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PBDE levels in franciscana dolphin (*Pontoporia blainvillei*): Temporal trend and geographical comparison

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HIGHLIGHTS

- PBDEs levels appears to be increasing in Franciscana dolphin from Southern Brazil
- Franciscana dolphin from SE showed higher levels than those from S Brazil
- PBDEs pattern were BDE 47 > BDE 99 > BDE 100

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ABSTRACT

Total PBDE concentrations determined in archived blubber samples from franciscana dolphins (*Pontoporia blainvillei*) unintentionally captured in the Brazilian coastal region off Rio Grande do Sul State (FMA III) between 1994 and 2004 (n = 73) ranged from 7.9 to 65 ng g^{-1} lipid weight in mature males, with an increase over the ten-year period. Total PBDE concentrations in blubber samples collected from the FAM II (n = 41) between 2002 and 2005 were higher (67.8 to 763.7 ng g^{-1} lw) than those from FMA III. This is possibly due to the proximity to important industrial development sites in the state of São Paulo. Despite the differences in total concentrations, PBDE profiles were comparable and the PBDE concentrations decreased in the following order BDE 47 > BDE99 > BDE 100 for both FMA and for males and females as well as adults, juveniles and pups.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are synthetic organic compounds used extensively as additive flame retardants in a wide variety of consumer products, such as plastics, textiles and electronic appliances (computers, televisions, fax machines, etc.) (de Wit, 2002). PBDEs are structurally similar to PCBs and DDTs with comparable chemical properties, persistence and environmental distribution (de Wit, 2002). While levels of organochlorines in different environmental matrices have demonstrated declining trends due to the ban on their use and production, a number of temporal trend studies indicate a continuous increase in PBDEs (Ikonomou et al., 2002; Akutsu et al., 2003; Ramu et al., 2006; Vorkamp et al., 2008) and others indicate a decrease (Kajiwara et al. (2004), Sellstrom et al. (2003)). Like organochlorines, PBDEs biomagnificate through the food chain and end up at high concentrations in top predators. Therefore, marine mammals are among the most vulnerable organisms to the long-term toxic effects of these compounds.

The franciscana dolphin (*Pontoporia blainvillei*), also known as the La Plata dolphin, is a small cetacean that inhabits shallow coastal and estuarine waters in tropical to temperate regions of the western South Atlantic Ocean from central Brazil to central Argentina. The existence of four Franciscana Management Areas (FMA I to IV) was proposted by Secchi et al. (2003) and it is used here to separate the samples. The FMA II referred to franciscana dolphins inhabiting northward of the state of Santa Catarina to the border between the states of São Paulo and Rio de Janeiro, in Brazil and the FMA III to those occurring in Rio Grande do Sul state (southern Brazil) and Uruguay. Due to its coastal/estuarine habits, the franciscana dolphin is particularly vulnerable to human activities (Secchi 2010) and is found in close proximity to

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pollution point sources. The International Union for Conservation of Nature and Natural Resources lists the species as "vulnerable" (Reeves et al., 2008).

The variety of contaminants in biota depends on transport rates, sources and contaminant inputs as well as absorption, distribution, metabolism and excretion processes acting on chemical, thus pollutant profiles can be used to differentiate populations of marine mammals (Aguilar, 1987). It may, therefore, be expected that franciscana dolphins from the two different FMAs exhibit different PBDE profiles and concentrations.

The primary objective of the present study was to assess temporal trends in PBDE concentrations in franciscana dolphins collected during 10 years (1994–2004) from FAM III area. In addition, differences in PBDEs levels between two management stocks (FMA III and FMA II) were also studied.

2. Materials and methods

2.1. Samples

Blubber samples were obtained from 73 and 41 franciscana dolphins accidentally captured by gillnet fisheries operating in the coastal waters of Rio Grande do Sul state (FMA III) (1994 to 2004) and São Paulo state (FMA II) (2002 to 2005) of Brazil, respectively (Fig. 1).

2.2. Age estimation

For estimating the age of the analyzed individuals of FMA III, teeth were extracted from the center of the left lower jaw and processed according to standard procedures established for franciscana dolphin (e.g. Pinedo and Hohn, 2000).

2.3. Reproductive status estimation

In FMA III male sexual maturity status was determined by examining the testicular sections magnified (100×) under a microscope according to Danilewicz et al. (2004) and the classification criteria followed was based on Hohn et al. (1985). For females, ovaries were examined externally for recording the presence or absence of corpus luteum, corpus albicans, and the largest follicles. The determination of the reproductive status followed the terminology recommended by the International Whaling Commission (Perrin et al. 1984).

Since there was no data of age and reproductive status for FMA II, franciscana dolphins were divided according to total length as described by Bertozzi, 2009: mature/adult males (larger than 107 cm), mature/adult females (larger than 119 cm); pups (smaller than 95 cm), juveniles (size between adult and pup).

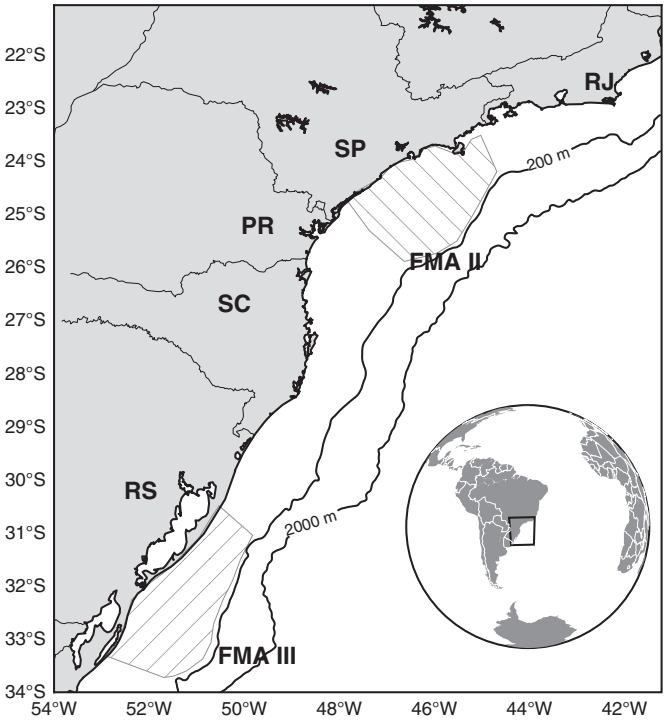

Fig. 1. Map showing sampling locations of franciscana dolphin (FMA II = franciscana management area II, FMA III = franciscana management area III).

2.4. Chemical analysis

Preparation of subsamples of blubber (~0.25 g) was based on standard procedures published in Lauenstein and Cantillo, 1998. Briefly, about 0.250 g of blubber was homogenized with 40 g of anhydrous Na_2SO_4 and 300 mL of methylene chloride (MeCl) using a tissumizer (PRO Scientific Inc. model PRO 250) after adding surrogate standards (PCB 103 and PCB 198). After the extracts were concentrated and the solvent was changed to hexane, they were initially cleaned using silica/alumina column chromatography and further purified using high-performance liquid chromatography-size exclusion column system: two phenogel 100A (22.5 × 250 mm) columns and a 7.8 × 50 mm precolumn. MeCl was used as mobile phase at a flow rate of 5 mL min^{-1} to remove excess lipids. To determine recovery rates, an internal standard (2,4,5,6-tetrachlorometaxylene (TCMX)) was added to extracts. Lipid content was gravimetrically determined.

2.5. Instrumental parameters

Extracts were analyzed with a Agilent 6890 gas chromatograph equipped with a 30 m × 0.25 mm DB-5MS fused silica capillary column with 0.25 μm film thickness associated to an mass selective detector, which was operated in the electron impact ionization mode and selected ion monitoring mode at 70 eV. Peaks were identified by retention time and mass spectra fragmentation patterns in comparison to known standards (from Cambridge Isotope Laboratory Inc.). Target PBDEs were quantified using calibration curves generated from four standard solutions. The oven temperature was programmed to start at 130 °C, held for 1 min., increased to 154 °C at 12 °C min^{-1}, increased to 210 °C min^{-1} at 2 °C min^{-1} and increased to 300 °C min^{-1} at 3 °C min^{-1}. The final temperature was held for 5 min.

2.6. Quality control

For quality assurance/quality control method blank, matrix duplicate, reference material, matrix spike and matrix spike duplicate were processed with each analytical batch (Lauenstein and Cantillo, 1998; EPA, 2003). To matrix spike and matrix spike duplicate were added known amounts of the following BDEs: 28, 47, 66, 85, 99, 100, 138, 153 and 154. The average recovery of internal standards was 86 ± 16 ($p = 0.05$) and the average recovery of POPs standards in the spiked matrices was 97 ± 11 ($p = 0.05$). The relative percent difference between the matrix duplicates was 8.1 ± 2.3 ($p = 0.05$) and between the spiked duplicates was 13 ± 6.1 ($p = 0.05$). Concentrations reported in the SRM 1945 were in good agreement with the acceptable limit of ±30%. Concentrations found in the blanks were never greater than three times the detection limit and were subtracted from respective samples. Method detection limit (MDL) was based on the standard deviation ($3 \times \sigma$) of seven replicates of a fish liver sample containing target compounds at a level of one to three times the expected MDL, which ranged from 0.5 to 1.25 ng g^{-1}.

2.7. Data management and statistical analysis

Blubber samples were analyzed for 39 PBDE congeners (1, 2, 3, 7, 8, 11, 10, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183 and 190). To minimize variability in contaminant concentrations due to varying lipid content in the samples, concentrations are expressed as ng g^{-1} on a lipid weight (lw) basis (Aguilar et al., 1999). For the statistical procedures, a value of half the detection limit was assigned for samples below the method detection limit, which was determined for all compounds (range: 1.2 to 3.7 ng g^{-1} lw) based on the guidelines established by the US Environmental Protection Agency (EPA, 1984).

To compare the two stocks all samples from the FMA II were used, but for FMA III only samples collected from 2001 to 2003 were used. Samples from the same time period were used for this comparison to minimize the effects from temporal variation. The Lilliefors test demonstrated a lack of normality in the distribution of the PBDE concentrations. Thus, nonparametric Kruskal–Wallis analysis of variance followed by a post hoc multiple comparison tests (Tukey's honestly significant difference) was used for the statistical comparison of populations and the determination of the influence of sex and age (pups, juveniles and adults). Regression analysis was conducted to examine differences between sampling years and concentrations.

3. Results and discussion

3.1. Correlation with biological parameters

A number of biological factors, such as age, sex, reproductive status, nutritional status and feeding habitat, can affect levels and patterns of contaminants in marine mammals (Aguilar et al., 1999). Thus, the relationship between contaminant levels and biological variables was examined prior to the analysis of temporal and geographical variations in the present study.

No statistically significant differences were detected in either FMA between PBDE concentrations and age/size or sex. This lack of significant differences may be due to 1) the considerable individual variation in total PBDE levels; 2) the small sample sizes of pups in the FAM III (Table 1); 3) interference from temporal variation (for FMA III) and 4) the relatively recent introduction of PBDEs compared to DDTs and PCBs. Lack of difference among sex and age/size and PBDE levels were also reported for the beluga whale (*Delphinapterus leucas*) and ringed seal (*Phoca hispida*) from Canada (Lebeuf et al., 2004; Ikonomou et al., 2002), the grey seal (*Halichoerus grypus*) from the North Sea (Kalantzi et al., 2005), and the guiana dolphin (*Sotalia guianensis*) from southeastern Brazil (Dorneles et al., 2010).

Although no associations were found between PBDE concentrations and age/size or sex, to control the variability (especially that from juveniles), only data from adult male individuals were used to examine temporal trends and compare the findings with previous data.

Table 1
PBDE concentrations (median values) in blubber of franciscana dolphins from FMA III and FMA II ng g^{-1} lipid weight, intervals (between parentheses) and number of samples (n).

	FMA III	FMA II
Adults males	26 (7.9–65) n = 22	289.3 (67.8–763.7) n = 11
Adult females	18.1 (<0.65–43.39) n = 6	64.8 (<0.65–227.8) n = 10
Juveniles	13.9 (<0.65–144) n = 37	198.6 (72.8–500.9) n = 8
Pups	10.88 (<0.65–124.43) n = 7	65.1 (31.1–210.4) n = 12

3.2. PBDE levels and congener profile in the two stocks

Table 2 displays the results of the PBDE determination in adult males of the FMA III and FMA II sampled from 1994 to 2004 and from 2002 to 2005, respectively. Total PBDE concentrations in the FMA III (7.99 to 65.02 ng g^{-1} lw) were lower than those found in the FMA II (67.8 to 736.7 ng g^{-1} lw). The higher values in the latter samples confirm the fact that PBDEs, like most other persistent organic pollutants, are found at higher concentrations in environmental matrices collected near industrial or highly populated centers (Lebeuf et al., 2004). Alonso et al. (2012) analyzed liver samples of franciscana from different regions of Brazil and found similar concentrations in samples from the FMA III, but lower values than those reported in the present study in the samples from the FMA II. This evaluation should be considered with caution, since there are difficulties associated to comparison between different organs.

The samples from the FMA II were collected from areas adjacent to the Santos and São Vicente Estuary System in the state of São Paulo. This region is the home of the Cubatão Industrial Complex, which is one of the most important petrochemical, chemical and metallurgical industrial centers in Brazil, as well as the Port of Santos, which is the largest commercial harbor in South America and represents another potential source of various contaminants, including PBDEs. Although these data are not enough to suggest a connection between the presence of the industrial complex and total PBDE concentrations detected in the blubber of the franciscana dolphin, the source of these chemicals may be linked to their use in these industries. Moreover there could be many other sources, such as coastal development, sewage, shipping and industrial discharge. Leonel et al. (2012) found high levels of PBDEs in the Atlantic spotted dolphin (*Stenella frontalis*) which appears to feed in the same region.

PBDE concentrations decreased in the following order BDE 47 > BDE99 > BDE 100 (Fig. 2), the only congeners detected in the franciscana dolphin samples. In Alonso et al. (2012) these congeners also presented the same distribution pattern. On the other hand, Dorneles et al. (2010) found BDE 47 to be the predominant, but BDE 100 had higher values than BDE 99 in another species (*Sotalia guianensis*) from the Brazilian coast. The difference among the two species can be species-specific related.

In FMA III and FMA II the composition of PBDEs suggests exposure to a similar technical mixture of PBDEs. Although some difference can be noted (mature females and pups) they are not significant since in FMA III only 1 out of 10 mature females and 3 out of 11 pups were detected BDE 99 and BDE 100, all the other individuals presented only BDE 47, a similar pattern detected in FAM III.

No difference was detected in the composition of PBDEs between the two FMAs, which suggests exposure to a similar technical mixture of PBDEs combined with a species-specific metabolism for PBDEs by franciscana dolphins. BDE 47 was the major congener, accounting for 23 to 98% in the FMA III and 46 to 99% in the FMA II. Alonso et al. (2012), Dorneles et al. (2010) and Leonel et al. (2012) also found BDE 47 to be the predominant congener in cetacean samples on the Brazilian coast. This profile suggests sources originating from the use of the penta-BDE mixture. However, the technical penta-BDE mixture has a higher proportion of BDE 99 than BDE 47 (La Guardia et al., 2006). Thus, the lower proportion of BDE 99 in comparison to BDE 47 suggests the preferential elimination or metabolic degradation of BDE 99. In vivo laboratory exposures have shown that some fish can debrominate BDE 99 to form BDE 47 (Stapleton et al., 2004; Pieroni, 2012). It is possible that the franciscana dolphin possesses a similar metabolic capacity to debrominate BDE 99, resulting in an increased accumulation of BDE 47 in the tissues and a relative depletion of BDE 99. However, one cannot rule out the possibility that this congener pattern in the tissue of the franciscana dolphin reflects the pattern of the source of exposure, which is primarily diet.

Table 2
Blubber PBDE concentrations (median) in adult male franciscana dolphins from FMA III and FMA II ng g^{-1} lipid weight.

	1994	1996	1999	2000	2001	2002	2003	2004	2005
FMA III									
Ages (years)	5	3 ± 0	4 ± 3.2	5 ± 1.4	3 ± 0.8	4 ± 2.9	5 ± 2.4	4	
	7.99	27.2	18.	30.5	9.7	33.9	13.4	65.02	
		11.5	48.6	37.1	16.	17.6	32.9		
			25.		30.9	20.4	34.9		
					14.7	15.3	26.9		
							33.2		
Median	7.99	19.3	25	33.8	15.3	18.9	32.9	65.02	
FMA II									
						436.2		655.7	92.62
						275.7		289.3	596.4
						67.79		212.1	101.4
									736.7
Median						436.2		289.3	348.9

3.3. Temporal variation

A number of studies have shown that PBDE levels increased exponentially from the 1970s to the 1990s, as found in the blubber from the San Francisco harbor seal from 1989 to 1998 (She et al., 2002), in the Arctic ringed seal from 1981 to 2000 (Ikonomou et al., 2002), in the eggs of the Great Lakes herring gull from 1981 to 2000 (Norstrom et al., 2002) and in the northern fur seal collected in Japan between 1972 and 1998 (Kajiwara et al., 2004). In the first decade of the 21st century, however, some studies indicated a decrease in PBDE levels. Kajiwara et al. (2004) observed an apparent decrease in concentration in the fur seal from 1994 to 1998 and Sellstrom et al. (2003) observed a significant decrease from the mid 1980s to 2001 in guillemot eggs from the Baltic Sea. These recent decreases are likely the result of changes in industrial practices and/or regulations in Europe and Japan that have gradually controlled the use of PBDEs, especially penta-BDE (Zhu and Hotes, 2004).

Based on the present findings, median concentrations of total PBDEs in adult male franciscana dolphins from FMA III appears to have increased exponentially ($r^2 = 0.63$), even after the year 2000 (Fig. 3), suggesting that total PBDE concentrations in this species have not yet reached a peak or that the use of PBDEs in the southern hemisphere is not regulated. Ramu et al. (2006) report similar findings in cetaceans from China and the authors propose that PBDE levels have kept increasing in developing countries, where recent economic development coupled with agricultural and industrial activities has resulted in the increased production and usage of these chemicals.

3.4. Comparison with other species

Concentrations of total PBDEs in the FMA III were two orders of magnitude lower than those found in samples from the North Atlantic: *Tursiops truncates* from Florida coast (Johnson-Restrepo et al., 2005) and the pelagic species *Lagenorhynchus acutus* and *Steno bredanensis* (Tuerk et al., 2005); and coastal species from the China Sea (*Neophocaena phocaenoides* and *Sousa chinensis*) (Ramu et al., 2005), which are considered "hot spots" for PBDEs due to the large usage of these chemicals. However, the concentrations were similar to those found in samples from India and the Philippines (Kajiwara et al., 2006), where PBDE levels are considered low. In contrast, total PBDE concentrations in samples from the FMA II were in the middle of the global contamination range, with concentrations similar to those found in the beluga whale (*D. leucas*) from St. Lawrence Estuary, Canada (Lebeuf et al., 2004) and the bottlenose dolphin (*T. truncates*) from the Mediterranean coast (Pettersson et al., 2004).

In general, the total PBDE levels encountered in this study in franciscana dolphins from the coastal regions off Brazil are lower than concentrations reported for other cetaceans in others parts of the world (Fig. 4). As the habitat of the franciscana dolphin is vulnerable to degradation, efforts should be made to decrease the amount of chemical pollution. Moreover, further efforts to conserve this endangered species should also focus on establishing protected areas, raising public awareness and managing fisheries to decrease the rate of incidental kills and ensure the sustainability of prey species.

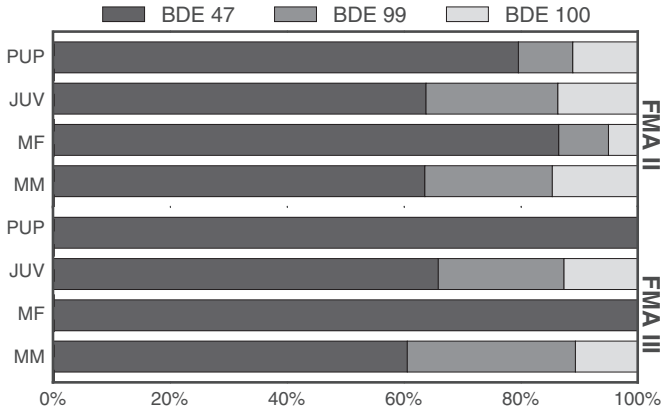

Fig. 2. Relative contribution of the PBDE congener groups to the ΣPBDE (FMA II = franciscana management area II, FMA III = franciscana management area III).

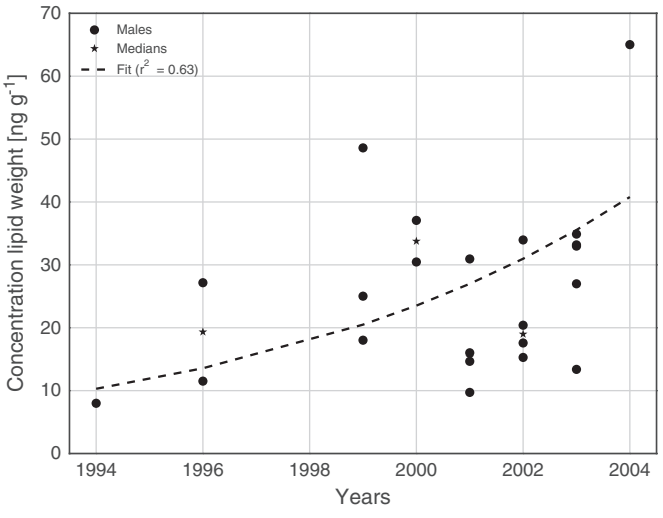

Fig. 3. Temporal trends of total PBDE concentrations in FMA III from 1994 to 2004.

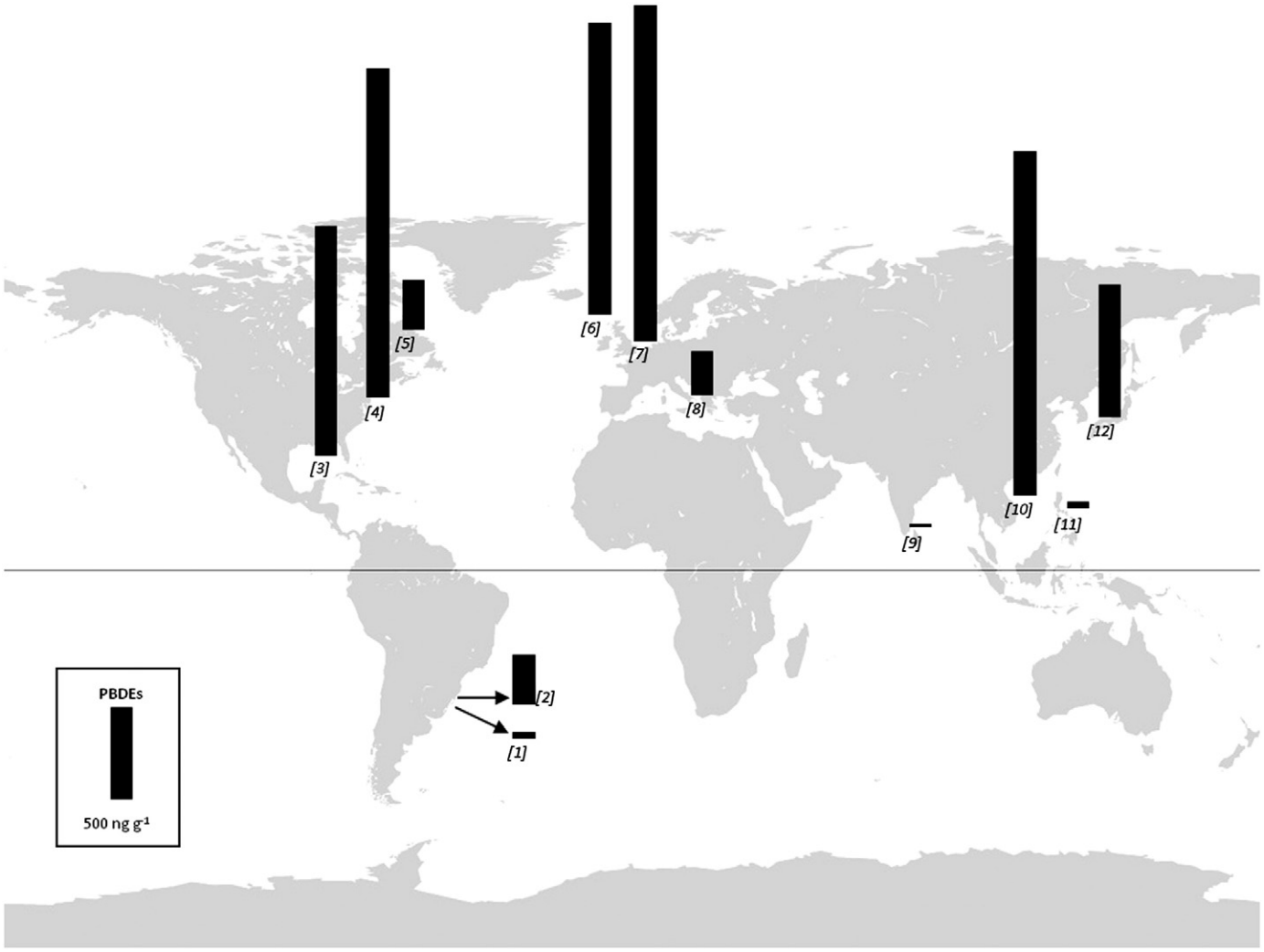

Fig. 4. Comparison of concentrations of PBDEs in blubber of cetaceans from various regions; [1] and [2] present study; [3] bottlenose dolphin (Johnson-Restrepo et al., 2005); [4] white-sided dolphin (Tuerk et al., 2005); [5] beluga whale (Lebeuf et al., 2004); [6] long-finned pilot whale (Lindström et al., 1999); [7] harbor porpoise (Boon et al., 2002); [8] bottlenose dolphin (Pettersson et al., 2004); [9] spinner dolphin (Kajiwara et al., 2006); [10] Indo-Pacific humpback dolphin (Ramu et al., 2005); [11] spinner dolphin (Kajiwara et al., 2006); [12] finless porpoise (Kajiwara et al., 2006).

4. Conclusions

Concentrations of PBDEs in franciscana dolphin from the FMA III appear to increase exponentially. However, these levels were still lower than those detected in the sFMA II. The differences in concentrations between the sFMA III and FMA II stocks appear to be related to differences in industrial discharge and urbanization in the two regions studied.

Due to the environmental behavior of PBDE congeners as well as current changes in industrial applications and regulatory measures, the future trend of PBDEs is unclear specially in Brazil. Therefore, continuous, detailed monitoring surveys are warranted to investigate the environmental distribution and fate of PBDEs in marine mammals on the coast of Brazil.

Conflict of interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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