LEVELS OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN TWO SPECIES OF ANTARCTIC FISH (*Chionodraco hamatus* and *Trematomus bernacchii*)

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Introduction

Persistent organic pollutants (POPs) are released around the world and transported to polar regions by air masses according to global distillation and fractionation processes (Wania and Mackay, 1996). In 2001 the production of polybrominated diphenyl ethers (PBDEs) was estimated at 674,000 cubic tons per year. Nowadays the majority of emissions into the environment are the result of the use and recycling of end products containing PBDEs. Production of these compounds is confined to only a few areas of the planet (especially Western Europe and the US), although emissions also occur during the production processes (BSEF, 2000). Andersson and Blomqvist found the presence of PBDEs in fish analysed in Sweden for the first time in 1981, while the first evidence of global contamination was reported by Jansson et al. in 1987, when they detected the presence of these compounds in Baltic sea organisms. Many studies have highlighted the presence of PBDEs in various areas of the planet (Law et al., 2006; Wolkers et al., 2004), including the Antarctic (Corsolini et al., 2006a; Corsolini et al., 2006b; Chiuchiolo et al., 2004), confirming that these compounds are persistent, they are subject to long-distance transportation, and they are capable of bioaccumulating in the tissues of organisms.
Here we report preliminary levels of PCBs and PBDEs in the muscle and liver of two species of Antarctic fish, the *Chionodraco hamatus* and the *Trematomus bernacchii*, in order to examine the differences in contaminant concentrations between the two species. The study of POP levels in Antarctic environmental matrices is important in order to monitor processes of contaminant distribution on both local and global scales.

Materials and Methods

Collection of Samples. Samples of *C. hamatus* (n=6) and *T. bernacchi* (n=6) were collected in January-February 2005. The fishing area was south of the Italian scientific station (74° 42' 00''S 164° 08' 40''E); the organisms were taken to the laboratory where they were measured, weighed and dissected. An aliquot of muscle and liver tissue (10-15 g) was kept at -20°C until analysis.
Chemical analysis: PBDE and PCB congeners were analyzed following a method described elsewhere, with some modifications (Kannan et al., 2001; Corsolini et al., 2006b). PCBs were identified and quantified using a gas chromatograph (Autosystem, Perkin Elmer) equipped with a ^{63}Ni electron capture detector (GC-ECD), and a capillary column (DB-5, Supelco Inc.). PBDEs were identified and quantified using a GC/MS (ion trap mass detector; Trace^{TM} GC Polaris, ThermoFinnigan) equipped with a capillary column (SPB-5, Supelco Inc.). For HRGC/MS conditions see Corsolini et al., 2005. Blanks were analyzed throughout the analytical procedure to check for interference and laboratory contamination. Recoveries were greater than 90%. Detection limits were 0.1 a 0.13 pg/g for PBDE and 0.01 ng/g for PCB. PBDE and PCB congeners are represented by their IUPAC numbers throughout the text. ∑PCBs were calculated as the sum of the principal congeners identified (23 congeners), while ∑PBDE were calculated as the sum of the 9 congeners identified. Results are given on wet basis (wet wt).

Results and Discussion

The highest concentrations of PBDEs were found in the liver: 205.24 pg/g wet wt in *C. hamatus* and 789.87 pg/g wet wt in *T. bernacchii*. The PCB concentrations were also an order of magnitude greater in the liver compared to the muscle (2.25 and 0.34 ng/g wet wt in *C. hamatus*, and 15.11 and 1.63 ng/g wet wt in *T. bernacchi,* respectively). As well as having a higher lipid content (0.16% in muscle in both species; 3.52% and 1.06% in liver of *C. hamatus* and *T. bernacchii*, respectively), the liver is the organ in which endogenous substances are metabolised by detoxifying enzymes (Garcia et al., 2000). Weber and Goerke (2003) found higher concentrations of various classes of POPs in the hepatic tissue of some Antarctic species of fish that feed on benthic organisms, in comparison to the levels found in fish that mainly feed on krill. Ruus et al. (1999) reported similar results for organisms in the northern hemisphere.

The greater POP accumulation in the tissues of *T. bernacchii* may be attributable to the ecological differences between the two species. *T. bernacchii* is a benthic species that feeds mainly on other benthic organisms (polychaetes, gastropods, isopods, amphipods, echinoderms). *C. hamatus*, inhabits the continental shelf and mainly eats krill, fish larvae and other small fish (Kock, 1992). Once they have entered an aquatic environment, many contaminants adsorb onto the suspended particulate and are then deposited on the seabed with it, thus becoming more readily available and easily accumulated in the tissues of bentonic organisms. However, PCB levels found in this study were generally lower than those detected in other species of fish from the Ross Sea (Corsolini et al., 2002; Focardi et al., 1996) and in industrialised parts of the world (Storelli et al., 2004; Kannan et al., 2002).

Regarding PBDEs, congeners nos. 154 and 153 were prevalent in both types of tissues in *T. bernacchi*, while BDE100 was prevalent overall in *C. hamatus*, followed by BDE138 in the muscle and BDE28 in the liver (Figure 1). The BDE154 was always present in a higher percentage compared to PBDEs, even in the tissues of *C. hamatus.* These findings are in agreement with those of other studies that have found PBDE154 to be commonly detected in the tissues of species of fish and among the most abundant congeners (Hale et al., 2001). The high levels of this congener in fish tissues may be due to processes of debromination of 2,2',3,3',4,4',5,5',6,6' (deca-BDE209), whose presence, in contrast, is rarely found in the tissues of organisms (Stapleton et al., 2004). The higher levels of BDE100 in *C. hamatus* tissues in comparison to BDE153 and BDE154 may be attributed to hexa-BDE debromination processes. In particular, in the formation of 2,2',4,4',6 penta-DBE, debromination occurs in *meta* position 5 (Vives et al., 2004; Ikonomou et al., 2002). The levels of PBDE found in this study were higher than those reported by Corsolini et al. (2006a) in the muscle (0.05 ng/g wet wt) and in the whole organism (0.16 ng/g wet wt) of *T. bernacchii* analysed in the same area between 2000-2002. Although the values detected in this study are lower than those found in other fish species that inhabit more contaminated parts of the earth (Jacobs et al., 2002; Boon et al., 2002), this data seems to confirm the gradual increase in PBDE levels even in the tissues of organisms living in polar areas. De Boer et al. (2004) reported an increasing concentration of BDE209 in falcon eggs analysed in Sweden between 1975-2001. Increases in PBDE levels from the 1980s until 2000 were also reported in species living in the Arctic region (Lebeuf et al., 2004; Ikonomou et al., 2002). The differences found between the two species may be attributable to dissimilarities between them and/or the physiological characteristics of the organisms (age, sex and dietary habits) (Vives et al., 2004), as well as to processes of debromination of the substances and therefore to their depuration rate. The detection of PBDEs and PCBs in remote areas such as polar regions is due to their large scale employment and the fact that the materials to which they are added as flame retardants are very widespread and commonly used. The importance of the diffusion of PCBs on a global scale was not recognised until they had been in use for 50 years and not until 30 years after they had been banned in many countries. Despite the fact that the use of PBDEs has been banned in the European Union, these substances are still widely used in many countries, especially in north America. PBDE congeners differed from one

species of fish to another (Stapleton et al., 2004a). The presence of PBDEs and PCBs in the tissues of Antarctic organisms confirms that these compounds are dispersed into the environment via long distance transport and can reach remote regions of the planet (Wania and Dugani, 2003). Furthermore, the data brought to light in this study confirm the continued use of some PBDEs in industrialised areas of the planet and their growing accumulation in the tissues of organisms.

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References

Andersson O, Blomqvist G. 1981. Chemosphere 10: 1051.

Boon JP, Lewis WE, Tjoen-a-choy MR, Allchin CR, Law RJ, De Boer J, Ten Hallers-Tjabbes CC, Zegers BN. 2002. Environ Sci Technol 36: 4025.

BSEF (Bromine Science and Environmental Forum) 2000. www.bsef.com.

Chiuchiolo AL, Dickhut RM, Cochran MA, Ducklow HW. 2004. Environ Sci Technol 38: 3551.

Corsolini S, Romeo T, Ademollo N, Greco S, Focardi S. 2002. Microchemical Journal 73: 187.

Corsolini S, Ademollo N, Romeo T, Greco S, Focardi S. 2005. Microchemical Journal 79: 115.

Corsolini S, Covaci A, Ademollo N, Focardi S, Schepens P. 2006a. Environ Pollut 140: 371.

Corsolini S, Borghesi N, Schiavone A, Focardi S. 2006b. Environ Sci & Pollut Res (DOI: http://dx.doi.org/10.1065/espr200601.017).

De Boer J, Leslie LA, Leonards PEG, Bersuder P, Morris S, Allchin CR. 2004. In: Proceedings of the Third International Workshop on Brominated Flame Retardants BFR2004 Toronto, Canada, 125.

Focardi S, Corsolini S, Aurigi S. 1996. S.It.E. Atti 17: 91.

Garcia LM, Porte C, Albaigés J. 2000. Mar Pollut Bull 40: 764.

Hale R, La Guardia MJ, Harvey EP, Matteson Mainor T, Duff WH, Gaylor MO. 2001. Environ Sci Technol 35: 4585.

Ikonomou MG, Rayne S, Addison RF. 2002. Environ Sci Technol 36: 1886.

Jacobs MN, Covaci A, Schepens P. 2002. Environ Sci Technol 36: 2797.

Jansson B, Asplund L, Olsson M. 1987. Chemosphere 16: 2343.

Kannan K, Corsolini S, Imagawa T, Focardi S, Giesy J.P. 2002. Ambio 31: 207.

Kannan K, Hilsherova K, Imagawa T, Yamashita N, Williams LL, Giesy JP. 2001. Environ Sci Technol 35:441.

Kock KH. 1992. Antarctic fish and fisheries, Cambridge University Press, Cambridge.

Law RJ, Allchin CR, De Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, De Wit CA. 2006. Chemosphere 64: 187.

Lebeuf M, Gouteux B, Measures L, Trottier S. 2004. Environ Sci Technol 38: 2971.

Ruus A, Ugland KI, Espeland O, Skaare JU. 1999. Marine Environmental Research 48: 131.

Stapleton HM, Alaee M, Letcher RJ, Baker JE. 2004. Environ Sci Technol 38: 112.

Storelli MM, Storelli A, Barone G, Marcotrigiano GO. 2004. Mar Pollut Bull 48: 743.

Vives I, Grimalt JO, La corte S, Guillamón M, Barceló D. 2004. Environ Sci Technol 38: 2338.

Wania F, Dugani CB. 2003. Environ Toxicol and Chem 22: 1252.

Wania F, Mackay D. 1996. Environ Sci Technol 30: 390.

Weber K, Goerke H 2003. Chemosphere 53: 667.

Wolkers H, van Bavel B, Derocher AE, Wiig O, Kovacs KM, Lydersen C, Lindstrom G. 2004. Environ. Sci. Technol 38: 1667.

Table 1. ΣPBDE (pg/g wet wt) and ΣPCB (ng/g wet wt) average concentrations (X±SD), minimum and maximum values (min-max) in *Chionodraco hamatus* and *Trematomus bernacchii* tissues.

	Chionodraco hamatus				*Trematomus bernacchii*			
	Muscle		Liver		Muscle		Liver	
n	6		6		6		6	
Lipid %	0.16		3.52		0.16		1.06	
	X±SD	min-max	X±SD	min-max	X±SD	min-max	X±SD	min-max
ΣPBDEs	160.5±80.4	84.9-297.7	205.2±121.5	0.9-321.2	354.1±116.8	225.1-526.8	789.9±252.8	499.5-1068.9
ΣPCBs	0.3±0.3	0.1-0.9	2.2±0.9	0.7-3.3	1.6±1.4	0.3-4.2	15.1±8.2	5.2-28.1

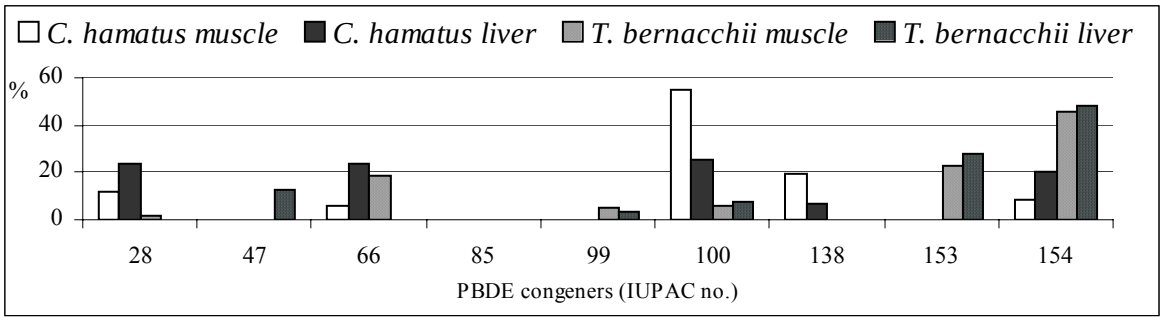

Figure 1: PBDE fingerprints of *Chionodraco hamatus* and *Trematomus bernacchii.*