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Abstract

Pollutants in Antarctic ecosystems are largely attributed to long range atmospheric transport. However, previous studies confirmed seabird colonies as relevant secondary sources of organic and inorganic pollutants. When comparing these data, higher trophic level seabird colonies, small and sparse, did not influence results as strongly as lower trophic level birds large dense colonies. Thus, we cross examined results of stable isotopes and pollutants from lichens, moss and soil samples from Antarctic seabird colonies with their data for population parameters to understand how these variables influence each other. Results showed colonies clearly supplying As, Cd, Hg, Se, Zn, HCB and PCBs and corroborated other local sources. Penguin colonies were the most important pollutants sources hereby studied due to their sheer size and also their recent relative growth. Finally, results suggest climate change should likely increase the concentration of contaminants and the overall burden trapped in Antarctic terrestrial ecosystems.

Keywords: Pollutants, Secondary sources, Antarctica, seabird, colonies, population

1 - Introduction

Antarctica, in spite of being the most isolated continent on Earth, is far from exempt of the input of several sorts of contaminants, including Persistent Organic Pollutants (POPs), such as PCBs and organochlorine pesticides and also Trace Elements (TEs) such as Hg, as reported in literature (Bargagli et al. 2007; Corsolini 2009; Cipro et al. 2017a). These inputs are classically attributed to a phenomenon labelled "Global distillation", briefly: volatile contaminants evaporate in warmer regions, undergo long-range transport and condensate in colder regions. In a lesser scale, TEs have natural sources as well (Mão de Ferro et al. 2013; Cipro et al. 2018a). Conversely, the input due to the movement of organisms, i.e., biologically mediated, is typically insufficiently considered or even ignored (Blais et al. 2007). Nevertheless, Antarctica is home to a large avifauna of both endemic and migratory species. Some studies (e.g. Roosens et al. 2007; Choy et al. 2010), including recent ones by the authors of the present work (Cipro et al. 2018a, 2019), confirmed the role of seabird colonies in Antarctic ecosystems as relevant secondary sources of POPs and TEs as well.

Birds undergo bioaccumulation and biomagnification of such pollutants throughout their lives and, during their reproductive period, they gather in large numbers into large colonies and excrete and die on land. Both extant and abandoned colonies (Tatur et al. 1997; Liu et al. 2006; Outridge et al. 2016) represent a local source of not only nutrients (Smykla et al. 2007) to terrestrial and possibly coastal marine ecosystems (Cipro et al. 2018b), but also of POPs and TEs. Moreover, some material within the colony other than the excretion itself, such as eggs (Brasso et al. 2012), carcasses and prey (Emslie et al. 2014) also contribute to this input. The use of stable isotope analyses (SIA), in turn, was proven able to provide a deeper insight on the origin of both organic matter and pollutants in previous studies of the authors (Cipro et al. 2011, 2018a, 2019), particularly due to fractionation steps during the decay of animal derived organic matter (Heaton 1986) and the relative volatility of the decay products and the pollutants themselves (Cipro et al. 2011).

When comparing the data obtained within our previous works and published literature, in most cases colonies of birds of higher trophic level (therefore more prone to biomagnification), generally small and sparse, did not present an influence as stark and as frequent as the large and dense colonies of

birds with a lower trophic level, typically penguins. This demonstrated that the role of population parameters and dynamics needed further investigation

The aim of the present work is, therefore, to cross examine the results of stable isotopes of C and N, POPs and TEs analyses from lichens, moss and soil samples from Antarctic seabird colonies with results from population parameters and dynamics from the very same colonies in order to understand whether and how these variables influence their role as relevant secondary sources of these pollutants.

2 - Material and Methods

2.1 -Sampling

A subset of the samples is taken from previous works of the authors (Cipro et al. 2018a, 2019), i.e., the samples from the austral summers of 2013-14 and 2014-15. To those, a new subset has been added, with samples collected in 2017-18 (n=3 for algae, 22 for lichen, 21 for moss, 10 for soil), always in locations comprised within the previous dataset. In those previous studies, samples had been divided in two types: "colony" (within the colony itself for soil and within the colony or bordering it for vegetation) and “control” (at least 50m away from the respectively closest colony, and 150m in most cases). Since the interest of the present study is to understand the influence of population parameters in the concentrations of contaminants found in lichens, mosses and soil, only "colony" type samples were considered for the present work. Having said that, a total of 51 samples of lichen, 58 of moss and 36 of soil were suited for Spearman correlations, model building and PCA during statistical analyses from an overall total of 77, 79 and 47, respectively.

Samples for TEs and SIA of C and N were collected according to Cipro et al. (2018a). Briefly, samples were collected with plastic gear (spoons and tweezers) firstly rinsed in an acid bath (35mL L^{-1} nitric acid, 50 mL L^{-1} hydrochloric acid), then further rinsed with Milli-Q water. Soil samples were dug no deeper than 5 cm. They were chosen at the field mainly by their availability, avoiding fresh faeces which could mask the results for the formed ornithogenic soil. Samples were kept in hermetically sealed plastic bags.

Conversely, samples for organic contaminants analyses were collected according to Cipro et al. (2019). Briefly, all the samples for organics analyses were collected using steel gear (spoons and tweezers) previously rinsed with n-

hexane. Soil samples underwent the same restrictions as for TEs. Once collected, all samples for POPs analyses were wrapped in previously combusted (420°C, 4h) aluminium foil.

All samples were frozen aboard and kept frozen (-20°C) until arrival at the Marine Organic Chemistry Laboratory (LabQOM, University of São Paulo/Brazil). POPs analyses were performed at the very same facility with no drying process whatsoever. Samples for TEs and SIA underwent lyophilisation before being sent to the University of La Rochelle, France, where vegetation samples were ground to a fine powder in a ceramic mortar before analyses. Soil samples, in turn, were sifted in a 1mm mesh in order to avoid larger rocks and debris. Also, soil samples were not ground in any part of the process to assure that only the chosen granulometry would undergo analyses.

For seabird colonies, population estimations were performed according to a previous study of the authors (Petry et al. 2016). Briefly, population censuses were conducted during each species' incubation period (CCAMLR 2014). Three observers counted the nests to estimate the numbers of breeding pairs with one nest representing one breeding pair. The average of the three counts with an error no larger than 10 % (CCAMLR 2014) was used to estimate the population size. All species recorded were mapped with a handheld GPS receiver; breeding groups were mapped via edges, while smaller breeding areas or isolated nests were mapped by point estimation. These estimations are taken from yet unpublished field data from the authors. With the results from the austral summers of 2013-14 and 2017-18, two parameters were estimated: the average population for any given colony and its relative increase/decrease, from now on labelled as "dynamics".

2.2 - Analyses (already published and newly performed)

SIA for all samples were performed as described in the studies from which the samples from 2013-14 and 2014-15 were taken (Cipro et al. 2018a, 2019). SIA was performed as described in previous literature (Chouvelon et al. 2012; Cipro et al. 2017a), with some modifications, especially the decarbonation of soil samples. Due to the negligible lipid content and influence in the results verified during previous studies (Cipro et al. 2011, 2017a), all samples have not undergone delipidation. Soil samples, however, have undergone 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 was as follows: up to 100mg of ground sample were put in a glass vial, 1mL of HCl 0.1 N were added and the vial was placed in a microwave bath, observing bubble formation as an indicator of carbonates digestion. After one minute, 100 ml of the same acid was added to verify that no more bubble formation was shown. If that was the case, this first step was repeated as many times as needed. Next, the vials were put in a 60°C dry bath (Techne) coupled to an evaporation system consisting of tubes gently blowing filtered analytical quality compressed air into the vials overnight in order to evaporate the liquid acidic phase. The following day, samples were recovered with 1mL of Milli-Q water, homogenised in a microwave bath for 1 min, frozen and finally lyophilised. SIA themselves were performed as follows: an aliquot of ground prepared sample (0.8 up to 1.5mg for vegetation, 1.5 up to 8mg for colony soil) was encapsulated in tin cups and injected in a Thermo Scientific Delta V Advantage ConFlo IV interface (NoBlank and SmartEA) coupled to a Thermo Scientific Flash EA1112 Elemental Analyser. Pee Dee Belemnite and atmospheric nitrogen were used as standards for calculation of $\delta^{13}C$ and $\delta^{15}N$, respectively. Based on replicate measurements of internal laboratory standards, experimental precision is of ± 0.10‰ and ± 0.15‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively.

TEs analyses for all samples were also performed as described in the study from which the data from the two first comprehended seasons were taken (Cipro et al. 2018a). Such analyses were performed in the “Plateforme Analyses Elementaires" of LIENSs, University of La Rochelle, France, according to their own protocols, further detailed. Hg analyses were carried out with an Automatic Mercury Analyser spectrophotometer, ALTEC AMA 254, which does not require an acid digestion of the samples, following (Blévin et al. 2013). According to the Hg content, limit of detection and calibration curves, aliquots ranging from 4 to 150 mg of freeze-dried sample were directly analysed after being inserted in the oven of the apparatus. After drying, the samples were heated under an oxygen atmosphere for 3 min, and the Hg liberated and subsequently amalgamated on an Au-net. The net was then heated to liberate the collected Hg, which was measured by Atomic Absorption Spectrometry. Accuracy and reproducibility of the method were tested using dogfish liver(DOLT-2 and DOLT-5), dogfish muscle

(DORM-2) for the first two seasons, and for the last season, lobster hepatopancreas (TORT-2) certified reference materials (CRMs, all from the NRCC, National Research Council, Canada). All certified reference materials were analysed along with each set of samples, and recoveries of the certified values and recoveries of Hg ranged from 79 to 94%. Hg concentrations are expressed in dry weight (dw) in order to compensate eventual moisture loss during freezing and to facilitate comparison between tissues and with other studies. Blanks were analysed at the beginning and end of each set of samples, and the detection limit of the method was 0.05 ng.

The analyses of the other trace elements (Ag, As, Cd, Co, Cr, Cu,Fe, Mn, Ni, Pb, Se, V, and Zn) were performed as described by (Lucia et al. 2016): analyses were carried out using a Varian Vista-Pro ICPOES and a Thermo Fisher Scientific X Series 2 ICP-MS. Aliquots of the samples (from 90 to 257 mg) were digested with 6ml 67-70% HNO3 and 2ml 34-37% HCl (Fisher Scientific, trace element grade quality). This acidic digestion was performed overnight at room temperature, then using a Milestone microwave (30 min with constantly increasing temperature up to 120°C, then 15 min at this maximal temperature). Each sample was completed to 50 ml with milli-Q water. Three control samples (two CRMs and one blank) treated and analysed in the same way as the samples, were included in each analytical batch. CRMs were dogfish liver DOLT-4 (NRCC) and lobster hepatopancreas TORT-3(NRCC). Mean recovery rates were for the samples of the first two seasons, in regard to those CRMs, of 101% for As, 99% for Cd, 101% for Co, 94% for Cr, 96% for Cu, 94% for Fe, 91% for Mn, 99% for Ni, 89% for Pb, 99% for Se, 92% for V and 101%for Zn. For the 2017-18 season, average results were 77% for Ag, 97% for As, 97% for Cd, 93% for Co, 59% for Cr, 94% for Cu, 96% for Fe, 93% for Mn, 112% for Ni, 106% for Pb, 119% for Se, 87% for V and 98% for Zn in regard to PACS-1 (NRCC), DOLT-5 (NRCC) and IAEA-470 CRMs. TE concentrations are expressed in µg g^{-1}dw. Measurements were also validated by IAEA inter-calibration exercises (Coquery et al. 2001).

Regarding POPs, analyses were performed for three classes of contaminants: polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). All sample extraction followed the work from which data were taken (Cipro et al. 2019).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 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 1mL 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 rotoevaporation (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

Organics analyses themselves, however, underwent a different method for the 2017-18 season in regard to the previous ones. Samples for the 2013-14 and 2014-15 austral summers were analysed as described in the work from which data were taken (Cipro et al. 2019). 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 x 250μm x 0.25 μm, internally coated with5% 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, $\gamma$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.

In turn, samples for the 2017-18 were analysed with a different method due to the arrival of a new equipment at the LabQOM. The same organochlorine compounds have been analysed in a 7010B Agilent Technologies chromatograph coupled to a triple quadrupole mass spectrometry system (GC/MS/MS). An ultra inert chromatographic column (Agilent J&W, 30m x 250μm x 0.25 μm, internally coated with5% phenyl - 95% dimethylpolysiloxane) was used. The temperature ramp for the oven was programmed as follows: 50°C during 1 min, then increased at 20°C min^{-1} up to 200°C, then 10°C min^{-1} up to 300°C, remaining as so for 5 minutes for a total run time of 23.5 minutes. Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}. Temperatures for the injector, interface and source were at 300°C and the quadrupoles (Q1 and Q2) were at 150°C. The injected volume was of 1μL in pulsed splitless mode. MDL for this method was defined as 0.05 pg μl^{-1} for PCBs and 0.1 pg μl^{-1} for OCPs and PBDEs, for the extract.

2.3 - Statistics

Statistics were performed using Microsoft Excel, Minitab 18 and Statsoft Statistica 13. Prior to analyses, data was checked for normality of distribution and homogeneity of variances by the Shapiro-Wilk and Brown-Forsythe tests, respectively. Pearson/Spearman correlations were chosen because of their linear/monotonic nature and not necessarily to parametric/non-parametric analyses.

Model building was performed as follows: normal distribution and generalised linear models (GLM) were constructed using the concentration of the contaminant of interest as dependent variable, matrix, main location, specific location, colony species and matrix species as categorical factors; $\delta^{13}C$, $\delta^{15}N$, %C, %N, average population and dynamics 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).

Principal Component Analyses (PCA) were performed with the continuous predictors previously cited in addition to the contaminants concentrations. Four components were included in every calculation, which was repeated for the whole dataset and each matrix subset as well.

Only contaminants described as sources or likely sources (POPs: HCB and PCBs; TEs: As, Cd, Hg, Se, and Zn) in the previous studies by the authors (Cipro et al. 2018a, 2019) were included in the models built (as dependent variable) and in the PCA as well.

3 - Results and discussion

Mean results for the POPs (HCB and PCBs) and TEs (As, Cd, Hg, Se, and Zn) verified as source or likely source in the previous studies (Cipro et al. 2018a, 2019), Main location, specific location, colony species, matrix species (when suitable), sampling number, SIA, C and N content for the 2017-18 austral summer are given in Table 1. The full dataset for the 2017-18 season is given as supplementary material (ST1).

Table 1 - Mean results for TEs (in µg g^{-1} dw), POPs (in ng g^{-1}dw), SIA (‰), C and N content (%) for the 2017-18 season. Colony species marked with an * indicate very sparse colonies. N/D stands for species not defined.

Main Location	Specific Location	Colony species	Matrix species	n	%C	%N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	As	Cd	Se	Zn	Hg	HCB	ΣPCBs
Deception Island	Whalers Bay	Control	N/D	3	3.22 ± 1.09	0.566 ± 0.131	-17.73 ± 0.47	17.98 ± 4.70	24.8 ± 4.83	0.022 ± 0.006	<0.04	13.8 ± 2.63	0.001 ± 0.000	<MDL	45.0

Lichen

Main Location	Specific Location	Colony species	Matrix species	n	%C	%N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	As	Cd	Se	Zn	Hg	HCB	ΣPCBs
Deception Island	Whalers Bay	Control	*Usnea sp*	3	39.7 ± 2.55	0.989 ± 0.084	-24.03 ± 0.35	-8.61 ± 0.33	0.356 ± 0.034	0.154 ± 0.033	1.43 ± 0.144	30.9 ± 1.07	0.240 ± 0.010	0.057	13.7
KGI	Arctowski	*Pygoscelis papua*	*Usnea sp*	4	39.3 ± 3.94	2.64 ± 1.26	-20.39 ± 3.21	3.78 ± 4.38	2.72 ± 1.52	0.093 ± 0.047	2.35 ± 1.34	43.5 ± 13.9	0.126 ± 0.038	<MDL	<MDL
	Hennequin Point	*Catharacta sp**	*Usnea sp*	1	36.6	0.762	-21.785	-2.387	0.760	0.069	2.39	29.0	0.093	0.014	10.7
		*Larus dominicanus**	*Usnea sp*	1	42.5	0.876	-22.358	-7.617	0.316	0.024	0.910	10.7	0.109	0.048	16.5
	Punta Plaza	Control	*Usnea sp*	1	36.7	0.699	-22.769	-8.652	0.185	0.040	1.28	14.8	0.250	0.069	22.9
	Punta Ullmann	*Larus dominicanus**	*Usnea sp*	1	40.3	0.697	-23.136	-2.562	0.575	0.084	1.16	13.0	0.119	0.036	12.4
	VLF	*Catharacta sp**	*Usnea sp*	1	41.5	0.471	-22.180	-7.834	0.444	0.042	1.85	23.7	0.169	<MDL	54.1
Livingston Island	Hannah Point	*Macronectes giganteus*	*Usnea sp*	3	39.2 ± 3.31	1.18 ± 0.037	-22.78 ± 0.86	-4.66 ± 1.89	1.11 ± 0.466	0.070 ± 0.005	2.19 ± 0.314	14.8 ± 5.93	0.205 ± 0.020	0.067 ± 0.012	10.6 ± 2.96
		Pygoscelis antarctica	*Ramalina terebrata*	3	39.3 ± 4.85	1.92 ± 0.375	-23.67 ± 0.37	7.95 ± 0.42	0.330 ± 0.024	0.092 ± 0.058	0.710 ± 0.022	12.1 ± 3.05	0.149 ± 0.040	0.033 ± 0.005	12.9 ± 0.705
Penguin Island	Penguin Island	*Sterna vittata*	*Usnea sp*	1	27.4	0.871	-24.916	-3.805	0.193	0.019	2.29	14.8	0.504	0.034	16.1
Two Summits	Two Summits	*Macronectes giganteus*	*Usnea sp*	3	43.3 ± 1.00	1.04 ± 0.136	-20.51 ± 0.87	-6.92 ± 0.10	0.429 ± 0.005	0.073 ± 0.006	1.40 ± 0.245	12.4 ± 3.50	0.184 ± 0.008	0.023 ± 0.006	12.9 ± 2.17

Moss

Main Location	Specific Location	Colony species	Matrix species	n	%C	%N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	As	Cd	Se	Zn	Hg	HCB	ΣPCBs
Deception Island	Whalers Bay	Control	N/D	3	2.70 ± 1.77	0.155 ± 0.071	-25.64 ± 0.93	4.31 ± 2.76	0.824 ± 0.129	0.032 ± 0.006	0.669 ± 0.089	17.3 ± 2.66	0.009 ± 0.004	0.001	4.57
KGI	Arctowski	*Pygoscelis papua*	N/D	1	14.0	0.945	-26.841	10.4	5.88	0.074	2.47	63.1	0.041	0.011	9.24
	Hennequin Point	*Catharacta sp**	N/D	1	11.2	0.812	-24.575	2.96	1.99	0.131	2.62	49.6	0.041	0.006	9.97
		*Larus dominicanus**	N/D	1	39.4	1.98	-25.546	7.68	1.74	0.064	2.42	30.0	0.097	0.012	19.9
	Punta Plaza	Control	N/D	1	36.1	2.04	-25.664	8.36	2.60	0.307	4.53	42.0	0.112	0.003	16.2
	Punta Ullmann	*Larus dominicanus**	N/D	1	30.8	2.48	-24.201	5.73	3.09	0.193	3.99	43.2	0.068	0.005	11.5
	VLF	*Catharacta sp**	N/D	3	28.6 ± 3.49	1.34 ± 0.150	-25.91 ± 0.03	7.03 ± 0.39	4.98 ± 0.575	0.173 ± 0.016	3.12 ± 0.271	48.9 ± 1.99	0.060 ± 0.003	0.005	13.0
Livingston Island	Hannah Point	*Macronectes giganteus*	N/D	3	7.34 ± 0.549	0.560 ± 0.025	-25.42 ± 0.29	11.33 ± 0.72	4.31 ± 0.122	0.126 ± 0.004	2.19 ± 0.138	48.5 ± 0.874	0.046 ± 0.003	0.001 ± 0.000	11.4 ± 0.511
		Pygoscelis antarctica	*Colobanthus quitensis*	3	29.1 ± 1.03	1.94 ± 0.070	-24.87 ± 0.32	3.08 ± 0.58	2.33 ± 0.117	0.236 ± 0.026	1.34 ± 0.093	54.9 ± 1.03	0.029 ± 0.002	0.005 ± 0.001	14.6 ± 1.50
Penguin Island	Penguin Island	*Pygoscelis adeliae*	*Prasiola crispa*	1	14.7	2.69	-23.820	22.8	6.94	1.47	16.9	175	0.051	0.009	8.68
Two Summits	Two Summits	*Macronectes giganteus*	N/D	3	42.8 ± 1.32	3.09 ± 0.185	-24.97 ± 0.36	6.90 ± 1.54	1.96 ± 0.494	0.998 ± 0.217	4.65 ± 1.17	38.1 ± 1.75	0.241 ± 0.051	0.003 ± 0.001	12.4 ± 0.391

Soil

Main Location	Specific Location	Colony species	n	%C	%N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	As	Cd	Se	Zn	Hg	HCB	ΣPCBs
KGI	Hennequin Point	*Catharacta sp**	1	1.46	0.611	-23.801	0.735	1.77	0.113	1.59	65.1	0.009	<MDL	11.1
	VLF	*Catharacta sp**	1	1.68	0.712	-23.855	5.65	8.74	0.138	2.53	80.7	0.015	<MDL	14.1
	Yellow Point	Control	1	0.934	0.580	-24.596	-2.274	12.1	0.380	2.75	71.5	0.008	0.001	5.88
Livingston Island	Hannah Point	*Pygoscelis antarctica*	3	10.8 ± 1.65	2.29 ± 0.247	-28.69 ± 0.28	23.29 ± 0.14	10.8 ± 0.522	2.77 ± 0.105	32.6 ± 2.88	291 ± 10.6	0.241 ± 0.012	0.025 ± 0.008	16.4 ± 1.82
Penguin Island	Penguin Island	*Pygoscelis adeliae*	1	9.76	2.76	-28.649	28.1	8.41	2.04	22.4	234	0.082	0.050	4.05
Two Summits	Two Summits	*Macronectes giganteus*	3	32.3 ± 2.05	3.93 ± 0.102	-23.28 ± 0.06	13.41 ± 0.12	7.55 ± 0.238	3.80 ± 0.316	22.8 ± 1.06	77.6 ± 6.61	1.17 ± 0.134	0.012 ± 0.003	12.1 ± 1.87

As previously stated, the whole sample set is comprised of the data in Table 1 in addition to two previous publications of the authors (Cipro et al. 2018a, 2019). The results for this last season come overall in agreement with the two previous ones, with some noticeable features. Firstly, for this last season, a set of algae samples was collected from a seasonal melting water lake (likely brackish indeed due to seawater infiltration, since one of its borders was only a few meters away from the shore) in Deception Island. These samples presented the second highest average PCBs levels within the subset, reinforcing the conclusion of the previous study (Cipro et al. 2019) that there is likely a local source of this contaminant group in the area. Moreover, the levels of As in this particular matrix are two to three orders of magnitude higher than any other for this season, all matrixes comprised. This has definitely not been the case in previous analyses (Cipro et al. 2018a), raising the likelihood of a local source for this trace element as well. A previous study on TEs levels in water from Antarctic lakes (Conca et al. 2017) showed that TEs concentrations in these environments depend not only on the marine aerosol but also on the different geomorphological conditions of the lake, such as the total surface area, the elevation and the mineralogical characteristics of soils surrounding it. Nevertheless, no concentrations of this order of magnitude have been found in any of the matrixes from any of the studies in this location. Since this element has both natural and anthropic sources, further research is needed in order to assess a likely pathway for the impressive concentration hereby found.

Yet again, the same previous reasoning may be repeated for some other cases: concentrations from control sites overcame colony ones, indicating likely local sources of contaminants. This is true for PCBs, HCB and Hg in lichens from Punta Plaza and PCBs, Hg and Cd in mosses from the same location. Again, the discussion of control samples is limited to this section of the study.

3.1 - Correlations

Pearson correlations have been calculated only in order to avoid multicollinearity during model building as previously stated. For data interpretation, Spearman correlations were chosen due to their monotonic nature and biological meaning, and are presented for the whole colony dataset in Table 2.

Table 2 - Significant Spearman correlations for the whole colony dataset

All samples		Lichen	
$\delta^{13}C$	+%C,- $\delta^{15}N$,-As,-Cd,-Se,-Zn,-Dynamics	$\delta^{13}C$	+As,-Hg
%C	+ $\delta^{13}C$,- $\delta^{15}N$,-As,-Cd,-Se,-Zn,+Hg	%C	-Se,+PCBs
$\delta^{15}N$	- $\delta^{13}C$,-%C,+%N,+As,+Cd,+Se,+Zn,-PCBs	$\delta^{15}N$	+%N,+Cd,-Se,+Zn,-Hg,-PCBs,+Average
%N	+d15N,+As,+Cd,+Se,+Zn,-PCBs,+Average	%N	+ $\delta^{15}N$,+As,+Cd,-Se,+Zn,-Hg,+Average
As	- $\delta^{13}C$,-%C,+ $\delta^{15}N$,+%N,+Cd,+Se,+Zn,+Average	As	+ $\delta^{13}C$,+%N,+Cd,+Zn,-Hg,+Average
Cd	- $\delta^{13}C$,-%C,+ $\delta^{15}N$,+%N,+As,+Se,+Zn	Cd	+ $\delta^{15}N$,+%N,+As,+Zn,+Average
Se	- $\delta^{13}C$,-%C,+ $\delta^{15}N$,+%N,+As,+Cd,+Zn,-PCBs	Se	-%C,- $\delta^{15}N$,-%N,+Hg,-Average
Zn	- $\delta^{13}C$,-%C,+ $\delta^{15}N$,+%N,+As,+Cd,+Se	Zn	+ $\delta^{15}N$,+%N,+As,+Cd,-Hg,+Average
Hg	+%C,-Average	Hg	- $\delta^{13}C$,- $\delta^{15}N$,-%N,-As,+Se,-Zn,+HCB,-Average
HCB	-PCBs,-Dynamics	HCB	+Hg,-PCBs
PCBs	- $\delta^{15}N$,-%N,-Se,-HCB,+Dynamics	PCBs	+%C,- $\delta^{15}N$,-HCB
Average	+%N,+As,-Hg	Average	+ $\delta^{15}N$,+%N,+As,+Cd,-Se,+Zn,-Hg,
Dynamics	- $\delta^{13}C$,-HCB,+PCBs	Dynamics	

Moss		Soil	
$\delta^{13}C$	+%N,+Cd,+Se,+Zn,+HCB,+Average,-Dynamics	$\delta^{13}C$	-As,-Cd,-Se,-Average,-Dynamics
%C	+%N,-As,-Zn,+Hg	%C	- $\delta^{15}N$,+%N,+As,+Cd,+Se,+Hg,+Dynamics
$\delta^{15}N$	-PCBs	$\delta^{15}N$	-%C,-Average
%N	+ $\delta^{13}C$,+%C,+Cd,+Se,+Hg,+HCB,-PCBs,+Average	%N	+%C,+As,+Cd,+Se,+Zn,+Hg,+Dynamics
As	-%C,+Se,+Zn,+Average	As	- $\delta^{13}C$,+%C,+%N,+Cd,+Se,+Hg,+PCBs,+Dynamics
Cd	+ $\delta^{13}C$,+%N,+Se,+Zn,+Hg	Cd	- $\delta^{13}C$,+%C,+%N,+As,+Se,+Zn,+Hg,+Dynamics
Se	+ $\delta^{13}C$,+%N,+As,+Cd,+Zn,+Hg	Se	- $\delta^{13}C$,+%C,+%N,+As,+Cd,+Zn,+Hg,+Dynamics
Zn	+ $\delta^{13}C$,-%C,+As,+Cd,+Se	Zn	+%N,+Cd,+Se,+Hg,+Dynamics
Hg	+%C,+%N,+Cd,+Se	Hg	+%C,+%N,+As,+Cd,+Se,+Zn
HCB	+ $\delta^{13}C$,+%N,-PCBs	HCB	-PCBs
PCBs	- $\delta^{15}N$,-%N,-HCB,-Average	PCBs	+As,-HCB
Average	+ $\delta^{13}C$,+%N,+As,-PCBs	Average	- $\delta^{13}C$,- $\delta^{15}N$
Dynamics	- $\delta^{13}C$	Dynamics	- $\delta^{13}C$,+%C,+%N,+As,+Cd,+Se,+Zn

Overall, the average population presented significant positive correlation with %N and As. This reinforces the role of colonies of sources of both organic matter and As, which had been classified as likely supplied by colonies in our previous study (Cipro et al. 2018a). The significant negative correlation of the average population to Hg might be due to several factors, including the redistribution via resuspension/revolatilisation, in addition to speciation processes between its volatile and deposited forms in a local scale (Góngora et al. 2018), and also due to the effect of different matrixes comprised in this analysis, since they have previously shown very different, and oftentimes,

opposite behaviour regarding the absorption of contaminants (Yogui and Sericano 2008; Cipro et al. 2011; Colabuono et al. 2015). The population dynamics, in turn, presented positive significant correlation with PCBs, meaning that, in general, one can assume that recent inputs due to colony growth are likely absorbed by soil and vegetation around the colonies. Conversely, two significant negative correlations were found: with $\delta^{13}C$ and HCB. This could be interpreted as, firstly, that organic matter freshly supplied by the colonies is relatively depleted in ^{13}C and also that the growth of the colonies is somehow related to lower levels of HCB, a pollutant of relatively high volatility (Colabuono et al. 2015) and, therefore, mobility. Because of that, two non exclusive hypotheses arise: it might be there is an important temporal shift in HCB revolatilisation from growing colonies, which could bias the data in the way we found, partially supported by the fact that colony samples presented overall soil concentrations one order of magnitude higher than mosses, and these latter, one order of magnitude higher than lichens (Cipro et al. 2019). Also, we hypothesise that an eventual decline in large colonies with a considerable pollutants burden to be supplied in and around them and also a growing population in relatively new colonies could definitely bias the data in the way we found out, which is highly consistent with the reports from literature (Petry et al. 2016).

Lichen samples presented significant correlations only with the average population and not with the dynamics, which was not expected since this matrix absorbs contaminants directly from the atmosphere (Yogui and Sericano 2008) and should, at a first glance, reflect changes in the input to this compartment. This result, however, reinforces the importance of the average population variable, meaning that some processes in the pathways from colony to lichen or even the slow growth rate of these organisms (Sancho and Pintado 2004) when compared to the birds input, might play a more important role than the dynamics of atmospheric concentrations of pollutants. In turn, several significant correlations with the average population appeared: $\delta^{15}N$, %N, As, Cd and Zn, corroborating the role of colonies of relevant sources of organic matter and these trace elements in the long term. The positive correlation with $\delta^{15}N$ is again somewhat unexpected since a previous work (Cipro et al. 2011) found a general trend of volatile contaminants correlating negatively to $\delta^{15}N$ due to fractionation

during ammonia formation resulting from the decay of animal derived organic matter (Heaton 1986). This previous work, however, comprehended samples near and far from colonies with no strict separation as in the present study, which might have played a role in this result. Moreover, literature indicates a wide range of $\delta^{15}N$ even within the same colony (Wainright et al. 1998; Erskine et al. 1998) as result of the previously cited process and likely of the mixing of old and new guano. Yet, there is also another factor at play: the fact that the influence of colonies might go beyond the 50/150m limit adopted in our previous works. More recent literature suggests that this influence, at least for nutrients, might reach over 1000m (Bokhorst et al. 2019). The significant negative correlation with Hg and Se might have a similar explanation to HCB in the overall case, particularly for Hg due to its volatility in several chemical species (Bloom and Fitzgerald 1988).

Moss samples presented significant correlations for the average population with $\delta^{13}C$, %N and As, again confirming the role of colonies as source of organic matter and As, particularly because mosses are highly sensible to deposited N due to the lack of a true root system to uptake it from the substratum (Liu et al. 2010). A significant negative correlation with PCB levels might, in addition to the previously hypothesised explanation for As and HCB, be due to its comparatively low solubility during interaction with the water phase (Cipro et al. 2011), since mosses, when compared to lichens, are much more water dependent and have tremendous ability to sequester water (Glime 2007). Colony dynamics, on the other hand, presented a significant negative correlation to $\delta^{13}C$, contrary to the average population parameter, which presented positive correlation with the same variable. This could suggest a process during which the input organic matter undergoes an important fractionation favouring the enriched ^{13}C in the long term by means of organic matter decay or water solubility for the same reasons as previously stated.

Soil samples, which have proven to be the most reliable to assess colonies as relevant pollutants sources (Cipro et al. 2018a, 2019), presented two significant negative correlations of the average population, with $\delta^{13}C$ and $\delta^{15}N$. In an analogous manner to what was previously discussed for lichens, this is somewhat contrary to our previous findings, which had presented a similar profile

for control samples only. Population dynamics presented the same significant negative correlation to $\delta^{13}C$ in a similar way to mosses and the overall sample set. Nevertheless, several significant positive correlations appeared: with %C, %N, As, Cd, Se and Zn, corroborating again the role of colonies as sources of organic matter and several TEs. Indeed, of those four, three (As, Se, and Zn) had been classified (Cipro et al. 2018a) as likely sourced by colonies, but the present data makes it clear that colonies indeed function as clear sources of those TEs.

Considering the other correlations, in all cases HCB and PCBs correlated negatively to one another. The same trend had been noticed, in a lesser degree, in a previous work for the whole data and also the lichens subset (Cipro et al. 2011). In any case, this reinforces the difference in mechanisms and pathways between these two contaminants, likely due to their volatilities and excretion rate in seabird colonies (Roosens et al. 2007; Rudolph et al. 2016; Finger et al. 2017).

In turn, when the congeneric composition (the sum of the concentrations of congeners according to the chlorination level) of PCBs is compared to HCB, some patterns arise. For lichen samples, significant correlations for HCB are found with penta- and hexa-chlorinated PCBs. For mosses, HCB correlates significantly with tetra-, penta-, hexa- and hepta-chlorinated PCBs. Finally, for soils, significant correlations are found between HCB and penta- and hexa-chlorinated PCBs. This pattern had already been presented in previous literature and is likely due to the fact that most of the more persistent PCBs locate in the interval from 4 to 6 chlorine substitutions (Cipro et al. 2019, Roosens et al., 2007).

3.2 - Factors influencing POP and TE concentrations

The relative importance of categorical variables together with continuous predictors was assessed by means of GLM building and model selection using AICc, as previously described. The results for the model building for each pollutant of interest as dependent variable is presented in Table 3.

Table 3 - Parameters for the best GLM for each contaminant of interest according to AICc

Dependent variable	Parameters for the best model	w_i
As	$\delta^{15}N$, Average, Dynamics, Main location, Matrix species	0.022
Cd	%C, Average, Specific location, Colony species, Matrix species	0.021
Hg	%C, Colony species, Matrix species	0.038
Se	$\delta^{13}C$, %N, Main location, Colony species, Matrix species	0.052
Zn	%C, %N, Dynamics, Colony species	0.103
HCB	-	-
PCBs	%N, Dynamics, Colony species, Matrix species	0.247

Unfortunately, due to the fact that some results remained under the MDLs, it was only possible to build the GLMs for the whole colony sample set and not for the subsets broken down by matrix. Nevertheless, with the aid those models, some patterns arise. Out of the seven contaminants of interest, model building was possible for six and in four of them a populational parameter appears in the most accurate model, being the average population present once, population dynamics twice and both of them together once. This information coupled to the fact that the "colony species" factor also appears four times allows the conclusion that penguin colonies, the overall most populous and most growing (with a few exceptions) within the present study, are therefore, the ones that most likely represent the most important sources of contaminants for these terrestrial ecosystems. The "matrix species" factor corroborates data from previous studies (Cipro et al. 2018a, 2019) for HCB in lichen colony samples, Hg in lichen control and colony samples, and mosses colony samples; and also for Cd in lichen control and colony samples, and mosses control and colony samples as well.

With the exception of PCBs and likely Zn, the models for all other contaminants presented rather low Akaike weights (between 2.2 and 5.5%), meaning that their explanatory power was rather divided and some other tools as the previously discussed correlations or a PCA could greatly enhance data interpretation.

3.3 - PCA

In order to obtain a better understanding of how the variables relate, PCA was performed and its results are presented in Figure 1 for all colony samples and also broken down by matrix subset.

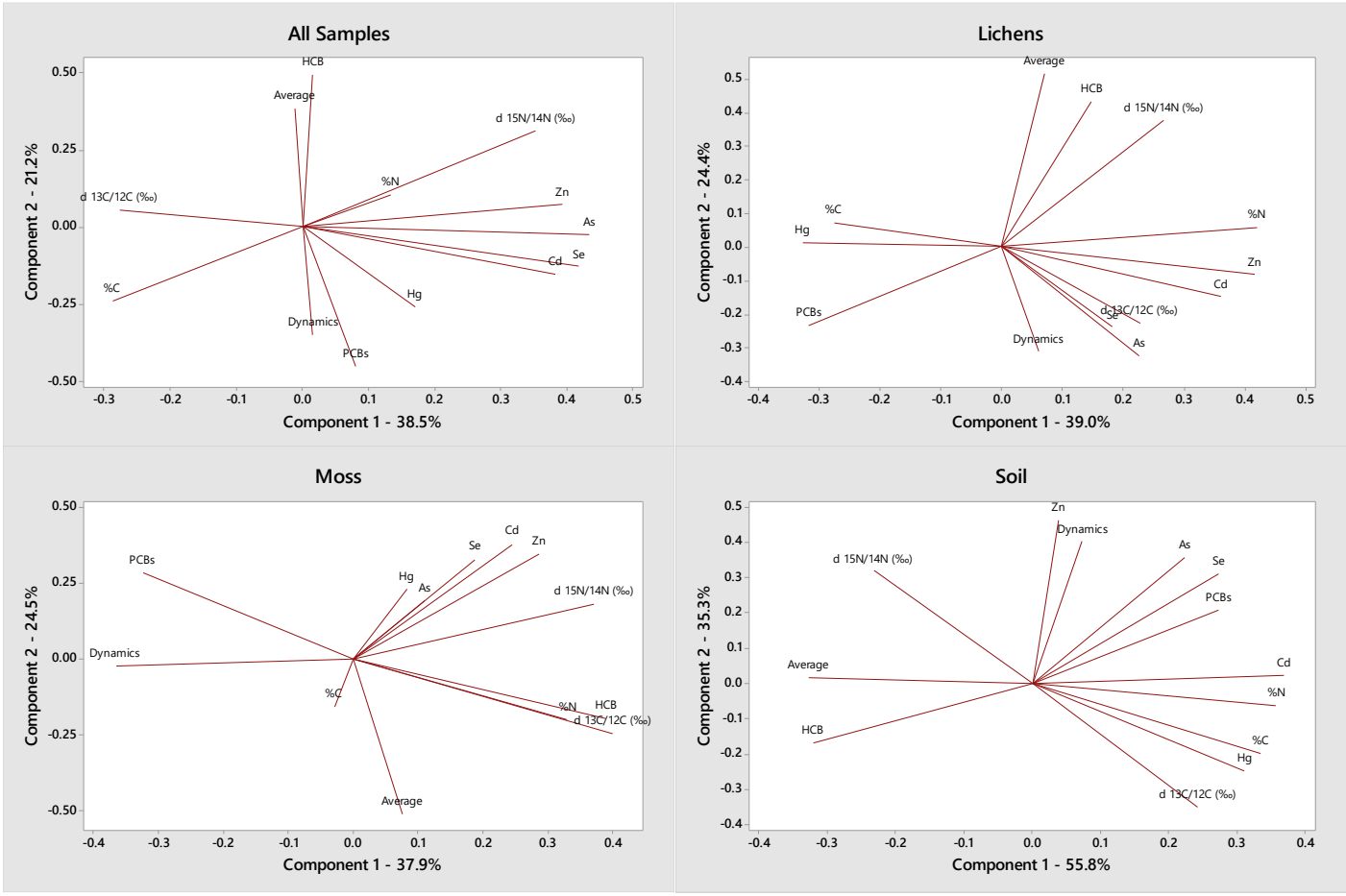

Figure 1 - PCA for the whole dataset and broken down by matrix subset

Firstly, it is noticeable that the opposite behaviour of HCB and PCBs previously inferred from correlations is corroborated by the PCA results for the whole dataset and each of the subsets broken down by matrix. As a general trend, the behaviour of HCB was more likely correspondent to the average population (except for moss), whereas those of PCBs was closest to population dynamics (except for lichens). These exceptions could be likely explained by the relatively high volatility and interference from the water phase for the former case and relatively low volatility for the latter. Nevertheless, this is somewhat unexpected precisely because of the volatility of the compounds. However, the

same two non exclusive hypotheses raised in the previous discussion on correlations can be raised again here.

TEs in the overall set were roughly grouped together with the exception of Hg, likely due to its particular behaviour on lichens, where it is clearly opposite from the rest because of its volatility and the fact that lichens absorb pollutants from atmospheric deposition without interaction with the substratum (Yogui and Sericano 2008) and Hg has volatile and non-volatile chemical species in its cycle (Góngora et al. 2018), contrary to the other TEs. In mosses, the grouping of TEs is clear, but the loading factor for Hg is also lower than the rest, likely for the same reasons as before, in addition to the interference of the water phase. For soil samples, the group is more spread than in the rest of the cases likely due to the interference of natural sources and different biogeochemical pathways (Cipro et al. 2018a). Moreover, the highest factor loadings of components 1 and 2 of the PCA were presented for this matrix, corroborating the conclusions from the previous works stating it is the most adequate for assessing colonies as relevant secondary sources of both organic and inorganic pollutants (Cipro et al. 2018a, 2019).

3.4 - Possible influences of climate change

According to Petry et al. (2016), the Antarctic Peninsula has undergone rapid climate changes when compared to other parts of Antarctica (Schofield et al. 2010). Bottom-up effects influence a large array of species of the Antarctic food webs at many levels (Schofield et al. 2010). In the long term, most studies verify a trend of population decrease for Adélie (*Pygoscelis adeliae*) and Chinstrap (*P. antarcticus*) penguins, especially in King George and Penguin Islands (Sander et al. 2007a, b; Trivelpiece et al. 2011), even if it might be increasing in some other sites (Lynch et al. 2008). Also, a more recent study using an unmanned aerial vehicle (Korczak-Abshire et al. 2019) detected a 68.3% decline in their population in Turret Point and Penguin Island, sampling sites also comprehended in our study. A similar situation as for the other two pygoscelids can be reported for the Gentoo (*P. papua*): despite an overall increase of population in Antarctica, a substantial decline was observed and predicted in Admiralty Bay (Woehler et al. 2001). Moreover, the temperature anomaly presented significant negative correlation for the number of breeding pairs of *P.*

antarcticus and *P. papua* and positively for Skuas in a previous study (Petry et al. 2016). Phenological changes (Barbraud and Weimerskirch 2006) and sea-ice extension (Croxall et al. 2002) also do play a role in colony population size. Taking all of that in consideration in addition to the paleoecological record, penguins are more likely to respond to climate change by dispersion rather than adaptation (Forcada and Trathan 2009), meaning that even if in our area of study populations might overall decline, colony pollutants input is likely to increase in southward breeding sites, extant or yet to be colonised.

Next, there is the issue of pollutants themselves. Simulations and estimations (Wöhrnschimmel et al. 2013) suggest a reduction of atmospheric POPs transported to Antarctica. However, the increase in temperature is known to enhance the release of pollutants previously trapped in snow, glaciers and has been verified in field studies in Antarctica (Geisz et al. 2008; Cipro et al. 2017b). These previous factors (population and pollutants input) combined resulted in a gradual decrease of pollutant concentrations in penguin fat and eggs over the last 50 years (Ellis et al. 2018). Nevertheless, the issue of remobilisation of contaminants due to the increasing temperature of the ecosystems compartments functioning as a sink remains, notably for soil and vegetation. This matter was analysed in a previous publication (Cabrerizo et al. 2013). The authors stated that whereas an increase of 1°C in ambient temperature due to climate change would increase current Antarctic atmospheric inventories of PCBs by 21−45%, a concurrent increase of 0.5% soil organic matter would counteract the influence of warming by reducing the POP fugacity in soil. A 1°C increase in Antarctic temperatures will induce an increase of the soil−vegetation organic carbon and associated POPs pools by 25%, becoming a net sink of POPs, and trapping up to 70 times more POPs than the amount remobilized to the atmosphere. Taking this last piece of information into account, it is reasonable to assume that concentrations in soil and vegetation should increase and, moreover, the overall mass of POPs and TEs trapped in Antarctic terrestrial ecosystems is expected to increase as well.

4 - Conclusions

Previous studies stated that colonies were clear sources of some TEs and likely sources of others. Our current results allow the placement of As, Se and Zn among those clearly supplied by seabird colonies instead of likely sourced. Therefore, colonies are clearly sources of As, Cd, Hg, Se, Zn, HCB and PCBs.

There were some rather unexpected results likely linked to isotopic fractionation or some other biogeochemical process that went undetected in previous studies and deserve further inquiry. Also, the presence of relevant local sources other than colonies, including natural ones, deserves future attention.

Penguin colonies, due not only to their sheer population size, but also due to their recent relative growth, are the most important TEs and POPs relevant secondary sources among those comprehended in this study.

Climate change should likely increase the concentration of contaminants and the overall burden trapped in Antarctic terrestrial ecosystems.

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