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Trace elements in Antarctic penguins and the potential role of guano as source of recycled metals in the Southern Ocean

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ABSTRACT

Penguins dominate the Antarctic avifauna. As key animals in the Antarctic ecosystem, they are monitored to evaluate the ecological status of this pristine and remote region and specifically, they have been used as effective bioindicators suitable for long-term monitoring of metals in the Antarctic environment. However, studies about the role of this emblematic organism could play in the recycling of trace metals (TMs) in the Antarctic ecosystem are very limited. In this study we evaluate, using the peer review research articles already published and our own findings, the distribution of metals (i.e., Ca, Fe, Al, Na, Zn, Mg, Cu, K, Cd, Mn, Sr, Cr, Ni, Pb, Hg, V, Ba, Co, La, Ag, Rb, Hf, Sc, Au and Cs) and metalloids (As and Sb), measured in different biotic matrices, with emphasis on guano, of the Chinstrap (*Pygoscelis antarcticus*), Adélie (*Pygoscelis adeliae*) and Gentoo (*Pygoscelis papua*) penguins.

Regarding bioactive metals, the high concentrations (μg g^{-1} dry weight) of Cu (2.0 ± 1.4) x 10^2, Fe (4.1 ± 2.9) x 10^2, Mn (30 ± 34) and Zn (210 ± 90) reported in the guano from all the penguin species studied including our data, are of the same order of magnitude as those reported for whale feces (μg g^{-1} dry weight): Cu (2.9 ± 2.4) x 10^2, Fe (1.5 ± 1.4) x 10^2, Mn (28 ± 17) and Zn (6.2 ± 4.3) x 10^2, and one order of magnitude higher than the metal contents in krill (μg g^{-1} dry weight) of Cu (10.2 ± 5.5), Fe (24 ± 29) and Zn (13.5 ± 1.7).

This suggest that penguin's excretion products could be an important source of these essential elements in the surface water, with an estimated annual release on a breeding season for Cu, Fe, Mn, Zn respectively of 28, 56, 4 and 29 tons, for the Chinstrap, Adélie and Gentoo penguins. The results provide evidence on the potential influence of penguins recycling TMs in the surface layer of the water column.

1. Introduction

The Southern Ocean (SO) is one of the most extensive High-Nutrient Low-Chlorophyll (HNLC) regions worldwide (Longhurst et al., 1995), characterized by a consistent abundance of nutrients such as nitrate, phosphate and silicate but a low phytoplankton biomass (e.g., de Baar et al., 1997; Boyd et al., 2000; Blain et al., 2001). It is known that this low phytoplankton biomass is a consequence of the scarce concentration of some trace metals, especially iron (Fe), which is the main limiting element that controls phytoplankton productivity and their community structure (de Baar et al., 2005; Martin, 1990). Besides Fe, other trace metals (TMs), such as copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co), or zinc (Zn), are essential for the biological functions of organisms, and once assimilated they become part of biochemical processes and enzymatic systems (Morel et al., 2003).

The main sources of TMs in the SO are known to come from natural origins and processes, such as melting sea ice and icebergs (Lannuzel et al., 2016; Tovar-Sánchez et al., 2019; Schmidt et al., 2016), continental sediments and hydrothermal vents (Mão de Ferro et al., 2014; Tovar-Sanchez et al., 2009), volcanic depositions (Deheyn et al., 2005; Smichowski et al., 2006; Wardell et al., 2008), the mixing of water masses (mostly the deep mixing in winter) (Castrillejo et al., 2013;

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Tagliabue et al., 2014), upwelling and biogeochemical cycling (Boyd et al., 2017) and atmospheric deposition (Bargagli, 2008; Chu et al., 2019; Sañudo-Wilhelmy et al., 2002). Despite these sources, the concentrations of TMs in surface waters in the SO are low, mainly due to the short residence time in oxygenated marine waters and because additional external sources are scarce (Bowie et al., 2001; de Baar et al., 1995). Therefore, any processes that can supply essential trace metals in surface waters or help to increase their persistence in an available form, would be relevant for primary production (Shatova et al., 2016, 2017).

Remineralization of organic matter (Gerringa et al., 2020) or biological recycling are mechanisms that contribute to maintain high levels of TMs in the upper-oxygenated layers of seawater (Ratnarajah et al., 2017). Indeed, it is assumed that marine organisms not only remove the available nutrients and TMs from the environment, but they reinsert the digested components in the euphotic zone, through excretion products, recycling and making them bioavailable again (Ratnarajah et al., 2018). Actually, several studies have already demonstrated that Antarctic krill (*Euphausia superba*), and whales (whose main food source is krill) contribute, via their excretion products, to the recycling of TMs in the surface waters of the SO (e.g., Lavery et al., 2010; Nicol et al., 2010; Ratnarajah et al., 2014; Tovar-Sanchez et al., 2007; Wing et al., 2014; Schmidt et al., 2016).

Seabirds have an important interactive role connecting the sea and land (De La Peña-lastra, 2021). Nesting on land, they are able to transfer the seawater nutrients assimilated to the surrounding soil through excretion, which has significant effects on the structure and dynamics of the terrestrial plant community, for example by producing greater biodiversity, or leading a zonation pattern of cyanobacteria, green algae, moss and lichens (Cipro et al., 2018; Ellis, 2005; Otero et al., 2018; Smykla et al., 2007). Among birds, penguins dominate the Antarctic avifauna (Boersma, 2008; Celis et al., 2015b; Croxall, 1987). The Chinstrap (*Pygoscelis antarcticus*), Adélie (*Pygoscelis adeliae*), Gentoo (*Pygoscelis papua*) and Emperor (*Aptenodytes forsteri*) are the most common and abundant species of penguins in the Antarctic, whose population has been estimated at about 16 million specimens (BirdLife International, 2020). Penguins, like whales, occupy a low/middle position in the Antarctic food chain, as their main feeding source is krill (Cherel, 2008; Borboroglu and Dee Boersma, 2013; Ratcliffe and Trathan, 2012; Cherel and Hobson, 2007). However, studies on the potential role of penguins in the recycling of TMs across the Southern Ocean has received scarce attention (Shatova et al., 2016, 2017; Wing et al., 2014, 2017).

In this study, we combined compiled data from the literature on the contents of metals in different parts of the penguin's body and biotic matrices, and our own analysis of guano from different penguins' species in order to: i) provide an overview of the background on the studies of metals in penguins, identifying general targets and results; ii) compare TMs levels found in biotic matrices (e.g., blood, brain, internal organs, bone, muscle, feathers and guano) in order to support our hypothesis that penguins guano can be an important source of TMs in the surface water of the SO and iii) compile all the information to discuss the potential influence of penguins in the recycling of TMs in the SO surface waters.

2. Materials and methods

2.1. Systematic revision of the data published

We compiled the data published concerning the concentration of metals (i.e., Ca, Fe, Al, Na, Zn, Mg, Cu, K, Cd, Mn, Sr, Cr, Ni, Pb, Hg, V, Ba, Co, La, Ag, Rb, Hf, Sc, Au and Cs) and the metalloids (As and Sb) in four species of Antarctic penguins: Chinstrap, Adélie, Gentoo and Emperor from different parts of the body, including feathers, blood, brain, internal organs, bone, muscle, fat and guano. The data was exclusively obtained from peer-reviewed articles from journals included in the Science Citation Index (SCI), published between 1986 and 2020. Data concerning metals coming from museum samples, zoo penguins or non-Antarctic penguin populations were not included in our study, we compiled data from samples collected on the Antarctic continent and the surrounding Antarctic islands. Here we used the term "guano", to refer to the different names for seabird excrements used in the literature, such as: "fecal material", "excreta" or "seabird droppings". All the data collected were transformed and expressed in μg g^{-1} dry weight (wet weight concentration data were converted to dry weight concentration as indicated on Supplementary Material 1). Values reported as "Not Determined" and "Not Analyzed" were not included in the analysis. Values reported as "Below Detection Limit" were included as the absolute value (Jerez et al., 2013a, 2013b). Maps of Fig. 2 have been created using the Quantarctica3 package (QGIS software).

2.2. Guano sample collection and metal analysis

In order to contribute to the scarce data on metal concentration in guano from Antarctic penguin species, fresh guano samples were collected from different colonies on King George Island in 2007 (Gentoo and Chinstrap penguin); Livingston Island in 2008 and in 2016 (Gentoo penguin); Deception Island in 2018 (Chinstrap penguin); Avian Island in 2019 (Adélie penguin) for metal analysis (guano samples of Emperor penguin were not collected) (see yellow dots in Fig. 2). At each location, about 5 g of superficial wet guano samples were collected manually in two polyethylene 15 ml vials by using a plastic spoon and stored frozen at −20 °C until the analyses. In the laboratory, the guano samples were lyophilized and the metals (Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and the metalloid As were extracted with a microwave acid digestion system (MARS-V, CEM) in accordance with the SW-846 EPA Method 3051A (USAEPA, 1987). TMs extraction involved the digestion of approx. 0.1 g of guano sample with 10 mL of nitric acid (65%, Suprapur quality) in Teflon vessels. After digestion, samples were diluted to 45 mL using Milli-Q water and then analyzed using an inductively coupled plasma-mass spectrometry (ICP-MS, iCAP Thermo). Blanks and certified material for digestion and analysis were treated like the samples. The accuracy of the analytical procedure was checked using a certified reference material (Mussel Tissue ERM®-CE278k), with concentration measured (μg g^{-1} dry weight) and recoveries (%) of Cd: 0.296 ± 0.004 (88.0 ± 1.2%); Fe: 150.88 ± 0.75 (93.71 ± 0.23%); Mn: 4.75 ± 0.02 (97.28 ± 0.21%); Ni: 0.58 ± 0.02 (84.8 ± 2.5%); Pb: 1.98 ± 0.05 (90.9 ± 1.2%); Zn: 70.8 ± 4.2 (99.7 ± 5.9%); As: 7.75 ± 0.13 (116 ± 2%); Cr 0.96 ± 0.87 (125 ± 9%).

2.3. Statistical analysis

Data of trace elements average concentrations between the literature and our results data, found in the penguin guano from the three *Pygoscelis* species, were analyzed by using Student's *t*-tests, to test for significant differences ($p < 0.05$). Previously, normality and homogeneity of variance were checked by using the Shapiro-Wilk and Levene tests, respectively ($p < 0.05$). Statistical analyses were performed with SPSS software (version 27). The *t*-values are provided in Supplementary Material 1.

3. Results and discussion

3.1. Background on Antarctic penguins' TMs data

Trace metal concentrations (e.g., Ag, Al, Br, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sr, Zn) and the metalloid (As) were reported in 64 articles, throughout different regions of the Southern Hemisphere. However, among these, 42 studies were used for discussion in this work since they reported data from penguin species living in the Antarctic continent: Chinstrap, Adélie, Gentoo and Emperor (dataset in Supplementary Material 2).

Most of the research papers compiled were focused on the study of penguin species as marine sentinels of environmental changes and pollution. Because penguins feed prevalently on krill, have a low/middle position in the food chain (Smichowski et al., 2006) and are long-lived with an average of 15–20 year lifespan (Ancora et al., 2002), they are considered useful species to biomonitor the contamination of ecosystems and environmental changes (Sun et al., 2020; Furness and Camphuysen, 1997; Carravieri et al., 2013; Espejo et al., 2017). Thus, for example, penguin droppings seem to reflect the contamination derived from the Industrial Revolution by showing increasing levels of Pb during the last 200 years (Sun and Xie, 2001a). Celis et al. (2015) suggested a common anthropogenic metal source (i.e., Cd, Cu, Cr, Mn, Ni, Pb and Zn) for the guano and feathers samples of Gentoo penguins, and also for the sediments near their colonies.

Geographically, the most studied area of the Antarctic is represented by the South Shetland Islands with the highest percentage of studies (60%), followed by the Queen Maud Land (18%) in the East Antarctica and the Antarctic Peninsula (14%) (Fig. 1A and Fig. 2). The Shetland Islands and the Antarctic Peninsula region, concentrate the highest number of studies probably due to: i) the significant presence of penguin rookeries (with more than 80 Important Bird Areas) (see Harris et al., 2015); ii) the major concentration of scientific bases (39 research scientific bases out of 115) which increases accessibility to the penguin colonies (COMNAP Programs, 2017); and iii) the increase of human impacts associated with fishing and tourism (Borowicz et al., 2018), which makes this region an interesting spot to assess the anthropogenic impacts.

Regarding the penguin species, the Adélie penguin with 44% of the total articles was the most studied, followed by the Gentoo (32%), the Chinstrap (22%) and the Emperor (2%) (Fig. 1B). The Adélie penguin is considered one of the best known Antarctic seabirds (Ainley et al., 2010), since is used as an indicator of the health of the ecosystem (Lynch and Larue, 2014; Trathan et al., 2015; Che-Castaldo et al., 2017).

Penguin feathers have been the biotic matrix most analyzed for TM contents (30% of the compiled papers; Fig. 1C) since they are considered a non-invasive sample and a good bioindicator of environmental quality (Metcheva et al., 2006). Other parts of the body and biotic matrices such as muscle, liver, guano, kidney, bones and stomach have been analyzed for TM content in a number of studies with a percentage of 13, 11, 10, 8, 7, 6, respectively (Fig. 1C). Most of the cases were focused on examining the anthropogenic pollution in the Antarctic ecosystem, with the exception of the study by Shatova et al. (2016), in which the composition of the metals in guano was analyzed to evaluate the impact of TMs originating from guano on marine phytoplankton.

The most studied metals were Cd, Cu, Pb and Zn, (11 and 10% of the

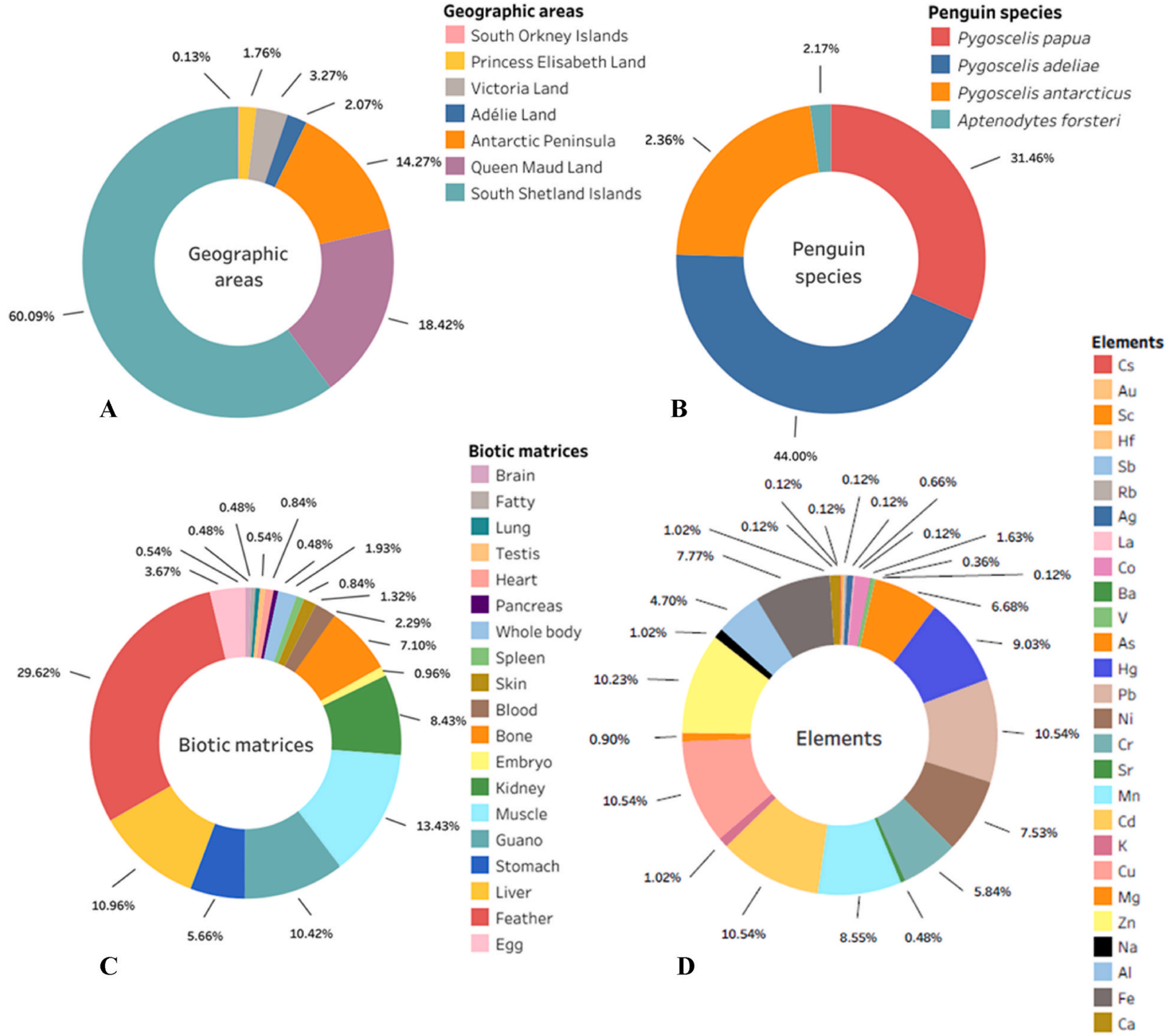

Fig. 1. Percentages of research articles published, according to geographic location (A), penguin species (B), body tissues and guano (C) and elements (D), (references in Supplementary Material 1).

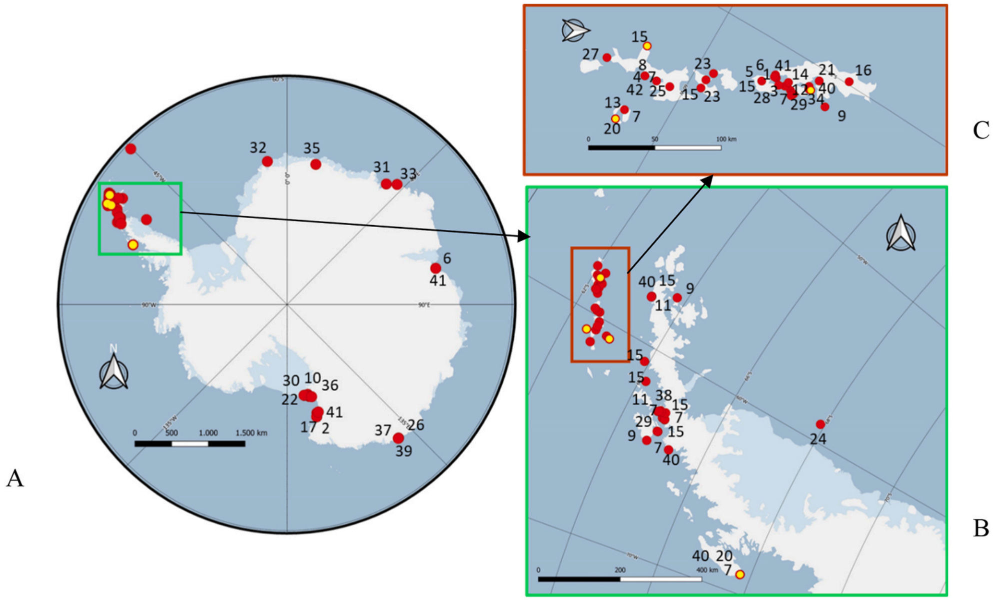

Fig. 2. Sample sites distribution in the whole Antarctic continent (A), in the Antarctic Peninsula (B) and in the South Shetland Islands (C). Numbers indicate the "Revision Code" and red dots indicate the sample sites of the reviewed studies from literature, indicated in Supplementary Material 1; the yellow dots represent this study sample sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

total data), and Mn, Hg, Fe, and Ni (between 8 and 9% of the total articles) (Fig. 1D), dealing with the incorporation route or the origin of sources (i.e., anthropogenic, dietary or natural). This finding agrees with the review done by Espejo et al. (2017) to evaluate the biological effect of metals in penguins. Concentrations of Fe, Cu, Zn, Cd and Hg found in penguins have been mainly associated with food intake and natural sources like upwellings or local volcanisms (Sanchez-Hernandez, 2000; Ancora et al., 2002; Smichowski et al., 2006; Jerez et al., 2011; Celis et al., 2012; Espejo et al., 2014; Polito et al., 2016; Metcheva et al., 2006). Sources also derived from anthropogenic activity (such as scientific bases, ship traffic or atmospheric inputs) were not excluded for some of the TMs, such as Pb, Ni, Hg and Cd, found in penguin samples (Metcheva et al., 2006; Nie et al., 2012; Celis et al., 2012, 2015; Espejo et al., 2014; Jerez et al., 2013a, 2013b; Barbosa et al., 2013; Sun and Xie, 2001a).

3.2. *Guano as a potential source of trace metals in the surface water*

The magnitude of metal levels in penguins' guano could provide relevant information that might help to evaluate the role of penguins as a source of recycled metals in the surface water layer, as previously suggested (e.g., Wing et al., 2014, 2017; Shatova et al., 2016, 2017).

A comparison of the average levels of TMs found in the different penguin biotic matrices, together with guano metal content here analyzed (Supplementary Material 3), is shown in Fig. 3. Guano is where the largest metal concentrations were found (no data available for the guano from the Emperor penguin; statistical tests for elements with less than three data,element in bold, were not performed, the symbol greater than in bold means statistically significant difference, $p < 0.05$), with the following order of metal abundances:

Adélie: **Al** > Cu > Zn > **Fe** > **Mn** > **Ag** > Cd > **Ni** > As > Pb > **Cr** > Hg > **Co**;

Chinstrap: **Al** > **Fe** > Ag **>** Zn > Cu > Mn **>** Cr > As > Cd > Ni > Pb > Co > Hg;

Gentoo: Ag > Al > Fe > Zn > Cu **>** Mn > Ni > Hg **>** Cr > As **>** Cd **>** Pb > Co.

Guano shows higher concentrations of the bioactive metals: Zn, Fe, Cu and Mn, and of Al and Ag (Fig. 3). The presence of high concentrations of TMs in guano can be linked to diet, foraging habitat, internal needs or environment (Metcheva et al., 2011). However, since it has been demonstrated that krill act as a reservoir of essential trace metals in surface waters (Ratnarajah et al., 2014; Tovar-Sanchez et al., 2009), is reasonable to think that these high concentrations in guano are mostly linked to the food source. Even high concentrations of non-essential metals (i.e., Ag and Al) in penguin's guano, could be linked to a krill-based diet, since it has been demonstrated that geothermal inputs could be a source of metals in krill (Tovar-Sanchez et al., 2009).

Once this cocktail of the metals in penguin's guano is released into the water it could fuel phytoplankton growth (Shatova et al., 2016, 2017). Iron and Zn are considered essential metals required for marine bacterial and phytoplankton growth. Specifically, Fe is required for many vital processes including chlorophyll synthesis and carbon and nitrogen fixation, among others (e.g., Koch and Trimborn, 2019). Furthermore, Zn acts as a cofactor in multiple metabolic processes including the uptake of CO_2 via the enzyme carbonic anhydrase (Hu et al., 2003) as well as the uptake of phosphorous via alkaline phosphatase (Shaked et al., 2006). Other metals, such as Cu and Mn, play an important role in phytoplankton growth: Cu as part of some metalloproteins that are essential for the transport of electrons, the mitochondrial one and in those of the process of photosynthesis (Twining and Baines, 2013); and Mn as a component of several metalloproteins involved in the reactions of photosynthesis, phosphorylation and with antioxidant functions (Twining and Baines, 2013).

The average metal contents in the guano ($\mu g\ g^{-1}$ dry weight) from the three species of penguins studied [i.e., Zn (210 ± 90), Fe (4.1 ± 2.9) x 10^2, Cu (2.0 ± 1.4) x 10^2 and Mn (30 ± 34) (Table 1);] were of the same magnitude as those reported in whale feces ($\mu g\ g^{-1}$ dry weight): Zn (6.2 ± 4.3) x 10^2, Fe (1.5 ± 1.4) x 10^2, Cu (2.9 ± 2.4) x 10^2 and Mn (28 ± 17) (Ratnarajah et al., 2014) and one order of magnitude higher than krill (the main prey of whales and penguins) with a metal composition ($\mu g\ g^{-1}$ dry weight) of Zn (13.5 ± 1.7); Fe (24 ± 29) and Cu (10.2 ± 5.5) (Tovar-Sanchez et al., 2009). Therefore, as suggested for whales (Smetacek, 2008; Nicol et al., 2010), defecation by Antarctic penguins could have a fertilizing effect by releasing essential TMs back into the surface layer, linked from a common source of food represented by krill.

A simple calculation seems to validate the magnitude and importance of penguin guano as a significant source of the TMs in the surface seawater. Provided a penguin abundance in the Southern Ocean of about

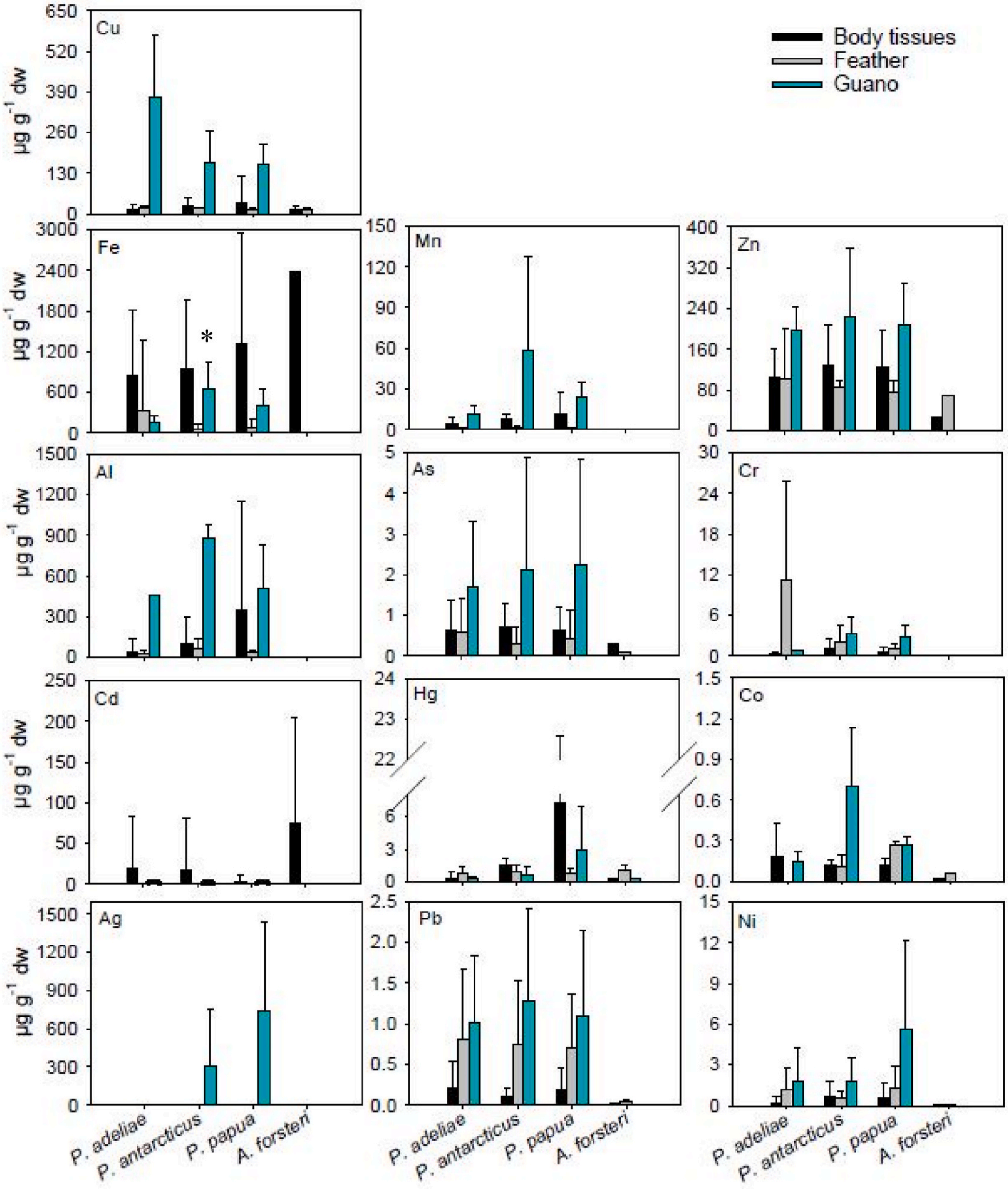

Fig. 3. Average trace metal concentrations (in µg g^{-1} dry weight) of each penguin species in body tissues (data include blood, brain, internal organs, skin, bone and muscle), feathers, and guano (included those measured in this study). * Data of Fe concentration in the guano of *P. antarcticus* reported by Szefer et al. (1993b) [i.e., (61 ± 5) x 10^2 µg g^{-1}] has been considered an outlier and it has not been plotted. Also the Cu and Zn data of Yin et al. (2008), which considers an average between species, have not been plotted. Black bars indicate standard deviation. The averages shown in this figure were extracted from data in Supplementary Material 1.

16 million individuals (with a population of the Adélie: 7.58 million; the Chinstrap: 8 million and the Gentoo: 774,000, see Otero et al., 2018), and the average concentration of the metals reported here in guano, we estimate an annual release of the metals Zn, Fe, Cu and Mn of 29, 56, 28 and 4 tons, respectively, during a breeding season. This conservative calculation was obtained assuming that: i) penguins excrete on average 84.5 g droppings (dry weight) each day (Sun and Xie, 2001b); ii) conservatively, only 60% of this guano excreted on land reaches the seawater by the runoff produced by glacial weathering or rainwater and by the strong winds that can spread the particles (De La Peña-lastra, 2021; Ratnarajah et al., 2018) and iii) the calculation is done for 165 days that is the estimated average of a breading period for the studied species of penguins (Borboroglu and Dee Boersma, 2013). Further studies will be necessary to evaluate the bioavailability fraction of these metals to phytoplankton (e.g., organic complexation and solubility, chemical speciation and redox states, etc.). The estimate of the annual amounts of TMs excreted by penguins were calculated by applying this equation:

$TM_{excr.} = [TMs]^{*}$ (84.5 g/day/penguin)*(16,354,000 penguins)*(165 days)*(0.60).

Penguins show a number of special characteristics and practical advantages over other marine vertebrates (including whales and other seabirds) that suggest they could play a key role in recycling TMs, contributing significantly to the nutritional supply of the upper layers of the SO and influencing phytoplanktonic communities and the carbon cycle. Among which we highlight that: i) unlike whales and other seabirds that migrate in northern waters during different life periods, penguins (i.e., the Chinstrap, Adélie and Gentoo species) are restricted

Table 1

Concentrations of trace metals in guano (μg g^{-1} dry weight), compiled from the literature and from this study of the Chinstrap (*Pygoscelis antarcticus*), Adélie (*Pygoscelis adeliae*) and Gentoo (*Pygoscelis papua*) penguins.

References	Geographic Area	Year	Specie	Pb	Cd	Hg	As	Fe	Mn	Co	Zn	Ni	Cu	Al	Ag	Cr	Sr
a	Terra Nova bay	1995–96	*P. adeliae*	0.43	5.8	0.34	–	–	–	–	–	–	–	–	–	–	–
b	King George Isl.	2001	*P. adeliae*	–	–	–	0.76	–	–	–	–	–	–	–	–	–	–
b	Nelson Isl.	1999	*P. papua*	–	–	–	4.1	–	–	–	–	–	–	–	–	–	–
c	Livingston Isl.	2006–07	*P. papua*	0.40	1.0	–	5.1	185	12.3	–	145.0	0.63	104.0	316.0	–	2.1	556.0
d	Ross Isl.		*P. antarcticus*	–	–	0.15	–	–	–	–	–	–	–	–	–	–	–
e	Paradise Bay	2011	*P. papua*	0.75	0.84	7.6	0.25	–	–	–	–	–	–	–	–	–	–
e	Paradise Bay	2011	*P. papua*	0.38	1.7	1.1	0.50	–	–	–	–	–	–	–	–	–	–
f	Paradise Bay	2011–12	*P. papua*	2.9	2.5	–	0.33	–	–	–	380.0	–	200.0	–	–	–	–
f	Greenwich Isl.	2011–12	*P. papua*	0.78	2.2	–	0.44	–	–	–	192.2	–	114.7	–	–	–	–
f	Palmer Archipel.	2011–12	*P. papua*	2.6	3.4	–	0.37	–	–	–	324.3	–	184.5	–	–	–	–
f	Errera Channel	2011–12	*P. papua*	0.87	2.2	–	0.43	–	–	–	195.4	–	130.1	–	–	–	–
f	Paradise Bay	2011–12	*P. papua*	2.7	2.1	–	0.36	–	–	–	201.2	–	222.5	–	–	–	–
f	Doumer Isl.	2011–12	*P. papua*	2.1	2.4	–	0.52	–	–	–	172.9	–	154.2	–	–	–	–
f	Paradise Bay	2011–12	*P. papua*	2.5	2.0	–	0.33	–	–	–	247.0	–	148.8	–	–	–	–
f	Palmer Archipel.	2011–12	*P. antarcticus*	1.1	3.3	–	0.43	–	–	–	295.7	–	168.8	–	–	–	–
f	Livingston Isl.	2011–12	*P. antarcticus*	1.1	1.9	–	0.40	–	–	–	246.8	–	229.9	–	–	–	–
f	King George Isl.	2011–12	*P. antarcticus*	1.3	3.1	–	0.70	–	–	–	227.8	–	260.0	–	–	–	–
f	Paradise Bay	2011–12	*P. antarcticus*	1.3	1.9	–	0.55	–	–	–	210.0	–	286.7	–	–	–	–
g	Terra Nova bay	1989–90/1990-91	*P. adeliae*	–	–	0.17	–	–	–	–	–	–	–	–	–	–	–
h	Antarctica	1989	*P. antarcticus*	3.8	0.16	–	–	–	138	1.2	456.0	3.5	37.6	–	0.20	5.0	–
i	South Shetland Isl.	1989	*P. antarcticus*	–	–	1.6	–	–	–	–	–	–	–	–	–	–	–
j	Neko Harbor	2014	*P. papua*	0.10	1.6	–	–	–	22.4	–	143.0	4.4	146.0	–	–	1.9	–
j	Doumer Isl.	2014	*P. papua*	0.10	1.2	–	–	–	17.8	–	109	4.9	201.5	–	–	1.7	–
j	King George Isl.	2014	*P. papua*	1.5	2.0	–	–	–	36.6	–	201	13	222.5	–	–	3.0	–
j	Paradise Bay	2014	*P. papua*	1.7	2.9	–	–	–	44.8	–	318	18	266.8	–	–	3.0	–
k	Ross Isl.	2013	*P. adeliae*	–	0.90	–	4.8	97.00	8.30	0.10	181	3.5	39.00	–	–	–	–
l	King George Isl.	2012–13	*P. adeliae*	2.0	4.0	0.52	1.1	–	–	–	263	–	558.3	–	–	–	–
l	Paradise Bay	2012–13	*P. adeliae*	1.5	2.8	0.40	1.0	–	–	–	216	–	586.0	–	–	–	–
l	Yalour Isl.	2012–13	*P. adeliae*	0.58	1.8	0.10	0.72	–	–	–	216	–	403.0	–	–	–	–
l	Avian Isl.	2012–13	*P. adeliae*	0.44	1.6	0.13	0.66	–	–	–	188	–	363.0	–	–	–	–
m	East Antarctica	2001	*P. adeliae*	2.1	–	0.20	–	–	–	–	–	–	–	–	–	–	–
m	King George Isl.	2000	*P. antarcticus*	1.4	–	0.11	–	–	–	–	–	–	–	–	–	–	–
m	King George Isl.	2002	*P. papua*	0.11	–	0.15	–	–	–	–	–	–	–	–	–	–	–
n	Livingston Isl.	2016	*P. papua*	0.14	1.3	–	5.8	759.1	22.0	0.26	98.3	0.0	171.0	964.7	40.00	0.81	–
n	King George Isl.	2007	*P. papua*	0.15	0.92	–	6.5	352.2	15.7	0.23	129	1.2	18.80	487.7	724.7	6.4	–
n	Livingston Isl.	2008	*P. papua*	0.19	2.4	–	6.1	370.3	21.0	0.33	256	1.9	64.30	294.1	1442	3.8	–
n	Deception Isl.	2018	*P. antarcticus*	0.10	1.1	–	3.1	930.2	17.1	0.65	40.7	0.0	125.3	946.2	88.30	0.61	–
n	King George Isl.	2007	*P. antarcticus*	0.22	1.3	–	7.4	358.8	20.6	0.30	92.4	1.7	20.80	819.2	823.0	4.4	–
n	Avian Isl.	2019	*P. adeliae*	0.0	1.6	–	3.0	223.4	15.9	0.20	127	0.0	286.9	463.4	3.500	0.91	–
Average				1.1	2.1	1.0	2.1	409.5	30.2	0.40	210	4.1	204.10	613.0	445.9	2.8	556.0
SDV				1.0	1.1	2.0	2.4	288.7	33.8	0.35	90.3	5.5	141.7	290.2	562.5	1.8	

[a] Ancora et al. (2002); [b] Xie and Sun (2008); [c] Metcheva et al. (2011); [d] Nie et al. (2012); [e] Celis et al. (2012); [f] Espejo et al. (2014); [g] Bargagli et al. (1998); [h] Szefer et al. (1993a); [i] Szefer et al. (1993b); [j] Celis et al., 2015a; [k] Shatova et al. (2016); [l] Celis et al. (2015b); [m] Yin et al. (2008); [n] This study.

to the SO all year long (Borboroglu, 2013); ii) their high abundance and wide distribution (Woehler et al., 2001); iii) with the exception of the Emperor penguins that feed more on Antarctic silverfish and to a lesser extent on cephalopods and krill (Cherel, 2008), they feed mainly on krill (>90% by mass) (Lynnes et al., 2004) which accumulate high concentrations of TMs (Tovar-Sanchez et al., 2007, 2009); iv) they feed within the upper 100 m of the water column (Borboroglu and Dee Boersma, 2013), which is the representative layer of the upper ocean and where primary production and photosynthetic fixation of carbon by phytoplankton occurs (Mahadevan, 2016); v) penguins migrate long distances using ocean currents with an annual average of 12,760 km, with the longest being 17,600 km for the Adélie penguins (Ballard et al., 2010), which favours the mobility, transport and distribution of metals released in seawater from their excretion products and; vi) on land, the large amount of droppings that characterizes their colonies (Karpouzi et al., 2007) can easily reach the surrounding surface waters thus influencing the supply of nutrient and TMs (Ancora et al., 2002; Otero et al., 2018; Wing et al., 2014).

4. Conclusions

Data compiled from the literature published on the composition of trace metals in penguins demonstrate a research effort aimed at evaluating the environmental changes and pollution in the Antarctic without paying attention to penguins' biogeochemical role. The high concentrations of metals found in guano together with their high population abundance and life cycle linked to the sea, suggest that penguins may release significant amounts of essential trace metals through a process based on their feeding on krill followed by defecation. Although, future investigations should focus on determining the bioavailability of the metal content in penguinś guano, this study can extend the role of penguins, just as for krill and whales, to include them as important factor of oceanic biogeochemical cycling for TMs.

Author contributions

All the authors equally contributed to the conceptualization, investigation, methodology, supervision, and writing of this manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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