



Bioaccumulation and biomagnification of classical flame retardants, related halogenated natural compounds and alternative flame retardants in three delphinids from Southern European waters



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ABSTRACT

Occurrence and behaviour of classical (PBDEs) and alternative (HNs, HBB, PBEB, DBDPE and HBCD) flame retardants, together with naturally produced MeO-PBDEs, were studied in short-beaked common dolphin (*Delphinus delphis*), bottlenose dolphin (*Tursiops truncatus*) and long-finned pilot whale (*Globicephala melas*) in two sampling locations from Southern European waters. PBDEs, Dec 602, Dec 603, DP, α -HBCD and two MeO-PBDEs were detected in all three species. Σ PBDEs were between 17 and 2680 ng/g lw; Σ HNs were between 1.1 and 59 ng/g lw; α -HBCD levels ranged between 3.2 and 641 ng/g lw; Σ MeO-PBDEs were between 34 and 1966 ng/g lw. Bottlenose dolphins were the most contaminated species and some individuals could present health risk for endocrine disruption since levels found were above the reported threshold (1500 ng/g lw). Stable isotope analysis was used to evaluate the biomagnification capacity of these compounds. PBDEs, MeO-PBDEs and Dec 602 showed a significant positive correlation with trophic position.

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1. Introduction

Odontocetes accumulate high concentrations of anthropogenic contaminants, many considered persistent, bioaccumulative and toxic (PBT) (Fossi et al., 2013a). Nowadays, there is no evidence that PBT chemicals are provoking direct mortalities of marine mammals, however these lipophilic contaminants cause immune and reproductive dysfunction that can have consequences at the population level (Hammond et al., 2005; Ross et al., 1995).

Flame retardants (FRs) have been used for many years in order to prevent fires, being applied to a wide range of materials such as

textiles, furniture, electronic materials and so on (Alaee et al., 2003). Halogenated flame retardants (HFRs) proved to be really effective and became one of the most used families of FRs, with an annual production constantly increasing (Birnbaum and Staskal, 2004). Some examples are polybromodiphenyl ethers (PBDEs) or Mirex. These compounds have been found in the environment, both in environmental matrices such as sediment (Hu et al., 2010), sludge (Gorga et al., 2013) or air (Harner et al., 2006), and in biological samples such as fish (Guerra et al., 2010), birds (Barón et al., 2014b), cetaceans (Alonso et al., 2012) or even humans (Covaci et al., 2003). PBDEs are lipophilic, persistent and toxic to wildlife and humans (Alaee et al., 2003; de Wit et al., 2010). In mammals, they present potential health risks such as thyroid disruption, neurobiological development and foetal toxicity/teratogenicity (Alonso et al., 2014). Due to its presence in the environment and its

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proved toxicity, Penta- and Octa-BDE mixtures were banned in 2006, while the production of Deca-BDE mixture was planned to be stopped by the end of 2013 (Schechter et al., 2010). As a result, other alternative FRs were developed, and were given the name of emerging FRs (EFRs). Some examples of brominated EFRs are hexabromocyclododecane (HBCD), hexabromobenzene (HBB), pentabromoethyl benzene (PBEB) and decabromodihphenyl ethane (DBDPE). The family of halogenated norbornenes (HNs) includes some chlorinated FRs such as dechlorane 602 (Dec 602), 603 (Dec 603), 604 (Dec 604) and dechlorane plus (DP), with its *syn*- and *anti*-isomers. DP was also the replacement of Mirex when this compound was banned as FR in 1976 (Sverko et al., 2011). With the exception of HBCD, included in the list of global elimination compounds under the Stockholm Convention in May 2013 (Al-Odaini et al., 2015), these compounds are still not legislated, even though they have been found in several environmental and biological matrices (Alonso et al., 2014; Covaci et al., 2011; Guerra et al., 2011; Sverko et al., 2011; Xian et al., 2011). Besides, despite HBCD was included in the Stockholm convention, its use is still permitted in expanded polystyrene and extruded polystyrene in buildings, as long as materials are clearly labelled, indicating that they contain HBCD (Al-Odaini et al., 2015). DP can interfere with the metabolism of some species and has been associated to proteins regulating the apoptosis and cell differentiation in liver cells (Liang et al., 2014). DBDPE and DP have been proposed as a specific alternative for BDE-209 (De la Torre et al., 2011; De la Torre et al., 2010) and consequently their concentrations in the environment might increase in the next years. Despite the increase of studies focussing on these contaminants in recent years, more information regarding their bioaccumulation and biomagnification capacities is needed. To date, there is only one study reporting the presence of DP in cetaceans from Brazil (De La Torre et al., 2012a), while PBDEs have been found in cetaceans at high concentrations worldwide, as reviewed by Alonso et al. (2014). Furthermore, some studies have revealed that cetaceans can be sensible to some families of organic contaminants (Fossi et al., 2013b) and, consequently, the study of the bioaccumulation of these contaminants, including FRs, is of special interest.

On the other hand, methoxylated PBDEs (MeO-PBDEs) are naturally produced halogenated compounds, called halogenated natural products (HNPs). There are more than 4000 HNPs mainly produced by algae, sponges or bacteria (Vetter, 2006) and, consequently, they are considered only a marine problem. These compounds have been found in different species like fish (Barón et al., 2013), polar bears (Letcher et al., 2009) or cetaceans (Alonso et al., 2012). Several studies report that its toxic potential could be similar to dioxins (Su et al., 2012). Furthermore, MeO-PBDEs are structurally similar to compounds shown to exert toxic effects such as endocrine disruption (Fu et al., 1995).

One of the main concerns about Persistent Organic Pollutants (POPs) is their bioaccumulation capacity (Alaee et al., 2003). Besides, it gets worse if the contaminant can also biomagnify in wild animal populations. Previous studies suggest that the uptake of organohalogen compounds occurs through the diet rather than directly from the environment (Vetter et al., 2002). Stable isotope analysis has become a powerful tool to study dietary exposure and biomagnification of contaminants in wild animal populations (Cullon et al., 2012; Chouvelon et al., 2012). $\delta^{15}\text{N}$ is commonly taken as indicator of trophic level (Cabana and Rasmussen, 1996), due to the increase of $\delta^{15}\text{N}$ from prey to predator throughout the food web (Jardine et al., 2006) and thus the correlation between the concentration of the contaminant in the sample (lipid-normalized) with the $\delta^{15}\text{N}$ is used to evaluate the biomagnification capacity of the contaminant.

Despite the fact that the Southern Iberian Peninsula is of special

interest for cetaceans because of its diversity of species (Cañadas et al., 2005; De Stephanis et al., 2008; Esteban et al., 2014; Verborgh et al., 2009) and its location as the unique natural connexion between the Mediterranean Sea and the Atlantic Ocean, there is only one recent study reporting FRs in the area, in striped dolphin (*Stenella coeruleoalba*) (Fossi et al., 2013a). Publications about these organic contaminants in cetaceans are not rare, except for halogenated norbornenes, however most studies were undertaken in both west and east coasts of USA, the Baltic Sea, Japan's Sea and the south east coast of Brazil (Alonso et al., 2014).

The aim of this work was to evaluate the presence of several classical and emerging FRs in the blubber from three cetacean species from southern Iberian Peninsula waters, to compare the anthropogenic burden with the levels of naturally-produced MeO-PBDEs and to evaluate the biomagnification capacity of these different FR families.

2. Materials and methods

2.1. Sampling

A total of 67 blubber samples from 3 cetacean species were obtained by remote biopsy sampling in the Strait of Gibraltar and the Gulf of Cadiz during 2012. Bottlenose dolphins and long-finned pilot whales were sampled via a crossbow and a modified dart with sterilised stainless-steel biopsy tips designed by Finn Larssen, following the protocols described in Giménez et al. (2011) to ensure a low impact sampling method. A pole and smaller biopsy tips were used to sample bow-riding individuals of common dolphins. All samples were collected under a special permit from the Spanish Ministry of Environment. Adults and sub adults were the main target and no calf under 2 years-old was sampled. In the Gulf of Cádiz, 15 samples of short-beaked common dolphin (*Delphinus delphis*) and 20 samples of bottlenose dolphin (*Tursiops truncatus*) were obtained. Furthermore, 2 samples of short-beaked common dolphin, 20 samples of bottlenose dolphin and 10 samples of long-finned pilot whale (*Globicephala melas*) were obtained in the Strait of Gibraltar.

2.2. Nitrogen stable isotope determination

Prior to the isotope determination, lipid content was extracted from the sample with several rinses of chloroform:methanol (2:1) solution in order to reduce the isotopic variability due to the differential content of lipids (Logan et al., 2008). Each sample was covered with the solvent mixture for 24 h, solvent was then removed and fresh solvent was added. This process was repeated for at least 3 times until the solvent appeared clean. Samples were dried at 50 °C for 24 h. Subsamples of powdered materials were weighed to the nearest μg and placed into tin capsules for $\delta^{15}\text{N}$ determinations. Isotopic analyses were carried out at the "Laboratorio de Isótopos Estables de la Estación Biológica de Doñana" (LIE-EBD, Spain; www.ebd.csic.es/lie/index.html). All samples were combusted at 1020 °C using a continuous flow isotope-ratio mass spectrometry system by means of Flash HT Plus elemental analyser coupled to a Delta-V Advantage isotope ratio mass spectrometer via a CONFLO IV interface (Thermo Fisher Scientific, Bremen, Germany). The isotopic compositions are reported in the conventional delta (δ) per mil notation (‰), relative to atmospheric N_2 ($\delta^{15}\text{N}$). Replicate assays of standards routinely inserted within the sampling sequence indicated analytical measurement errors of $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$. The standards used were: EBD-23 (cow horn, internal standard), LIE-BB (whale baleen, internal standard) and LIE-PA (feathers of Razorbill, internal standard). These laboratory standards were previously calibrated with international standards supplied by the International Atomic Energy Agency (IAEA,

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