Polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) in environmental samples from Ny-Ålesund and London Island, Svalbard, the Arctic

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HIGHLIGHTS

- PCBs including chiral compounds and PBDEs were investigated in various matrices from Arctic region.
- CB-11 was the major contributor of the total PCBs concentration.
- The concentrations of PCBs and PBDEs are at very low levels in the soil, plants and reindeer dung.
- Bioaccumulation factors of PCBs in six plants were less than 1, whereas those of PBDEs were higher than 1.

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ABSTRACT

Polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) were determined in environmental samples collected from Ny-Ålesund and London Island, Svalbard, the Arctic. Total PCB concentrations ($\sum_{25}\text{PCBs}$) varied from 0.57 to 2.52 ng g⁻¹ dry weight (dw) in soil, 0.30 to 1.16 ng g⁻¹ dw in plants and 0.56 to 0.98 ng g⁻¹ dw in reindeer dung. The non-Aroclor congener of CB-11 was predominant in most samples compared to other congeners, accounting for 16.0 ± 9.8% to the $\sum_{25}\text{PCBs}$. The $\sum_{13}\text{PBDEs}$ concentrations were 1.7–416, 36.7–495 and 28.1–104 pg g⁻¹ dw in soil, plants and reindeer dung, respectively. The signature of enantioselective biotransformation was observed in all samples for chiral CB-95, whereas in parts of samples for other chiral PCBs. Bioaccumulation factors (BAFs) in six plant species varied within individual contaminant congeners and plant species, with BAFs less than 1 for $\sum\text{PCBs}$ and higher than 1 for $\sum\text{PBDEs}$. BAF values decreased with increasing soil concentrations, suggesting that high background levels in soil restricted the accumulation of these contaminants by plants.

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1. Introduction

Arctic ecosystems, without significant human activities and emission sources, are subject to potential contamination of various agricultural, industrial chemicals and their by-products (Corsolini et al., 2002; McKinney et al., 2011). Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) have been widely detected in various environmental media and biota in the Arctic (Muir and Norstrom, 2000; Ikononou et al., 2002; de Wit et al., 2006; Ross et al., 2008). A number of studies pointed out long-range atmospheric transport, ocean currents and precipitation as

possible pathways of these pollutants in the Arctic (Fisk et al., 2002; Braune et al., 2007).

PCBs were widely used as dielectric fluids in transformers and capacitors in the 1960s, but their production and use was banned in the late 1970s due to persistent nature in the environment and adverse effect on human's health (Muir and Norstrom, 2000; Ockenden et al., 2003; Choi et al., 2008). Of the 209 PCB congeners, the twelve dioxin-like and six indicator PCBs were usually concerned due to their high toxicity and high concentrations in the environment. In recent years, 3,3'-dichlorobiphenyl (CB-11), an non-Aroclor PCB congener, has attracted great attention due to its ubiquitous presence and specific potential emission sources associated with pigment yellow production (Choi et al., 2008; Ross et al., 2008; Lehmler et al., 2009; Shang et al., 2014).

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Signature of chiral PCBs provide a useful tool to investigate biotransformation mechanisms of PCBs (Dang et al., 2010). Chiral pollutants exist in two forms as optical isomers, called enantiomers (Fisk et al., 2002). Although the two enantiomers have identical physical and chemical properties, they present different biological and toxicological effects in mammals (Ross et al., 2008; Lehmler et al., 2009). They are frequently observed as nonracemic mixtures in various organisms tissues (Ross et al., 2008; Zhai et al., 2011). To our knowledge, knowledge on the enantioselective biotransformation of chiral PCBs in the Arctic environments is still scarce.

PBDEs are man-made brominated flame retardants used in a wide range of consumption products such as insulation materials, electronic equipments and furniture (Herzke et al., 2003; Yogui and Sericano, 2008). Since PBDEs were first reported in 1987 in muscle tissues of animals collected in the Baltic Sea, North Sea and Arctic Ocean (Jansson et al., 1987), they were widely detected in various environmental media and different regions including the Arctic (de Wit et al., 2010; McKinney et al., 2011). PBDEs present comparable toxicological behavior with PCBs based on available toxicity data and chemical structures (McDonald, 2002). As endocrine disruptors, PBDEs can cause neurobehavioral deficits and cancer in animals (Ikonomou et al., 2002; McDonald, 2002). They could also transfer between different matrices (such as from soil to plant), bioaccumulate strongly in adipose tissues and biomagnify through the food chains (Hargrave et al., 2000; Corsolini et al., 2002; Pier et al., 2002).

Plants are indicative of deposition from air, providing evidence of long-range transport (de Wit et al., 2006). A certain of plants have a high lipid fraction to accumulate lipophilic compounds from

air precipitates and therefore play an important role in the global cycling of contaminants (Lead et al., 1996). Soils are considered as a sink for toxic chemicals. Therefore, they are influential for fate and distribution of POPs in the global scale (Negoița et al., 2003; Ockenden et al., 2003). In this study, soils, plants and reindeer dung samples were collected in Ny-Ålesund and London Island, Svalbard, the Arctic, to investigate the current contamination levels and spatial distribution of PCBs and PBDEs. Enantioselective biotransformation of PCBs and bioaccumulation of PCBs and PBDEs from soil to plant were also discussed.

2. Materials and methods

2.1. Sample collection

Environmental samples were collected from Ny-Ålesund and London Island, Svalbard, the Arctic, between September 2011 and September 2012. Details of the longitude and latitude for all sampling sites are presented in Table S1 (see Supplementary material). A total of 36 samples, including 10 moss (*Drepanocladus aduncus*), 1 tufted saxifrage (*Saxifraga cespitosa*), 3 arctic bell-heather (*Cassiope tetragona*), 3 mountain avens (*Dryas octopetala*), 4 sooty sedge (*Carex misandra*), 2 Alpine hair grass (*Deschampsia alpina*), 6 reindeer dung, and 7 soil samples, were collected at different sites (Fig. 1). The samples were wrapped in aluminum foil, transferred into a polyethylene bags with a zip locks and labeled with a permanent marker. They were then transported to the laboratory and kept in a freezer maintained at -20°C prior to extraction.

Fig. 1. Distribution of the sampling sites in Ny-Ålesund and London Island, Arctic.

2.2. Standards, reagents and chemicals

Standard solutions of PCBs (US EPA defined 68A-LCS, 68A-IS), and PBDEs (BDE-LCS, ^{13}C -BDE-47, -99, and -153) were all obtained from Wellington Laboratories (Guelph, Ontario, Canada). Pesticide-grade solvents, dichloromethane (DCM), *n*-hexane, toluene and acetonitrile (HPLC-grade) were purchased from J.T. Baker Company Inc. (Fairfield, OH, USA). Silica gel 60 (0.063–0.100 mm) was obtained from Merck (Darmstadt, Germany). C_{18} reversed-phase SPE columns (3 mL, 20 μm porosity) were bought from Supelco Inc. (Bellefonte, PA, USA). The carbon mixture (18% w:w) was prepared using 9 g carbon (Carbopak C, Supelco 10258, USA) dispersed 41 g Celite (545 coarse, Fluka 22140, USA). Anhydrous sodium sulfate, concentrated sulfuric acid and sodium hydroxide were of guaranteed grade from the domestic market. Prior to use, silica gel, and anhydrous sodium sulfate and carbon mixture were baked at 550 °C for 12 h, at 660 °C for 6 h and at 130 °C for 6 h, respectively. Acid silica gel, basic silica gel were prepared following our previous work (Wang et al., 2012).

2.3. Sample preparation

Prior to extraction, the samples were homogenized and freeze-dried. The extraction and clean-up procedures followed the method reported by Liu et al. (2006). Briefly, 2 g of plant/reindeer dung or 10 g of soil was mixed with 10 g of anhydrous sodium sulfate and spiked with ^{13}C -labeled surrogate standards (BDE-LCS and US EPA defined 68A-LCS). The mixture was then extracted on an accelerated solvent extraction device (ASE300, Dionex, USA) using 1:1 v/v mixture of *n*-hexane/DCM.

For biota, the extract was concentrated to dryness in order to determine the lipid content and was later redissolved in 50 mL of *n*-hexane. The solution was then passed through a column packed with acidified silica gel and anhydrous sodium sulfate to remove lipids and moisture, respectively. The resulting eluate was cleaned up with multi-layer silica gel column (packed from bottom to top with 1 g silica gel, 4 g basic silica gel, 1 g silica gel, 8 g acidic silica gel, 2 g silica gel, and 4 g anhydrous sodium sulfate), followed by a basic aluminum column (packed with 6 g basic alumina and 4 g anhydrous sodium sulfate at the top) and then a carbon column (1.5 g carbon mixture and 2 g anhydrous sodium sulfate at the top). The clean eluate was concentrated to 1 mL using a rotary evaporator and transferred into vials containing 20 μL nonane. The contents of the vials were further evaporated to 20 μL using a gentle stream of nitrogen and later spiked with injection standards (US EPA defined 68A-IS) prior to instrumental analysis.

2.4. Instrumental analysis

The analysis of thirteen PBDE congeners (BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183 and -190) and twenty-five PCBs congeners including six indicator PCBs (CB-28, -52, -101, -138, -153, and -180), twelve dioxin-like PCBs (CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, and -189), seven other PCBs (CB-3, -11, -15, -202, -205, -208 and -209) were performed using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS, AutoSpec Ultima, Waters, USA). The GC working conditions and other instrumental parameters are described in detail by Shang et al. (2013).

Chiral PCBs (CB-95, -136, -149, -174 and -176) were analyzed using a DFS system (Thermo Fisher, USA) with an electron impact (EI) ion source. The HRMS was operated in VSIR mode at a resolution ≥ 8000 , source temperature was 250 °C and electron emission energy was 45 eV. Chromatographic separation was achieved by injecting 1 μL of sample on a fused silica capillary column (Chirasil-Dex, 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm thickness). The

temperature conditions of the GC were as follows: initial temperature 60 °C for 1 min, increased to 150 °C at 5 °C min^{-1} , then to 192 °C at 0.4 °C min^{-1} , and finally to 220 °C at 10 °C min^{-1} . The injection port and transfer line temperature were held at 240 °C. The carrier gas was helium at a constant flow rate of 1.5 mL min^{-1} .

2.5. Quality assurance/quality control (QA/QC)

To ensure quality of the data, a laboratory blank was run after every ten samples. The recoveries based on spiked surrogate standards were 57.4–149% for PCBs and 63.2–146% for PBDEs. The limit of detection (LOD) for individual compounds was determined as three times of signal-to-noise ratio (S/N). The LOD was a function of the extracted mass and varied between analytes (0.01–16.2 pg g^{-1} dw for PCBs and 0.03–1.49 pg g^{-1} dw for PBDEs). Several indicator PCBs (CB-28, -52, -101 and -153) and PBDEs (BDE-47, -99 and -153) were detected in blank samples at relatively low levels (<15% of the levels in samples). Therefore, the detected concentrations of PCBs and PBDEs in samples were not blank corrected.

2.6. Statistical analysis

Statistical analysis was performed using SPSS Software for Windows Versions 20 (SPSS, Chicago, IL). The Mann–Whitney U-test was used to determine any significant differences between means of the analytes. Principle component analysis (PCA) was applied to investigate specific PCB congeners contributions between different matrices while one sample T-test was used to test for differences between enantiomeric fractions (EFs) and theoretical EFs of racemic mixtures. EFs were calculated using the equation, $\text{EFs} = (+)/[(+) + (-)]$ or $\text{EFs} = E_1/(E_1 + E_2)$, where (+) and (–) represent the concentrations of the (+) and (–) enantiomers, and E_1 and E_2 represent the first and second eluting enantiomers in GC column (Ross et al., 2008).

3. Results and discussion

3.1. PCBs and PBDEs concentrations

The mean concentrations of PCBs and PBDEs in different matrices (soils, reindeer dung, mosses and the other five plant species) are presented in Tables 1 and S2. The $\Sigma_{25}\text{PCBs}$ concentrations in soil varied from 0.57 to 2.52 ng g^{-1} dry weight (dw). They were consistent with those in the same region reported by Jartun et al. (2010) (4.2 ng g^{-1} dw) and in background surface soil from Svalbard (Kallenborn et al., 2013) (1–5 ng g^{-1} dw), but lower than those in the Canadian Arctic (Pier et al., 2002) and United Kingdom and Norway (Meijer et al., 2002) (Table S3). Different PCB concentrations in soils were observed at seven sampling sites (Fig. S1),

Table 1

Mean concentrations of $\Sigma_{25}\text{PCBs}$ (ng g^{-1} dw) and $\Sigma_{13}\text{PBDEs}$ (pg g^{-1} dw) in different samples.

	$\Sigma_{25}\text{PCBs}$	$\Sigma_{13}\text{PBDEs}$
Moss (<i>Drepanocladus aduncus</i>)	0.75(0.43–1.16) ^a	119(36.7–495)
Mountain avens (<i>Dryas octopetala</i>)	0.49(0.42–0.58)	45.7(42.1–48.1)
Arctic bell-heather (<i>Cassiope tetragona</i>)	0.57(0.48–0.63)	70.1(42.2–121)
Sooty sedge (<i>Carex misandra</i>)	0.45(0.3–0.55)	80(54.7–111)
Alpine hair grass (<i>Deschampsia alpine</i>)	0.41(0.37–0.46)	74.4(73.4–75.3)
Tufted saxifrage (<i>Saxifraga cespitosa</i>)	0.37	41.9
Reindeer dung	0.77(0.56–0.98)	52(28.1–104)
Soil	1.38(0.57–2.52)	65.5(1.7–416)

^a Arithmetic mean, minimum and maximum concentrations are listed.

and they were significantly higher than those in plants ($p < 0.05$, Mann–Whitney U-test).

The Σ_{25} PCBs levels in moss (*D. aduncus*) varied from 0.39 to 1.02 ng g⁻¹ dw, comparable to those in the same region reported by Ma et al. (2008) (0.92–1.97 ng g⁻¹ dw), and in moss (*Sanionia uncinata*) (0.41–0.95 ng g⁻¹ dw) from King George Island and Ardley Island in the Antarctica (Wang et al., 2012). PCBs levels in reindeer dung were 0.56–0.98 ng g⁻¹ dw, equally distributed at different sampling sites (Fig. S1). The Σ_{25} PCBs in *D. alpine*, *D. octopetala*, *C. tetragona*, *C. misandra* and *S. cespitosa* were 0.37–0.46, 0.42–0.58, 0.48–0.63, 0.30–0.55 and 0.37 ng g⁻¹ dw, respectively (Tables 1 and S2).

The Σ_{13} PBDEs concentrations in soil ranged from 1.7 to 416 pg g⁻¹ dw. They were lower than those reported in Norway (Hassanin et al., 2004), and the Antarctica (Cipro et al., 2011), but in the same levels with those from Canada (Danon-Schaffer et al., 2007) (Table S3). Although PCBs in soils were higher than those in *D. aduncus*, the reverse trend was found for PBDEs (Table 1). The Σ_{13} PBDEs levels in *D. aduncus* varied from 36.7 to 118 pg g⁻¹ dw with an outlier at site 6 (Fig. S1). These data were in the same range as those in mosses (*Sanionia uncinata*, *Syntrichia princeps*, *Brachythecium* sp.) from King George Island in the Antarctica (Cipro et al., 2011; Yogui et al., 2011), and comparable to those in *H. splendens* from Norway (Mariussen et al., 2008) and *S. uncinata* from the Antarctica reported by Wang et al. (2012) (Table S3). The Σ_{13} PBDEs concentrations were 28.1 to 104 pg g⁻¹ dw in reindeer dung, 73.4–75.3 pg g⁻¹ dw in *D. alpine*, 42.1–48.1 pg g⁻¹ dw in *D. octopetala*, 42.2–121 pg g⁻¹ dw in *C. tetragona*, 54.7–111 pg g⁻¹ dw in *C. misandra*, 41.9 pg g⁻¹ dw in *S. cespitosa*, respectively (Tables 1 and S2).

3.2. Congener profiles of PCBs and PBDEs

Most of the 25 PCB congeners were detected in all samples except CB-15, -81, -169, and -189. CB-11 was the predominant congeners in most samples, which contributed 26.2 ± 8.4% to the Σ_{25} PCBs in reindeer dung and 31.7 ± 7.6% in *D. alpine*. CB-11 was observed in water, suspended particulate material, and mussel tissues in Halifax Harbor (King et al., 2002) and in the air of Chicago (Hu et al., 2010). High levels of CB-11 were also reported in air samples in Ny-Ålesund, Arctic (Choi et al., 2008), air, soil, sediment, moss and lichen in King George Island, West Antarctica (Li et al., 2012; Wang et al., 2012). The abundant CB-11 in the present study was different to explain, and further investigations are required to reveal unidentified global sources. CB-28, -101, -138 and -153 were also the dominating PCB congeners, which accounted for 41.6–70.5% to the Σ_{25} PCBs in all samples. The primary sources

of PCBs in the Arctic could be associated with long-range atmospheric transport and global fractionation (King et al., 2002; Choi et al., 2008).

The homologue profiles of PCBs were different between plants and soils, especially for the low chlorinated homologue (Fig. 2a). The dominant PCB homologues in plants were mono- to hexa-CBs, whereas high proportions of tetra- and hexa-CBs were observed in soil. For instance, mono-CBs accounted for about 3.7% to the Σ PCBs in plants and 0.7% in soil. Varied homologue profiles could be attributed to different accumulation routes. Soil accumulates POPs mainly through dry and wet deposition of particles, whereas apart from these routes, POPs in plants could also come from accumulation and transport from soil, and gaseous deposition to leaf via cuticle and stomata (Collins et al., 2005; Wang et al., 2009). Tetra-CBs represented 49.9% of the Σ PCBs in *S. cespitosa*, whereas it was not the case for soil, *D. aduncus* and reindeer dung at different sampling sites (Fig. S2). The higher chlorinated homologues were detected at low levels in all samples, indicating that they are not easily transported to high latitudes by atmospheric deposition (Sericano et al., 2001; Choi et al., 2008).

The dominant PBDE congeners were BDE-47, -99 and -183, accounting for 51.2%, 17.8% and 7.9% to the Σ_{13} PBDE, respectively (Fig. 2b). The high percentage of BDE-47 and -99 (69%) was compatible with commercial penta-BDEs products, such as Bromkal 70-5DE, in which BDE-47 and -99 cover 72% of its formulation (Hassanin et al., 2004). The BDE-47/99 ratio in this study was 3.45 ± 1.52, 1.53 ± 0.27 and 1.92 ± 0.47 in soils, *D. aduncus* and reindeer dung, respectively, which were higher than those in commercial products (1:1 in Bromkal 70-5DE). This deviation could be due to the global distillation of these compounds through long-range transport (Lead et al., 1996). Another probable reason might be environmental debromination along congener pathways BDE-154 → BDE-99 → BDE-47 (Ikonomou et al., 2002). The proportion of BDE-183 was relatively high in soil samples at S2 and S4 (80.0% and 60.9%), *D. aduncus* at S6 (77.6%) and reindeer dung at S4 (36.3%) (Fig. S3). Penta-BDE, octa-BDE, and deca-BDE are used in a wide range of materials as technical PBDEs mixtures (Ikonomou et al., 2002), and BDE-183 is considered a marker congener of the octa-BDE products (Hassanin et al., 2004). The higher proportion of BDE-183 indicated the existence of a local pollution source.

3.3. Principal component analysis (PCA) of PCBs

In this study, principal component analysis (PCA) was carried out to investigate the specific PCB congeners partitioned in various environmental matrices. The first and second components (PC1

Fig. 2. Congener profiles of PCBs and PBDEs in different samples.

Fig. 3. Loading (a) and scores (b) plots of principal component analysis (PCA) for individual PCB congeners. The circles represent similar cluster conditions and scores.

and PC2) described 44.1 and 20.8% of the total variance. Loading plots of PCA revealed that 25 PCB congeners were clearly separated into two clusters: the upper-left cluster including five indicator PCBs (CB-52, -101, -138, -153 and -180) and CB-205, and the other one consisted of eleven dl-PCBs (except CB-169) and some other PCBs (Fig. 3a). Based on score plots of PCA (Fig. 3b), it was observed that soils and plants had markedly variant scores on PC1 and PC2. Percentage of the five indicator PCBs and CB-205 to $\sum_{25}\text{PCBs}$ in soils (87.8%, range 76.8–94.8%) was greatly higher than those in plants (49.2%, range 29.8–72.9%). The contributions of dl-PCBs to $\sum_{25}\text{PCBs}$ were 0.21 and 7.5% in soils and plants, respectively. These varied congener distributions between soils and plants could be explained by the different accumulation routes of PCBs (Collins et al., 2005; Wang et al., 2009). As discussed above, the PCA results provide a visual display on different congener distributions in analyzed environmental samples.

3.4. Chiral signatures of PCBs

Chiral PCBs could modulate the stereochemical ratio between enantiomers in environmental biota, which are regarded as good molecular indicators of biological metabolic processes, and usually be assessed using enantiomeric fraction (EFs) (Moisey et al., 2001; Fisk et al., 2002; Zhai et al., 2011). In the present study, five chiral PCBs (CB-95, -136, -149, -174 and -176) were investigated and they were detected in all analyzed environmental matrices (soil, reindeer dung and six plant species) except for CB-174 in reindeer

Fig. 4. Enantiomeric fractions (EFs) of five chiral PCBs in different samples. Red dash line represents the theoretical EF (0.5) of racemic mixtures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dung and CB-176 in *D. octopetala*. The mean EF values fluctuated around theoretical EF value of racemic mixtures of 0.5 (Fig. 4).

The EFs of CB-95 in all matrices were greatly lower than 0.5, indicating nonracemic signatures and enrichment of the second-eluted enantiomer or (–) enantiomer. Similar enantioselective biotransformation of CB-95 was also reported in poplars (*Populus deltoides*) after 20 days exposure (Zhai et al., 2011). The EF values of CB-136 in analyzed matrices were slightly higher than 0.5, but the consistent results between soils and plants were not observed for other chiral PCBs. The EFs of CB-174 in soil (0.555 ± 0.044) were significantly higher than those in *D. aduncus* ($\text{EF} = 0.485 \pm 0.039$, $p = 0.011$) and *D. alpine* ($\text{EF} = 0.495 \pm 0.011$, $p = 0.023$). They were also significantly higher than those in racemic mixtures, suggesting that CB-174 in soil showed enantioselective degradation. These results are consistent with EFs of CB-95, -149 and -174 in background soils collected in the United Kingdom and Norway (Schuster et al., 2011). Non-racemic EFs of CB-95, -136, and -149 were also found in top soils in the United Kingdom and Canada (Lehmle et al., 2009). Compared with CB-95, chiral PCBs with large molecular weight (such as CB-136, -174 and -176) presented nearly racemic or slightly enantioselective biotransformation. Chiral CB-95 was more easily enantioselectively biotransformed than other chiral PCBs in soils and plants. This result could be ascribed to the decreasing metabolism rates of PCBs with ascending molecular mass and compound-specific reactions with different enzymes or other biochemical processes (Zhai et al., 2011).

In short, the signature of enantioselective biotransformation was observed in all samples for CB-95, in soil, reindeer dung, *C. misandra*, and *C. tetragona* for CB-136, in *C. tetragona*, and *S. cespitosa* for CB-149 and in soil for CB-174 (Fig. 4). These varied signatures could be contributed to microbial enantioselective transformation by microorganisms in soil, and selective absorption in organisms (Zhai et al., 2011). Some other complex factors, such as soil organic carbon, organic matter and pH could also influence enantioselective degradation in environmental matrices (Bidleman et al., 2012).

3.5. Bioaccumulation in plants

Bioaccumulation factors (BAFs) were calculated from the ratio of contaminant concentrations in plant to those in soils. In this paper, BAF values of $\sum_{25}$ PCBs in six plant species were lower than 1, ranging from 0.28 in *D. alpine* to 0.71 in *D. aduncus* (Table S3). Similarly, lower BAFs were also observed for CB-52 and -101 in *D. aduncus*, CB-52, -101, -138, -153, -180 and -250 in plant species except for *D. aduncus*. The BAFs for CB-28, CB-118 and other PCB congeners were higher than 1. For example, CB-28 in plants varied from 2.89 in *S. cespitosa* to 9.93 in *D. octopetala*. All the BAF values of PCBs in this study were consistent with those in Arctic vascular plants comprising 31 genera from Canadian Arctic and Subarctic (Pier et al., 2002). The bioaccumulation trends were observed for $\sum$ PBDEs, increasing in the order of *S. cespitosa* (BAF: 2.41) < *D. octopetala* (7.93) < *C. tetragona* (8.13) < *C. misandra* (18.8) < *D. aduncus* (26.2) < *D. alpine* (44.3) (Table S3).

Plants physiology (such as water, lipid, carbohydrate and fiber content) and morphology characteristics (leaves, stems, or bark), physical–chemical properties of contaminants (K_{OW} or K_{OA}) and different sampling sites with different rhizosphere in soil could account for the variant BAFs (Collins et al., 2005; Vrkslavová et al., 2010). *D. aduncus* reported higher BAFs of PCBs because they have one-cell thick leaves, covering a thin stem, and do not have vascular tissue which could enhance them to take up contaminants from the surrounding environments. Low BAFs in *D. alpine* and *S. cespitosa* could be ascribed to their morphological characteristics or contaminants redistribution through active translocation (Pier et al., 2002).

A bell-shaped correlation ($R^2 = 0.46$, $p < 0.006$) was observed between BAFs and K_{OW} of PCBs, with the maximum BAF corresponding to hexa-CBs with $\log K_{OW}$ values of 7.2–7.6 (Fig. 5). This result may be explained by the fact that lower chlorinated PCBs are easily metabolized by plants, whereas higher chlorinated PCBs with large K_{OW} are more tightly bound to the soils and less available for plants uptake (Pier et al., 2002). With regard to PBDEs, a slightly declining trend was observed in the present study with the increase of number of bromine atoms. Vrkslavová et al. (2010) reported BAFs value of BDE-47, -99, -100 and -209 negatively correlated with their $\log K_{OW}$ in tobacco (*Nicotiana tabacum*) and nightshade (*Solanum nigrum*), which was consistent with the result in this study. A negative correlation was also observed between BAFs and $\log K_{OW}$ values from paddy soils to rice plant (She et al., 2013). The descending BAFs for PBDE congeners with high K_{OW} could be due to hydrophobicity and large molecular weight, which restricted contaminant penetration into cellular membranes (She et al., 2013).

Log-transformed BAFs exhibited significantly negative correlations to log-transformed PCBs concentration in soil ($R^2 = 0.73$, $p < 0.0001$) and log-transformed PBDEs concentration in soil ($R^2 = 0.91$, $p < 0.0001$) (Fig. S4). Similar trends was also reported by Pier et al. (2002), who indicated that BAFs of vascular plants in the Canadian Arctic and Subarctic negatively correlated with PCBs concentration in soil ($R^2 = 0.55$). Low BAFs of PCBs and PBDEs corresponded to high contaminant levels in soil, which suggested

Fig. 5. Relationships between BAFs and $\log K_{OW}$ values for PCB (a) and PBDE (b). Those BAFs corresponding to congeners whose concentrations were lower than limit of detection were not shown.

that high background levels of contaminants in soil could restrict the accumulation of these contaminants by plants (Pier et al., 2002). This could also explain why reverse variation trend of PCBs and PBDEs levels in the present study existed between soils and plants.

4. Conclusions

The present study examined the current contamination levels, distributions, homologue profiles and bioaccumulation of PCBs and PBDEs in plants and soil samples from the London Island, Svalbard, the Arctic. The results revealed that the current concentrations of PCBs and PBDEs were low on the global scale and they were not evidently affected by research stations in Ny-Ålesund. The mean concentrations of PCBs in soils were higher than those in plants. However, the reverse trend was observed for PBDEs. CB-11, -28, -101, -138 and -153 were the dominated PCB congeners, and BDE-47 was predominant for PBDEs. Chiral CB-95 in all analyzed matrices presented accordant enantioselectivity biotransformation, and varied enantioselectivity between matrices was observed for other chiral PCBs. Bioaccumulation factors of PCBs and PBDEs varied within different contaminant congeners and plant species. Further research is needed to better understand the enantioselectivity and bioaccumulation properties of these contaminants in the Arctic environment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.01.043>.

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