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Highlights

► We studied accumulation and magnification of trace elements in Antarctic penguin chicks. ► We evaluated their bioavailability in rookeries during the breeding season. ► Common sources and elimination routes could exist for several elements. ► Levels of some elements were similar to those found in seabirds from other regions.





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Monitoring trace elements in Antarctic penguin chicks from South Shetland Islands, Antarctica

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ABSTRACT

The concentration of human activities in the near-shore ecosystems from the northern Antarctic Peninsula area can cause an increasing bioavailability of pollutants for the vulnerable Antarctic biota. Penguin chicks can reflect this potential impact in the rookeries during the breeding season. They also can reflect biomagnification phenomena since they are on the top of the Antarctic food chain. The concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb were measured by ICP-MS in samples of liver, kidney, muscle, bone, feather and stomach content of gentoo, chinstrap and Adélie penguin chicks ($n = 15$ individuals) collected opportunistically in the Islands of King George and Deception (South Shetland Islands, Antarctica). The detected levels of some trace elements were not as low as it could be expected in the isolated Antarctic region. Penguin chicks can be useful indicators of trace elements abundance in the study areas. **Capsule:** Carcasses of Antarctic penguin chicks were used to evaluate the bioavailability of trace elements in the Islands of King George and Deception.

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1. Introduction

In the last years there has been a rising interest in the use of test organisms for pollution monitoring studies (e.g. Burger et al., 2008; Butt et al., 2010; Mochizuki et al., 2008; Yin et al., 2008). Specifically in marine coastal environments, the use of marine birds to monitor pollutants offers some advantages over the analysis of other biotic or abiotic matrices (Smichowski et al., 2006). These organisms occupy high positions in food chains, accumulate metals and other toxic elements in their tissues at concentrations several orders of magnitude above the environmental levels, and they only accumulate the biologically available forms (Tessier and Turner, 1995).

Pygoscelid penguins present populations distributed in Antarctic lands and they can be useful indicators of regional pollution, where information on trace elements concentrations is still scarce and fragmentary (Smichowski et al., 2006). Particularly the study of trace elements levels in penguin chicks makes it possible to assess their bioavailability in a specific place (the penguin rookery) during a specific time (the breeding season) in contrast with adult specimens that can reflect chronic exposures.

Although Antarctica is usually perceived as a symbol of the last great wilderness untouched by human disturbance, in the last years some researchers have suggested that the Antarctic

environment is not escaping the impact of local and global anthropogenic pollution (e.g. Barbosa et al., 2012; Bargagli, 2008; Jerez et al., 2011, 2012; Sun and Xie, 2001; UNEP Chemicals, 2002). In this way, the northern part of the Antarctic Peninsula and its associated islands are especially vulnerable due to their proximity to South America and the increasing local human pressure (mainly related to tourism and research activities; Tin et al., 2009).

In this area is located King George Island (62°15'S 58°37'W, South Shetland Islands), where human activities date since the early 19th century (Kennicutt, 2009). Nowadays this Island has the greatest concentration of multinational research in Antarctica (nine permanent stations and an airstrip exist) and it is a favorite destination for tourist cruises (IAATO, 2011; Kennicutt, 2009). This high human presence and its associated activities (use of fuels, waste disposal, vehicle transportation, etc.) cause adverse effects on the local environment (e.g. Bicego et al., 2009; Choi et al., 2008; Harris, 1991).

Deception Island is also located in this area (62°55'S 60°37'W, South Shetland Islands). It is a popular tourist location in Antarctica too (11800 visitors during 2010–2011 season according to IAATO, 2011) and two research stations are currently active. Deception Island is a horseshoe-shaped volcano and its caldera is a unique natural harbor in the region (Deheyn et al., 2005). For this reason, during several decades an important whaling activity was carried out there (a whaling station was working until 1967; Baker et al., 1969) and a heavy traffic of vessels still exists to this day.

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All these anthropogenic activities could have a significant effect on the accumulation of trace elements, including heavy metals, in the local biota. The aim of this study is to investigate the presence of trace elements in the tissues and stomach contents of chicks of gentoo penguin (*Pygoscelis papua*) and Adélie penguin (*P. adeliae*) from King George Island and chinstrap penguin (*P. antarctica*) from Deception Island, in order to increase the information in this issue and to evaluate the potential impact of human pressure in the area. Our goal is also to identify target organs for trace elements accumulation in these organisms as well as signs of biomagnification and inter-specific differences.

2. Materials and methods

The penguin carcasses (15 penguin chicks between 4 and 8 weeks old, see Table 1) were opportunistically collected during the 2008–2009 austral summer season in the Islands of King George and Deception (South Shetland Islands, Antarctica, see Fig. 1). The samples of liver ($n = 15$), kidney ($n = 15$), muscle ($n = 15$), bone ($n = 11$), feather ($n = 15$) and stomach content (composed mainly of krill, $n = 15$) were taken by necropsies of the penguin carcasses and frozen individually in polyethylene bags.

The analytical method used in this study was the one described by Jerez et al. (2011) with minor modifications. Before analysis, the penguin tissues were rinsed and all the samples were homogenized and dried at 75–80 °C till constant weight. Between 0.0816 and 0.4314 g of the material, according to availability, were submitted to microwave digestion with HNO₃ (65%), H₂O₂ (30%) and H₂O. The concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS Thermo-Optek Serio X7). All of the reagents used were Suprapur (Merck) and the water was double distilled and deionized (Milli-Q system, Millipore, USA). The analytical precision was verified by using blanks every five samples, initial calibration standards and certified reference materials (DORM-2 and DOLT-2). The detection limit value of each element, the reference material values and the percentages of recovery obtained are shown in Table 2.

According to Smith et al. (2007), the values below the instrumental detection limits were predicted from expected normal scores when more than 50% of all the samples showed detectable levels within each data set.

Data were analyzed by using the statistical software SPSS version 15.0. Differences in trace elements concentrations in the penguin internal tissues, feathers and stomach contents, and inter-specific differences were analyzed by using one-way ANOVAs (with Bonferroni post hoc tests) and Student's *t*-tests, although

Table 1
Studied specimens.

Specie	Location	Weight (kg)	Samples
<i>P. papua</i>	King George Island	1.50	L, K, M, B, F, SC
<i>P. papua</i>	King George Island	0.40	L, K, M, F, SC
<i>P. papua</i>	King George Island	NA	L, K, M, F, SC
<i>P. papua</i>	King George Island	NA	L, K, M, F, SC
<i>P. papua</i>	King George Island	NA	L, K, M, F, SC
<i>P. adeliae</i>	King George Island	0.62	L, K, M, B, F, SC
<i>P. adeliae</i>	King George Island	0.70	L, K, M, B, F, SC
<i>P. adeliae</i>	King George Island	0.77	L, K, M, B, F, SC
<i>P. adeliae</i>	King George Island	1.02	L, K, M, B, F, SC
<i>P. adeliae</i>	King George Island	2.69	L, K, M, B, F, SC
<i>P. antarctica</i>	Deception Island	2.65	L, K, M, B, F, SC
<i>P. antarctica</i>	Deception Island	2.15	L, K, M, B, F, SC
<i>P. antarctica</i>	Deception Island	NA	L, K, M, B, F, SC
<i>P. antarctica</i>	Deception Island	1.85	L, K, M, B, F, SC
<i>P. antarctica</i>	Deception Island	2.00	L, K, M, B, F, SC

L: liver; K: kidney; M: muscle; B: bone; F: feather; SC: stomach content; NA: not available.

non-parametric tests (Kruskal–Wallis and Mann–Whitney U tests) were used when the assumptions of normality and homocedasticity were not met. Post-hoc tests were carried out for Kruskal–Wallis analyses (least significant difference between mean ranks). Spearman rank correlation coefficients were calculated between pairs of elements. A *p* value less than 0.05 was considered to indicate statistical significance. Trace elements levels are presented as mean ± standard deviation in $\mu\text{g g}^{-1}$ dry weight (Table 3).

3. Results and discussion

The highest levels of Cd in this study were detected in the hepatic and renal tissues ($H_{4,66} = 46.59$, $p = 0.000$, post hoc test $p < 0.05$) which is a normal pattern of Cd accumulation in seabird chicks (e.g. Smichowski et al., 2006; Wenzel and Gabrielsen, 1995). We observed a ratio liver/kidney for Cd concentrations lower than 1 (ratio = 0.26) that showed a higher Cd affinity for renal tissue. Despite the short life of the studied specimens, this low ratio usually indicates a long exposure to Cd (chronic or sub-chronic exposure) that could have begun during egg development by maternal transfer of little Cd inputs as occurs in other seabirds (Agusa et al., 2005) and other oviparous organisms (Guirlet et al., 2008; Nagle et al., 2001). Our results are similar to those previously described by Smichowski et al. (2006) in soft tissues of chick penguins (*P. adeliae*) from King George Island. However, we found strongly lower Cd levels than those measured in renal tissues of adult penguins and other adult seabirds from Antarctic (Honda et al., 1986; Jerez et al., 2012; Nygard et al., 2001; Szefer et al., 1993), higher than $300 \mu\text{g g}^{-1}$ d.w. These great differences among chicks and adult specimens point out that there exists an accumulation of Cd during the Antarctic penguins life cycle.

Despite their short life, the feathers of some penguin chicks showed Cd levels (maximum level: $0.23 \mu\text{g g}^{-1}$ d.w.) similar to those considered as toxic for other seabirds ($0.10\text{--}2.00 \mu\text{g g}^{-1}$ d.w.; Burger and Gochfeld, 2000) and indicated a high exposure to this toxic metal during the period of feather growth. These results seem to be reflecting the well-known high natural environmental bioavailability of Cd in the Antarctic coastal ecosystems (e.g. Bargagli et al., 1996). In comparison to other studies that recently analyzed Cd levels in chicks or young specimens of seabirds from other regions of the world such as the Arctic (Burger et al., 2008; Hegseth et al., 2011a; Malinga et al., 2010) or the southwest Atlantic Ocean (Barbieri et al., 2010), we did not observed a clear pattern. We found similar Cd levels or even higher in the feathers ($0.02\text{--}0.03 \mu\text{g g}^{-1}$ d.w.; Barbieri et al., 2010; Burger et al., 2008) and similar or lower in the soft tissues ($0.21\text{--}0.53$, 0.90 and $0.41 \mu\text{g g}^{-1}$ d.w. in the liver, kidney and muscle, respectively; Hegseth et al., 2011a; Malinga et al., 2010).

We found the highest Cu levels in the liver ($F_{4,66} = 27.92$, $p = 0.000$, post hoc test $p = 0.000$) in accordance to previous studies in penguin chicks and other Antarctic seabirds (e.g. Schneider et al., 1985; Smichowski et al., 2006). In comparison to other seabird chicks from other regions of the world, we found similar levels in the feathers of chick penguins from King George Island to those detected in the feathers of seabird chicks from the Brazilian coasts ($13.76 \mu\text{g g}^{-1}$ d.w.; Barbieri et al., 2010) and even higher in the feathers of chick penguins from Deception Island (see Table 3). We also found similar Cu levels in the kidney and muscle of chick penguins to those detected in chicks of Arctic seabirds (12.80 and $4.30 \mu\text{g g}^{-1}$ d.w. in the kidney and muscle, respectively; Malinga et al., 2010) but we found Cu levels in the liver one order of magnitude higher ($11.50 \mu\text{g g}^{-1}$ d.w.; Malinga et al., 2010). In this way, Nygard et al. (2001) suggested that Antarctic seabirds usually present high Cu levels in the liver because of their main prey, Antarctic krill, naturally contains high amounts of this metal.



Fig. 1. Sampling sites.

Table 2

Detection limit values (ng g^{-1}), reference material values ($\mu\text{g g}^{-1}$) and percentages of recovery obtained.

Element	Detection limits	DORM-2/percentage of recovery	DOLT-2/percentage of recovery
Al	3.88	$10.90 \pm 1.70/80.20$	$25.20 \pm 2.40/97.43$
As	0.20	$18.00 \pm 1.10/93.44$	$16.60 \pm 1.10/95.39$
Cd	0.21	$0.043 \pm 0.008/93.02$	$20.80 \pm 0.50/97.34$
Cr	0.20	$34.70 \pm 5.50/85.63$	$0.37 \pm 0.08/90.81$
Cu	0.80	$2.34 \pm 0.16/94.36$	$25.80 \pm 1.10/102.13$
Fe	1.70	$142.00 \pm 10.00/97.84$	$1103.00 \pm 47.00/89.97$
Pb	0.80	$0.065 \pm 0.007/110.7$	$0.22 \pm 0.02/89.15$
Mn	0.40	$3.66 \pm 0.34/103.93$	$6.88 \pm 0.56/86.44$
Ni	0.40	$4.64 \pm 0.26/84.87$	$2.14 \pm 0.28/107.00$
Se	0.70	$19.40 \pm 3.10/93.36$	$0.20 \pm 0.02/94.54$
Zn	2.70	$1.40 \pm 0.09/85.414$	$6.06 \pm 0.49/94.89$

192 However it is important to consider the possibility that these high
 193 Cu levels in the liver of penguin chicks could be influenced by
 194 anthropogenic sources of pollution, since it was proved that human
 195 activities can contribute to increase Cu concentrations in coastal
 196 marine birds (Eiser, 1981).

197 The highest levels of Mn were found in the liver, kidney and
 198 bone of penguin chicks ($H_{4,66} = 48.30$, $p = 0.000$, post hoc test
 199 $p < 0.05$) in accordance with previous studies (Honda et al., 1986;
 200 Jerez et al., 2012; Smichowski et al., 2006). We found Mn levels
 201 in the soft tissues similar to those detected by Smichowski et al.
 202 (2006) in penguin chicks from King George Island (10.00, 9.40

and $1.50 \mu\text{g g}^{-1}$ d.w. in the liver, kidney and muscle, respectively).
 On the contrary, we found levels of Mn slightly higher than those
 detected two decades ago by Honda et al. (1986) in adult Antarctic
 penguins from Rumpa Island (1.48, 1.43, 1.51, 1.51 and 2.22 times
 higher in the liver, kidney, muscle, bone and feather, respectively)
 and by Szefer et al. (1993) in adult Antarctic penguins from the
 Antarctic Peninsula area (1.19–1.77 and 5.54–1.49 times higher
 in the liver and muscle, respectively). Although these comparisons
 must be cautiously considered due to data are still scarce and come
 from different Antarctic areas, an increase in the environmental
 Mn levels can be occurring in Antarctica. Similar results were

Table 3
Concentrations of trace elements (means \pm standard deviation in $\mu\text{g g}^{-1}$ dry weight; n : number of non-detectable levels) in chick penguins from Antarctica and inter-specific differences.

Tissues	Specie (Location)	Al	n	Cr	n	Mn	n	Fe	n	Ni	n	Cu	n
Liver	<i>P. papua</i> (King George I.)	2.12 \pm 2.05	0	0.18 \pm 0.08	0	10.51 \pm 3.74	0	854.55 \pm 136.61	0	0.01 \pm 0.01	0	142.40 \pm 63.85	0
	<i>P. adeliae</i> (King George I.)	6.81 \pm 11.91	0	0.12 \pm 0.06 ^a	0	12.01 \pm 5.80	0	1364.01 \pm 351.09	0	0.01 \pm 0.01 ^a	4	92.06 \pm 74.53	0
	<i>P. antarctica</i> (Deception I.)	15.52 \pm 15.55	0	1.11 \pm 0.95 ^b	0	11.42 \pm 3.24	0	2075.44 \pm 1745.28	0	0.07 \pm 0.07 ^b	0	95.10 \pm 48.67	0
	K–W Chi Square values (p)	NS		$H_{2,12} = 7.22$ (0.03)		NS		NS		$H_{2,12} = 7.76$ (0.02)		NS	
Kidney	<i>P. papua</i> (King George I.)	6.91 \pm 3.95	0	0.21 \pm 0.14	0	7.54 \pm 3.47	0	302.35 \pm 103.68	0	0.06 \pm 0.05	0	14.26 \pm 4.33	0
	<i>P. adeliae</i> (King George I.)	4.09 \pm 7.05	0	0.21 \pm 0.13 ^a	0	11.18 \pm 6.12	0	327.03 \pm 112.89	0	0.01 \pm 0.01 ^a	0	11.85 \pm 3.69	0
	<i>P. antarctica</i> (Deception I.)	10.93 \pm 10.57	0	0.75 \pm 0.54 ^b	0	10.19 \pm 2.63	0	397.49 \pm 82.35	0	0.08 \pm 0.06 ^b	0	13.64 \pm 2.28	0
	K–W Chi Square values (p)	NS		$H_{2,12} = 7.76$ (0.02)		NS		NS		$H_{2,12} = 6.96$ (0.03)		NS	
Muscle	<i>P. papua</i> (King George I.)	43.71 \pm 21.93	0	0.94 \pm 0.56	0	1.46 \pm 0.43	0	180.07 \pm 81.65	0	0.04 \pm 0.01 ^a	0	4.43 \pm 1.46	0
	<i>P. adeliae</i> (King George I.)	6.14 \pm 6.72 ^a	0	0.46 \pm 0.23	0	1.13 \pm 0.40	0	154.97 \pm 66.71	0	0.04 \pm 0.03 ^a	0	5.52 \pm 1.97	0
	<i>P. antarctica</i> (Deception I.)	114.88 \pm 125.59 ^b	0	1.49 \pm 0.55	0	2.55 \pm 1.53	0	328.59 \pm 102.73	0	1.83 \pm 2.67 ^b	0	6.82 \pm 1.20	0
	K–W Chi Square values (p)	$H_{2,12} = 9.98$ (0.01)		NS		NS		NS		$H_{2,12} = 9.39$ (0.01)		NS	
Bone	<i>P. papua</i> (King George I.)	69.95	0	0.57	0	11.01	0	154.13	0	3.37	0	0.79	0
	<i>P. adeliae</i> (King George I.)	11.89 \pm 3.69	0	0.14 \pm 0.08	0	8.31 \pm 3.11	0	78.67 \pm 33.16	0	1.02 \pm 0.37	0	0.96 \pm 0.53	0
	<i>P. antarctica</i> (Deception I.)	7.38 \pm 2.93	0	0.20 \pm 0.12	0	12.50 \pm 2.13	0	117.49 \pm 40.10	0	3.82 \pm 2.52	0	0.71 \pm 0.36	0
	K–W Chi Square values (p)	NS		NS		NS		NS		NS		NS	
Feather	<i>P. papua</i> (King George I.)	68.55 \pm 76.39	0	0.13 \pm 0.06 ^a	0	0.95 \pm 0.69	0	42.85 \pm 37.05	0	0.01 \pm 0.01 ^a	3	6.87 \pm 1.54 ^a	0
	<i>P. adeliae</i> (King George I.)	64.30 \pm 61.75	0	0.18 \pm 0.12	0	2.01 \pm 0.52	0	79.80 \pm 62.22	0	0.05 \pm 0.03	0	13.32 \pm 8.22	0
	<i>P. antarctica</i> (Deception I.)	142.00 \pm 206.33	0	0.68 \pm 0.49 ^b	0	2.25 \pm 3.17	0	173.86 \pm 173.09	0	0.13 \pm 0.10 ^b	0	18.57 \pm 2.78 ^b	0
	K–W Chi Square and F-ANOVA values (p)	NS		$H_{2,12} = 8.34$ (0.02)		NS		NS		$H_{2,12} = 10.21$ (0.000)		$F_{2,12} = 6.63$ (0.01)	
Stomach cont.	<i>P. papua</i> (King George I.)	2010.15 \pm 3231.82	0	1.15 \pm 1.27	0	36.89 \pm 66.39	0	2595.45 \pm 5015.93	0	0.50 \pm 0.56	0	58.69 \pm 28.48	0
	<i>P. adeliae</i> (King George I.)	282.01 \pm 235.63	0	1.06 \pm 0.77	0	10.57 \pm 8.76	0	277.18 \pm 135.74	0	0.41 \pm 0.41	0	57.81 \pm 35.82	0
	<i>P. antarctica</i> (Deception I.)	477.85 \pm 192.75	0	5.77 \pm 7.14	0	12.40 \pm 6.46	0	1051.56 \pm 819.46	0	0.57 \pm 0.12	0	65.67 \pm 50.01	0
	K–W Chi Square values (p)	NS		NS		NS		NS		NS		NS	
Organs and tissues	Specie/Location	Zn	n	As	n	Se	n	Cd	n	Pb	n		
Liver	<i>P. papua</i> (King George I.)	152.91 \pm 45.53	0	0.45 \pm 0.18	0	6.00 \pm 0.96	0	0.08 \pm 0.04	0	0.0008 ^a	5		
	<i>P. adeliae</i> (King George I.)	133.88 \pm 71.42	0	0.60 \pm 0.40	0	7.65 \pm 2.95	0	0.06 \pm 0.05	0	0.04 \pm 0.07	3		
	<i>P. antarctica</i> (Deception I.)	132.20 \pm 64.40	0	0.47 \pm 0.14	0	8.25 \pm 2.33	0	0.11 \pm 0.08	0	0.18 \pm 0.02 ^b	0		
	K–W Chi Square values (p)	NS		NS		NS		NS		$H_{2,12} = 10.18$ (0.01)			
Kidney	<i>P. papua</i> (King George I.)	125.43 \pm 12.60	0	0.40 \pm 0.23	0	5.57 \pm 0.33	0	0.20 \pm 0.05 ^a	0	0.0008 ^a	5		
	<i>P. adeliae</i> (King George I.)	85.74 \pm 19.49	0	0.44 \pm 0.24	0	6.62 \pm 2.82	0	0.20 \pm 0.15 ^a	0	0.05 \pm 0.12	4		
	<i>P. antarctica</i> (Deception I.)	92.83 \pm 32.19	0	0.50 \pm 0.09	0	11.20 \pm 4.03	0	0.54 \pm 0.29 ^b	0	0.14 \pm 0.02 ^b	0		
	K–W Chi Square values (p)	NS		NS		NS		$H_{2,12} = 7.98$ (0.02)		$H_{2,12} = 8.27$ (0.02)			
Muscle	<i>P. papua</i> (King George I.)	106.60 \pm 37.42	0	0.40 \pm 0.23	0	2.04 \pm 0.35	0	0.01 \pm 0.01	0	0.0008 ^a	5		
	<i>P. adeliae</i> (King George I.)	104.34 \pm 49.70	0	0.39 \pm 0.25	0	2.37 \pm 0.51	0	0.01 \pm 0.02	0	0.04 \pm 0.10 ^a	4		
	<i>P. antarctica</i> (Deception I.)	105.08 \pm 55.41	0	0.59 \pm 0.30	0	2.67 \pm 0.57	0	0.01 \pm 0.01	0	0.20 \pm 0.06 ^b	0		
	K–W Chi Square values (p)	NS		NS		NS		NS		$H_{2,12} = 10.41$ (0.01)			
Bone	<i>P. papua</i> (King George I.)	184.11	0	0.13	0	0.82	0	0.001	0	0.19	0		
	<i>P. adeliae</i> (King George I.)	227.01 \pm 121.11	0	0.13 \pm 0.08	0	1.15 \pm 0.33	0	0.01 \pm 0.004	0	0.04 \pm 0.10	4		
	<i>P. antarctica</i> (Deception I.)	235.01 \pm 40.62	0	0.14 \pm 0.13	0	1.03 \pm 0.30	0	0.004 \pm 0.001	0	0.14 \pm 0.02	0		
	K–W Chi Square values (p)	NS		NS		NS		NS		NS			
Feather	<i>P. papua</i> (King George I.)	80.59 \pm 10.85	0	0.12 \pm 0.05 ^a	0	2.61 \pm 0.80	0	0.06 \pm 0.04	0	0.87 \pm 0.86 ^a	0		
	<i>P. adeliae</i> (King George I.)	61.11 \pm 20.30 ^a	0	0.17 \pm 0.11	0	5.71 \pm 3.62	0	0.13 \pm 0.08 ^a	0	0.24 \pm 0.38	0		
	<i>P. antarctica</i> (Deception I.)	94.99 \pm 5.29 ^b	0	0.48 \pm 0.30 ^b	0	3.67 \pm 0.71	0	0.02 \pm 0.03 ^b	0	0.06 \pm 0.04 ^b	0		
	K–W Chi Square values (p)	$H_{2,12} = 11.18$ (0.004)		$H_{2,12} = 8.54$ (0.01)		NS		$H_{2,12} = 6.14$ (0.04)		$H_{2,12} = 6.74$ (0.03)			
Stomach content	<i>P. papua</i> (King George I.)	31.46 \pm 12.52	0	2.04 \pm 2.92	0	4.08 \pm 1.69	0	0.24 \pm 0.15	0	0.17 \pm 0.14	0		
	<i>P. adeliae</i> (King George I.)	71.16 \pm 48.82	0	2.00 \pm 1.58	0	5.97 \pm 1.40	0	0.23 \pm 0.17	0	0.40 \pm 0.26	0		
	<i>P. antarctica</i> (Deception I.)	31.04 \pm 10.02	0	1.92 \pm 1.11	0	6.13 \pm 1.96	0	0.32 \pm 0.34	0	0.33 \pm 0.11	0		
	K–W Chi Square values (p)	NS		NS		NS		NS		NS			

^{a,b} Concentrations marked with different letters were significantly different among species; NS: $p > 0.05$.

* Detection Limit Value.

found in a previous study including adult penguins (Jerez et al., 2012). Increases on the environmental Mn levels have also been described in other regions of the world and have been related to the current use of Mn as additive in combustibles (e.g. Burger and Gochfeld, 2000). A similar tendency could exist in our study area. In comparison to the levels detected in other regions, we found similar or even higher levels of Mn in penguin chicks than those detected in the feathers of seabird chicks from Alaska or the Brazilian coasts (0.96–1.18 $\mu\text{g g}^{-1}$ d.w.; Burger et al., 2008) and the soft tissues of Arctic seabird chicks (7.97, 4.20 and 1.03 $\mu\text{g g}^{-1}$ d.w. in the liver, kidney and muscle, respectively; Malinga et al., 2010).

We did not find a clear pattern of Pb accumulation in a specific tissue of penguin chicks ($p > 0.05$). Pb is a non-essential element that generally exhibits levels lower than 1 $\mu\text{g g}^{-1}$ in seabirds (Norheim, 1987) as occurs in the present study. If we compare our results with those obtained in other regions of the world, we found that the internal tissues of penguin chicks showed Pb levels similar to those detected in young specimens of seabirds from the Northern Hemisphere (ranging from non-detectable levels to 0.70 $\mu\text{g g}^{-1}$ d.w.; Hegseth et al., 2011a; Ribeiro et al., 2009). Regarding the feathers, we found lower levels in the chicks of *P. adeliae* and *P. antarctica* than those detected in young specimens from the Northern Hemisphere and South Atlantic Ocean (ranging from 0.64 to 1.47 $\mu\text{g g}^{-1}$ d.w.; Barbieri et al., 2010; Burger et al., 2008; Burger and Gochfeld, 2000; Ribeiro et al., 2009), whereas the *P. papua* feathers in this study showed similar levels to those mentioned before (maximum level detected in this study: 2.27 $\mu\text{g g}^{-1}$ d.w.). This toxic metal is usually analyzed for studying the presence of anthropogenic pollution in the environment since several human activities contribute to increase natural Pb levels (e.g. Schwarz et al., 2012), even in the Antarctic ecosystems (e.g. Sun and Xie, 2001). The obtained results suggest that the local anthropogenic activities can be increasing the Pb environmental levels in the study area since the Pb levels detected in some samples of penguin chicks were comparable to those detected in seabirds coming from “a priori” more polluted regions (the Northern Hemisphere or South Atlantic Ocean). However, the levels found in this study were below the levels known to cause adverse effects in seabirds (4 $\mu\text{g g}^{-1}$ in feathers; Burger and Gochfeld, 2000).

Burger et al. (2008) suggested that bird feathers can play an important role in Pb elimination from the organism due to its high affinity to calcified tissues. Due to this affinity, Pb levels used to be higher in the feathers and bones than in other bird internal tissues (e.g. Castro et al., 2011; Ribeiro et al., 2009; Thomas et al., 2009). According to this, our samples of *P. papua* chicks showed detectable Pb levels only in the feathers and bones whereas the soft tissues did not showed detectable amounts. On the contrary, this pattern was not clearly observed in *P. adeliae* and *P. antarctica* chicks.

The highest As levels in this study were found in the soft tissues ($H_{4,66} = 26.10$, $p = 0.000$, *post hoc* test $p < 0.05$) which is indicative of a recent exposure to this element that is rapidly distributed and retained in these tissues when goes into the organisms (ATSDR, 2007). We found As levels in the soft tissues similar to those described by Smichowski et al. (2006) in penguin chicks (0.50–0.81 $\mu\text{g g}^{-1}$ d.w.) which are usual levels and non-toxic for seabirds (usual levels are lower than 3 $\mu\text{g g}^{-1}$ d.w. and toxic levels are higher than 50 $\mu\text{g g}^{-1}$ d.w.; Braune and Noble, 2009; Neff, 1997). The diet seems to be an important As source for penguin chicks as relatively high As levels were detected in their stomach contents (ranging from 0.25 to 4.02 $\mu\text{g g}^{-1}$ d.w.). These high As levels in krill can be caused by the presence of volcanic activity and volcanic rocks in the study area (Baker et al., 1969; Baker and McReath, 1971; Thomson et al., 2001; Vodopivec et al., 2001) which constitutes an important natural input of elements such as

As (Smichowski et al., 2006), although local human activities could also be related to (Ribeiro et al., 2011).

The highest Se levels were found in the liver and kidney ($F_{4,66} = 37.55$, $p = 0.000$, *post hoc* test $p = 0.000$) in accordance with previous studies in Antarctic seabirds (Jerez et al., 2012; Nygard et al., 2001; Smichowski et al., 2006). We observed Se concentrations similar to those described by Smichowski et al. (2006) in penguin chicks but lower than the concentrations detected in adult Antarctic penguins in the same study area (ranging from 3.17 to 69.88 $\mu\text{g g}^{-1}$ d.w. in soft tissues; Jerez et al., 2012) and adult specimens of other Antarctic seabirds (ranging from 10.20 to 136.00 $\mu\text{g g}^{-1}$ d.w. in soft tissues; Nygard et al., 2001). These results suggest that penguins can accumulate Se during their life cycle. In comparison to seabird chicks from other regions of the world, we found similar or higher Se levels in the feathers of penguin chicks than those detected in the feathers of seabird chicks from the Arctic Ocean or the Mediterranean Sea (0.85–3.62 $\mu\text{g g}^{-1}$ d.w.; Abdennadher et al., 2010; Burger et al., 2008; Burger and Gochfeld, 2009). We also found higher Se levels in the liver of penguin chicks than those detected in the liver of Arctic seabird chicks (1.40–4.40 $\mu\text{g g}^{-1}$ d.w.; Hegseth et al., 2011b). These high Se levels detected in the studied specimens can be related with the relatively high Se amount present in the Antarctic krill (Se levels in the stomach contents ranged from 1.66 to 8.26 $\mu\text{g g}^{-1}$ d.w.). The 93.33% of the analyzed stomach contents showed Se concentrations above the level considered as potentially toxic for aquatic birds (more than 3 $\mu\text{g g}^{-1}$ d.w.; Lemly, 1993).

The highest levels of Ni were found in the bones ($H_{4,66} = 32.11$, $p = 0.000$, *post hoc* test $p < 0.05$) which is a common accumulation pattern for this metal in birds and mammals (Outridge and Scheuhammer, 1993a). Unlike other metals, data on nickel levels in seabirds are still scarce. Barbieri et al., 2010 analyzed Ni levels in the feathers of juvenile seabirds from the Brazilian coasts and found levels 1 or 2 orders of magnitude higher than ours (2.23 $\mu\text{g g}^{-1}$ d.w.; Barbieri et al., 2010). It has been proposed that the tissues of wild birds from uncontaminated environments generally contain between 0.1 and 5 $\mu\text{g Ni g}^{-1}$ d.w. (Outridge and Scheuhammer, 1993a). In accordance with this, our results suggest that penguin chicks were exposed to relatively low Ni environmental levels.

The highest Cr levels were found in the muscle tissue ($H_{4,66} = 16.62$, $p = 0.002$, *post hoc* test $p < 0.05$) which is indicative of a recent exposure to this metal. On the contrary, Cr tends to accumulate in the bones of animals chronically exposed (Outridge and Scheuhammer, 1993b). Regarding seabird chicks from other regions of the world, we did not found clear differences in the Cr concentrations. On the one hand, we observed Cr levels in the liver of penguin chicks similar or higher (0.80–22.20 times higher) than those detected in the liver of Arctic seabird chicks (Hegseth et al., 2011a). On the other hand, the feathers of penguin chicks showed Cr levels lower (1.49–12.46 times lower) than those detected in the feathers of chicks and juvenile specimens of other seabirds from the Arctic and South Atlantic Ocean (Barbieri et al., 2010; Burger et al., 2008; Burger and Gochfeld, 2009). Regarding Cr levels previously detected in Antarctic penguins, as in the case of Ni, data are still scarce. Szefer et al. (1993) found Cr levels in the soft tissues of penguins from the Antarctic Peninsula area (ranging from non-detectable to 0.09 $\mu\text{g g}^{-1}$ d.w.) lower than the levels we found. These results suggest that an increasing trend of the Cr levels could have existed in this area during the last two decades coinciding with an increase of the human presence. Similar results were found in samples of adult penguins (Jerez et al., 2012). The human presence and its associated activities (traffic of vessels, aircrafts and road vehicles, accidental oil spills, fuel combustion, waste incineration, etc.) could be responsible, at least partially, of this slight increase of the Cr environmental levels as it has been described in

other areas in Antarctica (Alam and Sadiq, 1993) and other regions (Caccia et al., 2003).

We found the highest Zn levels in the bones ($F_{4,66} = 22.42$, $p = 0.000$, *post hoc* test $p = 0.000$) as was observed in other seabirds (Nam et al., 2005). Zn levels in the muscle and bone of penguin chicks were similar or even higher than the levels detected in the same tissues of adult specimens (35.70–149.95 $\mu\text{g g}^{-1}$ d.w. in the muscle and 106.15–221.29 $\mu\text{g g}^{-1}$ d.w. in the bone; Honda et al., 1986; Jerez et al., 2012; Szefer et al., 1993). These high Zn levels can be related with the large requirements of this metal that bird chicks present in comparison to adult specimens (Mas, 1993). Despite these large requirements, the penguin chicks showed higher Zn levels than other seabird chicks from the Arctic (64.70, 73.70 and 53.30 $\mu\text{g g}^{-1}$ d.w. in the liver, kidney and muscle; Malinga et al., 2010) and South Atlantic Ocean (60.85 $\mu\text{g g}^{-1}$ dry weight in the feathers; Barbieri et al., 2010), which could be indicative of a higher Zn presence in the study area. These results can also be related with a probable protection role of Zn against the exposure to elevated Cd levels (see below).

The highest Fe levels were found in the liver and kidney ($H_{4,66} = 53.85$, $p = 0.000$, *post hoc* test $p < 0.05$) in accordance with previous studies in penguins (Honda et al., 1986; Jerez et al., 2012; Szefer et al., 1993). In comparison to other regions, we found higher Fe levels in the soft tissues than those found in Arctic seabird chicks (98.70–700.70, 254.00 and 9.60 $\mu\text{g g}^{-1}$ d.w. in the liver, kidney and muscle, respectively; Hegseth et al., 2011a; Malinga et al., 2010). These results can indicate that Fe levels are higher in the study area in comparison to the Arctic, which can be related to a high availability of this metal in the sediments of King George and Deception Islands (Almendros et al., 1997; Deheyn et al., 2005; Rey et al., 1995; Santos et al., 2005).

We found the highest Al levels in the muscle and feather of penguin chicks ($H_{4,66} = 28.69$, $p = 0.000$, *post hoc* test $p < 0.05$). This metal seems to have a high affinity to the feathers as other seabirds also exhibited the highest Al levels in these samples (Lucia et al., 2010). Data on Al levels in seabird or bird tissues from anywhere in the world are scarce despite this metal can cause them important adverse effects, for example, disruptive effects on calcium homeostasis and phosphorus metabolism, metabolic diseases in bone, muscle weakness, decreased growth rates, defective eggshell formation, impaired breeding or intrauterine bleeding (Capdevielle et al., 1998; Nyholm, 1981; Scheuhammer, 1987). We found similar Al levels to those described in the liver, kidney and feather of seabirds from the French Atlantic coasts, but higher in the muscle (3.20–11.80, 6.10–8.90, 96.00–226.00, 2.50–17.20 $\mu\text{g g}^{-1}$ d.w., respectively; Lucia et al., 2010). The high Al concentrations detected in the muscle of penguin chicks can be related to a recent exposure to high levels through diet (the stomach contents also showed elevated Al concentrations), in accordance with previous studies that pointed out the abundance and bioavailability of Al in the study area (Deheyn et al., 2005; Santos et al., 2005). Our results suggest that the feather and muscle can be more useful samples for Al monitoring than the liver or kidney that often show low Al concentrations and do not reflect exposures to high environmental levels (Lucia et al., 2010; Scheuhammer, 1987).

In general, our results in the feathers of penguin chicks are in accordance to those previously detected in the feathers of adult specimens from the same Islands (Jerez et al., 2011), although we found lower levels for Cr (5.48–35.39 times lower) and Ni (7.00–57.00 times lower) in chicks.

Comparisons among the levels of trace elements detected in the stomach contents of penguin chicks and their tissues did not indicate signs of biomagnification for Al, Cr, Mn, As, Cd or Pb. On the contrary, biomagnification phenomena in the Antarctic food web could be occurring for trace elements such as Fe, Ni, Cu, Zn and

Se since the levels in penguins tissues were higher than those detected in their preys (stomach contents). Fe and Cu levels in the liver of penguins were significantly higher than the levels detected in their stomach contents (Fe: $U = 47.00$, $p = 0.01$, $n_1 = 15$, $n_2 = 15$; Cu: $t = 2.74$, $p = 0.01$, $n_1 = 15$, $n_2 = 15$), as well as Ni levels in the bones ($U = 14.00$, $p = 0.000$, $n_1 = 11$, $n_2 = 15$), Zn levels in all the studied tissues (liver: $U = 16.00$, $p = 0.000$, $n_1 = 15$, $n_2 = 15$; kidney: $U = 22.00$, $p = 0.000$, $n_1 = 15$, $n_2 = 15$; muscle: $U = 24.00$, $p = 0.000$, $n_1 = 15$, $n_2 = 15$; bone: $U = 3.00$, $p = 0.000$, $n_1 = 11$, $n_2 = 15$; feather: $U = 34.00$, $p = 0.001$, $n_1 = 15$, $n_2 = 15$) and Se levels in the liver and kidney (liver: $t = 2.26$, $p = 0.03$, $n_1 = 15$, $n_2 = 15$; kidney: $t = 2.17$, $p = 0.04$, $n_1 = 15$, $n_2 = 15$). According with these results it has been proposed that trace elements can be magnified along the Antarctic food web due to the slow-growth and long-life of the organisms so higher concentrations than those of comparable species from temperate ecosystems can be reached (Clason et al., 2003; Kahle and Zauke, 2003). Anyway, these results should be confirmed in future studies analyzing the different tissues of the penguins prey Antarctic krill instead the whole body (Gray, 2002). The high levels of Fe, Cu and Zn detected in the tissues of penguin chicks can also be due to young specimens usually present high requirements of these essential metals (Mas, 1993) that can be metabolically regulated in seabird tissues (Smichowski et al., 2006).

Most of the observed inter-specific differences (Table 3) showed higher concentrations of trace elements in the tissues of chinstrap penguins than in gentoo and Adélie penguins except for Cd and Pb in the feathers (see Table 3). These results can be due to ecological or physiological differences among species such as a different specific capacity for detoxification and elimination of trace elements, different absorption–elimination rates or variations in their diet. In fact, the diet of penguins varies spatially and makes it difficult to compare concentrations of individuals from different colonies (Bargagli, 2005). It could be the main reason of the observed differences in this study since the tissues of penguins cohabiting the same area (gentoo and Adélie penguins from King George Island, see Table 1) did not show inter-specific differences. However, when the feathers of the three species were collected in the same location (Jerez et al., 2011), most of the inter-specific differences also showed the highest concentrations of trace elements in the chinstrap penguins feathers. A large number of positive correlations were observed between pairs of elements in the tissues of penguin chicks (54 positive correlations, 85.71% of all of them, see Table 4) in accordance with previous studies of seabirds (e.g. Jerez et al., 2012; Mendes et al., 2008; Nam et al., 2005; Pérez-López et al., 2006; Ribeiro et al., 2009). These correlations may suggest common sources of exposure, storage pathways or detoxification processes for these elements (Ribeiro et al., 2009). In addition, similar or parallel metabolic processes could exist for essential elements known to be internally regulated in birds (e.g. Cu, Zn, Mn, Se or Fe), which are reflected in positive relationships in the soft tissues such as the liver and kidney (34.92% of all the detected correlations). Some of them were previously reported in seabirds (e.g. Cu–Zn by Kim et al., 1998; Pérez-López et al., 2006; Ribeiro et al., 2009) confirming the close metabolic regulation for these elements in these animals.

A relevant number of positive correlations (17.46% of the total) were particularly observed in the muscle that is a short-term accumulation tissue and those could be reflecting a recent exposure to the involved elements (Al, Cr, Mn, Fe, Ni, Se, Cd and Pb).

In the case of the feathers, these samples showed 30.16% of all the detected correlations and 31.48% of all the positive ones involving ten different elements (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se and Cd). So many positive correlations seem to indicate that certain amount of trace elements migrated to the feathers through blood flow during the feathers growth and were retained there (Metcheva et al.,

Table 4
Correlations among elements in tissues of penguin chicks.

Elements	Al	Cr	Mn	Fe	Ni	Cu	Zn	As
Al	-	L* (Rho = 0.63) M (Rho = 0.53)	M** (Rho = 0.70) B* (Rho = -0.65) F*** (Rho = 0.84)	K* (Rho = 0.53) M* (Rho = 0.63) F*** (Rho = 0.89)	M* (Rho = 0.54)	B* (Rho = 0.61)		
Cr	-	-		K* (Rho = 0.59)	L** (Rho = 0.69) M* (Rho = 0.62) F** (Rho = 0.70)	B* (Rho = 0.66)	B*** (Rho = -0.91) F* (Rho = 0.59)	F* (Rho = 0.58)
Mn	-	-	-	M* (Rho = 0.63) F*** (Rho = 0.80)			L*** (Rho = 0.85)	
Fe	-	-	-	-				F** (Rho = 0.67)
Ni	-	-	-	-	-	F* (Rho = 0.56)		F** (Rho = 0.78)
Cu	-	-	-	-	-	-	L* (Rho = 0.63) B** (Rho = -0.80)	F** (Rho = 0.68)
Zn	-	-	-	-	-	-	-	F* (Rho = 0.59)
As	-	-	-	-	-	-	-	-
Se	-	-	-	-	-	-	-	-
Cd	-	-	-	-	-	-	-	-
Pb	-	-	-	-	-	-	-	-
			Se			Cd		Pb
Al								L*** (Rho = 0.84) K* (Rho = 0.56) M* (Rho = 0.58) L** (Rho = 0.75) K** (Rho = 0.59)
Cr					B* (Rho = -0.70)			
Mn			L* (Rho = 0.64) K** (Rho = 0.68) M* (Rho = 0.60) F** (Rho = 0.68)		L* (Rho = 0.64) K* (Rho = 0.61) F** (Rho = 0.76)			
Fe			L* (Rho = 0.57) F* (Rho = 0.55)		B** (Rho = -0.85)			K* (Rho = 0.53) M* (Rho = 0.59) B* (Rho = 0.74) M*** (Rho = 0.81) B* (Rho = 0.67) F** (Rho = -0.79)
Ni					B** (Rho = -0.81)			
Cu			F** (Rho = 0.67)		L* (Rho = 0.54)			
Zn			L* (Rho = 0.59)		L*** (Rho = 0.82)			
As			L** (Rho = 0.66) F* (Rho = 0.58)					
Se			-		L* (Rho = 0.59) K*** (Rho = 0.89) M** (Rho = 0.74) F* (Rho = 0.58)			F* (Rho = -0.55)
Cd			-		-			B*** (Rho = -0.80)
Pb			-		-			-

L = liver; K = kidney; M = muscle; B = bone; F = feather.

* p < 0.05.

** p < 0.01.

*** p < 0.0001.

2006), in accordance with previous results (Jerez et al., 2012). It can be a common pattern for trace elements elimination from the penguin body.

It is important to highlight that some pairs of elements showed simultaneously positive relationships in several tissues (Al-Fe, Al-Pb, Fe-Pb, Cr-Ni, Mn-Se, Mn-Cd and Se-Cd). It would confirm the existence of common inputs, regulation-storage pathways and/or detoxification-elimination processes for them.

Previous studies detected positive relationships between Se-Cd and Zn-Cd in the tissues of penguins and other polar seabirds (e.g. Jerez et al., 2011, 2012; Norheim, 1987) and the existence of a protective role of Se and Zn against the exposure to elevated Cd levels in Polar Regions was proposed. In accordance with this, we observed a strong positive relationship between Se and Cd in the kidney where Cd tends to accumulate and cause adverse effects. We also observed slighter positive relationships between Se and Cd in the liver, muscle and feather as well as between Zn and Cd in the liver supporting this hypothesis. Ribeiro et al. (2009) also suggested that Se may be involved in As storage-detoxification processes in seabirds and in accordance with them we observed significant Se-As relationships in the liver and feather of penguins.

We also observed positive relationships between pairs of elements known to be directly related with anthropogenic activities that take place in Antarctica (Section 1) such as Cr-Ni, Cr-As, Cr-Pb, Mn-Cd, Ni-As and Ni-Pb. These results support the idea that common anthropogenic sources existed for them.

Several authors have studied samples of soils, sediments, water and invertebrates in the proximity of scientific basis in King George and Deception Islands. Some of them have described an insignificant influence of human activities on the presence of environmental contamination (Ahn et al., 1996; Guerra et al., 2011) whereas others have proved a low to moderate anthropogenic influence (Bicego et al., 2009; Curtosi et al., 2007; Lu et al., 2012; Ribeiro et al., 2011; Santos et al., 2005). Differences of our results from some of these previous studies and the relatively high levels that we detected for some trace elements can be explained due to processes of bioaccumulation and biomagnification in penguins.

4. Conclusions

Several positive relationships between pairs of elements known to be emitted from anthropogenic activities such as Cr, Ni, Pb, Mn, Cd or As were observed in penguin tissues reflecting that common

sources of pollution could exist. Other positive relationships between essential elements such as Cu, Zn, Mn, Se or Fe suggested similar regulation processes for them in penguins. Similar elimination routes for toxic elements could also exist, especially through feathers. In general, non-toxic levels were observed for the studied elements except for Cd. The detected high Se and Zn levels could have played a protective role against the adverse effects produced by an exposure to high Cd levels. These results should be considered in future monitoring studies as well as the possible increase of Cr and Mn levels in the study area during the last years and the possible existence of biomagnification phenomena for elements such as Fe, Ni, Cu, Zn or Se.

In summary, the concentrations of trace elements in our samples were not as low as it could be expected and reflected that the exposition to some trace elements in the study sites is in general as high as in other places outside Antarctica such as the Arctic.

5. Uncited reference

Vodopivec and Curtosi (1998).

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