Accumulation of PBDEs and MeO-PBDEs in notothenioid fish from the South Shetland Islands, Antarctica : an interspecies comparative study

Accumulation of PBDEs and MeO-PBDEs in notothenioid fish from the South Shetland Islands, Antarctica: an interspecies comparative study

Juan Manuel Ríos[a,i], Sabrina B. Mammana[a,b,h], Eugenia Moreira[c,d], Giulia Poma[e], Govindan Malarvannan[e], Esteban Barrera-Oro[c,f], Adrian Covaci[e], Nestor F. Ciocco[b, g], and Jorgelina C. Altamirano[a,b]

[a]*Laboratorio de Química Ambiental, Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales (IANIGLA, CCT-CONICET), Mendoza 5500, Argentina*

[b]*Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza, Argentina*

[c]*Instituto Antártico Argentino (IAA), Buenos Aires, Argentina*

[d]*Laboratorio de Biología Funcional y Biotecnología (BIOLAB), INBIOTEC-CONICET. Facultad de Agronomía, UNCPBA, Azul 7300, Buenos Aires, Argentina*

[e]*Toxicological Centre, Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium*

[f]*Museo Argentino de Ciencias Naturales Bernardino Rivadavia and CONICET, Buenos Aires, Argentina*

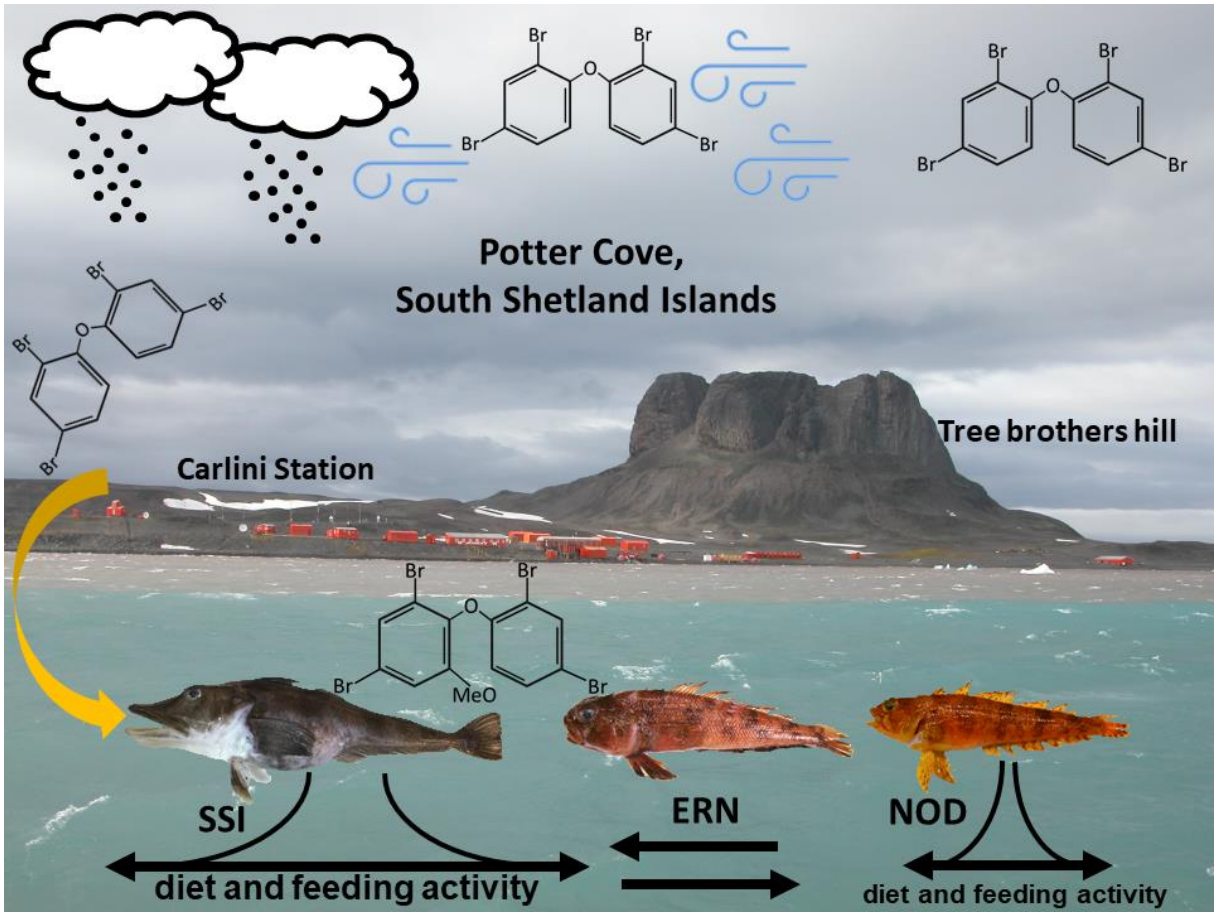
[g]*Instituto Argentino de Investigaciones de las Zonas Áridas (IADIZA, CCT- CONICET), Mendoza 5500, Argentina*

[h]*Instituto de Biología Agrícola de Mendoza (IBAM, CCT-CONICET), Mendoza 5505, Argentina*

[i]*Instituto de Medicina y Biología Experimental de Cuyo (IMBECU, CCT-CONICET), Mendoza 5505, Argentina*

* Corresponding author: jaltamirano@mendoza.conicet.gob.ar

Graphical Abstract



HIGHLIGHTS

- Marked interspecific differences for notothenioid fish in MeO-PBDE accumulation.
- BDE-47 and 6-MeO-BDE-47 contributed 53 and 90% to the total load, respectively.
- *C. aceratus* and *N. nudifrons* showed the highest and lowest MeO-PBDE levels, respectively.
- *C. aceratus* and *N. nudifrons* had a broader and narrower diet, respectively.

Abstract. Concentrations of polybrominated diphenyl ethers (PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs); are reported in specimens of fish notothenioids *Chaenocephalus aceratus* (SSI), *Trematomus bernacchii* (ERN), and *Nototheniops nudifrons* (NOD) from the South Shetland Islands, Antarctica. Significant differences in the accumulation of 2'-MeO-BDE-68 and 6-MeO-BDE-47 were detected among the analysed species. MeO-BDEs were significantly higher in SSI (11.7, 8.6, and 14.1 ng g^{-1} lw) than in NOD (1.63, 1.63, and 3.0 ng g^{-1} lw) in muscle, liver, and gill, respectively. Feeding ecology traits explain the accumulation patterns of MeO-PBDEs. SSI has a higher feeding activity with a broader diet, followed by ERN, whereas NOD is a benthic/sedentary fish with a narrower diet. The accumulation of PBDEs was neither species-, nor tissue-specific. The current study expands the knowledge concerning the accumulation of PBDEs and MeO-PBDEs in Antarctic marine fish and supports the importance of species-specificity in the accumulation of MeO-PBDEs.

Keywords: Antarctic fish; MeO-PBDEs; PBDEs; Notothenioidei; Species-specific accumulation

1. Introduction

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs); have been widely used in commercial and household products to prevent the spreading of fire (Choo et al., 2019). Once released into the environment, PBDEs represent a risk for wildlife and human health due to their persistence, bioaccumulation potential, and toxic effects on reproductive, endocrine, and nervous systems (De Wit et al., 2010). PBDEs can be spread away from emission sources through long-range atmospheric and/or water transport as a gas phase, dissolved, and/or associated with particulate matter (Gouin et al., 2006). Cold-condensation and cold-trapping are the main mechanisms whereby organic chemicals reach polar regions (Wania and Westgate, 2008; Ko et al., 2018). Due to their physicochemical properties, PBDEs can accumulate in the biota and biomagnify through the food web in polar regions (De Wit et al., 2010; Ríos et al., 2017).

Experimental research on PBDE metabolism suggests that methoxylated polybrominated diphenyl ethers (MeO-PBDEs) are formed by microsomal methylation of the hydroxylated polybrominated diphenyl ethers (OH-PBDEs) in hepatocytes (Lui et al. 2012; Kim et al. 2015). On the other hand, reports suggest that MeO-PBDEs are also naturally produced by marine biota (Wan et al., 2009). The predominant MeO-PBDEs in the environment and marine-biota are the tetrabrominated 6-MeO-BDE-47 and 2'-MeO-BDE-68 (Sinkkonen et al., 2004; Vetter et al., 2007; Covaci et al., 2008; Ríos et al., 2017). Their toxicity is still under investigation, although adverse effects on biota cannot be ruled out since their chemical structure only differs from the PBDEs on by one methoxy substituent (Dirtu et al., 2013). Consequently, studies on the transport, bioaccumulation, and biomagnification of MeO-PBDEs are of interest for environmental and toxicological sciences.

79 The perciform suborder Notothenioidei is the dominant group of the Antarctic
80 ichthyofauna (i.e., 129 species) in terms of diversity (35%), abundance, and biomass,
81 comprising 97% of endemic species (Near et al. 2015). Notothenioid fish are mostly demersal
82 and have developed a variety of feeding behaviours, including a wide range of prey and
83 diversity of benthic, epibenthic, nektonic, and planktonic organisms (Daniels, 1982; Barrera-
84 Oro, 2002; Ko et al., 2018). The Antarctic notothenioids, blackfin icefish *Chaenocephalus*
85 *aceratus* [(Lönnberg 1906), acronym: SSI], emerald rockcod *Trematomus bernacchii*
86 [(Boulenger 1902), acronym: ERN], and yellowfin notie *Nototeniops nudifrons* [(Lönnberg
87 1905), acronym: NOD] are demersal and typical representatives of the western Antarctic
88 Peninsula ichthyofauna (Kock 1992). They have similar habits in the fjords, living commonly
89 in shallow inshore waters from 20–25 m deep on rocky bottoms with macroalgae beds to
90 offshore shelf waters down to depths of 450 m (DeWitt 1971; Eastman, 2017), yet they differ
91 in diet and feeding activity (Barrera-Oro, 2002; Casaux et al., 2003; Casaux and Barrera-Oro,
92 2013). The wide Antarctic distribution, relative abundance, and feeding habits of these species
93 make them suitable sentinels of pollution in the Antarctic marine environment.

94 Considering the feeding ecology of the fish species studied in this work, we hypothesize
95 that PBDEs and MeO-PBDEs have a species-specific pattern of accumulation. We aimed to
96 determine and compare the occurrence and profiles of these contaminants in different tissues
97 (muscle, liver, and gill) of specimens from the three aforementioned species.

98 **2. Materials and methods**

99 *2.1. Fish sampling and storage*

100 Fish samples (n = 17) were collected at Potter Cove, King George Island/Isla 25 de
101 Mayo, South Shetland Islands, close to the Scientific Station Carlini (62°14' S; 58°40' W) in
102 the austral summer from November 2014 to January 2015. The low number of collected

individuals was mainly affected by the rigid environmental conditions of Antarctic sea and the severe restrictions in the permits regarding the number of fish specimens that can be collected from the Antarctic continent. Specimens of *Chaenocephalus aceratus* (n = 6), *Trematomus bernacchii* (n = 5), and *Nototeniops nudifrons* (n = 6) were collected with trammel nets (length 25 and 35 m; width 1.5 m; inner mesh 2.5 cm; outer mesh 12 cm) set for 6–96 h at 5-50 m depths in sites where the seabed is a uniform rocky bottom covered mainly with red and brown macroalgae. The abiotic and biotic characteristics of Potter Cove are detailed in Barrera-Oro et al. (2019). The fish samples were wrapped and kept in single aluminum foils and transported to the laboratory where they were measured (total length in cm), weighed (g), and dissected before freezing at -20 °C until further analysis.

2.2. Reagents

The following compounds were included in the analysis: 7 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, and -183), and 2 MeO-PBDEs (6-MeO-BDE-47 and 2'-MeO-BDE-68). PBDE and MeO-PBDE commercial standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). BDE-77 and CB-207 at 25 and 50 pg μL^{-1} in isooctane were used as internal standard (IS) and recovery standard (RS), respectively. Acetone, *n*-hexane, dichloromethane (DCM), isooctane (all pesticide grade), and sulfuric acid (analytical grade) were purchased from Merck (Darmstadt, Germany). Silica gel 60 (63–230 mesh) and anhydrous sodium sulfate (Na_2SO_4, Merck) were of analytical grade, pre-washed with *n*-hexane aliquots and dried at 140 °C for 24 h before use. Solid-phase cartridges were prepared using acidified silica (H_2SO_4, 44 % w/w) before use.

2.3. Sample preparation

Dissected tissues (muscle, liver, and gills) were weighed, lyophilized and stored at -18 °C until analysis. The analytical methodology used for determining PBDEs and MeO-PBDEs

in the analysed tissues was reported previously (Malarvannan et al., 2014). Briefly, dry-tissue aliquots (liver ca. 0.8 g, muscle and gills, ca. 1 g each) were homogenized in an agate mortar, transferred to a 15 mL polypropylene tube, mixed with Na_2SO_4, and spiked with 50 µL of IS solution. A 3 mL aliquot of *n*-hexane: acetone (3:1, v/v) was added to the tube containing the sample, vortexed for 1 min, sonicated for 10 min, and centrifuged at 3500 rpm for 3 min. The process was repeated once more with fresh solvent. An aliquot of the supernatant (ca. 1/8) was taken and used for the gravimetrical determination of the lipid content (Malarvannan et al., 2015). The remaining supernatant was transferred to an empty glass tube and evaporated to near 100 µL by a gentle nitrogen stream at 32 °C. The concentrated extract was cleaned-up on ~6 g acidified silica (H_2SO_4 44 %, w/w) column pre-washed with 15 mL of *n*-hexane. The analytes were eluted with 20 mL *n*-hexane and 15 mL DCM from the column. The eluent was rotary evaporated to ca.1 mL, further evaporated to ca. 50 µL in a glass tube under a gentle nitrogen stream at 32 °C, and finally reconstituted with 50 µL of isooctane and 50 µL of RS.

2.4. Analysis of PBDEs and MeO-PBDEs

Determination of PBDEs and MeO-PBDEs was carried out on an Agilent 6890 (Palo Alto, CA, USA) gas chromatograph (GC) equipped with mass spectrometry (Agilent 5973 MS) operated in electron capture negative ionization (ECNI) source. A DB-5 capillary GC column (30 m × 0.25 mm × 0.25 µm; J&W Scientific, Folsom, USA) was used. The GC system was equipped with electronic pressure control and a programmable temperature vaporizer (PTV) inlet. The injection temperature was set at 92 °C, held 0.03 min, ramped at 700 °C/min to 300 °C, held 30 min. The injection (1 µL) was performed under a pressure of 10.06 psi until 1.25 min and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature ramp started from 92 °C, held 1.25 min, ramped at 10 °C/min to 300 °C, held 1 min, ramped at 40 °C/min to 310 °C, held 9.5 min. Helium was used as carrier gas with a flow rate of 1.0 mL min^{-1} until 25 min, then increased to 1.5 mL/min. The ion source and quadrupole temperatures were set at

170 °C and 150 °C, respectively. The mass spectrometer was operated in selected ion monitoring (SIM) for the quantification of BDE-28, -47, -99, -100, -153, -154, and -183 and 6-MeO-BDE-47, and 2'-MeO-BDE-6 with ions m/z 79 and 81 monitored for each compound.

2.5. Quality assurance and quality control

Multi-level calibration curves in the linear response interval of the detector were created for the quantification, and good correlation (r > 0.999) was achieved. The identification of analytes was based on the relative retention times to the IS used for quantification, ion chromatograms, and intensity ratios of the monitored ions (Malarvannan et al., 2014). The peaks were identified as target analytes if their retention time matched that of the corresponding reference standard within ± 0.1 min and their signal/noise ratio (S/N) was >3:1. Procedural blanks were included in every batch to control interferences and/or contamination from solvents and/or glassware. The procedural blanks (n = 7) were stable (relative standard deviation: RSD < 17 %, Table S1), and therefore, if there was a positive detection of the analytes in the procedural blanks, those levels were afterwards subtracted from the ones measured in the samples. The limit of quantification (LOQ) of the methodology was calculated as 3*SD of the mean of the procedural blank. The LOQ for the 7 PBDEs and the 2 MeO-PBDE was 1.5 ng g^{-1} lipid weight (lw) [30 pg g^{-1} wet weight (ww)]. The analysis was further validated by determining the targeted analytes in the certified material SRM 1945 (organic contaminants in whale blubber). The concentrations of target PBDEs and MeO-PBDEs in the analysed SRM 1945 were satisfactory, showing a deviation lower than 10 % of the certified values (Table S1). The mean ± SD recovery of the internal standard BDE-77 was 101±17%.

2.6. Data analysis

For calculating sums, median, and means, a value of f * LOQ was assigned to concentrations of compounds < LOQ, where *'f'* is the detection frequency (James et al. 2002).

Contaminant concentrations data were log-transformed (Zar, 2013) to fit normal distribution (Shapiro-Wilks W test $P < 0.05$). A generalized linear model (GLM) with a full factorial design was performed to detect differences in the contaminant concentrations among the analysed fish species and tissues. In particular, full-factorial designs represent all possible combinations of the levels of the categorical predictors (e.g., in the present study the categorical predictors, are "species" and "tissues"). Therefore, the full-factorial design provides more information about the relationships between categorical predictor variables and responses on the dependent variables than is provided by corresponding one-way or main effect designs (Rutherford, 2011). Fisher's LSD (Least Significant Difference) *a posteriori* tests were used to make multiple comparisons. To verify our hypothesis, a significant effect in the categorical predictor factor "species" is expected from this GLM approach. The non-parametric Spearman's Rho correlations were used to explore for possible intraspecific associations between fish morphometry (total weight and length) and contaminants body burden. Since the lipid content in tissues is usually associated with accumulation of PBDEs in fish (Ondarza et al., 2011; Gewurtz et al., 2011a, b; Ríos et al., 2019), intraspecific correlations between lipid content and PBDE and MeO-PBDE levels (on a wet weight basis) were used to explore for possible (positive) associations using Spearman's Rho correlations. Statistical analyses were carried out using the InfoStat 2011 software (Di Rienzo et al., 2011). A p value < 0.05 was considered significant, except for Spearman's correlations adjusted by Bonferroni correction (Zar, 2013), and the α error was divided by the number of comparisons (i.e., three fish species). Thus, correlations were considered significant for $p < 0.016$.

3. Results and Discussion

3.1. Concentrations of PBDEs and MeO-PBDEs in fish specimens

Mean and median values along with standard errors of all compounds measured in muscle, liver, and gill tissues of the three fish species here considered are presented in Table 1. The measured median BDE-47 concentrations found in muscle tissue of SSI, ERN and NOD were 2.93, 2.22, and 8.32 ng g^{-1} lw, respectively, while in liver tissue were <LOQ, 1.36, and <LOQ, respectively (Table 1). The measured median BDE-47 concentrations found in gill tissue of SSI, ERN, and NOD, were 2.57, 2.28, 6.06 ng g^{-1} lw, respectively. BDE-100 was only detected in muscle tissue of ERN (2.25 ng g^{-1} lw). For the remaining species and tissues here analysed, BDE-100 concentrations were <LOQ. The measured median BDE-99 concentrations found in muscle tissue of SSI, ERN and NOD, were 3.77, 8.26, and 3.10 ng g^{-1} lw, respectively. BDE-99 was only detected in gill tissue of ERN (4.98 ng g^{-1} lw). For the remaining species and tissues analysed, BDE-99 concentrations were < LOQ. BDE-154 was only found in gill tissue of SSI (2.07 ng g^{-1} lw), and BDE-183 was only found in muscle tissue of NOD (5.84 ng g^{-1} lw). BDE 28 and 153 were not detected in any investigated sample.

The contribution of each BDE congener to the total load (when considering all tissues and species combined) was as follows: BDE-47 (53%), followed by BDE-99 (30%), BDE-183 (10%), BDE-100 (4%), and BDE-154 (3%). This pattern denotes that BDE-47 is, overall, the major congener in the total load. The contribution of 7 PBDEs and 2 MeO-PBDEs assessed in the target tissues of each analysed species is shown in figure Fig. S1 and Fig. S2 of the supplementary section, respectively. A plausible explanation regarding the predominant accumulation of PBDEs in gill and muscle tissues, and to a lesser extent in liver, could be due to differences in the specific metabolism for each congener. For example, the accumulation pattern of PBDEs found in gill could be linked to the morpho-physiological functions of this organ. Gills have a wide diffusion surface for gaseous exchange, osmotic and ionic regulation, acid-base balance, and nitrogenous waste excretion (Ahmad et al., 2008). Therefore, gills are in continuous contact with the external medium and thus are an uptake route of pollutants from

224 the water column as well as seabed (Playle, 1998). On the other hand, the liver is the organ
225 where xenobiotics are metabolized by detoxifying enzymes, resulting in a lower PBDE
226 concentration comparing it against gills and muscles (Borghesi et al., 2008).

227 In the present study, the sum of BDE-47 and BDE-99 contributed to ca. 83% of the total
228 PBDE load. The levels of BDE-47, -100, and -99 found in muscle, liver, and gill tissues of the
229 three species were similar to those previously reported for other three notothenioid fish species
230 (*Notothenia coriiceps, Notothenia rossii,* and *Trematomus newnesi*) from the same sampling
231 site (Lana et al., 2014). This pattern is comparable to commercial mixtures (e.g. 70-5DE
232 Bromkal), in which BDE-47 and -99 are ca. 70% of the formulation (Ikonomou et al., 2002).
233 Additionally, the relative abundance of BDE-47 was consistent with previous reports of fish
234 from other regions of the world (Voorspoels et al., 2003; Vives et al., 2004; Corsolini et al.,
235 2008). The high levels found may be either due to an elevated uptake rate or a debromination
236 of BDE-99 (Stapleton et al., 2004). The results suggest that PBDE burden in this Antarctic area
237 could have reached a steady state (Lana et al., 2014). However, it cannot be ruled out that there
238 are still reservoirs of PBDEs (soils and snow/ices) in this Polar region which could be
239 remobilized due to climate change-driven warmer conditions (Cabrerizo et al., 2013).

240 Regarding the analysed MeO-PBDEs (2'-MeO-BDE-68, 6-MeO-BDE-47), both were
241 consistently detected at variable concentrations in all tissue samples of the studied species
242 (Table 1). The measured median 2'-MeO-BDE-68 concentrations found in muscle tissue of
243 SSI, ERN, and NOD were the same (0.40 ng g^{-1} lw); while in liver tissue they were 1.41, 0.40,
244 and 0.40 ng g^{-1} lw, respectively. Regarding the gill tissue, median levels of 2'-MeO-BDE-68
245 found for SSI, ERN, and NOD were 1.93, 0.40, and 0.40 ng g^{-1} lw, respectively (Table 1). The
246 measured median 6-MeO-BDE-47 concentrations found in muscle tissue of SSI, ERN, and
247 NOD were 10.9, 9.36, and 1.23 ng g^{-1} lw, respectively, while in liver tissue they were 7.29,
248 6.08, and 1.23 ng g^{-1} lw, respectively. Finally, the measured median 6-MeO-BDE-47

concentrations found in gill tissue of SSI, ERN and NOD were 12.5, 6.19, and 2.62 ng g^{-1} lw, respectively. Likewise, as stated above for PBDEs, MeO-PBDE tissue concentrations found in the three species were similar to those previously reported for other two notothenioid fish species (*N. rossii* and *T. newnesi*) from the same sampling site (Ríos et al. 2017). The contribution of each MeO-PBDE congener to the total contamination load (when considering all tissues and species combined) was 90% and 10% for 6-MeO-BDE-47 and 2'-MeO-BDE-68, respectively. A similar profile with a predominance of 6-MeO-BDE-47 was also reported in the Antarctic notothenioid species *N. rossii* and *T. newnesi* (Ríos et al., 2017). In other marine fish species, with a different position in the food web, including hollowsnout grenadier *Trachyrinchus trachyrinchus*, roughsnout grenadier *Coelorhynchus coelorhynchus*, Atlantic salmon *Salmo salar*, and arctic cod *Cadus callarias,* the predominance of 6-MeO-BDE-47 was also reported (Sinkkonen et al., 2004; Vetter et al., 2007; Covaci et al., 2008).

3.2. Testing for interspecific differences in contaminants burden in fish

The GLM approach showed significant statistical differences in the accumulation of 2'-MeO-BDE-68 and 6-MeO-BDE-47 among the analysed fish species (Table 2). Besides, the GLM approach showed that there were no significant statistical differences among the tissues analysed within each species (Table 2). The highest levels of 2'-MeO-BDE-68 and 6-MeO-BDE-47 were found for SSI followed by ERN, while the lowest levels were found for NOD specimens (Table 1). Multiple interspecific comparisons (*A posteriori* Fisher's LSD tests) revealed that the burden of 2'-MeO-BDE-68 and 6-MeO-BDE-47 in tissues of SSI were statistically different from those found in NOD specimens. No significant differences were detected (*A posteriori* Fisher's LSD tests) between SSI and ERN, neither between ERN and NOD specimens when comparing 2'-MeO-BDE-68, nor 6-MeO-BDE-47 tissue levels. On the other hand, there were no significant differences for the levels of BDE-47 among species in all tissues (Table 2). The statistical GLM full-factorial approach used to test the hypothesis requires

274 homogeneous data set regarding the categorical predictors (factors: species and tissues) among
275 the cases considered. Therefore, the concentrations of BDE-28, -100, -99, -154, -153, and -183
276 were omitted from this statistical analysis because they could not be quantified in all the tissues
277 of the three species considered (Table 1).

278 The source of MeO-PBDEs in fish occurs mainly through two pathways: direct uptake
279 of these contaminants through diet (i.e., from the prey they eat) and the uptake of PBDEs
280 followed by biotransformation to HO-PBDEs; and then reversible biotransformation of HO-
281 PBDEs to MeO-PBDEs (Weijs et al., 2015; Liu et al., 2012). The observed differences between
282 the SSI and NOD for the concentration of the major MeO-PBDEs, 6-MeO-BDE-47 (Fig. 1)
283 could be attributed to the species-specific feeding ecology, as suggested in previous reports on
284 other notothenioid species (Ríos et al., 2017), and marine fish from South Korean (Choo et al.,
285 2019). This scenario is discussed below.

286 A compilation of literature information on the trophic ecology of the studied species at
287 the western Antarctic Peninsula area, including feeding type categories, feeding
288 strategies/behavior and diet composition, is shown in Table 3. It is known that in the Antarctic
289 marine ecosystem fish and krill are preys of higher energetic value compared to other
290 invertebrates (Table S3). Among the notothenioids considered, SSI is the largest species and
291 feeds in the water column on large prey like fish and cephalopods, and also on krill and mysids.
292 In contrast, NOD is a smaller and benthic species that inhabit on the bottom-feeding on small
293 invertebrates that are in a lower food web level. Regarding ERN, it is an epibenthic species with
294 size and diet breadth intermediate between the other two species (Table 3). In summary, SSI
295 exhibits higher feeding activity with a diet constituted by invertebrates and vertebrates –fish,
296 followed by ERN, whereas NOD is the least active feeder –a more sedentary fish species– with
297 a narrower diet that only includes invertebrates (Table 3). Consequently, a higher predation
298 activity on organisms with a higher position in the food web would plausibly involve a higher

intake of pollutants through diet. Recently, Choo et al. (2019) found species-specific differences in the accumulation of BFR and PBDE metabolites, in marine organisms from South Korea. Interestingly, higher concentrations of MeO-PBDEs in fish with higher trophic position than in benthic fish were detected, suggesting biomagnification of these chemicals through the food web. This assumption is reasonable since, for example, the estimation of lipophilic character identified by the octanol-water partition coefficient (log K_{ow}) for 6-MeO-BDE-47 is 5.9 (Yu et al., 2008). Accordingly, MeO-PBDEs are lipophilic enough to be excreted through the fish kidney function, and therefore these compounds have a high bioaccumulation and biomagnification potential (Weijs et al., 2015).

Another plausible scenario could be due to species-specific biotransformation capacity linked to food habits (e.g., differences in the activity of the xenobiotic-metabolizing enzyme between SSI and NOD). It has been demonstrated that a broad diet exposed fish to the intake of a high diversity of xenobiotics, such as PBDEs and their analogues MeO-PBDEs (Choo et al., 2019). In this sense, the computed interspecific differences in the 2'-MeO-BDE-68 and 6-MeO-BDE-47 level profiles could plausibly be explained by the feeding ecology of the fish species here considered. Few studies directly testing whether differences in diet breadth lead to differences in xenobiotics detoxification have been conducted in fish. For example, Solé et al. (2009) and Ribalta et al. (2015) reported species-specific differences in the xenobiotic-metabolizing enzymes linked with fish diet type. They suggest that Mediterranean fish species with an omnivorous diet had a higher intake of pollutants through diet (Solé et al., 2009; Ribalta et al., 2015). Specifically, marked differences were found between the fish with a broader (*Trachyrhynchus scabrus*) and narrower (*Alepocehalus rostratus*) diet (Ribalta et al., 2015).

3.3. Exploring associations among fish body size, lipid content and contaminant accumulation capability

323 It has been previously reported that PBDE congeners (e.g., BDE-28, -47, -100, and -
324 99), as well as 6-MeO-BDE-47, were linked to the body size (total weight and length) of the
325 notothenioid fish *Notothenia rossii* and *Trematomus newnesi* (Ríos et al., 2017). The lipid
326 content of tissues could also be associated with the accumulation of PBDEs, as showed in
327 several studies focusing on other fish species (Kuo et al., 2010; Gewurtz et al., 2011a; Ríos et
328 al., 2019). Therefore, intraspecific correlations were performed to explore possible associations
329 between fish biological characteristics (including body size and lipid content) and the PBDE
330 and MeO-PBDE burden in the considered fish specimens. Since there were no significant
331 differences between muscle, liver, and gill tissue for each analysed fish species (Table 2), all
332 intraspecific correlations were performed considering the levels of BDE-47, BDE-99, 2'-MeO-
333 BDE-68, and 6-MeO-BDE-47 for all tissues combined. Spearman correlation coefficients (rho)
334 indicated that there were no significant associations between the concentration levels of the
335 targeted compounds and fish biological characteristics (i.e., total weight, length, and lipid
336 content) for any of the analysed specimens (Table S2). It is worthwhile to mention that findings
337 related to correlations between PBDE levels and fish size or lipid content are controversial;
338 while several studies found positive relationships between these factors (Kou et al., 2010;
339 Gewurtz et al., 2011a; Ríos et al., 2019), other authors reported no clear correlation (reviewed
340 in Ríos et al., 2015), highlighting species-specificity when using this approach.

341 The increased concentration of PBDEs with the size of the specimen could be due to
342 differences in food habits, pollutants uptake, as well as to pollutant exposure over time
343 (Gewurtz et al., 2011a, b). Fish tend to consume only what they can swallow, so larger fish will
344 usually eat larger prey and thus may feed at a higher trophic level than smaller fish (Daniels
345 1982; Kock 1992). However, the correlational approach performed in the present study could
346 not detect any association that supports this statement. Lipid content in tissues is another factor
347 associated with the accumulation of PBDE concentrations in fish (Gewurtz et al., 2011a. b; Ríos

et al., 2019). PBDEs concentration reported in lipid-rich tissues were generally higher than those reported in other tissues owing to the lipophilic character of these compounds [log Kow > 5.5, (Goutte et al., 2013)]. However, the lipid content in tissues is dynamic and therefore could differ among seasons and habitats in terms of food availability and environmental characteristics (Gewurtz et al., 2011a). In this sense, another scenario, such as the fish feeding ecology, could help to explain the lack of correlations in the present study. Studies that directly test whether differences in trophic position of Antarctic fish lead to differences in xenobiotics biotransformation are needed to extend the above generalizations.

4. Conclusions

Results showed marked interspecific differences in 2'-MeO-BDE-68 and 6-MeO-BDE-47 accumulation levels among the analysed fish species. Such differences were significant between SSI (the most active species with a broader diet) and NOD (the less active species with a narrower diet), which showed the highest and lowest MeO-PBDE levels, respectively. The current study supports the importance of the feeding habits of fish and the species-specificity to explain the accumulation patterns found here for MeO-PBDEs. Our results add new information to the scarce data on MeO-PBDEs concentrations in Antarctic marine organisms and can be taken as baseline for Antarctic notothenioids fish species.

Acknowledgements

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Table 1. Mean, median (in brackets), limit of quantification (LOQ), and standard error (SE) of PBDEs and MeO-PBDEs [ng g^{-1} lw] and lipids [%] in muscle, liver and gill tissues of *Chaenocephalus aceratus* (SSI); *Trematomus bernacchii* (ERN), and *Nototheniops nudifrons* (NOD) from South Shetland Islands, Antarctica.

	SSI (n=6)						ERN (n=5)						NOD (n=6)					
	muscle		liver		gill		muscle		liver		gill		muscle (n=6)		liver *		gill *	
	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE	Mean (median)	SE
% lipids	3.17 (1.00)	1.97	12.6 (14.0)	1.31	5.67 (5.50)	0.33	1.22 (1.00)	0.48	15.6 (20.0)	4.20	4.26 (3.30)	0.78	1.38 (1.00)	0.39	13.0 (13.0)	1.00	3.50 (3.50)	0.50
BDE-28	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ		<LOQ	a	<LOQ	a	<LOQ	a
BDE-47	3.23 (2.93)	0.71	<LOQ	a	3.35 (2.57)	0.98	5.75 (2.22)	2.90	1.36 (1.36)	0.16	2.28 (2.28)	0.34	8.96 (8.32)	3.29	<LOQ	a	6.06 (6.06)	3.99
BDE-100	<LOQ	a	<LOQ	a	<LOQ	a	2.25 (2.25)	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a
BDE-99	3.60 (3.77)	0.72	<LOQ	a	<LOQ	a	6.23 (8.26)	2.12	<LOQ	a	4.98 (4.98)	3.06	2.92 (3.10)	0.80	<LOQ	a	<LOQ	a
BDE-154	<LOQ	a	<LOQ	a	2.07 (2.07)	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a
BDE-153	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a
BDE-183	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	<LOQ	a	5.84 (5.84)	a	<LOQ	a	<LOQ	a
PBDEs	**6.83 (6.70)**				**5.42 (4.64)**		**14.2 (12.7)**		**1.36 (1.36)**		**7.26 (7.26)**		**17.7 (17.2)**				**6.06 (6.06)**	
2-MeO-BDE68	0.74 (0.40)	0.34	1.33 (1.41)	0.35	1.84 (1.93)	0.52	0.40 (0.40)	a	1.07 (0.40)	0.41	0.40 (0.40)	0.00	0.40 (0.40)	0.00	0.40 (0.40)	0.00	0.40 (0.40)	0.00
6-MeO-BDE47	11.0 (10.9)	2.35	7.28 (7.29)	0.75	12.3 (12.5)	1.52	9.09 (9.36)	1.20	6.96 (6.08)	1.09	7.42 (6.19)	1.28	1.23 (1.23)	0.00	1.23 (1.23)	0.00	2.62 (2.62)	0.70
MeO-BDE	**11.7 (11.3)**		**8.61 (8.70)**		**14.1 (14.4)**		**9.49 (9.77)**		**8.03 (6.48)**		**7.82 (6.59)**		**1.63 (1.63)**		**1.63 (1.63)**		**3.02 (3.02)**	

Total (in bold) = sum of PBDEs (#28, 47, 100, 99, 154, 153, 183); sum of MeO-BDE (2-MeO-BDE-68, and 6-MeO-BDE-47). <LOQ: below the limit of quantification. a: no standard error could be calculated since only one value was available or values are <LOQ. * Due to limitations in the sample size, liver and gill tissues of NOD were pooled in two groups of three specimens each (n = 2) to perform their analysis. .

Table 2. Output of the GLM used to detect differences among species in the accumulation of BDE-47, 2-MeO-BDE-68, 6-MeO-BDE-47 in fish tissue.

Variable	*F*	*df*	*p-value*
BDE-47 (ng g^{-1} lw)			
Species	1.138	2	0.336
Tissue[A]	1.759	1	0.197
Interaction	1.070	2	0.358
2-MeO-BDE68 (ng g^{-1} lw)			
Species	6.033	2	0.005*
Tissue	1.702	2	0.197
Interaction	1.287	4	0.294
6-MeO-BDE47 (ng g^{-1} lw)			
Species	41.146	2	<0.001*
Tissue	2.304	2	0.115
Interaction	1.124	4	0.361

Significant effects are denoted with an asterisk*. [A]Since BDE-47 in liver tissue was only detected and quantified for ERN specimens, only muscle and gill tissue of the three fish species were included as categorical factors in GLM. *F*: Fisher statistic; *df*: degrees of freedom).

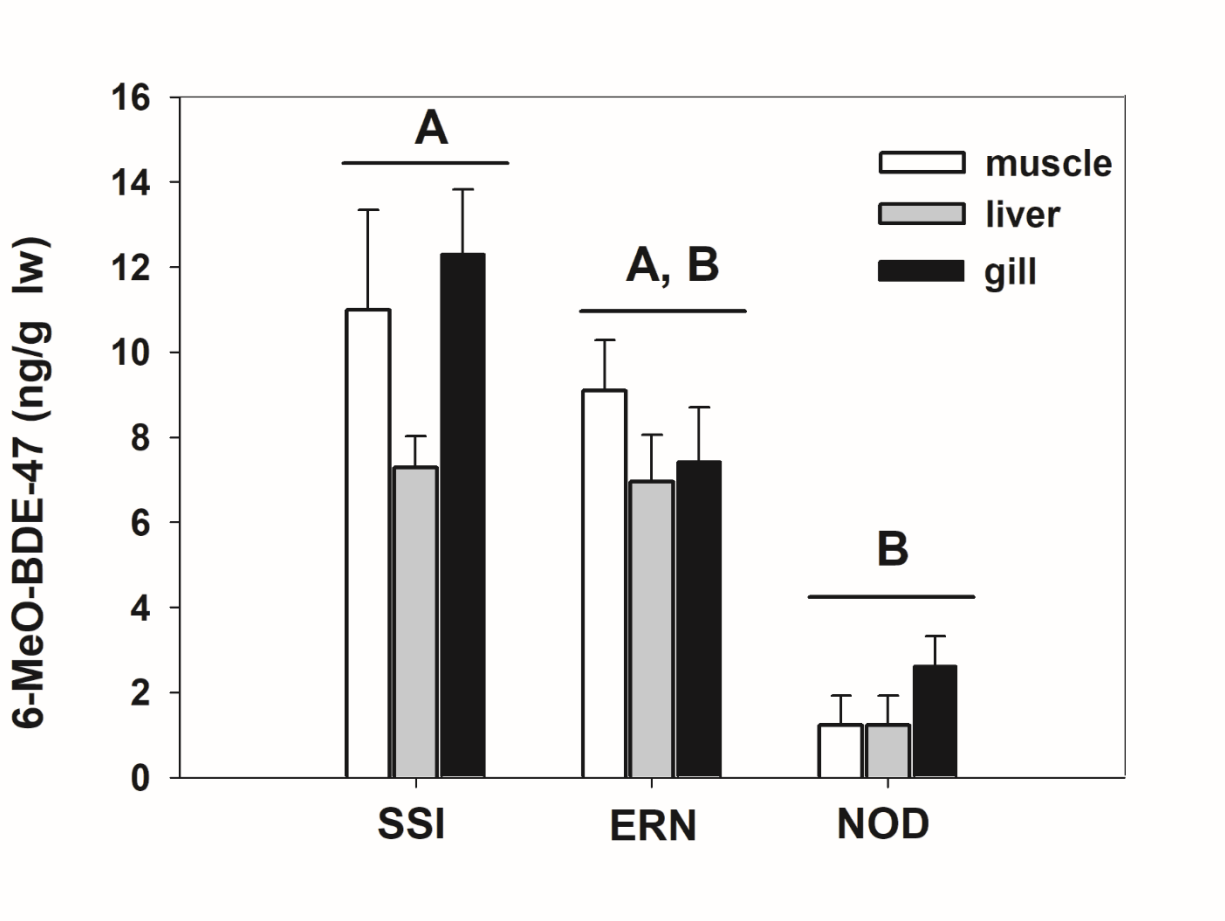
Table 3. Morphometric data of *Chaenocephalus aceratus* (SSI), *Trematomus bernacchii* (ERN), and *Notothenios nudifrons* (NOD) collected at Potter Cove, South Shetland Islands, linked with feeding habits information of these notothenioid species at the western Antarctic Peninsula.

Species	**Total weight (g)**	**Total length (cm)**	**n**	**Feeding categories***	**Diet items***	**Feeding behaviour***
SSI	2206±95.5 (1852−2426)	62.4±0.80 (59.4−63.9)	6	Nekton and plankton feeder	Fish, krill, cephalopods, mysids	water column
ERN	138±30.1 (64.6−248)	21.6±1.60 (16.9−26.8)	5	benthos and plankton feeder	Algae, polychaetes, gastropods, gammarideans, isopods, krill, hyperiids	water column, ambush and grazing near bottom
NOD	47.9±3.64 (38.0−64.1)	16.1±0.31 (15.2−17.4)	6	benthos feeder	polychaetes, gammarideans, isopods, krill (occasional in summer)	ambush on bottom

Morphometric values for fish size is mean ± standard error, and range (in brackets). *Feeding categories, diet items, and feeding behaviour information was taken from the compilation in Barrera-Oro (2002, Tables 2 and 3) and from Casaux et al. (2003).

536 **Figure Caption**

537 **Fig. 1.** Accumulation of 6-MeO-BDE-47 (ng g^{-1} lw) in muscle, liver and gill tissues of the notothenioid fish
538 species collected at Potter Cove, South Shetland Islands: *Chaenocephalus aceratus* (SSI), *Trematomus*
539 *bernacchii* (ERN), and *Nototheniops nudifrons* (NOD). Different capital letters indicate significant
540 differences in the 6-MeO-BDE-47 concentration levels among the fish species (full factorial GLM, followed
541 by Fisher's LSD *a posteriori* multiple comparisons, $p < 0.05$).
542



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Supplementary material

Accumulation of PBDEs and MeO-PBDEs in notothenioid fish from the South Shetland Islands, Antarctica: an interspecies comparative study

Juan Manuel Ríos[a,i], Sabrina B. Mammana[a,b,h], Eugenia Moreira[c,d], Giulia Poma[e], Malarvannan Govindan[e], Esteban Barrera-Oro[c,f], Adrian Covaci[e], Nestor F. Ciocco[b, g], and Jorgelina C. Altamirano[a,b]

[a]*Laboratorio de Química Ambiental, Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales (IANIGLA, CCT-CONICET), Mendoza 5500, Argentina.*

[b]*Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza, Argentina.*

[c]*Instituto Antártico Argentino (IAA), Buenos Aires, Argentina.*

[d]*Laboratorio de Biología Funcional y Biotecnología (BIOLAB), INBIOTEC-CONICET. Facultad de Agronomía, UNCPBA, Azul 7300, Buenos Aires, Argentina.*

[e]*Toxicological Centre, Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.*

[f]*Museo Argentino de Ciencias Naturales Bernardino Rivadavia and CONICET, Buenos Aires, Argentina.*

[g]*Instituto Argentino de Investigaciones de las Zonas Áridas (IADIZA, CCT- CONICET), Mendoza 5500, Argentina.*

[h]*Instituto de Biología Agrícola de Mendoza (IBAM, CCT-CONICET), Mendoza 5505, Argentina.*

[i]*Instituto de Medicina y Biología Experimental de Cuyo (IMBECU, CCT-CONICET), Mendoza 5505, Argentina.*

* Corresponding author: jaltamirano@mendoza.conicet.gob.ar

The supplementary material contains two Tables and two Figures.

Table S1. PBDE and MeO-PBDE concentrations, relative standard deviation (RSD), and certified values for the SRM-1945 (whale blubber).

Congener	Obtained values (ng g^{-1}) (n=3)	Certified values SRM-1945 (ng g^{-1})	RSD	Accuracy (%)
BDE-47	38.1	39.6	0.2	96
BDE-100	10.1	10.3	1.1	98
BDE-99	17.9	18.9	2.3	95
BDE-154	14.1	13.3	1.7	106
2-MeO-BDE-68	53.7	53.5	3.3	100
6-MeO-BDE-47	66.5	66.5	4.7	101

Table S2. Output of the Spearman's correlations used to explore intraspecific associations between fish biological characteristics (size and lipid content) and BDE-47, BDE-99, 2-MeO-BDE-68, 6-MeO-BDE-47 burden in fish. Spearman's correlations were adjusted by Bonferroni correction, thus, correlations were considered significant for $p = 0.016$. n.a. = not available

congener	SSI		ERN		NOD	
	Spearman r	*p-value*	*Spearman r*	*p-value*	*Spearman r*	*p-value*
Total weight & BDE-47	0.30	0.21	-0.90	0.74	0.04	0.90
Total weight & BDE-99	-0.17	0.49	-0.35	0.19	-0.39	0.26
Total weight & 2-MeO-BDE-68	0.09	0.70	-0.11	0.69	n.a.	n.a.
Total weight & 6-MeO-BDE-47	0.29	0.23	0.06	0.81	0.32	0.35
Total length & BDE-47	0.25	0.31	-0.90	0.74	0.04	0.90
Total length BDE-99	-0.20	0.42	-0.35	0.19	-0.39	0.26
Total length 2-MeO-BDE-68	-0.13	0.58	-0.11	0.69	n.a.	n.a.
Total length 6-MeO-BDE-47	0.11	0.64	0.06	0.81	0.32	0.35
Lipid content & BDE-47	-1.41	0.08	0.09	0.74	0.67	0.03
Lipid content & BDE-99	n.a.	n.a.	-0.25	0.36	n.a.	n.a.
Lipid content & 2-MeO-BDE-68	0.11	0.65	1.63	0.12	n.a.	n.a.
Lipid content & 6-MeO-BDE-47	0.02	0.92	0.09	0.72	0.41	0.23

Table S3. Energy content of fish and invertebrates from western Antarctic Peninsula. Compiled in Barrera-Oro (2002, Table 4).

Species	Month	Energy (kJ 100 g^{-1})
Fish		
Nothothenia coriiceps	March	395
Gobionotothen gibberifrons	Jan-March	344
Chaenochephalus aceratus	March	327
Champsocephalus gunnari	March	345
Electrona carlsbergi	January	587
Gymnoscopelus nicholsi	March	843
Pleurogramma antarcticum	March	484
Invertebrates		
Euphausia superba (Krill)	March	531
Mollusca		237
Polychaeta		271
Amphipoda		327
Echinodermata		217

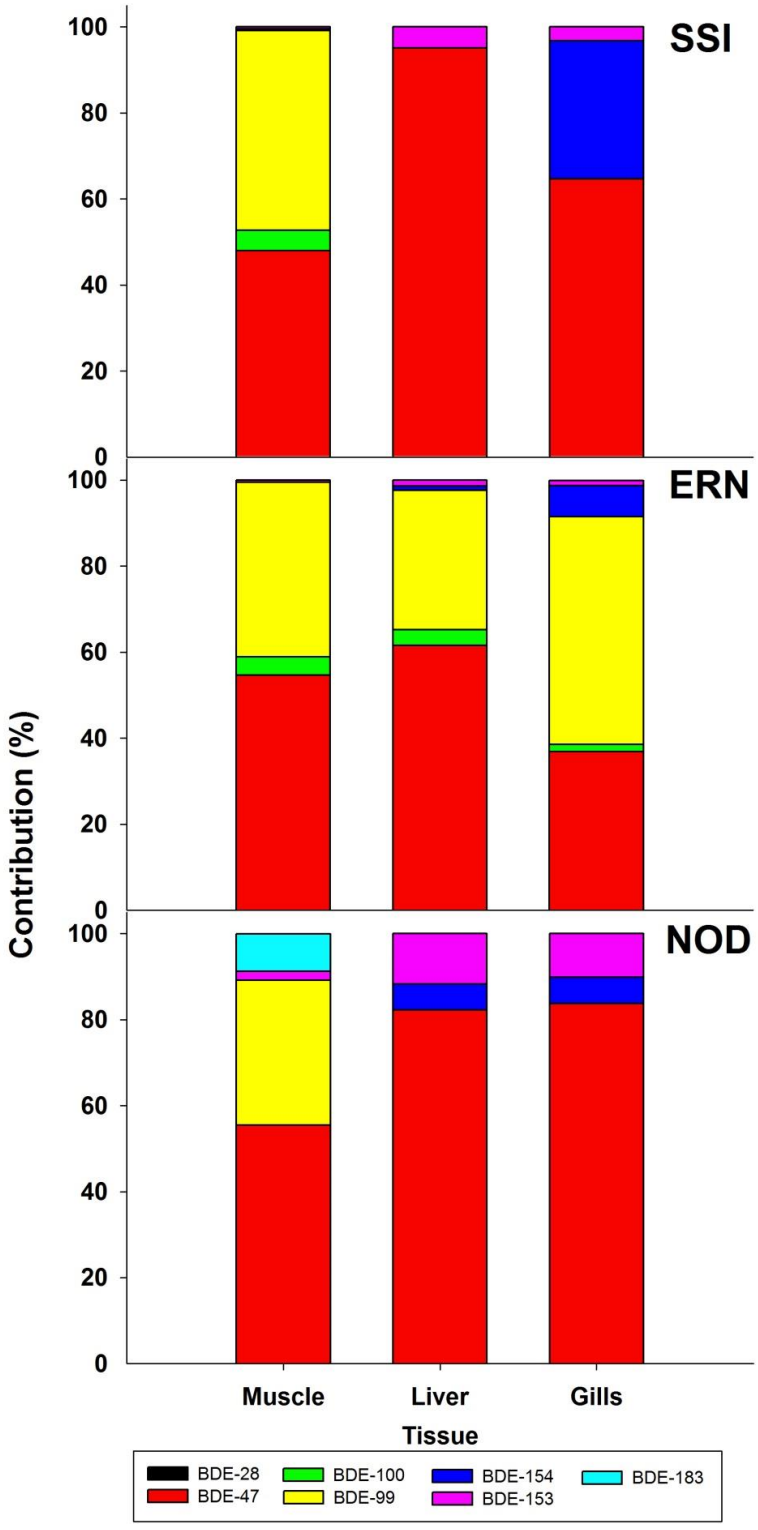

Fig. S1. Contribution (%) of BDE congeners in muscle, liver and gill tissue of *Chaenocephalus aceratus* (SSI); *Trematomus bernacchii* (ERN), and *Nototheniops nudifrons* (NOD) from South Shetland Islands, Antarctica.

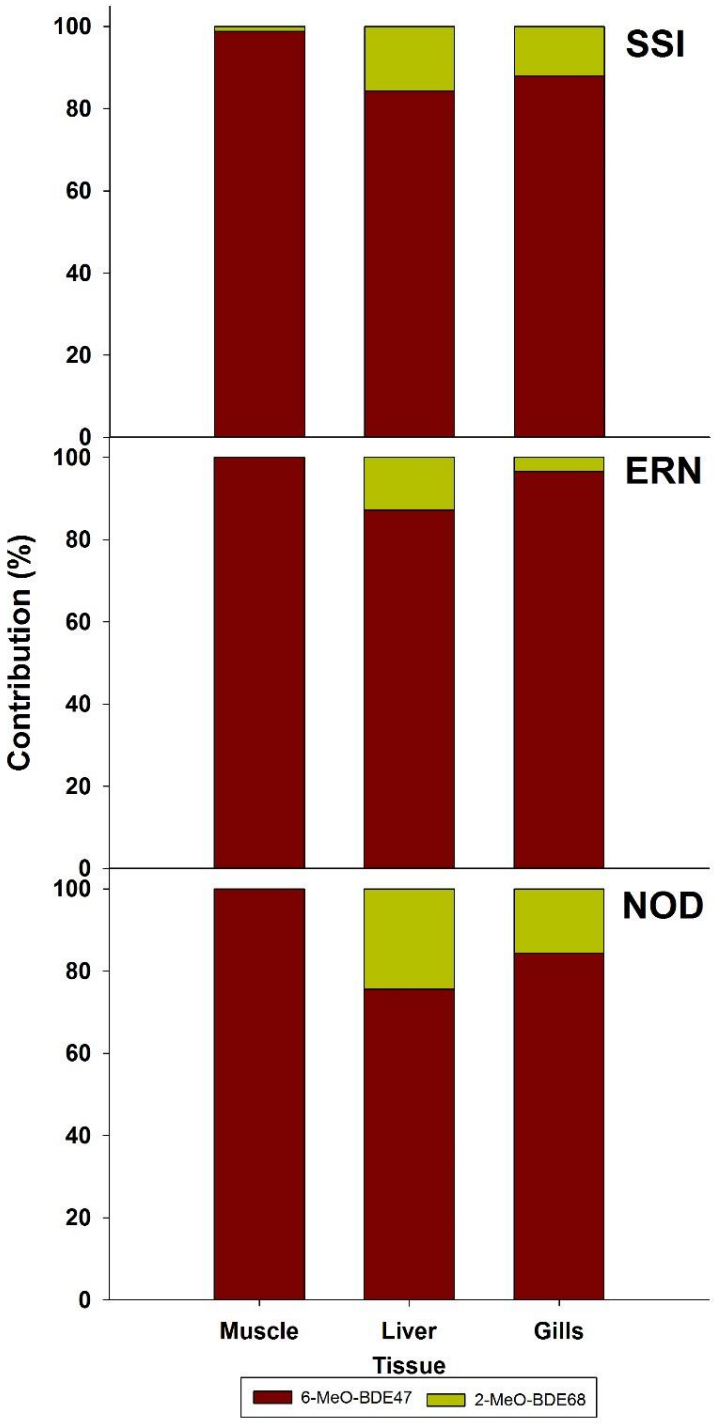

Fig. S2. Contribution (%) of MeO-PBDE congeners in muscle, liver and gill tissue of *Chaenocephalus aceratus* (SSI); *Trematomus bernacchii* (ERN), and *Nototheniops nudifrons* (NOD) from South Shetland Islands, Antarctica.