Environmental Research 146 (2016) 263–273

Contents lists available at ScienceDirect

Environmental Research

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

# Contrasted accumulation patterns of persistent organic pollutants and mercury in sympatric tropical dolphins from the south-western Indian Ocean

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ARTICLE INFO

*Article history:*
Received 20 October 2015
Received in revised form
9 December 2015
Accepted 4 January 2016

*Keywords:*
POPs
Hg
stable isotopes
La Réunion
Stenella longirostris
Tursiops aduncus

ABSTRACT

Due to their high trophic position and long life span, small cetaceans are considered as suitable bioindicators to monitor the presence of contaminants in marine ecosystems. Here, we document the contamination with persistent organic pollutants (POPs) and total mercury (T-Hg) of spinner (*Stenella longirostris*, $n = 21$) and Indo-Pacific bottlenose dolphins (*Tursiops aduncus*, $n = 32$) sampled from the coastal waters of La Réunion (south-western Indian Ocean). In addition, seven co-occurring teleost fish species were sampled and analyzed as well. Blubber samples from living dolphins and muscle from teleosts were analyzed for polychlorinated biphenyls (PCBs), DDT and metabolites (DDTs), chlordanes (CHLs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and polybrominated diphenyl ethers (PBDEs). Methoxylated PBDEs (MeO-PBDEs), reported as having a natural origin, were also analyzed. T-Hg levels were measured in blubber and skin biopsies of the two dolphin species. Stable isotopes $\delta^{13}C$ and $\delta^{15}N$ values were determined in skin of the dolphins and in the muscle of teleosts. For PCBs, HCHs and T-Hg, concentrations were significantly higher in *T. aduncus* than in *S. longirostris*. For other POP levels, intra-species variability was high. MeO-PBDEs were the dominant compounds (55% of the total POPs) in *S. longirostris*, while PCBs dominated (50% contribution) in *T. aduncus*. Other contaminants showed similar profiles between the two species. Given the different patterns of POPs and T-Hg contamination and the $\delta^{15}N$ values observed among analyzed teleosts, dietary and foraging habitat preferences most likely explain the contrasted contaminant profiles observed in the two dolphin species. Levels of each class of contaminants were significantly higher in males than females. Despite their spatial and temporal overlap in the waters of La Réunion, *S. longirostris* and *T. aduncus* are differently exposed to contaminant accumulation.



## 1. Introduction

Due to their physicochemical properties and environmental behavior, Persistent Organic Pollutants (POPs) are one of the most intensively studied among the organohalogenated contaminants. Although POPs are regulated in many countries within the Stockholm Convention (www.pops.int), their resistance to degradation, persistence, and lipophilic properties facilitate their bioaccumulation and biomagnification in the environment. The marine environment is a global sink for legacy anthropogenic POPs, e.g. organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) (Dachs et al., 2002). Although structurally similar to metabolites of anthropogenic PBDEs, methoxylated analogs (MeO-PBDEs) are of biogenic origin (Teuten et al., 2005). Apart from POPs, mercury (Hg) pollution can also reach elevated concentrations worldwide including the open ocean (Hylander and Goodsite, 2006), although data on the oceanic distribution of Hg is limited (Sunderland et al., 2009; Savery et al., 2013; Fitzgerald et al., 2007). Mercury

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http://dx.doi.org/10.1016/j.envres.2016.01.006
0013-9351/

biomonitoring might be used as an indicator of foraging habitats and trophic position of large marine predators, because body burden concentrations are highly correlated to size/age, environmental parameters and geographic location (Power et al. 2002; Cai et al. 2007). Total Hg (T-Hg) levels in pelagic fishes increase with median depth of occurrence in the water column and mesopelagic habitats are probably major entry points of mercury into marine food webs as a result of increased methylation at these depths (Monteiro et al., 1996; Choy et al., 2009; Chouvelon et al., 2012). Marine top predators feeding on mesopelagic prey, such as large predatory fishes, exhibit significantly higher T-Hg concentrations than epipelagic predators (Thompson et al., 1998; Kojadinovic et al., 2006; Choy et al., 2009). As a consequence, depending on their habitat influenced by their feeding ecology and diet, this might have a significant impact on the T-Hg, but also on the exposure to POPs of marine mammals (Balmer et al., 2011; Shaul et al., 2015).

The accumulation of organic and inorganic contaminants in marine food chains represents an important stress factor for marine mammals since they can have significant negative effects on health and reproductive ability (Wells et al., 2005; Schwacke et al., 2011; Murphy et al., 2015). Cetaceans are particularly susceptible to POP accumulation in blubber (Ross et al., 2000; Pierce at al., 2008; Yordy et al., 2010; Ellisor et al., 2013), since these species have long lifespans, large fat deposits and occupy high trophic positions. The adverse health effects of POPs on marine mammals are difficult to assess, although some studies have shown that for such contaminants toxicity thresholds are commonly exceeded (Kannan et al., 2000; Jepson et al., 2005; García-Alvarez et al., 2014; Murphy et al., 2015). Consequently, marine mammals such as cetaceans are considered as good indicators of POP contamination in aquatic ecosystems (Dachs et al., 2002; Bachman et al., 2014).

Apart from sampling of stranded or bycaught animals, non-lethal remote biopsy sampling of skin and blubber has become a routine method for sampling free-ranging cetaceans with relatively limited behavioral impact (Best et al., 2005; Jefferson and Hung 2008; Kiszka et al., 2010). T-Hg measurements in skin reflected T-Hg in liver of small cetaceans and can provide valuable information on the status of Hg contamination, and even to inform on potential spatial variations (Aubail et al., 2013).

At least 10 species of cetaceans are regularly observed in the waters of La Réunion, in the south-western tropical Indian Ocean (Dulau-Drouot et al., 2008). Spinner (*Stenella longirostris*) and Indo-Pacific bottlenose dolphins (*Tursiops aduncus*) are the most common species found around the island year-round. Indo-Pacific bottlenose dolphins occur in shallow inshore waters (depth $< 80$ m) within 3 km of the coastline. Spinner dolphins have a wider depth range ($< 700$ m) and use the coastal and insular slope waters of the island during daylight hours, mainly to rest and socialize (Dulau-Drouot et al., 2008). At night, spinner dolphins feed upon mesopelagic organisms (primarily fish and squids) as deep as 400 m (Perrin et al., 1973; Dolar et al., 2003). Indo-Pacific bottlenose dolphins can feed on a range of small- and medium-sized inshore prey (Amir et al., 2005a). Some insular populations could be more specialized and feed on demersal and epipelagic predators (Kiszka et al., 2014).

The present study aimed to investigate anthropogenic POPs (OCPs, PCBs, and PBDEs), naturally-occurring MeO-PBDEs, and T-Hg concentrations in skin and blubber tissues of spinner and Indo-Pacific bottlenose dolphins around La Réunion. Given the differences reported in the foraging behavior of spinner (offshore mesopelagic prey) and Indo-Pacific bottlenose dolphins (coastal demersal prey), stable carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$ values) were used to investigate the effect of habitat preferences and diet on the bioaccumulation of these contaminants (Jardine et al., 2006).

## 2. Materials and methods

### 2.1. Study area

La Réunion (21°07′S, 55°32′E) is a French oceanic volcanic island located in the south-west Indian Ocean, 700 km east of Madagascar and 60 km west of Mauritius (Fig. 1). The island is relatively small, extending over 2512 $km^2$, and is characterized by a steep insular slope and fringing reef off the west coast. The island faces increasing human pressures and coastal development. Very little is known on POP and trace element contamination of marine ecosystems and species, including marine fauna. Studies on seabirds and pelagic fishes from oceanic islands, including La Réunion, suggest that mercury availability in the south-western Indian Ocean is relatively low compared to other regions (Kojadinovic et al., 2006, 2007a, 2007b).

### 2.2. Sample collection

In order to document POP and Hg loadings from the coastal waters of the La Réunion, skin and subcutaneous blubber biopsy samples were collected between 2010 and 2011 from both spinner ($n=21$) and Indo-Pacific bottlenose dolphins ($n=32$) (Fig. 1). A total of 62 boat-based surveys dedicated to biopsy sampling were conducted during the study period. Biopsies were collected by using a crossbow (BARNETT Veloci-Speed® Class, 150 lb draw weight) with Finn Larsen (Ceta-Dart, Copenhagen, Denmark) bolts and tips (dart 25-mm long, 7-mm-diameter). The dolphins are hit below the dorsal fin when sufficiently close (3–10 m) to the research boat. Samples were exclusively collected from adult or subadult individuals (based on body size). A maximum of $0.5 \times 1$ $cm^2$ of tissue was collected per individual biopsy. Samples were stored individually at $-20$ °C and transported in dry ice. Biopsy permit was delivered by the French Ministry for Environment in November 2009 (reference number MC/2009/336). Supplementary information on the sampling (geographical coordinates, sampling date and time, species sampled and gender) is presented in Tables SI.1 and SI.2 from Supporting Information. Additionally, seven fish species were sampled in the same area and during the same campaign as the dolphin biopsies; additional information is given in Supplementary Information file. For each species, one composite muscle sample was prepared.

### 2.3. Target analytes

All samples were analyzed for T-Hg and organic contaminants, as follows: polychlorinated biphenyls (PCBs) – 37 tri- to decachlorinated congeners (IUPAC numbers: CB 18, 31, 28, 52, 49, 44, 74, 70, 66, 95, 101, 99, 87, 110, 105, 118, 151, 149, 146, 153, 138, 128, 167, 156, 187, 183, 174, 177, 171, 172, 180, 170, 199, 196/203, 194, 206, and 209), Dichlorodiphenyl trichloroethane (DDT) and metabolites (*p,p′* DDT, *o,p′*-DDT, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD) discussed here as DDTs, chlordanes (*cis*-chlordane (CC), *trans*-chlordane (TC)) and metabolites (*oxy*-chlordane (OxC), *cis*-nonachlor (CN), *trans*-nonachlor (TN)) discussed in text as CHLs, hexachlorocyclohexanes ($\alpha$-, $\beta$-, and $\gamma$-HCH) discussed as HCHs, hexachlorobenzene (HCB), and polybrominated diphenyl ethers (PBDEs) – 7 tri- to hepta-BDE congeners (BDE 28, 47, 100, 99, 154, 153, and 183). Two most abundant naturally-occurring MeO-PBDEs (2′-MeO-BDE68 and 6-MeO-BDE47) were also targeted.