PCDD, PCDF, AND COPLANAR PCB CONGENERS IN FRANCISCANA DOLPHINS, *Pontoporia blainvillei*, FROM SOUTH AND SOUTHEAST BRAZILIAN REGIONS: LEVELS AND PROFILES

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Introduction

Special concern has been raised since the 1960s about the environmental persistence, bioaccumulative capacity, toxicity of dioxins and related compounds (DRCs), such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (coplanar PCBs). Despite the high toxicity of these compounds and the awareness of the scientific community about the environmental problem, studies on environmental levels of DRCs in Brazil are scarce. The present study constitutes part of the first scientific investigation on DRC levels in marine biota from Brazil, which used samples from cetaceans for screening the neritic environment in search of this class of pollutants. Determination of organic micropollutants in cetaceans is of special interest, owing to their top position in the food web, their long life-span and, for some species, their year-round presence in polluted and relatively small areas[1].

The franciscana dolphin (*Pontoporia blainvillei*) occurs exclusively in the western Atlantic coastal waters of South America, from southeastern Brazil (18°25'S) to central Argentina (~42º35'S)[2]. Due to its nearshore distribution, the franciscana dolphin may be vulnerable to the effects of human activities. Considering this vulnerability, it is also of great interest to investigate if accumulation of persistent bioaccumulative toxicants can pose an additional threat to this dolphin species. This study presents results of DRC bioaccumulation in franciscana dolphins from Southeastern and Southern Brazilian coast.

Materials and methods

Liver samples were collected from franciscana dolphins either incidentally captured in fishing operations or stranded on the beaches. Samples comprised fourteen males from Rio Grande do Sul (RS=3), Santa Catarina (SC=2), São Paulo (SP=6 males) and Espírito Santo (ES=3) states, as well as six female franciscana dolphins from São Paulo (SP=6 females) state, Southern (RS, SC) and Southeastern (ES, SP) Brazilian coast.

The analytical procedure was detailed elsewhere[3]. Briefly, samples were fortified with $^{13}C_{12}$-labelled PCDD/F and $^{13}C_{12}$-labelled PCB quantification standard solutions (Wellington Laboratories Inc., Canada), EPA 1613 LCS and WP-LCS, and extracted using a Dionex ASE100 apparatus. Sulphuric acid was used for removing organic matter from the extracts. Clean-up stage was performed in an automated purification Power Prep™ System (FMS, Inc., USA) including acidic silica gel and basic alumina columns for mono-ortho PCB purification and an additional carbon column for PCDD/F and coplanar PCB cleanup. The final extracts were concentrated avoiding dryness, spiked with EPA1613-ISS and WP-ISS internal standard solutions (Wellington Laboratories Inc., Canada) and further analyzed by GC–HRMS. The following dioxins and furans were targeted for analysis: 2,3,7,8– Tetra CDD; 1,2,3,7,8– Penta CDD; 1,2,3,4,7,8– Hexa CDD; 1,2,3,6,7,8– Hexa CDD; 1,2,3,7,8,9– Hexa CDD; 1,2,3,4,6,7,8– Hepta CDD; Octa CDD (OCDD); 2,3,7,8– Tetra CDF; 1,2,3,7,8– Penta CDF; 2,3,4,7,8– Penta CDF; 1,2,3,4,7,8– Hexa CDF; 1,2,3,6,7,8– Hexa CDF; 1,2,3,7,8,9– Hexa CDF; 2,3,4,6,7,8– Hexa CDF; 1,2,3,4,6,7,8– Hepta CDF; 1,2,3,4,7,8,9– Hepta CDF; Octa CDF (OCDF). Concerning dioxin-like (coplanar) PCBs, the following congeners (IUPAC numbers) were targeted for analysis: 77; 81; 126; 169; 105; 114; 118;

123; 156; 157; 167 and 189. Toxic equivalent (TEQ) concentrations of PCDD/Fs and coplanar PCBs were calculated using the World Health Organization (WHO)-2005 toxic equivalency factors (TEF)[4]. Concentrations below detection limits were considered as zero (lower bound TEQ).

Results and discussion:

PCDD, PCDF and coplanar (non-ortho and mono-ortho) PCB concentrations and TEQ values (pg.g^{-1}, l.w.), as well as percentages to ∑TEQ, in liver of franciscana dolphins from Rio Grande do Sul (RS), Santa Catarina (SC), São Paulo (SP) and Espírito Santo (ES) states, Brazil, are presented in the Table 1.

Dioxin-like (coplanar) PCBs accounted for 83-96% of the total TEQs in the hepatic tissues of franciscana dolhins. In this context, non-ortho coplanar PCBs deserve to be highlighted, since the group contributed to 82% of the total TEQs, on average. Among the later group, PCB-126 was by far the congener of greatest importance. In fact, of the measured DRCs, PCB-126 contributed the majority of the total TEQ in all franciscana dolphins (mean 78%, SD 11%). However, PCB-118 occurred in the highest concentrations, which varied from 19.7 to 563.9 ng/g (l.w.). PCDDs and PCDFs accounted for, on average, 10% of the total TEQs. The predominant PCDD/F congener found in the livers of franciscana dolphins was OCDD, with concentrations ranging between 32 and 1093 pg/g (l.w.). Concentrations of PCDDs were greater than those of PCDFs in all individuals. However, regarding the TEQ values (TEQ pg/g l.w.), levels were in general higher for PCDFs. Among furans, 2,3,4,7,8- PeCDF provided the highest contribution to total TEQ.

It is important to keep in mind that while analyzing franciscana dolphins from RS, SC, SP and ES, individuals from three different management areas are being considered. It has been proposed[2] that franciscana should be splitted into four stocks for management purposes, three of which occur in Brazilian waters. Each stock inhabits discrete areas named Franciscana Management Areas (FMA): FMA I, including coastal waters of ES and Rio de Janeiro states; FMA II, covering SP to SC states; and FMA III, comprising the coastal waters of RS state. A recent study from our research team[5] has shown that different ecological franciscana dolphin populations could exhibit remarkably distinct organochlorine compound bioaccumulation profiles, characterized by different ΣDDT/ΣPCB ratios, even within the same management area (FMA II). However, taking into account the compounds measured and the individuals analyzed in the present study, no distinction among areas was more noteworthy than the individual variation, which can be visualized through the example provided by Figure 1.

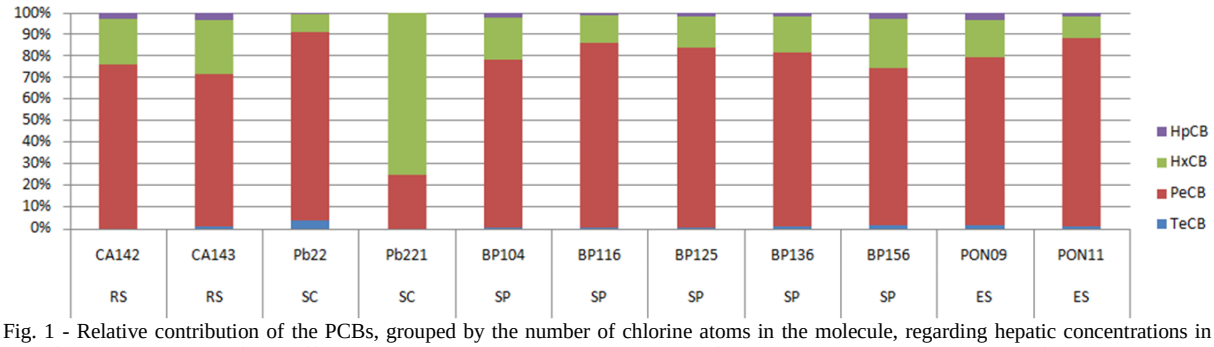

Fig. 1 - Relative contribution of the PCBs, grouped by the number of chlorine atoms in the molecule, regarding hepatic concentrations in male franciscana dolphins from different Brazilian states (RS, SC, SP, ES). The figure exposes the individual codes of each dolphin (e.g. CA142, CA143, Pb22 and etc) as well.

It is interesting to highlight differences in PCDF profiles between franciscana dolphins from SP state and air samples from São Paulo city[6] (Figure 2). For all individuals from SP state, with the exception of BP136, a higher contribution of PeCDF in dolphins than in air could be observed. A possible explanation for this lays on the selective biomagnification of 2,3,4,7,8- PeCDF reported in literature[7].

From the toxicological point of view, it is important to draw attention to the fact that three franciscana dolphins (two males from SP and SC, and 1 female from SP) presented ∑TEQ concentrations within the range (160 to 1400 pg.g^{-1}, l.w.) of threshold levels for TEQs in livers of aquatic mammals that are capable of eliciting physiological effects[8]. In this context, it is important to mention that the hepatic PCDD and PCDF concentrations of franciscana dolphins can be considered as high when compared to cetaceans from different regions of the globe (Table 2).

Table 1 – Hepatic DRC concentrations and TEQ values, in pg.g^{-1} l.w., as well as percent contribution to Total-TEQ (T-TEQ) (Mean (Median) ± SD; [*n*] Min - Max) of Franciscana dolphins from Brazil

	RS	SC	SP (males)	SP (females)	ES
∑PCDDs	113 (93) ± 67 [3] 59 - 188	[2] 69 - 354	422 (174) ± 473 [5] 62 - 1174	348 (390) ± 163 [5] 113 - 539	66 (76) ± 19 [3] 44 - 77
∑PCDDs TEQ	1.5 (0.1) ± 2.4 [3] 0.1 - 4.3	[2] 0.2 - 10	2.6 (1.1) ± 3.2 [5] 0.8 - 8.3	3.3 (3.4) ± 1.8 [5] 1.1 - 5.2	0.1 (0.1) ± 0.1 [3] 0.02 - 0.2
∑PCDDs TEQ % T-TEQ	[2] 0.2 - 6.4	[2] 0.3 - 4.8	2.3 (1.7) ± 1.5 [5] 0.7 - 4.6	4.6 (4.0) ± 3.0 [5] 1.1 - 9.1	[2] 0.1 - 0.3
∑PCDFs	77 (66) ± 41 [3] 42 - 123	[2] 42 - 204	178 (127) ± 152 [5] 44 - 380	100 (90) ± 54 [5] 49 - 184	35 (33) ± 11 [3] 25 - 46
∑PCDFs TEQ	4.2 (3.8) ± 0.7 [3] 3.7 - 4.9	[2] 2.4 - 18	10 (5.7) ± 10 [5] 1.6 - 27	7.2 (4.7) ± 5.8 [5] 2.2 - 17	4.9 (5.5) ± 1.4 [3] 3.3 - 6.0
∑PCDFs TEQ % T-TEQ	[2] 5.5 - 6.7	[2] 4.1 - 8.7	7.5 (7.6) ± 2.1 [5] 4.2 - 9.7	7.7 (7.5) ± 2.1 [5] 5.1 - 10	[2] 5.6 - 6.2
∑non-ortho PCBs	629 (691) ± 390 [3] 211 - 983	[2] 5 182 - 8 171	3 081 (2 693) ± 2 147 [5] 915 - 5 573	4 224 (2 613) ± 4 449 [6] 1 398 - 13 120	1 882 (1 813) ± 593 [3] 1 327 - 2 506
∑non-ortho PCBs TEQ	42 (52) ± 22 [3] 17 - 57	[2] 49 - 90	96 (56) ± 80 [5] 34 - 224	67 (58) ± 37 [6] 29 - 133	57 (49) ± 29 [3] 34 - 90
∑non-ortho PCBs TEQ % T-TEQ	[2] 85 - 91	[2] 43 - 85	83 (85) ± 6.2 [5] 73 - 88	83 (83) ± 2.2 [5] 80 - 85	[2] 90 - 90
∑ortho PCBs	[2] 35 017 - 79 563	[2] 208 300 - 3 000 297	270 606 (234 377) ± 216 116 [6] 43 314 - 566 064	138 532 (86 990) ± 123 932 [6] 61 543 - 384 608	[2] 67 127 - 139 709
∑ortho PCBs TEQ	[2] 1.1 - 2.4	[2] 6.3 - 90	8.1 (7.0) ± 6.5 [6] 1.3 - 17	4.2 (2.6) ± 3.7 [6] 1.8 - 12	[2] 2.0 - 4.2
∑ortho PCBs TEQ % T-TEQ	[2] 1.8 - 3.6	[2] 11 - 43	7.5 (5.6) ± 6.4 [5] 3.3 - 19	4.8 (4.6) ± 1.5 [5] 3.3 - 7.1	[2] 3.7 - 4.2
∑TEQ pg/g	[2] 57 - 67	[2] 58 - 209	117 (78) ± 98 [5] 39 - 276	87 (85) ± 49 [5] 34 - 164	[2] 54 - 100

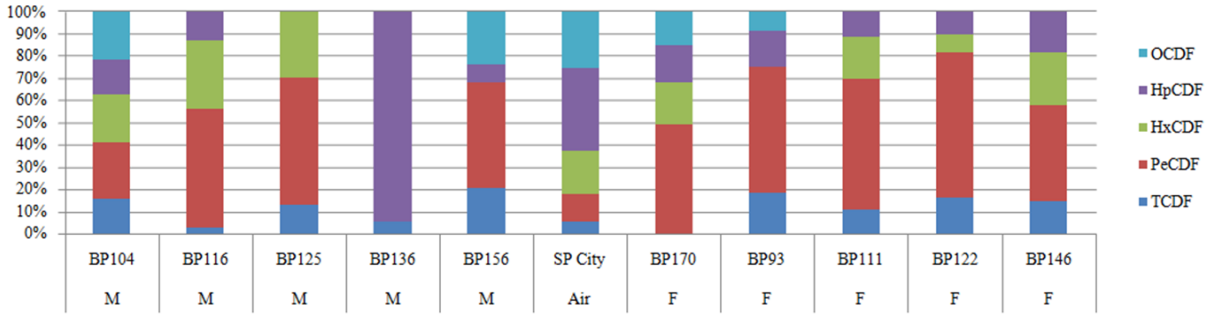

Figure 2 -Relative contribution of the PCDFs, grouped by the number of chlorine atoms in the molecule, regarding hepatic concentrations in male and females (M and F) franciscana dolphins from SP state in comparison with air levels in São Paulo city. The figure exposes the individual codes of each dolphin (e.g. BP104, BP116, BP125 and etc) as well.

Table 2 - Mean ∑PCDD and ∑PCDF concentrations (pg/g, l.w.) in blubber (B) and liver (L), with standard deviation (± SD), number of individuals of each species/area of sampling of cetaceans from all over the world.

Species - Common name	Area	PCDDs Mean±S.D.	PCDFs Mean±S.D.	SEX	Tissue	n	Ref.
Finless porpoise	Japan	60.9	6.0	NS	B	1	9
Killer whale	Japan	N.D.	344.8	M	B	1	10
Hector's dolphin	New Zealand	38.7 ±8.1	41.6 ±11.1	M	B	4	11
False killer whale	N. America	41.9	117.2	M	B	1	12
Harbor porpoise	N. America	84.8 ±112.2	13.1 ±14.4	M	B	4	12
Bottlenose dolphin	Italy	72.3 ±46.0	75.3 ±44.6	M	L	4	13
Striped dolphin	Italy	271.0 ±148.0	92.3 ±70.6	M	L	3	13
Pilot whale	Italy	183.3	195.5	M	L	1	13
Franciscana dolphin	S-SE Brazil	236.3 ±323.1	113.2 ±113.0	M	L	13	PS
Franciscana dolphin	SP, Brazil	348.2 ±163.4	100.0 ±53.8	F	L	5	PS

NS, non-specified; PS, present study

The DRC concentrations verified in the present study constitute a matter of concern for the conservation of the species. This apprehension is enhanced if it is taken into account that franciscana dolphins inhabit anthropogenically disrupted environments, facing a number of potential and known threats[2], as well as that molecules of this class of pollutants have been shown to be risk factors for cancer, immune deficiency and reproductive abnormalities[14].

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