Environmental Pollution 236 (2018) 785–794

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Contamination status by persistent organic pollutants of the Atlantic spotted dolphin (*Stenella frontalis*) at the metapopulation level☆

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ARTICLE INFO

Article history:
Received 27 March 2017
Received in revised form
23 January 2018
Accepted 4 February 2018

Keywords:
Bioaccumulation
Contamination assessment
Persistent organic pollutants
Stenella frontalis
Atlantic ocean

ABSTRACT

The Atlantic spotted dolphin (*Stenella frontalis*) is an endemic species of the tropical-temperate Atlantic Ocean with widespread distribution. Although this species has been the subject of a large number of studies throughout its range, it remains in the "data deficient" category of the International Union for Conservation of Nature (IUCN). Chemical pollution by persistent organic pollutants (POPs) has been listed as one of the major threats to this species, however, there is no information on a wide scale. Thus, the aim of the present study was to investigate the contamination status of spotted dolphins on the metapopulation level as well as determine spatial and temporal variations in POP concentrations and bioaccumulation. A total of 115 blubber samples collected from a large part of the Atlantic basin were analysed for PCBs, DDTs, PBDEs, chlordanes, HCB and mirex. Although PCBs and DDTs were the predominant compounds in all areas, inter-location differences in POP concentrations were observed. Dolphins found at São Paulo, southeastern coast of Brazil, had the highest PCB concentrations (median: 10.5 μg/g lw) and Canary Islands dolphins had the highest DDT concentrations (median: 5.13 μg/g lw). Differences in PCB patterns among locations were also observed. Dolphins from the Azores and São Paulo demonstrated a similar pattern, with relatively highly contributions of tetra- (6.8 and 5.2%, respectively) and penta-CBs (25.6 and 23.8%, respectively) and lower contributions of hepta-CBs (20.8 and 23.5%, respectively) in comparison to other areas. Moreover, the sex of the animals and the year in which sampling or capture occurred exerted an important influence on the majority of the POPs analysed. Comparisons with toxicity thresholds available in the literature reveal that the São Paulo and Canary Island dolphins are the most vulnerable populations and should be considered in future conservation and management programs for the Atlantic spotted dolphin.

1. Introduction

The Atlantic spotted dolphin (*Stenella frontalis*, ASD) is an endemic species of the tropical-temperate Atlantic Ocean (Perrin et al., 1987, 1994; Moreno et al., 2005; Paro et al., 2014), primarily encountered from the continental shelf (<200 m) to the continental slope waters (200–2000 m) (Mullin and Fulling, 2003). This species has been the subject of a large number of studies throughout its

☆ This paper has been recommended for acceptance by Prof. von Hippel Frank A..

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https://doi.org/10.1016/j.envpol.2018.02.009
0269-7491/

range, but remains in the "data deficient" category of the International Union for Conservation of Nature (IUCN, 2014).

To assess the contemporary conservation status of the ASD, it is essential to gain a better understanding of several aspects of its ecology, such as population structure, key drivers of population dynamics, feeding ecology, and the major threats to which the species is exposed. Marine mammals face an array of threats stemming from human activities, including incidental captures, collisions, prey resources depletion, hunting, habitat degradation and loss, and pollution. However, due to the challenges of sampling marine wildlife, global data, particularly species-specific data on threats to marine mammals is generally lacking. Special attention has been given to incidental captures of the ASD in Brazil, the Caribbean, the United States and Mauritania and to hunting for human consumption practiced on small islands of the Caribbean Sea (Fielding and Evans, 2014; Mignucci-Giannoni et al., 1999; Perrin et al., 1994). However, little is known about chemical pollution in this species, especially on the metapopulation level.

Persistent organic pollutants (POPs) (*e.g.*, PCBs, polychlorinated biphenyls, DDTs, dichloro diphenyl trichloroethane, PBDEs, polybrominated diphenyl ethers) merit special attention. POPs are man-made contaminants that enter aquatic environments directly (*e.g.*, transformer spills, agricultural runoff) or indirectly via atmospheric transport, ocean currents (Breivik et al., 2004; Li and Macdonald, 2005) and through plastics (*e.g.*, microplastic particles, plastic resin, etc.), where they are adsorbed and transported via ocean currents (Rios et al., 2007; Teuten et al., 2009). These pollutants are a primary concern in marine ecosystems and are cited on the OSPAR list of Chemicals for Priority Action (OSPAR, 2010). POPs are lipophilic synthetic organic compounds, which because of their chemical and physical properties, have been used in agriculture, industry and human health since the 1940s (Clark, 2001). The production and use of these compounds were restricted or banned approximately 15 years ago at the Stockholm Convention (UNEP, 2001) due to their environmental persistence and toxicity to humans and wildlife. Nevertheless, considerable amounts of these persistent compounds continue cycling in the environment.

Marine mammals bio-accumulate and bio-magnify large amounts of POPs due to the fact that they are top predators with high longevity and low biodegradation capacity (Borrel and Aguilar, 2007; Tanabe et al., 1988). Moreover, since POPs are highly lipophilic, they reach the highest concentrations in fatty tissues and particularly in the hypodermic fat or blubber of marine mammals. Several studies have shown the adverse effects of POPs on marine mammals. For instance, significant reductions in total reproductive outcome have been found to coincide with increased long-term exposure to highly biomagnified levels of PCBs in the Baltic grey seal population (Helle et al., 1976). High levels of organochlorines have been correlated with pathological uterus lesions, a disease complex including lesions on skin, claws, intestines, kidneys and adrenal glands, as well as immunosuppression (Bergman and Olsson, 1985; Jepson et al., 2005; Kannan et al., 2000). It is also important to highlight the effect of the exposure to a complex mixture of chemical contaminants present in the environment. Even when individual stressors are present at concentrations lower than the "no-observable-effect" concentration (Brian et al., 2007; Kortenkamp, 2007; Silva et al., 2002). Therefore, marine mammals are largely considered as good sentinel organisms in aquatic and coastal environments when evaluating the presence of chemical contaminants (Reddy et al., 2001; Wells et al., 2004).

Numerous studies have shown that several ecological as well as biological factors, such as age and sex, affect the pollutant burden in marine mammals and have to be taken in consideration (Borrell et al., 1996; Borrell and Aguilar, 2005; Tanabe et al., 1982). These compounds enter marine mammal tissues almost exclusively through feeding and contamination levels therefore vary greatly depending on intake factors (*i.e.*, trophic level and prey type) (Aguilar, 1989) and local environmental pollution. Each compound may have its own trophic source. Consequently, a complete POP profile may be used as a kind of fingerprint to infer dietary behaviour and feeding habitat as well as to differentiate among different species or populations (Wells et al., 1996; Borrell et al., 2006; Pierce et al., 2008; Méndez-Fernandez et al., 2017).

Thus, the aim of the present study was to assess contamination by POPs (PCBs, DDTs, PBDEs, chlordanes, HCB and mirex) in the ASD on the metapopulation level and in light of bio-ecological factors. For such, blubber samples from a large geographic area of ASD distribution were analysed to investigate variations in POP concentrations and accumulation in this species. This paper also addresses the toxicological implications of contaminant concentrations on the health of the Atlantic spotted dolphin.

2. Material and methods

2.1. Sample collection

A total of 115 blubber samples were collected from stranded ASDs in São Paulo ($n = 10$, southeast Brazil), the Canary Islands ($n = 11$, Spain) and Guadalupe Island ($n = 1$, French Caribbean) between 2005 and 2015 (Table 1). An experienced stranding network personnel performed complete necropsies whenever the condition of the animal permitted. Only samples collected from fresh or moderately decomposed animals (decomposition state ≤ 3 based on the classification proposed by Kuiken and Hartmann [1991] and category 2 using the classification proposed by Geraci and Lounsbury [1993]) were used for POP analyses to prevent sampling biases associated with tissue decomposition. Biopsies of skin and blubber from São Paulo ($n = 39$) and the Azores ($n = 54$, Portugal) collected using a crossbow (BARNETT 125 and 150 l b) with tips specially designed for small cetaceans (dart 25 mm in length and 5 mm in diameter) were also used. Dolphins were hit below the dorsal fin when sufficiently close to the research boat. At sea, samples were stored on ice from 1 to 8 h. On land, skin and blubber were separated. Blubber samples were wrapped in aluminium foil and preserved frozen (−20 °C) until analysis.

2.2. Sex determination

Molecular sexing techniques were performed for the sex determination of the specimens sampled through biopsy darting (using skin samples). The protocol proposed by Rosel (2003) was used for samples from São Paulo. Molecular sexing was performed on samples from the Azores by co-amplification of a short fragment of the male-specific SRY gene and a tetranucleotide microsatellite used as a PCR control for positive identification of females (Quérouil et al., 2010).

2.3. Persistent organic pollutant (POP) analyses

Atlantic spotted dolphins exhibit a slight stratification of POPs at different blubber depths (Méndez-Fernandez et al., 2016). Therefore, the entire dorsal blubber of stranded individuals and the more superficial blubber from the biopsy samples were used for the analyses of POPs. Approximately 0.2 g of blubber were ground with anhydrous Na_2SO_4 and extracted using a Soxhlet apparatus for 8 h with 80 mL of *n*-hexane and methylene chloride (1:1, v:v). Prior to extraction, surrogates (PCB 103 and 198) were added to samples, blanks and reference material. The extract was then concentrated by rotary evaporation to 2 mL, 200 µL of which were used to determine the amount of lipids by gravimetry. The remaining