status, beak length and development, and stomach content. These variables were used as potential predictors in subsequent analyses to assess differences in metal accumulation between individuals and tissues.

2.3. Analytical methodology

The concentrations of Cu, Cr, Zn, Hg, Cd, Pb, As, and Se in tissue samples (liver, muscle, feathers, and kidney) were determined following the protocol for metal determination in fish tissues [24]. The samples (0.1 g dry weight (dw)) were digested with 4.5 mL of concentrated nitric acid and 1 mL of hydrogen peroxide (69 %, 30 %, respectively) in a closed Teflon PFA container in microwaves (Milestone, Ultrawave Model) for 20 min at 220∘ C in five times and finally diluted with 10 mL of ultrapure water (18.2 MΩ) from a Merck Milipore Mili-Q Rerefence A+ water purification system. The calibration curve was prepared from a multi-element standard solution (CertiPUR, Merck).

Two "blanks" (reagents only) were analysed, and accuracy was verified with Standard Reference Material analysis (Merck ICP IV Certipur Multi-Element Standard Solution, Merck ICP Mercurio Certipur Standard, and Agilent Technologies Initial Calibration Verification Standard) to check reagent purity and contamination. The recoveries ranged from 96.2 % to 104.8 % using fortified continental water and 86.9–107.1 % using a reference biological matrix (muscle tissue, ERM®, certified reference material). Detection and quantification of metals were carried out using inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies Model 7900). The detection limits established for each metal were as follows: Cr (0.03 ppb), Cu (0.03 ppb), Zn (0.16 ppb), As (0.05 ppb), Se (1.33 ppb), Cd (0.03 ppb), Hg (0.01 ppb), and Pb (0.02 ppb).

To ensure the reliability of the results, rigorous quality control measures were implemented, including repeated analyses and verification of data using internal standards. ICP-MS was selected for its high sensitivity and ability to conduct multi-elemental analysis at extremely low concentrations, making it ideal for studying trace elements in biological tissues. All identified inorganic element concentrations were expressed in $\mu g/g^1$ dw.

2.4. Statistical analysis

Data were analyzed using IBM SPSS Statistics software (version 26.0, Chicago, IL, USA). Descriptive statistics (mean, median, standard deviation, maximum, and minimum values) were calculated for the concentrations of eight heavy metals and trace elements (Cr, Cu, Zn, Hg, Cd, Pb, As, and Se) in the analyzed tissues. The normality of the data was assessed using the Kolmogorov-Smirnov test, which indicated that only feather concentrations followed a normal distribution ($p > 0.05$). Therefore, non-parametric statistical analyses were applied to the remaining tissues due to their robustness in handling non-normally distributed data.

The Mann-Whitney and Kruskal-Wallis tests were used to identify significant differences between groups defined by sex, weight, beak length, nutritional status, and stomach content. The significance level was set at $\alpha = 0.05$. Spearman's correlation coefficient was used to explore relationships between metal concentrations across different tissues.

Additionally, the molar ratio of Se to Hg was calculated to evaluate the potential protective effect of Se against Hg toxicity, using the formula: Hg. Se/Hg = ([Se]/78,96) / ([Hg]/200,59), where 78.96 and 200.59 $gmol^{-1}$ are the atomic weights of Se and Hg, respectively. This analysis allowed for an estimation of detoxification mechanisms within the studied tissues, following previously established methodologies [25, 26].

3. Results and discussion

3.1. Metal distribution

In Table 1 are showed the concentrations of Cr, Cu, Zn, As, Se, Hg, Cd, and Pb (mg/kg dry weight) in the analyzed tissues of Guanay cormorants. As observed, all metals were detected in the four studied

Table 1
Concentrations of Cr, Cu, Zn, As, Se, Hg, Cd, and Pb (mg/kg dry weight) in tissues of Guanay Cormorant (*Leucocarbo bougainvilliorum*) from Mejillones Bay (Antofagasta. Chile). Data from this study are presented as mean ± standard deviation and maximum and minimum values.

Tissue / Element	Cr	Cu	Zn	As	Se	Hg	Cd	Pb
Liver								
Mean ± SD	0.07 ± 0.02	6.83 ± 1.09	25.77 ± 2.81	0.31 ± 0.06	1.24 ± 0.23	0.31 ± 0.036	1.43 ± 0.34	0.35 ± 0.32
Maximum	0.12	9.41	29.57	0.44	1.73	0.38	1.94	1.10
Minimum	0.04	5.53	19.79	0.21	0.91	0.27	0.87	0.06
% Detected	3	19	15	28	29	22	27	28
n	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Muscle								
Mean ± SD	0.13 ± 0.12	5.68 ± 0.43	16.25 ± 2.91	0.30 ± 0.59	0.38 ± 0.08	0.10 ± 0.01	0.02 ± 0.01	0.17 ± 0.16
Maximum	0.48	6.57	21.17	0.39	0.50	0.13	0.05	0.55
Minimum	0.07	5.26	11.27	0.23	0.23	0.08	0.01	0.06
% Detected	5	16	9	28	9	7	0.4	14
n	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Feather								
Mean ± SD	2.03 ± 0.63	19.72 ± 3.82	109.84 ± 11.95	0.27 ± 0.37	1.41 ± 0.31	0.83 ± 0.40	0.24 ± 0.11	0.60 ± 0. 24
Maximum	3.16	25.53	125.57	0.35	2.03	1.55	0.50	1.11
Minimum	1.36	11.55	86.08	0.22	0.98	0.37	0.07	0.22
% Detected	79	55	64	25	33	57	4.6	49
n	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Kidney								
Mean ± SD	0.33 ± 0.75	3.55 ± 0.88	20.63 ± 1.91	0.20 ± 0.02	1.28 ± 0.25	0.20 ± 0.03	3.63 ± 1.79	0.11 ± 0.03
Maximum	2.35	5.76	23.35	0.24	1.73	0.25	6.76	0.19
Minimum	0.04	2.85	18.07	0.17	0.91	0.15	1.98	0.07
% Detected	13	10	12	19	29	14	68	9
n	9.00	9.00	9.00	9.00	9.00	9.00	9.00	9.00

*DS: Standard deviation
*n: Number of samples

tissues.

Feathers accumulated the highest amounts of metals, serving as the primary detoxification pathway, followed by the liver, kidneys, and muscle. Feathers serve as a major detoxification mechanism, isolating contaminants and preventing their impact on vital organs (Fig. 2). During their growth, metals incorporate into keratin, ensuring long-term immobilization [27,28]. This process not only facilitates excretion but also makes feathers valuable tools for environmental monitoring [27]. Cr, Cu, Zn, Hg, Pb, and Se showed the highest accumulation in feathers, ranging from 33 % to 79 % of the total detected in the body.

The liver plays a central role in metabolizing and detoxifying metals due to its homeostatic regulation of essential and non-essential elements [29]. It is particularly important for Cu regulation, which is crucial for enzyme production and metallothionein synthesis [30,31]. In our study, the liver played a significant role in metal retention, particularly for Se (29 %), As (28 %), Pb (28 %), Cd (27 %), Hg (22 %), and Cu (19 %), reflecting its detoxification function. Se, known for its antioxidant and thyroid functions, accumulated primarily in the liver and kidneys, likely due to its biological role. However, excretion through feathers also plays a critical role in reducing its toxicity [31]. On the other hand, the kidneys showed a marked affinity for Cd (68 %), as well as similar accumulation levels to the liver for Zn (12 % vs. 15 %) and Se (29 % in both tissues). Kidneys filter and excrete toxic metals, particularly Cd, which binds to metallothioneins and accumulates in this organ, posing a risk of renal damage [32]. The Cd liver/kidney ratio in our study (0.3) suggests prolonged exposure to moderate levels of the metal [30,33]. Muscle, in contrast, exhibited lower concentrations, but As (28 %), Zn (9 %), and Se (9 %) were present in notable amounts. Although the homogeneous distribution of As between liver and muscle (28 %) suggests its ability to affect multiple organ systems [31,34].

In summary, most heavy metals accumulated predominantly in feathers, followed by the liver, kidneys, and muscle. Feathers act as efficient reservoirs, reflecting environmental exposure by incorporating metals into keratin during their growth [35]. Once deposited, these metals remain immobilized, reinforcing feathers as a key matrix for monitoring heavy metal exposure in seabirds.

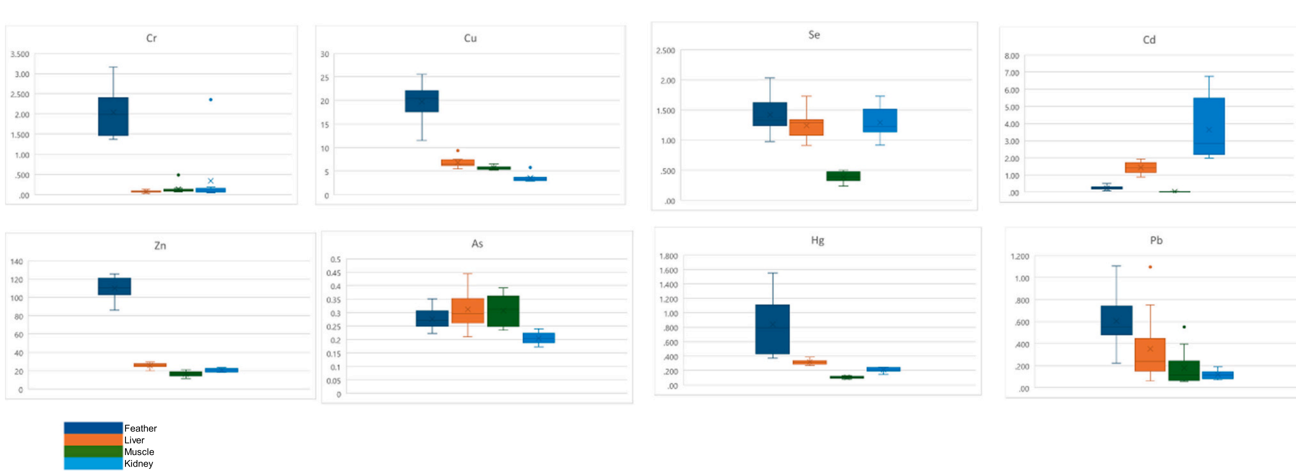

Fig. 2. Box plot on concentrations of Cr, Cu, Zn, As, Se, Hg, Cd, and Pb (mg/kg dry weight) in tissues of Guanay Cormorant (Leucocarbo bougainvilliorum) from Mejillones Bay (Antofagasta. Chile).

3.1.1. Relationships of elements among variables

No significant differences among metal concentration have been observed between variables (age, weight, length, nutritional status, beak length and development, and gastric content) only variable sex showed statistically significant differences being Cu and Pb in muscle and Cr in kidney higher in females (Cu_Muscle ($r = 0.01$, $p < 0.05$), Pb_Muscle ($r = 0.033$, $p < 0.05$), Cr_Kidney ($r = 0.039$, $p < 0.05$).

Sex-related differences in metal accumulation are influenced by physiological, hormonal, and behavioral factors. Estrogens impact the absorption and retention of essential metals, and the increased nutritional demand during reproduction reinforces their storage. Additionally, elevated metal levels in female seabirds have been associated with reduced egg viability and lower reproductive success [36–41].

Estrogens enhance the retention of Cu and Zn, which are essential for reproduction and embryonic development [41]. During reproduction, Cu is crucial for egg production and physiological functions, leading females to absorb it in greater amounts [39,40]. In our study, the higher Cu concentrations found in the muscle tissue of adult females in the reproductive period suggest that this physiological process influences the bioaccumulation of this metal. The accumulation of Pb may be influenced by differences in diet and migratory routes, leading to unequal exposure [40,42]. The significantly higher Pb levels detected in the muscle tissue of adult females in reproduction could be explained by the mobilization of Pb from bones during eggshell formation, as has been documented in other birds [38,41]. Although migratory behavior can influence metal accumulation in some seabird species due to sex-specific differences in movement or exposure [43], this explanation is unlikely in *Leucocarbo bougainvillii*, which is considered a marine resident along the Chilean coast and shows strong site fidelity [44]. Moreover, there is no evidence of sex-based differences in movement patterns. Therefore, the observed Pb concentrations are more plausibly attributed to physiological factors rather than spatial differences in exposure.

Similarly, Cr metabolism and oxidative stress also differ between sexes, which could explain its higher accumulation in female kidneys [40]. In this study, the higher Cr concentrations observed in the kidneys of adult females support this hypothesis, indicating that metabolic and hormonal differences during reproduction may influence the accumulation of this metal. Differences in body size and metabolic rate may also affect metal bioaccumulation, as males, being larger, could metabolize and store metals differently [41]. Furthermore, females may excrete certain metals through egg-laying, providing a detoxification pathway that is not available to males [32,39].

However, this excretion route is limited to the reproductive period and may not be sufficient to counterbalance increased internal mobilization, especially of Pb, which is transferred from bone stores to soft tissues during eggshell formation [40]. The efficiency of this detoxification pathway also depends on the physiological state and reproductive effort of the female. Conversely, males may eliminate part of their metal burden through feather molt, a mechanism proposed as an alternative detoxification route in seabirds [32,45]. During feather growth, metals such as Hg, Pb, and Zn are incorporated into the keratin matrix and irreversibly sequestered, allowing their elimination upon molting.

While both sexes undergo molt, studies in passerines have shown that females often delay or reduce molting due to the energetic costs associated with breeding, resulting in a sex-specific molting schedule where males tend to molt earlier or more synchronously than females [46]. This physiological and temporal trade-off may explain why females, despite having egg-laying as a detoxification pathway, still accumulate higher metal concentrations in tissues.

3.1.2. Relationships among metals and tissues

The correlation coefficients obtained in this study highlight interrelationships between different heavy metals and the tissues of the Guanay cormorant, suggesting distribution and bioaccumulation patterns influenced by shared physiological and environmental processes (Table 2).

Table 2
Significant correlation coefficients considered in this study between the concentrations of Cd, Pb, As, Se, Hg, Cr, Cu, and Zn in each type of analyzed tissue.

Correlation	Correlation coefficient	*p*-value
Hg_Kidney / Zn_Muscle	0.717	0.03*
Cd_Kidney / Pb_Liver	0.767	0.016*
Hg_Kidney / Hg_Muscle	0.833	0.005**
Cd_Kidney / Hg_Muscle	0.767	0.016*
Cd_Kidney / Cd_Muscle	0.717	0.03*
Cu_Kidney / As_Muscle	0.667	0.05*
Zn_Kidney / As_Muscle	0.767	0.016*
Hg_Kidney / Pb_Liver	0.967	0.001**
As_Kidney / Cr_Kidney	0.733	0.025*
Cd_Kidney / Hg_Kidney	0.867	0.002**
Pb_Kidney / Cu_Liver	−0.783	0.013*
Pb_Kidney / Se_Liver	−0.833	0.005**
Hg_Muscle / Hg_Liver	0.745	0.013*
Cd_Muscle / Cd_Liver	0.636	0.048*
Pb_Muscle / Pb_Liver	0.709	0.022*
Hg_Muscle / Pb_Liver	0.697	0.025*
Hg_Muscle / Zn_Muscle	0.709	0.022*
Cr_Músulo / Zn_Liver	−0.745	0.013*
Hg_Feathers / Hg_Liver	0.782	0.008**
Se_Feathers / Cd_Liver	0.636	0.048*
Hg_Feathers / Cd_Liver	0.685	0.029*
Zn_Feathers / Pb_Liver	0.636	0.048*
Pb_Feathers / Pb_Liver	0.673	0.033*
Se_Feathers / Se_Muscle	0.636	0.048*
Hg_Feathers / Hg_Muscle	0.733	0.016*
Se_Feathers / Cd_Muscle	0.758	0.011*
Hg_Feathers / Cd_Muscle	0.879	0.001*
Cd_Feathers / Cd_Muscle	0.745	0.013*
Zn_Feathers / Pb_Muscle	0.709	0.022*
Pb_Feathers / Pb_Muscle	0.745	0.013*
Se_Feathers / Cd_Kidney	0.717	0.03*
Hg_Feathers / Cd_Kidney	0.7	0.036*
As_Feathers / Pb_Kidney	0.667	0.05*
Pb_Feathers / Sex	0.64	0.046*
Se_Feathers / Zn_Feathers	0.794	0.006**
Hg_Feathers / Se_Feathers	0.709	0.022*
Pb_Feathers / Pb_Liver	0.745	0.013*
Cu_Feathers / Zn_Muscle	−0.673	0.033*
Cr_Feathers / As_Kidney	−0.7	0.036*
Cd_Feathers / Hg_Feathers	−0.733	0.016*
Zn_Liver / Cu_Liver	0.721	0.019*

*The correlation is significant at the 0.05 level.
**The correlation is significant at the 0.01 level.

The strongest correlation was observed between Hg levels in the kidney and liver ($r = 0.967$, $p = 0.001$), suggesting that both organs work together in the detoxification of heavy metals, reflecting similar bioaccumulation mechanisms in birds [41]. Additionally, a significant correlation was found between Hg in the kidney and muscle ($r = 0.833$, $p = 0.005$), which could be due to Hg's ability to bind to proteins and be transported via the circulatory system. Previous studies have shown that Hg tends to accumulate in soft tissues due to its affinity for proteins [8].

Conversely, negative correlations were identified between Pb in the kidney and Pb in the liver ($r = -0.783$, $p = 0.013$) and between Pb in the kidney and Se in the liver ($r = -0.833$, $p = 0.005$). These correlations may indicate competition between these elements for protein-binding sites or differential regulation in these tissues [33]. Since the liver and kidney are key organs in detoxification and heavy metal storage, these correlations suggest they may serve as substitute samples in avian metal accumulation studies [41].

Cd also showed significant correlations between the kidney and liver ($r = 0.767$, $p = 0.016$) and between the kidney and muscle ($r = 0.717$, $p = 0.03$), suggesting shared transport and accumulation mechanisms among these organs. High Cd concentrations in birds have been documented to cause renal damage, reduced egg production, and behavioral changes [47], as well as anemia, growth retardation, and testicular damage [48]. Although the correlation between Cd in the kidney and muscle was weaker than that between the kidney and liver, it remained significant, indicating that muscle serves as a secondary reservoir for certain heavy metals [29,41].

Overall, the results indicate that the liver and muscle play a joint role in heavy metal accumulation, showing significant correlations with Hg, Cd, Pb, Zn, and Cr (Table 2). For instance, a positive correlation was found between Pb in muscle and Pb in liver ($r = 0.709$, $p = 0.022$), suggesting that the liver, as the primary detoxification organ, and muscle, as a secondary storage site, contain related amounts of Pb due to their roles in regulating and excreting this metal. Similarly, the correlation between Hg in muscle and Hg in liver ($r = 0.745$, $p = 0.013$) confirms that both tissues reflect the organism's total Hg burden [29, 49].

Feathers exhibited the highest number of significant correlations with other organs (22 in total). They are recognized for their role in heavy metal excretion, as evidenced by positive correlations between metal concentrations in feathers and in tissues such as the liver and muscle [29,41]. This supports their use as bioindicators of long-term environmental contamination exposure [50,51]. For example, the correlation between Hg in feathers and liver ($r = 0.782$, $p = 0.008$) and between Hg in feathers and muscle ($r = 0.733$, $p = 0.016$) suggests that feathers can reliably indicate the total Hg burden in the body [8,50–52].

Furthermore, as aforementioned, feathers exhibited the highest metal concentrations compared to other tissues, except for As and Cd. This indicate that feathers not only accumulate metals during growth but also facilitate their excretion, which is crucial in metal homeostasis in birds. Besides, it has been suggested that certain metals may have an affinity for feather pigments; for instance, darker black feathers tend to contain more Cu, while iridescent blue feathers accumulate higher Zn levels [53]. The numerous correlations between feathers and other tissues support their utility for non-invasive heavy metal monitoring. However, it has been suggested that feather analysis should not completely replace the study of internal tissues, as each tissue type reflects distinct metabolic processes [50].

Respect to the molar ratio Hg:Se, this ratio is a crucial indicator for assessing the detoxification capacity of Hg in organisms exposed to environmental contamination. Various studies have demonstrated that Se can mitigate the toxic effects of Hg by forming inert mercury selenide (HgSe) complexes in biological tissues, reducing its bioavailability and toxicity [54,55]. Hg, especially in its organic forms such as methylmercury (MeHg) and dimethylmercury (DMeHg), is highly toxic and has a strong bioaccumulation capacity in aquatic trophic networks [56]. Se-mediated detoxification is particularly relevant in seabirds, which are frequently exposed to high levels of Hg due to their position in the food chain and reliance on contaminated marine environments [57]. It has been documented that Se plays a role in the demethylation of MeHg, facilitating the formation of inert compounds such as HgSe, which primarily accumulate in the liver and kidneys without apparent adverse effects [54].

In the present study, the Hg:Se ratio was calculated in all analyzed organs (Table 3). It has been proposed that Hg:Se values ≥ 1 indicate that the amount of Se is insufficient to neutralize the Hg present in the tissue, whereas values close to 0 suggest that detoxification has been effective [26,58]. Our results show that the obtained ratios are consistently below 1 in all analyzed samples, suggesting that Se exerts a significant detoxifying role in this population of Guanay cormorants. This finding aligns with previous studies in seabirds, where Se accumulation has been demonstrated as a key mechanism in mitigating Hg toxicity [55,59]. The observed relationship could be explained by the combination of two factors: on the one hand, the high concentrations of Se in tissues facilitate the formation of HgSe complexes, enabling their safe storage in the liver and kidneys without detectable toxic effects; on the other hand, the low concentrations of Hg in tissues indicate that the baseline Se levels present in these individuals are sufficient to neutralize any Hg exposure. Additionally, it has been suggested that the presence of selenoneine, an organic form of Se with antioxidant properties, may play a key role in modulating Hg toxicity in seabirds [54].

Table 3
Mean concentrations of Hg and Se, expressed in mg/kg, detected in the different studied organs and their corresponding Hg:Se ratios.

Tissue	[Hg] mg/kg	[Se] mg/kg	Hg:Se
Liver	0.31	1.24	0.10
Muscle	0.1	0.38	0.10
Feather	0.83	1.41	0.23
Kydney	0.2	1.28	0.06

These results reinforce the importance of Se as a protective factor in the environmental toxicology of marine species and suggest that the evaluation of the Hg:Se ratio could be used as a reliable biomarker of Hg contamination status in seabirds [55,58]. However, future studies should assess potential seasonal variations in Se and Hg levels, as well as the effect of diet on the accumulation of these metals.

3.1.3. Global comparison and risk assessment

In Table 4 are showed the concentrations of Cr, Cu, Zn, As, Se, Hg, Cd, and Pb (mg/kg, dry weight) in different species of the *Phalacrocoracidae* family.

The levels of heavy metals in the feathers of red-legged cormorant (*Poikilocarbo gaimardi)* obtained by García-Cegarra and Martínez-López [3] in Antofagasta Bay, within the same geographic region as this study, show concentrations similar to those recorded in the present work. The elevated Cu concentrations in feathers, compared to other studies (Table 4), may be attributed to intense mining contamination in this region. Cu extraction activities have increased the concentration of this metal in the marine ecosystem, affecting aquatic organisms and their top predators [3,4,59]. However, the levels of Se, Pb, Cd, As, and Cr in this study are significantly lower than those reported by these authors (Table 4). This difference could be related to diet and nesting behaviour, as *P. gaimardi* has a more generalist feeding strategy, consuming fish, mollusks, crustaceans, polychaetes, and algae [60] and nest in artificial seaport structures of the industrial area of Mejillones Bay [61], whereas the Guanay cormorant relies almost exclusively on Peruvian anchoveta (*Engraulis ringens*), which could influence the lower accumulation of certain heavy metals and nest in natural cliffs far from the industrial area [14].

The concentrations of Zn, Cu, Pb, and Hg in muscle are consistent with those found in other studies, while the levels recorded in the liver and kidney of the Guanay cormorant were generally lower than those found in other cormorant species (Table 4). Specifically, the Zn, Cu, and Hg concentrations in liver, muscle, and kidney were lower compared to studies conducted by Irena et al. [62] in *Phalacrocorax carbo* from the Danube River (Serbia) and by Nam et al. [63] in populations of the same species in Lake Biwa (Japan). In Serbia, 95 % of industrial wastewater is discharged untreated into rivers and lakes, resulting in severe heavy metal contamination [62]. In Japan, Lake Biwa receives water from 460 rivers, functioning as a sink for industrial and urban pollutants, which explains the high metal concentrations in the cormorants from that area [63]. It has been documented that freshwater fish accumulate more heavy metals than marine fish due to differences in osmoregulation. Freshwater fish tend to lose salts and absorb more water, which increases the uptake of heavy metals, whereas marine fish do the opposite, reducing their vulnerability to metal contamination [64]. From a dietary perspective, this could explain the greater bioaccumulation of metals in freshwater and estuarine cormorants compared to predominantly marine species.

Beyond comparing metal levels across species, it is essential to analyze their toxicological relevance to Guanay cormorants. This analysis helps evaluate whether the recorded concentrations may pose risks to the species' health and survival

Hg is one of the most commonly studied metals in toxicity assessments due to its high bioaccumulation and toxicity. Sublethal effects in

Table 4
Concentrations of Zn, Cu, Se, Pb, Cd, As, Hg, and Cr (mg/kg dry weight) in feathers, muscle, liver, and kidney of Guanay Cormorants (*Leucocarbo bougainvilliorum*) observed in this study and in other studies. Data are presented as mean ± standard deviation.

Specie	Tissue	Country	Zn	Cu	Se	Pb	Cd	As	Hg	Cr	Reference
Leucocarbo bouganvilliorum	**Feathers**	**Chile**	**109.84 ± 11.95**	**19.72 ± 3.82**	**1.41 ± 0.31**	**0.60 ± 0. 24**	**0.24 ± 0.11**	**0.27 ± 0.37**	**0.83 ± 0.40**	**2.03 ± 0.63**	**This study**
Poikilocarbo gaimardi	Feathers	Chile	110.87 ± 10.82	17.44 ± 1.18	2.85 ± 0.29	2.82 ± 0.96	1.49 ± 0.37	0.87 ± 0.12	0.66 ± 0.04	0.61 ± 0.07	García-Cegarra y Martínez-López. 2023
Phalacrocorax capensis	Feathers	Namibia	-	-	1.47 ± 0.22	4.34 ± 0.36	1.42 ± 0.37	0.91 ± 0.25	0.25 ± 0.11	4.24 ± 0.66	Burger y Gochfeld. 2001
Phalacrocorax carbo	Feathers	Serbia	89.22 ± 21.33	5.21 ± 0.80	-	2.18 ± 0.74	-	-	13.14 ± 4.89	0.99 ± 0.45	Irena et al. 2017
			90.21 ± 4.91	11.60 ± 1.93	-	0.63 ± 0.28	-	-	14.62 ± 14.95	0.36 ± 0.10	
Leucocarbo atriceps	Feathers	FalklandIslands	-	-	-	-	-	0.54 ± 0.13	2.69 ± 0.77	-	Furtado et al. 2019
Phalacrocorax carbo	Feathers	PersianGulf	157.5 ± 30.23	9.11 ± 2.15	-	0.67 ± 0.24	0.02 ± 0.02	-	-	-	Mirsanjari et al. 2014
Phalacrocorax fuscescens	Feathers	Tasmania	182.9 ± 42.2	12.1 ± 3.1	1.53 ± 0.8	10.6 ± 5.9	1.7 ± 1.2	1.2 ± 0.8	19.3 ± 6.9	1.8 ± 1.2	Einoder et al. 2018
Phalacrocorax carbo	Feathers	Japan	161 ± 3	6.71 ± 0.66	1.5 ± 0.2	1.65 ± 0.50	0.04 ± 0.002	-	2.8 ± 2.7	0.27 ± 0.05	Nam et al. 2005
Phalacrocorax carbo	Feathers	Spain	92.60 ± 7.93	9.21 ± 7.93	0.16 ± 0.31	22.50 ± 20.06	0.19 ± 0.25	0.51 ± 0.53	-	4.83 ± 1.83	Navarro et al. 2010
Leucocarbo bouganvilliorum	**Muscle**	**Chile**	**16.25 ± 2.91**	**5.68 ± 0.43**	**0.38 ± 0.08**	**0.17 ± 0.16**	**0.02 ± 0.01**	**0.30 ± 0.59**	**0.10 ± 0.01**	**0.13 ± 0.12**	**This study**
Phalacrocorax carbo	**Muscle**	Serbia	43.53 ± 7.80	15.74 ± 0.89	-	0.26 ± 0.41	-	-	9.48 ± 1.17	-	Irena et al. 2017
Phalacrocorax carbo	**Muscle**	Hungary	14.8 ± 2.5	7.2 ± 1.4	-	0.5 ± 0.2	-	0.6 ± 0.1	0.9 ± 0.3	-	Lehel et al. 2022
			16.1 ± 6.4	6.5 ± 1.0	-	0.4 ± 0.1	-	-	1.1 ± 0.5	-	
			16.6 ± 5.7	2.8 ± 0.7	-	0.3 ± 0.2	-	-	0.8 ± 0.3	-	
			17.9 ± 4.3	3.1 ± 1.1	-	0.5 ± 0.3	-	-	0.9 ± 1.1	-	
Phalacrocorax carbo	**Muscle**	Japan	49.7 ± 0.8	22.5 ± 4.0	1.8 ± 0.1	0.09 ± 0.11	0.02 ± 0.01	-	1.1 ± 0.3	0.16 ± 0.01	Nam et al. 2005
Phalacrocorax carbo	**Muscle**	Spain	0.48 ± 0.31	19.13 ± 2.14	3.34 ± 1.28	0.054 ± 0.615	0.001 ± 0.01	3.98 ± 3.08	.	0.47 ± 0.30	Navarro et al. 2010
Leucocarbo bouganvilliorum	**Liver**	**Chile**	**25.77 ± 2.81**	**6.83 ± 1.09**	**1.24 ± 0.23**	**0.35 ± 0.32**	**1.43 ± 0.34**	**0.31 ± 0.06**	**0.31 ± 0.036**	**0.07 ± 0.02**	**This study**
Phalacrocorax carbo	Liver	Japan	166 ± 4	36.5 ± 1.1	8.2 ± 1.7	0.053 ± 0.015	1.15 ± 0.24	-	12 ± 9	0.23 ± 0.02	Nam et al. 2005
Phalacrocorax carbo	Liver	Serbia	83.20 ± 13.19	18.04 ± 4.04	-	0.22 ± 0.15	0.22 ± 0.22	-	30.67 ± 14.08	-	Irena et al. 2017
Phalacrocorax carbo	Liver	Spain	105.56 ± 23.10	30.33 ± 10.16	7.73 ± 2.46	0.15 ± 0.16	0.22 ± 0.12	6.96 ± 5.06	-	0.41 ± 0.24	Navarro et al. 2010
Leucocarbo bouganvilliorum	**Kidney**	**Chile**	**20.63 ± 1.91**	**3.55 ± 0.88**	**1.28 ± 0.25**	**0.11 ± 0.03**	**3.63 ± 1.79**	**0.20 ± 0.02**	**0.20 ± 0.03**	**0.33 ± 0.75**	**This study**
Phalacrocorax carbo	Kidney	Serbia	57.92 ± 7.47	9.81 ± 3.98	-	0.26 ± 0.16	0.82 ± 0.87	-	17.41 ± 5.68	0.27 ± 0.11	Irena et al. 2017
Phalacrocorax carbo	Kidney	Japan	78.9 ± 3.1	11.6 ± 0.1	12 ± 4	0.31 ± 0.39	3.31 ± 0.36	-	14 ± 9	0.22 ± 0.09	Nam et al. 2005
Phalacrocorax carbo	Kidney	Spain	61.09 ± 9.48	9.27 ± 1.64	9.28 ± 4.09	0.50 ± 0.62	0.70 ± 0.51	8.85 ± 5.98	-	0.49 ± 0.42	Navarro et al. 2010
Phalacrocorax carbo	Kidney	Iran	6.23	-	-	0.60	0.47	-	-	-	Behrooz y Burger. 2022

birds exposed to Hg have been documented, including alterations in growth, development, reproduction, blood chemistry, and behavior [65–69]. In our study, the Hg concentrations in the liver (maximum 0.38 mg/kg) fall within the background levels reported for wild birds (1–10 mg/kg in the liver) [67,70]. The renal concentrations (maximum 6.76 mg/kg) are well below the levels considered toxic in American black ducks (*Anas rubripes*), where brain lesions and reproductive disorders have been recorded at levels exceeding 16 mg/kg in the kidney [65,67]. Therefore, the Hg levels in the liver and kidneys of Guanay cormorants do not appear to be high enough to cause adverse effects.

Additionally, Pb and Cd toxicity in the liver was evaluated. According to Franson [71] and Clark & Scheuhammer [72], Pb concentrations exceeding 6.0–30.0 mg/kg are considered toxic, while values above 30 mg/kg are lethal. In our study, the maximum Pb concentration was 1.1 mg/kg, indicating safe environmental exposure [73]. For Cd, Scheuhammer [33] established a toxicity threshold of 3 mg/kg, whereas the maximum level in our study was 1.94 mg/kg. It has been documented that Cr concentrations of 2.80 mg/kg in feathers can affect hatching success in birds such as mallards [49,74–76]. Comparing these values with the data from this study, none of the analyzed metals exceeded the toxic limits established for bird feathers, which are as follows: As (30 mg/kg), Cd (10 mg/kg), Cr (500 mg/kg), Cu (250 mg/kg), Hg (2 mg/kg), Pb (10 mg/kg), and Zn (500 mg/kg) [77].

In light of these results, it is suggested that, although Guanay cormorants are exposed to heavy metals in their environment, current concentrations in the liver, kidneys and feathers do not represent a significant toxicological risk and do not appear to be responsible for the detriment of this species. However, continued monitoring is essential to assess whether these concentrations increase over time and to include other risk assessment tools such as enzymatic and biochemical biomarkers that would help us to better understand the potential threat to the health and conservation of the species from these compounds. Nevertheless, even low levels of heavy metals may pose sublethal risks to wildlife, especially when interacting with other environmental stressors such as food scarcity, parasitism, or climate-driven changes in prey availability. Subclinical effects, including endocrine disruption, oxidative stress or immunosuppression, may accumulate over time and contribute to population declines in Near Threatened species [8,67]. Therefore, these findings should be interpreted with caution and integrated into broader ecotoxicological frameworks considering multi-stressor exposures.

CRediT authorship contribution statement

Martínez-Lopez Emma: Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Data curation, Conceptualization. **Jorge Carretero:** Writing – original draft, Methodology, Formal analysis. **Ana M. García-Cegarra:** Writing – review & editing, Resources, Funding acquisition, Data curation, Conceptualization.

Declaration of Competing Interest

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

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