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Organic pollutants and their correlation with stable isotopes in

vegetation from King George Island, Antarctica

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Abstract: Vegetation samples from King George Island, Antarctica (62°05'S, 058°23'W) were collected in the austral summer of 2004-05. Lichens (Usnea aurantiaco-atra and Usnea antarctica), mosses (Sanionia uncinata, Syntrichia princeps and Brachytecium sp.), and one angiosperm (Colobanthus quitensis) species were analyzed for persistent organic pollutants as well as δ^{13} C and δ^{15} N stable isotopes. The following contaminants were found above the method detection limit (MDL): HCB (0.141 to 1.06 ng g⁻¹ dry weight), HCHs (< MDL to 1.20 ng g⁻¹ dw), DDTs (< MDL to 1.73 ng g⁻¹ dw), PCBs (7.76 to 18.6 ng g⁻¹ dw) and PBDEs (0.146 to 0.811 ng g⁻¹ dw). In all cases, levels in mosses were higher than in lichens (one order of magnitude higher for OCs), suggesting that specific biogeochemical processes were involved in the transport, exposure and absorption for each group. Carbon stable isotope ratios showed clearly different ranges for lichens (δ^{13} C from -21.13 up to -18.43%) and mosses (-25.99 to -21.64‰). The only angiosperm species investigated exhibited ¹³C signature within the moss range. A large range of δ^{15} N was found (-7.67 to 20.75%) and seemed to be related to nitrogen uptake from different animal-derived sources. Pearson's correlation showed significant results for some contaminants (e.g. HCHs/HCB and PCBs/DDTs) and suggested the influence of the origin of both nitrogen and pollutants, notably taking secondary sources (animal excrements/remains, for instance) into consideration.

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40 **Keywords:** Antarctica; lichens; mosses; PBDEs; POPs; stable isotopes

1. INTRODUCTION

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43 Antarctica still is one of the least polluted regions on Earth, what provides unique 44 opportunities for studying environmental pollution processes at both local and global scales 45 (Borghini et al., 2005). Even though Antarctica has had limited direct exposure to persistent 46 organic pollutants (POPs), the atmosphere represents a source of contaminants through long 47 range transport. According to a mechanism known as "global distillation", semi-volatile 48 compounds evaporate in warmer regions and are atmospherically transported to colder 49 regions (i.e., high altitudes/latitudes) where they are deposited and enter the ecosystem (ARQP, 2007; Cipro et al., 2010). Oceanic currents and animals also play a minor role in this 50 51 transport as described in (Roosens et al. (2007) and Choy et al. (2010). 52 Lichens and mosses have been extensively used in environmental pollution studies 53 throughout the world, since their collection is relatively easy and they can absorb 54 contaminants directly from the air. In the Antarctic environment, a variety of contaminants 55 has been reported in these organisms such as trace metals (Poblet et al., 1997) and 56 radioactive elements (Mietelski et al., 2000). Information on POPs, especially PBDEs, is 57 scarce in these matrices (see Borghini et al., 2005; Yogui & Sericano, 2008). According to Liu et al. (2010), δ^{13} C has been extensively used to examine physiological, 58 59 ecological, and biogeochemical processes related to C cycling, providing insights to the 60 interactions between plants and environmental factors at a variety of temporal and spatial scales (Farquhar et al., 1989; Israeli et al., 1996). $\delta^{15}N$, on the other hand, has been 61 62 recognized as an effective tool holding source-specific information for tracing the deposition 63 of N pollutants and N availability to plants (Robinson, 2001). Because of the close correlation between C and N, δ^{13} C and δ^{15} N are recognized as a biologically important 64 65 stable isotope pair and are frequently used in combination to investigate N supply and C 66 fixation occurring from individual organism to ecosystem level (e.g. Hietz et al., 1999;

- Robinson et al., 2000). Xiao et al. (2010) state that this isotope pair is used to understand
- 68 mixing processes, transport pathways, deposition, and history of atmospheric pollutants in
- the environment (Xiao and Liu, 2002; Liu et al., 2009). The $\delta^{15}N$ values of atmospheric N
- sources range from -15 to +10%, with the oxidized N (NO_x) more positive and the reduced
- 71 N (NH_x) more negative (Heaton, 1990; Xiao and Liu, 2002).
- 72 The aim of this work is to determine concentration of several POPs in Antarctic vegetation as
- vell as their carbon and nitrogen stable isotope signatures. Correlation between these
- variables is also investigated in order to better understand pollution processes in Antarctica.

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2. MATERIAL AND METHODS

2.1. Area of study and sample collection

King George Island (62°05′S 58°23′W), the largest one of the South Shetlands Islands, is separated from the northern portion of the Antarctic Peninsula by the Bransfield Strait. The island is mostly ice-covered and even during summer an ice cap remains over at least 90% of its surface area (SCAR, 2010). Ice-free areas are abundantly vegetated by lower plants such as lichens and mosses (Lee et al. 2009). In the present study, plants were collected at eleven sites along the coast of Admiralty Bay, the largest fjord-like embayment on King George Island encompassing a surface area of 122 km² (Rakusa-Suszczewski et al., 1993). The coast of Admiralty Bay is fairly irregular alternating between gravel/sandy beaches, rocky shores and glaciers along its ca. 84 km long shoreline (Rakusa-Suszczewski, 1995). Its climate is predominantly cold oceanic, characteristic of maritime Antarctica. It can be considered relatively warm and humid, supporting a substantial bryophyte flora including mosses and liverworts, lichens, and some freshwater algae. Bryophytes predominate in moister and more sheltered habitats, while lichens in more arid and exposed rocky habitats (Kim et al., 2007).

Samples were collected in the austral summer, from early December 2004 to early January

2005. Plants were collected by hand, and carefully shaken to remove animal-related debris and/or soil particles. They were then stored in clean containers (previously combusted at 450°C for 4 hours), frozen at -20°C upon return to the Brazilian Research Station (Estação Antártica Comandante Ferraz), and kept frozen until analysis.

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2.2. Chemical analyses

98 Organochlorine (OC) analyses were performed at University of São Paulo (Brazil). 99 Laboratory protocol was based on MacLeod et al. (1986) and quality assurance/quality 100 control (QA/QC) followed guidelines described by Wade & Cantillo (1994). Briefly, 10 g of 101 wet sample were ground with anhydrous Na₂SO₄ and surrogate (PCB103) was added before 102 extraction in a Soxhlet apparatus for 8 h with 80 mL of n-hexane and methylene chloride 103 (1:1, v/v). The extract was concentrated to 1 mL and cleaned up in a column filled (from top 104 to bottom) with 16 g alumina and 8 g silica gel (both 5% deactivated with water). The extract 105 was eluted with 100 mL of methylene chloride and subsequently concentrated to 900 µL. 106 Finally, internal standard (TCMX, used to estimate surrogate recovery) was added to the 107 purified extract prior to injection in the gas chromatograph. 108 OC analyses were run in a gas chromatograph equipped with an electron capture detector 109 (GC-ECD, Agilent Technologies, model 6890N). Hydrogen was used as carrier gas at 110 constant pressure (13.2 psi, i.e. 91.01 kPa). The injector was operated in splitless mode and 111 kept at 300 °C. The capillary column used was a DB-5 (30 m length × 250 µm internal 112 diameter \times 0.25 µm film thickness). The detector operated at 320 °C using N₂ as makeup gas at a flow rate of 58 mL min⁻¹. The oven was programmed as follows: 70°C for 1 min, 5°C.min⁻¹ 113 to 140°C (1min), 1.5°C.min⁻¹ to 250°C (1 min) and 10°C to 300°C (5 min). The investigated 114 115 compounds were PCBs (IUPAC Nos. 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 77, 87, 116 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157,

117 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 201, 203, 206 and 209), 118 DDTs (o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, and p,p'-DDT), HCB, HCHs 119 (α, β, γ) and δ isomers), chlordanes $(\alpha$ - and γ -chlordane, heptachlor, and heptachlor epoxide), 120 mirex and drins (aldrin, dieldrin, and endrin). Surrogate recovery ranged from 98% to 111%. 121 Detection limits were set as three times the standard deviation (σ) of seven method blank 122 replicates. Spiked matrices were recovered within the acceptance ranges (i.e., 40-130% for at 123 least 80% of the spiked analytes) suggested by Wade & Cantillo (1994). Method validation 124 was performed using NIST SRM 1945. Blanks were included in every analytical batch 125 (usually 10–12 samples) and all data were blank-subtracted. 126 PBDE analyses were performed at Texas A&M University (USA) following procedures 127 described in Yogui & Sericano (2008). Briefly, approximately 10 g of wet plant tissue was 128 mixed with 40 g of anhydrous Na₂SO₄ and extracted with 300 mL of methylene chloride 129 using a tissumizer (PRO Scientific Inc., model PRO250). Plant extracts were extensively 130 cleaned up with sulfuric acid, silica/alumina chromatography and gel permeation 131 chromatography/high performance liquid chromatography (GPC/HPLC). A suite of 36 di-132 through hepta-BDEs was measured including the following congeners: 7, 8, 10, 11, 12, 13, 133 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 134 153, 154, 155, 166, 181, 183 and 190 (numeration according to the same IUPAC system used 135 for PCBs. Dry and lipid weights were gravimetrically determined using an analytical 136 balancefollowing standard procedures used at the Geochemical and Environmental Research 137 Group (GERG) facilities. 138 Stable isotope analyses were performed at University of La Rochelle (Plateau Analyses 139 Elémentaires et Isotopiques). Samples were ground and lyophilized. Clean up was performed 140 in a test tube containing 100 mg of sample and 4 mL of cyclohexane. The mixture was 141 shaken for an hour, then centrifuged for separation (as many times as needed, until the liquid phase, which is discarded, comes out clear) and dried at 50°C for 48h. Purified samples were analyzed using a Thermo Scientific Delta V Advantage, ConFlo IV interface (NoBlank and SmartEA) and Thermo Scientific Flash EA1112 Elemental Analyzer. Each injection corresponded to 1 mg of sample encapsulated in tin cups, and there were no replicates. Pee Dee Belemnite and atmospheric nitrogen were used as standards for calculation of δ^{13} C and δ^{15} N, respectively. Based on replicate measurements of internal laboratory standards, experimental precision is of \pm 0.15 and \pm 0.20 ‰ for δ^{13} C and δ^{15} N, respectively.

3. RESULTS AND DISCUSSION

3.1. Organic pollutants

Average concentrations of POPs are shown in Table 1. PCBs presented the highest concentration among POPs in all plant species, exhibiting values at least an order of magnitude higher than all other contaminants. Similar distribution of POPs was observed by Borghini et al. (2005) for several moss species (*Bryum argenteum*, *Pottia heimii* and *Ceratodon purpureus*) collected in Antarctica at latitudes ranging from 72° to 77° S, sites possibly subject to distinct contaminant trapping effects due to colder temperatures. Total PCBs found by Borghini et al. (2005) ranged from 23 to 34 ng g⁻¹ dry weight. DDTs were an order of magnitude lower, while HCB and HCHs were 1-2 orders of magnitude lower than PCBs. Similar trends in organochlorine pattern between both studies may be an indication of the long range transport and exposure characteristics. Bacci et al. (1986), whose work investigated the genus *Usnea* and *Sanionia uncinata* (there described as *Drepanocladus uncinatus*, a synonym), had observed similar patterns two decades ago. This may be associated to the long lifespan of such organisms, whose age estimation may reach over 500 years (Tatur et al., 1997) as well as very low productivity rates (Glime, 2007). The combination of such factors may account for a large difference in PCBs and PBDEs

concentrations due to the more recent environmental inputs of the latter. Levels of POPs in eggs of gentoo penguin collected at King George Island also revealed large differences between PCBs and PBDEs (Yogui and Sericano, 2009a; Cipro et al., 2010). Roosens et al. (2007) also show this difference in soil from Adélie penguin colonies and reference sites at Hop Island, Antarctica: PCBs totals reach up to 328 pg g⁻¹ dw and PBDEs totals were in none of the cases superior to the limit of quantification of 200 pg g⁻¹ dw.

Distribution of PCBs and PBDEs as a function of their respective chlorination

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and bromination numbers (i.e., molecular weight) in plant species is shown in Figure 3. In the case of PCBs, there is a prevalence of tetra-, followed by penta- and tri- CBs, except for Sanionia uncinata which exhibited a balanced distribution (~20%) from trithrough hexa-CBs. Although concentration levels are on the same order of magnitude, the pattern of PCBs in lichens in this study is slightly different from the one found by Park et al. (2010) that had a different congener composition aimed. Negoita et al. (2003) presents results within this same quantitative range for lichens from East Antarctica coast, however an even different distribution: hexa, penta and tri-CBs, in this order. Nevertheless, both of these previous studies strongly suggested the influence of PCBs resulting from anthropogenic activity and/or local biotic origin rather than sole atmospheric transport as a significant pathway of contamination. Indeed, it has been demonstrated that seabird colonies represent a secondary source of contamination with persistent organic pollutants (Roosens et al., 2007) or heavy metals (Choy et al. 2010). In this respect, large colonies of penguins at King George Island would likely constitute an input of POPs contamination to terrestrial organisms such as lower plants. Since Montone et al. (2001) found no evidence of local sources after analyzing the marine macroalgae *Desmarestia* sp., it is hereby hypothesized that terrestrial plants are more likely to be affected by these secondary sources (such as the local transport of pollutants in runoff water or physiological factors, for instance).

With regard to PBDEs, tetra and penta homologues represented over 90% of the total composition (Figure 1). Such a distribution is similar to commercial mixtures of Penta-BDE, which has over 70% of its formulation comprised of BDE-47 (tetrabrominated) and BDE-99 (pentabrominated) which also dominated the composition of plants. These are congeners of great environmental concern since they are known to best bioaccumulate among PBDEs (de Wit, 2002; Alcock et al., 2003; Darnerud, 2003; Hale et al., 2003; Yogui and Sericano, 2009b). Homologue pattern correspondence between Penta-BDE technical mixtures and Antarctic vegetation suggests that PBDEs do not undergo major fractionation during transport to Antarctica. The composition of brominated homologues in the samples resembles patterns observed in penguin eggs (with deviation of samples in regard to Penta-BDE not superior to 5% for skuas and chinstrap penguins) and other vegetation samples collected at King George Island (Yogui and Sericano, 2008; 2009a). BDEs 47 and 99 were also prevalent congeners in the composition of mosses from Norway (Mariussen et al., 2008), probably due to the use of Penta-BDE mixtures in Europe.

3.2. Stable isotopes

Stable isotope ratios of δ^{13} C and δ^{15} N are plotted in Figure 2. Carbon stable isotope analysis showed a clearly different range for lichens (δ^{13} C from -21.13 up to -18.43‰) and mosses (δ^{13} C from -25.99 up to -21.64‰). The sole angiosperm sample (*Colobanthus quitensis*) was within the mosses range. A previous study (Lee et al., 2009), also in King George Island, showed similar trends, however with some overlapping between moss and lichen ranges, attributing the differences probably to plant physiology and biochemistry. Overall, the δ^{13} C values of the mosses are more consistent with that of C3 photosynthesis (Smith and Epstein, 1971).

Regarding nitrogen isotopes, Heaton (1986) suggests that once deposited, urea and uric acid

hydrolyze, producing a temporary rise in pH, favoring the formation of ammonia, which easily volatilizes to the atmosphere. The kinetic fractionations accompanying these steps result in strongly ¹⁵N-depleted ammonia, while the remaining ammonium is ¹⁵N-enriched. These fractionations result in plants around the excrement zone assimilating ¹⁵N enriched in inorganic nitrogen while the species at the upland sites have $\delta^{15}N$ signatures that reflect the δ^{15} N of the isotopically depleted ammonia source. That is the reason why animal-derived nitrogen uptake is associated with large δ^{15} N ranges (e.g. Erskine et al., 1998). Typical values of $\delta^{15}N$ of seabird excrement and soil under influence of the colonies range between 6 and 26‰ (Wada et al., 1981; Mizutani and Wada, 1988; Cocks et al., 1998; Wainright et al., 1998), which comes in agreement to the values hereby presented, ranging from -7.67 up to 4.30% for lichens and from -0.53 up to 20.75% for mosses. Mosses are characterized by higher sensitivities to atmospheric N supply due to the lack of a true root system to acquire N from substratum (Liu et al. 2010). Unlike some lichens and algae, mosses can barely utilize atmospheric N2 due to the lack of azotobacteria, but the deposited N, which accounts for higher variability as well. Overall, moister habitats and marine influence were related to lower δ^{13} C and higher δ^{15} N (Lee et al. 2009), which comes in agreement with our results, since mosses are more water dependant than lichens. Interestingly, the only plant species with true root system, Colobanthus quitensis, exhibited one of the highest ¹⁵N enrichments. This may be explained by water uptake via roots since dissolved ammonium (and its byproducts) is ¹⁵N-enriched.

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3.3. Correlation between variables

Pearson's product-moment correlation analysis was performed between paired variables (see Table 2). Since a large range of $\delta^{15}N$ was found (from -7.67 up to 20.75‰, i.e. a range of 28.42‰), which is related to animal-derived nitrogen uptake, this variable was also included

242 in order to investigate if these nitrogen sources would act as a secondary organic pollutants 243 sources as well. 244 Significant positive correlations were found between HCB and HCHs when all plants are 245 taken into account. This is probably a consequence of similar long range atmospheric 246 transport processes since these chemicals have high volatility. DDTs showed significant 247 correlation with both PCBs and PBDEs. These POPs have intermediate to low volatility. The 248 moderate association between DDTs and PCBs is hypothesized to be related to the plants 249 long lifespan that would contribute to proportional contaminant burdens being deposited after 250 several depositional cycles in spite of the discrepancy between the restrictions for these 251 groups. This observation is also plausible when mosses are taken separately. In regard to 252 mosses only, HCHs correlation with both DDTs and PCBs could be related to the interaction 253 of HCHs with the water phase (resulting from recent snowpack melting, or even water from 254 glacier melting that percolates a bird or seal colony, for instance), as they are more water 255 soluble, and not directly atmosphere-moss, since mosses have tremendous ability to sequester 256 water (Glime, 2007). The absence of correlation between PCBs and PBDEs is probably due 257 to the temporal shifts in production, utilization and restriction/banning policies throughout 258 the world. The differences in volatility might also play a role, since a PCB is more volatile 259 than its PBDE equivalent. δ¹⁵N correlations should be examined carefully. Two significant correlations were observed 260 when all plants are taken into consideration: a negative correlation between $\delta^{15}N$ and HCHs, 261 and a positive correlation between $\delta^{15}N$ and PBDEs. As described above, uptake of 262 volatilized ammonia from animal-derived nitrogen sources leads to depletion in $\delta^{15}N$, while 263 uptake of dissolved ammonium leads to enrichment in $\delta^{15}N$. Therefore, it is suggested that 264 265 plant species relying on the latter would have positive correlation between low volatility contaminants and $\delta^{15}N$. Conversely, plants relying on volatilized ammonia would have 266

negative correlation. This may explain the significant negative correlation between $\delta^{15}N$ and HCHs (high volatility chemicals) and the positive correlation between $\delta^{15}N$ and PBDEs (low volatility compounds). When lichens and mosses are taken separately, no significant correlation is found probably due to the relatively small sampling number and occasional cross interference of nitrogen sources in a smaller sample set; however it is noticeable that lichens results are generally more negative than the ones for mosses, which indicates a higher dependency on volatilized ammonia. The absence of correlation with PCBs could be due to temporal issues already considered in this work, but also to the comparatively higher volatility of PCBs when compared to PBDEs.

4. CONCLUSIONS

Lichens and mosses present similar contamination patterns. Overall, there is a predominance of PCBs, being one order of magnitude higher than the other organochlorines (DDTs, HCB and HCHs) and one to two orders of magnitude higher than PBDEs. Considering the contamination levels, our results for lower plants from King George Island are consistent with findings of previous studies. Nonetheless, the use of carbon and nitrogen stable isotopes provides a deeper insight on the origin of POPs in these terrestrial plants.

Lichens and mosses exhibited clearly distinct fractionation of carbon as observed in $\delta^{13}C$ ratios. Nitrogen stable isotope signatures are less specific, but they apparently indicate a sensitivity to the influence of animal-derived nitrogen and therefore, to its source.

Correlation analyses showed significant results in some historically linked contaminant groups and suggested the influence of the origin of both nitrogen and pollutants, notably taking secondary sources into consideration.

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Table 1. Average concentration of POPs (ng g⁻¹ dry weight) and standard deviations (when possible) in plants collected at King George Island, Antarctica during the austral summer 2004-05.

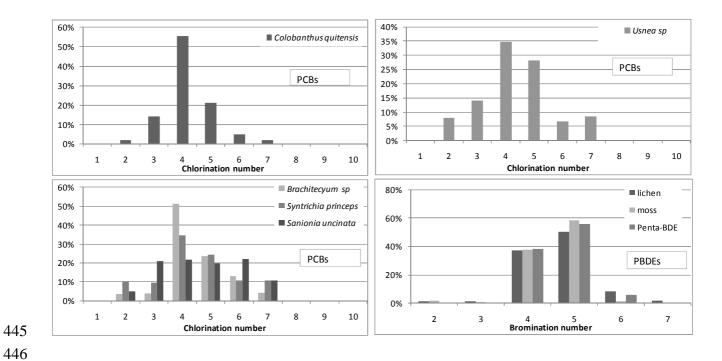
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	Angiosperm	Mosses			Lichen	
	Colobanthus quitensis	Brachitecyum sp.	Syntrichia princeps	Sanionia uncinata	Usnea spp.	
	n=1	n=1	n=2	n=7	n=6	
НСВ	1.01	0.779	1.06	0.811 ± 0.18	0.141 ± 0.10	
Σ HCHs	1.05	< 0.18	< 0.18	1.20 ± 0.81	0.205 ± 0.08	
Σ DDTs	< 0.11	1.22	1.73	1.62 ± 0.58	0.353 ± 0.04	
Σ PCBs	14.5	15.7	16.8	18.6 ± 2.5	7.76 ± 2.3	
Σ PBDEs	0.328	0.276	0.718	0.893 ±0.28	0.236 ± 0.05	

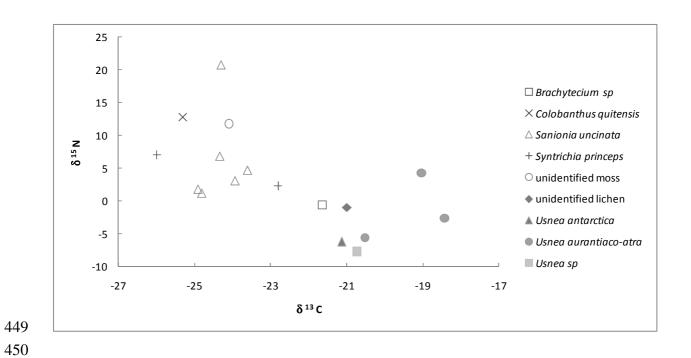
Table 2. Pearson's product-moment correlation matrix between all paired variables investigated in plants collected at King George Island, Antarctica during the austral summer 2004-05. Significant results at α = 0.05 are marked with an asterisk.

		НСВ	Σ HCHs	Σ DDTs	Σ PCBs	PBDEs	$\delta^{^{15}}$ N
	НСВ	1.00					
	Σ HCHs	0.48*	1.00				
Samples	Σ DDTs	-0.33	0.17	1.00			
	Σ PCBs	-0.17	0.18	0.49*	1.00		
	PBDEs	-0.35	-0.21	0.51*	0.33	1.00	
	$\delta^{^{15}}$ N	-0.19	-0.60*	-0.01	0.17	0.55*	1.00
		НСВ	Σ HCHs	Σ DDTs	Σ PCBs	PBDEs	$\delta^{^{15}}$ N
	НСВ	1.00					
Mosses	Σ HCHs	0.14	1.00				
	Σ DDTs	0.49	0.91*	1.00			
	Σ PCBs	0.41	075*	0.64*	1.00		
	PBDEs	-0.21	0.52	0.30	0.13	1.00	
	$\delta^{\scriptscriptstyle 15}$ N	0.39	-0.28	-0.42	-0.03	0.23	1.00
		HCB	$\Sigma HCHs$	$\Sigma DDTs$	$\Sigma PCBs$	PBDEs	$\delta^{^{15}}$ N
Lichens	НСВ	1.00					
	Σ HCHs	0.37	1.00				
	Σ DDTs	-0.50	0.01	1.00			
	Σ PCBs	-0.13	0.40	-0.44	1.00		
	PBDEs	0.15	0.72	-0.32	0.36	1.00	
	$\delta^{^{15}}$ N	0.24	-0.28	-0.54	-0.28	0.38	1.00

437 438	Caption to figures
139	Figure 1. Percent distribution of PCB and PBDE homologues in plants collected at King
440	George Island, Antarctica during the austral summer 2004-05.
441	
442	Figure 2 – δ 13C and δ 15N values (‰) of lower plants (lichens are represented in closed, full
443	markers) collected at King George Island, Antarctica during the 2004-05 austral summer.
1/1/1	



447 Figure 3



451 Figure 2