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Seabird colonies as relevant sources of pollutants in Antarctic ecosystems: Part 2 - Persistent Organic Pollutants

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HIGHLIGHTS

- Seabird colonies are verified as secondary POPs sources.
- Soil and vegetation samples in/around colonies are compared to control away from them.
- Seabird colonies act as a source of PCBs and likely of HCB.
- SIA, C and N content confirm the animal-derived organic matter influence on results.
- Other local sources, particularly of PCBs, are hypothesised.

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ABSTRACT

Despite typically not being taken into account (usually in favour of the 'global distillation' process), the input of persistent organic pollutants (POPs) through biological activities can be indeed relevant at the local scale in terrestrial polar environments when seabird colonies are considered. Seabirds can bioaccumulate and biomagnify POPs, gather in large numbers and excrete on land during their reproductive season, thus making them locally as relevant secondary sources of POPs. The first part of this study indicated that these colonies act as so for several essential and non-essential trace elements, and this second part tests the same hypothesis concerning POPs using the very same samples. Lichens (n = 55), mosses (n = 58) and soil (n = 37) were collected from 13 locations in the South Shetlands Archipelago during the austral summers of 2013–14 and 2014–15. They were divided in colony (within the colony itself for soil and within and surrounding the colony for vegetation) and control (at least 150 m away from any colony interference) and analysed for POPs such as organochlorine pesticides, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers and stable isotopes (C and N). Results showed that colonies act clearly as a secondary source for PCBs and likely for hexachlorobenzene. As in the first part, probable local sources other than the colonies themselves are hypothesised because of high concentrations found in control sites. Again, soil seemed the most adequate matrix for the intended purposes especially because of some particularities in the absorption of animal-derived organic matter by vegetation, pointed out by stable isotope analyses.

1. Introduction

As presented in part 1 of our work (Cipro et al., 2018a), 'global distillation', the mechanism by which contaminants volatilise in warmer locations with subsequent atmospheric long-range transport and condensation in colder regions is majorly held responsible as the main, or even the only pollutant input process in Polar environments, whilst the biologically mediated transport is

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frequently not taken into account (Blais, 2005; Blais et al., 2007). However, literature presents evidence suggesting the role of seabird colonies as relevant secondary sources at the local or regional level for both organic and inorganic contaminants (Cipro et al., 2018a, 2011; Roosens et al., 2007). The particular fact that several species of seabirds assemble in colonies containing a large number of individuals (penguins, for instance, may form colonies of hundreds of thousands of individuals, e.g., Ballance et al., 2009) excreting on land, notably during the reproductive season, results in a substantial input regarding the terrestrial ecosystems in and around such colonies.

This input from seabird colonies added to the organic matter deriving from eggs (Brasso et al., 2012), bird tissues and prey present in these structures (Emslie et al., 2014) represents the major source of nutrients for Antarctic terrestrial ecosystem (Smykla et al., 2007). This has been verified for both extant and abandoned colonies (Liu et al., 2006; Outridge et al., 2016; Tatur et al., 1997). The availability of the nutrients resulting from this input induces a pattern of green algae/cyanobacteria, Antarctic hair grass, mosses and lichens, in this order, as the distance to the colony increases (Smykla et al., 2007). In this regard, water availability also plays an important role not only because of the differences in water dependency of these organisms but also that seasonal melting and runoff water are known to have a key influence on marine primary production (Anderson and Polis, 1999) and on carrying organic contaminants (Cipro et al., 2017b) to be absorbed by marine life (Cipro et al., 2018b). This introduction of nutrients brings contaminants along, not only by a direct influence of the excretion (Rudolph et al., 2016) but also through cycles of resuspension and redeposition, for instance.

The suitability of matrices for this objective (the assessment of seabird colonies as secondary contaminant sources) is largely confirmed by the literature (e.g. Borghini et al., 2005; Cocks et al., 1998; Negoita et al., 2003; Tarcau et al., 2013). However, differently from the trace elements presented in the first part of the present study (Cipro et al., 2018a), persistent organic pollutants (POPs) analysed in this second part do not present natural environmental sources but only anthropic ones. Because of their physico-chemical properties (mainly high stability and lipophilicity; and somewhat low vapour pressure), POPs are (1) transported to long distances through the atmospheric pathway and (2) undergo an increase in their concentrations during the lives of organisms (i.e. bioaccumulation process) and also according to their trophic position (i.e. biomagnification process). The cold conditions of Antarctic environments favour the persistency of these compounds with respect to temperate and tropical environments, particularly because of the seasonal storage and consumption of lipids in these environments (Cipro et al., 2013; Loganathan and Kannan, 1991).

Taking all the previous considerations into account, in an analogous manner to the first part of the study, the present study aimed at assessing seabird colonies as secondary sources of selected POPs using both soil and vegetation as indicators in several Antarctic terrestrial ecosystems considering geographical variation, distance to the colonies and the use of different seabird species with different feeding ecology strategies.

2. Material and methods

2.1. Sampling

Because this is a two-part study, the present work was performed with the same samples used in the first one (Cipro et al., 2018a). Samples of lichen (n = 55), mosses (n = 58) and soils (n = 37) were collected from 13 locations in the South Shetlands Archipelago in the austral summers of 2013–14 and 2014-15 during cruises of the Brazilian Antarctic Programme and divided into two types: 'colony' (within the colony itself for soil and within and surrounding the colony for vegetation) and 'control' (at least 150 m away from the respectively closest colony. Lichens and soil were collected at higher elevations than the colony, whereas mosses, because of their water dependency, were collected from lower sites. All the samples for POP analyses were collected using a steel gear (spoons and tweezers) previously rinsed with *n*-hexane. All the samples for stable isotope analysis (SIA) were collected using a plastic gear (spoons and tweezers) first rinsed in an acid bath (35 mL L^{-1} nitric acid and 50 mL L^{-1} hydrochloric acid) and then with Milli-Q water. The soil samples were collected from no deeper than 5 cm. They were chosen at the field mainly by their availability, avoiding fresh faeces, which could mask the results of the formed ornithogenic soil. The samples were collected in triplicates whenever possible.

In some cases, the samples were collected from more than one spot in each area of interest, and these spots were labelled as 'main location' and 'specific location'. Thus, the comparison between control and colony sites was made within the same specific location, when available, otherwise the closest control sample within the same main location was adopted.

Once collected, samples for POP analyses were stored in previously combusted aluminium foil, and samples for SIA were stored in hermetically sealed plastic bags. They were frozen aboard (−20 °C) and kept frozen until arrival at the Marine Organic Chemistry Laboratory (LabQOM, University of São Paulo/Brazil), where all POP analyses were performed and, also, where the SIA samples underwent lyophilisation. Vegetation species were identified by Prof. Jair Putzke (Universidade Federal do Pampa, São Gabriel, Brazil). SIA samples were then sent to the University of La Rochelle, France, where they were ground to a fine powder in a ceramic mortar before analyses. Soil samples were sifted (1 mm mesh) after freeze-drying to remove larger rock fragments and debris. Soil samples were not ground in any part of the process whatsoever in order to assure that only the granulometry of choice underwent analyses.

2.2. Analyses

Analyses for POPs were performed for three classes of contaminants: polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs).

Samples were extracted according to a previously described method (Cipro et al., 2013), which was adapted from the literature (Macleod et al., 1986). Briefly, wet samples (10 g for vegetation and colony soil, 20 g for control soil) were manually ground with anhydrous Na_2SO_4, and a surrogate (PCB 103) was added before extraction in a Soxhlet apparatus for 8 h with 80 mL of *n*-hexane and methylene chloride (1:1, v/v). During the extraction, metallic copper was added to the flasks to retain sulphur. The extract was then concentrated to 1 mL and cleaned up in a column filled (from top to bottom) with 16 g alumina and 8 g silica gel (both 5% deactivated with water). A second rotorevaporation (up to 900 μl) followed, and finally, an internal standard (100 ng of TCMX, used to estimate the surrogate recovery) was added to the purified extract before injection in the gas chromatograph. The same extract was used for all POP analyses.

PCB and PBDE analyses were performed by gas chromatography in an Agilent 6890 Plus attached to an MS 5973N Mass Selective Detector (GC/MS) in selective ion monitoring (SIM) mode, with a HP-5MS column (30m × 250μm × 0.25 μm, internally coated with 5% phenyl–95% dimethylpolysiloxane). Helium was used as carrier gas at a constant flow (1.1 mL min^{-1}). The injection volume was 1 μl in the splitless mode. The injector, interface and ion source

operated at 280 °C, 280 °C and 300 °C, respectively. The oven ramp was programmed as follows: 75 °C for 3 min, then increased at 15 °C min^{-1} up to 150 °C, then increased at 2 °C min^{-1} up to 260 °C, and finally increased at 20 °C min^{-1} up to 300 °C and remained at this temperature for 10 min, thus making a total run time of 75 min. The analysed PCB congeners were IUPAC 8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, 74, 77, 81, 87, 95, 97, 101, 105, 114, 118, 123, 126, 128, 132, 138, 141, 149, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 201, 203, 206 and 209. In turn, the analysed PBDE congeners were IUPAC 28, 47, 99, 100, 153, 154 and 183.

OCP analyses were run in a gas chromatograph equipped with an electron capture detector (GC-ECD, Agilent Technologies, model 6890N). Hydrogen was used as carrier gas at a constant pressure (13.0 psi). The injector was operated in the splitless mode and kept at 300 °C. The capillary column used was the same HP-5MS. The detector was operated at 320 °C using N_2 as makeup gas at a flow rate of 60 mL min^{-1}. The oven was programmed as follows: the initial temperature was 60 °C, then increased at 5 °C min^{-1} up to 150 °C and remained at this temperature for 6 min, then increased at 1 °C min^{-1} up to 200 °C, and finally increased at 18 °C min^{-1} up to 300 °C and remained at this temperature until a final run time of 90 min. The compounds analysed were hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT), (dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) in op' and pp' configurations; hexachlorocyclohexanes (HCHs in α, β, γ and δ isomers), chlordanes (α- and γ-chlordane, oxychlordane, heptachlor and heptachlor epoxide), mirex, methoxychlor, endosulfan and drins (aldrin, dieldrin, isodrin and endrin). OCP quantifications were performed in GC-ECD only after confirmation in GC/MS, which decreased the number of detected compounds, as further discussed.

Method detection limits (MDLs) were calculated as being three times the standard deviation after seven blank replicates. Spiked matrices were recovered within the acceptance ranges (i.e. 40–130% for at least 80% of the spiked analytes) suggested by QA/QC standards (Wade and Cantillo, 1994). Method validation was performed using NIST SRM 1945. Blanks were included in every analytical batch (usually 10–12 samples), and all data were blank subtracted. The average surrogate recovery was 93.27%.

SIA was performed as described in the first part of this work (Cipro et al., 2018a), with the same restrictions, especially the decarbonation of soil samples. Because of the negligible lipid content and influence in the results verified during previous studies (Cipro et al., 2017a, 2011), the samples did not undergo delipidation. The soil samples, however, underwent a decarbonation procedure to avoid the interference of carbonates, which are depleted in ^{13}C and could represent a bias in data interpretation. The decarbonation procedure was as follows: up to 100 mg of the ground sample were placed in a glass vial, 1 mL of HCl 0.1 N was added, and the vial was placed in a microwave oven; bubble formation was observed as an indicator of carbonate digestion. After 1 min, 100 μl of the same acid was added to verify that there was no more bubble formation. If that was the case, this first step was repeated many times as needed. Next, the vials were placed in a 60 °C dry bath (Techne) coupled to an evaporation system consisting of tubes for gently blowing filtered analytical quality compressed air into the vials overnight to evaporate the liquid acidic phase. The following day, the samples were recovered with 1 mL of Milli-Q water, homogenised in a microwave bath for 1 min, frozen and finally lyophilised.

SIA was performed as follows: an aliquot of ground prepared sample (0.8–1.5 mg for vegetation, 1.5–8 mg for colony soil, and 8–16 mg for control soil) was encapsulated in tin cups and injected in a Thermo Scientific Delta V AdvantageConFlo IV interface (NoBlank and SmartEA) coupled to a Thermo ScientificFlash EA1112 Elemental Analyser. Pee Dee Belemnite and atmospheric nitrogen were used as standards for the calculation of $\delta^{13}C$ and $\delta^{15}N$, respectively. On the basis of replicate measurements of internal laboratory standards, the experimental precision was found to be ±0.15‰ and ±0.20‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively.

2.3. Statistics

Statistics were performed using Microsoft Excel, Minitab 18 and Statsoft Statistica 10 and 13. Before analyses, data were checked for normality of distribution and homogeneity of variances by the Shapiro–Wilk and Brown–Forsythe tests, respectively. Statistically significant results were set at $\alpha = 0.05$ unless stated otherwise. Differences of colony and control datasets were assessed by t-tests, and Pearson/Spearman correlations were chosen because of their linear/monotonic nature and not necessarily to parametric/non-parametric analyses.

Normal distribution and log-link function generalised linear models (GLMs) were built as follows: POP concentrations as the dependent variable; matrix, main location, specific location, colony species and matrix species as categorical factors; and $\delta^{13}C$, $\delta^{15}N$, %C and %N as continuous predictors. Biologically relevant models were constructed by incorporating different variables and their interactions, considering the removal of continuous variables that were significantly correlated before model building in each dataset and its subsets as well. Model selection was based on the Akaïke's Information Criteria (AIC) adjusted for small sample sizes (AICc). The model with the lowest AICc value was considered to be the most accurate. Models with AICc values differing by less than 2 have a similar level of support in the data, and the model including the least number of parameters can be regarded as the most accurate, according to the principle of parsimony (Burnham and Anderson, 2002). The overall model support was assessed using Akaike weights (w_i), following Johnson and Omland (2004). Residual (R^2adj) analyses should be restricted to description and not be used in model selection (Burnham and Anderson, 2002). Only models with AICc values differing by less than 10 are presented.

3. Results and discussion

The most commonly present compounds in both vegetation and soil samples were HCB and PCBs. None of the PBDEs or HCHs exceeded the MDL in any sample. Because of a methodology modification regarding a previous work (direct GC-ECD quantification in Cipro et al., 2011 *versus* ECD quantification after GC-MS confirmation in the present study), the remaining POPs could be detected and quantified in only a small fraction of the samples and unfortunately do not allow further discussion: chlordanes were present in detectable amounts in only 5 samples, DDTs in 4, Drins in 4 and mirex in 5 from a total of 150 samples. Table 1 presents the data for HCB, PCBs, and SIA and centesimal composition for C and N. Nevertheless, the full dataset is provided as supplementary material (Table S1).

Regarding the concentrations presented in Table 1, some patterns appear. In a general way, for control samples, lichens and mosses presented similar PCB concentrations and both were one order of magnitude above those found in the control soils. Considering colony samples, the pattern is somewhat similar: lichens presenting concentrations slightly higher than mosses, and both are one order of magnitude higher than soil in average again. Therefore, the main difference in PCB distribution between colony and control samples would be a relative increase in lichen concentration in colony samples, meaning that, proportionally, most of the input derived from the colony ends up absorbed by this matrix, possibly by volatilisation and/or resuspension. HCB, in turn,

Table 1
Mean ± standard deviation results for POPs concentrations in (ng g^{-1} ww), SIA (‰) and C and N content (%) separated by location, colony species and matrix species. Colony species marked with an * indicate very sparse colonies.

Lichen

Main Location	Specific Location	Colony species	Matrix Species	n	ΣPCBs	HCB	$\delta^{13}C$	%C	$\delta^{15}N$	%N
Deception Island	Deception Island	Control	*Usnea antarctica*	3	65.5 ± 2.58	6.75 ± 2.07	-22.175 ± 3.69	30.8 ± 16.7	-0.680 ± 11.0	2.13 ± 1.22
Half Moon	Half Moon	Control	*Usnea aurantiaco-ater*	3	11.5 ± 14.8	1.43 ± 0.613	-22.300 ± 0.136	41.7 ± 0.264	-5.730 ± 0.947	0.960 ± 0.060
		Pygoscelis antarcticus	*Ramalina terebrata*	3	60.4 ± 1.58	3.72	-23.940 ± 0.840	41.3 ± 0.326	-0.343 ± 1.53	2.21 ± 0.466
KGI	Cape Vauréal	*Macronectes giganteus*	*Usnea antarctica*	3	5.65 ± 0.843	5.07 ± 1.25	-21.960 ± 0.701	40.1 ± 0.895	-0.028 ± 0.793	0.668 ± 0.025
	Ferraz	Control	*Usnea aurantiaco-ater*	3	5.04 ± 4.31	1.82 ± 0.187	-20.750 ± 0.125	39.4 ± 1.67	-6.612 ± 4.83	0.341 ± 0.046
	Punta Hennequin	*Catharacta sp**	*Usnea antarctica*	3	5.85 ± 3.87		-23.175 ± 0.403	40.4 ± 1.28	0.250 ± 1.35	1.64 ± 0.464
	Stenhouse	*Larus dominicanus**	*Usnea antarctica*	3	10.5 ± 5.38	6.02 ± 2.37	-22.395 ± 0.864	40.6 ± 0.886	-5.904 ± 0.814	0.526 ± 0.065
	Turret Point	Control	*Ramalina terebrata*	3	6.44 ± 4.69		-24.366 ± 0.191	40.5 ± 0.774	0.852 ± 0.922	1.67 ± 0.161
			Usnea antarctica	3	4.53 ± 2.96	7.14 ± 7.75	-22.702 ± 0.223	40.3 ± 1.21	-3.155 ± 0.555	1.40 ± 0.311
			Usnea aurantiaco-ater	3	10.8 ± 2.97	7.48 ± 0.321	-21.486 ± 0.297	39.9 ± 0.520	-5.875 ± 0.599	1.44 ± 0.076
		Phalacrocorax atriceps	*Ramalina terebrata*	3	1.72 ± 1.38	2.53 ± 0.413	-22.880 ± 0.152	38.5 ± 0.522	1.25 ± 0.420	1.50 ± 0.205
		Pygoscelis adeliae	*Usnea antarctica*	3	4.10 ± 0.529	3.55 ± 0.042	-23.339 ± 0.102	38.4 ± 1.39	-1.594 ± 1.83	1.42 ± 0.478
	Yellow Point	Control	*Usnea aurantiaco-ater*	1	1.87		-22.066	39.0	-1.949	1.34
Livingston	Hannah Point	*Macronectes giganteus*	*Ramalina terebrata*	2	4.65 ± 1.56	1.79	-24.050 ± 0.137	42.1 ± 3.29	-1.693 ± 7.07	1.85 ± 0.662
			Turgidiusculum complicatulum	1	0.710	0.845	-16.170	33.7	9.78	4.18
		Pygoscelis papua	*Ramalina terebrata*	3	2.86 ± 1.64	3.58 ± 1.98	-22.731 ± 0.333	40.2 ± 1.04	11.2 ± 0.588	2.02 ± 0.071
Nelson Island	Nelson Island	*Daption capense***	*Usnea aurantiaco-ater*	3	2.39 ± 0.433	3.42 ± 0.442	-22.837 ± 0.525	41.5 ± 2.18	5.04 ± 6.30	1.12 ± 0.171
Penguin Island	Penguin Island	Control	*Usnea aurantiaco-ater*	3	2.91 ± 0.560	2.55 ± 0.356	-22.184 ± 0.745	41.3 ± 0.328	-5.393 ± 0.864	0.869 ± 0.151
		Sterna vittata	*Ramalina terebrata*	3	3.08 ± 1.16	1.59 ± 0.559	-24.832 ± 0.335	34.1 ± 2.38	-2.575 ± 0.336	0.923 ± 0.022
			Usnea aurantiaco-ater	3	3.58 ± 0.828	4.70 ± 0.576	-23.389 ± 0.332	39.2 ± 0.299	-7.417 ± 0.159	0.724 ± 0.054

Moss

Main Location	Specific Location	Colony species	Matrix Species	n	ΣPCBs	HCB	$\delta^{13}C$	%C	$\delta^{15}N$	%N
Deception Island	Deception Island	Control	*Bryum pseudotrichetrum*	4	34.0 ± 31.2		-25.235 ± 1.34	34.2 ± 12.6	1.60 ± 6.59	1.80 ± 0.777
Half Moon	Half Moon	Control	*Sanionia uncinata*	3	3.20 ± 2.18		-24.298 ± 0.213	43.6 ± 0.392	13.1 ± 0.735	2.27 ± 0.315
		Pygoscelis antarcticus	*Prasiola crispa*	3	1.84 ± 0.014	47.0 ± 42.7	-21.493 ± 1.08	42.2 ± 1.57	0.426 ± 0.988	6.53 ± 0.130
KGI	Cape Vauréal	*Macronectes giganteus*	*Colobanthus quitensis*	3	21.9 ± 3.59		-26.233 ± 0.172	28.0 ± 6.61	8.79 ± 1.18	1.28 ± 0.235
			Polytrichastrum alpinum	3	3.98 ± 2.26	1.19	-26.085 ± 0.395	37.9 ± 3.96	12.2 ± 0.593	1.06 ± 0.071
	Chabrier Rock	*Pygoscelis antarcticus*	*Prasiola crispa*	3	37.9 ± 37.9	2.36	-20.553 ± 0.187	35.9 ± 2.59	12.8 ± 0.793	5.61 ± 0.360
	Ferraz	Control	*Sanionia uncinata*	3	6.01 ± 4.08		-27.509 ± 0.401	41.6 ± 1.53	6.27 ± 0.901	1.11 ± 0.276
	Punta Hennequin	*Catharacta sp**	*Sanionia uncinata*	3	20.4 ± 18.4		-25.882 ± 0.473	43.7 ± 0.924	9.51 ± 0.406	2.04 ± 0.094
	Punta Ullmann	*Larus dominicanus**	*Sanionia uncinata*	3	9.13 ± 6.76		-25.439 ± 0.424	35.4 ± 1.27	2.93 ± 0.742	1.65 ± 0.168
	Stenhouse	*Larus dominicanus**	*Sanionia uncinata*	3	6.21 ± 4.03	1.23 ± 0.787	-25.374 ± 0.599	31.4 ± 6.35	2.33 ± 0.241	1.52 ± 0.410
	Turret Point	Control	*Sanionia uncinata*	3	15.9 ± 20.1		-25.629 ± 0.172	33.0 ± 1.05	11.9 ± 0.113	2.62 ± 0.034
		Pygoscelis adeliae	*Sanionia uncinata*	3	2.06 ± 0.608		-26.593 ± 0.342	39.5 ± 0.939	11.5 ± 0.140	1.86 ± 0.062
	Yellow Point	Control	*Syntrichia sp*	1	1.41	6.55	-25.562	31.9	7.08	1.17
Livingston	Hannah Point	*Macronectes giganteus*	*Prasiola crispa*	3	1.72 ± 1.23		-28.007 ± 0.166	35.4 ± 2.28	12.7 ± 0.832	3.85 ± 0.256
		Phalacrocorax atriceps	*Prasiola crispa*	3	7.01 ± 4.17	60.0 ± 22.1	-21.806 ± 0.267	20.2 ± 4.53	21.0 ± 2.81	3.53 ± 0.621
		Pygoscelis antarcticus	*Prasiola crispa*	2	1.69 ± 0.431		-24.147 ± 0.114	25.6 ± 3.45	16.5 ± 0.727	3.85 ± 0.461
		Pygoscelis papua	*Prasiola crispa*	3	0.207 ± 0.021	61.3 ± 19.2	-20.161 ± 0.400	26.6 ± 3.32	15.1 ± 0.352	4.06 ± 0.588
Nelson Island	Nelson Island	*Daption capense***	*Sanionia uncinata*	3	1.16 ± 0.239		-25.513 ± 0.282	43.0 ± 0.890	19.5 ± 0.581	3.01 ± 0.219
Penguin Island	Penguin Island	Control	*Polytrichastrum alpinum*	3	2.72 ± 1.63		-27.178 ± 0.117	40.0 ± 6.86	5.43 ± 0.205	1.12 ± 0.255
		Pygoscelis antarcticus	*Prasiola crispa*	3	1.81 ± 1.23		-21.733 ± 0.448	37.6 ± 1.85	5.80 ± 1.08	6.83 ± 0.404

Soil Main Location	Specific Location	Colony species	Matrix Species	n	ΣPCBs	HCB	$\delta^{13}C$	%C	$\delta^{15}N$	%N
Deception Island	Deception Island	Control		3	0.763 ± 0.640	0.956 ± 0.440	-25.752 ± 0.234	0.095 ± 0.046	29.6 ± 3.12	0.053 ± 0.008
Half Moon	Half Moon	*Pygoscelis antarcticus*		3	0.420	404 ± 470	-28.470 ± 0.529	17.2 ± 2.12	20.1 ± 0.942	4.42 ± 0.262
KGI	Chabrier Rock	*Pygoscelis antarcticus*		3	2.14 ± 1.46	41.7 ± 6.42	-28.079 ± 0.924	21.6 ± 1.98	13.5 ± 5.19	9.58 ± 4.48
	Shag Island	*Phalacrocorax atriceps*		3	1.96 ± 0.693		-24.745 ± 0.409	9.87 ± 1.40	30.9 ± 0.802	2.76 ± 0.408
	Turret Point	Control		3	3.62 ± 2.97	8.49	-23.414 ± 0.294	0.540 ± 0.335	13.0 ± 7.42	0.156 ± 0.073
		Phalacrocorax atriceps		3	0.380	578 ± 655	-24.508 ± 0.401	8.66 ± 1.11	30.7 ± 0.718	2.52 ± 0.359
		Pygoscelis adeliae		3	5.88 ± 9.53	4.26 ± 0.047	-26.813 ± 0.267	9.65 ± 2.24	16.8 ± 0.746	2.03 ± 0.458
	Yellow Point	Control		1	0.960		-22.081	0.814	9.12	0.097
Livingston	Hannah Point	*Phalacrocorax atriceps*		3	1.92 ± 1.70		-24.423 ± 0.330	7.54 ± 1.42	25.7 ± 2.06	1.94 ± 0.626
		Pygoscelis antarcticus		3	1.87	18.8 ± 4.80	-28.139 ± 0.317	8.84 ± 0.938	18.8 ± 0.137	1.95 ± 0.186
		Pygoscelis papua		3	2.23 ± 2.64	16.5 ± 6.07	-27.402 ± 0.560	1.55 ± 0.127	22.4 ± 1.78	0.523 ± 0.051
Penguin Island	Penguin Island	Control		3	1.04 ± 0.332	0.394	-22.317 ± 0.232	1.23 ± 0.392	18.8 ± 0.441	0.228 ± 0.076
		Pygoscelis adeliae		3	12.5 ± 16.5		-28.461 ± 0.462	24.6 ± 2.22	17.4 ± 1.53	5.72 ± 0.637

presented mean concentrations in control samples in mosses approximately 50% higher than those found in lichens; which in turn presented values that were double those found in soil, all of them within the same order of magnitude. In colony samples, however, HCB presented overall concentrations in soil samples one order of magnitude above those found in mosses (with the exception of the Gentoo Penguin *Pygoscelis papua* from Hannah Point likely due to some local effect such as water percolation); and mosses, on the other hand, presented concentrations one order of magnitude higher than lichens. This leads to the conclusion that first, HCB is proportionally more excreted than PCBs. Moreover, HCB-dominated seabird profiles are reported in the literature (Carravieri et al., 2014) and, in this regard, similar data from chicks (Carravieri et al., 2017) evidentiate this phenomenon because most of their POP burden comes from that not accumulated by the mother. In addition, several previous works demonstrated proportionally lighter profiles in excreta (Roosens et al., 2007; Rudolph et al., 2016). Another consideration is yet to be made: the very high levels found in the Imperial Shag *Phalacrocorax atriceps* soil colony samples is likely because they form dense colonies in high and dry spots; thus, very little water percolation occurs when compared to penguin colonies for instance.

Second, volatilisation and/or resuspension play a proportionally lesser role in this case when compared to PCBs, likely because of its higher water solubility (therefore, a lower K_{ow} of HCB than most PCBs) than HCB and also a higher water dependency of mosses than that of lichens (see Cipro et al., 2011). This interpretation, however, hangs on the lack of data concerning the absorption mechanism of POPs in mosses. Simple diffusion can explain our results, but there is probably some non-linearity in the absorption process. The results for the even more water-soluble HCHs could enlighten this issue, but unfortunately, they have remained under the method detection level.

To obtain a deeper understanding of POP occurrence and dynamics, correlation analyses and PCA were performed. The Spearman correlation results are presented in Table 2, and PCA results are presented as supplementary material (Fig. S1).

Lichens in control sites presented two significant correlations for POPs. First, a positive one of PCBs and %N, meaning that a common source is possibly shared, likely atmospheric deposition from long-range transport (Montone et al., 2005, 2003), even if the role of colonies as sources by resuspension/volatilisation cannot be discarded at this point. A negative correlation for HCB and %C was also found for this subgroup, leading to two possible, non-mutually excluding hypotheses: the range of the resuspended/volatilised HCB from sources is greater than that of organic carbon and that some organic matter decomposition process might play a role as hypothesised in the previous work (Cipro et al., 2018a). This would mean that HCB might be liberated into the atmosphere, but the organic carbon might be trapped by some previous step of its biogeochemical cycle. Lichens in colony sites, however, presented several significant correlations. PCBs correlated positively with %C and negatively with $\delta^{15}N$, and HCB presented the same with %C and $\delta^{15}N$ and a negative correlation with %N. The first two correlations can be explained by the decomposition of animal-derived organic matter. The kinetic fractionations during the decomposition of deposited urea and uric acid lead to the formation of starkly ^{15}N-depleted highly volatile ammonia, whereas the remaining ammonium, much less volatile, was conversely ^{15}N-enriched (Heaton, 1986). This indicates that vegetation around the excrement zone is more exposed to ^{15}N-enriched inorganic nitrogen, whereas upland sites are more exposed to ^{15}N-depleted nitrogen (Cipro et al., 2018a, 2011). Moreover, and as a consequence of the previous statement, animal-derived nitrogen uptake is associated with large $\delta^{15}N$ ranges, with typical values ranging between 6‰ and 26‰ (e.g. Cipro et al., 2011; Cocks et al., 1998; Erskine et al., 1998; Mizutani and Wada, 1988). The negative correlation between HCB and %N is likely explained in an analogous manner to the previous negative correlation between this contaminant and %C in control sites, i.e. the contaminant might be released into the atmosphere, but this time, we hypothesise that the nitrogen might be trapped by some previous step of its biogeochemical cycle. Some of these same patterns were found for SIA and trace elements, particularly the more volatile Hg in the previous study (Cipro et al., 2018a).

Mosses in control sites presented no significant correlation for any of the contaminants. In colony sites, however, a negative

Table 2
Significant Spearman correlations among the studied variables.

		Control sites	Colony sites
Lichen	$\delta^{13}C$		
	%C	-HCB	+ΣPCBs, +HCB
	$\delta^{15}N$		+%N, -ΣPCBs, -HCB
	%N	+ΣPCBs	+$\delta^{15}N$, -HCB
	ΣPCBs	+%N	+%C, -$\delta^{15}N$
	HCB	-%C	+%C, -$\delta^{15}N$, -%N
Moss	$\delta^{13}C$	+%N	+%N, +HCB
	%C		
	$\delta^{15}N$		
	%N	+$\delta^{13}C$	+$\delta^{13}C$, -ΣPCBs
	ΣPCBs		-%N
	HCB		+$\delta^{13}C$
Soil	$\delta^{13}C$	+%C, -$\delta^{15}N$, +%N	-%C, +$\delta^{15}N$
	%C	+$\delta^{13}C$, -$\delta^{15}N$, +%N	-$\delta^{13}C$, -$\delta^{15}N$, +%N
	$\delta^{15}N$	-$\delta^{13}C$, -%C	+$\delta^{13}C$, -%C
	%N	+$\delta^{13}C$, +%C	+%C
	ΣPCBs		
	HCB		

correlation between PCBs and %N and a positive one between HCB and $\delta^{13}C$ were detected. The first correlation, besides the previously discussed occurrence in lichens, was also found in several trace elements (Co, Fe, Mn, Ni, Pb and V) analysed in the first part of the study (Cipro et al., 2018a). Some of these, particularly Mn and Pb, have already been reported with comparatively higher concentrations in Gentoo penguins (*P. papua*) faeces (Celis et al., 2015) and, therefore, might confirm the role of colonies as secondary sources for PCBs in an analogous manner. The correlation between HCB and $\delta^{13}C$ is, at a first glance, somewhat contrary to the previous literature that suggests that lower $\delta^{13}C$ values are related to moister habitats and marine influence (Cipro et al., 2011; Huiskes et al., 2006; Lee et al., 2009) because mosses are more water dependent than lichens, negative correlations were to be expected. However, this intra-group correlation means that the samples in dryer locations are more exposed to HCB, which is consistent with its comparatively higher volatility.

Soil presented no significant correlations for any of the contaminants in the present study neither for control nor for colony sites.

PCA results (Fig S1, supplementary material) reinforce the previously discussed correlations on the subsets of samples. Nevertheless, when broader data were considered, two interesting trends showed up: the pattern for all lichen samples taken together resembles closely that for its control sites, whereas the pattern for all moss samples taken together resembles even more closely that for its colony sites. This likely means that the mechanisms for POP exposure in control sites are more representative for all the lichens, i.e. long-range atmospheric transport is probably the major force in this case. Mosses, on the other hand, that presented patterns for the whole dataset even closer to the ones of the colony samples, allow an analogous interpretation: the input through water from colony percolation, as hypothesised in previous works (Cipro et al., 2018b, 2011) would be the more relevant specific exposure phenomenon. This similarity does not occur for soil samples, likely meaning that specific mechanisms at the local scale regulate each situation.

3.1. PCB chlorination level

The average relative chlorination number of the PCBs found in the matrices is shown in Fig. 1.

In all cases, the profile from the control sites was lighter than the one from colony sites, meaning that lower molecular weight congeners are more subject to undergo a transport process by resuspension/volatilisation. Yet, the results show congeners with 5 and 4 chlorine substitutions as the most frequent, in this order, except for lichens from control sites, in which case this order was inverted. These results reinforce the hypothesis that the exposure to PCBs occurs only through atmospheric deposition because of the lack of a true root system to absorb compounds from the substratum (Liu et al., 2010).

Moreover, the comparison with the data from King George Island only, in a study in which the samples were collected further away from any interference of seabird colonies (Cipro et al., 2011), shows PCB profiles in vegetation even lighter than the ones from the present study, reinforcing the fact that heavier congeners are less mobile regarding both primary (see von Waldow et al., 2010) and secondary sources: with the increase in the distance from colonies, the profiles become proportionally lighter because of a lesser input of heavier congeners and a higher input of lighter ones. Because heavier congeners are more environmentally persistent (Fuoco and Ceccarini, 2001), these also have to be taken into account when considering this proportionally heavier profiles from colonies. The overall profiles for both vegetation subgroups closely agree with those in previous literature, particularly for snow samples (Cipro et al., 2017b), which is subject to a much similar input mechanism from the atmosphere.

Soil samples, however, concentrated roughly 90% of their congeners in tetra-and penta-chlorinated congeners, with the latter representing approximately 75%. This distribution is corroborated by the literature (Roosens et al., 2007), where pentachlorinated congeners also prevailed. This distribution is due to the fact that most of the more persistent PCBs locate in the interval from 4 to 6 chlorine substitutions. As the authors stated, the profiles were dominated by comparatively heavier congeners indicating penguins as the main source rather than long-range atmospheric deposition, in which case a lighter profile would be expected.

3.2. Factors influencing PCB and HCB concentrations

To evaluate the relative importance of the categorical variables (main location, specific location, colony species and matrix

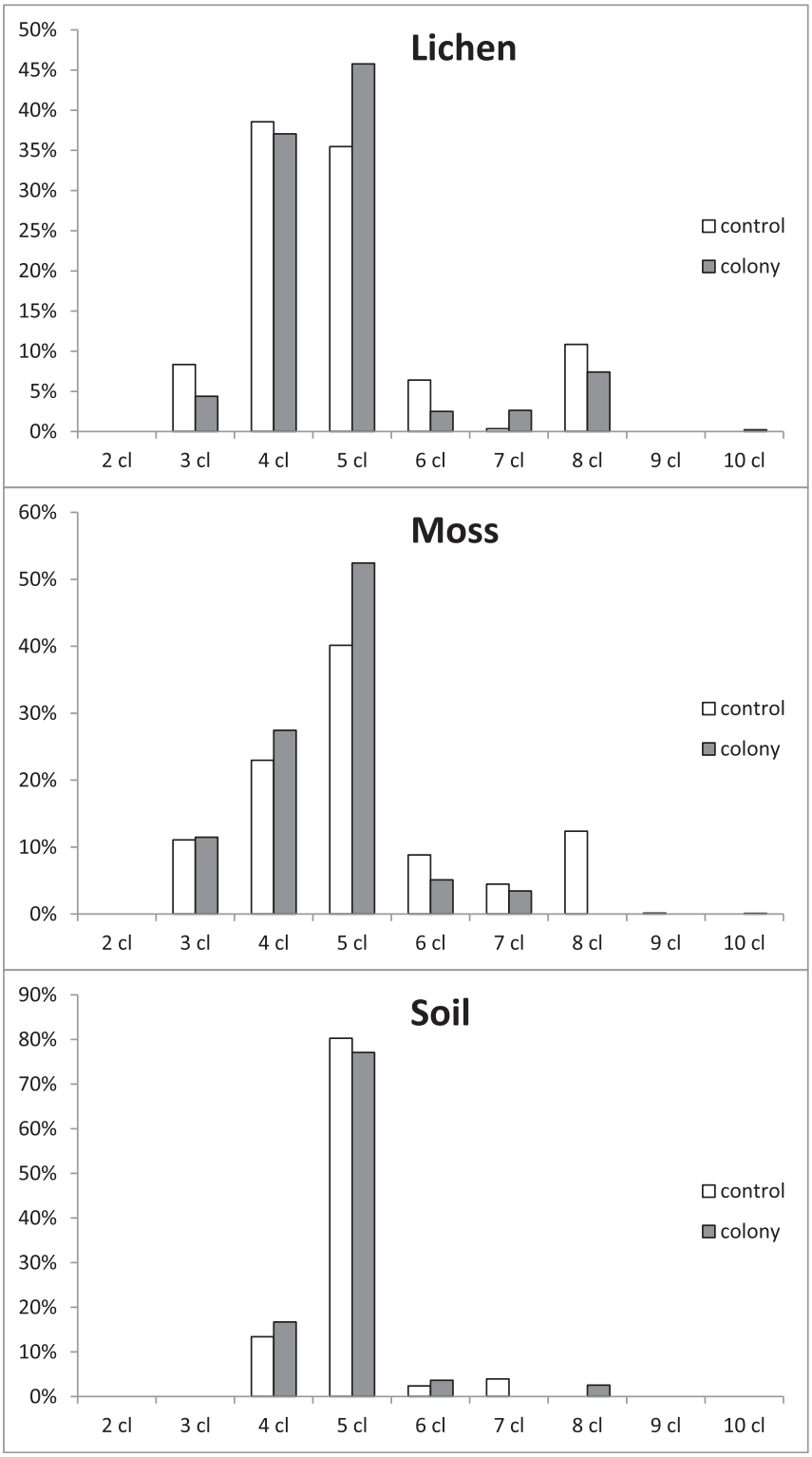

Fig. 1. Relative average PCBs chlorination number in the sampled matrixes.

Table 3
Parameters composition and relative weights (wi) for the most accurate model for each of the subsets according to AICc.

		PCBs		HCB	
		parameters	w_i	parameters	w_i
Lichen	control	Specific Location	0.24	–	–
	colony	$\delta^{13}C + \%C$	0.74	%C + Matrix Species	0.44
Moss	control	%C	0.52	–	–
	colony	$\delta^{15}N$	0.41	–	–
Soil	control	Specific Location	0.44	–	–
	colony	–	–	–	–

species), GLMs were built, and model selection was based upon AICc as previously explained. Results are presented in Table 3.

No model building was possible for the soil colony subgroup neither for PCBs nor for HCB because the number of samples under the MDL paired with other variables that were considered.

The results partially agree with those of the first part of the study. In a general way, models with less factors were more accurate in the present study, and those with only one factor was the most accurate in almost half of the cases. Specific location and %C were the frequently found factors in the chosen models, whereas for trace elements, specific location and matrix species seemed to play a more important role. This means that for POPs, because of their comparatively higher tendency to volatilise/resuspend than trace elements, the organic matter concentration and matrix species seem to have a less important role than the sheer quantity of organic matter, except for lichens. This is also in agreement with previous works suggesting that a migration into the liquid phase is likely to precede the absorption of POPs by more water-dependent organisms (Cipro et al., 2018b, 2011) when compared to lichens that will not interact with the substratum and absorb contaminants directly from the atmosphere (Yogui and Sericano, 2008).

3.3. Control sites versus colony sites

First, Tukey HSD/ANOVA tests were performed to understand why some control sites with apparently abnormal concentrations were in fact not grouped with their counterparts, by which it was confirmed that there were some hypothesised local sources other than the colonies. Even with apparent huge disparities among the data subsets, the only case when the homogenous groups after the post hoc test indicated a separation was for PCBs in lichens from Deception Island. Indeed, this site presented the highest concentrations for PCBs from control sites in both lichens and mosses but was the least contaminated control soil dataset. This pattern, however, was not observed for HCB. These results for vegetation are much higher than those found in previous literature (Cabrerizo et al., 2012), which presented higher levels of PCBs in locations closer to ancient stations (such as our location) than those found in the vicinity of more recent ones. This means that ancient contamination and eventual spillages might have not yet been completely revolatilised in a homogenous manner as the authors hypothesised (Cabrerizo et al., 2012), at least not in our area of sampling within Deception Island, different from theirs. In other words, if a seabird colony can act as a relevant secondary source, an abandoned station also can. Yet, we hereby hypothesise another factor, namely the local volcanic activity through fumaroles, which increases the temperature in some zones and favours the revolatilisation of PCBs and thus the exposure of vegetation to them.

The results for the t-tests of colony sites compared to the closest control site are presented in Table 4.

Lichens presented significant differences in POP concentrations between control and colony sites in two cases: for PCBs from a chinstrap penguin *Pygoscelis antarcticus* colony from Half Moon Island and for HCB from an Antarctic tern *Sterna vittata* colony from Penguin Island. In both cases, there was also a significant difference in the organic matter content, corroborating the statement that the role of nutrient source is not separated from that of contaminant source.

Mosses, on the other hand, did not present any significant difference in POP concentrations. Despite some huge differences found, they were not statistically significant likely because of the relatively high standard deviation in these cases. Moreover, in some cases, the control sites did not overcome the MDLs, and a proper comparison was not possible.

Soil samples, however, presented significant differences in one occasion: Adélie penguin *Pygoscelis adeliae* colony samples from Turret Point, King George Island, in similar conditions to the ones previously discussed for lichens: significant differences in organic matter content and also SIA indicating that the nutrient and contaminant sources are indeed the same. Again, the same issues were repeated: some samples presented elevated standard deviations suggesting higher levels than the control sites, but not in a statistically significant manner.

Comparing the matrices among them and also with the first part of the study (Cipro et al., 2018a), some trends seem clear. First, the accumulation of contaminants is correlated to the contents of organic matter and SIA results, but in different ways. In lichens, %N seems to be the common factor for the most contaminated samples, whereas in mosses, the response is somewhat mixed but $\delta^{13}C$ seems to correlate in the cases when differences from control to colony sites were the highest for both POPs and trace elements. Soil, in turn, presents %C clearly as the common factor for the highest differences in both studies. However, the interpretation for these specific cases is rather limited and has to be considered with caution. However, it is not possible to affirm that if one proxy correlates to a significant difference, then a high level for such proxy will imply a significant difference in POP levels between control and colony sites.

Considering all these together, a broader, more robust approach for interpreting both POP and trace element datasets is clearly given by AICc.

4. Conclusions

Seabird colonies act as secondary sources of PCBs and likely of HCB as well. The role of colonies as secondary HCB sources is not demonstrated as clear as for PCBs, particularly for lichens, likely due to two reasons. Given the comparatively higher HCB volatility, the 150 m distance adopted to qualify a site as control might not be fully adequate for this analysis and could be reviewed in the future. The second reason is that some control sites have again presented somewhat high concentrations likely because of local sources other than the colonies themselves. For other matrices, especially soil, the role of such colonies as relevant secondary sources seemed clearly

Table 4
Results for the t-tests of colony sites compared to the closest control site, by matrix. *, ** and *** stand for p = 0.05, 0.01 and 0.001 respectively. Underline indicates control values higher than colony ones. Colony species marked with an * indicate very sparse colonies.

Lichen

Main Location	Specific Location	Colony species	Matrix Species	n	ΣPCBs	HCB	$\delta^{13}C$ (‰)	%C	$\delta^{15}N$ (‰)	%N
Half Moon	Half Moon	*Pygoscelis antarcticus*	*Ramalina terebrata*	3	**		*		**	*
KGI	Cape Vauréal	*Macronectes giganteus*	*Usnea antarctica*	3			*			***
	Punta Hennequin	*Catharacta sp**	*Usnea antarctica*	3			***			**
	Stenhouse	*Larus dominicanus**	*Usnea antarctica*	3			*			*
	Turret Point	*Phalacrocorax atriceps*	*Ramalina terebrata*	3			***	*		
		Pygoscelis adeliae	*Usnea antarctica*	3			*			
Livingston	Hannah Point	*Macronectes giganteus*	*Ramalina terebrata*	2			***			
			Turgidiusculum complicatulum	1			***	**	**	***
		Pygoscelis papua	*Ramalina terebrata*	3					***	***
Nelson Island	Nelson Island	*Daption capense***	*Usnea aurantiaco-ater*	3			**			**
Penguin Island	Penguin Island	*Sterna vittata*	*Usnea aurantiaco-ater*	3		*		**	*	

Moss

Main Location	Specific Location	Colony species	Matrix Species	n	ΣPCBs	HCB	$\delta^{13}C$ (‰)	%C	$\delta^{15}N$ (‰)	%N
Half Moon	Half Moon	*Pygoscelis antarcticus*	*Prasiola crispa*	3			*		***	***
KGI	Cape Vauréal	*Macronectes giganteus*	*Colobanthus quitensis*	3			**	*	*	
			Polytrichastrum alpinum	3			*		***	
	Chabrier Rock	*Pygoscelis antarcticus*	*Prasiola crispa*	3			***	*	***	***
	Punta Hennequin	*Catharacta sp**	*Sanionia uncinata*	3			*		**	**
	Punta Ullmann	*Larus dominicanus**	*Sanionia uncinata*	3			**	**	**	*
	Stenhouse	*Larus dominicanus**	*Sanionia uncinata*	3			**		**	
	Turret Point	*Pygoscelis adeliae*	*Sanionia uncinata*	3			*	**	*	***
Livingston	Hannah Point	*Macronectes giganteus*	*Prasiola crispa*	3			***	**		**
		Phalacrocorax atriceps	*Prasiola crispa*	3			***	***	**	*
		Pygoscelis antarcticus	*Prasiola crispa*	2				**	*	*
		Pygoscelis papua	*Prasiola crispa*	3			***	***	*	**
Nelson Island	Nelson Island	*Daption capense***	*Sanionia uncinata*	3			**		***	***
Penguin Island	Penguin Island	*Pygoscelis antarcticus*	*Prasiola crispa*	3			***			***

Soil										
Main Location	Specific Location	Colony species	n	ΣPCBs	HCB	$\delta^{13}C$ (‰)	%C	$\delta^{15}N$ (‰)	%N	
Half Moon	Half Moon	*Pygoscelis antarcticus*	3			***	***		***	
KGI	Chabrier Rock	*Pygoscelis antarcticus*	3			**	***		*	
	Shag Island	*Phalacrocorax atriceps*	3			*	***	*	***	
	Turret Point	*Phalacrocorax atriceps*	3			*	***	*	***	
		Pygoscelis adeliae	3		**	***	**		**	
Livingston	Hannah Point	*Phalacrocorax atriceps*	3			*	**	*	**	
		Pygoscelis antarcticus	3			***	***		***	
		Pygoscelis papua	3			***	**		**	
Penguin Island	Penguin Island	*Pygoscelis adeliae*	3			***	***		***	

demonstrated. Soil seemed the most adequate matrix to study this phenomenon, and more detailed research is needed on vegetation because of specific uptake mechanisms that could not be deeply considered in the present study, particularly for lichens. Finally, future studies on population parameters and dynamics could clarify some of the interspecific differences found.

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Appendix A. Supplementary data

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