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Halogenated and organophosphorus flame retardants in cetaceans from the southwestern Indian Ocean

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HIGHLIGHTS

- PBDE levels in South African dolphins were as high as in more industrialised areas.
- HBCD, DBDPE, PBEB and HBB were rarely detected or at very low concentrations.
- Dec 602 was the only quantifiable dechlorane at 232 ± 549 ng g^{-1} lw.
- OPFR levels were one or two orders of magnitude higher than PBDE levels.
- Natural MeO-PBDEs, analogous to man-made PBDEs, showed outstanding levels.

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ABSTRACT

PBDEs, HBCD, DBDPE, PBEB and HBB, dechloranes and OPFRs, as well as natural MeO-PBDEs were monitored in muscle tissue of three dolphin species from the southwestern Indian Ocean (*Delphinus delphis*, *Sousa plumbea* and *Tursiops aduncus*) collected between 2012 and 2015. The mean PBDE concentration was 416 ± 333 ng g^{-1} lw. BDE-47 was found in all samples and was almost half the total PBDE contamination. BDE-209, BDE-100 and BDE-99 were present in ≥85% of the samples. HBCD was detected in just two samples at 20 and 330 ng g^{-1} lw. PBEB and HBB were not detected, while DBDPE was in all samples but always below its limit of quantification. Dec 602 was the only quantifiable dechlorane at 232 ± 549 ng g^{-1} lw. Mean OPFR concentration was 10452 ± 11301 ng g^{-1} lw. TBOEP was found in all samples making up most of the total OPFR contamination. MeO-PBDEs were detected in all samples at 114 ± 137 ng g^{-1} lw. Data on flame retardants in biota and environmental samples from the southwestern Indian Ocean are scarce and, as a result, comparisons are difficult. However, data from other marine predators in the region, such as penguins, suggest that further studies are needed to determine if these concentrations are the consequence of a high local contamination or widespread thoughout the Indian Ocean.

1. Introduction

Flame retardants (FRs) are compounds applied to all kind of materials, such as household appliances, office electronics, textiles and furniture, to prevent them from ignition. Polybrominated diphenyl ethers (PBDEs) are the most used FRs in a great variety of indoor and outdoor products (Alaee et al., 2003). Penta-BDE, Octa-BDE and Deca-BDE are PBDEs commercial mixtures produced at different levels of bromination. PBDEs leach out of materials since they are not covalently bonded with the polymers, but simply blended with them (Alaee et al., 2003). Hence, PBDEs have been found in all kinds of environmental matrices (Harner et al., 2006; Guerra et al., 2010; Sánchez-Avila et al., 2011; Gorga et al., 2013) and biological matrices (Norén and Meironyté, 2000; Lacorte et al., 2010; Guerra et al., 2012). PBDEs persist in the environment,

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bioaccumulate through the food chain and show toxicity on hormonal regulation, neuronal, thyroid and liver activity (Branchi et al., 2003; Mikula and Svobodova, 2006; Costa and Giordano, 2011).

The effects of FRs on human health and the environment have been a growing concern through time. In 2009, Penta-BDE and Octa-BDE were added to the Stockholm Convention on Persistent Organic Pollutants (POPs) (SC, 2008). There were a few exceptions for specific uses, and North America and Europe decided to reduce their presence in formulations and committed to stop producing them by 2013 (Schecter et al., 2010; EPA, 2014). Appart from their persistence, bioaccumulation and adverse effects, POPs also have potential for long-range transport. POPs are often halogenated and have high lipid solubility, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, which promotes air transportation before deposition far from their sources. The use of Penta-BDE, Octa-BDE and Deca-BDE has also been restricted or banned by several European directives and regulations (REACH, 2006; HSEEE, 2011; PSWP, 2013). After ten years included in the REACH regulation, Deca-BDE was also added to the Stockholm Convention in 2017.

Previously, in 2013 hexabromocyclododecane (HBCD), a FR already included in the REACH regulation, had also been added to the Stockholm Convention (REACH, 2006; SC, 2008). Like PBDEs, HBCD is likely to leach out of the materials and can be transported long distances (Alaee et al., 2003; de Wit et al., 2006). HBCD is very toxic to aquatic organisms and neuroendocrine and developmental toxicity has been observed in humans (SC, 2008). It has been detected in environmental and biotic samples (Eljarrat et al., 2004, 2009).

Novel FRs act as substitutes for the banned compounds due to their health and environmental concerns (Betts, 2008). Some of them are decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB). DBDPE is the marketed alternative to Deca-BDE as their structures are similar; therefore their properties are also expected to be (Hardy et al., 2002). With a production peak in the 1970s, PBEB persists in environmental matrices and bioaccumulates (Covaci et al., 2011). Japan and China are the main producers of HBB (Cruz et al., 2015). Additionally, Dechlorane Plus (DP) and dechloranes 602, 603 and 604 (Dec 602, Dec 603, Dec 604) are chlorinated alternatives to mirex, which was banned in the United States of America due to its toxicity. Research groups around the world are currently studying novel FRs to assess their behaviour and occurrence in the environment. Brominated novel FRs have been found in environmental matrices and biota (Zhu et al., 2014; Barón et al., 2015b; Aznar-Alemany et al., 2017; Giulivo et al., 2017) and so have dechloranes (Hong et al., 2010; Torre et al., 2010; Guerra et al., 2011; Houde et al., 2014).

A growing alternative to halogenated flame retardants (HFRs), are organophosphorus flame retardants (OPFRs). They comprised 20% of the amount of FRs used in 2006 in Europe —doubling the amount of brominated FRs used that year— and the ban on PBDEs increased their popularity (Van der Veen and de Boer, 2012). OPFRs are also released from materials and access environmental matrices through washout, infiltration, deposition, etc. (Andresen et al., 2004; Schreder and La Guardia, 2014). Moreover, OPFRs are used as plasticisers that can leak from the tones of plastic that reach seas and oceans. Their presence has been reported in sediments, water and fish (Chung and Ding, 2009; Gao et al., 2014; Giulivo et al., 2016). OPFRs show toxic effects on the reproductive and endocrine systems, as well as systemic and carcinogenic effects (Van der Veen and de Boer, 2012; Hou et al., 2016).

Finally, methoxylated PBDEs (MeO-PBDEs) are natural analogs to PBDEs that are synthesized by some marine sponges, algae and their associated cyanobacteria (Malmvarn et al., 2008). They have been found in cetaceans and seafood (Losada et al., 2009; Alonso et al., 2014; Aznar-Alemany et al., 2017). MeO-PBDEs can be detected in marine mammals at similar levels to manufactured halogenated organic compounds (Vetter et al., 2002; Vetter, 2006).

The present article assesses the occurrence of the aforementioned compounds in three species of dolphin from the Indian Ocean; the long-beaked common dolphin (*Delphinus delphis*), Indian Ocean humpback dolphin (*Sousa plumbea*) and the Indo-Pacific bottlenose dolphin (*Tursiops aduncus*). This study also provides data about FRs in marine mammals from a region with little data published about these contaminants in environmental samples and little to none in biota.

2. Materials and methods

2.1. Sampling

Thirteen muscle samples of three species of dolphin were collected from individuals accidently caught in shark nets of KwaZulu-Natal (east-coast South Africa), in the Indian Ocean (Fig. 1), between 2012 and 2015. The samples included two individuals of long-beaked common dolphin, five individuals of Indian Ocean humpback dolphin and six individuals of Indo-Pacific bottlenose dolphin. For brevity purposes in this article, the species will be referred to as simply common dolphin, humpback dolphin and bottlenose dolphin. The samples contained individuals of different age groups. Age groups were assigned according to the size of the dolphins (Cockcroft and Ross, 1990; Best, 2007; Plön et al., 2015). Samples were freeze-dried prior to shipping to the analytical laboratory. Lipid content referenced to dry weight (dw) was between 0.65 and 11.7%. See Table 1 for details.

2.2. Standards and reagents

Native and ^{13}C-labelled standard mixtures of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209); *syn*-DP, *anti*-DP and ^{13}C-*syn*-DP; α-, β- and γ-HBCD and their deuterated congeners were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Dec 602 (95%), Dec

Fig. 1. Sample location for the present study and other studies discussed.

Table 1
Sampling data.

species	gender	size (cm)	age group	year	fat (%) from dry weight
Long-beaked common dolphin (*Delphinus delphis*)	female	222	adult	2012	1.04
	male	239	adult	2012	2.19
Indian Ocean humpback dolphin (*Sousa plumbea*)	female	125	new-born	2015	4.53
	male	183	juvenile	2014	1.60
		214	juvenile	2014	1.68
		245	adult	2013	0.74
		249	adult	2015	11.7
Indo-Pacific bottlenose dolphin (*Tursiops aduncus*)	female	146	calf	2013	8.97
		154	juvenile	2014	8.50
		205	juvenile	2014	1.48
	male	180	juvenile	2014	0.65
		224	juvenile	2014	2.26
		248	adult	2014	1.74

603 (98%) and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). HBB, DBDPE, PBEB and the standard mixture of MeO-PBDEs (5-MeO-BDE-47, 6-MeO-BDE-47, 4′-MeO-BDE-49, 2′-MeO-BDE-68, 5′-MeO-BDE-99, 5′-MeO-BDE-100, 4′-MeO-BDE-101 and 4′-MeO-BDE-103) were bought from Wellington Laboratories Inc. (Guelph, ON, Canada). Tris(2-butoxyethyl) phosphate (TBOEP), tris(chloroethyl) phosphate (TCEP), tris(chloroisopropyl) phosphate (TCIPP), trihexyl phosphate (THP) and tris(2-ethylhexyl) phosphate (TEHP) were purchased from Santa Cruz Biotechnology (SantaCruz, CA, USA). Isodecyldiphenyl phosphate (IDPP) and 2-ethylhexyldiphenyl phosphate (EHDPP) were purchased from AccuStandard (New Haven, CT, USA). Diphenylcresyl phosphate (DCP), tri-*n*-butyl phosphate (TNBP), triphenyl phosphate (TPHP), triphenylphosphine oxide (TPPO) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tricresyl phosphate (TMCP) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Isopropyl phenyl phosphate (IPPP) was purchased from Chiron (Trondheim, Norway). Labelled d_{15}-TDCPP, d_{27}-TNBP, d_{12}-TCEP and $^{13}C_2$-TBOEP were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Labelled d_{15}-TPHP was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Dichloromethane (DCM), methanol and sulphuric acid were purchased from Merck (Darmstadt, Germany). Acetone and hexane for organic trace analysis were purchased from J.T. Baker (Center Valley, PA, USA).

2.3. Sample preparation

The extraction of OPFRs was carried out by ultrasound assisted extraction according to an existing method (Giulivo et al., 2016). Freeze-dried muscle tissue (0.5 g dw) was extracted twice by sonication with hexane:acetone (1:1 v/v). The combined extract was reconstituted in 5 ml of hexane:methanol (1:3 v/v). The solution was centrifuged and an aliquot of 200 μl was used for the instrumental analysis. Labelled OPFR standards were added prior to analysis by turbulent flow chromatography-(TFC)-LC-MS/MS.

For all the other FRs, sample extraction was carried out with a different existing method (de la Cal et al., 2003; Labandeira et al., 2007). Freeze-dried sample (1.5 g dw) was spiked with the ^{13}C-labelled standards. Pressurized liquid extraction (PLE) was used with a mixture of hexane:DCM (1:1 v/v). Afterwards, the lipid content was determined gravimetrically and the extract was redissolved in hexane and treated with concentrated sulphuric acid to remove the fat. Then, the organic phase was cleaned by solid phase extraction (SPE) using Al–N cartridges (5 g) and eluted with hexane:DCM (1:2 v/v). The extract was reconstituted with 40 μl of toluene prior to the instrumental analysis.

2.4. Instrumental analysis

For OPFRs, online sample purification and analysis was performed with a Thermo Scientific TurboFlow™ system (Giulivo et al., 2016). CycloneTM-P (0.5 × 50 mm) and C18-XL (0.5 × 50 mm) columns were used in combination for purification. Chromatographic separation was achieved with an analytical column Purosphere Star RP-18 (125 mm × 0.2 mm). Mobile phase was a gradient of water (0.1% formic acid) and methanol (ammonium acetate) at 0.75 ml min^{-1}. Spectrometric analysis was performed with a triple quadrupole with a heated-electrospray ionization source. LC flow rate was 5 μl min^{-1}, ion transfer tube temperature was 320 °C and vaporizer temperature was 50 °C. For all compounds, selective reaction monitoring (SRM) mode was used with two transitions monitored for each one. Recoveries for individual compounds ranged 47–98% and RSDs were 2.4–16%. LOQs and LODs were, respectively, 0.97–24.8 ng g^{-1} lipid weight (lw) and 0.19–19.3 ng g^{-1} lw.

PBDEs, MeO-PBDEs, HBB, DBDPE and PBEB were analysed with an Agilent 7890A gas chromatograph coupled to an Agilent 7000B triple quadrupole mass spectrometer (Eljarrat et al., 2002, 2007). Chromatographic separation was carried out with a DB-5ms column (15 m × 0.25 mm × 0.1 μm of film thickness). For the spectrometric determination (Barón et al., 2014), electronic ionization at 300 °C was used, with helium as carrier gas. BDE-209 and DBDPE were analysed with the same chromatographic conditions and the same column as PBDEs using an Agilent 5975A mass spectrometer because of better sensibility. For the spectrometric determination (Eljarrat et al., 2004), negative chemical ionization at 250 °C was used. For the analysis of dechloranes (Barón et al., 2012), the same column and negative chemical ionization at 175 °C was used, with methane as ionization gas and helium as carrier gas. SRM mode was used for all compounds, except for BDE-209 and DBDPE, analysed using selected ion monitoring (SIM). Recoveries for individual compounds ranged from 51 to 99% and RSDs were 1.1–22%. LOQs and LODs were, respectively, 7.7 pg g^{-1} lw to 35.4 ng g^{-1} lw and 2.3 pg g^{-1} lw to 10.6 ng g^{-1} lw.

After analysis of the previous HFRs, extracts were redissolved in methanol and 1 ng of d_{18}-HBCD was added. HBCD was analysed using an Agilent HP 1100 binary pump LC system coupled to a hybrid triple quadrupole/linear ion trap 4000QTRAP (Guerra et al., 2008). Recoveries for α-, β- and γ-HBCD ranged 85–105% and RSDs were 3.1–8.3%. LOQs and LODs were, respectively, 0.4–4.4 ng g^{-1} lw and 0.2–2.0 ng g^{-1} lw.

2.5. Data analysis

A t-test was used for the statistical analysis taking $p < 0.05$ as the

criterion for statistical difference. In box plots figures, outliers (×) were calculated as values above Q3 + 1.5 IQR and below Q1 − 1.5 IQR (Q3 = third quartile, IQR = interquartile range, Q1 = first quartile). For all means and standard deviations (SD), concentrations below LOQ were given the LOD value and concentrations below LOD were considered to be 10% of the LOD.

To compare the proportional compositions or *fingerprints* of the different species, sexes, and age classes, we used multivariate ordinations (non-metric multidimensional scaling (NMS), with Sørensen as distance measure) using PC-Ord version 6.20 (MjM Software Design, www.pcord.com). Concentration data were relativized per sample to compensate for the large differences in concentrations. Of the 18 compounds analysed, we eliminated those compounds with less than three quantifiable values; 12 remained. A maximum of six axes were allowed, random starting conditions, 200 maximum number of iterations, 50 runs with real data followed by 50 runs with randomised data, the latter to stress-test the final ordination. Convex hulls were drawn on the same ordination for species, sex and age class. Final stress of less than five gives an excellent representation of the relationships between samples (McCune and Grace, 2002).

3. Results and discussion

FRs concentrations in muscle of Indian Ocean dolphins are summarized in Table 2 (for individual compound results see *Supplementary information*). Results are expressed in ng g^{-1} lw. FRs were detected in all samples. PBDEs and OPFRs were detected in all samples ranging from 33.3 to 1309 ng g^{-1} lw and from 1630 to 31861 ng g^{-1} lw, respectively. HBCD was detected in just two samples at 20 and 330 ng g^{-1} lw. DBDPE was detected in all samples, but always below its LOQ (0.26 ng g^{-1} lw). The novel FRs PBEB and HBB were not detected in any sample (<0.2 ng g^{-1} lw). Dechloranes were present in 84.6% of the samples. However, Dec 602 was the only quantifiable congener at concentrations from 58.0 to 2034 ng g^{-1} lw in 69.2% of the samples. One sample contained Dec 603 and *anti*-DP, and two other samples contained *anti*-DP too, both compounds always below their LOQs (0.02 and 0.01 ng g^{-1} lw). MeO-PBDEs were quantifiable in all the samples with a mean concentration of 114 ± 137 ng g^{-1} lw.

3.1. Legacy HFRs

Mean PBDE concentration was 416 ± 333 ng g^{-1} lw (Table 2). BDE-47 was found in all samples and was almost half the total PBDE contamination (42 ± 16%). BDE-209, BDE-100 and BDE-99 were present in 100, 92 and 85% of the samples, respectively, representing an average 20, 9 and 19% of the PBDE contamination. BDE-183 was not detected.

Published data about FRs in dolphins from the Indian Ocean is very scarce. Comparisons should be made with caution since different factors such as species analysed, sampling period or tissue studied, can affect the levels of contamination. Total PBDEs in blubber of Indo-Pacific humpback dolphin (*Sousa chinensis*, 1992) and Irrawaddy dolphin (*Orcaella brevirostris*, 2000–2001) from India were always below 20 ng g^{-1} lw (Kannan et al., 2005; Kajiwara et al., 2006). One would expect PBDE levels on the Asian coast to be higher than on the African coast, but counterintuitively, these levels were much lower than the ones we obtained in the present study. Similarities could be found, though, as BDE-47, BDE-99 and BDE-100 were detected in all the samples and accounted for 66, 16 and 9% of the total PBDE contamination. BDE-209 was not analysed by Kannan et al. (2005) and Kajiwara et al. (2006). However, our results were lower than those obtained in blubber of Indo-Pacific humpback dolphin (*Sousa chinensis*, 1997–2001) from Hong Kong, which ranged from 280 to 6000 ng g^{-1} lw (Kajiwara et al., 2006). Some studies from the last two decades on different dolphin species showed mean concentrations values between 420 and 880 ng g^{-1} lw in Europe, with the highest values at 2340 ng g^{-1} lw (Barón et al., 2015a, 2015b) and of 166 ng g^{-1} lw in Brasil, ranging from 6 to 1800 ng g^{-1} lw (Alonso et al., 2012). These results seem to be similar to the ones of the present study.

Looking at the admittedly limited sample size from South Africa, sewage sludge and effluent samples of a wastewater treatment plant in Cape Town (west South Africa) showed levels of the same sum of congeners of 400 ± 490 ng g^{-1} dw and 5100 ± 6900 ng l^{-1}, respectively, with BDE-47 and BDE-209 as the main contributors (Daso et al., 2012). Sludge from wastewater treatment plants from

Table 2
Concentration of contaminants (ng g^{-1} lw).

species	gender	age group	∑PBDEs[a]	HBCD	DBDPE[b]	Dec 602[c]	∑MeO-PBDEs[d]	∑OPFRs[e]
Delphinus delphis	female	adult	97.7	< LOD	< LOQ	150	52.4	1961
	male	adult	165	< LOD	< LOQ	< LOQ	112	2030
Sousa plumbea	female	new-born	494	< LOD	< LOQ	58.0	37.6	1630
	male	juvenile	244	< LOD	< LOQ	127	64.0	3965
		juvenile	573	20.7	< LOQ	321	220	25239
		adult	667	< LOD	< LOQ	< LOQ	132	14212
		adult	33.3	< LOD	< LOQ	49.1	23.1	3449
Tursiops aduncus	female	calf	563	< LOD	< LOQ	81.8	76.8	3772
		juvenile	382	330	< LOQ	132	529	3083
		juvenile	264	< LOD	< LOQ	< LOD	65.3	31861
	male	juvenile	1309	< LOD	< LOQ	2034	1.50	30595
		juvenile	189	< LOD	< LOQ	< LOD	51.3	7951
		adult	424	< LOD	< LOQ	59.5	123	6131
		LOD	0.04	0.20	0.08	0.02	0.43	0.19
		LOQ	0.12	0.40	0.26	0.07	1.42	1.03
frequency of detection (%)			100	15.4	100	69.2	100	100

[a] BDE-183 was not detected (BDE-183 < 6.24 ng g^{-1} lw).
[b] The other novel brominated FRs were not detected (PBEB, HBB < 0.2 ng g^{-1} lw).
[c] The other dechloranes were mostly not detected (<0.002–0.007 ng g^{-1} lw).
[d] 5-MBDE-47, 4-MBDE-99, 4-MBDE-100, 5-MBDE-99 and 4-MBDE-101 were not detected (<0.43–3.75 ng g^{-1} lw).
[e] THP, TCEP, TCIPP, DCP and IDPP were not detected (<0.88–2.96 ng g^{-1} lw).

26 cities in China were reported to have a mean of 94 ng g^{-1} dw (5.1–1115 ng g^{-1} dw), including five PBDE congeners more (Wang et al., 2007). On the other hand, sediments and leachate from Gauteng (Fig. 1), closer to KwaZulu-Natal, showed maximum PBDE concentrations of 114 ng g^{-1} dw and 3.7 ng l^{-1} (Olukunle et al., 2015). Eggs of African penguin (*Spheniscus demersus*) from Robben Island (Cape Town, n = 10) collected during the same period as the present samples had a mean PBDE concentration (including BDE-209) of 15 ng g^{-1} lw (between 1.8 and 120 ng g^{-1} lw), and eggs from Bird Island (Port Elizabeth, n = 10) had a mean (including BDE-209) of 3.8 ng g^{-1} lw (ranging between 3.5 and 7.2 ng g^{-1} lw) (Bouwman et al., 2015). Both dolphins and penguins are predators consuming similar prey, such as sardine and squid. Penguins are, however, more restricted in their feeding ranges than dolphins. The 'fingerprints' of the two breeding populations of penguin (Robben Island and Bird Island) based on POPs showed distinct differences. The overlap of the dolphin convex hulls (section 3.5 of this article) probably indicates much greater feeding ranges.

In short, a lack of published information on PBDEs in South Africa makes it hard to comment on the high levels in the present study. However, some of the available data on environmental samples show high levels, suggesting high environmental contamination in the area, which would explain the results from the present study.

Possible explanations for high levels of HFRs would be atmospheric transportation, air-water exchange, deposition and exposure (direct or indirect) to plastics (Bouwman et al., 2015). Asia has been reported as a source of marine pollution for HFRs with a stress on BDE-209 and the shift to alternative FRs (Möller et al., 2011). Another reason could be the city of Durban as a local source. PBDE levels in dust collected in Durban in 2012 and 2013 reached concentrations of 27.5 ng g^{-1} in e-waste recycling sites samples and of 11.8 ng g^{-1} in automobile samples (Abafe and Martincigh, 2015, 2016).

HBCD was detected in just two juvenile dolphins; α-HBCD in a female humpback dolphin (20.7 ng g^{-1} lw) and β- and γ-HBCD in a male bottlenose dolphin (173 and 158 ng g^{-1} lw). HBCD was quantifiable in only one African penguin egg from Robben Island (0.15 ng g^{-1} lw) and in seven eggs from Bird Island (mean 0.12 ng g^{-1} lw, ranging between 0.10 and 0.13 ng g^{-1} lw) (Bouwman et al., 2015). The difference of three orders of magnitude in concentrations between dolphins and penguins suggests trophic differences, differences in prey size with larger prey presumably having larger amounts of accumulated pollutants or that dolphins (mammal) and penguins (bird) accumulate and metabolize POPs differently.

3.2. Emerging HFRs

PBEB and HBB were not detected, while DBDPE was in all samples but always below its LOQ, 0.26 ng g^{-1} lw. As DBDPE is the marketed alternative to Deca-BDE (which consists in 97–98% of BDE-209), it seems logical to detect the presence of DBDPE in modern samples where BDE-209 accounts for 20% of the total PBDEs. This percentage of BDE-209 is quite high for biota samples, suggesting a previous abundant usage of Deca-BDE, which would have been replaced by the usage of DBDPE, hence its presence in these samples.

Dec 602 was the only quantifiable dechlorane at 232 ± 549 ng g^{-1} lw. Dec 602 has a higher bioaccumulation potential than other dechloranes (Shen et al., 2011). Dec 603 was detected in one adult common dolphin and anti-DP was found in both adult common dolphins and an adult humpback dolphin, both compounds below their LOQ. It must be noted, however, that other species of dolphins from the Mediterranean Sea had total dechloranes levels in blubber below 60 ng g^{-1} lw (Barón et al., 2015a).

3.3. Organophosphorus flame retardants

The mean OPFR concentration was 10452 ± 11301 ng g^{-1} lw. TBOEP was found in all samples making 82 ± 28% of the total OPFR contamination. TPPO and TDCPP were detected in 53.8% of the samples. TDCPP was always below 1.03 ng g^{-1} lw, while TPPO mean concentration was 27.6 ± 45.9 ng g^{-1} lw. IPPP, TEHP, TNBP, EHDPP and TMCP were detected in one to three samples at concentrations up to 1749 ng g^{-1} lw; except for IPPP and TEHP in a juvenile male bottlenose dolphin with 17591 and 5581 ng g^{-1} lw, respectively. Published works on OPFR levels in biota are scarce, and even more for marine mammals. A study from 2012 on blubber and liver of harbour porpoises from the United Kingdom also found TBOEP to be present at higher concentrations than the other OPFRs included in our study (Papachlimitzou et al., 2015). Their highest concentration was 205 ng g^{-1} ww in blubber. Assuming an approximate 80% of water content and a 5% of lipid from dw (based on data from 42 Mediterranean dolphins from a different study), that would translate to 20500 ng g^{-1} lw, in line with our highest values 23489 and 31841 ng g^{-1} lw. A study including seals (blubber and plasma), Artic foxes (liver) and polar bears (plasma) from Norway showed concentrations below 10 ng g^{-1} ww for most OPFRs (Hallanger et al., 2015). Conversely, TCIPP reached 372 ng g^{-1} ww in seal plasma and TBOEP reached 590 ng g^{-1} ww in seal blubber and 2198 ng g^{-1} ww in fox liver. In our study, TCIPP was never detected and the conversion of the maximum TBOEP values in seal blubber and fox liver would clearly exceed our results. On the other hand, a different study on polar bear fat and ringed seal blubber from East Greenland found concentrations of individual OPFRs mostly below limits of quantification (Strobel et al., 2018). For both species TPHP showed the highest levels (up to 7.2 ng g^{-1} ww), while TPHP was only detected in two of our samples. Our results are in the same order of magnitude as other studies in mammals, except for the study from East Greenland, where the impact of human activity might be weaker.

A recent work (Sala et al., 2019) carried out by our group reported OPFRs in common dolphin (*Delphinus delphis*) samples from the Alboran Sea, western Mediterranean Sea (2004–2010). OPFR concentrations in muscle tissue ranged between 69.5 and 2939 ng g^{-1} lw, with a mean value of 994 ng g^{-1} lw. These values were one order of magnitude lower than those obtained in the present study (mean value of 10452 ng g^{-1} lw).

It is important to note that OPFRs were at concentrations clearly higher than dechloranes (t-test $t = 3.07$, df = 22, $p < 0.05$) and even PBDEs ($t = 2.97$, df = 22, $p < 0.05$). Higher bioaccumulation potential of HFRs versus OPFRs has been described (Giulivo et al., 2017), as well as limited OPFR biomagnification through the food web (Hallanger et al., 2015) probably due to biotransformation processes (Strobel et al., 2018). This would suggest that OPFR levels in dolphins, belonging to a high trophic level, should be lower than those of HFRs. Therefore, the present results might indicate a greater input of OPFRs to the environment, arguably as a result of OPFRs not being used only as FRs but also as plasticisers. This draws the attention to further monitoring of these compounds.

The present study was conducted with individuals that were accidently caught in shark nets. Thus, the number of samples, the species, the sex and the maturity stage of the dolphins were impossible to control. POPs levels should show a characteristic trend during the lifetime of the dolphins, with males showing increasing levels with age, as POPs are bioaccumulated. Females should show a decrease after giving birth due to the mother-to-calf

transfer.

With the present samples, no differences among age groups could be assessed statistically for any family of compounds, except for OPFRs (Fig. 2). Female adult dolphins were excluded in case they had reproduced and transferred their contamination to their calves.

As seen in Fig. 2, OPFRs showed an increase between calves and juveniles ($t = 2.56$, df = 6, $p < 0.05$), but there was no increase from juveniles to adults ($t = 1.73$, df = 8, $p > 0.1$). Some congeners (e.g. TBOEP, TCIPP, TDCPP, TPHP) can be metabolised and they would not follow the POP increasing pattern with age, but their levels could stabilise or decrease in male individuals (Van den Eede et al., 2013; Greaves et al., 2016). TBOEP accounted for 82 ± 28% of the total OPFR contamination, greatly influencing this pattern. The increase in OPFR concentrations from calves to juveniles that did not occur from juveniles to adults hints at the metabolic transformation of this congener after reaching maturity.

3.4. Natural compounds

MeO-PBDEs showed in all the samples with a mean concentration of 114 ± 137 ng g^{-1} lw. These levels are similar to those found in other dolphin species from Tanzania (65 ± 43 ng g^{-1} lw), in the same region of the Indian Ocean (Rayne et al., 2004; Mwevura et al., 2010). There are reports of MeO-PBDEs in delphinids from more distant regions, like the Mediterranean Sea (Barón et al., 2015a, 2015b) or Brazil (Alonso et al., 2012). In agreement with the most occurring congeners in those studies, 6-MBDE-47 and 2-MBDE-68 were detected in 92.3% of our samples. Additionally, 5-MBDE-100 was found in 69.2% of them. Levels reported in blubber of the Mediterranean delphinids were up to 2506 ng g^{-1} lw and in liver of Franciscana dolphin from Brazil, mostly up to 3939 ng g^{-1} lw. Contrary to what happened with the relative contribution of the congeners, the levels of contamination in those more distant regions are quite different. MeO-PBDEs were present in the dolphins from this study in the same order of magnitude as the FRs, including the analogous PBDEs. Sharing levels with a POP of similar structure and properties is a good reason to consider these natural compounds in routine monitoring. While compounds of natural origin cannot be controlled by regulation, it is important to take into account that MeO-PBDEs' effects on marine biota could add to PBDEs' effects. High levels of the natural compounds could make a case for a tougher legislation on the analogous anthropogenic contaminants in order to keep the balance.

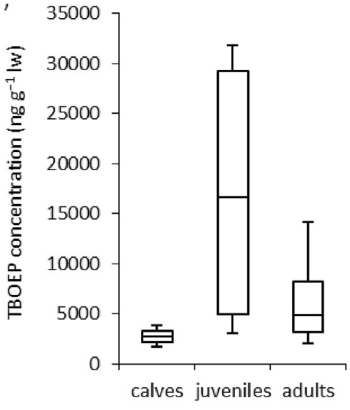

Fig. 2. Box plots of TBOEP concentrations for all maturity stages. Adults include only males.

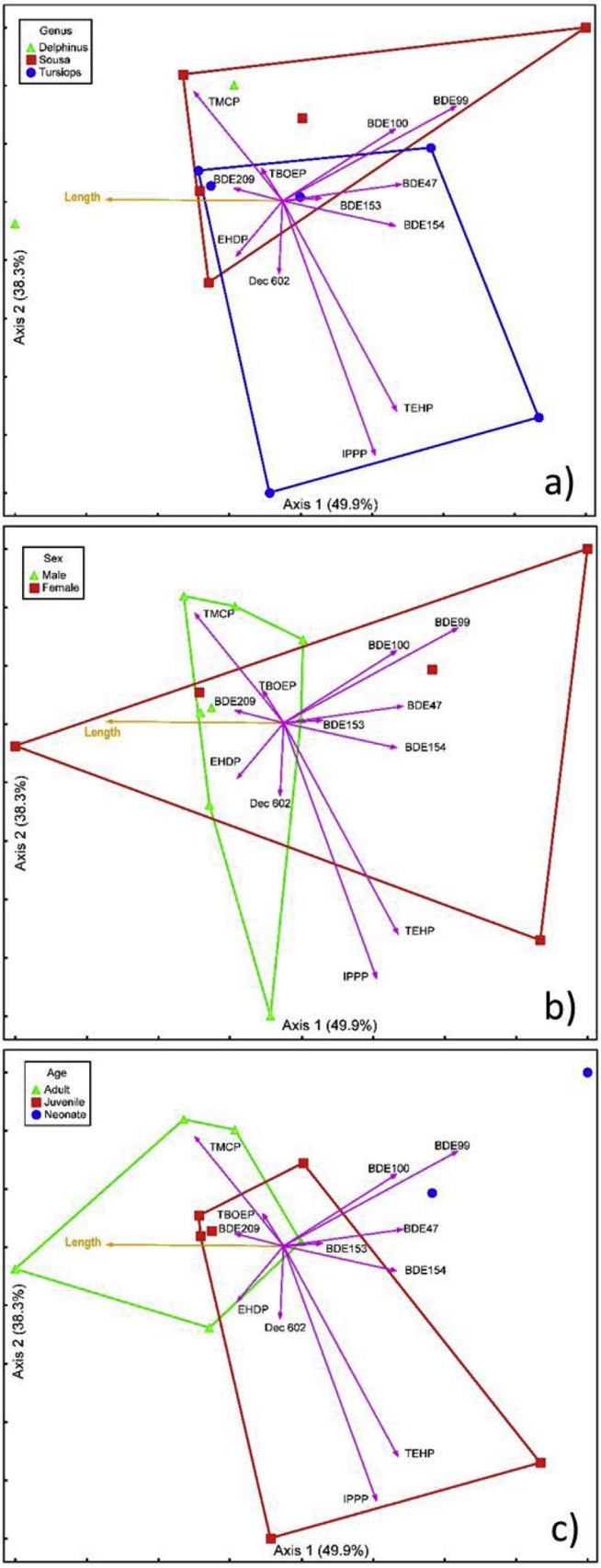

Fig. 3. NMS ordination for species, sex and age group.

3.5. Ordination of proportional composition

To compare the proportional compositions or *fingerprints* of the different species, sexes, and age classes, we used multivariate ordinations (see 2.5. Data analysis). Although the number of individuals was limited, this analysis serves as a preliminary assessment of similarities or differences among the mentioned groups.

The NMS ordination required three axes, with axis 1 explaining 59.9% of the variation, axis 2 explained 49.9% and axis 3, 38.3%, for a cumulative explanation of 88.2%. Axes 1 and 2 are represented in Fig. 3. The closer each sample point is to another, the more commonality in relative composition. The final instability was 0.647, indicating an excellent representation. The final stress was 0.00000, reached after 77 iterations, with no improvement in stress versus iteration after 48 iterations. The convex hulls of the species overlapped (common dolphin had only two samples, so no convex hull drawn) indicating no differences in proportional composition of the compounds in the samples, relative to species (Fig. 3a). Similarly, there was no differences between sexes (Fig. 3b), nor for the age classes, except for the two neonate samples (Fig. 3c).

The low stress value indicates that the ordination is an excellent representation of the relative positions or *fingerprints* of each sample (Fig. 3). Neither species (Fig. 3a) nor sex (Fig. 3b) showed any differences, as the convex hulls overlapped. This may indicate similar exposures to the compounds, possibly through shared or similar prey. The two neonates (the blue dots in Fig. 3c) did show some separation from the older age classes, strongly associated with higher relative proportions of BDE-99 and BDE-100.

IPPP, TEHP and Dec 602 ordinated perpendicularly to PBDEs and opposite to TBOEP. This suggests three different sources of the compounds from the prey that is consumed.

4. Synthesis and conclusions

PBDEs and dechloranes (only Dec 602) were found in dolphins from the eastern coast of South Africa at levels as high as in more industrialised areas, such as Europe. BDE-47, as well as BDE-209, BDE-100 and BDE-99, dominated the PBDE profiles.

DBDPE was the only brominated alternative FR detected in the samples, but always below its LOQ. HBCD was detected in just two samples. Mean OPFR concentration was 10452 ± 11301 ng g^{-1} lw, with TBOEP as the main contributor. These concentrations were one or two orders of magnitude higher than PBDE concentrations. This highlights the need for further monitoring of OPFRs. Additionally, adult dolphins might be metabolising TBOEP successfully as the bioaccumulation trend from calves to juveniles seemed to stop in the adult age.

Finally, the natural MeO-PBDEs showed outstanding levels for a compound that is analogue to a family of POPs.

Reports about FRs in biota and environmental samples from South Africa and the Indian Ocean are scarce. This region should be further studied to see if these levels are the consequence of a high local contamination, if they are an isolated case influenced by the small number of samples or the variations between individuals, if bioaccumulation occurs, and if these compounds contribute towards population declines.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.03.165.

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