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Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica

Caio V.Z. Cipro [a,*], Gilvan Takeshi Yogui [b], Paco Bustamante [c], Satie Taniguchi [a], José L. Sericano [d], Rosalinda Carmela Montone [a]

[a] Universidade de São Paulo, Instituto Oceanográfico, Praça do Oceanográfico, 191, 05508-900 São Paulo, SP, Brazil
[b] Universidade Federal de Pernambuco, Centro de Tecnologia e Geociências, Departamento de Oceanografia, Av. Arquitetura s/n, 50740-550 Recife, PE, Brazil
[c] Littoral Environnement et Sociétés (LIENSs), UMR 6250, CNRS, Université de La Rochelle, 2 rue Olympe de Gouges, 17042 La Rochelle Cedex 01, France
[d] Geochemical and Environmental Research Group, College of Geosciences, Texas A&M University, 833 Graham Road, College Station, TX 77845, USA

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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 2004–2005. 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 $\delta^{13}C$ and $\delta^{15}N$ stable isotopes. The following contaminants were found above the method detection limit (MDL): HCB (0.141–1.06 ng g^{-1} dry weight), HCHs (<MDL to 1.20 ng g^{-1} dw), DDTs (<MDL to 1.73 ng g^{-1} dw), PCBs (7.76–18.6 ng g^{-1} dw) and PBDEs (0.146–0.811 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 ($\delta^{13}C$ from −21.13‰ up to −18.43‰) and mosses (−25.99‰ to −21.64‰). The only angiosperm species investigated exhibited ^{13}C signature within the moss range. A large range of $\delta^{15}N$ 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.

1. Introduction

Antarctica still is one of the least polluted regions on Earth, what provides unique opportunities for studying environmental pollution processes at both local and global scales (Borghini et al., 2005). Even though Antarctica has had limited direct exposure to persistent organic pollutants (POPs), the atmosphere represents a source of contaminants through long range transport. According to a mechanism known as "global distillation", semi-volatile compounds evaporate in warmer regions and are atmospherically transported to colder 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 transport as described in Roosens et al. (2007) and Choy et al. (2010).

Lichens and mosses have been extensively used in environmental pollution studies throughout the world, since their collection is relatively easy and they can absorb contaminants directly from the air. In the Antarctic environment, a variety of contaminants has been reported in these organisms such as trace metals (Poblet et al., 1997) and radioactive elements (Mietelski et al., 2000). Information on POPs, especially PBDEs, is scarce in these matrices (see Borghini et al., 2005; Yogui and Sericano, 2008).

According to Liu et al. (2010), $\delta^{13}C$ has been extensively used to examine physiological, ecological, and biogeochemical processes related to C cycling, providing insights to the 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 recognized as an effective tool holding source-specific information for tracing the deposition of N pollutants and N availability to plants (Robinson, 2001). Because of the close correlation between C and N, $\delta^{13}C$ and $\delta^{15}N$ are recognized as a biologically important stable isotope pair and are frequently used in combination to investigate N supply and C 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 mixing processes, transport pathways, deposition, and history of atmospheric pollutants in the environment (Xiao and Liu, 2002; Liu et al.,

* Corresponding author.
E-mail address: caiovzc@usp.br (C.V.Z. Cipro).

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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 N (NH_x) more negative (Heaton, 1990; Xiao and Liu, 2002).

The aim of this work is to determine concentration of several POPs in Antarctic vegetation as well as their carbon and nitrogen stable isotope signatures. Correlation between these variables is also investigated in order to better understand pollution processes in Antarctica.

2. Materials 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 km^2 (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 h), frozen at −20 °C upon return to the Brazilian Research Station (Estação Antártica Comandante Ferraz), and kept frozen until analysis.

2.2. Chemical analyses

Organochlorine (OC) analyses were performed at University of São Paulo (Brazil). Laboratory protocol was based on MacLeod et al. (1986) and quality assurance/quality control (QA/QC) followed guidelines described by Wade and Cantillo (1994). Briefly, 10 g of wet sample were ground with anhydrous Na_2SO_4 and surrogate (PCB103) was added before extraction in a Soxhlet apparatus for 8 h with 80 mL of n-hexane and methylene chloride (1:1, v/v). The extract was 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). The extract was eluted with 100 mL of methylene chloride and subsequently concentrated to 900 μL. Finally, internal standard (TCMX, used to estimate surrogate recovery) was added to the purified extract prior to injection in the gas chromatograph.

OC 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 constant pressure (13.2 psi, i.e. 91.01 kPa). The injector was operated in splitless mode and kept at 300 °C. The capillary column used was a DB-5 (30 m length × 250 μm internal diameter × 0.25 μm film thickness). The detector operated at 320 °C using N_2 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} to 140 °C (1 min), 1.5 °C min^{-1} to 250 °C (1 min) and 10–300 °C (5 min). The investigated compounds were PCBs (IUPAC Nos. 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 77, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 201, 203, 206 and 209), DDTs (*o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, and *p,p′*-DDT), HCB, HCHs (α, β, γ, and δ isomers), chlordanes (α- and γ-chlordane, heptachlor, and heptachlor epoxide), mirex and drins (aldrin, dieldrin, and endrin). Surrogate recovery ranged from 98% to 111%. Detection limits were set as three times the standard deviation (σ) of seven method blank replicates. Spiked matrices were recovered within the acceptance ranges (i.e., 40–130% for at least 80% of the spiked analytes) suggested by 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.

PBDE analyses were performed at Texas A&M University (USA) following procedures described in Yogui and Sericano (2008). Briefly, approximately 10 g of wet plant tissue was mixed with 40 g of anhydrous Na_2SO_4 and extracted with 300 mL of methylene chloride using a tissumizer (PRO Scientific Inc., model PRO250). Plant extracts were extensively cleaned up with sulphuric acid, silica/alumina chromatography and gel permeation chromatography/high performance liquid chromatography (GPC/HPLC). A suite of 36 di- through hepta-BDEs was measured including the following congeners: 7, 8, 10, 11, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183 and 190 (numeration according to the same IUPAC system used for PCBs. Dry and lipid weights were gravimetrically determined using an analytical balance following standard procedures used at the Geochemical and Environmental Research Group (GERG) facilities.

Stable isotope analyses were performed at University of La Rochelle (Plateau Analyses Elementaires et Isotopiques). Samples were ground and lyophilized. Clean up was performed in a test tube containing 100 mg of sample and 4 mL of cyclohexane. The mixture was 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 48 h. 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 $\delta^{13}C$ and $\delta^{15}N$, respectively. Based on replicate measurements of internal laboratory standards, experimental precision is of ±0.15‰ and ±0.20‰ for $\delta^{13}C$ and $\delta^{15}N$, 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

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 2004–2005.

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

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 and bromination numbers (i.e., molecular weight) in plant species is shown in Fig. 1. In the case of PCBs, there is a prevalence of tetra-, followed by penta- and tri-CBs, except for *S. uncinata* which exhibited a balanced distribution (~20%) from tri- through 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 (Fig. 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

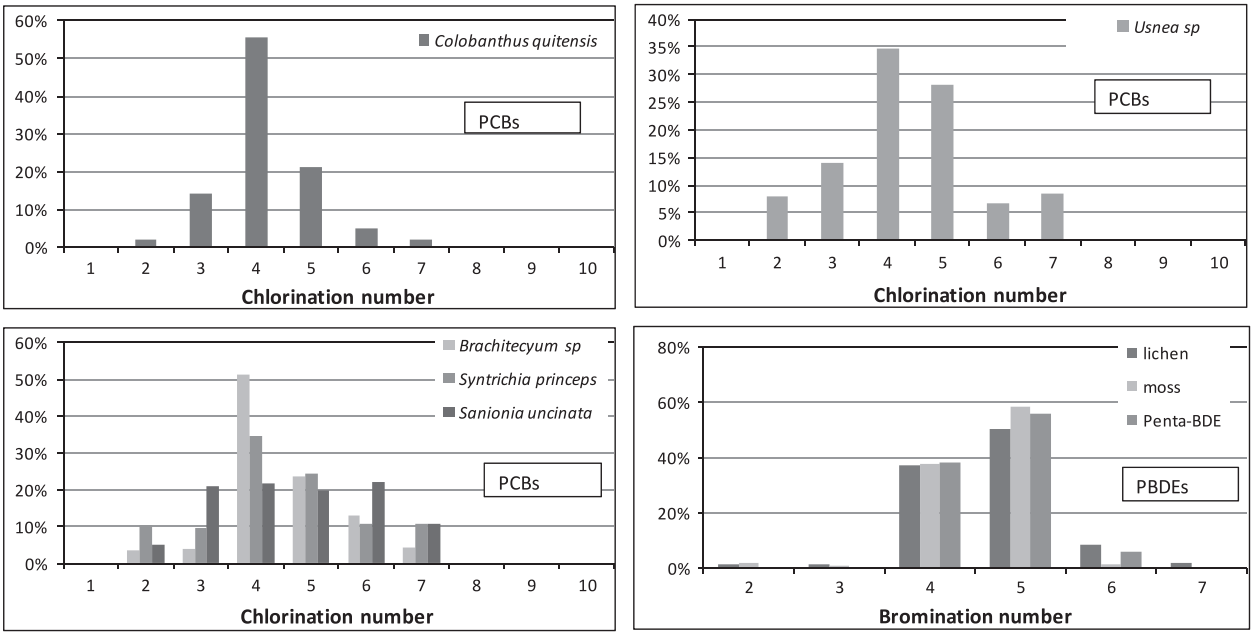

Fig. 1. Percent distribution of PCB and PBDE homologues in plants collected at King George Island, Antarctica during the austral summer 2004–2005.

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 $\delta^{13}C$ and $\delta^{15}N$ are plotted in Fig. 2. Carbon stable isotope analysis showed a clearly different range for lichens ($\delta^{13}C$ from −21.13‰ up to −18.43‰) and mosses ($\delta^{13}C$ 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 $\delta^{13}C$ 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 ^{15}N-depleted ammonia, while the remaining ammonium is ^{15}N-enriched. These fractionations result in plants around the excrement zone assimilating ^{15}N enriched in inorganic nitrogen while the species at the upland sites have $\delta^{15}N$ signatures that reflect the $\delta^{15}N$ of the isotopically depleted ammonia source. That is the reason why animal-derived nitrogen uptake is associated with large $\delta^{15}N$ 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 N_2 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 $\delta^{13}C$ and higher $\delta^{15}N$ (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, *C. quitensis*, exhibited one of the highest ^{15}N enrichments. This may be explained by water uptake via roots since dissolved ammonium (and its byproducts) is ^{15}N-enriched.

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 2004–2005. Significant results at $\alpha = 0.05$ are marked with an asterisk.

	HCB	∑HCHs	∑DDTs	∑PCBs	PBDEs	$\delta^{15}N$
All samples						
HCB	1.00					
∑HCHs	0.48*	1.00				
∑DDTs	−0.33	0.17	1.00			
∑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
Mosses						
HCB	1.00					
∑HCHs	0.14	1.00				
∑DDTs	0.49	0.91*	1.00			
∑PCBs	0.41	0.75*	0.64*	1.00		
PBDEs	−0.21	0.52	0.30	0.13	1.00	
$\delta^{15}N$	0.39	−0.28	−0.42	−0.03	0.23	1.00
Lichens						
HCB	1.00					
∑HCHs	0.37	1.00				
∑DDTs	−0.50	0.01	1.00			
∑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

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 in order to investigate if these nitrogen sources would act as a secondary organic pollutants sources as well.

Significant positive correlations were found between HCB and HCHs when all plants are taken into account. This is probably a consequence of similar long range atmospheric transport processes since these chemicals have high volatility. DDTs showed significant correlation with both PCBs and PBDEs. These POPs have intermediate to low volatility. The moderate association between DDTs and PCBs is hypothesized to be related to the plants long lifespan that

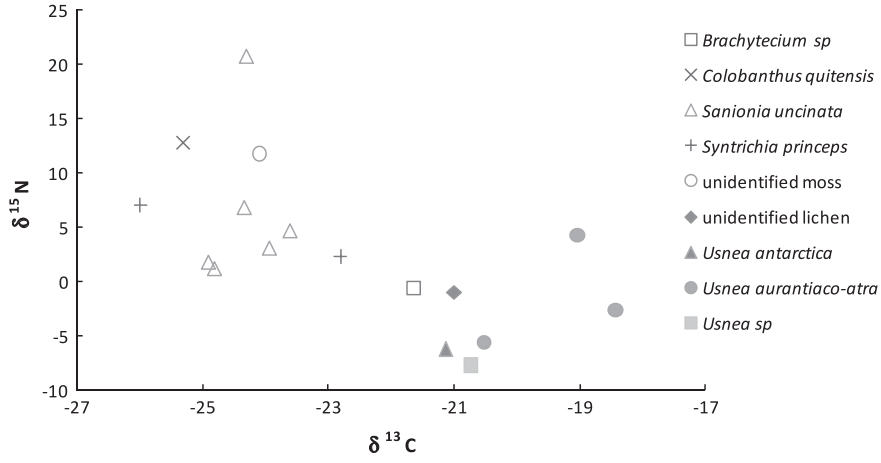

Fig. 2. $\delta^{13}C$ and $\delta^{15}N$ values (‰) of lower plants (lichens are represented in closed, full markers) collected at King George Island, Antarctica during the 2004–2005 austral summer.

would contribute to proportional contaminant burdens being deposited after several depositional cycles in spite of the discrepancy between the restrictions for these groups. This observation is also plausible when mosses are taken separately. In regard to mosses only, HCHs correlation with both DDTs and PCBs could be related to the interaction of HCHs with the water phase (resulting from recent snowpack melting, or even water from glacier melting that percolates a bird or seal colony, for instance), as they are more water soluble, and not directly atmosphere-moss, since mosses have tremendous ability to sequester water (Glime, 2007). The absence of correlation between PCBs and PBDEs is probably due to the temporal shifts in production, utilization and restriction/banning policies throughout the world. The differences in volatility might also play a role, since a PCB is more volatile than its PBDE equivalent.

$\delta^{15}N$ correlations should be examined carefully. Two significant correlations were observed when all plants are taken into consideration: a negative correlation between $\delta^{15}N$ and HCHs, and a positive correlation between $\delta^{15}N$ and PBDEs. As described above, uptake of volatilized ammonia from animal-derived nitrogen sources leads to depletion in $\delta^{15}N$, while uptake of dissolved ammonium leads to enrichment in $\delta^{15}N$. Therefore, it is suggested that 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 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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