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Novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in fish, penguin, and skua from the King George Island, Antarctica

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Abstract

Persistent organic pollutants (POPs), including legacy pollutants polychlorinated biphenyls (PCBs) and emerging contaminants polybrominated diphenyl ethers (PBDEs), are a challenge to the biota in the polar regions. Frequent and increasing detection of PCBs and PBDEs were reported in Antarctica, whereas no data were available for novel flame retardants (N-FRs). N-FRs are being used in global range as alternatives of PBDEs and have similar properties to POPs. This study presented the occurrence of several N-FRs, PBDEs, and PCBs in tissue samples of an Antarctic rock cod (*Trematomus bernacchii*), a young gentoo penguin (*Pygoscelis papua*), and a brown skua (*Stercorarius antarcticus*) collected from the King George Island. Among all N-FRs, only Dec-602 was detected in 75% of the biota samples and the detection frequencies only ranged from 3.5% to 28.6% for PBBz, HBBz, PET, PBEB, BTBPE, 1,2-DPMA, *anti*-DP, and Dec-604. No DPTE and *syn*-DP were found, while PBDEs and dioxin-like PCBs (DL-PCBs) can be detected in almost all samples. The total concentrations of N-FRs (ΣN-FRs; mean: 931 pg/g dry weight (dw)) were comparable to those of PBDEs (Σ_8PBDEs; 681 pg/g dw), both of which were much lower than those of PCBs (ΣDL-PCBs; 12,800 pg/g dw). Overall, skua contained two to three orders of magnitude higher N-FRs, PBDEs, and DL-PCBs than penguin and fish. For a specific species, liver generally contained the highest pollutant levels compared to muscle, spleen, and stomach in fish and penguin. However, for skua, the highest values were found in muscle and spleen for PBDEs and DL-PCBs and N-FRs, respectively. The significant correlations were observed among three types of contaminants in biota, indicating the similar sources from either long-range transportation or local sources. More attention should be paid on the fate of N-FRs in Antarctica, which are used in increasing amounts after the ban of PCBs and PBDEs. To our knowledge, this is the first report on the levels of N-FRs in biota from Antarctica.

Keywords: Novel brominated flame retardants, polybrominated diphenyl ethers, dioxin-like polychlorinated biphenyls, bioaccumulation, Antarctica

1. Introduction

Polychlorinated biphenyl (PCBs) and polybrominated diphenylether (PBDEs) are typical anthropogenic chemicals which were used over decades. Because of the persistent and the environmental dispersal mechanism linked with the high production level they are highly distributed all over the world. Both groups are lipophilic, they accumulate through the food web and adversely affect ecosystems. In 2004 together with other chlorine semi-volatile substances the PCBs were banned as “dirty dozen” in the Stockholm convention and the usage were phased out. As well in 2004 the PBDEs were restricted in the EU and North America. In 2009, together with other highly chlorinated, two of the three major commercial PBDE mixtures, penta-BDE and octa-BDE, have been banned globally because of their strong bioavailability, persistence, and toxicity (Xiang et al., 2014). Therefore, novel flame retardants, such as 2,3-bibromopropyl-2,4,6-tribromophenyl ether (DPTE), bis(2-ethylhexyl)tetrabromophthalate (TBPH), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), hexabromobenzene (HBBz), and dechlorane plus are produced and used with increasing volume (Vorkamp and Riget, 2014).

Antarctica is a cold and isolated continent which was never direct under anthropogenic activity like settlement, mining or farming excepting discovery and scientific work. Unfortunately many studies have shown that the continent has reached by persistent organic pollutants (POPs) (Bengtson Nash, 2011). The long range atmospheric transportation (LRAT) is generally regarded as the main contaminant source (Kallenborn et al., 1998; Klanova et al., 2008). Compounds enter the environment in the urban areas and over the atmosphere they were global distributed. Along the latitude and altitude temperature gradients the compounds are under a fractionation process according their volatility. In the cold remote environment of polar areas they were deposited and trapped by precipitation and

cold condensation (Wania and Mackay, 1996) Recently, local sources such as research stations and tourism activities have been gradually recognized as an important input pathway of pollutants to the polar environment (Hale et al., 2008). Currently, except for PCBs and PBDEs, emerging contaminants such as novel brominated and chlorinated flame retardants mentioned above have been found in Arctic (Vorkamp and Riget, 2014), however, no data were reported in Antarctica currently.

This study collected fish, penguin, and skua samples from the King George Island, Antarctica, with main aims: (1) to investigate the occurrence of N-FRs with comparisons with PBDEs, and PCB; (2) to examine the specie and tissue distributions of these contaminants.

2. Methods and materials

2.1. Sample collection

Samples including an Antarctic rock cod (*Trematomus bernacchii*), a young gentoo penguin (*Pygoscelis papua*), and a brown skua (*Stercorarius antarcticus*) were collected around the Chinese Great Wall Station on King George Island, Fildes Peninsula, Antarctica during November 2010 to January 2011. The skua as well as the penguin at a young age were found naturally death.

2.2. Extraction and clean-up

Detailed descriptions of used chemicals including analytical standards are listed in Table S1-S2 ("S" indicates Table or Figure in the Supporting Information here and thereafter). The freeze-dried samples were homogenized by mortar. Approximately 1–3 gram of samples were filled in an extraction thimble, covered with Na_2SO_4 and spiked with mass labeled internal standards to control the extraction and analysis (the analogous labelled standards for PCBs, labelled BDE-77, and 138 for PBDEs, and labelled HBB and s-DP for N-FRs). The thimbles were soxhlet extracted for 12 h using dichloromethane (DCM) as solvent. After

extraction the samples were reduced to approximately 2 mL using rotary evaporator. The clean-up procedure is adapted from Suehring et al. (2013). For the first clean-up a manually gel permeation chromatography (GPC) with 35 g Bio-Beads S-X3 (Bio-Rad Laboratories) and DCM: Hexane (1: 1; v/v) was used as elute. The extracts were again reduced and the solvent transferred to hexane. As second step the samples were further purified by silica clean-up with 10% deactivated silica gel. The elute was reduced to 150 µL under a gentle stream of nitrogen and transferred to measurement vials. 10 µL labelled PCB-141/PCB-208 (50 ng mL^{-1}) was added as injection standards and finally extracts were evaporated to 30 µL for measurement.

2.3. Instrumental Analysis

The instrumental analysis done by a GC/MS-system (6890 GC/5973 MSD) in negative chemical ionisation mode (NCI) with methane as ionization gas fitted with a HP-5MS column (30m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific). The instrument was operated in selected ion monitoring mode. Samples were analysed in a first chromatographic run for PCB, in a second run were following PBDEs and N-FRs analysed. Details information about GC-MS conditions and assignation of target compounds and internal standards are given in Table S3.

2.4. QA/QC

Extraction and clean-up were conducted in a clean lab (class 10000). Recovery rates of internal standards were determined for every sample. Mean relative recoveries of internal standard for PCBs, PBDEs, and N-FRs were 94 ± 3%, 70 ± 19%, and 63 ± 18 %, respectively.

The limit of detection (LOD) was calculated from a signal to noise ratio of ten or else from the blank. The LOD for PCBs is given with 1 pg/g dry weight (dw) for PBDEs and N-FRs 3 pg/g dw. A blank test, using Na_2SO_4 as sample material treated similar to real

samples, was conducted with every extraction batch of nine samples. All Blanks were under LOD or else 1–2 magnitudes lower as lowest samples. Because of the possible drying process between dying and the sample pick up, all results will be given by contaminants based on dry weight (dw).

3. Results and discussion

3.1. Levels

The detailed concentration information of N-FRs, PBDEs, and DL-PCBs in fish, penguin, and skua from the King George Island, Antarctica were listed in Table S4-S6.

N-FRs. Among all N-FRs, only Dec-602 was detected in 75% of the biota samples (n = 28). Much higher concentrations (range: 324–12, 400 pg/g dw) were observed in skua than those in penguin (range: <LOD–238 pg/g dw) and fish (range: <LOD–4.8 pg/g dw), indicating the bioaccumulation and biomagnification potential of Dec-602 in the polar environment. However, for other chlorinated flame retardants, the detection frequencies were only 21%, 11%, and 7.1% for DPMA, Dec-604, and *anti*-DP with the highest levels of 136, 165, and 8.9 pg/g dw, respectively. No *syn*-DP was found in any investigated samples. Similarly, Dec-602 was detected in beluga whale (range: 25–300 pg/g lipid) from the Canadian Arctic whereas Dec-604 and DPs were below detection limits (Shen et al., 2012).

DPs was originally produced in the 1960s as a replacement of the insecticide Mirex and is a current-use flame retardant with a world production of 800 tons annually, as an alternative of Deca-BDE (Vorkamp and Riget, 2014). The resulting material consists of the *syn* and *anti* isomers with a ratio of about 1:3 (Sverko et al., 2011). Dec-602 and Dec-604 are dechlorane-based flame retardants used in certain applications and the residues were reported in the environment such as the Great Lakes region, but the information on the production volumes and applications of these compounds is not available (Sverko et al., 2011).

Generally, Dec-602 was evidenced to have greater bioaccumulation potentials than Dec-604 and DPs based on calculated biota-sediment accumulation factors (BSAFs) in Lake Ontario (Shen et al., 2011) and near the Bohai and Huanghai Sea shore area of northern China (Jia et al., 2011), possibly because of the lower log K_{ow} compared to others (7.1, 8.5, and 9.0 for Dec-602, Dec-604, and DPs, respectively) (Feo et al., 2012). Moreover, the higher vapor pressure (5.53×10^{-7} Pa) and water solubility (8.49 ng/L) of Dec-602 compare to those of Dec-604 (8.47×10^{-8} Pa and 2.21 ng/L) and DPs (4.71×10^{-8} Pa and 0.04 ng/L) (Feo et al., 2012) are more prone to its long-range transportation from production and/or usage regions to the polar environment.

As monoadducts of DPs, two isomers of DMPA (1,3-DPMA and 1,5-DPMA) could be formed by the incomplete reaction of hexachlorocyclopentadiene with 1,3-cyclooctadiene (a reported impurity) or with DP's starting material, 1,5-cyclooctadiene (Sverko et al., 2011). The monoadducts (DMPA) was indicated to have bioaccumulation potential, with the properties similar to DPs. In the present study, 1,3-DPMA was found in all tissue samples of skua except for blood with a variation of 52.8−136 pg/g dw, however, the levels in fish and penguin were below the detection limit. Few studies have been done on the occurrence of DPMA in biota. DPMA was widely distributed in Spanish and Canadian peregrine (*Falco peregrines*) eggs with concentrations from 1.7 to 469 ng/g lipid and 1.2 to 1660 ng/g lipid, respectively, even much higher than DPs (Guerra et al., 2011). Sverko et al. (2010) also reported as high as approximately 30 ng/g lipid of 1,3-DPMA in Lake Ontario lake trout. In a Lake Ontario (Canada) food web, 1,3-DPMA was measured in all trophic levels (0.12−199 ng/g lipid), whereas 1,5-DPMA was measured only sporadically in the food web and was not detectable in the apex predator, lake trout (*Salvelinus namaycush*). 1,5-DPMA is more readily metabolized than 1,3-DPMA by lake trout, which was indentified through

biotransformation kinetic experiments using in vitro lake trout liver microsomal exposures by Tomy and co-workers (2013).

Interestingly, PBBz was frequently found in fish tissue with concentrations of 2.5–17.0 pg/g dw whereas no detection in penguin and skua samples, the reason of which is unclear currently. PBBz was reported as a flame retardant introduced in the 1980s and no further information on its production and/or consumption. In addition, PBBz could be a degradation product of HBBz or other brominated compounds . The occurrence of PBBz was reported in air and snow pit, but not in water samples from the Arctic (Vorkamp and Riget, 2014), and no data is available for biota. HBBz were observed only in one sample (stomach contents of fish) with the concentration as low as 7.8 pg/g dw. The production volume HBBz is in the order of some 100 tons per year and was mainly used in Japan. In the recent years, the monitoring of HBBz have been conducted extensively in biota from the Arctic, with a large concentration variation depending on sampling locations (Vorkamp and Riget, 2014). For example, all polar bear samples from East Greenland contained detectable HBBz, while the detection frequencies of HBBz were only about 15–45% for the polar bear samples from Alaska and Canada (McKinney et al., 2011). For DPTE, the production volume as a brominated flame retardant and the distribution pattern in the environment are unclear (Vorkamp and Riget, 2014). Meanwhile, no DPTE was detected in our samples, which may indicate that DPTE was not largely and widely used in the world.

Unexpectedly, the detection frequency of PBT in our samples is very low (18%; mainly in fish) with concentrations of less than 7.3 pg/g dw, although the production quantity is up to 5000 tons per year (de Wit et al., 2010). PBT was also undetectable in a variety of biota samples from Svalbard, the Faroe Islands, Iceland, Alaska, Canada, and Greenland (McKinney et al., 2011; Vorkamp and Riget, 2014), suggesting the bioacccumation potential of PBT is low. PBEB was found in 29% of samples with a low concentration of <LOD–7.6

pg/g dw. Similar to PBT, fish contained relatively higher contents compared to penguin and skua. In a previous study, however, PBEB was found in all samples of egg yolk of glaucous gull from the Norwegian Arctic (Verreault et al., 2007), which is inconsistent with our result. It is interesting to note that four skua tissue samples contained BTBPE (range: <LOD–26.3 pg/g dw), but no BTBPE in fish and penguin samples. According to a review by de Wit et al. (2010), BTBPE is a replacement of OctaBDE and it can be long-transported and accumulate in high trophic level biota. A trophic magnification factor of 1.8 was calculated for BTBPE in a food web in Lake Winnipeg in Canada (Law et al., 2006). However, the current concentration of BTBPE is much lower when compared to PBDEs and PCBs, such as in Greenland shark (*Somniosus microcephalus*) (0.61 ng/g lipid for BTBPE *vs* 24 ng/g lipid for BDE-47 *vs* 1100 ng/g lipid for PCB-153) (Strid et al., 2013).

PBDEs. PBDEs were detected in all biota samples except for a skua blood (Table S4-S6). The total concentrations of targeted PBDE congeners (Σ_8PBDEs) in fish (9.1–294 pg/g dw) and penguin (6.2–188 pg/g dw) were far lower than those in skua (<LOD–6460 pg/g dw). The congener profiles of PBDEs were similar in different tissues of fish, penguin, and skua, in which BDE-47 was the predominate congener with the mean contributions of 58.7–73.9%, followed by BDE-99 (9.3–20.2%) and BDE-100 (5.1–14.7%) (Figure 2 and S2). BDE-47, BDE-99, and BDE-100 are the main compounds in PentaBDE (BromKal 70-5DE and DE-71) (La Guardia et al., 2006; Li et al., 2014). However, the contents of BDE-99 in commercial products (44.8–48.6%) are slightly higher than those of BDE-47 (38.2–42.8%), which was common and interesting in fish and marine mammals (Meng et al., 2009; Meng et al., 2008). The possible reasons may due to the relatively lower bioaccumulation ability and higher biodegradation rate of BDE-99 compared to those of BDE-47. The contributions of BDE-153 and BDE-154 in our samples were low (2.1–3.6% and 1.6–5.2%, respectively), which may relate with their small percentages in PentaBDE and OctaBDE (5.32–5.44% and

0.15−8.66% for BDE-153; 2.68−4.54% and 0.04−1.07% for BDE-154, respectively) (La Guardia et al., 2006). BDE-183 is a main component of one OctaBDE commercial product (DE-79) (La Guardia et al., 2006), however, the percentage as low as 0.25% of BDE-183 was found in our samples. More PentaBDE was used historically than OctaBDE in the global range and currently both of them have been added to the list of banned chemicals included in the Stockholm Convention on Persistent Organic Pollutants since 2009 due to their persistence and ubiquitous occurrence in the environment (Xiang et al., 2014).

Several researchers reported the occurrence of PBDEs in biota from the Antarctica (Borghesi et al., 2008; Borghesi et al., 2009; Corsolini et al., 2006; Goutte et al., 2013; Hale et al., 2008; van den Brink et al., 2011; Yogui and Sericano, 2009), however, the data cannot be compared among differ studies because of inconsistent units. Goutte et al. detected PBDEs in 9 of the 30 analyzed biological samples (starfish, Antarctic yellowbelly rockcod, Antarctic krill, egg of snow petrel, and bald notothen) collected from the pointe Géologie Archipelago, Adélie Land, Antarctica and BDE-47 was predominant in two upper trophic level species, the snow petrel and the Antarctic yellowbelly rockcod (Goutte et al., 2013). Borghesi et al. sampled Antarctic fish (*Chionodraco hamatus*, *Chaempsocephalus gunnari*, *Gymnoscopelus nicholsi*, *Trematomus eulepidotus*) from the Ross Sea, south of the Italian "Mario Zucchelli" scientific station in 2001−2002 and found PBDE levels ranged from 90 to 440 pg/g wet weigh (Borghesi et al., 2009), which were comparable to those reported for muscle samples of *Trematomus bernacchii* from the same area and for other Antarctic species (Corsolini et al., 2006). In 2005, Borghesi et al. collected two species of Antarctic fish from the above area and PBDE concentrations varied from 160.5 pg/g wet weight in *Chionodraco hamatus* muscle to 789.9 pg/g wet weight in *Trematomus bernacchii* liver (Borghesi et al., 2008). The average concentration of PBDEs in seabird eggs was 6.78 ng/g lipid (range: 3.13−33.0 ng/g lipid; geometric mean: 5.59 ng/g lipid) for chinstrap penguin, 8.12 ng/g lipid

(range: 3.03–22.7 ng/g lipid; geometric mean: 6.87 ng/g lipid) for gentoo penguin and 146 ng/g lipid (range: 19.0–558 ng/g lipid; geometric mean: 84.7 ng/g lipid) for south polar skua collected from the Admiralty Bay, Antarctic Peninsula (Yogui and Sericano, 2009).

DL-PCBs. DL-PCBs were detected in all samples (Table S4-S6), with the range of 32.2–191 pg/g dw in fish (mean: 102 pg/g dw), 91.8–3370 pg/g dw in penguin (mean: 560 pg/g dw), and 7 090–85, 800 pg/g dw (mean: 50, 100 pg/g dw), respectively for ΣDL-PCBs (sum of all investigated PCB congeners). Similar congener patterns of DL-PCBs were observed in fish, penguin, and skua, in which PCB-180, 118, and 170 were the predominant compounds with the mean contributions of 30.2–45.0%, 22.4–29.6%, and 10.4–12.5%, respectively (Figure 2). PCBs still can be detected in biota from the Antarctic although its production and usage have been banned since 1970s globally. Corsolini et al. collected emerald rockcod (*Trematomus bernacchii*) from the Ross Sea, Antarctic in 2000 and detected 56 PCB congeners with the average of 6.35 ng/g wet weight in muscle samples (Corsolini et al., 2006). Focardi et al. investigated 22 PCB congeners in seven species of Antarctic fish from Terra Nova Bay (Ross Sea) collected from 1987-1990 and the levels ranged from 2.8 ng/g dw in *Cygnodraco mawsoni* to 12.8 ng/g dw in *Pagothenia bernacchii* (Focardi et al., 1992). PCBs were quantitated in four species of Antarctic fish collected around the Japanese Antarctic Research Station during January to December 1981 and the concentrations ranged between 0.08 and 0.77 ng/g wet weight basis in whole body homogenates (Subramanian et al., 1983). Fish (*Trematomus pennelli*, *Chionodraco hamatus*, *Pleuragramma antarcticum*), were collected from the Ross Sea (Antarctica) in Terra Nova Bay, during the X (1994/1995) and XI (1995/96) Italian Expeditions and the concentrations varied from 4.2 to 175 ng/g dw (Corsolini et al., 2002).

3.2. Species and tissue distribution

Overall, skua contained much higher N-FRs, PBDEs, and DL-PCBs than penguin and fish (Figure 3). Taking muscle samples as example, the concentrations of N-FRs in skua were 1770 pg/g dw, approximately two orders of magnitude higher than those in penguin (11.0 pg/g dw) and fish (20.8 pg/g dw). For PBDEs, more than two orders of magnitude in levels were found between skua (2390 pg/g dw) and penguin (6.2 pg/g dw) and fish (9.1 pg/g dw). Even three orders of magnitude difference were observed for DL-PCBs in skua (54, 100 pg/g dw) and penguin (154 pg/g dw) and fish (32.2 pg/g dw). Similar findings were also shown for other tissues (Figure 3). The possible reasons of species distribution may contribute to their different tropic positions and living habitats. Rock cod is a benthic species that mainly feeds on other benthic organisms (polychaetes, gastropods, isopods, amphipods, echinoderms), which generally contaminated with high POPs concentrations in comparison to fish that mainly feed on krill (Borghesi et al., 2008; Weber and Goerke, 2003). Gentoo penguin lives mainly on crustaceans such as krill, with fish making up only about 15% of the diet. Therefore, the levels of N-FRs, PBDEs, and DL-PCBs were comparable between fish and penguin because of their similar diet (Figure 3). Compared to fish and penguin, brown skua (*catharacta lonnbergi)* occupy a higher trophic level in food chain of Antarctic. Skua is a large marine bird which are highly predatory, feeding mainly on fish, other birds, small mammals, eggs and carrion. In addition, brown skua is a migratory seabird moving further north when not breeding, while gentoo penguins are endemic species that live year round south of the Antarctic Convergence, suggesting that skua is more exposed to contaminants during the non-breeding season when they migrate to waters of the northern hemisphere. Yogui et al. also found that PBDEs in south polar skua eggs are approximately 20 times higher than in penguin eggs (Yogui and Sericano, 2009).

For different tissues of fish and penguin, liver generally contained the highest ΣDL-PCBs and PBDEs compared to muscle, spleen, and stomach (Figure 3). However, for skua, the

highest values were found in muscle and spleen for PBDEs and DL-PCBs and N-FRs, respectively. Currently, no clear reason can be given because of small sample size in the present study. As expected, all targets can be found in stomach or stomach contents of fish, penguin, and skua, indicating dietary is a main route for their exposure to POPs (Table S4-S6). In addition, the occurrence of pollutants in fish egg, penguin yolk, and skua ovarian indicated that they cannot be degraded or assimilated completely by its body and can be transferred to its baby. For example, up to 85,700 pg/g dw of DL-PCBs were detected in a skua ovarian sample, which even higher than those in muscle, liver, and spleen.

3.3. Potential sources

Significant and positive relationships were found among N-FRs, PBDEs, and PCBs in tissues of fish, penguin, and skua from the King George Island, Antarctica, as shown in Table 1 (all $r > 0.65$ and $p < 0.01$), suggesting these chemicals have similar sources. Many researchers indicated that pollutants in the polar areas originate mainly from their production and/or usage regions via long-range transportation either by atmosphere or by seawater (Bengtson Nash, 2011; Goutte et al., 2013). Soils and snow/ice in polar regions is regarded as the reservoirs of POPs, which can be remobilized due to decreasing primary emissions or due to climate change-driven warmer conditions (Cabrerizo et al., 2013). Additionally, local sources such as touristic or research activities cannot be ignored. For example, Hale et al. (2008) investigated PBDEs in indoor dust and wastewater sludge from the U.S. McMurdo and New Zealand-operated Scott Antarctic research bases and indicated that import of personal and professional goods (e.g. plastics, fabrics, electronic equipment) to Antarctic research stations might enhance the local release of this deca-brominated congener. Following the ban of PBDE commercial products, more attention should be paid on the occurrence and fate of N-FRs in the Antarctic, which are used in increasing amounts as alternatives of PBDEs (Vorkamp and Riget, 2014).

4. Conclusions

The levels and distributions of N-FRs, PBDEs, and dioxin-like PCBs were investigated in tissues of fish, penguin, and skua from the King George Island, Antarctica. Several N-FRs were observed in biota samples, especially for Dec-602 with the detection frequencies as high as 75%, indicating its potential of bioaccumulation and long-range transportation. N-FRs levels are similar to PBDEs, but one order of magnitude lower than PCBs. In addition, skua contained two to three orders of magnitude higher N-FRs, PBDEs, and DL-PCBs than penguin and fish. The significant positive relationships among three types of chemicals suggest they share similar sources in Antarctica and more studies are needed to explore their fates in polar areas, especially for emerging contaminants N-FRs.

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Table 1. Spearman correlation (two-tailed) among the levels of novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in tissues in fish, penguin, and skua from the King George Island, Antarctica.

Compounds	ΣN-FRs	Σ_8PBDEs	ΣDL-PCBs
ΣN-FRs	1.000		
Σ_8PBDEs	0.753**	1.000	
ΣDL-PCBs	0.777**	0.659**	1.000

** $p < 0.01$.

Figure Captions

Figure 1. Map of studied areas. The red dots are the sampling sites

Figure 2. Congener profiles of polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in fish, penguin, and skua

Figure 3. Tissue distributions (muscle, liver, spleen, and stomach) of novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in tissues in fish, penguin, and skua

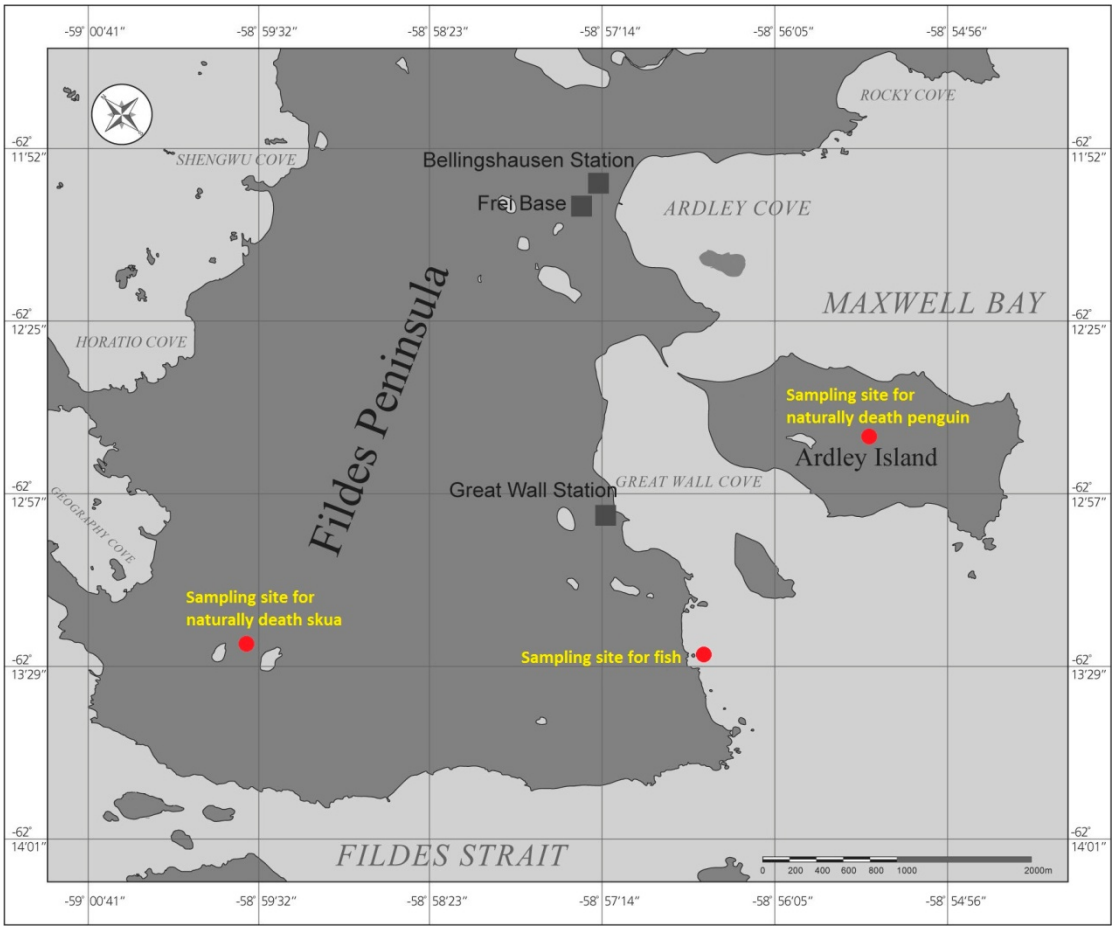
-59° 00'41"
-58° 59'32"
-58° 58'23"
-58° 57'14"
-58° 56'05"
-58° 54'56"
-62° 11'52"
-62° 12'25"
-62° 12'57"
-62° 13'29"
-62° 14'01"
ROCKY COVE
SHENGWU COVE
Bellingshausen Station
Fre Base
ARDLEY COVE
MAXWELL BAY
HORATIO COVE
Fildes Peninsula
Sampling site for naturally death penguin
Ardley Island
Great Wall Station
GREAT WALL COVE
GEOGRAPHY COVE
Sampling site for naturally death skua
Sampling site for fish
FILDES STRAIT
0 200 400 600 800 1000 2000m

Figure 1.

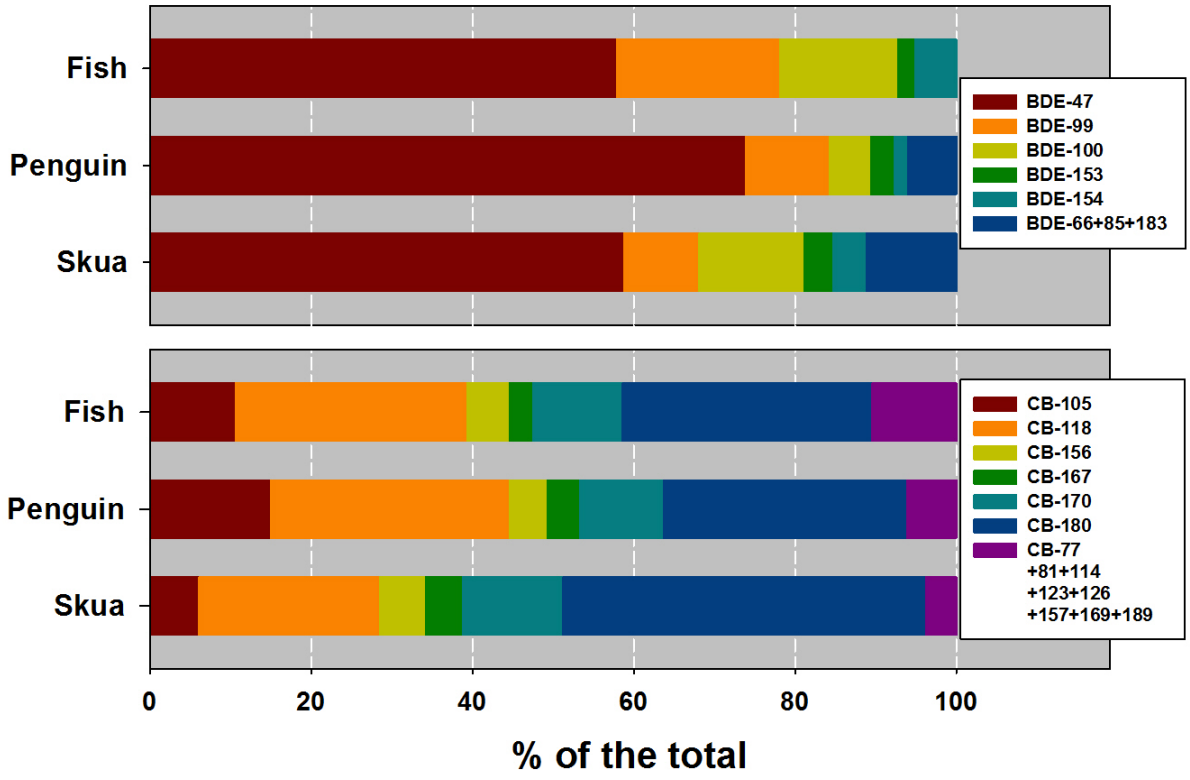
Fish
Penguin
Skua
BDE-47
BDE-99
BDE-100
BDE-153
BDE-154
BDE-66+85+183
Fish
Penguin
Skua
CB-105
CB-118
CB-156
CB-167
CB-170
CB-180
CB-77
+81+114
+123+126
+157+169+189
0
20
40
60
80
100
% of the total

Figure 2.

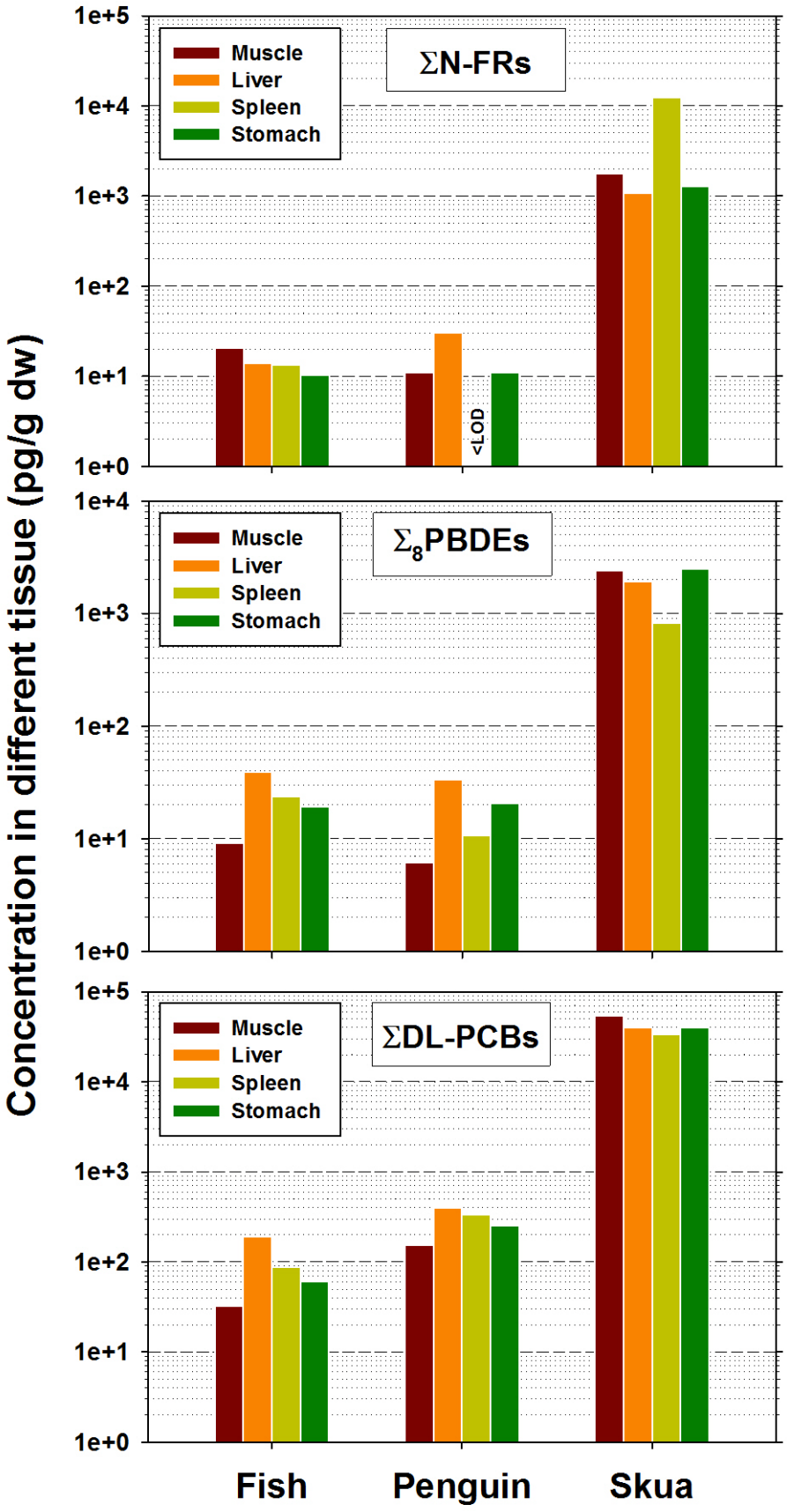
Concentration in different tissue (pg/g dw)
ΣN-FRs
Muscle
Liver
Spleen
Stomach
<LOD
Σ8PBDEs
ΣDL-PCBs
1e+0
1e+1
1e+2
1e+3
1e+4
1e+5
Fish
Penguin
Skua

Figure 3.