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Trace elements in feathers and eggshells of brown booby *Sula leucogaster* in the Marine National Park of Currais Islands, Brazil

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Abstract Levels of trace elements were investigated in feathers of 51 adults and 47 eggshells of brown boobies *Sula leucogaster* from one bird colony in the Marine National Park of Currais Islands, Brazil, between December 2013 and October 2014. Average concentrations (μg g^{-1}, dry weight) in feathers and eggshells, respectively, were Al 50.62–9.58, As 0.35–2.37, Cd 0.05–0.03, Co 0.38–2.1, Cu 15.12–0.99, Fe 47.47–22.92, Mg 815.71–1116.92, Ni 0.29–11.85, and Zn 94.16–1.98. In both arrays, the average concentration of Mg was the highest among all the elements analyzed, while the lowest was recorded for Cd. As and Ni presented levels at which biological impacts might occur. Zn concentrations were higher than those considered normal in other organs. Levels of Al, Fe, Cu, Zn, and Cd were higher in feathers, whereas higher contents of Mg, Co, Ni, and As occurred in eggshells. The comparison between the elements in eggshells collected at different seasons showed no significant difference ($p > 0.05$) due, probably, to the lack of temporal variation on foraging behavior and/or on bioavailability of trace elements. Metals and arsenic in feathers and eggshells were mostly not correlated. Future studies on Paraná coast should focus on the speciation of the elements, especially As, Ni, and Zn, which proved to be a possible problem for the environment and biota. It is necessary to investigate both matrices, shell and internal contents of the eggs, in order to verify if the differences previously reported in other studies also occur in eggs of brown boobies in the Marine National Park of Currais Islands.

Keywords Seabirds · Contamination · Metals · Sulidae · Marine National Park of Currais Islands · Subtropical coastal systems

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Introduction

Due to their location in the trophic chain as top predators and their long-life spans, seabirds are susceptible to bioaccumulation of a wide range of pollutants by the air, water, and by the consumption of contaminated prey and are commonly used as marine and coastal pollution tracer (Burger and Gochfeld 2004). Once ingested, pollutants can be stored in several tissues, eliminated directly through excreta, eggs, and eggshells, deposited in uropygial glands and salt glands or even sequestered in feathers (Burger and Gochfeld 1985; Burger 1993;

Lam et al. 2005; Burger et al. 2009, Trefry et al. 2013). Samples of feathers and eggs are useful for measuring levels of metals in birds because they present several methodological advantages over other tissues, such as non-invasive, easily and quickly obtained matrices. This allows sampling time series data, less interference to the individuals during sampling, and possibility of systematic resampling (Burger 2013). The brown booby, *Sula leucogaster*, is the most common Sulidae species on the Brazilian coast. However, according to BirdLife International (2017), the population trend of *S. leucogaster* appears to be decreasing. On the coast of Paraná, Brazil, data obtained in 1995/1996 (Krul 2004) and 2012 (Dolci, unpublished. data) showed a marked decrease in the number of *S. leucogaster* nests, from 277 nests in 1995/1996 to only 98 in 2012, that may be associated with a contamination of water and/or fish by metals, although the cause of these declines is unknown. Widely distributed in all tropical and subtropical oceans, *S. leucogaster* nests in both remote oceanic islands and coastal regions (Nelson 1978). The Paranaguá Estuarine Complex (PEC), situated in the coast of Paraná, is one of the main areas used by the brown booby for feeding (Krul 2004), where some studies have found levels above the critical threshold established by environmental legislation, such as arsenic (As), copper (Cu), nickel (Ni) and zinc (Zn) in sediments (Sá et al. 2006; Choueri et al. 2009), As, Cu and Zn in oysters *Crassotrea rhizophorae* (Castello 2010) and As in catfish *Cathorops spixii* and *Genidens genidens* (Angeli et al. 2013). In addition, cadmium (Cd) and Cu are also reason for general concern because of their already known presence in the marine environment. However, the status of contamination by these elements in seabirds on the coast of Paraná has not yet been evaluated and studies on metals in biota normally do not include elements considered less potentially toxic such as aluminum (Al), cobalt (Co), iron (Fe), and magnesium (Mg). On Brazilian coast, Ferreira (2010) already showed elevated levels of metals in the liver and kidney of *S. leucogaster* but the use of feathers and eggshells of brown booby for analysis of trace elements is unprecedented.

Considering that levels of trace elements surpassed the critical threshold found in the biota and in the sediments of PEC and, since brown boobies use this area to feed, it is believed that there may be contamination also in top-chain animals, such as *S. leucogaster*. This study was drove by the necessity to assess the role of these potential contaminants on population decline of this specie. In this context, the main goals were to determine metal and arsenic levels in feathers and eggshells of *S. leucogaster* on southern Brazilian coast and compare them with other studies with seabirds; to evaluate if there are temporal variations on the levels of trace elements in brown booby eggs, which would reflect a variability on metal sources that would affect seasonally seabirds on the Paraná coast and; to examine if there are differences in trace element concentrations between feather and egg tissues, which would contribute to elucidate different exposition routes in top predators, as the brown booby.

Materials and methods

Study area

The Paranaguá Estuarine Complex (PEC) (25° 16′ and 25° 34′ S; 48° 17′ and 48° 42′ W) is located on the coast of the state of Paraná, Southern Brazil (Fig. 1). Despite its great ecological, economic, and social importance, represented by extensive areas of mangroves, fishing activities, aquaculture, and tourism, PEC undergoes influence of anthropic agents as result of industrial facilities, domestic effluent supply, and the presence of the largest port for grains export of the South America, where industrial products, fertilizers, minerals, and petroleum products are also present (Marone et al. 2000; Noernberg 2001; Kolm et al. 2002; Choueri et al. 2009; Liebzeit et al. 2011; Angeli et al. 2013). Moreover, dredging activities carried out periodically also contribute to the negative impacts on the region (Sá 2003). In addition, Paranaguá City, situated in the middle sector, has urbanized areas without basic sanitation and dumping ground without legal sanitary convention (Lautert et al. 2006). Areas with relatively lower environmental pressure are found in the Antonina Bay, where there is a local port and agricultural activities.

On the continental shelf of Paraná is located the Marine National Park of Currais Islands (25° 44′ S and 48° 22′ W), created in 2013, third of this category in Brazil (Fig. 1). It is formed by three islands that are approximately 6 nm from the shoreline of Paraná. The Marine National Park of Currais has great ecological relevance, since it shelters important colonies of *S. leucogaster*, frigatebirds *Fregata magnificens*, seagulls

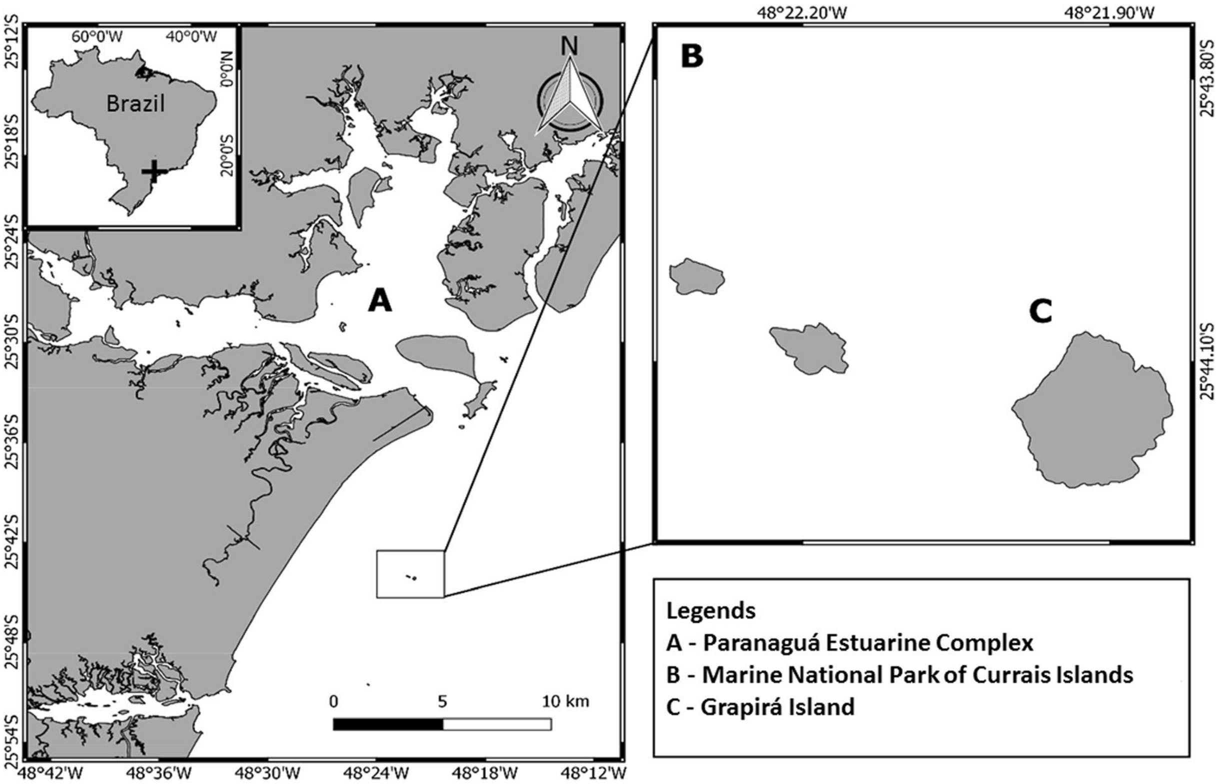

Fig. 1 Map of Paranaguá Estuarine Complex (PEC) and Marine National Park of Currais Islands on the coast of Paraná state. PEC (a), Marine National Park of Currais Islands (b) e Grapirá Island (c)

Larus dominicanus, South American terns *Sterna hirundinacea*, black-crowned night herons *Nycticorax nycticorax*, and great egrets *Ardea alba* actives throughout the year. Sampling was performed in short campaigns (2 to 3 days) on the largest of the islands, Grapirá, located in the eastern portion of the archipelago, where *S. leucogaster* can be found breeding throughout the year and all over the island. Samples were collected throughout the island, within the same bird colony and according to the nest distribution.

Sampling

Under appropriate state and federal legal permits, external rectrices of 51 adult individuals of brown boobies, with no separation by gender, and 47 samples of newly hatching eggshells were collected for analysis of trace elements. Eggshells were sampled in February ($n = 9$), May ($n = 14$), August ($n = 15$), and October ($n = 9$) 2014 and feather samples were collected in December 2013 ($n = 9$) and February ($n = 11$), May ($n = 19$) and October ($n = 12$) 2014. All the samples were properly identified, stored in acrylic vials previously decontaminated and frozen (− 20 °C) until further analysis in the laboratory.

All the reagents used in the analytical procedures were of high purity (Merck) and all materials used during the sampling, extraction, and chemical analysis were previously decontaminated through immersion on 2% neutral Extran solution for 24 h, followed by immersion on a 10% HNO_3 solution for at least 72 h and rinsed with ultrapure water (Milli-Q system, Millipore, USA).

Chemical analysis

The analysis of metals in feather samples was adapted from Dauwe et al. (2000) and Burger et al. (2009) and for eggshells, the methodology proposed by Abduljaleel et al. (2011) was followed. In laboratory, the feathers were washed alternately with ultrapure water (Milli-Q system, Millipore, USA) and acetone (P.A. 99.5%), for removal of external contaminations, and placed in metal-free acrylic vials. After drying in an oven (60 °C) for 24 h, feathers were cut into pieces of up to 2 mm and approximately 0.05 g of each sample were extracted through microwave-assisted acid digestion in a microwave system (Microwave Digestion System—Milestone) using HNO_3 (65%) and H_2O_2 (30%) in the ratio of 6:4. After digestion, samples were transferred to decontaminated centrifuge tubes and diluted to 50 ml with a 2% HNO_3 solution. Eggshell samples were abundantly washed with ultrapure water and dried in an oven (60 °C) for 24 h. After powdering on agate mortar, approximately 0.5 g of each sample was mineralized in a 1:1 mixture HNO_3 (65%) and H_2O_2 (30%) and transferred to decontaminated centrifuge tubes and diluted to 50 ml with a 2% HNO_3 solution. After cooling, extracts of feathers and eggshells were filtered via a Whatman·TM cellulose acetate filter and kept refrigerated (4 °C) until determination of the concentration of the elements.

The concentrations of Al, As, Cd, Co, Cu, Fe, Mg, Ni, and Zn in extracts of feathers and eggshells were determined by using inductively coupled plasma mass spectrometry (ICP-MS 7500cx, Agilent Technologies). To discriminate possible analytical spectral interferences, collision cell (He and H gas, ORS3 system, Agilent Tecnologies®) was used to determine the elements considered. A standard tuning solution containing 1.0 μg l^{-1} of ^{7}Li, ^{24}Mg, ^{59}Co, ^{89}Y, ^{140}Ce, and ^{205}Tl in 2.0% HNO_3 was used to adjust the reduction of oxides and the formation of doubly charged ions, optimizing the ICP-MS conditions.

A multielement internal standard (Internal Standard Mix—Bi, Ge, In, Li, Sc, Tb, and Y, Agilent Technologies) was used to correct possible fluctuations in the measurements of the signals from the elements analyzed. Calibration curves were constructed using standards multielement (ICP multi-element standard solution XXI for MS, CentiPUR® MERCK, Darmstadt-Germany). The accuracy of the quantified element concentrations was evaluated by measuring two certified reference materials: (NRCC—National Research Council of Canada), DORM-3 (Fish protein) and DOLT-4 (Dogfish liver). The detection limits (DL) were obtained from three times the standard deviation in seven replicates of method blanks and limits of quantification were calculated as 3.3 times DL. In at least 80% of the analyzed elements, the concentrations for the certified material were in agreement with the certified levels. For samples whose levels were below the limit of quantification, the arithmetic means between the limit of detection and the limit of quantification was calculated. The concentrations for the certified material, the percent recovery, and the limits of detection and quantification for each element are presented in Table 1.

Data analysis

We tested data for normality using the Shapiro-Wilk test (*W* test) and for homogeneity of variances using the Bartlett test (*K* test). When non-normality or heterocedasticity where found, Box-Cox transformation was applied. Mean differences of element concentrations in eggshells among seasons (autumn, summer, spring, and winter) were tested using one-way ANOVA. To compare the mean concentrations between metals and arsenic levels in feathers and eggshells, the non-parametric Mann-Whitney test was chosen because of the low replication. Spearman's rank correlation test was performed to evaluate relationships among the elements analyzed in each matrix.

Results

The mean concentrations of the elements analyzed in feathers and eggshells of *S. leucogaster* are shown in Table 2. The mean level of cadmium was the lowest among all elements analyzed in both matrices and the levels in feathers surpassed the limit of quantification in only 39% of samples (0.0095–0.29 μg g^{-1}) while in eggshells, it was above in 44% of the samples (0.0095–0.14 μg g^{-1}). The element Mg, in turn, presented the highest levels in feathers of brown boobies in comparison with the other elements analyzed in this work and showed also high variation (491.26–1395.64 μg g^{-1}). In eggshells, the levels were high (510.82–1393.13 μg g^{-1}). For the other elements, the levels found in feathers and eggshell matrices, respectively, were as follows: As (0.11–0.97 and 0.06–3.20 μg g^{-1}), Cu (3.25–108.34 and 0.24–2.31 μg g^{-1}), Zn (62.30–181.58 and 0.033–13.37 μg g^{-1}), Ni (0.01–1.13 and 8.17–17.96 μg g^{-1}), Al (11.35–147.92 and 2.27–26.22 μg g^{-1}), Co (0.04–2.56 and 1.26–2.63 μg g^{-1}), and Fe (0.075–188.64 and 12.53–42.56 μg g^{-1}).

The comparison between the levels of trace elements in eggshells collected at different seasons of the year

Table 1 Average recoveries and standard deviation (n = 3) of certified values for metals and arsenic (μg g^{-1}). Standard reference material (DORM-3 and DOLT-4), recovery (% recovery), method detection limit (MDL; μg g^{-1}), method quantification limit (MQL; μg g^{-1}) and coefficient of determination (r^2) for each analyzed element

Element	DORM-3	Present study (DORM-3)	% recovery	DOLT-4	Present study (DOLT-4)	% recovery	MDL	MQL	r^2
Al[a]	1700	1501.43 ± 20.13	88.32	200	58.98 ± 6.15	29.49	0.207	0.684	0.9999
As	6.88 ± 0.30	6.62 ± 0.18	99.93	9.66 ± 0.62	8.83 ± 0.13	91.44	0.025	0.083	0.9998
Cd	0.290 ± 0.020	0.25 ± 0.04	86.57	24.3 ± 0.8	22.57 ± 0.73	92.88	0.006	0.019	0.9997
Co[a]	–	–	–	0.25	0.17 ± 0.02	96.17	0.035	0.115	0.9997
Cu	15.5 ± 0.63	17.09 ± 4.31	110.25	31.2 ± 1.1	39.10 ± 2.80	125.33	0.156	0.514	0.9999
Fe	347 ± 20	309.13 ± 74.45	89.09	1833 ± 75	1703.72 ± 120.67	92.95	0.065	0.216	0.9999
Mg[a]	–	–	–	1500	1397.55 ± 81.81	93.17	0.094	0.31	0.9999
Ni	1.28 ± 0.24	1.24 ± 0.18	96.57	0.97 ± 0.11	0.62 ± 0.02	63.77	0.171	0.565	0.9998
Zn	51.3 ± 3.1	49.77 ± 1.86	97.02	116 ± 6.0	116.30 ± 0.59	100.26	0.02	0.067	0.9997

[a] Information value

through ANOVA revealed no significant difference (Table 3). Significant differences ($p < 0.05$) were detected when comparing the levels of metals and arsenic among the different matrices analyzed. Considering the arithmetic averages, the concentrations of Al, Fe, Cu, Zn, and Cd were higher in feathers while Mg, Co, Ni, and As were higher in eggshells. The correlations between the levels of trace elements in feathers and eggshells were significant ($p < 0.001$) only for four of the 36 possible correlations (Table 4). Al levels in feathers were positively correlated with Mg, whereas As was correlated negatively with Ni and positively with Cu. Cd, in contrast, showed only positive correlation with Co. For eggshells, positive significant correlations occurred between As and Ni; and Fe and Ni and negative correlations were found between the elements As and Cd, and Cd and Co.

Discussion

Levels of trace elements reported in feathers of seabirds in studies elsewhere and the comparison with the present study are shown in Table 5. Table 6 summarizes the levels of trace elements reported in bird eggs in studies elsewhere. Due to the scarce information available in the literature about the concentration of metals in seabird eggshells, the results were compared with data from other groups of birds. Additionally, most of the studies report levels of contaminants in the internal contents of eggs, not in their shells, given its importance due to nutritional value and its role in embryo development (Surai 2002).

Levels of As in feathers of *S. leucogaster* were higher than those recorded in feathers of red-footed booby *Sula*

Table 2 Concentrations (arithmetic mean ± standard deviation) of metals and arsenic (μg g^{-1}, dry weight) in feathers of adult individuals and eggshells of *Sula leucogaster* collected in the Marine National Park of the Currais Islands. The column in the right side reports the differences by Mann-Whitney

Element	Feathers (n = 51)	Eggshells (n = 47)	W statistic	(p)
Al	50.62 ± 31.27	9.58 ± 5.23	2339.5	< 0.001
As	0.35 ± 0.18	2.37 ± 1.01	357	< 0.001
Cd	0.05 ± 0.06	0.03 ± 0.03	318	0.004
Co	0.38 ± 0.52	2.10 ± 0.31	47	< 0.001
Cu	15.12 ± 15.70	0.99 ± 0.48	2397	< 0.001
Fe	47.47 ± 36.33	22.92 ± 8.77	1763	< 0.001
Mg	815.71 ± 199.36	1116.92 ± 153.33	253	< 0.001
Ni	0.29 ± 0.23	11.85 ± 2.92	0	< 0.001
Zn	94.16 ± 21.23	1.98 ± 3.06	2244	< 0.001

Table 3 ANOVA results of metals and arsenic concentrations in eggshells among seasons (summer, winter, autumn, and spring) of *Sula leucogaster* collected in the Marine National Park of the Currais Islands. The column in the right side reports the differences by Mann-Whitney

Element	*f* statistic	(*p*)
Al	0.656	NS
As	0.471	NS
Cd	0.367	NS
Co	0.207	NS
Cu	1.856	NS
Fe	1.064	NS
Mg	0.398	NS
Ni	0.113	NS
Zn	0.673	NS

NS not significant

sula and frigatebirds *F. magnificens* in the Midway Atoll, north of Pacific Ocean (Burger and Gochfeld 2000). Higher levels of As are reported in feathers of gulls *L. dominicanus* and *Leucophaeus pipixcan* in Chile (Sepúlveda and Gonzalez-Acuña 2014). The average level in eggshells was approximately twice higher than the concentrations recorded in seagulls *Larus glaucescens* in Alaska (Burger et al. 2009) and about five times higher than reported by Lam et al. (2005) on eggs of terns *Sterna anaethetus* in China. Levels of As in living organisms are generally < 1 μg g^{-1} (Eisler 1988) and are usually present in a harmless organic form (Woolson 1975). Therefore, the mean concentration of As in feathers in the present study (0.35 μg g^{-1}) probably reflects normal concentrations in seabirds and is below the levels at which biological impacts may occur (2–10 μg g^{-1}; Eisler 1988). In eggshells, in contrast, the mean level of As (2.37 μg g^{-1}) is within the range considered to be harmful.

Arsenic was reported by the Agency for Toxic Substances and Disease Registry (ATSDR 2007) as the most dangerous among 275 toxic substances. It occurs naturally in the environment in the form of sulfides and as iron, nickel, and cobalt sulfide complexes due to the natural weathering of rocks and soils. Arsenic is used in pigments, pesticides, herbicides, defoliants, wood preservatives, steel mills, coal-fired plants, and foundries (Eisler 1988). The high levels found in the eggshells suggest the ability of this element to be excrete in this matrix and probably reflects high concentrations of As in the blood of *S. leucogaster*. Angeli et al. (2013)

Table 4 Correlation of metal and arsenic levels in feathers and eggshells of *S. leucogaster* in the Marine National Park of the Currais Islands. They are given: rho (*p* value). *NS* not significant

	Al	As	Cd	Co	Cu	Fe	Mg	Ni	Zn
Feathers									
Al		NS	NS	NS	NS	0.39 (0.004)	0.62 (< 0.001)	NS	NS
As			NS	− 0.47 (0.01)	0.54 (< 0.001)	0.33 (0.01)	− 0.40 (0.003)	− 0.52 (0.0009)	NS
Cd				0.73 (0.0003)	NS	NS	NS	NS	NS
Co					NS	NS	NS	NS	NS
Cu						0.29 (0.03)	NS	− 0.33 (0.04)	NS
Fe							NS	NS	− 0.28 (0.04)
Mg								0.35 (0.03)	NS
Ni									NS
Zn									
Eggshells									
Al		NS	NS	NS	NS	NS	NS	NS	NS
As			− 0.76 (< 0.001)	NS	NS	0.31 (0.0317)	NS	0.55 (< 0.001)	NS
Cd				− 0.8 (< 0.001)	NS	NS	NS	NS	NS
Co					NS	NS	NS	NS	NS
Cu						− 0.37 (0.01)	0.35 (0.01)	− 0.37 (0.008)	NS
Fe							NS	0.56 (< 0.001)	0.37 (0.01)
Mg								− 0.39 (0.006)	NS
Ni									NS
Zn									

Table 5 Mean concentrations (μg g^{-1}) of metals and arsenic reported in feathers of seabirds elsewhere in the world. For studies reporting levels of metals and arsenic in more than one species of bird, the lower and upper average concentrations for each element are given. <DL: below to the method detection limit

Location	Specie	Al	As	Cd	Co	Cu	Fe	Mg	Ni	Zn	Reference
Chilsando Island (South Korea)	*Larus crassirostris*	10.4	–	0.14	–	4.16	92.1	–	–	46.5	Kim and Oh (2015)
Hara Biosphere Reserve (Iran)	*Phalacrocorax carbo*	–	–	0.027	–	9.51	–	–	–	159.7	Mirsanjari et al. (2014)
Talcahuano (Chile)	*Larus dominicanus Leucophaeus pipixcan*	–	0.64–0.75	0.03–0.15	–	4.20–19.5	–	–	–	–	Sepúlveda and Gonzalez-Acuña (2014)
Hara Biosphere Reserve (Ira)	*Larus heuglini*	–	–	1.16	0.5	4.58	171.85	–	–	45.66	Mansouri et al. (2012)
Patgonia (Argentina)	*Procellaria aequinoctialis*	–	–	<DL	–	5.89	72.56	–	–	75.98	Seco Pon et al. (2012)
National Park of Atlantic I slands (Spain)	*Phalacrocorax aristotelis* and *Larus michahellis*	–	–	–	–	1.5–10.0	–	–	–	104.2–206.5	Moreno et al. (2011)
Florianópolis (Brazil)	*Larus dominicanus*	–	–	0.072	4.48	13.3	–	–	5.92	68.97	Barbieri et al. (2010)
Yeongjong Island (South Korea)	Aves costeiras	–	–	0.38–1.13	–	4.08–10.4	–	–	–	67.9–103	Kim and Koo (2008)
Ilhas Shetland do Sul (Antarctica)	*Pygoscelis papua* and *P. antarctica*	26–46	< 0.6–4	< 0.15–0.43	0.19–0.25	16–19	42–56	981–1108	0.65–0.84	75–106	Metcheva et al. (2006)
Midway Atoll (Central Pacific)	*Sula sula* and *Fregata magnificens*	–	0.125–0.158	0.051–0.204	–	–	–	–	–	–	Burger and Gochfeld (2000)
Long Island (EUA)	*Rynchops niger*	–	–	0.031–0.098	–	25.44–29.42	–	–	–	–	(Burger and Gochfeld 1992)
Marine National Park of Currais Islands (Brazil)		50.62	0.35	0.05	0.38	15.12	47.47	815.71	0.29	94.16	This study

Table 6 Average concentrations (μg g^{-1}) of metals and arsenic reported in eggs of birds in studies elsewhere. For studies reporting levels of metals and arsenic in more than one species of bird, the ranges of the lower and upper medium concentrations are given. <DL: below to the method detection limit

Location	Specie	Matrix	Al	As	Cd	Co	Cu	Fe	Mg	Ni	Zn	Reference
Condrington (Antígua and Barbuda)	*Fregata magnificens*	Conteúdo	9.61	–	0.1	–	5.24	–	–	0.24	10.98	Trefry et al. (2013)
Livingston Island (Antarctica)	*Pygoscelis papua ellsworthii*	Casca	28.96	< 0.3	< 0.05	–	1.24	13.95	818	< 0.05	4.07	Metcheva et al. (2011)
Aleutian Islands (Alaska)	*Larus glaucescens*	Conteúdo	–	0.126	0.084	–	–	–	–	–	–	Burger et al. (2009)
Hong Kong (China)	*Sterna anaethetus*	Casca	–	0.39	0.002	0.39	1.23	–	–	–	2.35	Lam et al. (2005)
		Conteúdo		1.38	0.002	0.02	3.92				47.62	
Hong Kong (China)	*Egretta garzetta* and *Nycticorax nycticorax*	Casca	–	–	0.006–0.008	0.355–0.356	1.11–1.6	–	–	–	5.39–9.63	Lam et al. (2004)
		Conteúdo		<DL-0.22	<DL-0.001	0.02–0.03	6.28–6.58				39.87–51.38	
Flórida (EUA)	*Aphelocoma coerulescens*	Conteúdo	–	0.010–0.017	0.002–0.003	–	–	–	–	–	–	Burger et al. (2004)
New Jersey (EUA)	*Sterna hirundo*	Conteúdo	–	0.14–0.38	0.0001–0.017							(Burger and Gochfeld 2003)
New Jersey (EUA)	Charadriiformes	Conteúdo	–	0.1–0.529	0.002–0.005	–	–	–	–	–	–	Burger (2002)
Long Island (EUA)	*Sterna dougallii*	Conteúdo	–	–	0.021–0.189	–	–	–	–	–	–	Gochfeld and Burger (1998)
Marine National Park of Currais Islands (Brazil)	*Sula leucogaster*	Casca	9.58	2.37	0.03	2.1	0.99	22.92	1116.92	11.85	1.98	This study

identified levels of As above the limit allowed by the legislation in catfish in the Paranaguá Estuary Complex. Although they are not part of the specific diet of brown boobies (Krul 2004), catfish have demersal habits and can easily bioaccumulate contaminants in their tissues. Moreover, brown boobies frequently feed on demersal fish discarded by shrimp trawling in the coastal waters of Paraná (Krul 2004) and may, therefore, be ingesting elevated levels of As. Although the source of the high levels of As for birds in the Marine National Park of Currais Islands has not been determined, four potential sources could be considered (Sá et al. 2006): (i) strong natural enrichment of As in the region coming from rocks enriched with such element; (ii) the intense traffic of ships in the Port of Paranaguá, periodic activities of dredging and boats with antifouling paint; (iii) the grounding of an old area used by the Barão de Teffé Port in Antonina City as a coal deposit, after the closure of its activities; (iv) the phosphate fertilizer industry located west of the Port of Paranaguá with an auxiliary pier for landing of the raw material (apatite), where arsenic can substitute part of the phosphate group (Abouzeid 2008). However, the total concentration of an element is limited information, especially on potential damage to biota. The physical, chemical, and biological properties are dependent on their chemical form (Burguera and Burguera 1993), so the chemical speciation of As must be considered in future works to better evaluate its potential risk for brown boobies.

In feathers, the mean concentration of cadmium is lower or similar to several studies conducted on seabirds elsewhere (Burger and Gochfeld 1992; Burger and Gochfeld 2000; Kim and Koo 2008; Barbieri et al. 2010; Mansouri et al. 2012; Sepúlveda and Gonzalez-Acuña 2014; Kim and Oh 2015). Lower levels of Cd have been reported on the southern coast of Iran in feather of cormorant *Phalacrocorax carbo* (Mirsanjari et al. 2014). In eggshells, the mean concentration of Cd is lower than levels found in *F. magnificens* in Antigua and Barbuda (Trefry et al. 2013) and *L. glaucescens* in Alaska (Burger et al. 2009) and higher than those reported by Lam et al. (2005) in *S. anaethetus* eggs in China and by Burger (2002) in Charadriiformes eggs in the USA.

The average level of Cd found in feathers (0.05 $\mu g\ g^{-1}$) and eggshells (0.03 $\mu g\ g^{-1}$) of brown boobies is within the range reported in feathers of seabirds, which is generally less than 0.2 $\mu g\ g^{-1}$ (Burger 1993). Although levels in feather have not yet been determined from laboratory studies, Burger (1993) estimated that levels associated with adverse effects range from 0.1 $\mu g\ g^{-1}$ in petrels to 2 $\mu g\ g^{-1}$ in terns. Therefore, the levels of Cd found in eggshells and feathers of brown boobies in the Marine National Park of Currais Islands are below the values of negative effects for other seabirds. However, it is known that birds accumulate excess of Cd in two main organs, liver and kidney, and the kidney is considered the critical organ in Cd toxicity (Leach et al. 1979; Cain et al. 1983). In other tissues, Cd levels tend to be much lower except in cases where the bird has recently been exposed to high levels of Cd (Scheuhammer 1987). In addition, Cd in feathers are often poorly correlated with levels in internal tissues (Furness and Monaghan 1987) and Sell (1975) and White and Finley (1978) report that little Cd is transferred from the birds to the eggs, regardless of the levels consumed through the diet. Thus, low levels of Cd in eggs and feathers do not necessarily reflect a low intake of Cd by the birds and the mean level found in this study for both matrices may not represent the real concentration of this metal in the body. Chick feathers may be better indicators of dietary levels of Cd since the load of contaminants in young birds comes from food provided by parents or levels kidnapped in the eggs during their development (Burger and Gochfeld 2004). Added to that, in general, higher levels of Cd are found in birds that feed primarily on squid, such as albatrosses, compared to those whose diet is fish-based (Cherel and Klages 1998; Muirhead and Furness 1988). Since brown boobies feed primarily on fish (Krul 2004), the low levels of Cd in this study may be also partly related to the predominance of fish items in its diet, nevertheless, previous studies in sediments (Sá et al. 2006; Choueri et al. 2009), oysters and fish (Castello 2010; Angeli et al. 2013) suggest that Cd does not represent a problem for the biota in PEC.

The mean concentration of Copper is lower or similar to the levels found on the south coast of Brazil in feathers of seagulls *L. dominicanus* (Barbieri et al. 2010), *L. dominicanus* and *L. pipixcan* in Chile (Sepúlveda and Gonzalez-Acuña 2014), and *Rynchops niger* on the North American coast (Burger and Gochfeld 1992). Lower levels are found in feathers of cormorants *P. carbo* (Mirsanjari et al. 2014) in Iran, *Phalacrocorax aristotelis* and seagulls *Larus michahellis* on the coast of Spain (Moreno et al. 2011), and Charadriiformes on the coast of South Korea (Kim and Koo 2008). Levels of Cu in eggshells were lower than those recorded in eggs of *F. magnificens* in Antigua and Barbuda (Trefry et al. 2013) and *S. anaethetus* in China (Lam et al. 2005).

There are few data on Cu toxicity on wild birds; however, birds inhabiting contaminated sites present concentrations from 9 to 28 μg g^{-1} Cu in their eggs, muscles, and stomach contents, from 43 to 53 μg g^{-1} in kidneys, feces, and feathers and approximately 367 μg g^{-1} in livers (Eisler 1998a). Both levels in eggshells (0.99 μg g^{-1}) and feathers (15.12 μg g^{-1}) of brown boobies in the present study are below those reported in birds from contaminated sites. However, Lam et al. (2005) revealed in their study that the concentrations of metals present in the internal contents of the egg and that are effectively transferred to the chick may be higher than that registered in the shell and this should, therefore, be an alert. Additionally, one sample of feather exhibited 108.34 μg g^{-1} of Cu, suggesting that a special attention should be given for this metal in a future monitoring.

Levels of zinc are similar to those reported in feathers of Charadriiform birds in South Korea (Kim and Koo 2008). For the southern coast of Brazil, the mean concentration recorded in feathers of *L. dominicanus* by Barbieri et al. (2010) is lower, as well as the levels reported by Kim and Oh (2015) in feathers of *Larus crassirostris* in South Korea and by Mansouri et al. (2012) in feathers of *Larus heuglini* in Iran. Higher levels were found in a few studies such as on the coast of Spain using feathers of *P. aristotelis* and *L. michahellis* (Moreno et al. 2011) and on the coast of Iran in feathers of *P. carbo* (Mirsanjari et al. 2014). In eggshells, the levels of Zn are lower than those recorded in the internal contents of *F. magnificens* eggs (Trefry et al. 2013) and similar to those reported by Lam et al. (2005) on eggshells of *S. anaethetus* in China. However, the same study points out that the Zn levels in the internal content of eggs may be higher than in the shell, which explains the difference between the levels in eggs of brown boobies and frigates and draws attention to possible transfers of higher levels of Zn to the chicken than those recorded in this work.

In seabirds, Zn concentrations are usually between 12 μg g^{-1} in eggs and 88 μg g^{-1} in the liver. Zn poisoning usually occurs in birds whose levels are higher than 2.1 g/kg in the kidneys or liver (Eisler 1993). Most studies in laboratory indicate concentrations related only to food but do not depict the critical values in tissues making it difficult to compare data. Despite the levels of Zn in this study are far below the levels associated with poisoning, levels found in feathers (94.16 μg g^{-1}) are higher than those considered normal in eggs and liver. Nevertheless, Zn, as well as Cu, is an essential micronutrient homeostatically regulated at optimal levels by physiological mechanisms in most organisms so its incorporation by biota is independent of concentration in the environment (Bowen 1979; ATSDR 2005b; Scherer et al. 2015).

The mean concentration of Nickel in samples of brown booby feathers is lower than the levels previously reported on the coast of Santa Catarina in feathers of *L. dominicanus* (Barbieri et al. 2010). However, due to temporal and spatial differences in the abundance and availability of prey, seagulls *L. dominicanus* frequently alter their natural diet for anthropogenic items from dumps (Yoda et al. 2012), which may lead to the accumulation of contaminants in their tissues. For eggshells, the mean concentration of Ni (8.18–17.96 μg g^{-1}) in this work is almost 50 times higher than that recorded by Trefry et al. (2013) in frigatebirds *F. magnificens* in the Condrington National Park, the largest and better preserved wetland complex in Antigua and Barbuda (Environment Division Antigua and Barbuda 2009). As the samples in the present study were also collected in a well-preserved area and protected by legislation, this discrepancy may have occurred due to differences in physiological and biological processes of the species, such as eating habits, growth, and reproduction (Kim and Koo 2008). However, the available data on this metal in eggs of birds are insufficient for a more comprehensive evaluation.

Ni concentrations normally range from 0.1 to 2.0 μg g^{-1} in various bird organs, occasionally reaching 5 μg g^{-1} (Eisler 1981; Outridge and Scheuhammer 1993). In contaminated regions, the mean levels of Ni reported in ducks *Anas platyrhynchos*, terns *Sterna hirundo*, and eggshells of tree swallow *Tachycineta bicolor* is between 31 and 36 μg g^{-1} (Eisler 1998a, b). Although the maximum acceptable concentrations of Ni in eggs and feathers of birds for prevention of harmful effects on growth and survival are not presented in the literature, levels exceeding 10 μg g^{-1} in the kidneys and 3 μg g^{-1} in the livers are associated with adverse effects by Eisler (1998b). Thus, the concentrations in eggshells in the present study (11.85 μg g^{-1}) are in excess of those found in non-polluted environments, also within the levels at which probable negative effects are expected and close to those recorded in ducks (0.7–12.5 μg g^{-1}), which may have already been accumulated (Eisler 1998b). Ni is a micronutrient essential for the healthy growth of most vertebrates but may have carcinogenic effects when ingested at high concentrations (Eisler 1998b). Naturally abundant in the earth's crust, its main anthropogenic source for aquatic environments is mining, foundry activities, refinement, Ni alloy processing, burning of fossil fuels, waste incineration, and its use as a catalyst in industrial activities (ATSDR 2005a). Therefore, special attention should be given to Ni.

Although there is considerable attention devoted to As, Cd, Cu, Ni, and Zn in marine environments, there are relatively few studies on Al, Co, Fe, and Mg in feathers of seabirds, and data on the contamination by Al, Co, Cu, Fe, Mg, Ni, and Zn in seabird eggs are even more scarce, making difficulty its interpretation. More data are needed for a better assessment on contamination at higher trophic organisms, as brown bobby.

Levels of Al in feathers of *S. leucogaster* were higher than those reported by Kim and Oh (2015) in feathers of *L. crassirostris* in South Korea. For the eggshells, the levels of Al are similar to the levels reported in eggs of *F. magnificens* in Antigua and Barbuda. Absorption of Al salts ingested through the feed is very poor and the small amount that is absorbed is almost completely removed from the body through the urine, resulting in low or no retention of Al under normal kidney conditions (Scheuhammer 1987). Its chronic toxicity is mainly due to its effects on decreased egg production, testicular and nephrological damage, and altered behavioral responses and growth rates (Furness 1996). Al concentrations above 10 μg g^{-1} (dry weight) in bone are indicative of elevated exposure to Al or decreased ability to excrete Al (Scheuhammer 1987). However, for feather and egg, the levels have not yet been established.

Co concentrations in feathers of brown boobies are high compared to that reported by Mansouri et al. (2012) on the coast of Iran in feathers of seagulls *L. heuglini* and *L. dominicanus* on the south coast of Brazil (Barbieri et al. 2010). The mean concentration of Co in eggshells is higher than levels reported for *S. anaethetus* eggshells in Hong Kong, China (Lam et al. 2005). In feathers, the mean concentration of Fe is lower than the concentrations in *L. crassirostris* in South Korea (Kim and Oh 2015) and *L. heuglini* in Iran (Mansouri et al. 2012) while the average concentration in eggs is higher than the levels reported in eggshells of *Pygoscelis papua ellsworthii* penguins (Metcheva et al. 2011). The element Mg, in turn, despite the highest levels in feathers in comparison with the other elements analyzed in this work, showed a mean concentration lower than the levels previously reported in penguins *Pygoscelis papua* and *P. antarctica* feathers on Livingston Island, Antarctica (Metcheva et al. 2006). In eggshells, the levels were high compared to those recorded in eggshells of *P. papua ellsworthii* (Metcheva et al. 2011).

In summary, As and Ni presented worrying levels at which biological impacts may occur. Zn was above levels considered normal in other organs. Cd and Cu showed normal levels. There are few laboratory studies for other metals in seabirds, making it difficult to interpret the significance of the levels found in this study. This lack of data stresses the importance of further studies, both for analysis of the effects of particular doses and for determining the levels of contaminants in feathers, eggshells, and other tissues.

Comparison of the levels of trace elements in eggshells among seasons

A set of data on contaminant levels that extends over a year are useful in determining whether the sources of these compounds are intermittent or punctual. However, the comparison of the levels of metals and arsenic in eggshells collected at different seasons of the year through ANOVA revealed no significant difference ($p > 0.05$) due, probably, to the lack of temporal variation on foraging behavior and/or on bioavailability of trace elements that affects seasonally seabirds on the Paraná coast.

Differences between feather and eggshell tissues

Birds can excrete contaminants directly or sequester them in their feathers. Additionally, females may excrete the excess in eggs and their eggshells (Burger 1993; Burger et al. 2009, Tefry et al. 2013, Sepúlveda and Gonzalez-Acuña 2014). The differences between the different matrices possibly reflects the ability of some of these elements, such as Al, Fe, Cu, Zn, and Cd to be better sequestered in feathers than eggs. Trace elements in feathers are derived from the bloodstream during the period in which the feathers are formed. During this period, essential elements and non-essential toxic elements can be supplied to the growing feather and those with affinity for the sulfhydryl groups of the keratin protein are likely to be sequestered in the feathers (Burger 1996). Although other studies considered external contamination as a possible explanation for higher levels of certain feathered elements (Dauwe et al. 2003), the cleaning protocol used in the present study minimizes this possibility.

Correlations between trace elements

For individuals of the *S. leucogaster* from the Marine National Park of the Currais Islands, metals and arsenic were, mostly, uncorrelated. Our data do not permit to explain the correlations found for trace elements in feathers and eggshells of brown booby eggs. However, it is important to examine them carefully, since the presence of one element may potentiate or reduce the effect of the other. In addition, the data allow the construction of a reference baseline for the monitoring of trace elements in the investigated region, as well as for comparison intra- and interspecific of contamination on marine birds.

Conclusions

Mean concentrations of most elements were similar to levels reported elsewhere but As and Ni presented levels at which biological impacts may occur. Zn levels were above those considered normal in other organs. Insufficient data on Al, Co, Fe, and Mg highlights the need for further studies not only to analyze the effects of particular doses, but also to examine levels in feathers, eggs, and other tissues thus allowing conversion among matrices.

The average concentrations of Al, Fe, Cu, Zn, and Cd were higher in feathers while the highest levels of Mg, Co, Ni, and As occurred in eggshells. The comparison of the levels of trace elements in eggshells collected at different seasons did not reveal a significant difference, suggesting no temporal variation on foraging behavior and/or on the bioavailability of these elements. Also, metals and arsenic in feathers and eggshells were generally uncorrelated.

Future studies on Paraná coast should focus on the speciation of the elements, especially As and Ni, which is a potential problem for the environment and biota due to the high levels in eggshells from brown boobies, surpassing the critical threshold values associated with harmful effects. Although such levels could have contributed, at least partially, to the populations decline, the role of other pollutants, such as POPs, should be investigated. In addition, more studies are needed to investigate both matrices, shell and internal contents of the eggs, in order to verify if the differences previously reported in other studies in the levels of trace elements among different matrices also occur in eggs of brown boobies in the Marine National Park of the Currais Islands.

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