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Concentration of trace elements in feathers of three Antarctic penguins: Geographical and interspecific differences

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ABSTRACT

Antarctica is often considered as one of the last pristine regions, but it could be affected by pollution at global and local scale. Concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb were determined by ICP-MS in feathers ($n = 207$ individuals) of gentoo, chinstrap and Adélie penguin collected in 8 locations throughout the Antarctic Peninsula (2006–2007). The highest levels of several elements were found in samples from King George Island (8.08, 20.29 and 1.76 μg g^{-1} dw for Cr, Cu and Pb, respectively) and Deception Island (203.13, 3.26 and 164.26 μg g^{-1} dw for Al, Mn and Fe, respectively), where probably human activities and large-scale transport of pollutants contribute to increase metal levels. Concentrations of Cr, Mn, Cu, Se or Pb, which are similar to others found in different regions of the world, show that some areas in Antarctica are not utterly pristine.

1. Introduction

It is important to investigate baseline levels of trace elements in relatively uncontaminated areas to be taken as global reference values (Ancora et al., 2002), and Antarctica can be considered as one of the last pristine environments. However, at regional level, in addition to isolated incidents or impacts of the tourism increase, a continuous but low level of contamination due to research facilities and their associated activities has been detected (e.g. Vodopivez and Curtosi, 1998). On the other hand, contamination is a global phenomenon and transport of persistent pollutants may occur even to remote areas (Smichowski et al., 2006). Global change and development in countries of the Southern Hemisphere have increased the impact of anthropogenic contaminants on Antarctica (Bargagli, 2008), as contaminants have reached this continent from other areas of the world and have been deposited in waters and sediments (Bargagli, 2005). Research on environmental contamination in Antarctica has therefore increased in the last years trying to establish the levels of contamination from different sources (Bargagli, 2005).

Seabirds are considered among the most reliable indicators of environmental changes (Boersma, 2008). Specifically, seabirds are excellent subjects for heavy metal evaluation because they are long-lived, feed at different distances from land and exhibit different trophic levels (Walsh, 1990). In this context, Antarctic penguins have potential to be a standard biological indicator for monitoring the contamination of Antarctica nearshore ecosystems, because they have permanent ecological niches and represent an important part of the avian biomass in this region (Metcheva et al., 2006). In addition, the risk of persistent pollutant biomagnifications in Antarctica increases in these nearshore ecosystems because of the lengthening of the food chain (Bargagli, 2008).

Large-scale surveys on the chemical composition of some key species and the standardisation of non-invasive procedures for sampling (feathers, blood, excreta), allow detecting spatio-temporal changes in Antarctic environmental contamination (Bargagli, 2005). In this case, feathers are excellent for monitoring the Antarctica's environmental state, especially for the study of metal levels since metals have a high affinity for the sulfhydryl groups of the feather's structural proteins (Metcheva et al., 2006).

Currently, the available data on the levels of metals and trace and essential elements in feathers of Antarctic penguins are scarce and fragmented. Honda et al. (1986) studied levels of metals in feathers and other tissues (i.e. liver, kidney, heart or lung) of *Pygoscelis adeliae* (Rumpa Island). Ancora et al. (2002) used feathers, stomach contents and excreta of *P. adeliae* to investigate

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levels of cadmium, lead and mercury (Terra Nova Bay), and Metcheva et al. (2006) studied levels of different trace elements in feathers of *Pygoscelis papua* and *Pygoscelis antarctica* (Livingston Island). Our aim is to increase the information on this issue at a large geographical scale investigating the concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb in feathers of gentoo (*P. papua*), chinstrap (*P. antarctica*) and Adélie penguins (*P. adeliae*) from different locations along the Antarctic Peninsula.

2. Materials and methods

During 2005/2006 and 2006/2007 austral summer seasons, adult penguins were captured during moulting using a long-handled net in different locations (8) along the Antarctic Peninsula ranging from King George Island (62°15′S 58°37′W) to Avian Island (67°46′S, 68°64′W) (see Table 1 and Fig. 1). Feather samples were collected individually in polyethylene bags from a total of 207 adult individuals: 59 gentoo penguins, 80 chinstrap penguins and 68 Adélie penguins. Sample sizes for each locality and species are shown in Table 1.

The analytical method used in this study was obtained from the modification of the one described by Jerez et al. (2010). The feathers were rinsed with deionized water to eliminate adsorbed external contamination (Burger, 1993), and dried at 75–80 °C till constant weight (mean water content of penguin feathers: 11.12%). Between 0.0017 and 0.3925 g of the material, according to availability, were subjected to microwave digestion with HNO_3 (65%), H_2O_2 (30%) and H_2O in the proportion 5:3:2. Double-distilled and deionized water was added to the resulting samples to bring their volume to 25 ml. The elements Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb were determined by mass spectrometry with inductively coupled plasma (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 of blanks every five samples, initial calibration standards and CWW-TM-D certified reference material. The detection limit values, the reference material values and the percentage of reliability obtained for each element are shown in Table 2.

The detection limit of each element was calculated by using the formula DL = 3sB/a (DL: detection limit; sB: standard deviation of the number of counts corresponding to zero on the calibration line; a: the constant of the calibration line).

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

Differences among populations in the levels of the investigated elements were analysed by using one-way ANOVAs (with Bonferroni post hoc tests), although non-parametric tests (Kruskal–Wallis and Mann–Whitney *U* tests) were used when the assumptions of normality and homocedasticity were not met. Interspecific differences were analysed in King George Island (where the three species are present), Livingston Island (*P. papua* and *P. antarctica*) and Ronge Island (*P. papua* and *P. antarctica*) by means of one-way ANOVAs (Bonferroni post hoc tests), Student's *t*-tests, and non-parametric tests (Kruskal–Wallis and Mann–Whitney *U* tests). Spearman ranks and Pearson correlation coefficients were calculated between Zn and Cd, Se and Cd, and Zn/Se and Cd levels, in order to study the existence of relations that were observed by Norheim (1987) in seabirds from Polar Regions. A *p* value less than 0.05 was considered to indicate statistical significance. The detected levels are presented as mean ± standard deviation in $\mu g\ g^{-1}$ dry weight. Values reported in wet weight by other authors were converted to dry weight using the mean water content of penguin feathers. Data were analysed by using the statistical software SPSS 15.0.

3. Results

Concentrations of Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb in feathers of gentoo, chinstrap and Adélie penguins are shown in Table 3.

Table 1
Studied locations, species and sample size (*n*: number of individuals).

Locations	Species	*n*
Stranger Point, King George Island (62°15′S 58°37′W)	*P. papua*	20
Hannah Point, Livingston Island (62°39′S 60°36′W)	*P. papua*	14
George Point, Ronge Island (64°40′S 62°40′W)	*P. papua*	17
Paradise Bay (64°53′S, 62°53′W)	*P. papua*	8
Barton Point, King George Island (62°15′S 58°37′W)	*P. antarctica*	25
Hannah Point, Livingston Island (62°39′S 60°36′W)	*P. antarctica*	10
Vapour Col, Deception Island (63°00′S 60°40′W)	*P. antarctica*	25
George Point, Ronge Island (64°40′S 62°40′W)	*P. antarctica*	20
Stranger Point, King George Island (62°15′S 58°37′W)	*P. adeliae*	25
Yalour Island (65°15′S 64°11′W)	*P. adeliae*	21
Avian Island (67°46′S, 68°64′W)	*P. adeliae*	22

3.1. Geographical differences

The feathers of *P. papua*, *P. antarctica* and *P. adeliae* showed significant differences among the different locations for several trace elements.

With respect to Al and Mn, *P. papua* feathers showed that the levels in Stranger Point (King George Island) are significantly higher than in George Point (Ronge Island) (Table 4). Levels of Ni, Zn and Se in feathers of this species are significantly higher in Stranger Point in comparison to Paradise Bay, whereas there was significantly more Pb in Stranger Point than in Hannah (Livingston Island) and George Point (Table 4). Levels of Cr, Fe, Cu, As and Cd in *P. papua* feathers did not show significant differences among the studied locations.

P. antarctica feathers showed the highest levels of Al and Fe in Vapour Col (Deception Island), which are significantly higher than in Hannah and George Point. Al levels are also significantly higher in Barton Point (King George Island) than in George Point, whereas Fe levels are significantly higher in Barton Point than in Hannah and George Point (Table 4). *P. antarctica* feathers showed that Mn levels are higher in Vapour Col than in George and Hanna Point, and Cr levels are higher in Barton and George Point than in Hannah Point (Table 4). In the case of Ni, Zn and Se, the highest levels in feathers of this species were found in George Point, which are significantly higher than in Hannah Point, than in Barton and Hannah Point and than in Vapour Col, respectively (Table 4). *P. antarctica* feathers also showed that the levels of Cd are significantly higher in Vapour Col and George Point than in Hannah Point, whereas the levels of Pb are significantly higher in Barton Point than in Vapour Col, Hannah and George Point (Table 4). Levels of As and Cu in feathers of *P. antarctica* were similar in all the studied locations.

P. adeliae feathers showed that Al and Fe levels are significantly higher in Stranger Point than in Yalour and Avian Island, and Cr and Pb levels are higher in Stranger Point than in Avian Island (Table 4). On the contrary, Ni and Zn levels in *P. adeliae* feathers are significantly higher in Yalour Island in comparison to Stranger Point, and Zn levels are also higher in Avian Island in comparison to Stranger Point (Table 4). Levels of Mn, Cu, As, Se and Cd in feathers of *P. adeliae* did not show significant differences among the studied locations.

3.2. Interspecific differences

In King George Island, the feathers of *P. papua*, *P. antarctica* and *P. adeliae* showed significant differences for several trace elements. The highest levels of Al, Cr, Fe, Ni, Cu and Pb were detected in the feathers of *P. antarctica*, whereas the feathers of *P. papua* and *P. adeliae* showed the highest levels of Zn and Se, respectively (Table 5).

In Livingston Island, the feathers of *P. papua* and *P. antarctica* only showed significant differences for Se (Table 5). The highest Se levels were found in the feathers of *P. antarctica*.

In Ronge Island, the feathers of *P. antarctica* showed significantly higher levels of Cr, Ni, Cu, Zn, Se and Cd in comparison to the feathers of *P. papua* (Table 5).

3.3. Correlations between elements

Several significant positive correlations were observed between Zn and Cd, Se and Cd, and Zn/Se and Cd levels in penguin feathers (Table 6).

4. Discussion

Several researches have suggested a natural enrichment of Cd in polar food chains (Bustamante et al., 2003; Sanchez-Hernandez,

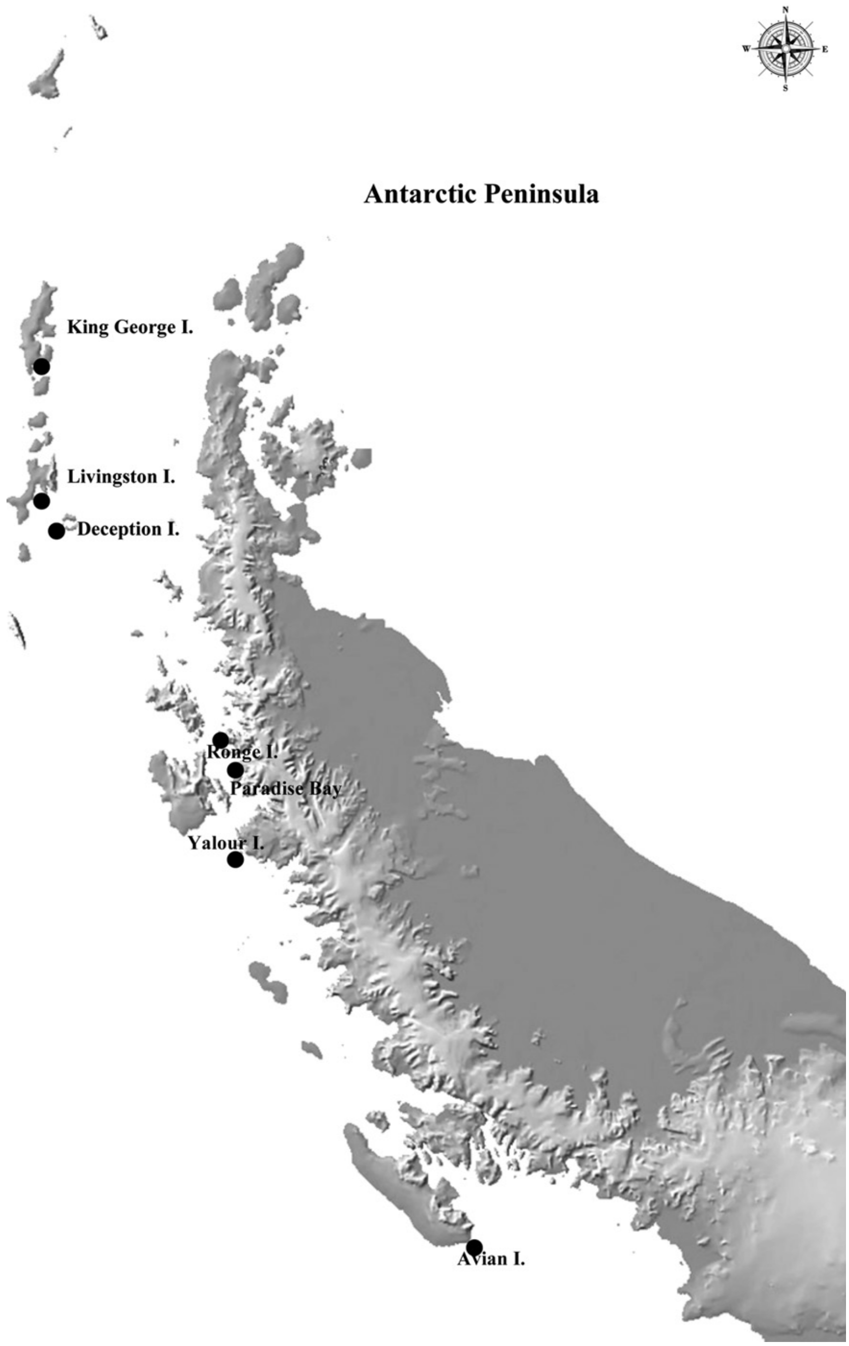

Fig. 1. Location of sampling sites.

2000), which could be favoured by different factors in Antarctica, for example, upwelling of Cd-rich waters, algal bloom (Bargagli et al., 1996) or local volcanism (Deheyn et al., 2005). In fact, Cd accumulation in Antarctic biota is well-documented and indicates its high bioavailability in the marine environment (Grotti et al., 2008). Several studies have detected relatively high Cd levels in different samples of Antarctic organisms such as plankton, marine benthic invertebrates (Ahn et al., 1996; Bargagli et al., 1996; Dalla Riva et al., 2004; Lohan et al., 2001; Mauri et al., 1990; Minganti et al., 1998; Negri et al., 2006; Nigro et al., 1997; Petri and Zauke, 1993) and different vertebrates, including fishes, seabirds and marine mammals (De Moreno et al., 1997; Grotti et al., 2008; Nygard et al., 2001; Szefer et al., 1993, 1994). Different samples of pygoscelid penguins (liver, kidney, pancreas, excreta or stomach content) have also shown relatively high Cd levels (2.80–236.22 $\mu g\ g^{-1}$ dry weight) (Ancora et al., 2002; De Moreno et al., 1997; Honda et al., 1986; Szefer et al., 1993). As krill-eating species, these penguin tissues reflect the naturally high Cd concentration found in the Antarctic krill (Barbante et al., 2000; Nygard et al., 2001; Petri and Zauke, 1993). However, Cd levels detected in penguin feathers in this study were relatively low compared to other penguin tissues, and were in agreement with relatively low Cd levels measured by Ancora et al. (2002), Honda et al. (1986) and Metcheva et al. (2006) in penguin feathers from different Antarctic areas (range from undetectable levels to 0.30 $\mu g\ g^{-1}$ dry weight). Similar Cd levels have been measured

Table 2
Detection limit values (ng g^{-1}), reference material values (ng g^{-1}) and the percentage of reliability obtained.

Element	Detection limit values	Reference material values obtained (dilution 1:100)	Percentage of reliability
Al	3.88	928.3 ± 30	92.8
Cr	0.2	984.6 ± 32	98.5
Mn	0.4	956.1 ± 40	95.6
Fe	1.7	951.2 ± 39	95.1
Ni	0.4	1034.2 ± 60	103.4
Cu	0.8	1043.5 ± 60	104.3
Zn	2.7	1259.5 ± 64	126.0
As	0.2	289.3 ± 4	115.7
Se	0.7	276.1 ± 3	110.4
Cd	0.1	293.9 ± 3	117.6
Pb	0.8	1107.0 ± 32	110.7

in seabird feathers from other regions of the world (0.01–0.40 μg g^{-1} dry weight) (Burger et al., 2008; Liu et al., 2006; Lucia et al., 2010; Ribeiro et al., 2009). These results suggest that feathers do not reflect the actual level of Cd exposure in penguins since feathers represent a minor site of Cd accumulation (Lucia et al., 2010). More research on alternative tissues such as liver or kidney is needed to evaluate a likely Cd bioaccumulation and its effects in these penguin localities.

The average levels of Pb detected in penguin feathers in the present study were higher than those found for Cd, and the ratio Pb/Cd in gentoo, chinstrap and Adélie penguins was 10.67, 8.75 and 6.75, respectively. These results are similar to those reported by Ancora et al. (2002) and Metcheva et al. (2006) in penguin feathers. Pb is known as a calcium-formations-seeking element (Lucky and Venugopal, 1977; O'Flaherty, 1998) and, unlike Cd, shows great bioaccumulation in bird feathers. This non-essential element (Smichowski et al., 2006) is not metabolically regulated (Gochfeld et al., 1996) and is one of the most suitable metals for monitoring of anthropogenic pollution (Metcheva et al., 2006). Our results showed the highest Pb concentrations in feathers from King George Island for the three studied species, which are similar to Pb levels measured in feathers of other seabirds from the Northern Hemisphere (0.71–1.88 μg g^{-1} dry weight) (Burger et al., 2008; Ribeiro et al., 2009). Different human activities are known as Pb sources, for example fuel combustion, waste incineration, sewage disposal, paint or accidental oil spills (Bargagli, 2008; Santos et al., 2005). In our case, Pb levels seem to be related to the great concentration of human activities that exists in King George Island, where most Antarctic scientific bases in the region are concentrated, including a small airport, and where there is heavy traffic of vessels, planes, and helicopters to transport tourists, scientists and support personnel (Tin et al., 2009).

Feathers of Adélie penguins, which have been collected along a wide geographic area of study (from 62°15′S 58°37′W to 67°46′S 68°64′W), showed a decrease of Pb abundance along the latitudinal gradient of the Antarctic Peninsula (Table 3). This decrease can be related to the decrease of human presence and activities from North to South. Feathers of gentoo and chinstrap penguins also showed the highest Pb concentration in the most northern location, King George Island, although a decrease of Pb abundance along the latitudinal gradient from North to South was not clearly observed due to some exceptions (Table 3): on one hand, relatively high Pb levels were found in feathers of gentoo penguins from Paradise Bay, which can be related to the location of research bases just beside the studied penguin rookery; on the other hand and as we expected, feathers of chinstrap penguins showed higher Pb levels in Deception Island in comparison to other locations further North, such as Livingston Island (see Fig. 1), since in Deception Island there has been a greater human presence from the beginning of the last century until now, and it is one of the most visited areas by tourist cruises nowadays. Probably, all these activities have contributed to increase Pb levels in these locations.

With respect to the rest of evaluated elements, we observe that the most of them decrease along the latitudinal gradient from North to South, with the exception of levels detected in Deception Island (Table 3). However, in some cases the differences among the studied locations were not statistically significant (Table 4).

Considering all the sampling sites together, the following relations among trace elements were observed:

Zn > Fe > Al > Cu > Se > Cr > Mn > Ni > Pb > As > Cd for *P. papua* and *P. adeliae*.

Al > Fe > Zn > Cu > Se > Cr > Mn > Ni > Pb > Cd > As for *P. antarctica*.

These relations are similar to those observed by Honda et al. (1986) in Adélie penguins from Rumpa Island and by Metcheva et al. (2006) in gentoo penguins from Livingston Island. It is important to point out that, unlike other vertebrates, feathers of penguins showed Zn levels higher than Fe levels in almost all the studied sites (Table 3). These high Zn levels can be related to an adaptive reaction of these Antarctic birds to elevated Cd and Hg levels (Metcheva et al., 2006), since increases of Zn levels are known to reduce the toxic effect of these toxic metals (Norheim, 1987; Underwood et al., 1977). In agreement with that we observe a significant positive correlation between Zn and Cd levels in feathers of chinstrap penguin (Table 6). On the contrary, we found a different proportion Fe–Zn in feathers of chinstrap and Adélie penguins from King George and Deception Island, where Fe levels are higher than Zn levels (Table 3). In Deception Island, these high Fe levels (and also high Al levels) could be due to the volcanic character of the Island, where geochemical analyses showed that Fe and Al are dominant elements in seafloor sediments (Almendros et al., 1997; Rey et al., 1995) and are available for the organisms (Deheyn et al., 2005). In King George Island, high levels of Fe and Al are present in sediments and soils too, which might be related to the abundance of pyrite/chalcopyrite in the volcanic rocks of the area (Deheyn et al., 2005; Santos et al., 2005).

We found the highest concentration of Mn in feathers of chinstrap penguins from Deception Island, where Mn levels were 4.18 times higher than those reported by Honda et al. (1986) in feathers of penguins near Syowa Station (Northeast of Antarctica). As in the case of Al and Fe, the abundance of Mn in seafloor sediment from Deception Island (Deheyn et al., 2005) would explain these results. If we compare Mn levels in penguin feathers with Mn levels measured in other regions, we observe that Mn range measured in the present study is similar to others detected in feathers of different seabirds from the Northern Hemisphere (0.75–2.84 μg g^{-1} dry weight) (Burger et al., 2008; Ribeiro et al., 2009). This comparison between Mn levels in penguin feathers and Mn levels in feathers of seabirds from other regions of the world can be indicative of the degree of pollution present in Antarctica. But it is important to point out that this comparison and others can also be influenced by differences in diet composition of each species.

The highest Cr concentrations were detected in King George Island and Deception Island (see Table 3), which could be related to the major human presence and contaminant activities in these locations. In fact, Cr is associated with oil contamination (Alam and Sadiq, 1993; Caccia et al., 2003) and our results are similar or even higher (1.06–5.25 times) than those found in seabirds from the Northern Hemisphere (Burger et al., 2008; Ribeiro et al., 2009). Our results contrast with those reported by Szefer et al. (1993) that found Cr levels below detection limits in soft tissues of pygoscelid

Table 3
Metal and trace element concentrations (μg g^{-1} dry weight) in feathers of adult penguins from different locations. Data shown are means ± standard deviation (*n*: number of detectable levels).

Species	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Pb
Pygoscelis papua											
King George Island	39.76 ± 24.74 (*n* = 20)	1.87 ± 1.56 (*n* = 20)	1.80 ± 1.28 (*n* = 20)	77.60 ± 134.55 (*n* = 20)	0.57 ± 0.35 (*n* = 20)	16.44 ± 3.16 (*n* = 20)	85.12 ± 14.84 (*n* = 20)	0.05 ± 0.04 (*n* = 20)	2.46 ± 0.70 (*n* = 20)	0.03 ± 0.03 (*n* = 7)	0.51 ± 0.46 (*n* = 20)
Livingston Island	40.17 ± 42.37 (*n* = 14)	2.71 ± 3.13 (*n* = 14)	1.17 ± 1.05 (*n* = 14)	35.13 ± 37.91 (*n* = 14)	0.49 ± 0.37 (*n* = 14)	13.88 ± 2.89 (*n* = 14)	75.41 ± 15.85 (*n* = 14)	0.02 ± 0.02 (*n* = 3)	2.25 ± 0.59 (*n* = 14)	0.02 ± 0.01 (*n* = 14)	0.17 ± 0.23 (*n* = 14)
Ronge Island	22.92 ± 27.87 (*n* = 17)	1.71 ± 1.17 (*n* = 17)	0.46 ± 0.58 (*n* = 17)	69.45 ± 109.94 (*n* = 17)	0.42 ± 0.27 (*n* = 17)	16.02 ± 2.09 (*n* = 17)	72.89 ± 7.46 (*n* = 17)	0.04 ± 0.02 (*n* = 8)	2.15 ± 0.80 (*n* = 17)	0.03 ± 0.01 (*n* = 8)	0.25 ± 0.44 (*n* = 17)
Paradise Bay	17.19 ± 11.90 (*n* = 8)	1.15 ± 0.89 (*n* = 8)	0.68 ± 0.66 (*n* = 4)	39.09 ± 24.33 (*n* = 8)	0.24 ± 0.08 (*n* = 8)	13.42 ± 5.09 (*n* = 8)	61.71 ± 18.01 (*n* = 8)	0.07 (*n* = 1)	1.51 ± 0.65 (*n* = 8)	0.03 ± 0.04 (*n* = 2)	0.31 ± 0.09 (*n* = 8)
Pygoscelis antarctica											
King George Island	132.38 ± 198.09 (*n* = 25)	8.08 ± 9.10 (*n* = 25)	1.66 ± 0.98 (*n* = 6)	126.28 ± 103.63 (*n* = 25)	0.97 ± 1.00 (*n* = 25)	20.29 ± 8.30 (*n* = 25)	77.12 ± 45.15 (*n* = 25)	0.10 (*n* = 1)	4.44 ± 1.71 (*n* = 25)	BDL (*n* = 0)	1.76 ± 1.74 (*n* = 25)
Livingston Island	26.07 ± 9.97 (*n* = 10)	1.15 ± 1.08 (*n* = 10)	0.92 ± 0.59 (*n* = 10)	32.06 ± 13.80 (*n* = 10)	0.52 ± 0.48 (*n* = 10)	14.93 ± 6.10 (*n* = 10)	72.21 ± 28.96 (*n* = 10)	0.01 ± 0.0001 (*n* = 2)	5.01 ± 2.26 (*n* = 10)	0.04 ± 0.03 (*n* = 10)	0.15 ± 0.12 (*n* = 10)
Deception Island	203.13 ± 194.65 (*n* = 25)	3.73 ± 4.19 (*n* = 25)	3.26 ± 2.68 (*n* = 25)	164.26 ± 149.75 (*n* = 25)	0.91 ± 0.90 (*n* = 25)	16.39 ± 3.44 (*n* = 25)	82.40 ± 15.64 (*n* = 25)	0.10 ± 0.10 (*n* = 8)	4.58 ± 2.27 (*n* = 25)	0.08 ± 0.04 (*n* = 25)	0.32 ± 0.22 (*n* = 25)
Ronge Island	14.26 ± 9.72 (*n* = 20)	2.81 ± 1.28 (*n* = 20)	0.29 ± 0.39 (*n* = 3)	22.47 ± 11.63 (*n* = 20)	1.18 ± 1.10 (*n* = 20)	19.23 ± 3.65 (*n* = 20)	97.27 ± 21.35 (*n* = 20)	0.05 ± 0.03 (*n* = 7)	6.77 ± 3.23 (*n* = 20)	0.10 ± 0.05 (*n* = 20)	0.14 ± 0.09 (*n* = 20)
Pygoscelis adeliae											
King George Island	43.36 ± 69.03 (*n* = 25)	6.37 ± 5.60 (*n* = 25)	1.30 ± 1.16 (*n* = 3)	59.74 ± 45.26 (*n* = 25)	0.55 ± 0.55 (*n* = 25)	12.68 ± 7.09 (*n* = 25)	50.84 ± 17.38 (*n* = 25)	BDL (*n* = 0)	6.37 ± 2.52 (*n* = 25)	BDL (*n* = 0)	0.64 ± 1.09 (*n* = 5)
Yalour Island	8.62 ± 6.41 (*n* = 21)	2.88 ± 1.95 (*n* = 21)	1.16 ± 1.26 (*n* = 3)	23.37 ± 11.25 (*n* = 21)	0.90 ± 0.48 (*n* = 21)	13.41 ± 2.60 (*n* = 21)	82.45 ± 13.10 (*n* = 21)	0.07 ± 0.04 (*n* = 21)	6.00 ± 2.30 (*n* = 21)	0.04 ± 0.05 (*n* = 6)	0.32 ± 0.36 (*n* = 21)
Avian Island	5.08 ± 3.03 (*n* = 22)	1.68 ± 0.78 (*n* = 22)	0.34 ± 0.49 (*n* = 5)	27.98 ± 41.20 (*n* = 22)	0.68 ± 0.25 (*n* = 22)	13.16 ± 3.04 (*n* = 22)	77.69 ± 15.17 (*n* = 22)	0.07 ± 0.03 (*n* = 3)	6.06 ± 3.05 (*n* = 22)	0.04 ± 0.02 (*n* = 22)	0.14 ± 0.21 (*n* = 22)

BDL = below detection limit.

Table 4
Significant differences in metal and trace element concentrations between the studied locations.

Pygoscelis papua	King George I.	Livingston I.	Ronge I.	Paradise Bay
King George I.		Pb^a ($H_{3,55} = 15.48$)	Al^a ($F_{3,55} = 3.74$) Mn^a ($H_{3,51} = 16.58$) Pb^a ($H_{3,55} = 15.48$)	Ni^a ($H_{3,55} = 9.53$) Zn^b ($F_{3,55} = 5.99$) Se^a ($F_{3,55} = 3.57$)
Livingston I.				
Ronge I.				
Paradise Bay				
Pygoscelis antarctica	**King George I.**	**Livingston I.**	**Deception I.**	**Ronge I.**
King George I.		Cr^a ($H_{3,76} = 21.28$) Fe^c ($F_{3,76} = 30.14$) Pb^a ($H_{3,76} = 38.49$)	Pb^a ($H_{3,76} = 38.49$)	Al^a ($H_{3,76} = 43.30$) Fe^c ($F_{3,76} = 30.14$) Zn^a ($H_{3,76} = 20.13$) Pb^a ($H_{3,76} = 38.49$)
Livingston I.			Al^a ($H_{3,76} = 43.30$) Mn^c ($F_{3,40} = 10.17$) Fe^c ($F_{3,76} = 30.14$) Cd^a ($H_{2,52} = 11.66$)	Cr^a ($H_{3,76} = 21.28$) Ni^a ($H_{3,76} = 8.45$) Zn^a ($H_{3,76} = 20.13$) Cd^a ($H_{2,52} = 11.66$)
Deception I.				Al^a ($H_{3,76} = 43.30$) Mn^b ($F_{3,40} = 10.17$) Fe^c ($F_{3,76} = 30.14$) Se^a ($F_{3,76} = 3.14$)
Ronge I.				
Pygoscelis adeliae	**King George I.**	**Yalour I.**	**Avian I.**	
King George I.		Al^a ($H_{2,65} = 29.06$) Fe^a ($F_{2,65} = 8.90$) Ni^b ($F_{2,65} = 4.95$) Zn^c ($F_{2,65} = 28.69$)	Al^a ($H_{2,65} = 29.06$) Cr^a ($H_{2,65} = 10.03$) Fe^c ($F_{2,65} = 8.90$) Zn^c ($F_{2,65} = 28.69$) Pb^a ($H_{2,45} = 7.64$)	
Yalour I.				
Avian I.				

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.0001$.

penguins, or those reported by Curtosi et al. (2010) that found undetectable Cr levels in different marine organisms near Stranger Point (King George Island); penguin feather appears to be a more useful sample for monitoring Cr levels in this region.

Currently, the information about Ni concentration in feathers of seabirds is very scarce. Honda et al. (1986) reported similar Ni levels in feathers of Adélie penguins (0.44 μg g^{-1} dry weight) near Syowa Station (Northeast of Antarctica) two decades ago to the ones we found in this study. Other penguin tissues analysed by different authors in this region showed levels below detection limits (Honda et al., 1986; Szefer et al., 1993), therefore feathers seem to be a better sample for Ni biomonitoring. Lucia et al. (2010) reported Ni levels in feathers of several seabirds from French coast to be similar to or higher than our results (0.90–14.10 μg g^{-1} dry weight). More research is needed for a better comprehension of Ni presence in penguins.

Our results on Cu concentrations were similar to those found two decades ago in feathers of Adélie penguins from the Northeast of Antarctica (14.49 μg g^{-1} dry weight, Honda et al., 1986). Our results were also similar to Cu levels found in feathers of gentoo and chinstrap penguin from Livingston Island (16.00–19.00 μg g^{-1} dry weight, Metcheva et al., 2006) or in liver of chick individuals of Adélie penguin from King George Island (18.00 μg g^{-1} dry weight, Smichowski et al., 2006). However, the same chick individuals of Adélie penguin showed Cu levels in kidney and muscle lower than

Table 5
Significant differences in metal and trace element concentrations between species from the same location.

King George I.	*P. papua*	*P. antarctica*	*P. adeliae*
P. papua		Cr^a ($H_{2,67} = 15.87$) Fe^a ($F_{2,67} = 5.00$) Zn^a ($H_{2,67} = 32.08$) Se^c ($F_{2,67} = 22.26$) Pb^a ($H_{2,47} = 10.40$)	Cr^a ($H_{2,67} = 15.87$) Zn^a ($H_{2,67} = 32.08$) Se^c ($F_{2,67} = 22.26$)
P. antarctica			Al^b ($F_{2,67} = 5.08$) Fe^a ($F_{2,67} = 5.00$) Ni^a ($H_{2,67} = 8.44$) Cu^b ($F_{2,67} = 7.94$) Zn^a ($H_{2,67} = 32.08$) Se^a ($F_{2,67} = 22.26$)
P. adeliae			
Livingston I.	***P. papua***	***P. antarctica***	
P. papua		Se^b ($t = 3.42$)	
P. Antarctica			
Ronge I.	***P. papua***	***P. antarctica***	
P. papua		Cr^a ($t = 2.70$) Ni^c ($U = 40.00$) Cu^b ($t = 3.34$) Zn^c ($t = 4.78$) Se^c ($U = 14.00$) Cd^b ($U = 20.00$)	
P. antarctica			

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.0001$.

Table 6
Significant correlations between Cd, Zn and Se levels in penguin feathers.

Pygoscelis papua		
Cd–Zn	Cd–Se *Pearson* $r = 0.40^a$	Cd–Zn/Se
Pygoscelis antarctica		
Cd–Zn *Spearman rho* $= 0.43^b$	Cd–Se *Spearman rho* $= 0.33^a$	Cd–Zn/Se *Spearman rho* $= 0.44^b$
Pygoscelis adeliae		
Cd–Zn	Cd–Se *Spearman rho* $= 0.43^a$	Cd–Zn/Se

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.0001$.

our results (1.60–6.40 μg g^{-1} dry weight, Smichowski et al., 2006), since Cu is mainly retained in penguin feathers and liver. In respect to other regions of the world, our results were comparable to Cu levels found in feathers of seabirds from the French coast (19.10–35.70 μg g^{-1} dry weight, Lucia et al., 2010). Besides, we found higher Cu concentrations in feathers of penguins than other authors have found in feathers of seabird species from China and Portugal (1.65–3.97 times higher) (Liu et al., 2006; Ribeiro et al., 2009). The higher Cu levels in penguins could be related to the high Cu levels present in Antarctic krill (Nygard et al., 2001). In spite of this, seabird feathers seem to be reflecting variations in Cu levels in the different regions. Although Cu is an essential element and it is important for the formation of feathers (Nygard et al., 2001), human activities such as oil spills, sewage, or solid waste among others could contribute to increase Cu levels in coastal marine birds (Eiser, 1981). In this way penguin feathers could be a reliable indicator of a possible Cu increase in Antarctic environments.

We found As levels 2.80–250.00 times lower than those measured in seabird feathers from other regions of the world (Burger et al., 2008; Lucia et al., 2010; Ribeiro et al., 2009). Smichowski et al. (2006) detected As concentrations one order of magnitude higher than our results in soft tissues of Adélie penguin chicks from Stranger Point. Volcanic activity constitutes an important natural input of elements such as As, but we found lower As levels than expected in volcanic areas. These results seem to point out that feathers do not reflect the actual exposure of penguins to As.

Se levels in our samples were similar to those detected by Metcheva et al. (2006) in feathers of gentoo penguin (1.80–2.00 μg g^{-1} dry weight), but higher than those detected by the same study in feathers of chinstrap penguin (<0.80 μg g^{-1} dry weight). A major exposure to Cd and Hg could explain the increase in Se levels, as is the case of Zn, since Se is also known to have a detoxifying effect on these metals (e.g. Smichowski et al., 2006). In agreement with this idea and with data reported by Norheim (1987), who observed significant correlations between Se/Zn and Hg/Cd levels in seabirds from the Arctic and the Antarctic, we found significant positive correlations between Se and Cd levels in feathers of gentoo, chinstrap and Adélie penguins, and between Zn/Se and Cd levels in feathers of chinstrap penguins (Table 6). Besides, our results were similar to Se levels recently detected in different seabirds from the Northern Hemisphere (0.40–8.70 μg g^{-1} dry weight) (Burger et al., 2008; Lucia et al., 2010; Ribeiro et al., 2009).

Finally, we observe interspecific differences in the presence of trace elements in penguin feathers (see Table 5), which could be due to ecological or physiological differences among the species. We found that most of the elements showed the highest levels in feathers of chinstrap penguin in comparison to the other studied species from King George Island (Al, Cr, Fe, Ni, Cu and Pb), Livingston Island (Se) and Ronge Island (Cr, Ni, Cu, Zn, Se and Cd). Ecological differences in penguin species living in the same place are usually expressed in terms of diet. In the case of the chinstrap penguin, the diet consists almost exclusively of Antarctic krill (Williams, 1995). Gentoo penguin diet consists of about 60–85% krill and different crustaceans, but they also prey upon fish and cephalopods (Williams, 1995). However, in Stranger Point (King George Island) krill was predominant in the summer diet for both gentoo (Carlini et al., 2009) and Adélie penguins (Volkman et al., 1980). Also inter-annual changes in the penguin diet can exist (Ropert-Coudert et al., 2002). But the three species of penguins have a similar diet and probably the small differences in diet are not enough to explain the differences found in the concentration of metals in their feathers. The incorporation of metals in the feathers occurs during moulting and, thus, the presence of metals should reflect the diet during the pre-moulting period. Unfortunately, as far as we know, there is no information about diet during this particular period in any of the three species. Therefore, we cannot exclude diet as the responsible of interspecies differences in metal concentrations. Alternatively, differences in metal levels could be due to intrinsic differences in the absorption–elimination rate among the three species. This possibility remains to be tested.

5. Conclusions

Our results are not completely in agreement with the idea of an uncontaminated Antarctic ecosystem compared with other regions of the world. Levels of Cr, Mn, Cu, Se or Pb in penguin feathers from several studied areas, such as King George or Deception Islands, are similar or even higher than levels of these elements detected in feathers of other seabirds from the Northern Hemisphere. Even though these results can be related to natural phenomena (e.g. local volcanism) they can also be related to anthropogenic pollution.

The study of penguin feathers is especially interesting for monitoring Pb and Cr levels, since these metals are directly connected with several human contaminant activities. Penguin feathers showed that these elements are more abundant in areas with major human presence, King George and Deception Islands. Feathers are also useful for monitoring other elements such as Ni and Cu, which previously showed lower or non-detectable levels in other penguin tissues. However, other biological samples should be analysed to evaluate penguin exposure to As or Cd, since these elements tend to accumulate in soft tissues. Probably, penguins in this region are exposed to greater Cd levels than those detected in feathers, which can be causing increases of Se and Zn levels.

In summary, different activities carried out locally may contribute to increase metal levels in the Antarctic environment. Most of the studied elements in our penguin samples showed the highest levels in locations where many human activities take place, thus, supporting the anthropogenic influence as responsible, at least partially, for the concentration of metals. Therefore, the increase of contaminant human activities such as plane and ship trips related to the tourism industry in the northern area of the Antarctic Peninsula (6704 tourists and 59 voyages in 1992–1993, and 36,875 tourists and 239 voyages in 2009–2010, IAATO, 2010) could have a significant effect on the accumulation of metals in Antarctic biota.

In addition to local pollution, elements such as Cr, Ni, Cu, Zn or Pb can be transported to Antarctica from other continents in the Southern Hemisphere (Bargagli, 2008). Therefore, population growth and industrial development in those continents and global changes can increase the impact of persistent contaminant in Antarctica.

Feathers of Antarctic penguins, together with other penguin tissues, are useful for long-term monitoring of trace elements in Antarctic marine environment and are reliable for a better understanding of spatio-temporal trends.

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