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Trace elements in migratory species arriving to Antarctica according to their migration range

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ABSTRACT

The levels of eighteen trace elements (TEs) were evaluated in association with stable isotopes ($\delta^{15}N$, $\delta^{34}S$, and $\delta^{13}C$) in feathers and eggs of five migratory species breeding on the Antarctic Peninsula to test the factors that influence their exposure to contaminants. The feathers of seabirds migrating to the Northern Hemisphere (South polar skua) have concentrations (mean ± SD, μg. g^{-1}) of Li (1.71 ± 2.08) and Mg (1169.5 ± 366.8) one order of magnitude higher than southern migrants, such as Snowy sheathbill Li (0.01 ± 0.005) and Mg (499.6 ± 111.9). Feathers had significantly higher concentrations for 11 of a total of 18 metals measured compared to eggs. South polar skua have higher concentrations of all TEs in eggs compared to antarctic tern. Therefore, the present study showed that migration and trophic ecology ($\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$) influence Fe, Mn, Cu, and Se concentrations in feathers of Antarctic seabirds. The concentrations of Cu, Mn, Rb, Zn, Pb, Cd, Cr are higher than previously reported, which may be due to increased local and global human activities.

1. Introduction

Anthropogenic activities disrupt the natural cycling of essential and non-essential trace elements (TEs) in different environments around the world, including pristine regions such as Antarctica (Bargagli, 2008; Carravieri et al., 2020; Jerez et al., 2011). TEs are of concern to living organisms due to their toxicity and bioaccumulation properties. Increasing concentrations of TEs in Antarctic environments are related to global and regional human activities (Bargagli, 2008; Padilha et al., 2021).

Seabirds are valuable sentinels of environmental pollution of trace elements, due to their high trophic position, wide distribution, and longevity (Burger and Gochfeld, 2000a; Polito et al., 2016; Souza et al., 2020). The migratory seabirds are vectors of nutrient and contaminant transfer from marine environments to land (Burger and Gochfeld, 2000a; Celis et al., 2014), which can have an impact on soil microorganisms (Espejo et al., 2017). This biotransport relocate nutrients and contaminants, including TEs, from foraging areas to breeding sites and these nutrients / contaminants are released through processes of molt, defecation, regurgitation, dropping food, or mortality (Cipro et al., 2018; Mallory et al., 2015). Migratory birds can act as carriers of contaminants to Antarctica, as they migrate during the austral winter, reaching more contaminated regions, and return to the Antarctic environment during the summer to reproduce (Cipro et al., 2018). The migratory Antarctic seabirds, such as south polar skua (*Stercorarius maccormicki*) disperses by routes through the Atlantic and Pacific oceans, reaching the Northern Hemisphere during winter (Kopp et al., 2011). On the other hand, Antarctic tern (*Sterna vittata*), snowy sheathbill (*Chionis albus*), giant petrel (*Macronectes giganteus*) and kelp gull (*Larus dominicanus*) disperse in marine environments of the

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Southern Hemisphere (Australia, New Zealand, South Africa, and South America) during winter (Patterson and Hunter, 2000).

For birds, feeding is the main form of exposure to pollutants, which accumulates in the tissues like the liver and kidney, and excreted by feather, guano, and also by laying eggs (Bargagli, 2008; Celis et al., 2018). Because of this, feathers and eggs provide an advantageous monitoring tool for assessing avian exposure to contaminants, including TEs, in many regions of the world (Bighetti et al., 2021; Espejo et al., 2018; Jerez et al., 2011; Padilha et al., 2018, 2021). Both feathers and eggs potentially represent different periods of exposure to contaminants (Metcheva et al., 2011). Feathers are considered matrices of choice for TEs measurements, because integumentary structures constitute excretion pathways for toxic elements and compounds (Burger, 1993; Jaspers et al., 2019). During its formation (2–3 weeks), TEs bind to the proteins of the feather structure through blood irrigation (Burger, 1993; Metcheva et al., 2006, 2011). The disulfide bonds, which are present in the protein of the feather, are readily reduced to sulfhydryls, which have a great affinity to metals, thus permanently storing them in the feather structure (Metcheva et al., 2006). Thus, the feathers constitute a potentially important detoxification pathway for toxic TEs and reflect levels in the blood during feather formation. Feathers display a relatively higher body burden of certain TEs compared to internal tissues such as blood (Burger, 1993; Metcheva et al., 2011). On the other hand, the contaminants deposited in eggs reflect circulating levels in the blood at the time of egg-laying (Burger and Gochfeld, 2003), and also represent the contaminant exposure of maternal tissue, once maternal lipid, protein, and contaminants are deposited into eggs during their synthesis (Drouillard and Norstrom, 2001).

Little is known about how the migratory patterns and different trophic ecologies of Antarctic seabirds can influence their exposure to TEs in Antarctic environments (Wing et al., 2020). To help fill this gap, this study aims to evaluate the species-specific differences in exposure of migratory (South polar skua, antarctic tern, snowy sheathbill, giant petrel, and kelp gull) Antarctic seabirds to 18 TEs (7 essential and 11 non-essential) through feather and eggs analysis. The influence of multiple spatial and ecological factors (e.g., food sources, trophic position, …) on these concentrations was investigated through the isotopic composition of carbon, sulfur, and nitrogen ($\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$). We hypothesized that: (1) seabirds that migrate to the Northern Hemisphere have higher concentrations of trace elements than those that migrate to the Southern Hemisphere; (2) trophic ecology will influence the concentration of trace elements in Antarctic seabirds (3) feathers have higher concentrations of most trace elements compared to eggs; and (3) the concentrations of TEs increased when compared to previous studies due to the increase in anthropic impacts in different regions of the globe.

2. Materials and methods

2.1. Sampling

The samples were collected in King George Island (61°50′ - 62°15′S and 57°30′ - 59°00′W) in the South Shetland Archipelago, Antarctic Peninsula region (Fig. 1), during 2010–2011, 2012–2013 and 2013–2014 austral summers. Snowy sheathbill (*Chionis albus*; $n = 5$) and antarctic tern (*Sterna vittata*; $n = 18$) were captured during the breeding season with long-handled fish nets, the south polar skua (*Stercorarius maccormicki*; $n = 16$) were captured using snare trap, and breast feathers of these animals were cut close to their base with stainless steel scissors. The feathers of the kelp gull (*Larus dominicanus*; $n = 6$) and southern giant petrel (*Macronectes giganteus*; $n = 23$) were collected in the colonies of these species following the protocol: 10 to 20 contour feathers (feathers on the chest, abdomen or back) at three distinct points in each colony. Each point collected within the same colony was considered as an independent sample. Each captured animal was weighed, measured (beak size, wing, tail) with digital caliper or ruler, banded with an aluminum ring, and freed after measurements and sampling as described by Sick et al. (1997). The feathers were packed in individual polyethylene ziplock bags, and the samples were kept at room temperature until the time of analysis. It was not possible to perform molecular recognition on sex, and as these species do not have sexual dimorphism, we do not know the percentage of males and females in the collected samples. Eggs of south polar skua ($n = 38$) and antarctic tern ($n = 8$) were collected in breeding territories. It was not possible to correlate the egg to the parents in the present study since the non-viable eggs were found abandoned outside the nests. The non-viable eggs were collected and stored in decontaminated jars and kept frozen for later lyophilization.

2.2. Sample preparation

Breast feather samples 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) again, for eliminating external contamination, and oven-dried at 50 °C for 24 h (Marques et al., 2007) before being grounded into a fine powder using ceramic scissors. The internal content of the egg was lyophilized for further analysis. For trace element measurements, aliquots of approximately 0.1 g of dry powdered feathers and eggs were subjected to acid digestion in the microwave in Teflon vessels, with the addition of 5 mL of nitric acid (HNO_3, 65 % suprapur Merck, Germany), 2 mL of hydrogen peroxide (H_2O_2, 30 % suprapur Merck, Germany) and

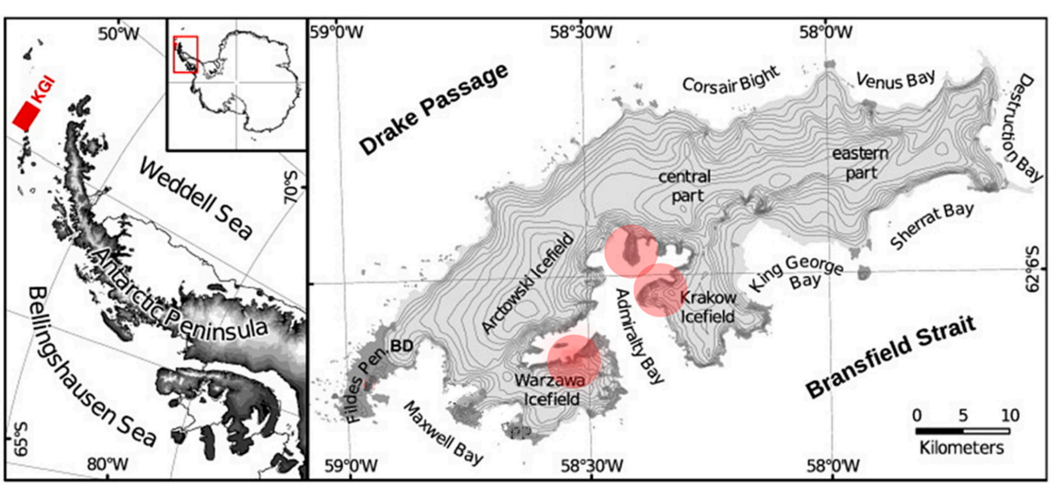

Fig. 1. Map of the Antarctic Peninsula, highlighting the King George Island. The sampling points are marked as a red circle (Adapted from Rückamp et al., 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1 mL of Milli-Q ultrapure water (Merck Millipore, USA).

2.3. Quality assurance

For trace elements measurements, blanks were carried through the procedure in the same way as the samples, as it was the case for the reference materials NIES - 1 and 2 (human hair) and Dorm-4 (fish protein). Reference material results (Table S1) were in good agreement (recovery between 90 and 110 %) with the values certified by the National Institute for Environmental Studies (NIES, $n = 6$) and National Research Council of Canada (NRC – Dorm, n = 6). The detection limits of the method, in μg. g^{-1}, were: 0.001 for Li; 0.006 for Be; 0.11 for Mg; 0.78 for Ca; 0.008 for Cr; 0.45 for Fe; 0.005 for Mn; 0.009 for Ni; 0.009 for Cu; 0.05 for Zn; 0.003 for As; 0.04 for Se; 0.002 for Rb; 0.006 for Sr; 0.003 for Cd; 0.0001 for Sn; 0.01 for Ba; and 0.004 for Pb.

For stable isotopes measurements, isotopic ratios were conventionally expressed as δ concentrations in ‰ (Coplen, 2011) and relative to the international standards: Vienna Pee Dee Belemnite, for carbon; Atmospheric Air, for nitrogen; and Vienna Canyon Diablo Troilite, for sulfur. We used International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials IAEA-C6 (δ^{13}C values = −10.8 ± 0.5 ‰; mean ± SD), IAEA-N2 (δ^{15}N values = 20.3 ± 0.2 ‰; mean ± SD) and IAEA-S1 (δ^{34}S values = −0.3 ‰; mean) as primary analytical standards. As secondary analytical standards we used sulfanilic acid (δ^{13}C values = −25.9 ± 0.3; δ^{15}N values = −0.12 ± 0.4; δ^{34}S values = 5.9 ± 0.6; mean ± SD in each case). Isotopic ratios of samples were calibrated using primary analytical standards. Standard deviations on multi-batch replicate measurements of secondary analytical (sulfanilic acid) and lab standards (feathers) analyzed interspersed among samples (one replicate of each standard every 15 analysis) were 0.2 ‰ for both δ^{13}C values and δ^{15}N values and 0.4 ‰ for δ^{34}S values.

2.4. ICP-MS analysis and stable isotope measurements

Lithium (Li), Be, Mg, Ca, Cr, Fe, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Ba and Pb concentrations were determined by inductively coupled plasma - mass spectrometry (ICP-MS), using a Perkin Elmer Elan 9000 spectrometer following the methodology described in Lehnert et al. (2016).

Stable isotope measurements were performed via continuous flow - elemental analysis - isotope ratio mass spectrometry (CF-EA-IRMS) using a Vario MICRO cube C-N-S elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) coupled to an IsoPrime100 isotope ratio mass spectrometer (Isoprime, Cheadle, United Kingdom).

2.5. Statistical analysis

Non-parametric (Mann-Whitney *U* test, Spearman correlation test-r and Kruskal-Wallis) tests were used. A Kruskal-Wallis test was used for comparing TEs concentration values among different species. The post hoc tests were conducted to test pairwise comparisons. Mann-Whitney U test was used to evaluate the possibility of a significant difference between the concentrations of TEs and two different species/matrices. Spearman rank correlation test were used to assess the relationship between TEs concentrations and stable isotope values (δ^{15}N, δ^{13}C, δ^{34}S) values. We investigated the relationship between trace element concentrations and stable isotope values among the species of migratory birds using a principal component analysis (PCA). Statistical analyses were performed in R (R Core Team, 2019) statistical software and Statistica 12.

3. Results

Essential (Mg, Ca, Fe, Mn, Cu, Zn, Se) and nonessential (Li, Be, Cr, Ni, As, Rb, Sr, Cd, Sn, Ba and Pb) trace element concentrations in feathers and eggs of five species of nesting seabirds in Antarctica were determined and are displayed in Table 1.

A Principal Component Analysis was conducted to determine if there are significant differences in the concentrations of TEs and stable isotope profiles among the two groups of migratory seabirds. The first principal component (PC1) explained 41.3 % (Fig. 2) of the total variability in the dataset, with the strongest positive contributions from Fe, Ba, Mn, and Ni and the weakest one from Be (Fig. 3a). The second principal component (PC2) expressed 19.4 % of the variation with the strongest positive contributions from Li and Mg (Fig. 3b). There was a clear overlap among the TEs and stable isotope profiles between migrants from the Southern Hemisphere. However, the horizontal axis tends to separate Northern Hemisphere migratory birds from Southern Hemisphere birds.

3.1. Interspecific differences in Antarctic seabirds

The concentrations of essential elements in feathers of different seabird species differed significantly (Ca > Mg > Fe > Zn > Cu > Mn > Se > Li > Be, Kruskal-Wallis - KW, Table S2), with south polar skua having higher concentrations of Li ($p = 0.002$), Be ($p < 0.001$), Mg ($p = 0.02$), and Zn ($p = 0.005$), but lower concentrations of Fe ($p = 0.04$) and Mn ($p = 0.001$) compared to other species. The snowy sheathbill had lower Fe ($p = 0.007$), Se ($p = 0.01$), and Mn (p = 0.01) levels, while kelp gull had lower Se (p = 0.005) concentrations compared to other species. The Cu concentration was higher in Snowy sheathbill (p = 0.02) than in south polar skua and kelp gull. Additionally, south polar skua eggs had higher concentrations of Fe (U- 237 2.8 = 18, p = 0.01) and Se (U-2.5 = 20, p = 0.01) than antarctic tern eggs.

The concentrations of non-essential elements Sr > Ni > Ba > As > Pb > Rb > Cd > Sn in feathers differed among seabird species (Kruskal-Wallis test, $p < 0.05$, Table S2). Antarctic tern had significantly higher concentrations of Ni ($p < 0.001$) and Cd ($p = 0.03$) than south polar skua and snowy sheathbill. Concentrations of Rb were significantly lower in snowy sheathbill ($p = 0.02$) compared to other seabird species, except for kelp gull. As and Pb concentrations were significantly higher in south polar skua (As: $p = 0.003$; Pb: $p = 0.04$) than other species, except for kelp gull. Ba values were significantly lower in south polar skua (p < 0.001) and snowy sheathbill ($p = 0.03$) than other seabird species, except for kelp gull. In eggs, a Mann-Whitney *U* test, south polar skua had higher concentrations of Ni (U-2.6 = 17, $p = 0.01$), As (U-2.2 = 26, p = 0.03), Cd (U-2.0 = 29, p = 0.04), and Ba (U-1.98 = 30, $p = 0.05$) than antarctic tern.

3.2. Stable isotope ratios and trace element patterns

Data from stable isotope analysis in the present study indicate that the south polar skua ($p = 0.003$) and giant petrel ($p = 0.007$) had significantly higher δ^{15}N values compared to other seabird species. Additionally, the south polar skua ($p < 0.001$), kelp gull ($p = 0.029$), snowy sheathbill ($p = 0.022$), and giant petrel (p = 0.022) all had significantly higher δ^{13}C values compared to the other seabird species. In terms of δ^{34}S, only the giant petrel ($p = 0.006$) had significantly higher values compared to the south polar skua.

Significant negative correlations were found between δ^{13}C and ten elements (Ca, Fe, Mn, Ni, Cu, Se, Rb, Sr, Cd, and Ba) and significant positive correlation between δ^{13}C and two elements (Zn and Sn; Table 2). Significant negative correlations were found between δ^{15}N and eight elements (Ca, Cr, Fe, Mn, Ni, Cu, Se, and Sr), and positive for two elements (Be and Sn; Table 2). Regarding δ^{34}S, significant negative correlations were observed for five elements (Li, Be, Zn, and Sn) and significant positive correlations for six elements (Fe, Mn, Cu, Se, Cd, and Ba; Table 2).

3.3. Differences between eggs and feathers

A Mann-Whitney *U* test was performed to determine the differences

Table 1
Concentrations (mean ± SD, μg. g^{-1}, dry weight) of trace elements in two matrices (M): feathers (F) and eggs (E) of migratory seabirds from King George Island, Antarctic Peninsula, Antarctica). <LD: below detection limit.

Species	M	*N*	Li	Be	Mg	Ca	Cr	Fe	Mn	Ni	Cu	Zn	As	Se	Rb	Sr	Cd	Sn	Ba	Pb
S. maccormicki	F	16	1.71 ± 2.08	0.02 ± 0.01	1170 ± 367	1046 ± 309	0.61 ± 1.08	18.8 ± 9.12	0.52 ± 0.31	0.29 ± 0.08	14.4 ± 5.45	114 ± 30.8	0.49 ± 0.09	3.65 ± 1.14	0.13 ± 0.06	12.6 ± 4.01	0.11 ± 0.11	0.02 ± 0.01	0.16 ± 0.06	0.29 ± 0.13
	E	25	0.04 ± 0.05	0.01 ± 0.01	473 ± 121	2835 ± 1387	0.02 ± 0.02	103 ± 35	1.18 ± 0.74	0.06 ± 0.03	3.37 ± 0.79	44.9 ± 14.2	0.28 ± 0.1	2.93 ± 0.68	1.97 ± 0.43	9.39 ± 4.67	<LD	0.28 ± 0.44	0.33 ± 0.55	0.04 ± 0.04
C. albus	F	5	0.01 ± 0.005	<LD	500 ± 112	600 ± 118	0.71 ± 0.39	16.6 ± 3.65	0.27 ± 0.24	0.14 ± 0.05	25.7 ± 1.71	132 ± 9.22	0.38 ± 0.09	1.18 ± 0.21	0.03 ± 0.01	7.00 ± 2.24	0.06 ± 0.02	0.04 ± 0.01	0.17 ± 0.08	0.18 ± 0.05
L. dominicanus	F	6	0.05 ± 0.02	<LD	790 ± 247	806 ± 150	24.9 ± 44.7	257 ± 316	3.31 ± 2.88	1.16 ± 1.77	13.9 ± 3.55	123 ± 19	0.14 ± 0.03	1.76 ± 0.28	0.08 ± 0.04	11.7 ± 3.1	0.12 ± 0.12	0.07 ± 0.09	0.72 ± 0.43	0.31 ± 0.28
M. giganteus	F	23	0.09 ± 0.07	0.01 ± 0.01	760 ± 333	891 ± 414	0.74 ± 0.92	297 ± 328	7.17 ± 7.45	0.69 ± 0.69	17.0 ± 6.27	81.9 ± 10.9	0.13 ± 0.09	5.34 ± 2.30	0.16 ± 0.14	11.3 ± 5.34	0.16 ± 0.14	0.03 ± 0.02	1.35 ± 1.38	0.13 ± 0.10
S. vittata	F	18	0.13 ± 0.09	0.01 ± 0.02	973 ± 663	1325 ± 658	18.2 ± 46.8	495 ± 488	11.2 ± 15.8	1.78 ± 1.83	21.1 ± 9.39	103 ± 38.4	0.19 ± 0.12	5.08 ± 2.51	0.49 ± 0.70	14.2 ± 6.93	0.43 ± 0.31	0.04 ± 0.03	4.44 ± 6.78	0.32 ± 0.32
	E	5	0.03 ± 0.04	0.01 ± 0.005	541 ± 145	3759 ± 1173	0.09 ± 0.16	259 ± 225	2.20 ± 1.50	0.11 ± 0.04	3.03 ± 1.03	57.3 ± 19.1	0.44 ± 0.15	4.18 ± 1.35	1.93 ± 0.79	13.1 ± 6.49	0.01 ± 0.01	0.72 ± 1.55	0.34 ± 0.15	0.04 ± 0.02

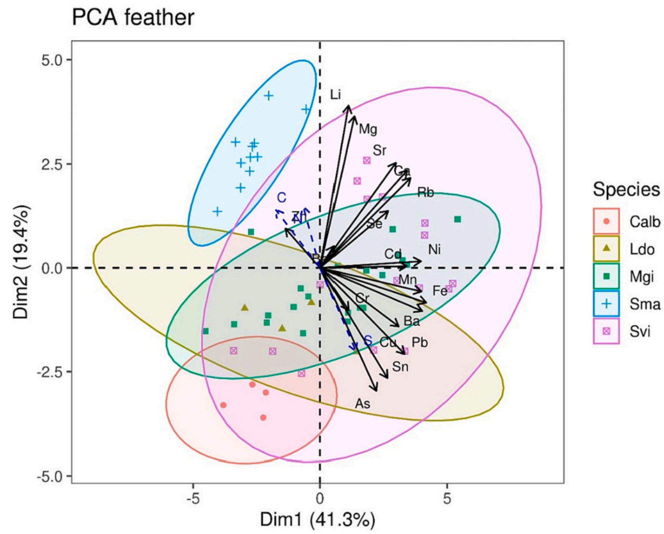

Fig. 2. PCA in feathers of *Chionis albus* (Calb), *Larus dominicanus* (Ldo), *Macronectes giganteus* (Mgi), *Stercorarius maccormicki* (Sma), and *Sterna vittata* (Svi) from Antarctic Peninsula. The length of the vector's projection reflects its contribution to the principal component. The angle between two vectors gives the correlation between the corresponding variables, as well as between variables and principal components.

between matrices (Table S3). It was found that concentrations of Li, Ca, Cr, Ni, Cu, Zn, As, Rb, Cd, Ba, and Pb were significantly higher in antarctic tern feathers than egg samples. In relation to south polar skua, Li, Ni, Be, Mg, Cr, Cu, Zn, As, Cd, and Pb concentrations are significantly higher in feathers than eggs. Additionally, Ca, Fe, Rb, Sn, Mn, Sr, and Ba concentrations are higher in eggs than feathers of south polar skua.

4. Discussion

4.1. Interspecific differences in Antarctic seabirds

According to the authors' knowledge, there are no data in the literature about most of the elements measured in the present study in eggs and feather of migratory Antarctic seabirds. Therefore, these data are pioneering and serve as a baseline for future studies.

To investigate if seabirds that migrate to the Northern Hemisphere have higher exposure to pollution than those that migrate to the Southern Hemisphere, we compared the concentrations of TEs and stable isotopes in south polar skuas and the other seabirds. The south polar skua are opportunistic predators, kleptoparasites and scavengers, feeding on nototenid fish (*Pleuragramma antarcticum*), eggs and adults, or chicks of seabirds nesting in nearby colonies, as well as carcasses of marine mammals (Borghello et al., 2019). This trophic ecology can be confirmed by the findings of the present study, as the high trophic position of south polar skua is established by the high values of $\delta^{15}N$. Furthermore, its transequatorial behavior, reaching the Northern Hemisphere during the southern winter (Kopp et al., 2011), confirms the high values of $\delta^{13}C$, once the baseline $\delta^{13}C$ across the Southern Ocean is known to increase from south to north, permitting the categorization of birds from foraging lands at different latitudes (Roscales et al., 2016). The post-breeding dispersal of south polar skua linked to its wide foraging areas that span populated coastal areas and high trophic position could also contribute to their higher concentrations of Li, Be, Mg, Zn, As, and Pb in feathers in comparison to the southern migrants.

Snowy sheathbill, giant petrel, antarctic tern, and kelp gull disperse in marine environments in the Southern Hemisphere (Australia, New Zealand, South Africa, and South America) during the winter (Patterson and Hunter, 2000). Antarctic tern presents $\delta^{15}N$ values and a diet similar to penguins (Casaux et al., 2008), which consists of krill and fish, being

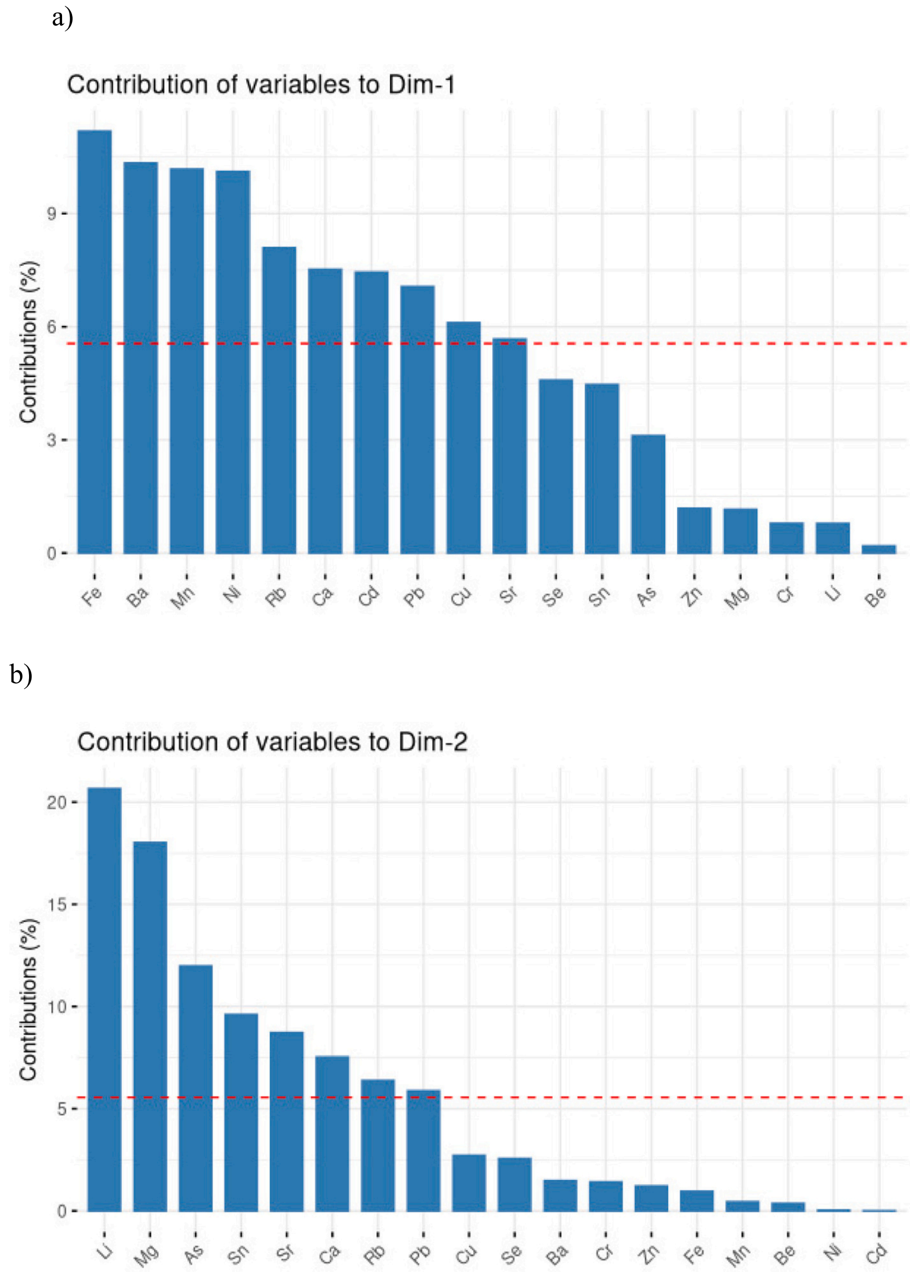

Fig. 3. Percentage of contribution (%) of variables (trace elements) for a) PC1 and b) PC2.

in a lower trophic position, which could also be observed in the principal component analysis and may explain the significantly lower concentrations of trace elements in relation to the top predator south polar skua. Giant petrel is one of the main predators of food webs sub-Antarctic and Antarctic regions, feeding on fish, and carcasses of marine mammals and penguins (Patterson and Hunter, 2000), as confirmed by our results of δ^{15}N values. This species forages in several marine regions during the breeding season, which explains the great variability of concentrations of δ^{13}C values (Roscales et al., 2019).

The influence of trophic ecology was evaluated to determine if it affects the concentration of trace elements in Antarctic seabirds. Our results showed that values of Fe, Mn, Cu, and Se are influenced by trophic position (δ^{15}N values), foraging area (δ^{13}C values), and dietary sources (δ^{34}S values). Padilha et al. (2021) observed that Fe, Mn, and Se are also influenced by those factors in *Pygoscelis* penguins from Antarctic Peninsula. Previous studies reported that Zn can biomagnify in polar organisms (Santos et al., 2006), however, in the present study this tendency was not observed once we did not observe a positive correlation between Zn and δ^{15}N values. Espejo et al. (2020) observed Zn biomagnification within the lower-trophic-level organisms (macroinvertebrates), but did not observe this tendency for top-of-the-chain animals such as birds. Rb is known to bioaccumulate through the food chain, once previous studies reported a significant correlation between Rb and δ^{15}N in marine organisms, potentially suggesting biomagnification, but in the present study no significant correlation was observed. Anderson et al. (2010) also did not observe a significant correlation between Rb and δ^{15}N in the blood of Procellariforms birds from South Georgia, as well as Padilha et al. (2021) in feathers of *Pygoscelis* penguins, indicating the Rb biomagnification through Antarctic food chains is unclear, and further studies into Rb bioaccumulation in the Antarctic environment are necessary.

Table 2
Spearman-test correlation between trace elements (TE) and stable isotopes (δ ^{13}C, δ ^{15}N, and δ ^{34}S).

TE	δ ^{34}S			δ ^{15}N			δ ^{13}C		
	R	t(N-2)	*p*-value	R	t(N-2)	p-value	R	t(N-2)	p-value
Li	−0.28	−2.79	**0.006**	0.09	0.95	0.344	0.09	0.95	0.345
Be	−0.22	−2.18	**0.032**	0,24	2.40	**0.018**	0.19	1.87	0.065
Mg	−0.09	−0.82	0.411	−0.13	−1.24	0.217	−0.15	−1.42	0.159
Ca	0.08	0.74	0.459	−0.26	−2.60	**0.011**	−0.37	−3.79	**<0.001**
Cr	−0.03	−0.34	0.740	−0.23	−2.26	**0.026**	−0.14	−1.38	0.169
Fe	0.29	2.95	**0.004**	−0.25	−2.49	**0.014**	−0.48	−5.26	**<0.001**
Mn	0.30	3.04	**0.003**	−0.23	−2.24	**0.028**	−0.46	−4.96	**<0.001**
Ni	0.02	0.22	0.825	−0.23	−2.32	**0.023**	−0.34	−3.51	**<0.001**
Cu	0.22	2.21	**0.029**	−0.39	−4.08	**<0.001**	−0.41	−4.38	**<0.001**
Zn	−0.28	−2.83	**0.006**	−0.04	−0.43	0.669	0.24	2.40	**0.018**
As	0.16	1.43	0.160	0.01	0.09	0.928	0.09	0.79	0.426
Se	0.32	3.18	**0.002**	−0.21	−2.09	**0.038**	−0.52	−5.74	**<0.001**
Rb	0.06	0.62	0.535	−0.19	−1.81	0.073	−0.28	−2.79	**0.006**
Sr	0,11	1.05	0.306	−0.28	−2.85	**<0.001**	−0.40	−4.20	**<0.001**
Cd	0.21	2.06	**0.042**	−0.17	−1.63	0.106	−0.26	−2.60	**0.011**
Sn	−0.22	−2.20	**0.030**	0.23	2.23	**0.028**	0.31	3.11	**<0.001**
Ba	0.31	3.08	**0.003**	−0.20	−1.97	**0.058**	−0.41	−4.25	**<0.001**
Pb	−0.30	−3.05	**0.003**	−0.01	−0.15	0.882	0.12	1.19	0.235

In bold, values with significance $p \leq 0.05$.

4.2. Differences between eggs and feathers

In order to gain a better understanding of the differences between the studied matrices, we compared the values of TEs between feather and eggs. This is because there is limited knowledge about the distribution of TEs in birds' bodies (Burger, 1993; Espejo et al., 2018; Jerez et al., 2013) and these values can vary greatly among different taxa (Padilha et al., 2018, 2021), and consequently more studies about TEs concentrations in different species of seabirds is needed. In the present study we observed that values of some TEs (Li, Ni, Be, Mg, Cr, Cu, Zn, As, Cd, and Pb), including toxic ones, were higher in the feathers than in eggs. Feathers may have presented higher concentrations for most metals compared to eggs due to the bioaccumulation process, which is the accumulation of a certain pollutant throughout the animal's life (Wang, 2016). Metcheva et al. (2011) also observed higher concentrations of Cu, Zn, Mn, Pb, and Cd in feather than in eggs of seabirds from Antarctica, and suggested that toxic metals are mainly present in feathers when compared to eggs, which have a higher proportion of essential metals in their internal content. Nygård et al. (2001) showed that the transport in the uterus of Cd, Cu, and Zn to the egg is low, which suggests that there is a protection in bird organisms regarding the maternal transfer of TEs to eggs.

Thus, more studies focusing on intraspecific differences are needed, since it was possible to observe that south polar skua has higher concentrations of some elements in eggs than in feathers, which may reflect sexual differences in the concentrations of trace elements, as noted previously in *Pygoscelis* penguins (Padilha et al., 2021), as eggs are also an excretion pathway. Improving the knowledge of TEs concentrations in Antarctic biota helps to fill gaps about sources and fate of these pollutants and explain questions about the global transport and distribution of TEs in pristine areas.

4.3. Concentration of TEs over the years

Comparing the results of the present work with previous studies, we observed that concentrations of TEs in feather of giant petrel from South Georgia collected in 2001 are almost 3 times lower for Cu (mean, 6.9 μg. g^{-1}, dw), 7 times lower for Mn (0.6 μg. g^{-1}, dw), and 8 times lower for Rb (0.2 μg. g^{-1}, dw) than the present study. TEs concentrations in feathers of kelp gull sampled in 2005 are lower for Cd (mean 0.07 μg. g^{-1}, dw), Cr (4.7 μg. g^{-1}, dw), and Zn (68.9 μg. g^{-1}, dw) in comparison to the present study. Santos et al. (2006) also have shown lower values of Zn (mean: 93.5 μg. g^{1}) compared to the present study in feathers of kelp gull from Antarctic Peninsula collected almost one decade ago. This may be an indication that the increase in local and global anthropogenic activities over the years may have influenced the increase in the availability of trace elements for Antarctic birds.

De Moreno et al. (1997) analyzing samples of antarctic tern eggs from Antarctic Peninsula 20 years ago found values 100 times lower for Zn and 60 times lower for Cu than the present study, which may be related to the increase in human activities over the years. Previous studies in South Shetland Islands have shown that *Pygoscelis* penguins' eggs from Antarctica, a resident Antarctic seabirds, presented one order of magnitude lower values of TEs (mean μg. g^{-1}, dw, Zn: 4.07; Mn: 0.82; Cu; Ni: <LD) compared to the migratory Antarctic birds from the present study (Espejo et al., 2018; Metcheva et al., 2011). Additionally, Padilha et al. (2021) observed values two orders of magnitude lower for Cr (mean μg. g^{-1}, dw, Cr: 0.20) and one order of magnitude lower for Ni (0.28) and Pb (<LD) in feathers of *Pygoscelis* penguins from King George Island compared to the present study. This demonstrates that migratory birds, by generally occupying higher trophic positions than penguins, as well as by migrating closer to polluting sources, have greater exposure to contaminants than resident birds, and can be vectors of pollutants to remote areas such as Antarctica (Calizza et al., 2021; Cipro et al., 2018).

Seabirds can deposit significant quantities of exogenous elements in Antarctic soils, through influence of excrement, carcass deterioration, molt (feather), and reproduction (eggshell) (Castro et al., 2021). Previous studies have demonstrated the potential of Antarctic seabirds in the biotransportation of trace elements from the ocean to soils (Castro et al., 2021; Cipro et al., 2018). Cipro et al. (2018) demonstrated, through soil analysis, that colonies of seabirds are clearly local sources of organic matter, Cd, Hg and likely of As, Se and Zn to Antarctic environment. Santamans et al. (2017) observed that bird activity influences the accumulation of As, Cd, Cu, Se, and Zn in the soils of the South Shetland Islands. Castro et al. (2021) showed the enrichment of Cu, Pb and Zn in ornithogenic soils, being the Cu the most common element biotransported by seabirds in Antarctic environment. Thus, according to the present study, the south polar skua can be an important vector of Zn, As and Pb through the feathers and vector of Se, As, and Cd through the eggs for Antarctic soils, as it presented higher concentrations of these elements when compared to migrant birds from the Southern Hemisphere.

4.4. Toxicity limits of elements in seabirds

Essential elements exert fundamental biochemical and physiological functions in a living being, however above a certain threshold have the potential to be toxic (Nordberg et al., 2014). Little is known about toxic threshold of TEs in seabirds, but the literature has shown that levels in feather starting at 200 μg. g^{-1} (dw) for Zn may be harmful for birds growth and reproduction (Einoder et al., 2018). Our results were 2 times lower than these values, which indicates that these essential elements levels represent either background or normal physiological and ecological levels. Suggested toxic effects of Cr may occur at feather concentration over 2.8 μg. g^{-1} (Burger and Gochfeld, 2000a, 2000b). Antarctic tern and kelp gull in the present study, presented values of Cr higher than 2.8 μg. g^{-1}, indicating that potential adverse effects due to Cr cannot be excluded. Previous studies reported 1–4 μg g^{-1} as a typically background concentrations of Se in feathers (Ohlendorf and Heinz, 2011). A Se concentration in feathers of 5 μg g^{-1} was identified as a provisional threshold of toxicity by several studies (Ashbaugh et al., 2018; Burger, 1993; Ohlendorf and Heinz, 2011). In the present study, giant petrel and antarctic tern showed mean feather values higher than 5 μg g^{-1}, indicating that potential adverse effects due to Se cannot be excluded.

Suggested toxic effects of non-essential TEs may occur at feather concentration over than 2 μg. g^{-1} for Cd and 4 μg. g^{-1} for Pb (Burger and Gochfeld, 2000a, 2000b). Our results showed higher concentrations of non-essential elements mainly in south polar skua (Li, Be, Sn, and Pb) and antarctic tern (Ni and Cd) compared to the other species. However, none of the species showed higher values of non-essential elements compared to those previously established as toxic to birds.

5. Conclusion

We observed that our hypotheses were confirmed, since migration and trophic ecology play an important role in the exposure of Antarctic seabirds to TEs. We highlight that: (1) Seabirds that migrate to the Northern Hemisphere have higher concentrations of Li, Be, Ca, As, Mg, Zn, Sn and Pb in feathers than Southern Hemisphere migratory seabirds; (2) Seabirds that migrate to the Northern Hemisphere have higher concentrations of all TEs in eggs compared to the Southern Hemisphere ones (3) Seabirds that migrate to the Southern Hemisphere have higher concentrations of Cu, Se, and Ni in feather than Northern Hemisphere migratory seabirds; (4) Trophic position ($\delta^{15}N$ values), foraging area ($\delta^{13}C$ values), and dietary sources ($\delta^{34}S$ values) influence Fe, Mn, Cu, and Se in feathers of Antarctic birds; (5) Foraging area ($\delta^{13}C$ values), and dietary sources ($\delta^{34}S$ values) influence Zn, Ba, Sn, Cd, Ba concentrations of migratory seabirds in Antarctica (6) the concentration of most TEs was higher in the feather than in the eggs, indicating a possible protection in the transfer of toxic elements from the mother to the offspring.

In addition, higher level of some of the TEs (Cu, Mn, Rb, Zn, Pb, Cd, Cr) compared to previous studies reinforces the need for monitoring studies in Antarctic seabirds, since the increase in human activities at a local and global scale may lead to higher exposure of these animals to pollutants.

Corroborating with previous studies on migratory birds in Antarctica, we were able to observe that migratory birds are excellent sentinels for studies of trace elements (Cipro et al., 2018; Santamans et al., 2017; Nygård et al., 2001), and that stable isotopes are valuable tools to ascertain the factors that influence the exposure of these animals to pollutants (Roscales et al., 2019). This work serves as a precursor for studies that focus on the potential of migratory birds as vectors of pollutants in remote regions. This study presents essential baseline data that will assist in future investigations seeking to use migratory Antarctic seabirds as sentinels for TEs availability in the Antarctic marine environments.

CRediT authorship contribution statement

Dr. Janeide de Assis Padilha: Investigation, Methodology, Sampling, Visualization, Formal analysis, and Writing – review & editing.

The first author headed the writing, sampling, review, editing, and structuring of the paper. Dr. Padilha actively participated in the sample collections, trace elements, and stable isotopes analysis, and the execution of the manuscript's statistics, formulation, and evolution of ideas and goals, and paper review.

MSc. Gabriel Oliveira de Carvalho: Visualization, Formal analysis, and Writing – review & editing.

The co-author contributed to the writing, review, editing and structuring of the paper. Mr. Carvalho actively participated in the formal analysis, and the execution of the manuscript's statistics, using techniques to analyze and synthesize the data, making graphics and bringing ideas that would make the information clearer and more consistent for the reader.

Dr. Winfred Espejo: Visualization, Formal analysis, and Writing – review & editing.

Dr. Winfred Espejo contributed to the writing, review, and editing. He played a fundamental role in the execution of the manuscript's statistics, and each step of the idealization of how the article would be written and how the ideas would be organized.

MSc. Adriana Rodrigues de Lira Pessoa: Investigation, Methodology and Writing – review & editing.

Ms. Pessoa contributed to the execution and organization of sample collections in Antarctica. The co-author also participated in the writing, review, formulation, and evolution of ideas and goals, and paper review.

Dr. Larissa S. T Cunha: Conceptualization, Methodology, Writing – review & editing.

Dr. Cunha contributed to the writing, execution, and administration of the Antarctic expedition to obtain all samples. In addition, she contributed to the sampling of feathers of seabirds in King George Island, conceptualization, writing, review of the paper.

Dr. Erli S. Costa: Conceptualization, Methodology, Writing – review & editing.

Ms. Costa contributed to the writing, execution, and administration of the Antarctic expedition to obtain all samples. In addition, she participated in scientific ship expeditions on seabirds' nests to collect samples, conceptualization, writing, review of the paper.

Dr. João Paulo Machado Torres: Conceptualization, Funding acquisition, Investigation and Writing – review & editing.

Professor Torres was responsible for the administration of the project that allowed the execution of the Antarctic expedition to obtain all collections. In this way, he was responsible for the coordination, planning and execution of sample collection expeditions. Professor João Paulo also obtained the acquisition of financial funds to carry out the collections and part of the analyzes, and review of the paper.

Dr. Gilles Lepoint: Funding acquisition, Investigation, Writing – review & editing and Supervision.

Professor Gilles contributed with the acquisition of funds for the analysis of stable isotopes at the University of Liege, in addition to participating in the analysis of isotopes, as well as conceptualization, writing, correction and revision of the paper.

Dr. Krishna Das: Conceptualization, Supervision, Funding acquisition, Investigation and Writing – review & editing.

Professor Das was responsible for funding acquisition, administration, and supervision of the project (CAPES - process numbers 88,881.154725/2017–0188887.154724/2017–00) and Wallonie Bruxelles International (WBI, from Belgium) that allowed the analysis of trace elements and stable isotopes at the University of Liége. She contributed to the conceptualization, writing, and review of the paper.

Dr. Paulo Renato Dorneles: Conceptualization, Supervision, Funding acquisition, Investigation and Writing – review & editing.

Professor Dorneles was responsible for the administration, and supervision of the project (CAPES - process numbers 88,881.154725/2017–0188887.154724/2017–00) and Wallonie Bruxelles International (WBI, from Belgium) that allowed the analysis of trace elements and stable isotopes at the University of Liége, Belgium. He was responsible for the coordination, planning and execution of sample analysis. Professor Dorneles contributed to the conceptualization, writing, and review of the paper.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2023.114693.

References

Anderson, O.R.J., Phillips, R.A., Shore, R.F., McGill, R.A.R., McDonald, R.A., Bearhop, S., 2010. Element patterns in albatrosses and petrels: influence of trophic position, foraging range, and prey type. Environ. Pollut. 158, 98–107. https://doi.org/10.1016/j.envpol.2009.07.040.

Ashbaugh, H.M., Conway, W.C., Haukos, D.A., Collins, D.P., Comer, C.E., French, A.D., 2018. Evidence for exposure to selenium by breeding interior snowy plovers (Charadrius nivosus) in saline systems of the Southern Great Plains. Ecotoxicology 27, 703–718. https://doi.org/10.1007/s10646-018-1952-2.

Bargagli, R., 2008. Environmental contamination in Antarctic ecosystems. Sci. Total Environ. 400, 212–226. https://doi.org/10.1016/j.scitotenv.2008.06.062.

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. Environ. Pollut. 285, 117222 https://doi.org/10.1016/j.envpol.2021.117222.

Borghello, P., Torres, D.S., Montalti, D., Ibañez, A.E., 2019. Diet of the Brown Skua (Stercorarius antarcticus lonnbergi) at Hope Bay, Antarctic Peninsula: differences between breeders and non-breeders. Polar Biol. 42, 385–394. https://doi.org/10.1007/s00300-018-2429-8.

Burger, J., 1993. Metals in avian feathers: bioindicators of environmental pollution. Rev. Environ. Toxicol. 5, 203–311.

Burger, J., Gochfeld, M., 2000a. Metal levels in feathers of 12 species of seabirds from Midway Atoll in the northern Pacific Ocean. Sci. Total Environ. 257, 37–52. https://doi.org/10.1016/S0048-9697(00)00496-4.

Burger, J., Gochfeld, M., 2000b. Metals in albatross feathers from midway atoll: influence of species, age, and nest location. Environ. Res. 82, 207–221. https://doi.org/10.1006/enrs.1999.4015.

Burger, J., Gochfeld, M., 2003. Spatial and temporal patterns in metal levels in eggs of common terns (Sterna hirundo) in New Jersey. Sci. Total Environ. 311, 91–100. https://doi.org/10.1016/S0048-9697(03)00135-9.

Calizza, E., Signa, G., Rossi, L., Vizzini, S., Careddu, G., Tramati, C.D., Caputi, S.S., Mazzola, A., Costantini, M.L., 2021. Trace elements and stable isotopes in penguin chicks and eggs: a baseline for monitoring the Ross Sea MPA and trophic transfer studies. Mar. Pollut. Bull. 170, 112667 https://doi.org/10.1016/j.marpolbul.2021.112667.

Carravieri, A., Bustamante, P., Labadie, P., Budzinski, H., Chastel, O., Cherel, Y., 2020. Trace elements and persistent organic pollutants in chicks of 13 seabird species from Antarctica to the subtropics. Environ. Int. 134, 105225 https://doi.org/10.1016/j.envint.2019.105225.

Casaux, R., Baroni, A., Ramón, A., Favero, M., Silva, P., 2008. Aspects of the foraging behaviour of the Antarctic Tern Sterna vittatagaini at Harmony Point, South Shetland Islands. Polar Biol. 31, 327–331. https://doi.org/10.1007/s00300-007-0362-3.

Castro, M.F., Neves, J.C.L., Francelino, M.R., Schaefer, C.E.G.R., Oliveira, T.S., 2021. Seabirds enrich Antarctic soil with trace metals in organic fractions. Sci. Total Environ. 785, 147271 https://doi.org/10.1016/j.scitotenv.2021.147271.

Celis, J.E., Barra, R., Espejo, W., González-Acuña, D., Jara, S., 2014. Trace element concentrations in biotic matrices of gentoo penguins (Pygoscelis papua) and coastal soils from different locations of the Antarctic Peninsula. Water Air Soil Pollut. 226, 2266. https://doi.org/10.1007/s11270-014-2266-5.

Celis, J.E., Barra, R., Chiang, G., González-Acuña, D., Espejo, W., 2018. Studying heavy metals on Antarctica by using non invasive biotic samples of penguins. Oceanogr. Fish.Open Access J. 7, 23–24.

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. https://doi.org/10.1016/j.chemosphere.2018.02.048.

Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid Commun. Mass Spectrom. 25, 2538–2560. https://doi.org/10.1002/rcm.5129.

De Moreno, J.E.A., Gerpe, M.S., Moreno, V.J., Vodopivez, C., 1997. Heavy metals in Antarctic organisms. Polar Biol. 17, 131–140.

Drouillard, K.G., Norstrom, R.J., 2001. Quantifying maternal and dietary sources of 2,2′,4,4′,5,5′-hexachlorobiphenyl deposited in eggs of the ring dove (Streptopelia risoria). Environ. Toxicol. Chem. 20, 561–567. https://doi.org/10.1002/etc.5620200315.

Einoder, L.D., MacLeod, C.K., Coughanowr, C., 2018. Metal and isotope analysis of bird feathers in a contaminated estuary reveals bioaccumulation, biomagnification, and potential toxic effects. Arch. Environ. Contam. Toxicol. 75, 96–110. https://doi.org/10.1007/s00244-018-0532-z.

Espejo, W., Sandoval, M., Celis, J.E., López, J., Riquelme, F., 2017. POSIBLES IMPLICANCIAS AMBIENTALES DEBIDO A LA RESISTENCIA A METALES PESADOS EN BACTERIAS AISLADAS DE EXCRETAS DEL PINGÜINO DE HUMBOLDT. Interciencia 42, 324–330.

Espejo, W., Celis, J.E., GonzÁlez-Acuña, D., Banegas, A., Barra, R., Chiang, G., 2018. A global overview of exposure levels and biological effects of trace elements in penguins. In: de Voogt, P. (Ed.), Reviews of Environmental Contamination And Toxicology, Reviews of Environmental Contamination And Toxicology, Vol. 245. Springer International Publishing, Cham, pp. 1–64. https://doi.org/10.1007/398_2017_5.

Espejo, W., Padilha, J.de A., Kidd, K.A., Dorneles, P., Malm, O., Chiang, G., Celis, J.E., 2020. Concentration and trophic transfer of copper, selenium, and zinc in marine species of the Chilean Patagonia and the Antarctic Peninsula Area. Biol. Trace Elem. Res. 197, 285–293. https://doi.org/10.1007/s12011-019-01992-0.

Jaspers, V.L.B., Covaci, A., Herzke, D., Eulaers, I., Eens, M., 2019. Bird feathers as a biomonitor for environmental pollutants: prospects and pitfalls. TrAC Trends Anal. Chem. 118, 223–226. https://doi.org/10.1016/j.trac.2019.05.019.

Jerez, S., Motas, M., Benzal, J., Diaz, J., Vidal, V., D'Amico, V., Barbosa, A., 2013. Distribution of metals and trace elements in adult and juvenile penguins from the Antarctic Peninsula area. Environ. Sci. Pollut. Res. 20, 3300–3311. https://doi.org/10.1007/s11356-012-1235-z.

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. In: Environmental Pollution, Nitrogen Deposition, Critical Loads And Biodiversity, 159, pp. 2412–2419. https://doi.org/10.1016/j.envpol.2011.06.036.

Kopp, M., Peter, H.-U., Mustafa, O., Lisovski, S., Ritz, M.S., Phillips, R.A., Hahn, S., 2011. South polar skuas from a single breeding population overwinter in different oceans though show similar migration patterns. Mar. Ecol. Prog. Ser. 435, 263–267. https://doi.org/10.3354/meps09229.

Lehnert, K., Ronnenberg, K., Weijs, L., Covaci, A., Das, K., Hellwig, V., Siebert, U., 2016. Xenobiotic and immune-relevant molecular biomarkers in harbor seals as proxies for pollutant burden and effects. Arch. Environ. Contam. Toxicol. 70, 106–120. https://doi.org/10.1007/s00244-015-0202-3.

Mallory, M.L., Mahon, L., Tomlik, M.D., White, C., Milton, G.R., Spooner, I., 2015. Colonial marine birds influence island soil chemistry through biotransport of trace elements. Water Air Soil Pollut. 226, 31. https://doi.org/10.1007/s11270-015-2314-9.

Marques, R.C., Garrofe Dórea, J., Rodrigues Bastos, W., de Freitas Rebelo, M., de Freitas Fonseca, M., Malm, O., 2007. Maternal mercury exposure and neuro-motor development in breastfed infants from Porto Velho (Amazon), Brazil. Int. J. Hyg. Environ. Health 210, 51–60. https://doi.org/10.1016/j.ijheh.2006.08.001.

Metcheva, R., Yurukova, L., Teodorova, S., Nikolova, E., 2006. The penguin feathers as bioindicator of Antarctica environmental state. Sci. Total Environ. 362, 259–265. https://doi.org/10.1016/j.scitotenv.2005.05.008.

Metcheva, R., Yurukova, L., Teodorova, S.E., 2011. Biogenic and toxic elements in feathers, eggs, and excreta of Gentoo penguin (Pygoscelis papua ellsworthii) in the

Antarctic. Environ. Monit. Assess. 182, 571–585. https://doi.org/10.1007/s10661-011-1898-9.
Nordberg, G.F., Fowler, B.A., Nordberg, M., 2014. Handbook on the Toxicology of Metals. Academic Press.
Nygård, T., Lie, E., Røv, N., Steinnes, E., 2001. Metal dynamics in an Antarctic food chain. Mar. Pollut. Bull. 42, 598–602. https://doi.org/10.1016/S0025-326X(00)00206-X.
Ohlendorf, H., Heinz, G., 2011. Selenium in Birds. USGS Staff – Published Research.
Padilha, J.D.A., 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: Electron. J. Chem. 10, 254–261. https://doi.org/10.17807/orbital.v10i2.1050.
Padilha, J.A., Carvalho, G.O., Espejo, W., Souza, J.S., Pizzochero, A.C., Cunha, L.S.T., Costa, E.S., Pessôa, A.R.L., Almeida, A.P., Torres, J.P.M., Lepoint, G., Michel, L.N., Das, K., Dorneles, P.R., 2021. Factors that influence trace element levels in blood and feathers of Pygoscelis penguins from South Shetland Islands,Antarctica. Environ. Pollut. 284, 117209 https://doi.org/10.1016/j.envpol.2021.117209.
Patterson, D.L., Hunter, S., 2000. Giant Petrel Macronectes spp. band recovery analysis from the International Giant Petrel Banding Project, 1988/89. Mar. Ornithol. 28, 69–74.
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. Environ. Pollut. 218, 196–206. https://doi.org/10.1016/j.envpol.2016.04.097.
R Core Team, 2019. R: A language and environment for statistical computing [Computer software]. R Foundation for Statistical Computing.
Roscales, J.L., González-Solís, J., Zango, L., Ryan, P.G., Jiménez, B., 2016. Latitudinal exposure to DDTs, HCB, PCBs, PBDEs and DP in giant petrels (Macronectes spp.) across the Southern Ocean. Environ. Res. 148, 285–294. https://doi.org/10.1016/j.envres.2016.04.005.
Roscales, J.L., Vicente, A., Ryan, P.G., González-Solís, J., Jiménez, B., 2019. Spatial and interspecies heterogeneity in concentrations of perfluoroalkyl substances (PFASs) in seabirds of the Southern Ocean. Environ. Sci. Technol. 53, 9855–9865. https://doi.org/10.1021/acs.est.9b02677.
Rückamp, M., Braun, M., Suckro, S., Blindow, N., 2011. Observed glacial changes on the King George Island ice cap, Antarctica, in the last decade. Glob. Planet. Chang. 79, 99–109. https://doi.org/10.1016/j.gloplacha.2011.06.009.
Santamans, A.C., Boluda, R., Picazo, A., Gil, C., Ramos-Miras, J., Tejedo, P., Pertierra, L. R., Benayas, J., Camacho, A., 2017. Soil features in rookeries of Antarctic penguins reveal sea to land biotransport of chemical pollutants. PLOS ONE 12, e0181901. https://doi.org/10.1371/journal.pone.0181901.
Santos, I.R., Silva-Filho, E.V., Schaefer, C., Maria Sella, S., Silva, C.A., Gomes, V., 2006. Baseline mercury and zinc concentrations in terrestrial and coastal organisms of Admiralty Bay, Antarctica. Environ. Pollut. 140, 304–311. https://doi.org/10.1016/j.envpol.2005.07.007.
Sick, H., Haffer, J., Alvarenga, H.F., Pacheco, J.F., Barruel, P., 1997. Ornitologia Brasileira. Nova Fronteira, Rio de Janeiro.
Souza, J.S., Kasper, D., da Cunha, L.S.T., Soares, T.A., de Lira Pessoa, A.R., de Carvalho, G.O., Costa, E.S., Niedzielski, P., Torres, J.P.M., 2020. Biological factors affecting total mercury and methylmercury levels in Antarctic penguins. Chemosphere 261, 127713. https://doi.org/10.1016/j.chemosphere.2020.127713.
Wang, W.-X., 2016. Bioaccumulation and biomonitoring. In: Marine Ecotoxicology. Elsevier, pp. 99–119.
Wing, S.R., Wing, L.C., O'Connell-Milne, S.A., Barr, D., Stokes, D., Genovese, S., Leichter, J.J., 2020. Penguins and seals transport limiting nutrients between offshore pelagic and coastal regions of Antarctica under changing sea ice. Ecosystems. https://doi.org/10.1007/s10021-020-00578-5.