Environmental Pollution 207 (2015) 391–402

Contents lists available at ScienceDirect

Environmental Pollution

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

Toxic heritage: Maternal transfer of pyrethroid insecticides and sunscreen agents in dolphins from Brazil

Mariana B. Alonso [a, b, c], Maria Luisa Feo [d], Cayo Corcellas [d], Pablo Gago-Ferrero [d], Carolina P. Bertozzi [c], Juliana Marigo [c], Leonardo Flach [e], Ana Carolina O. Meirelles [f], Vitor L. Carvalho [f], Alexandre F. Azevedo [b], João Paulo M. Torres [a], José Lailson-Brito [b], Olaf Malm [a], M. Silvia Diaz-Cruz [d], Ethel Eljarrat [d, *], Damià Barceló [d]

[a] Radioisotopes Laboratory Eduardo Penna Franca (LREPF), Biophysics Institute Carlos Chagas Filho (IBCCF), Federal University of Rio de Janeiro (UFRJ), Brazil
[b] Aquatic Mammals and Bioindicator Laboratory (MAQUA), School of Oceanography, Rio de Janeiro State University (UERJ), Brazil
[c] Laboratório de Biologia e Conservação da Megafauna Marinha – Biopesca – Instituto de Biociências, Universidade Estadual Paulista, Unesp, Campus Litoral Paulista, Brazil
[d] Department of Environmental Chemistry, IDAEA, CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
[e] Projeto Boto Cinza, Sepetiba, Rio de Janeiro, Brazil
[f] Associação de Pesquisa e Preservação de Ecossistemas Aquáticos (AQUASIS), Caucaia, Ceará, Brazil

ARTICLE INFO

Article history:
Received 19 March 2015
Received in revised form
9 September 2015
Accepted 14 September 2015
Available online 2 November 2015

Keywords:
Cetacean
Emerging pesticides
Fetus
Lactational uptake
Transplacental transfer
UV filters

ABSTRACT

Pyrethroids (PYR) and UV filters (UVF) were investigated in tissues of paired mother-fetus dolphins from Brazilian coast in order to investigate the possibility of maternal transfer of these emerging contaminants. Comparison of PYR and UVF concentrations in maternal and fetal blubber revealed Franciscana transferred efficiently both contaminants to fetuses (F/M > 1) and Guiana dolphin transferred efficiently PYR to fetuses (F/M > 1) different than UVF (F/M < 1). PYR and UVF concentrations in fetuses were the highest-ever reported in biota (up to 6640 and 11,530 ng/g lw, respectively). Muscle was the organ with the highest PYR and UVF concentrations ($p < 0.001$), suggesting that these two classes of emerging contaminants may have more affinity for proteins than for lipids. The high PYR and UVF concentrations found in fetuses demonstrate these compounds are efficiently transferred through placenta. This study is the first to report maternal transfer of pyrethroids and UV filters in marine mammals.

1. Introduction

The number of organic contaminants found in the environment is constantly increasing. Among those that have emerged recently are synthetic pyrethroid insecticides and active ingredients in sunscreen products. Along with the emerging POPs (persistent organic pollutants, e.g. emerging flame retardants), these both classes of chemicals have been detected in biota (Alonso et al., 2012a, 2012b; Gago-Ferrero et al., 2012), in human matrices (Corcellas et al., 2012; Kunisue et al., 2012) as well as in other environmental samples (Feo et al., 2010b; Gago-Ferrero et al., 2011). The main concern for these emerging contaminants is endocrine disrupting activity in non-target organisms (Schreurs et al., 2005; Weybridge, 2012).

Synthetic pyrethroids (PYR) are hydrophobic, particle reactive, and are found in low concentrations in water (e.g. up to 70 ng/L in California creeks and 40 ng/L in Ebro river) (Amweg et al., 2006; Feo et al., 2010b). They are applied to land and/or around man-made structures for the control of arthropod-borne diseases, and are also used in agricultural, garden and veterinary products (Feo et al., 2010a; Santos et al., 2007). This group of insecticides has a high degree of toxicity in standard laboratory studies with fish and arthropods (Maund et al., 2002; Woudneh and Oros, 2006; You et al., 2008). Studies suggested carcinogenic, neurotoxic, immunosuppressive, allergenic and reproductive potential toxicity in mammals (Jin et al., 2012; Scollon et al., 2011; Shafer et al., 2008). Newborn rats were reported as 4 to 17 times more vulnerable to acute

* Corresponding author. Department of Environmental Chemistry, IDAEA, CSIC, C/ Jordi Girona 18-26, Barcelona, Spain.
E-mail address: eeeqam@cid.csic.es (E. Eljarrat).

http://dx.doi.org/10.1016/j.envpol.2015.09.039
0269-7491/

toxicity of PYR than adults (Ostrea et al., 2013; Shafer et al., 2004). Recent studies have reported their accumulation in biotic matrices, such as human breast milk (Corcellas et al., 2012; Feo et al., 2012) and in liver of marine mammals (Alonso et al., 2012b).

Ultra-violet filters (UVFs) are sunscreen agents that reduce the intensity of UV light incidence on cells. UVFs can be found in many products, including cosmetics (e.g. perfumes, shampoos, creams and make up products), as well as in industrial and/or commercial products as an agent to minimize photodegradation. UVFs produced estrogenic and androgenic activity in *in vivo* and *in vitro* studies (Díaz-Cruz and Barceló, 2009; Schreurs et al., 2005). Oral administration of UVF to mammals during pre and postnatal life, has shown that the central nervous system and reproductive organs are targets for the damaging effects on the development of the offspring; resulting in changes in gene expression in organs and regions of the brain related to sexual dimorphism (Schlumpf et al., 2004). Ethylhexyl methoxycinnamate (EHMC) can alter the gene expression in zebrafish (*Danio rerio*) and showed multiple hormonal activities at environmentally relevant concentrations (Zucchi et al., 2011). Recent studies showed that these chemicals are detected in the environment (Gago-Ferrero et al., 2011; Jurado et al., 2014), in biota (Buser et al., 2006; Gago-ferrero et al., 2013) and in human breast milk, placenta and semen (Jiménez-Díaz et al., 2011; León et al., 2010; Schlumpf et al., 2004).

Long-lived marine mammals such as cetaceans are exposed to multiple persistent bioaccumulative toxicants compounds throughout their life history. Dolphins in particular serve as excellent sentinel species for contamination in the marine environment (Alonso et al., 2014; Bossart, 2011; Kucklick et al., 2011). When concentrations reach high enough levels, these sentinels may experience neurotoxic, immunologic and multiple endocrine effects (McDonald, 2002; Zhou et al., 2002). The two primary exposure routes are via the diet and through maternal transfer that in turn occurs via lactation and gestation (Bossart, 2011; Kajiwara et al., 2008). Thus, the exposure of a pregnant female cetacean to toxicants may pose a health threat to the developing fetus, resulting in an increased susceptibility to disease in adulthood (Desforges et al., 2012; Park et al., 2010).

Few works have focused on maternal transfer of organohalogenated compounds in marine mammals. Most data are derived from studies of lactational transfer of contaminants in seals and sea lions (Debier et al., 2012; Vanden Berghe et al., 2012; Wang et al., 2013). Prenatal exposure of cetaceans to organohalogen contaminants was slightly recorded, mainly due to difficulty in obtaining such samples. Some reports recorded the transplacental transfer of organochlorines and organobrominated compounds in cetaceans (Desforges et al., 2012; Dorneles et al., 2010; Hoguet et al., 2013; Kajiwara et al., 2008; Weijs et al., 2013), and rare researches on perfluorinated compounds were conducted (Dorneles et al., 2008a; Van De Vijver et al., 2007), however with a very limited number of samples from mother-fetus pairs.

Our previous studies reported on residues of PYR and UVFs in free-ranging dolphins, including in placenta and milk samples (Alonso et al., 2012b; Gago-Ferrero et al., 2013). However, no direct evidence of maternal transfer was found in these studies. In this paper, we investigated for the first time the likelihood of maternal transfer of pyrethroids and UV filters in cetaceans by analyzing paired samples of mother-fetus of Franciscana and Guiana dolphins from the Southwestern Atlantic Ocean.

2. Materials and methods

2.1. Target species

The Franciscana dolphin (*Pontoporia blainvillei)* is a small odontocete that occurs exclusively in the southwestern Atlantic where it is considered to be among the most threatened cetacean species along the east coast of Latin America (Secchi and Wang, 2002). It has a small coastal home range due to its limited movement patterns (Wells et al., 2012). The site fidelity exhibited by *P. blainvillei* makes this species a particularly useful sentinel for regional contamination (Alonso et al., 2012a, 2012b). The Guiana dolphin (*Sotalia guianensis)* is another exclusively coastal species, ranging from south Brazil northward into Central America. This small delphinid inhabits shallow waters and is often found year-round in bays and estuaries (Batista et al., 2014). Studies have shown *S. guianensis* to reside in Guanabara and Sepetiba bays in Rio de Janeiro State, Brazil (de Freitas Azevedo et al., 2004; Flach et al., 2008). Their largely near-shore distribution render *S. guianensis* particularly vulnerable to impacts due to human activities, such as fishing by-catch and exposure to organohalogenated contaminants (Alonso et al., 2010; Dorneles et al., 2010; Lailson-Brito et al., 2010).

2.2. Sample collection

Fig. S1 (Supplementary Information) shows the coastal areas of Brazil where dolphins were sampled for this study. The southeast region of Brazil, where the states of São Paulo (SP) and Rio de Janeiro (RJ) are located, is one of the most developed areas of South America. The coastal ecosystems near these urban centers historically receive discharges of industrial, domestic and agricultural effluents that contain chemical contaminants (Buruaem et al., 2013), as reflected in residue analysis of biota (Lailson-Brito et al., 2012). In contrast, the land use and economy associated with Ceará state (CE), located in northeastern Brazil, specially where the samples where collected (C3 region, following Santos-Neto et al. (2014)), is based on agriculture, fishing and tourism and the population density is very low (44 hab./Km^2) (CEARA, 2014).

Tissue samples from five mother-fetus pairs of Franciscana dolphins from the São Paulo coast (Baixada Santista) in southeastern Brazil were collected, along with samples from three mother-fetus pairs of Guiana dolphins (two pairs from Sepetiba Bay, Rio de Janeiro coast and one pair from Canoa Quebrada Beach, Ceará coast) from 2004 to 2011 (Fig. S1). Pregnant female dolphins as by-catch were brought to research labs, where they were classified as carcasses in early decomposition stage. After dissection, biological samples were stored in aluminum foil and kept frozen (−20 °C) until processing for analysis. Total length of females and fetuses were measured and pregnancy stages were estimated assuming Franciscana dolphins average 10.2 months of gestation and length at birth is 72 cm (Bertozzi, 2009); for Guiana dolphins, gestation averages 11.4 months and length at birth is 106 cm (Ramos et al., 2000). Blubber and muscle from both mother and fetus were taken from both species. Maternal blubber (n = 7), fetal blubber (n = 5), maternal muscle (n = 4) and fetal muscle (n = 4), as well as umbilical cord (n = 3), placenta (n = 4) and milk (n = 3) from Franciscana dolphins; and maternal blubber (n = 3), fetal blubber (n = 3), maternal muscle (n = 3) and fetal muscle (n = 3) from Guiana dolphins.

2.3. Standards and reagents

A standard mixture of six PYRs containing cyfluthrin, cypermethrin, deltamethrin, fenvalerate, permethrin and tetramethrin, and single analytical standards of bifenthrin, lambda-cyhalothrin, esfenvalerate, tau-fluvalinate, tralomethrin. d_6-*trans*-permethrin and d_6-*trans*-cypermethrin, used as internal standard, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The certified UVF standards 4-methylbenzylidene camphor (4MBC), 2-ethylhexyl-4-trimethoxycinnamate (EHMC), 2-ethyl-hexyl-4-dimethyl-