Science of the Total Environment 631–632 (2018) 239–245

Contents lists available at ScienceDirect

Science of the Total Environment

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

Transplacental transfer of persistent organic pollutants in La Plata dolphins (*Pontoporia blainvillei*; Cetartiodactyla, Pontoporiidae)

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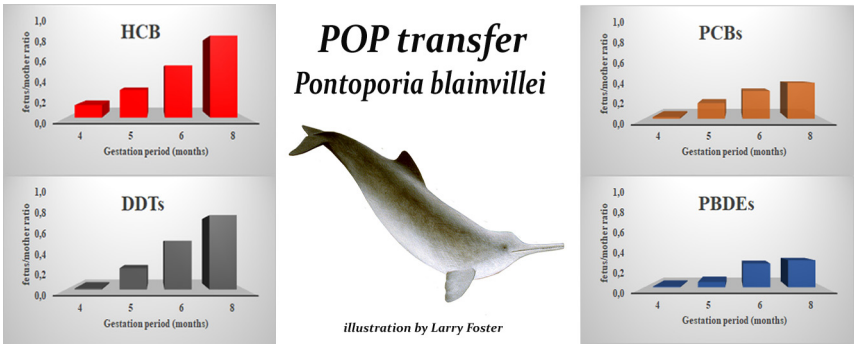
HIGHLIGHTS

- POPs are transferred via placenta in La plata dolphins.
- Dolphin blubber is the main tissue for accumulate POPs.
- POP transfer via placenta increases according to gestation period and fetal development of *Pontoporia blainvillei*.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 November 2017
Received in revised form 8 February 2018
Accepted 27 February 2018
Available online xxxx

Editor: Yolanda Picó

Keywords:
Bioaccumulation
Persistent organic pollutants
Mother-fetus
Marine mammals
Southeastern Brazil

ABSTRACT

Persistent organic pollutants (POPs) accumulate in the fat tissue of living organisms and are found in relatively high concentrations in animals at the top of the food chain, such as dolphins. The ability of these compounds to interact with the endocrine system of marine mammals constitutes a risk for the reproduction and conservation of species. The La Plata dolphin, *Pontoporia blainvillei*, is exclusive to the southwestern Atlantic Ocean and is classified on the IUCN red list as a vulnerable species. Blubber, liver, kidney and muscle samples from four *P. blainvillei* mother-fetus pairs were analyzed to evaluate the transfer of POPs to fetal tissues through the placenta. The presence of POPs in fetal tissues indicates the maternal transfer of compounds. In the pregnant females, blubber was the tissue with POP highest concentration, followed by the liver, kidneys and muscles. In the fetuses, POP accumulation mainly occurred in the blubber followed by the muscles, liver and kidneys. Polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDTs) were found in all tissues analyzed and had the highest concentrations among all compounds. The main PCB congeners in the fetal samples had five to seven chlorine atoms. The only polybrominated diphenyl ether (PBDE) in the fetal samples was 47 and was found only in blubber. The main DDT metabolite in the fetuses was *p,p′*-DDE. POP transfer via the placenta occurs in the first months of gestation and increases with fetal development, according to fetus/mother (F/M) ratio: HCB > DDT > PCB > PBDE > Mirex, which may follow the order of the octanol/water partition coefficient (K_{ow}) values.

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https://doi.org/10.1016/j.scitotenv.2018.02.325
0048-9697/

1. Introduction

Persistent organic pollutants (POPs) accumulate and are biomagnified in the fat tissue of organisms due to their lipophilic characteristics with higher concentrations found in animals at the top of the food chain (Aguilar et al., 1999; Tanabe et al., 1994). POPs include organochlorine pesticides, such as DDTs, mirex, chlordanes, hexachlorocyclohexanes (HCHs) and industrial products, such as PCBs and PBDEs (UNEP, 1995, 2009, 2011, USEPA, 2009). Such pollutants pose risks to marine mammal populations (Bila and Dezotti, 2007; Pestana et al., 2008).

Marine mammals bioaccumulate and biomagnify large amounts of POPs due to the fact they are top predators with high longevity and low biodegradation capacity (Borrel and Aguilar, 2007; Tanabe et al., 1988). Moreover, these mammals maintain a significant fat layer for energy and thermoregulation needs, making them particularly vulnerable to the lipophilic POPs (Weijs et al., 2010a). A series of chemical substances present in the environment can disturb the endocrine system of aquatic and terrestrial organisms by interacting with reproductive hormone receptors, exerting a negative influence on the reproduction and thus the conservation of a given species (USEPA, 1997). Known as environmental endocrine disruptors, these compounds are defined as exogenous agents that interfere with the production, release, transport, action, metabolism, link or elimination of natural hormones responsible for the maintenance, homeostasis, reproduction, development and/or behavior of organisms (USEPA, 2006). POP contents in dolphins vary widely depending on the species and their habitats (e.g. Weijs et al., 2010a, 2010b; Yogui et al., 2010; Lailson-Brito et al., 2011, Gui et al., 2014). Studies confirmed the occurrence of the maternal transfer of chemical contaminants in small cetaceans (Gerpe et al., 2002; Leonel et al., 2012; Borrell and Aguilar, 2005). Up to 90% of this transfer was reported to occur during lactation (Tilbury et al., 1999). However, some studies showed evidence of the transfer of halocarbons in cetaceans through the placenta (Yang et al., 2007; Tilbury et al., 1999; Weijs et al., 2013; Desforges et al., 2012; Alonso et al., 2015). The placental transfer of contaminants is of concern due to the incomplete development or absence of the blood-brain barrier in fetuses, which enables the accumulation of toxic substances in neural tissue. This may cause harmful effects in critical development phases, organ and skeletal abnormalities, and damages to reproduction and immune functions (Tilbury et al., 1999). Nevertheless, it is unknown the dimension of the impacts this might have on their development or survival in the longer term (Weijs et al., 2013).

The La Plata dolphin, *Pontoporia blainvillei* (Gervais and d'Orbigny, 1844), is a small cetacean that feeds on several species of demersal fish, cephalopods and crustaceans (Danilewicz et al., 2002). This species is exclusively distributed in coastal and estuarine waters of tropical and temperate regions of the southwestern Atlantic Ocean, from the Gulf of San Matías at the central coast of Argentina (Crespo et al., 1988), to the state of Espírito Santo in southeastern Brazil (Siciliano, 1994). Although dolphins have the ability to reach long distances, La Plata dolphins do not travel >100 km from their usual range (Wells et al., 2013). The species is listed as vulnerable to extinction by the International Union for Conservation of Nature (IUCN) (Reeves et al., 2012). The major threat this species faces is bycatch in gillnet operations (Secchi et al., 2003). However, besides incidental captures, other impacts such as chemical contamination have turned into a new cause of concern and may constitute an additional obstacle for the conservation of the species (Lailson-Brito et al., 2011).

Considering the limited available information on the maternal transfer of POPs during gestation and their potential risks in fetal development (e. g. Yang et al., 2007, Tilbury et al., 1999, Weijs et al., 2013, Desforges et al., 2012, Alonso et al., 2015), the aim of the present study was to evaluate the occurrence of the placental transfer of POPs, as well as the bioaccumulation of these compounds in the blubber, liver, kidneys and muscles of *P. blainvillei* fetuses.

2. Material and methods

2.1. Sampling

Between September 2013 and June 2015, four pregnant females (PA331, PA332, PA369, and PA397) with their respective fetuses (PA344, PA345, PA370 and PA401) (see Table 1 - considered as pairs A, B, C and D) were accidentally caught in fishing operations on the coast of the state of São Paulo (southeastern Brazil) (Fig. 1). Necropsies were conducted at the field research station of the *Instituto Oceanográfico – Universidade de São Paulo*. Blubber, muscle, kidney and liver samples were collected from fetuses and females. The samples were wrapped in aluminum foil and preserved at −20 °C until analysis at the *Laboratório de Química Orgânica Marinha do Instituto Oceanográfico – Universidade de São Paulo* [Marine Organic Chemistry Laboratory, Oceanographic Institute, University of São Paulo].

Muscle tissue from fetus/mother pairs C and D and liver and kidney tissue from fetus/mother pair D were not available for analysis. The gestation period was estimated based on the body length of the fetuses (see Danilewicz et al., 2002). Detailed information on the biometric data of fetus/mother pairs is found in Table 1. Based on the carcass classification proposed by Geraci and Lounsbury (1993), the individuals were grouped in the Code 2 category (fresh animals).

2.2. Chemical analysis

Samples of ~ 0.25 g of blubber, ~1.0 g of liver and kidney and ~2.5 g of muscle were ground with 15 g of anhydrous sodium sulfate and extracted in a Soxhlet apparatus for 8 h using approximately 80 mL of n-hexane and dichloromethane (1:1) (v/v). Before extraction, PCB 103 (2,2′,4,5′,6–pentachlorobiphenyl) and PCB 198 (2,2′,3,3′,4,5,5′,6–octachlorobiphenyl) were added as surrogate standards. The extract was concentrated to 2 mL, from which a 0.2 mL aliquot was removed for lipid content gravimetric analysis (UNEP/FAO/IOC/IAEA, 1986). The remaining extract was submitted to treatment with concentrated sulfuric acid (96%), followed by elution in a 5% water-deactivated alumina chromatographic column with 20 mL of a mixture of 30% dichloromethane and 70% of n-hexane. Tetrachloro-*m*-xylene (TCMX) was added before injection in a gas chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD) for the analysis of pesticides and a mass spectrometer detector (GC/MS) for the analysis of PCBs and PBDEs.

2.3. Instrumental parameters

2.3.1. GC-ECD

Agilent Technologies (model 6890 N) fused silica capillary column with 5% diphenylmethylsiloxane (30 m length, 0.25 mm i.d., 0.25 μm film thickness) was used for separation. The carrier gas was H_2 (0.7 mL min^{-1}) and the makeup gas was N_2. The compounds were identified based on retention time in comparison to certified external standards. The oven temperature used in the separation of compounds was set at 60 °C and increased to 150 °C (5 °C per min) held for 5 min, then up to 200 °C (1 °C per min) and finally reached 300 °C (8 °C per min), holding this temperature for 4.5 min (90 min run).

2.3.2. GC/MS

The column used was similar to that used in GC-ECD. MSD was operated in the electron impact ionization (EI) (70 eV) and select ion monitoring (SIM) mode. The carrier gas was He (1.1 mL min^{-1}). In addition to the retention times, compounds were identified based on each mass/charge (m/z) ratio of quantitation ion. The oven temperature used in the separation of PCB congeners was set at 75 °C, held for 3 min, increased 15 °C per min to 150 °C, then up to 260 °C (2 °C per min) and finally reached 300 °C (20 °C per min), holding this temperature for 10 min until the end of the analysis in a 66 min run. For PBDEs, the heating ramp started at 70 °C, holding for 1 min, increased to 154 °C