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Levels and profiles of chlorinated and brominated contaminants in Southern Hemisphere humpback whales, *Megaptera novaeangliae*

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ABSTRACT

The study documents the levels and profiles of selected contaminants [polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and methoxylated PBDEs (MeO-PBDEs)] in blubber biopsy samples collected from humpback whales (*Megaptera novaeangliae*) in Antarctic Peninsula waters. In addition, we investigated year-to-year and sex-related differences in the bioaccumulation patterns. Except for hexachlorobenzene (HCB), whose concentrations were in the same range as those found in whales from the Northern Hemisphere, levels of all other compounds were lower in Southern Hemisphere whales compared to literature data on animals from the Arctic and subarctic region. The mean contribution to the sum of all anthropogenic organohalogen compounds (ΣOHC) decreased in the following order ΣPCBs (44%) > HCB (31%) > ΣDDXs (13%) > ΣCHLs (4.6%) > ΣHCHs (4.4%) > ΣPBDEs (0.9%). The predominant compounds within each chemical class were: PCBs 153, 149, 101 and 138; *p,p′*-DDE; γ-HCH; *trans*-nonachlor; PBDEs 99 and 47. The most dominant MeO-PBDE congener was 6-MeO-BDE 47. As samples were collected during three consecutive summer seasons, year-to-year trends could be assessed indicating a significant decrease from 2000 to 2003 for ΣCHL levels. Higher ΣPBDE concentrations and higher values of the ΣPBDE / ΣMeO-PBDE ratio, as well as higher ratios between the two MeO-BDEs (2′-MeO-BDE 68/6-MeO-BDE 47) were found in females compared to males. Higher ΣMeO-PBDE concentrations and higher values of the ratios between the lower chlorinated and the higher chlorinated PCBs were found in males than in females. In addition, five out of six significant differences found through discriminant function analysis were gender-related. The literature reports both feeding in mid- to low-latitudes and sex-related differences in migration patterns for humpback whales from the Southern Hemisphere, indicating that the hypothesis of dietary differences between males and females cannot be excluded. Nevertheless, additional studies are required for further investigation of this hypothesis.

1. Introduction

Antarctica remains relatively protected from widespread human disturbance, with the exception of small areas of significant environmental pollution from military and scientific activities (Conlan et al., 2004). This relative protection is a consequence of its remoteness and extreme climate conditions, which makes the whole continent a region of high ecotoxicological interest. Taking

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into account the absence of industrial or agricultural activities in Antarctica, the continent was considered to be free of contamination by anthropogenically-produced organohalogen compounds (OHCs) until the late 1960s, when such contamination was first scientifically recorded (Reisebrough et al., 1968). Since then, a number of investigations have shown trace levels of these pollutants (Corsolini, 2009).

Environmental contamination by OHCs has received considerable attention due to their toxicity, persistency and bioaccumulative nature (Covaci et al., 2003; Fabre et al., 2005; Guo et al., 2009; Sonne, 2010). Environmental OHC pollution is caused by their past widespread use as dielectric fluid and in heat exchange systems (the case of polychlorinated biphenyls-PCBs), as well as their use as insecticides for fighting agricultural pests or controlling insect-borne diseases. This latter was the case for organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), hexachlorocyclohexane (HCHs) and chlordanes (Fabre et al., 2005; Guo et al., 2009; Newman and Unger, 2002; Sonne, 2010). Environmental concern has also been raised by the global utilization of polybrominated diphenyl ethers (PBDEs) as flame retardants, since they present similarities with the abovementioned organochlorine pollutants regarding toxicity, persistency and bioaccumulation (Covaci et al., 2003; de Wit, 2002; Law et al., 2006). The high long-range transport potential of OHCs enabled them even to reach remote polar areas (Sonne, 2010).

Methoxylated PBDEs (MeO-PBDEs) have been evidenced in marine environments, with the tetrabrominated 2'-MeO-BDE 68 and 6-MeO-BDE 47 being the most abundant compounds (Vetter et al., 2002). MeO-PBDEs have been reported as having a natural origin (Teuten and Reddy, 2007; Teuten et al., 2005), being formed by sponges (Vetter et al., 2002) or algae (Malmvärn et al., 2005). However, biotransformation of hydroxylated PBDEs (OH-PBDEs) to MeO-PBDEs has also been demonstrated (Wan et al., 2010). These naturally-produced compounds have been detected in marine mammals at concentrations comparable or even higher than those of organobrominated compounds of anthropogenic origin, such as PBDEs (Alonso et al., 2012; Dorneles et al., 2010; Rotander et al., 2012b).

OHCs have been detected in Antarctic marine biota since various species have been used for monitoring purposes (Bengtson Nash, 2011; Corsolini, 2009). The Southern Ocean constitutes feeding ground for several marine mammal species, including large whales. These animals are long-lived upper trophic level predators that are regarded as ideal repository for lipophilic compounds due to their large lipid reserves (O'Shea and Tanabe, 2003). The humpback whale (*Megaptera novaeangliae*) migrates from low latitude breeding regions to high latitude feeding areas (Clapham, 1996). During the end of spring through early fall, Southern Hemisphere humpback whales forage in Southern Ocean waters (Dalla Rosa et al., 2008). Humpback whales are among the most abundant cetaceans in Antarctic Peninsula waters (Secchi et al., 2001; Thiele et al., 2004) and photo-identification studies have shown that individuals of the species have strong site fidelity to the region (Dalla Rosa et al., 2001). These facts turn the humpback whale into the ideal species for ecotoxicological studies in the near-shore waters of the Western Antarctic Peninsula, the operation area of the Brazilian Antarctic Program.

This study reports on organohalogen compound concentrations in humpback whales that feed in nearshore Antarctic Peninsula waters, investigating possible year-to-year and sex-related differences in bioaccumulation patterns of these pollutants.

2. Materials and methods

2.1. Samples

Samples were obtained during research cruises conducted by the Brazilian Antarctic Program (PROANTAR) in the summers of 2000/2001, 2001/2002 and 2002/2003, corresponding to the Brazilian Antarctic Operations (AOs) XIX, XX and XXI, respectively. During these surveys, 65 blubber biopsy samples were obtained from humpback whales in the western Antarctic Peninsula waters. Samples were collected from a 4 m long inflatable boat, using a 120–150 lb crossbow with arrows and tips M8 × 40 mm modified for large cetaceans (Larsen, 1998). In order to reduce the possibility of analysing biopsy samples from the same individual, the sampled whales were photo-identified whenever possible. For sex determination, DNA was extracted from skin samples using the standard phenol–chloroform protocol (Sambrook and Russell, 2001). Subsequently, DNA was used for PCR amplification of the sex-specific ZFY/ZFX genes, as detailed elsewhere (Bérubé and Palsbøll, 1996; Cunha and Solé-Cava, 2007).

2.2. Targeted analytes

Thirty PCB congeners (IUPAC numbers: CB 18, 28, 49, 52, 87, 95, 99, 101, 105, 110, 118, 128, 138, 146, 149, 153, 156, 170, 171, 172, 174, 177, 180, 183, 187, 194, 195, 199, 205, and 209), seven PBDEs (IUPAC numbers: BDE 28, 47, 99, 100, 153, 154, and 183), six DDXs (*o,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT), chlordanes and metabolites (CHLs), such as oxychlordane (OxC), *trans*-nonachlor (TN), *cis*-nonachlor (CN), *cis*-chlordane (CC), and *trans*-chlordane (TC), three hexachlorocyclohexane (HCH) isomers (α-, β- and γ-HCH), as well as hexachlorobenzene (HCB) were targeted. Two MeO-PBDEs (2'-MeO-BDE 68 and 6-MeO-BDE 47) were also determined.

2.3. Sample preparation

Individual standards for PBDEs and MeO-PBDEs (Wellington Laboratories, Guelph, ON, Canada), as well as for PCBs and OCPs (Dr. Ehrenstorfer Laboratories, Augsburg, Germany) were used for identification and quantification. All solvents used for the analysis (*n*-hexane, acetone, dichloromethane, *iso*-octane) were of pesticide-grade (Merck, Darmstadt, Germany). Sodium sulfate and silica were pre-washed with *n*-hexane before use and dried at 150 °C overnight. Extraction thimbles were pre-extracted for 1 h with the extraction mixture used for the samples and dried at 100 °C overnight. The method used for the clean-up of the samples has been previously described and validated (Covaci et al., 2002; Voorspoels et al., 2003), and is briefly presented below. Between 0.04 and 0.24 g of subcutaneous adipose tissue was accurately weighted, homogenized with approximately 8 g anhydrous sodium sulfate, spiked with internal standards BDE 77/BDE 128 (25 ng) and PCB 46/ PCB 143 (75 ng) and extracted for 2 h by hot Soxhlet with 100 mL hexane/acetone (3/1; v/v). After lipid determination (performed gravimetrically on an aliquot of the extract), the extract was cleaned-up on 8 g of acidified silica. After elution with 15 mL hexane and 10 mL dichloromethane, the cleaned extract was evaporated to near dryness and further redissolved in 200 μL of *iso*-octane.

2.4. Instrumental analyses

PBDEs, MeO-PBDEs, CHLs, and HCHs were measured with an Agilent 6890 GC connected to an Agilent 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI) mode. The GC was equipped with a 20 m × 0.18 mm × 0.20 μm AT-5