Inter-Island Variability in Trace Elements and Trophic Ecology of Brown Booby (*Sula leucogaster*) in the South Atlantic

Padilha J.A.G., Almeida A.P., Souza-Kasprzyk J., Silva M., Cunha L.S.T., Soares T.A., Paiva T.C., Bighetti G.P., Torres J.P.M., Lepoint G., Michel L.N., Das K., Dorneles P.R.

PII: S0269-7491(24)02324-8

DOI: https://doi.org/10.1016/j.envpol.2024.125607

Reference: ENPO 125607

To appear in: *Environmental Pollution*

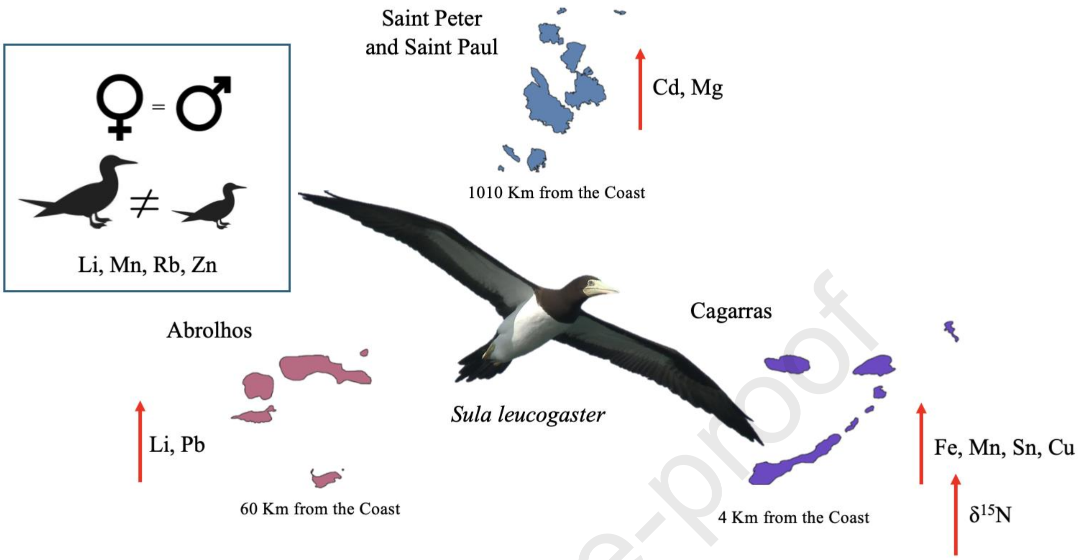
Received Date: 22 July 2024

Revised Date: 29 August 2024

Accepted Date: 27 December 2024

Please cite this article as: Padilha, J.A.G, Almeida, A.P, Souza-Kasprzyk, J, Silva, M, Cunha, L.S.T, Soares, T.A, Paiva, T.C, Bighetti, G.P, Torres, J.P.M, Lepoint, G, Michel, L.N, Das, K, Dorneles, P.R, Inter-Island Variability in Trace Elements and Trophic Ecology of Brown Booby (*Sula leucogaster*) in the South Atlantic , *Environmental Pollution*, https://doi.org/10.1016/j.envpol.2024.125607.

Graphical Abstract



Inter-Island Variability in Trace Elements and Trophic Ecology of Brown Booby (*Sula leucogaster*) in the South Atlantic

Padilha, J.A.G.[1*], Almeida, A.P.[2], Souza-Kasprzyk, J[3]., Silva, M.[1], Cunha, L.S.T.[2]; Soares, T. A.[2,4]; Paiva, T. C[2,5]; Bighetti, G. P.[2], Torres, J.P.M.[4], Lepoint, G.[8], Michel, L.N.[6,], Das, K.[7], and Dorneles, P.R.[2,7]

[1] CBMA – Centre for Molecular and Environmental Biology/ARNET-Aquatic Research Network & IB-S, Institute of Science and Innovation for Bio-Sustainability, Department of Biology, University of Minho, Campus Gualtar, Braga, Portugal

[2] Olaf Malm Laboratory of Environmental Studies (LEA-OM), Carlos Chagas Filho Biophysics Institute (IBCCF), Federal University of Rio de Janeiro (UFRJ), 21941-902, Rio de Janeiro, Brazil

[3] Department of Analytical Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Ul. Uniwersytetu Poznańskiego, Poznań, Poland

[4] Laboratory of Organic Micropollutant Jan Janpenga, Carlos Chagas Filho Biophysics Institute (IBCCF), Federal University of Rio de Janeiro (UFRJ), Rio de Janeiro, Brazil

[5] Institute of Biological Sciences. Laboratory of Limnology, Ecotoxicology and Aquatic Ecology. Federal University of Minas Gerais, Belo Horizonte, MG, Brazil

[6] Animal Systematic and Diversity, Freshwater and Oceanic Sciences Unit of Research (FOCUS), University of Liege, Belgium

[7] Laboratory of Oceanology, Freshwater and Oceanic Sciences Unit of Research (FOCUS), University of Liege, Belgium

[8] Laboratory of Trophic and Isotope Ecology (LETIS), Freshwater and Oceanic Sciences Unit of Research (FOCUS), University of Liege, Belgium

*Corresponding Author:
Janeide de Assis Guilherme Padilha
E-mail: janeide_padilha@bio.uminho.pt

Highlights

- Inter-island differences in elemental levels in Brown Booby feathers
- Higher contaminant levels in Cagarras, likely due to urban proximity.
- Stable isotope analyses reveal distinct dietary patterns
- No significant sex-based differences in metal concentrations.
- Juveniles have different contaminant profiles than adults.

Abstract

This study investigates essential (Mg, Ca, Fe, Mn, Cu, Zn, Se, Ni) and non-essential (Li, Be, Cr, Rb, Sr, Cs, Cd, Sn, Ba, and Pb) element concentrations and stable isotope ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) compositions in feathers of Brown Boobies (*Sula leucogaster*) from three distinct Atlantic islands: the Archipelagos of Saint Peter and Saint Paul (SPSP), Abrolhos, and Cagarras. We aimed to investigate the ecological and environmental factors influencing these seabird populations and assess potential variations in contaminant exposure and dietary habits based on location, sex, and maturity stages. Our finding revealed significant geographical differences in trace element concentrations. The Brown Boobies from Cagarras had higher concentrations (mean ± SD, $\mu g\ g^{-1}$) of Fe (29 ± 20) and Mn (0.82 ± 0.82) than those from Abrolhos (Fe: 21 ± 20; Mn: 0.24 ± 0.09) and SPSP (Fe: 15 ± 16; Mn: 0.21 ± 0.06). Tin concentrations were also higher in Cagarras (Sn: 0.02 ± 0.01) than in SPSP (Sn: 0.01 ± 0.01). Our analyses revealed significant differences in Li, Mg, Rb, and Zn concentrations between adults and juveniles. However, there were no sex-related differences in element concentrations within each locality. SIBER analyses revealed distinct dietary differences among the three Brown Boobies populations, with the Cagarras seabirds occupying a higher trophic position compared to the SPSP population. This study highlights the importance of considering different populations to understand contaminant exposure and ecological dynamics in Brown Boobies along the South Atlantic. The Cagarras population shows significantly higher contaminant levels, likely due to proximity to anthropogenic activities. These

results highlight the necessity for ongoing monitoring to evaluate long-term effects on the more impacted population and to ensure seabird health and sustainability in the Atlantic Ocean.

Keywords: Contaminant Exposure, Stable Isotopes, Bioaccumulation, Seabirds

1. **Introduction**

The biodiversity of coastal areas is often threatened by human activities, making it crucial to understand the ecology of these regions (Fuentes et al., 2020). Brazil's coastal zone harbors vital and dynamic ecosystems that support a range of critical ecological and socio-economic functions (Bighetti et al., 2021; Herbst et al., 2020). However, this zone also faces many significant threats, including habitat loss, pollution, overfishing, and climate change (Figueiredo et al., 2015). These threats endanger the diverse marine species inhabiting this region and impact the millions of people who rely on these resources for their livelihoods and well-being (Herbst et al., 2020).

To address these challenges, it is crucial to deepen our understanding on the ecology and biochemistry of key species in this ecosystem (Van Weerelt et al., 2013; Bighetti et al., 2021; Signa et al., 2021). Seabirds, in particular, are important bioindicators of environmental health and ecological processes in coastal areas (Signa et al., 2021; Bighetti et al., 2022). As top predators, they provide valuable means of monitoring the impacts of human activities on marine ecosystems (Cunha et al., 2012; Dias et al., 2013).

The Brown Booby (*Sula leucogaster*) is a pantropical species commonly found along the Brazilian coast. Studying these birds across various locations along the Brazilian coast enhances our understanding on the ecological dynamics and challenges affecting coastal ecosystems, thereby facilitating the development of targeted conservation strategies.

Trace elements (TEs) and stable isotopes serve as valuable tools for comprehending the ecology of seabirds (Cipro et al., 2018; Bond & Lavers, 2020; Padilha et al., 2021). Trace elements are crucial in various physiological processes and are often used to assess avian health (Zaman et al., 2022). They can also be used to discriminate among populations and species based on differences in exposure to environmental contaminants and dietary intake (Burger & Gochfeld, 2000, 2001; Moura et al., 2018). Additionally, stable isotope ratios are essential for understanding seabird foraging habitats ($\delta^{13}C$), trophic level ($\delta^{15}N$), and habitat use ($\delta^{34}S$) (Connolly et al., 2004; Cherel et al., 2014; Hobson et al., 2015; Polito et al., 2016; Pizzochero et al., 2018), helping to elucidate the relationships between seabirds and their environments and offering a comprehensive understanding of their ecological niches and responses to environmental changes.

Feathers are indicated as a suitable matrix for studying trace elements because birds eliminate these contaminants through this integumentary system (Dolan et al., 2017). During the molting period, there is a significant increase in the trace element concentrations in the blood of these animals, indicating the remobilization of elements stored in other tissues into the bloodstream (Burger, 1993; Dolan et al., 2017). As feathers develop, they have a blood supply, which will cease after the complete development of these integumentary structures (Burger, 1993). Once fully formed, feathers retain immobilized elements linked to sulfhydryl groups in their structure (Burger, 1993; Yao, et al., 2021). In this way, the feathers will reflect the plasmatic concentrations of these elements during the molting period, since there will be no further possibility of remobilizing trace elements stored in this matrix (Burger, 1993).

Few studies have examined the differences among populations of the same species across various geographic locations. In the case of the Brown Booby (*Sula leucogaster*), most of the research that has been conducted primarily focuses on organic pollutants (Cunha et al., 2012; Mello et al., 2012). Additionally, there is limited research on how proximity to the coast influences exposure to pollutants and the ecological responses of these seabirds (da Silva et al., 2023). To the authors' knowledge, no studies have compared different populations of this species across Saint Peter and Saint Paul, Abrolhos, and Cagarras Archipelagos in the Atlantic Ocean in terms of inorganic contaminant exposure. These gaps hinder our ability to fully understand the ecological dynamics and conservation needs of coastal ecosystems.

Studies have shown that TEs like Pb, Cd, Cu, and Sn are often elevated in seabird populations near urban and industrial areas due to pollution from sources such as urban runoff, industrial discharges, and maritime activities (Burger & Gochfeld, 2000; Dorneles et al., 2020; Moura et al., 2018). For example, seabirds in proximity to highly urbanized areas, such as Rio de Janeiro, have shown higher concentrations of these elements compared to seabirds from a less polluted area in the North Pacific (Burger & Gochfeld, 2000; de Assis Padilha et al., 2018). However, not all TEs are influenced by urbanization; some, like Mg and Sr, are more affected by natural geological factors or specific oceanographic conditions (Jerez et al., 2011; Gama et al., 2022; da Costa et al., 2023).

In addition to geographical differences, variations in TE concentrations are also influenced by the sex and age of seabirds. Previous research has indicated that juveniles may accumulate Zn and Cu because of their higher nutritional requirements during their development (Lerma et al., 2020). For instance, Zn is essential for growth and is typically found in higher concentrations in younger individuals (Lerma et al., 2020; Zaman et al., 2022). Additionally, sex-based differences have been reported in some studies, where females may exhibit different TE concentrations due to factors such as egg-laying, which can influence the mobilization and excretion of certain elements (Jerez et al., 2011; Bighetti et al., 2021).

However, these patterns are not universal across all species or environments. In some cases, studies have found no significant sex-based differences in TE concentrations, suggesting that both males and females are similarly exposed to environmental contaminants, particularly when both sexes occupy similar ecological niches and share similar diets (Bighetti et al., 2021). Therefore, it is crucial to consider the specific environmental context and species behavior when predicting how sex and age might influence TE accumulation.

To address these existing gaps in our understanding of seabird ecology and exposure to contaminants, our study investigates variations in trace element concentrations and stable isotope compositions in the feathers of Brown Boobies from different islands in the South Atlantic Ocean. By analyzing these biochemical markers, we aim to discern differences in diet, habitat use, and exposure to contaminants among distinct Brown Booby populations. The varying distances of the islands from the coast are essential in understanding how the proximity to coastal or oceanic environments influences dietary sources and bioaccumulation of trace elements (Cunha et al., 2012). This approach will enable us to evaluate the effects of environmental factors on these birds and the ecosystems they inhabit.

Therefore, our objectives are:

- To compare trace element concentrations among Brown Booby populations from the three archipelagos: Cagarras Islands, Abrolhos, and SPSP, focusing on the influence of the proximity to urban and industrial areas.
- To use stable isotope data ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) to assess trophic positions and dietary patterns of Brown Booby populations from the three archipelagos, identifying variations in the elemental concentrations influenced by local prey availability and nearby fishing and urban activities.
- To investigate the influence of maturity stage and sex on the trophic position and contaminant exposure in Brown Boobies, examining differences between juveniles and adults, as well as males and females, across the three populations.

We hypothesize that: 1) The Brown Booby population from the Cagarras Islands will exhibit higher concentrations of trace elements and has a higher δ^{15}N value compared to populations from Abrolhos and SPSP. This is due to their closer proximity to urban and industrial areas with intense anthropogenic activity, influencing their diet and exposure to environmental contaminants; 2) maturity stage and sex will influence the δ^{15}N values and exposure to contaminants, with juveniles and adults, as well as males and females, showing different profiles.

2. Materials and Methods

2.1 Study area and sampling

Samples were colleted from Saint Peter and Saint Paul Archipelago (SPSP, n = 32, 00°55.01'N, 029°20.76'W) in 2015, from Abrolhos Archipelago (Abrolhos, n = 20, 18°00.00'S, 38°40.00'W) in 2015, as well as from the Cagarras Islands Natural Monument (Cagarras, n = 35, 23°01.58'S, 43°11.56'W) between 2011 and 2015 (Figure 1). SPSP is the farthest archipelago from the coast, 1010 km away from Pernambuco state, while Abrolhos is located 70 km from Bahia state, and Cagarras is just 4 km from the coast of Rio de Janeiro city (Rio de Janeiro state). Adult male and female Brown Boobies were captured at all three locations, while juveniles were only sampled at the Cagarras Islands. As juveniles do not exhibit sexual dimorphism, the sex of the juveniles was not determined.

It is important to note that on 5th November 2015, one of Brazil's worst environmental disasters occurred when the Fundão dam collapsed, releasing approximately 50 million cubic meters of metal-rich mud into the Doce River (Coimbra et al., 2020). This mud flowed into the Atlantic Ocean, significantly impacting marine ecosystems, including the Abrolhos Archipelago, located about 200 km north of the river's mouth. Although the samples in this study were collected before the disaster, our data are essential as they provide a baseline and can be considered in future studies to assess potential long-term effects on trace element levels in the region's wildlife.

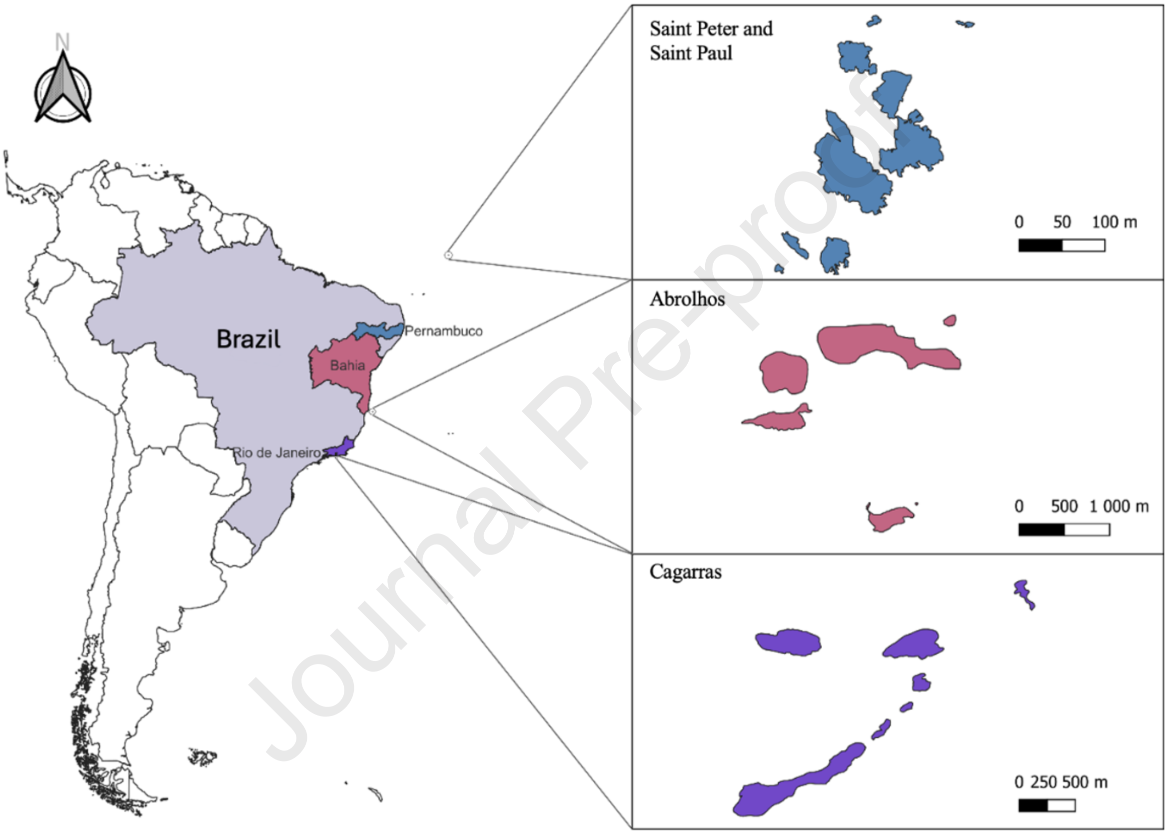


Figure 1. Study Area, highlighting the islands considered in the current study for the sampling of Brown Booby (*Sula leucogaster*) feathers. The map was created using QGIS 3.32 with the WGS 84 datum.

One feather was collected from the primary remiges (P8) for each individual, placed in polyethylene bags, and kept at room temperature until the analyses. The seabirds were captured in their nests with the help of a pull net. A digital caliper (accuracy: ±0.2 mm) was used to measure the beak and tarsus of the birds. Tail and wing measurements were taken with a 50 cm ruler. Body mass was measured using a 2,500 g dynamometer-type precision scale (Accuracy: ±0.3%). The captured birds were identified with metal bands provided by the National Center for Research and Conservation of Wild Birds (CEMAVE), from the Chico Mendes Institute for Biodiversity Conservation (ICMBio).

2.2 Sample preparation

The feathers were washed three times with a sequence of Milli-Q ultrapure water (Merck Millipore, USA), 0.01% EDTA (Spectrum, Tedia, USA), and finally Milli-Q ultrapure water (Merck Millipore, USA) to eliminate external contamination. They were then oven-dried at 50 °C for 24 h (Padilha et al., 2021) before being cut up using stainless steel scissors. An aliquot of 0.1 g of each sample was submitted to acid digestion (5 ml of HNO_3, 2 ml of H_2O_2, and 1 ml of ultrapure deionized water (Milli-Q system). The samples were submitted to the microwave digestion program for 15 min. After digestion, the samples were swelled to 50 mL with ultrapure water (Milli-Q system).

2.3 Elemental measurements

The concentrations of Barium (Ba), Calcium (Ca), Cadmium (Cd), Chromium (Cr), Cesium (Cs), Copper (Cu), Iron (Fe), Lithium (Li), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Lead (Pb), Rubidium (Rb), Selenium (Se), Tin (Sn), Strontium (Sr) and Zinc (Zn) were determined with an inductively coupled plasma mass spectrometer (ICP MS, Perkin Elmer Elan - 9000) at the University of Liege, Belgium. As a Quality Assurance / Quality Control (QA/CQ) procedure, the certified reference material was treated and analyzed in the same way as the samples. The concentrations of these elements were only considered valid when the results of the analyses of the NIES-1 (human hair; n = 8) were in agreement (between 90 and 110%) with the value certified by the National Institute for Environmental Studies of Japan (NIES) (Table S1). Additionally, blank solutions were analyzed using identical procedures as the samples. Such QA/QC procedure allows any contamination in any analytical step to be observed when reading such solutions. The limits of detection (LOD, in µg.L^{-1}) and quantification (LOQ, in mg.kg^{-1}) depend on the amount of sample mineralized and the dilution volume. The LOQ in mg.kg^{-1} is calculated as LOQ in µg.L^{-1} multiplied by the dilution volume divided by the weight of the mineralized sample. The LOD values for each element were calculated as 0.3 times the corresponding LOQ value, and the results are presented in Table S2.

2.4 Measurement of C, N, and S isotopic ratios

The elemental and isotopic composition of C, N, and S of the samples was determined by continuous flow elemental analyses - Isotope Ratio Mass Spectrometry (CF - EA - IRMS) at the University of Liège (Belgium), using a CNC elemental analyzer Vario MICRO cube (Elementary Analysensysteme GmBH, Hanau, Germany) coupled to an IsoPrime100 isotope ratio mass spectrometer (Isoprime, Cheadle, UK). Isotopic ratios were conventionally expressed as δ values according to the standard established by (COPLEN et al., 2011) relative to international standards C and N i.e. Vienna Pee Dee Belemnite (VPBD) for carbon, and atmospheric air for nitrogen. International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials IAEA-C6 ($\delta^{13}C = -10.8 \pm 0.5$ ‰, mean ± SD), IAEA-S1 ($\delta^{34}S = -0.3$‰; mean), and IAEA-N2 ($\delta^{15}N = 20.3 \pm 0.2$ ‰) as primary analytical standards, as well as sulphanilic acid ($\delta^{13}C = -25.9 \pm 0.3$; $\delta^{15}N = -0.12 \pm 0.4$; $\delta^{34}S = 5.9 \pm 0.6$; mean ± SD in each case) as secondary analytical standards. The isotopic ratios of the samples were normalized using primary analytical standards. Standard deviations in repeated measurements on multiple batches of secondary analyses (sulphanilic acid) and laboratory standards (seabird feather) analyzed interspersed between samples (one repeat of each standard every 15 samples) were 0.2 ‰ for $\delta^{13}C$ and $\delta^{15}N$ and 0.4‰ for $\delta^{34}S$.

2.5 Statistical analyses

The statistical analyses were conducted using the R statistical environment (R Core Team, 2019). Data normalization was performed by log-transforming the concentrations to base 10. Normality tests were then conducted to confirm that the log-transformed data followed a normal distribution. Parametric tests were used to explore differences in trace element concentrations and stable isotope compositions among the Brown Boobies from different localities and maturity stages.

Since juveniles do not exhibit sexual dimorphism, we treated them as a distinct group without distinguishing their sex. To assess differences in trace element concentrations and stable isotope compositions between different localities, sex (females and males), and among maturity stages (adults: females, males, and juveniles), we initially used ANOVA. If a significant difference was found in the ANOVA, the Tukey post-hoc test was applied to determine the specific pairs of groups that differed. Additionally, we applied the Benjamini-Hochberg (BH) method to adjust the p-values for multiple comparisons, reducing the risk of false discoveries due to the number of tests performed.

The SIBER (Stable Isotope Bayesian Ellipses in R) method (Jackson et al., 2011) was utilized to explore ecological niches across different species. The ellipse areas were estimated using the SEAc correction and Bayesian modeling for intergroup pairwise comparisons. The SEAb (Bayesian estimate of the standard ellipse area) provides a comparative measure of niche widths between groups based on the size of simulated ellipse areas and their estimated posterior distributions. Groups with similar SEAb values are inferred to have similar isotopic niche widths, indicating reliance on a similar diversity of prey items and feeding habitats. The SIBER 2.1.4 method (Jackson et al., 2011) was employed for these analyses. Additionally, the Pearson correlation coefficient test was conducted to identify significant relationships between trace elements and stable isotopes.

3. **Results**

Among the 18 trace elements measured (Table 1, Figure 2) in the feathers of Brown Booby, the ANOVA test ($p < 0.05$) demonstrated that 8 element concentrations (Li, Fe, Mn, Rb, Cd, Sn, Cs, and Pb) differed between islands. Beryllium was the only element below the limits of detection.

Table 1. Mean ± standard deviation (µg g^{-1} dw) of the concentrations of essential and non-essential elements in Brown Booby (*Sula leucogaster*) feathers.

	SPSP		**Abrolhos**		**Cagarras**		
Sex	Male	Female	Male	Female	Male	Female	Juvenile
n	18	14	7	13	12	13	10
Li	0.06± 0.02	0.07± 0.02	0.07± 0.01	0.07± 0.03	0.07± 0.03	0.06± 0.02	0.04± 0.02
Mg	577± 131	645± 147	651 ± 194	533 ± 87	623± 391	542± 151	316± 230
Ca	761± 140	896± 253	689± 91	789± 214	616± 210	690± 154	653± 117
Cr	0.68± 0.44	0.65± 0.49	0.62± 0.45	0.40± 0.19	0.77± 0.84	0.49± 0.28	0.97± 0.83
Fe	15± 16	11± 3.5	21± 20	15± 5.1	29± 20	21± 9.1	35± 24
Mn	0.21± 0.06	0.28± 0.21	0.24± 0.09	0.20± 0.05	0.82± 0.82	0.62± 0.41	0.84± 0.53

Ni	0.26±0.11	0.28±0.20	0.16±0.03	0.18±0.05	0.24±0.10	0.23±0.08	0.27±0.11
Cu	6.41±0.94	6.73±0.81	6.20±0.63	7.48±0.90	8.02±2.50	8.15±0.96	6.94±0.88
Zn	113±14	121±18	114±27	111±12	102±31	109±22	151±37
Se	2.48±0.34	2.54±0.45	2.70±0.25	2.75±0.35	1.78±0.88	2.07±0.99	1.59±0.79
Rb	0.05±0.02	0.05±0.01	0.05±0.01	0.05±0.01	0.07±0.04	0.06±0.02	0.12±0.08
Sr	7.27±1.62	8.15±2.61	8.19±2.93	6.47±0.81	5.59±2.27	6.76±7.52	3.76±3.19
Cd	0.06±0.04	0.05±0.02	0.02±0.01	0.01±0.01	0.02±0.01	0.03±0.04	0.02±0.01
Sn	0.01±0.01	0.02±0.01	0.02±0.02	0.01±0.002	0.02±0.01	0.02±0.01	0.02±0.01
Cs	0.001±0.00	0.001±0.00	0.001±0.00	0.001±0.00	0.002±0.00	0.001±0.01	0.002±0.00
Ba	0.09±0.08	0.09±0.03	0.07±0.01	0.10±0.06	0.13±0.07	0.15±0.05	0.12±0.04
Pb	0.22±0.15	0.35±0.12	0.20±0.01	0.23±0.15	0.37±0.12	0.38±0.14	0.28±0.18
δ^{15}N	12.0±0.65	12.0±0.46	12.0±1.42	13.0±1.51	15.0±0.92	15.0±0.93	13.0±1.37
δ^{13}C	-17±1.57	-17±1.45	-16±0.95	-16±1.35	-15±1.17	-15±1.86	-15±1.49
δ^{34}S	16.0±0.94	16.0±0.97	14.0±1.41	15.0±1.75	13.0±1.37	14.0±1.35	14.0±0.97

3.1 Geographical Comparison

The ANOVA test revealed significant differences in trace element concentrations among the Brown Booby populations from different islands (F = 5.23, $p < 0.001$). Brown Boobies from Cagarras had significantly higher concentrations of Fe ($p < 0.001$), Mn ($p < 0.001$), Rb ($p < 0.001$), and Cs ($p < 0.001$) compared to both Abrolhos and SPSP (Tukey post hoc Test). Tin concentrations were significantly higher in Cagarras ($p = 0.003$) compared to SPSP.

Cd concentrations were significantly higher in SPSP compared to both Cagarras ($p < 0.001$) and Abrolhos ($p < 0.001$). Brown Boobies from Abrolhos presented significantly higher Li concentrations ($p = 0.039$) than those from Cagarras. Lead concentrations were significantly higher in Abrolhos ($p = 0.032$) than SPSP.

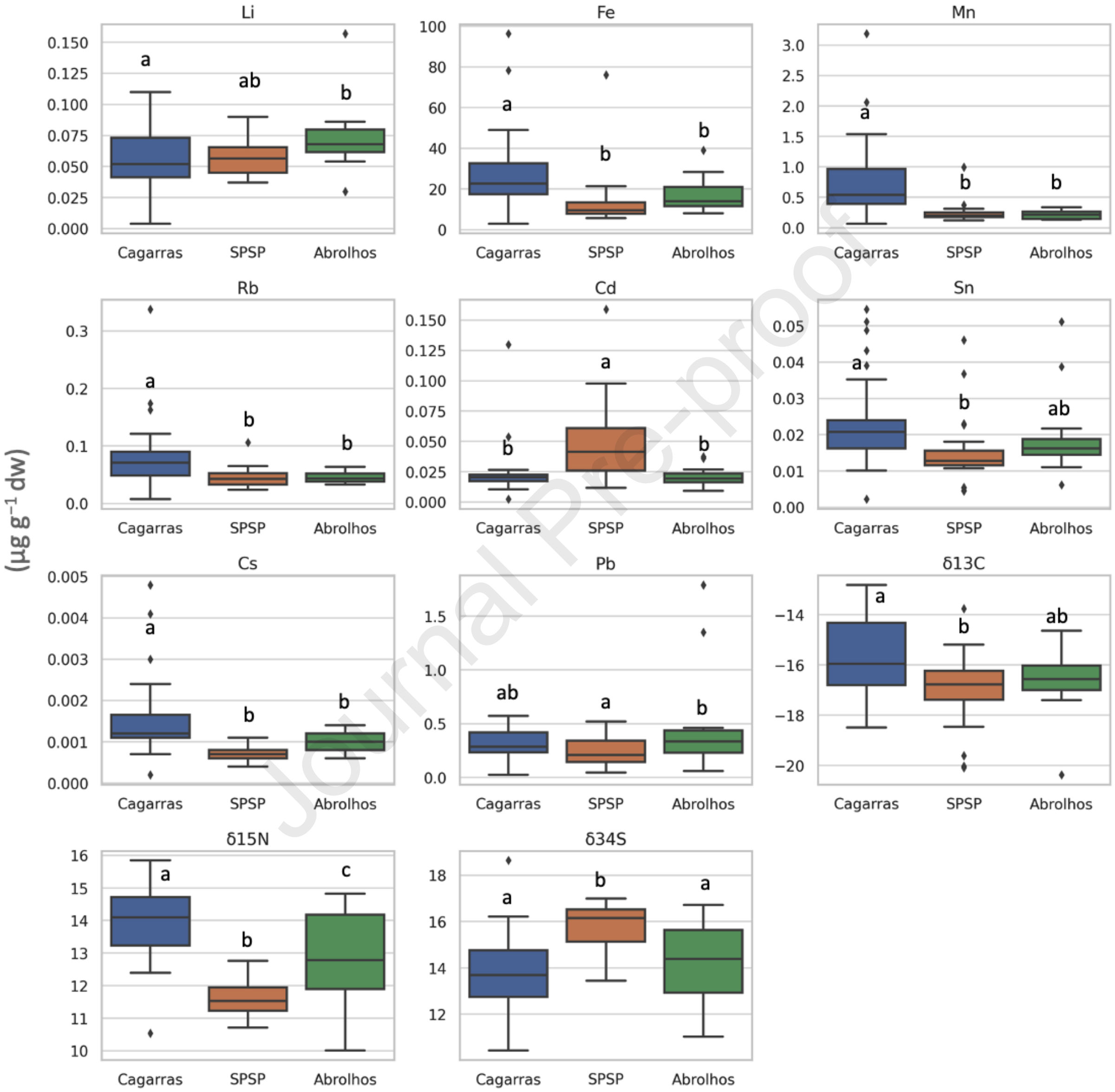


Figure 2. Boxplots of concentrations of essential and non-essential concentrations (Li, Fe, Mn, Rb, Cd, Sn, Cs, and Pb) and stable isotopes ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) in feathers of Brown Booby (*Sula leucogaster*) from Cagarras, Abrolhos, and SPSP archipelagos. Different letters (abc) indicate significant differences between groups.

3.2 Sex-Based Comparison and Maturity Stage

The ANOVA analyses conducted separately for each location did not reveal any significant differences in elemental concentrations between males and females for any of the elements studied ($p > 0.05$).

Elemental concentrations differed significantly between juveniles and male and female separately (Figure 3). Specifically, juveniles had significantly lower concentrations of Li ($F = 4.595$, $p = 0.018$) and higher concentrations of Zn ($F = 8.395$, $p = 0.001$) compared to adult males (post hoc test both $p = 0.01$). Magnesium levels ($F = 3.482$, $p = 0.043$) were significantly lower in juveniles compared to adult females ($p = 0.02$), and also compared to adult males ($p = 0.03$). Rubidium ($F = 5.019$, $p = 0.013$) was significantly higher in juveniles compared to adult females ($p = 0.01$), as well as between males and juveniles ($p = 0.05$).

The ANOVA analyses revealed significant differences in body measurements (weight, beak length, wing length, and tail length, Table S3) based on sex and maturity stage. Post hoc Tukey's HSD tests indicated that females were significantly larger than both males and juveniles across all measurements. Specifically, females had greater weight, beak length, wing length, and tail length (all $p < 0.001$ for weight, beak length, and tail length; $p = 0.002$ for wing length) compared to males and juveniles. Males were also significantly larger than juveniles in weight, beak length, and tail length (all $p < 0.001$).

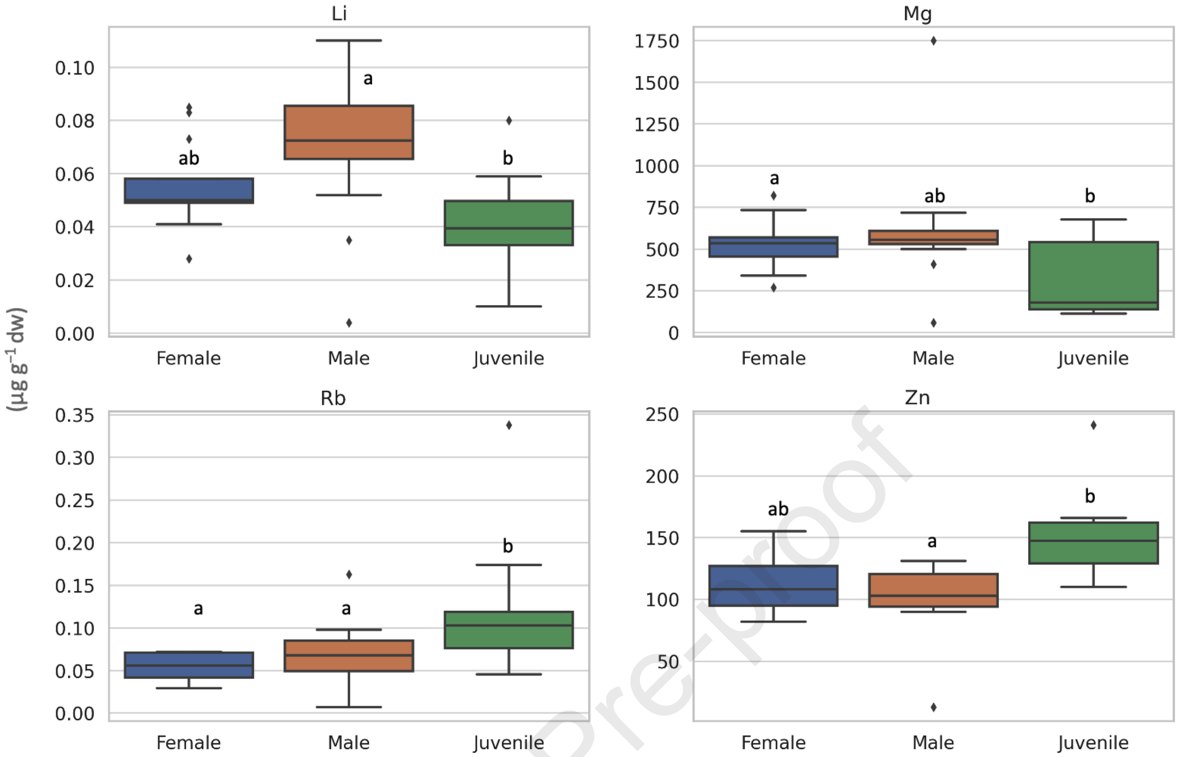


Figure 3. Boxplots of concentrations of metals (Li, Mg, Rb, and Zn) in Brown Boobies (*Sula leucogaster*) from the Cagarras location, categorized by adult female, juvenile (sex non-identified), and adult males. Different letters (abc) indicate significant differences between groups.

3.3 Trophic Niche Comparisons

Isotope values differed significantly among locations for $\delta^{13}C$ (F = 5.733, p = 0.005), $\delta^{15}N$ (F = 34.854, $p < 0.001$), and $\delta^{34}S$ (F = 15.421, $p < 0.001$) (Figure 2). For $\delta^{13}C$, SPSP showed significantly lower values compared to Cagarras (diff = -1.333, p = 0.003). For $\delta^{15}N$, Cagarras had significantly higher values compared to Abrolhos (diff = 1.295, $p < 0.001$), and SPSP had significantly lower values compared to Abrolhos (diff = -1.149, p = 0.001) and Cagarras (diff = -2.444, $p < 0.001$). For $\delta^{34}S$, SPSP had significantly higher values compared to Abrolhos (diff = 1.420, p = 0.003) and Cagarras (diff = 2.103, $p < 0.001$).

SIBER results (Figure 4) suggest that the core isotopic niches of the Brown Boobies from SPSP were markedly separated from those of the Cagarras group. In terms of the overlap between populations, Brown Boobies from SPSP and Abrolhos exhibited a 17% overlap in their isotopic niche areas. The overlap between the Cagarras and Abrolhos populations was 13% of their combined area.

In SPSP, the isotopic niche overlap between male and female Brown Boobies was $1.59‰^2$, which constitutes 46% of their area. In Abrolhos, this overlap was $4.16‰^2$, or 55% of their area, and in Cagarras, it was $2.72‰^2$, or 36% of their area. Additionally, in Cagarras, the overlap between male and juvenile Brown Boobies was $1.36‰^2$ (27% of their area), while the overlap between female and juvenile Brown Boobies was $3.27‰^2$ (46% of their area). The females from Abrolhos and Cagarras showed a significantly wider trophic niche area than males ($p < 0.001$) (Figure 4b).

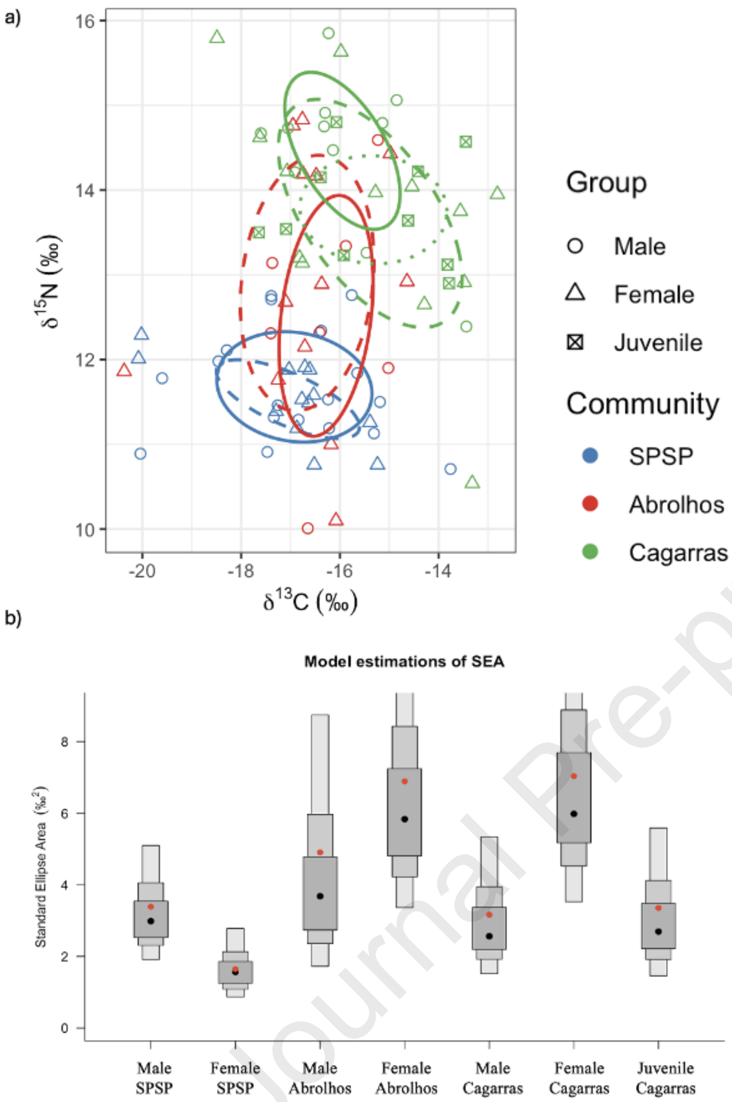


Figure 4. Isotopic niche sizes (a) for feathers of adult Brown Booby (*Sula leucogaster*), with their respective small sample-size corrected standard ellipses (b). Male (solid ellipse), Female (dashed ellipse), and Juvenile (dotted ellipse)

3.4 Stable isotope and element correlations

The Pearson correlation coefficient test (Figure 5) demonstrated several significant relationships. For $\delta^{13}C$, there is a moderate negative correlation with Se and a moderate positive correlation with Cs and Sn. For the $\delta^{15}N$, there is a strong negative correlation with Cd, a moderate negative correlation with Sr, Se, and Ca, a strong positive correlation with Cs and Mn, and a moderate positive correlation with Rb, Cu, Fe, and Cr. For the δ^{34}S, there is a moderate negative correlation with Cs, Sn, Rb, and Fe, and a moderate positive correlation with Cd and Se.

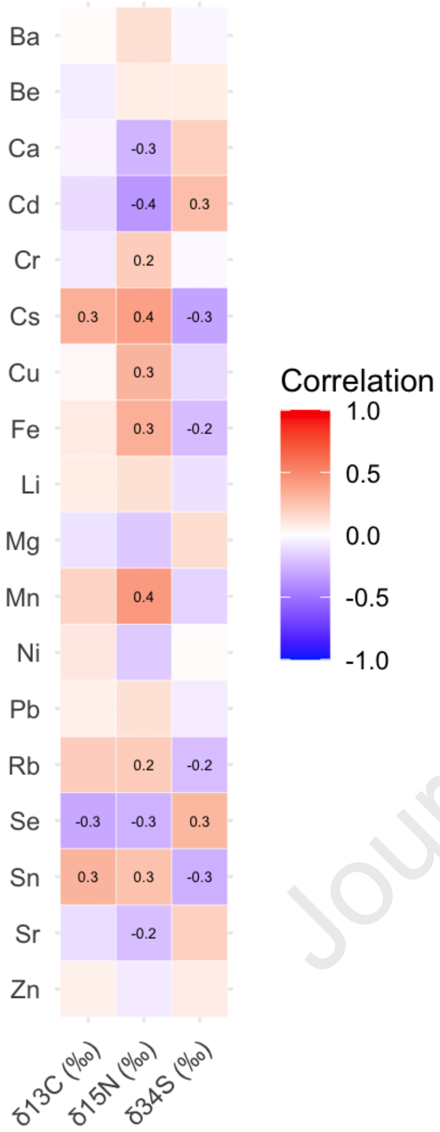


Figure 5. Results of the Pearson Correlation Test showing *r* values between essential and non-essential elements and stable isotopes (δ^{13}C, δ^{15}N, and δ^{34}S) for Brown Booby (*Sula leucogaster*) populations from the archipelagos of SPSP, Cagarras, and Abrolhos.

4. Discussion

This study explored the concentrations of essential and non-essential elements and the isotopic compositions of C, N, and S in the feathers of Brown Boobies from three distinct archipelagos in the Atlantic Ocean. Our findings indicate that Brown Boobies from different areas exhibit significant variations in elemental concentrations and stable isotope values, reflecting the differences in their local diets and exposure to contaminants. These results provide crucial insights into the environmental and ecological factors that influence these seabird populations.

4.1 Impact of Anthropogenic Proximity, Ecological Niches, and Dietary Influence on Elemental Concentrations

Our results revealed significant geographical differences in elemental concentrations. As expected, the Cagarras Archipelago population exhibited notably higher concentrations of Fe, Mn, Rb, Cs, and Sn. These elevated levels support the hypothesis that proximity to urban areas increases exposure to specific contaminants. However, this trend is not uniform for all elements, suggesting a complex relationship between proximity to urban areas and contaminant sources.

Our findings are aligned with previous studies indicating heightened pollutant levels in seabird populations near urban centers, due to increased anthropogenic activities (Gilmour et al., 2019). For example, Finger et al. (2016) found that seabirds, such as little penguins (*Eudyptula minor*), in areas with significant human influence have higher concentrations of elements like Al, As, B, Ca, Cu, Fe, Hg, Pb, Se, and Zn in their blood. Similarly, Cagarras' proximity to a megacity (Rio de Janeiro), with its substantial industrial and urban runoff, likely leads to the bioaccumulation of pollutants in local wildlife (Dorneles et al., 2020).

Industrial activities and urban runoff likely influence the presence of elevated Rb and Cs concentrations in Cagarras in the Rio de Janeiro area, where these elements are commonly associated with electronics and petroleum extraction industries, with cesium specifically utilized in drilling fluids and photoelectric cell production (Riley, 2019; Varala & Rao, 2015). Concerning tin concentrations, it is important to highlight that previous studies from our research team have demonstrated being possible to use total tin (ΣSn) concentrations for evaluating vertebrate exposure to organotin compounds (Dorneles et al., 2008; Dorneles et al., 2020). The rationale for this comes from the fact that inorganic tin forms are practically not absorbed through the digestive systems of vertebrates (Berman, 1980; Guruge et al., 1996; Schilithz et al., 2013). Furthermore, ΣSn biomagnification was found in the ichthyofauna of RJ waters at TMF (Trophic Magnification Factor) values that were similar to those found for tributyltin (TBT) (Dorneles et al., 2020). These aspects associated with the fact that the loss of integumentary structures has also been verified as an excretion route for organotins (OTs) in seabirds (Guruge et al., 1996) strengthen the suitability of the use of ΣSn concentrations for evaluating Brown Booby exposure to OTs. Additionally, the significant maritime traffic around Guanabara Bay, a major port area, contributes to elevated tin levels in Cagarras' Brown Booby population due to the extensive use of OTs in antifouling paints on ships and boats (Padilha et al. 2015, de Assis Padilha et al., 2018; Castro et al., 2021). Organotins are highly toxic compounds used to prevent biofouling, leach into the marine environment, affecting local wildlife. Despite international bans by the International Maritime Organization (IMO) in 2008, OT-based antifouling paints are still used in Brazil (Maciel et al., 2018; Castro et al., 2021). Elevated tin levels in the Cagarras Brown Boobies are concerning due to OT's toxicological effects, such as endocrine disruption, immunotoxicity, and reproductive issues in birds, potentially leading to population declines (Maciel et al., 2018; Frouin et al., 2010).

Although higher levels of some elements in the Cagarras population could be partially attributed to urban proximity, we cannot ignore the potential impact of differences in food webs and local geology across the islands. Previous studies have shown that certain elements, like Cd, can be elevated due to specific geological features, even in remote areas (Jerez et al., 2011). Therefore, it is likely that a combination of environmental and ecological factors is influencing the patterns observed. In this context, the higher concentrations of certain elements in Abrolhos and SPSP are likely due to different environmental factors. In Abrolhos, Brown Boobies exhibited elevated levels of Li and Pb. The Fundão dam collapse affected seabird foraging areas in the Atlantic Ocean, including the Abrolhos Archipelago (Coimbra et al., 2020), significantly altering the elemental levels in tropical seabirds from Abrolhos (Nunes et al., 2022). According to Nunes et al. (2022), the collapse led to increased levels of non-essential elements like As and Cd, while essential elements like Fe, Mn, and Zn decreased (Nunes et al., 2022). Furthermore, as shown in Table 2, when compared with other studies worldwide, the post-collapse Cd levels in seabirds from Abrolhos are notably higher, highlighting the severe impact of the disaster on contaminant bioaccumulation in this region. In addition, a recent study by Bauer et al. (2024) reported significant temporal changes in element concentrations in the blood and feathers of tropical seabirds, including Brown Boobies, following the Fundão Dam disaster. The study reported acute contamination events, notably observed in February 2021, which occurred after a major rainy season in the Doce River basin (Bauer et al., 2024). This surge likely remobilized contaminated sediments, which were transported into the ocean and led to elevated levels of non-essential elements like As, Cd, Hg, and Pb in Brown Booby feathers. Additionally, the Abrolhos Bank experiences frequent cold fronts and southern winds that resuspended sediments, potentially leading to the remobilization of certain elements (Gama et al., 2022), which could include Li and Pb. These findings underscore the role of tropical seabirds as indicators of marine pollution, revealing strong temporal patterns in elemental concentrations driven by climatic and environmental processes (Bauer et al., 2024). It is relevant to highlight that our study samples were obtained before the Fundão dam collapse. In our study, the concentrations of non-essential elements such as Cd (0.02 ± 0.01 μg g^{-1}, mean ± SD) and Pb (0.23 ± 0.01 μg g^{-1}) in the feathers of Brown Boobies from Abrolhos were lower compared to Nunes et al. (2022) and Bauer et al., 2024 post-collapse (Cd: 0.436 μg g^{-1}, Pb: 1.03 ± 0.01 μg g^{-1} respectively). Essential elements like Fe (15 ± 20 μg g^{-1}), and Mn (0.24 ± 0.09 μg g^{-1}) were also lower in our study compared to post-collapse levels (Fe: 40 μg g^{-1}, Mn: 19 ± 0.09 μg g^{-1}). This highlights the impact of severe anthropogenic events on element concentrations and underscores the need for continuous monitoring to assess long-term impacts on seabird populations.

SPSP, being the farthest from the mainland, showed higher concentrations of Cd, which may be linked to unique oceanographic conditions and the presence of deep-sea hydrothermal vents (da Costa et al., 2023). Cadmium concentrations in birds can vary based on age, diet, ecosystem use, and physiological status (Burger et al., 1993). Cadmium's high solubility, significant hydrophilicity, and low sedimentation rate facilitate its dissolution and dispersion in seawater, leading to higher bioavailability and accumulation in marine organisms (Barcellos, 1995). Differences in cadmium levels between coastal (e.g., Cagarras Archipelago) and oceanic (e.g., SPSP) environments were notable. Oceanic species tend to have higher Cd levels than coastal species, likely due to the higher cadmium concentrations found in oceanic cephalopods compared to those from coastal areas (Dorneles et al., 2007).

Concentrations of essential elements (Mg, Ca, Fe, Mn, Cu, Zn, Se) in the feathers of Brown Boobies from our study were within the range previously reported for seabirds worldwide (Burger & Gochfeld, 2000; Dolci et al., 2017; de Assis Padilha et al., 2018; Moura et al., 2018). This consistency is expected, as essential elements are under homeostatic control with nutritional requirements regulating their absorption (Walsh, 2018). A few studies have reported toxic levels of certain elements in feathers. For instance, levels starting at 200 μg g^{-1} (dw) for Zn and at 26 μg g^{-1} (dw) for Se have been identified as harmful to bird growth and reproduction (Burger & Gochfeld, 2000; Einoder et al., 2018).

Non-essential elements (Li, Be, Cr, Rb, Sr, Sn, Ba, and Pb) in the feathers of Brown Boobies from our study were also within the range previously reported for seabirds worldwide (Burger & Gochfeld, 2000; Dolci et al., 2017; de Assis Padilha et al., 2018; Moura et al., 2018). Toxic effects of non-essential elements may be observed at lower concentrations, such as over 2 μg g^{-1} for Cd and 4 μg g^{-1} for Pb (Burger & Gochfeld, 2000). The elemental levels reported in our study are below these harmful thresholds.

Geographical differences in elemental concentrations may also be attributed to local dietary habits and prey availability. The foraging behavior of Brown Boobies is an important factor influencing their exposure to contaminants. Brown Boobies are known to forage in both coastal and offshore areas, with variations in diet depending on local prey availability and oceanographic conditions (Branco et al., 2005; Cunha et al., 2012). Birds from the Cagarras Archipelago, located near the highly urbanized Rio de Janeiro, are likely foraging in coastal waters, where they may be exposed to higher levels of pollution (Cunha et al., 2012). In contrast, birds from SPSP, located in a more oceanic environment, encountering different prey, such as oceanic cephalopods, and their elemental sources, may also be associated with hydrothermal vent activity (Nunes et al., 2018; da Costa et al., 2023). These differences in foraging ranges and habitats could explain the observed variations in elemental concentrations among the populations.

For instance, Becker et al. (2016) found that diet and trophic position are key factors determining elemental concentrations in Southern Ocean seabirds. Our findings, using the SIBER method, revealed significant isotopic niche separation among populations from SPSP and Cagarras, indicating considerable dietary differences. This supports our hypothesis that the Cagarras population occupies a higher trophic position compared to those from Abrolhos and SPSP, influenced by the availability of higher trophic level prey and the impact of nearby fishing and urban activities (Cunha et al., 2012). Boobies from more oceanic areas primarily feed on flying fish and squid (Alves et al., 2004). Specifically, Brown Boobies in SPSP primarily consume flying fish (*Exocoetus volitans*) and cephalopods (Nunes et al., 2018), while those from Abrolhos have a diet that includes a mix of flying fish (*Exocoetus volitans*), reef-associated fish, and cephalopods (Mello et al., 2012). However, Brown Boobies from Cagarras Archipelago inhabit a coastal area heavily influenced by fisheries, which may lead them to consume a greater proportion of food items provided by these activities (Branco et al., 2005; Cunha et al., 2012). Thus, Brown Boobies from Cagarras feed more on sardines and fishing discards (Branco et al., 2005).

4.2 Variations in Elemental Concentrations Based on Maturity Stage and Sex

Our analyses revealed significant differences in elemental concentrations and trophic positions between adults and juveniles for Li, Mg, Rb, and Zn in the Cagarras Archipelago. This supports the hypothesis that the maturity stage influences the trophic position and contaminant exposure. This finding supports the hypothesis that the maturity stage influences both trophic position and contaminant exposure, consistent with studies by Bighetti et al. (2021, 2022) and Padilha et al. (2018). Juveniles tend to accumulate certain elements differently than adults due to variations in metabolic rates and dietary intake (Barbieri et al., 2010; Burger and Gochfeld, 2000; Pacyna et al., 2019). Specifically, our study found higher Zn concentrations in juveniles compared to adults, which is supported by similar findings in Blue-footed Booby nestlings (Lerma et al., 2020). Additionally, the SIBER analyses showed that juveniles in Cagarras had a greater isotopic niche overlap with females than with males, suggesting maternal influence on foraging behavior and dietary preferences. Females, being larger and heavier, may be selected for a greater food payload capacity and/or foraging range, providing more food for their offspring (Mellink et al., 2001; Abdennadher et al. 2017).

Similar findings were described for Brown Boobies at Peña Blanca Island, where the $\delta^{13}C$ values of chicks were similar to the values of their mothers (Abdennadher et al. 2017). A broader isotopic niche was observed in females, compared to males, during the post-breeding period, suggesting that females explore a wider range of foraging habitats and prey types (Abdenadher et al. 2017).

The role of body size in shaping the trophic structure of tropical seabird communities is particularly relevant in this study. Mancini et al. (2014) discussed that larger seabirds often occupy higher trophic positions due to their capacity to consume larger prey. This principle is evident in our findings which demonstrate trophic segregation between adults and juveniles. This observed body size-based trophic structure is consistent across different seabird communities and plays a crucial role in niche differentiation and reducing interspecific competition during the breeding season. Navarro et al. (2014) examined resource partitioning between incubating and chick-rearing Brown Boobies on Christmas Island. Their $\delta^{13}C$ values revealed spatial segregation in foraging grounds between species and different breeding stages of Brown Boobies. Specifically, Brown Boobies shifted their foraging habitats from incubation to chick-rearing to minimize competition for prey.

Contrary to our hypothesis, we did not observe significant sex-based differences in elemental concentrations. This finding aligns with studies by de Assis Padilha et al. (2018) and

Bighetti et al. (2021), which also reported no significant sex-related differences in elemental concentrations (Sn, Cd, Mn, Se, Cu, and Hg) in Brown Booby feathers.

In SPSP, there was substantial dietary overlap between Brown Boobies' males and females, with an even higher overlap in Abrolhos, indicating minimal sex-based dietary differences. This is consistent with findings by Lerma et al. (2020) on Masked Boobies, where overlapping isotopic niches during breeding stages implied minimal diet differences between sexes. Another potential factor contributing to sex-based differences in elemental concentrations is the egg-laying process by females. However, it does not appear to result in significant excretion of essential and non-essential elements in Brown Boobies females, likely explaining the lack of significant sex-based differences in elemental concentrations (Bighetti et al., 2021). Additionally, the transfer of most elements to the eggs is minimal, as the ovary restricts the passage of these elements. This selective permeability of the ovarian and oviductal membranes ensures that mostly essential nutrients pass through, while potentially harmful elements like non-essential elements are largely blocked, as supported by studies on avian reproductive physiology (Klein et al., 2012; Sasanami et al., 2017). Therefore, both sexes are equally exposed to and affected by local contamination sources, highlighting the uniform environmental pressures on these populations.

Table 2. Concentrations of elements (mean in μg g^{-1}, dry weight) found in the feathers of adult seabirds of the genus *Sula* worldwide.

Species	Location	Reference	Cd	Cr	Cu	Fe	Mn	Zn	Pb	Sn	Li	Mg	Ca	Ni	Se	Rb	Sr	Cs	Ba
Sula sula	North Pacific	Burger et al. (1992)	0.13	-	-	-	-	-	2.08	-	-	-	-	-	3.68	-	-	-	-
Sula sula	Midway Atol	Burger & Gochfeld (2000)	0.05	2.53	2.9	-	1.46	-	0.97	2.28	-	-	-	-	2.34	-	-	-	-
Sula leucogaster	Brazil	Dolci et al. (2017)	0.05	-	15	47	-	94	-	-	-	815	-	0.29	-	-	-	-	-
Sula leucogaster	Brazil	Padilha et al. (2018)	0.03	-	8.2	-	1.6	-	-	0.2	-	-	-	-	-	-	-	-	-
Sula leucogaster	Brazil	Nunes et al. (2020)	0.45	0.97	0.66	40	19	25	0.09	-	-	-	-	-	-	-	-	-	-
Sula leucogaster	Australia	Lavers et al. (2020)	0.04	-	2.86	-	-	-	0.59	-	-	-	-	-	-	-	-	-	-
Sula dactylatra	Australia	Lavers et al. (2020)	0.03	-	2.92	-	-	-	0.48	-	-	-	-	-	-	-	-	-	-
Sula leucogaster	Brazil	Bauer et al. (2024)	0.33	-	-	-	-	-	1.03	-	-	-	-	-	-	-	-	-	-
Sula leucogaster	SPSP	Present study	0.06	0.62	6.41	15	0.21	113	0.22	0.01	0.06	577	761	0.26	2.48	0.05	7.27	0.001	0.09
Sula leucogaster	Abrolhos	Present study	0.02	0.4	7.48	15	0.2	111	0.23	0.01	0.07	533	789	0.18	2.75	0.05	6.47	0.001	0.1
Sula leucogaster	Cagarras	Present study	0.02	0.77	8.02	29	0.82	102	0.37	0.02	0.07	623	616	0.24	1.78	0.07	5.59	0.002	0.13

5. Conclusion

This study provides a comprehensive analysis of trace element concentrations and stable isotope compositions in the feathers of Brown Boobies (*Sula leucogaster*) from three distinct archipelagos in the South Atlantic Ocean: Cagarras, Abrolhos, and Saint Peter and Saint Paul (SPSP). The results reveal significant geographical variations in elemental concentrations, indicating that brown booby populations in these regions are influenced by different environmental and ecological factors.

The Cagarras population, located near a major urban area, exhibited higher concentrations of elements such as Fe, Mn, Cu, Rb, Cs, and Sn, supporting the hypothesis that proximity to urban areas increases exposure to specific contaminants. This elevation in concentrations is likely related to the intense anthropogenic activity in the area, including maritime traffic and industrial pollutants. In contrast, the populations in Abrolhos and SPSP, which are farther from the coast and direct urban influences, showed higher concentrations of elements such as Li, Pb, Mg, and Cd, suggesting that local environmental factors, such as geological and oceanographic activities, also play a significant role in contaminant bioaccumulation. Additionally, the study highlights the lack of significant differences in elemental concentrations between sexes, suggesting that both males and females are equally exposed to local contaminants despite potential differences in foraging behavior. In contrast, juveniles were found to have different trace element profiles than adults, reflecting changes in diet and metabolism during development.

Isotopic analyses revealed differences in diet and trophic niches among populations, with the Cagarras population occupying a higher trophic position compared to those from Abrolhos and

SPSP. This could be attributed to the availability of higher trophic level prey and the influence of nearby fishing and urban activities.

Overall, our study underscores the complex interplay between environmental contamination, dietary habits, and habitat use in Brown Boobies. The findings highlight the need for comprehensive conservation measures and continued monitoring to protect Brown Boobies and other marine species from Atlantic Ocean.

Acknowledgments

This work was supported by the Brazilian National Council for Scientific and Technological Development (CNPq) through CNPq / MCT 557049/2009–1, as well as through a Universal Call CNPq - Project from PRD (proc. 432518/2016–9). This work was also supported by scientific cooperation established between the Brazilian Foundation for the Coordination and Improvement of Higher Level or Education Personnel (CAPES - process numbers 88881.154725/2017–01 88887.154724/2017–00) and Wallonie Bruxelles International (WBI, from Belgium), coordinated by PRD and KD, as well as by the Rio de Janeiro State Government Research Agency [FAPERJ - E-26/111.505/2010 and E - 26/210.464/2019 (249593)]. We would like to thank the Brazilian Navy, which provided logistical support in Antarctica through the "Secretariat of the Interministerial Commission for the Resources of the Sea" (SECIRM). GL is a F.R.S.-FNRS research associate, and KD is a Senior F.R.S.- FNRS research associate. PRD has a research grant from CNPq (PQ-2 proc. 08733/2019–3).

6. References

Abdennadher, A., Moreno Carillo, R., Hernandez, S., Aguilar, B., Gonzalez, D., Sanpera, C., & Jover, L., 2017. Trophic segregation by sex and age in Brown Booby Sula leucogaster, a reversed sexual size dimorphic species. Bulletin de l'Institut National des Sciences et

Technologies de la Mer (INSTM Salammbô), 20, 29-33.

Alves, V. S., Soares, A. B. A., & Couto, G. S., 2004. Aves marinhas e aquáticas das ilhas do litoral do Estado do Rio de Janeiro. In: Branco, J.O. (Ed.), Aves marinhas insulares brasileiras: bioecologia e conservação. Editora da UNIVALI, Itajaí, pp. 83-100.

Barbieri, E., Passos, E.D.A., Filippini, A., dos Santos, I.S., Garcia, C.A.B., 2010. Assessment of trace metal concentration in feathers of seabird (Larus dominicanus) sampled in the Florianópolis, SC, Brazilian coast. Environmental Monitoring and Assessment, 169, 631-638.

Barcellos, C., 1995. Geodinâmica de Cádmio e Zinco na Baía de Sepetiba. MSc Thesis, UFRJ, Rio de Janeiro.

Bauer, A. de B., Linhares, B. de A., Nunes, G.T., Costa, P.G., Zebral, Y.D., Bianchini, A., Bugoni, L., 2024. Temporal changes in metal and arsenic concentrations in blood and feathers of tropical seabirds after one of the largest environmental disasters associated with mining. Environmental Research, 248, 118240. https://doi.org/10.1016/j.envres.2024.118240

Becker, P. H., Goutner, V., Ryan, P. G., & González-Solís, J., 2016. Feather mercury concentrations in Southern Ocean seabirds: variation by species, site and time. Environmental Pollution, 216, 253-263. https://doi.org/10.1016/j.envpol.2016.05.061

Berman, E., 1980. Toxic Metals and Their Analysis. Heyden and Son, London.

Bighetti, G.P., Padilha, J.A., Cunha, L.S.T., Kasper, D., Malm, O., Mancini, P.L., 2021. Bioaccumulation of mercury is equal between sexes but different by age in seabird (Sula leucogaster) population from southeast coast of Brazil. Environmental Pollution, 285, 117222. https://doi.org/10.1016/j.envpol.2021.117222

Bighetti, G. P., Padilha, J. A., Cunha, L. S. T., Malm, O., & Mancini, P. L., 2022. Ventral feathers contained the highest mercury level in Brown Booby (Sula leucogaster), a pantropical seabird species. Chemosphere, 298, 134305.

Branco, J.O., Fracasso, H.A.A., Machado, I.F., Bovendorp, M.S., Verani, J.R., 2005. Rev. Bras. Zool. 22, 1044.

Burger, J., Schreiber, E.A.E., & Gochfeld, M., 1992. Lead, cadmium, selenium and mercury in seabird feathers from the tropical mid-pacific. Environmental Toxicology and Chemistry, 11(6), 815-822.

Burger, J., 1993. Metals in avian feathers: bioindicators of environmental pollution. Reviews of Environmental Contamination and Toxicology, 5, 203-311.

Burger, J., 1995. Heavy metal and selenium levels in feathers of herring gulls (Larus argentatus):

differences due to year, gender, and age at Captree, Long Island. Environmental Monitoring and Assessment, 38, 37-50.

Burger, J., & Gochfeld, M., 2000. Metal levels in feathers of 12 species of seabirds from Midway Atoll in the northern Pacific Ocean. Science of the Total Environment, 257(1), 37-52.

Burger, J., & Gochfeld, M., 2001. Effects of chemicals and pollution on seabirds. In: Schreiber, E. A., Burger, J. (Eds.), Biology of Marine Birds. CRC Press, pp. 503-544.

Burger, J., & Gochfeld, M., 2000. Metals in Albatross Feathers from Midway Atoll: Influence of Species, Age, and Nest Location. Environmental Research, 82, 207-221. https://doi.org/10.1006/enrs.1999.4015

Castro, Í.B., Machado, F.B., de Sousa, G.T., Paz-Villarraga, C., & Fillmann, G., 2021. How protected are marine protected areas: A case study of tributyltin in Latin America. Journal of Environmental Management, 278, 111543.

Cherel, Y., Connan, M., Jaeger, A., & Richard, P., 2014. Seabird year-round and historical feeding ecology: blood and feather δ13C and δ15N values document foraging plasticity of small sympatric petrels. Marine Ecology Progress Series, 505, 267-280.

Cipro, C.V.Z., Bustamante, P., Petry, M.V., & Montone, R.C., 2018. Seabird colonies as relevant sources of pollutants in Antarctic ecosystems: Part 1-Trace elements. Chemosphere, 204, 535-547.

Coimbra, K.T.O., Alcântara, E., & de Souza Filho, C.R., 2020. Possible contamination of the Abrolhos reefs by Fundao dam tailings, Brazil–New constraints based on satellite data. Science of the Total Environment, 733, 138101.

Connolly, R.M., Guest, M.A., Melville, A.J., & Oakes, J.M., 2004. Sulfur stable isotopes separate producers in marine food-web analyses. Oecologia, 138, 161-167.

Cunha, L.S.T., Torres, J.P.M., Muñoz-Arnanz, J.A., & Jiménez, B., 2012. Evaluation of the possible adverse effects of legacy persistent organic pollutants (POPs) on the Brown Booby (Sula leucogaster) along the Brazilian coast. Chemosphere, 87(9), 1039-1044.

Cunha, L., Alves, V., Rajão, H., & Lanna, A., 2013. Aves do Cagarras Islands Natural Monument. In: História, pesquisa e biodiversidade do Cagarras Islands Natural Monument. Série Livros, 48, pp. 177-205.

de Assis Padilha, J., da Cunha, L.S.T., de Castro, R.M., Malm, O., Dorneles, P.R., 2018. Exposure of Magnificent Frigatebird (Fregata magnificens) and Brown Booby (Sula leucogaster) to Metals and Selenium in Rio de Janeiro State (Brazil) Coastal Waters. Orbital: The Electronic Journal of Chemistry, 10(3), 254-261.

da Costa, T.F.C., Araujo, J.H., Sichel, S.E., da Silva Pastura, V.F., Motoki, K.F., Barão, L.M., ... & Brunelli, D., 2023. Mapping of surface radiogenic heat production from in situ gamma spectrometry and chemical data of exhumed mantle peridotites at the St. Peter and St. Paul archipelago (equatorial Atlantic). Applied Radiation and Isotopes, 192, 110608.

da Silva, D.A.M., Colabuono, F.I., Taniguchi, S., Petry, M.V., & Montone, R.C., 2023. Persistent organic pollutant patterns in seabirds from marine protected areas in the tropical Atlantic Ocean. Marine Pollution Bulletin, 186, 114461.

de Seixas, J.T., Mello, S.C.R.P., Faria, A.S., Souza, L.L., & Melo, C., 2020. Análise socioambiental da poluição por esgoto da Baía de Guanabara do Rio de Janeiro. Revista Valore, 5, 5022.

Dehnhard, N., Achurch, H., Clarke, J., Michel, L.N., Southwell, C., Sumner, M.D., ... & Emmerson, L., 2020. High inter-and intraspecific niche overlap among three sympatrically breeding, closely related seabird species: generalist foraging as an adaptation to a highly variable environment? Journal of Animal Ecology, 89(1), 104-119.

Dias, P.S., Cipro, C.V.Z., Taniguchi, S., Montone, R.C., 2013. Persistent organic pollutants in marine biota of Saint Peter and Saint Paul Archipelago, Brazil. Marine Pollution Bulletin, 74, 435-440. https://doi.org/10.1016/j.marpolbul.2013.06.025

Dolan, K.J., Ciesielski, T.M., Lierhagen, S., Eulaers, I., Nygård, T., Johnsen, T.V., ... & Jaspers, V.L.B., 2017. Trace element concentrations in feathers and blood of Northern goshawk (*Accipiter gentilis*) nestlings from Norway and Spain. Ecotoxicology and Environmental Safety, 144, 564-571.

Dolci, N.N., Sá, F., da Costa Machado, E., Krul, R., & Rodrigues Neto, R., 2017. Trace elements in feathers and eggshells of Brown Booby Sula leucogaster in the Marine National Park of Currais Islands, Brazil. Environmental Monitoring and Assessment, 189, 1-14.

Dorneles, P.R., Lailson-Brito, J., Dos Santos, R.A., da Costa, P.A.S., Malm, O., Azevedo, A.F., & Torres, J.P.M., 2007. Cephalopods and cetaceans as indicators of offshore bioavailability of cadmium off Central South Brazil Bight. Environmental Pollution, 148(1), 352-359.

Dorneles, P.R., Lailson-Brito, J., Fernandez, M.A., Vidal, L.G., Barbosa, L.A., Azevedo, A.F., ... & Malm, O., 2008. Evaluation of cetacean exposure to organotin compounds in Brazilian waters through hepatic total tin concentrations. Environmental Pollution, 156(3), 1268-1276.

Dorneles, P.R., Schilithz, P.F., Paiva, T.D.C., Flach, L., Barbosa, L.A., Domit, C., ... & Lailson-Brito, J., 2020. Total tin (TSn) biomagnification: Evaluating organotin trophic flow and dispersion using hepatic TSn concentrations and stable isotope (C, N) data of nektonic organisms from Brazil. Marine Environmental Research, 161, 105063.

Einoder, L.D., MacLeod, C.K., & Coughanowr, C., 2018. Metal and isotope analyses of bird feathers in a contaminated estuary reveals bioaccumulation, biomagnification, and potential toxic effects. Archives of Environmental Contamination and Toxicology, 75, 96-110.

El Hanafi, K., Pedrero, Z., Ouerdane, L., Marchán Moreno, C., Queipo-Abad, S., Bueno, M., Pannier, F., Corns, W.T., Cherel, Y., Bustamante, P., Amouroux, D., 2022. First Time Identification of Selenoneine in Seabirds and Its Potential Role in Mercury Detoxification. Environmental Science & Technology, 56, 3288-3298. https://doi.org/10.1021/acs.est.1c04966

Fan, C., Yu, B., & Chen, D., 2009. Effects of different sources and levels of selenium on performance, thyroid function and antioxidant status in stressed broiler chickens. International Journal of Poultry Science, 8(6), 583-587.

Finger, A., Lavers, J.L., Orbell, J.D., Dann, P., Nugegoda, D., & Scarpaci, C., 2016. Seasonal variation and annual trends of metals and metalloids in the blood of the Little Penguin (Eudyptula minor). Marine Pollution Bulletin, 110, 261-273. https://doi.org/10.1016/j.marpolbul.2016.06.055

Frouin, H., Pelletier, E., Lebeuf, M., Saint-Louis, R., & Fournier, M., 2010. Toxicology of organotins in marine organisms: a review. Organometallic Compounds: Preparation.

Fuentes, M.M.P.B., Wildermann, N., Gandra, T.B.R., Domit, C., 2020. Cumulative threats to juvenile green turtles in the coastal waters of southern and southeastern Brazil. Biodiversity and Conservation, 29, 1783-1803. https://doi.org/10.1007/s10531-020-01964-0

Gama, I.H., de Almeida, M.G., Rangel, T.P., Marques, J.S., de Oliveira, B.C., Araújo, B.F., ... & de Rezende, C.E., 2022. Metals and organic matter baselines in sediments in a cross-shelf gradient at Abrolhos Bank, SW Atlantic. Science of the Total Environment, 802, 149867.

Gilmour, M.E., Hudson, S.T., Lamborg, C., Fleishman, A.B., Young, H.S., & Shaffer, S.A., 2019. Tropical seabirds sample broadscale patterns of marine contaminants. Science of the Total Environment, 691, 631-643.

Guruge, K.S., Tanabe, S., Iwata, H., Taksukawa, R., & Yamagishi, S., 1996. Distribution, biomagnification, and elimination of butyltin compound residues in common cormorants (Phalacrocorax carbo) from Lake Biwa, Japan. Archives of Environmental Contamination and Toxicology, 31, 210-217.

Herbst, D.F., Gerhardinger, L.C., Vila-Nova, D.A., de Carvalho, F.G., Hanazaki, N., 2020. Integrated and deliberative multidimensional assessment of a subtropical coastal-marine ecosystem (Babitonga bay, Brazil). Ocean and Coastal Management, 196, 105279. https://doi.org/10.1016/j.ocecoaman.2020.105279

Jerez, S., Motas, M., Palacios, M.J., Valera, F., Cuervo, J.J., & Barbosa, A., 2011. Concentration of trace elements in feathers of three Antarctic penguins: geographical and interspecific differences. Environmental Pollution, 159(10), 2412-2419.

Klein, R., Bartel-Steinbach, M., Koschorreck, J., Paulus, M., Tarricone, K., Teubner, D., Wagner, G., Weimann, T., & Veith, M., 2012. Standardization of egg collection from aquatic birds for biomonitoring-a critical review. Environmental Science & Technology, 46(10), 5273-5284.

Kopp, D., Lefebvre, S., Cachera, M., Villanueva, M.C., & Ernande, B., 2015. Reorganization of a marine trophic network along an inshore–offshore gradient due to stronger pelagic–benthic coupling in coastal areas. Progress in Oceanography, 130, 157-171.

Lailson-Brito, J., Dorneles, P.R., Azevedo-Silva, C.E., Azevedo, A.F., Vidal, L.G., Zanelatto, R.C., ... & Malm, O., 2010. High organochlorine accumulation in blubber of Guiana dolphin, Sotalia guianensis, from Brazilian coast and its use to establish geographical differences among populations. Environmental Pollution, 158(5), 1800-1808.

Lavers, J.L., Humphreys-Williams, E., Crameri, N.J., & Bond, A.L., 2020. Trace element concentrations in feathers from three seabird species breeding in the Timor Sea. Marine Pollution Bulletin, 151, 110876.

Lerma, M., Castillo-Guerrero, J.A., García-Hernández, J., & Fernández, G., 2020. Zinc concentrations in Blue-footed booby (Sula nebouxii) eggs, nestlings, and adults. Journal of Sea Research, 165, 101952.

Lerma, M., Dehnhard, N., Luna-Jorquera, G., Voigt, C.C., & Garthe, S., 2020. Breeding stage, not sex, affects foraging characteristics in masked boobies at Rapa Nui. Behavioral Ecology and Sociobiology, 74, 1-16.

Maciel, D.C., Castro, Í.B., de Souza, J.R.B., Yogui, G.T., Fillmann, G., & Zanardi-Lamardo, E., 2018. Assessment of organotins and imposex in two estuaries of the northeastern Brazilian coast. Marine Pollution Bulletin, 126, 473-478.

Mancini, P.L., Hobson, K.A., & Bugoni, L., 2014. Role of body size in shaping the trophic structure of tropical seabird communities. Marine Ecology Progress Series, 497, 243-257.
trophic variation in Brown Booby (*Sula leucogaster*) from the Southwestern Atlantic. Marine Biology, 170(1), 1.

Mancini, P. L., Valim, E. E. M., de Barros Bauer, A., & Fischer, L. G., 2023. Intraspecific trophic variation in Brown Booby (*Sula leucogaster*) from the Southwestern Atlantic. Marine Biology, 170(1), 1.

Mellink, E., Domínguez, J., Luévano, J., & Dominguez, J., 2001. Diet of Eastern Pacific Brown Boobies Sula leucogaster brewsteri on Isla San Jorge, north-eastern Gulf of California, and an April comparison with diets in the Middle. Marine Ornithology, 28, 23-28.

Mello, F. V., Cunha, L. S. T., & Torres, J. P. M., 2012. Persistent organic pollutants in the diet of Brown Boobies (Sula leucogaster) from three different archipelagos of Brazil. Organohalogen Compounds, 74, 524-527.

Moura, J. F., Tavares, D. C., Lemos, L. S., Acevedo-Trejos, E., Saint'Pierre, T. D., Siciliano, S., & Merico, A., 2018. Interspecific variation of essential and non-essential trace elements in sympatric seabirds. Environmental Pollution, 242, 470-479.

Navarro, J., Moreno, R., Braun, L., Sanpera, C., & Hennicke, J. C., 2014. Resource partitioning between incubating and chick-rearing Brown Boobies and red-tailed tropicbirds on Christmas Island. Zoological Studies, 53, 1-6.

Neto, J. A. B., Gingele, F. X., Leipe, T., & Brehme, I., 2006. Spatial distribution of heavy metals in surficial sediments from Guanabara Bay: Rio de Janeiro, Brazil. Environmental Geology, 49, 1051-1063.

Nunes, G. T., Bertrand, S., & Bugoni, L., 2018. Seabirds fighting for land: phenotypic consequences of breeding area constraints at a small remote archipelago. Scientific Reports, 8(1), 665.

Nunes, G. T., Efe, M. A., Barreto, C. T., Gaiotto, J. V., Silva, A. B., Vilela, F., ... & Bugoni, L., 2022. Ecological trap for seabirds due to the contamination caused by the Fundão dam collapse, Brazil. Science of the Total Environment, 807, 151486.

Ohlendorf, H. M., 2002. Ecotoxicology of selenium. In: Hoffman, D. J., Rattner, B. A., Burton Jr., G. A., & Cairns Jr., J. (Eds.), Handbook of Ecotoxicology. CRC Press, Boca Raton, pp. 489-524.

Pacyna, A.D., Jakubas, D., Ausems, A.N.M.A., Frankowski, M., Polkowska, Ż., & Wojczulanis-Jakubas, K., 2019. Storm petrels as indicators of pelagic seabird exposure to chemical elements in the Antarctic marine ecosystem. Science of the Total Environment, 692, 382–392. https://doi.org/10.1016/j.scitotenv.2019.07.137

Padilha, J. A., Castro, R.M., Cunha, L.S.T., Paiva, T. C., Malm, O., & Dorneles, P.R., 2013. Concentrações de cádmio, estanho e cobre em penas de atobás (*Sula leucogaster*) e fragatas (*Fregata magnificens*) do Cagarras Islands Natural Monument, Rio de Janeiro, Brasil. Natural Resources, 3, 14-14. https://doi.org/10.6008/ESS2237-9290.2013.002.0009

Padilha, J. A., Carvalho, G. O., Espejo, W., Souza, J. S., Pizzochero, A. C., Cunha, L. S. T., ... & Dorneles, P. R., 2021. Factors that influence trace element levels in blood and feathers of Pygoscelis penguins from South Shetland Islands, Antarctica. Environmental Pollution, 284, 117209.

Pereira, E., Baptista-Neto, J. A., Smith, B. J., & Mcallister, J. J., 2007. The contribution of heavy metal pollution derived from highway runoff to Guanabara Bay sediments: Rio de

Janeiro/Brazil. Anais da Academia Brasileira de Ciências, 79, 739-750.

Pizzochero, A. C., Michel, L. N., Chenery, S. R., McCarthy, I. D., Vianna, M., Malm, O., ... & Dorneles, P. R., 2018. Use of multielement stable isotope ratios to investigate ontogenetic movements of Micropogonias furnieri in a tropical Brazilian estuary. Canadian Journal of Fisheries and Aquatic Sciences, 75(6), 977-986.

Polito, M. J., Brasso, R. L., Trivelpiece, W. Z., Karnovsky, N., Patterson, W. P., & Emslie, S. D., 2016. Differing foraging strategies influence mercury (Hg) exposure in an Antarctic penguin community. Environmental Pollution, 218, 196-206.

Riley, W. J., 2019. A history of the rubidium frequency standard. IEEE UFFC-S History, 2, 1-10.

Hobson, K. A., Blight, L. K., & Arcese, P., 2015. Human-induced long-term shifts in gull diet from marine to terrestrial sources in North America’s coastal Pacific: more evidence from more isotopes (δ2H, δ34S). Environmental Science & Technology, 49(18), 10834-10840.

Roman, L., Kastury, F., Petit, S., Aleman, R., Hardesty, B. D., & Wilcox, C., 2023. Nutrients and seabird biogeography: Feather elements differ among oceanic basins in the Southern Hemisphere, reflecting bird size, foraging range and nutrient availability in seawater. Global Ecology and Biogeography, 32(4), 495-510.

Sasanami, T. (Ed.), 2017. Avian Reproduction: From Behavior to Molecules. Springer, Tokyo.

Schilithz, P. F., Dorneles, P. R., & Brito, J. L., 2013. Exposição de cetáceos a compostos butilestânicos: uma revisão. Oecologia Australis, 17(3), 429-448.

Signa, G., Mazzola, A., & Vizzini, S., 2021. Seabird influence on ecological processes in coastal marine ecosystems: An overlooked role? A critical review. Estuarine, Coastal and Shelf Science, 250, 107164.

Van Weerelt, M., Cunha, L., Dorneles, P. R., Padilha, J., Ormond, J., Torres, F., Torres, J. P., Batista, D., Nudi, A., & Wagener, A., 2013. Monitoramento da qualidade das águas e dos poluentes no MoNa das Ilhas Cagarras e entorno. História, pesquisa e biodiversidade do Monumento Natural das Ilhas Cagarras, Rio de Janeiro. Museu Nacional, pp. 229-243.

Varala, R., & Rao, K. S., 2015. Cesium salts in organic synthesis: A review. Current Organic Chemistry, 19(13), 1242-1274.

Walsh, P. M., 2018. The use of seabirds as monitors of heavy metals in the marine environment. In: Furness, R. W., & Rainbow, P. S. (Eds.), Heavy Metals in the Marine Environment. CRC Press, pp. 183-204.

Wróblewski, M., Wróblewska, J., Nuszkiewicz, J., Pawłowska, M., Wesołowski, R., & Woźniak, A., 2023. The role of selected trace elements in oxidoreductive homeostasis in patients with thyroid diseases.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: