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Levels and profiles of POPs (organochlorine pesticides, PCBs, and PAHs) in free-ranging common bottlenose dolphins of the Canary Islands, Spain

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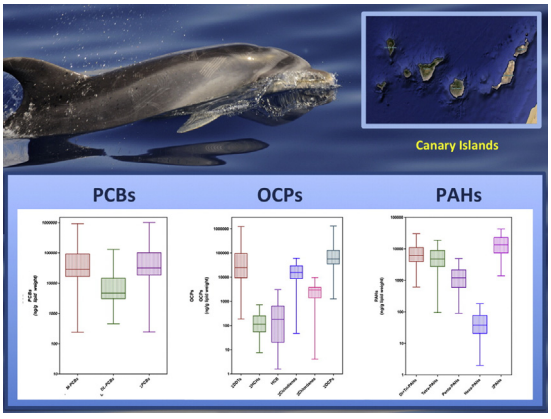
HIGHLIGHTS

- Baseline levels of POPs in free-ranging bottlenose dolphins of the Canary Islands
- Bottlenose dolphins of this area are facing a high exposure to organic pollutants.
- Median concentrations of PCBs and TEQs widely exceeded the toxicity thresholds.
- Surprisingly the levels of contamination by OCPs and PCBs seem to be increasing.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of anthropogenic pollution in marine mammals worldwide has become an important issue due to the high concentrations found in many areas. The present study represents the first report of pollutants in free-ranging cetaceans from the Canary Islands, where there are 12 marine Special Areas of Conservation (SACs), because of the presence of bottlenose dolphins (*Tursiops truncatus*). We selected this resident population of dolphins as a bioindicator to gain knowledge concerning the toxicological status of the cetaceans of this protected area. In 64 biopsy samples of live free-ranging animals sampled from 2003 to 2011, we determined the concentrations of 18 polychlorinated biphenyls (PCBs), 23 organochlorine pesticides (OCPs) and 16 polycyclic aromatic hydrocarbons (PAHs). We found high levels of many of these pollutants, and some of them were detectable in 100% of the samples. The median value for $\sum$OCPs was 57,104 ng g^{-1} lipid weight (lw), and the dichlorodiphenyldichloroethylene (p,p′-DDE) accounted for 70% of this amount. Among PCBs, congeners 180, 153 and 138 were predominant (82% of $\sum$PCBs; median = 30,783 ng g^{-1} lw). Concerning the analyzed PAHs, the total median burden was 13,598 ng g^{-1} lw, and phenanthrene was the compound measured at the highest concentration followed by pyrene and by naphthalene. Surprisingly, we have found that organohalogen pollutants exhibit an upward trend in recent years of sampling. Thus, according to the

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guidelines outlined in the EU's Marine Strategy Framework Directive, further monitoring studies in Canary Islands are required to contribute to the conservation of the resident populations of marine mammals in this region.

1. Introduction

Currently, marine mammals face a great variety of threats, many of which are of human origin. Among all anthropogenic threats (e.g., habitat loss and degradation, maritime traffic, accidental capture, overfishing, commercial whaling, tourist human interactions, whale watching activities and acoustic pollution), the exposure to pollutants and to debris occupies a prominent place (Tanabe, 2002). Thereby, the role of persistent organic pollutants (POPs) in the habitat of marine mammals, as causative factor of poor survival and the continued decline of their populations, is an area of ongoing research (Aguilar et al., 1999; Aguilar and Borrell, 1994; Balmer et al., 2011; Kakuschke et al., 2010; Kuehl et al., 1991).

Although the adverse health effects of POPs are difficult to assess, some studies have demonstrated that POPs adversely affect the endocrine and immune system, or cause reproductive impairment in these animals (Letcher et al., 2010; Miyazaki et al., 2004; Schwacke et al., 2012; Tanabe, 2002). Moreover, some massive die-off and stranding episodes of marine mammals have been related to chemical pollutants, which have been proposed as contributors of the emergence and pathogenicity of infectious disease epidemics (Aguilar and Borrell, 1994; Hall et al., 2006; Van Bressem et al., 2009). Various authors have established thresholds for toxicity in different tissues and endpoints in marine mammals (AMAP, 2002; Kannan et al., 2000; Letcher et al., 2010), and numerous studies worldwide have shown that these thresholds are commonly exceeded in these animals. However, the majority of these studies have been performed on samples taken from the remains of stranded animals. It is well known that pollutant concentrations found in stranded animals may not be indicative of levels of live individuals, because disease is often the cause of death in strandings, and the possibility exists that these animals may carry abnormal pollutant loads (Aguilar et al., 1999; Camacho et al., 2014). Thus far, relatively few investigations have been performed on healthy live captive or free-ranging marine mammals primarily due to the complexity and cost of sampling (Balmer et al., 2011; Berrow et al., 2002; Fair et al., 2010; Formigaro et al., 2014; Hansen et al., 2004; Kucklick et al., 2011; Yordy et al., 2010). To date, none of these investigations on live animals has been performed in cetaceans from the Canary Islands, which have been declared a "Particularly Sensitive Sea Area" by the International Maritime Organization (IMO) and are considered a protected marine area. This archipelago is an area of great diversity of cetaceans, and its geographical location and oceanographic conditions have caused the establishment of year-round resident populations of cetaceans, such as the common bottlenose dolphin (*Tursiops truncatus*), among others (Arbelo et al., 2013).

Bottlenose dolphin is a species of high interest for the study of pollutants for various reasons: a) its worldwide distribution (MMC, 1999), b) the great amount of available studies concerning different aspects of its biology and physiopathology, and c) the fact that there are many coastal populations throughout the planet with a potential to reflect the contamination because their proximity to urban and industrial sources increases their POP exposure (Kucklick et al., 2011). For all these reasons, this species has been proposed as a good bioindicator of marine pollution, and many of the above-mentioned studies have been performed on these dolphins.

The primary objective of the present monitoring study was to obtain a baseline of many relevant anthropogenic pollutant loads in bottlenose dolphins from the Canary Islands to assess the potential toxic impact of these pollutants in cetacean species of this area with conservation aims. Although life history data of wild animals are difficult to obtain, blubber biopsy samples collected from these 64 free-ranging bottlenose dolphins can be representative of this population and are preferred over samples collected from necropsies (Aguilar and Borrell, 1994).

2. Materials and methods

2.1. Study area

The Canary Islands are located 1600 km away from southwest Spain, in the Atlantic Ocean, and 100 km away from the nearest point on the North African coast (southwest of Morocco) (Fig. 1). Thus, although geographically part of the African continent, from political and socioeconomic points of view, the Canary Islands belong to the European Union. As above-mentioned, this region is a protected marine area. However, notably large quantities of organochlorine pesticides (OCPs) have been used in the past in this archipelago because of the important role of agriculture in the economy of the region. In fact, high loads of OCPs and other anthropogenic pollutants have been described in the human population (Luzardo et al., 2012, 2009) and in biota of this archipelago, including marine wildlife in nearby areas (Camacho et al., 2012, 2013a, 2013b, 2013c; Luzardo et al., 2014; Zumbado et al., 2005).

There are 12 marine Special Areas of Conservation (SACs, Natura 2000 network) in the Canary Islands due to the presence of bottlenose dolphins, which are listed on Annex II and IV in the European Habitats Directive. By means of individual identification (individual photo-ID) it has been shown that this population is year-round resident with inter-island movements of animals, at least for the last 15 years. The populations of bottlenose dolphin in at least three of these SACs are under the same synergistic threats (e.g. maritime traffic, whale-watching, professional fishing, high-speed ferries and coastal degradation).

2.2. Sample collection and ethics statement

The biopsy samples were collected by the Society for the Study of Cetaceans in the Canary Archipelago (SECAC), from 2003 to 2011, through monitoring surveys in the SACs of the Canary Islands and in the eastern waters of the islands of Lanzarote and Fuerteventura. The use of crossbows and the Ceta-Dart® bolt and cutting head (Ceta-Dart, Copenhagen, Denmark) allows efficient, minimally invasive, and humane sampling of cetaceans in the wild (Wenzel et al., 2010). Biopsy sampling on individual cetaceans, if performed responsibly, is likely to cause only low-level and short-term reactions and is not likely to produce any long-term deleterious effects. Therefore, this sampling is deemed as relatively irrelevant for the animals' welfare. In this study, we have used this methodology to collect 64 blubber samples from bottlenose dolphins during the period 2003–2011 (Table 1). In Fig. 1, we depict the exact location of each sampling. Samples were responsibly collected by trained personnel using a modified arrow that was fired with a stainless hollow cylindrical head of 0.8 cm in internal diameter and 2.5 cm in length. After removing the tissue from the tip, the skin was separated from the blubber using solvent-rinsed scalpel and forceps. The skin was used for both trophic studies (stored at −20 °C) and genetic studies (stored in a saturated salt solution of 20% DMSO). The blubber samples were stored in pre-solvent-cleaned Eppendorf® vials and frozen at −20 °C (ship) and at −80 °C (laboratory) until chemical analyses. All biopsies were collected from the dorsal and mid-lateral regions near the dorsal fin. A limitation of this type of remote sampling is that reliable data concerning the age and sex of individuals cannot be recorded. However, all animals were photographed and videotaped for later stock identification. Besides, the individuals were classified as