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# Long-term trends of polychlorinated biphenyls and chlorinated pesticides in franciscana dolphin (*Pontoporia blainvillei*) from Southern Brazil

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ABSTRACT

Selected POPs were analyzed in blubber samples of Pontoporia blainvillei from Southern Brazil to appraise temporal trend over a 10 year period (1994–2004). Overall, levels of POPs were relatively low, especially when compared to Northern Hemisphere concentrations. Apart from Mirex and PCBs, which showed stable concentrations, DDTs, HCB, CHLs, Dieldrin levels presented a slight decrease over the studied period. In addition, the increase in the PCBs/DDTs ratio supports the idea that inputs of DDTs are decaying faster than PCBs.



## 1. Introduction

Over the last two decades, there has been growing concern about the bioaccumulation and toxic effects of persistent organic pollutants (POPs) in marine ecosystems (Clark, 2001; Tanabe et al., 1994). POPs are a group of synthetic organic compounds that have been produced for industrial and agricultural purposes, or are by-products of other industrial processes. In addition to being resistant to degradation, most POPs are lipophilic and, consequently, tend to accumulate in organisms and biomagnify throughout the food chain reaching the highest levels in top predators (Clark, 2001).

In this regard, marine mammals have been widely used as bioindicators/biomonitors of POPs (Muir et al., 1990; Tanabe and Subramanian, 2006). Because they are long-lived, they are at the top of the aquatic food chain (Reijnders, 1986), they can transfer PCBs and chlorinated pesticides through lactation over generations and most have low capacity for xenobiotic degradation (Tanabe et al., 1988). Marine mammals may also be used to assess the bioavailability and bioaccumulation of selected POPs in the marine environment worldwide and over long time spans, and may provide a model for human exposure to organochlorines from seafood consumption (Aguilar, 1987). Moreover, they can be considered as "model systems" for studying low-dose, long-term effects of pollution by POPs (Tanabe and Subramanian, 2006).

The franciscana, *Pontoporia blainvillei*, is a small cetacean with a distribution restricted to the southwest Atlantic Ocean (Bastida et al., 2007). Some studies have been done with this dolphin (Borrel et al., 1995; Kajiwara et al., 2004; O'Shea et al., 1981), but long-term temporal trends of POPs in this cetacean are unknown. Although several studies have indicated a continuous decrease of POP concentrations in cetaceans from the Northern Hemisphere (e.g. Borrel and Aguilar, 2007; Dietz et al., 2004), the only long-term study available in the Southern Hemisphere did not indicate a decrease, but rather slightly increasing concentrations in the minke whale (*Balaenoooptera acutorostrata*) from Antarctica (Aono et al., 1997). Organochlorine pesticides were not totally banned in South American countries, their use was only restricted from mid-eighties, but some are still allowed in pest control of tropical and subtropical epidemic disease (such as malaria), emergencies use in agriculture, wood preservations and forestation/reforestation activities (PNUMA, 2002). Although prohibited in most of the South American countries, in Brazil PCBs have been allowed in transformers already installed before their exchange for a PCB free-oil (Barreto et al., 1988). Other diffuse sources (for example, dumpsites) are also inputting PCBs to the environment. Considering these possible sources it is still very important to appraise POPs levels and trends in South America. Therefore, the present study is the first attempt to assess long-term trends of selected POPs in blubber samples of *P. blainvillei* from Southern Brazil.

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## 2. Materials and methods

### 2.1. Samples

Blubber samples were obtained from 73 individual of franciscana dolphins incidentally caught in gillnet fisheries operating in coastal waters off Southern Brazil (state of Rio Grande do Sul) between 1994 and 2004 (see Fig. 1).

### 2.2. Age estimation

For estimating the age of the analyzed individuals, teeth were extracted from the center of the left lower jaw and processed according to standard procedures established for franciscana (e.g. Kasuya and Brownell, 1979; Pinedo and Hohn, 2000).

### 2.3. Reproductive status estimation

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).

### 2.4. Chemical analysis

Subsamples of blubber (~0.25 g), included the entire blubber layer from skin to muscle, were extracted and cleaned up following standard procedures routinely used at the Geochemical and Environmental Research Group (GERG) and published elsewhere (e.g. Lauenstein and Cantillo, 1998). Briefly, sample aliquots were macerated with 40 g of anhydrous $Na_2SO_4$ and 300 mL of methylene chloride (MeCl) using a tissumizer (PRO Scientific Inc. model PRO 250). Extracts were initially cleaned by silica/alumina column chromatography and then purified with gel permeation using a high performance liquid chromatography (HPLC). Then, extracts were concentrated to 1 mL in hexane and 0.5 mL was used to analyze PCBs and pesticides. The remaining 0.5 mL (for non-*ortho* PCBs) was passed through a glass column packed with silica gel and activated carbon (20:1). The first fraction eluted with 10% of toluene in DCM and the second fraction, contained non-*ortho* PCBs, was eluted with toluene only. Surrogates ((PBB 77 for non-*ortho* PCBs and PCB 103 and PCB 198 for the other PCBs and pesticides) and an internal standard (tetrachloro *meta* xilene – TCMX) were added to samples for quantification and to determine recovery rates, respectively. Lipid content was gravimetrically determined.

### 2.5. Instrumental parameters

Samples were analyzed with a HP6890 gas chromatograph (GC) equipped with a mass spectrometer detector (MSD). A DB-5MS fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) was used for separation. The MSD was operated in the electron impact ionization (EI) (70 eV) and selected ion monitoring (SIM) mode. The peaks were identified by retention time, target ion, and conformation ions ratios (five ions were monitored for each compound) in comparison to external standards. Target POPs were quantified with a calibration curves generated from four standard solutions. For chlorinated pesticides and non-*ortho* PCBs all compounds were injected to generate the calibrations curves and for other PCBs only 21 PCBs were used (PCB 8, PCB 18, PCB 28, PCB 29, PCB 44, PCB 52, PCB 66, PCB 87, PCB 101, PCB 105, PCB 110, PCB 128, PCB 153, PCB 160, PCB 170, PCB 180, PCB 187, PCB 195, PCB 201, PCB 206, PCB 209).

For non-*ortho* PCBs the oven temperature was programmed to start at 120 °C (hold for 1 min) and increased to 300 °C at 6 °C/min; the final temperature was held for 1 min. For other PCBs and pesticides the oven temperature was programmed to start at 75 °C (hold for 3 min), increased to 150 °C at 15 °C/min, increased

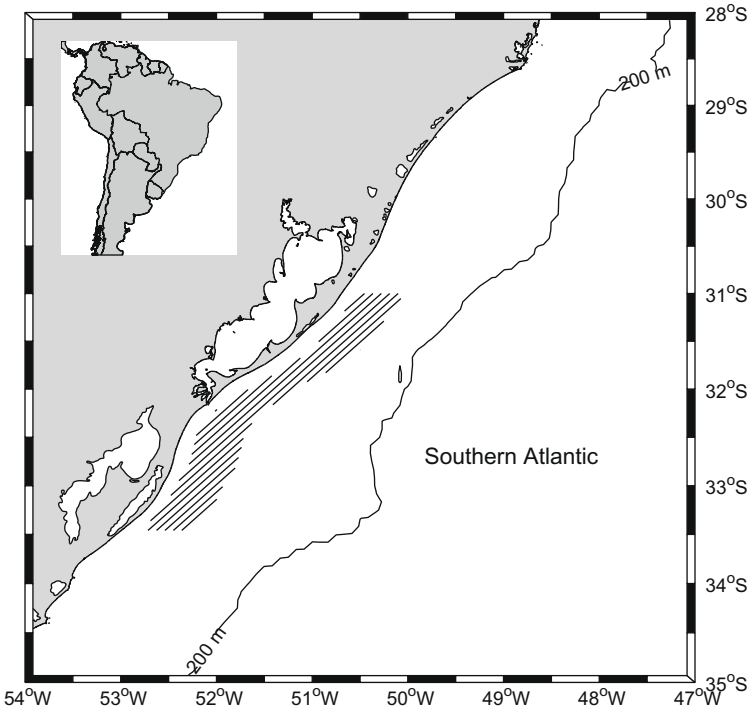


**Fig. 1.** Map showing sampling locations of franciscana in Southern Brazil; insert shows South America and zoom in show Rio Grande do Sul State (RS-Brazil).

to 260 °C/min at 2 °C/min, and increased to 300 °C/min at 20 °C/min. The final temperature was held for 10 min.

### 2.6. Quality control

For quality control (QC), a method blank, sample duplicate, matrix spike, matrix spike duplicates, and standard reference material (SRM 1945) were processed with each sample preparation batch (Lauenstein and Cantillo, 1998; EPA, 2003). The average recovery of internal standards was 86 ± 16 (95% of confidence) and the average recovery of POPs standards in the spiked matrices was 97 ± 11 (95% of confidence). The relative percent difference between the matrices duplicates was 8.1 ± 2.3 (95% of confidence) and between the spiked duplicates was 13 ± 6.1 (95% of confidence). 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.

### 2.7. Data management and statistical analysis

In order to standardize contaminant concentrations due to variation on the sample lipid contents, concentrations are expressed as ng $g^{-1}$ on a lipid weight (lw) basis. The method detection limits (MDL) for all compounds (range = 1.13–3.62 ng $g^{-1}$ lw) were determined in accordance with EPA Protocol (EPA, 1984) and taking into consideration the lowest calibration level of a particular analyte and the amount of sample extracted. A value of one half of the detection limit was assigned for samples with concentrations below the (MDL).

Data were examined for independence and normality and, whenever appropriate, were log-normalized. Differences in the contaminant group were established between sex- and size-classes using an analysis-of-variance (ANOVA) with a "multiple comparison procedure" for pairwise comparison of sex/size-classes. For statistical analyses, the level of significance was defined at $p \leqslant 0.05$.

To examine the current status of POP concentrations only adult males from 2002 to 2004 were considered in order to avoid effects from age and reproductive status differences. Due to sample size, only males from 2002 to 2004 and females from 1996 to 1997 were used for assessing age-related accumulation. Moreover, a regression analysis was conducted with adult specimens to examine differences among years of sampling.

## 3. Results and discussion

### 3.1. Status of organochlorine contamination

Blubber samples were analyzed for PCBs (sum of all 209 congeners, including coplanar congeners), Hexachlorobenzene (HCB), Aldrin, Endrin, Dieldrin, DDTs (*o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD and *p,p′*-DDD), Hexachlorocyclohexane isomers (α-HCH, β-HCH, δ-HCH and γ-HCH), selected Chlordanes (CHLs) (i.e. Heptachlor, Heptachlor Epoxide, α-Chlordane, γ-Chlordane, *cis*-nonachlor, *trans*-nonachlor and oxychlordane), 1,2,3,4-Tetrachlorobenzene, 1,2,4,5-Tetrachlorobenzene, Pentachlorobenzene, Pentachloroanisole, Mirex and Endosulfan II. Mean concentrations (and standard deviation) of PCBs and chlorinated pesticides, with concentrations above the MDL, in adult franciscana are shown in Table 1.

Among the organochlorines compounds detected in *P. blainvillei*, PCBs showed the predominant concentrations followed by DDTs, CHLs, Mirex, Dieldrin and HCB. Concentrations of Aldrin, Endrin, HCHs, 1,2,3,4-Tetrachlorobenzene, 1,2,4,5-Tetrachlorobenzene, Pentachlorobenzene, Pentachloroanisole, Endosulfan II, Heptachlor and oxychlordane were lower than their MDL in all samples.

PCBs concentrations range from 1270 to 10,555 ng $g^{-1}$ lw (mean 5120 ± 3122 ng $g^{-1}$ lw), which contributed up to 78% of the total load of measured POPs. Among all PCBs analyzed, non-*ortho* coplanar PCBs represent 0.11%, (mean 5.16 ± 1.16 ng $g^{-1}$ lw). DDTs were detected in concentrations between 230 and 3447 ng $g^{-1}$ lw (mean concentration of 1037 ± 942 ng $g^{-1}$ lw).

Although Rio Grande do Sul state (Southern Brazil) has historically been an agricultural region, the predominance of PCBs over DDTs (ΣDDT/ΣPCB ratio was 0.2) implies the presence of significant sources of PCBs in and nearby the region's coastline, possibly

**Table 1**
Concentrations (ng $g^{-1}$ lw) of organochlorines in blubber of franciscana sampled from 1994 to 2004.

| Code | Year | Sex | Age | Length | PCBs | DDTs | CHLs | HCB | Mirex | Dieldrin |
|---|---|---|---|---|---|---|---|---|---|---|
| CA 97 | 1994 | Female | 6 | 142 | 3113 | 769 | 114 | 52.8 | 60 | 54.8 |
| CA 108 | 1995 | Female | 11 | 157 | 3240 | 1451 | 189 | 87.3 | 45.2 | 149 |
| CA 118 | 1996 | Male | 3 | 132 | 4483 | 1798 | 154 | 58.5 | 83.8 | 141 |
| CA 120 | 1996 | Male | nd | 131.2 | 3506 | 905 | 82 | 33.6 | 58.4 | 57.2 |
| CA 126 | 1997 | Female | 6 | 157 | 1135 | 219 | 28.7 | 7.52 | 42.4 | 52.8 |
| CA 127 | 1997 | Female | 4 | 152 | 6061 | 2845 | 297 | 114 | 60.1 | 189 |
| CA 129 | 1997 | Female | 6 | 148 | 4259 | 737 | 89.5 | 13.7 | 49 | nd |
| CA 198 | 1999 | Male | 2 | 131.5 | 3470 | 876 | 136 | 54.3 | 44.7 | 66.7 |
| CA 208 | 1999 | Male | 3 | 132.5 | 7331 | 1348 | 130 | 35.3 | 110.6 | 81.9 |
| CA 230 | 2000 | Male | 6 | 138 | 8090 | 2125 | 173 | 29.1 | 70 | nd |
| CA 242 | 2000 | Male | 4 | 138 | 5987 | 1431 | 180 | 73.6 | 119 | 107 |
| CA 248 | 2001 | Male | 4 | 125 | 3618 | 749 | 46.5 | 20.7 | 84.5 | nd |
| CA 251 | 2001 | Male | 3 | 116 | 2442 | 459 | 37.1 | 17.7 | 32.9 | nd |
| CA 254 | 2001 | Male | 2 | 119 | 2138 | 438 | 43.7 | 25.5 | 22.4 | 37.4 |
| CA 256 | 2001 | Male | 3 | 119 | 3121 | 615 | 54.6 | 26.1 | 42.3 | nd |
| CA 260 | 2002 | Male | 8 | 127 | 10,555 | 3447 | 261 | 45.8 | 80.6 | 347 |
| CA 275 | 2002 | Male | 2 | 129 | 2550 | 516 | 48.8 | 25.8 | 41.4 | 45.7 |
| CA 281 | 2002 | Male | 3 | 137 | 4138 | 855 | 77.5 | 37.7 | 64.2 | 63.5 |
| CA 290 | 2002 | Male | 2 | 125 | 1937 | 273 | 10.8 | 20.5 | 38.7 | nd |
| CA 295 | 2003 | Male | 3 | 146 | 4051 | 763 | 71.5 | 38.9 | 58 | 48.8 |
| CA 304 | 2003 | Male | 6 | 133 | 7138 | 949 | 66.3 | 27.1 | 71.9 | 61.3 |
| CA 309 | 2003 | Male | 3 | 127 | 6964 | 1196 | 90.1 | 35.1 | 67.9 | nd |
| CA 315 | 2003 | Male | nd | 135.4 | 3628 | 562 | 45.2 | 22 | 33.8 | nd |
| CA 320 | 2003 | Male | 8 | 130 | 8975 | 1583 | 132 | 46.7 | 106 | nd |
| CA 338 | 2004 | Male | 4 | 153.5 | 1271 | 230 | 21.1 | 4.83 | 55.5 | nd |
| CA 359 | 2004 | Female | 2 | 143 | 3280 | 462 | 58.2 | 37.1 | 42.3 | 45.5 |

arising from the significant industrial usage (e.g. dielectric fluid for the manufacture of capacitors and transformers) in the area drained by the Plata River (~2,000,000 km$^2$) and Patos Lagoon (~200,000 km$^2$) (Menone et al., 2001; PNUMA, 2002).

The compound *p,p′*-DDE is the most persistent DDT metabolite and it is not significantly present in commercial DDT mixture (WHO, 1979). Consequently, high values for the ratio *p,p′*-DDE/ΣDDT (>0.6) is an indication of ageing of the initial product (Aguilar, 1985; Borrel and Aguilar, 1987). In *P. blainvillei*, the value of 0.78 for this ratio strongly indicate that no new inputs of DDT have occurred in Southern Brazilian waters, probably as a consequence of the legal restrictions on production and use of almost all chlorinated pesticides in the 1980s–1990s (PNUMA, 2002).

CHLs, Mirex, Dieldrin and HCB concentrations were about two orders of magnitude lower than PCBs and DDTs concentrations. CHLs levels ranged from 10.7 to 261 ng g$^{-1}$ lw (mean of 82.5 ± 71.7 ng g$^{-1}$ lw), while Mirex levels were between 34 and 106 ng g$^{-1}$ lw (mean of 61.8 ± 21.8 ng g$^{-1}$ lw). Dieldrin concentrations were very similar to those of Mirex, ranging from <0.71 to 347 ng g$^{-1}$ lw (mean of 56.8 ± 105.7 ng g$^{-1}$ lw), and HCB presented the lowest levels ranging from 4.8 to 47 ng g$^{-1}$ lw (mean of 30.5 ± 12.9 ng g$^{-1}$ lw).

Among the CHLs compounds, *trans*-nonachlor was the predominant (40%) followed by *cis*-nonachlor (38%). Kajiwara et al. (2004) analyzed franciscana samples from another population (Northern population) and *trans*-nonachlor was also the predominant compound. Nevertheless, elevated percentage of oxychlordane was reported in Kajiwara's study, indicating that this species has a high metabolic capacity to decompose or transforms CHLs compounds. The absence of oxychlordane in franciscana from Rio Grande do Sul (Southern population) suggests different sources of contamination.

### 3.2. Variation with age, reproductive status and sex

In the present study no statistically significant differences in contaminant levels were found between males and females of franciscana. However, the absence of significant differences between genders might be biased by the small number of adult females analyzed. Similar findings were reported for other species of dolphin (Borrel and Aguilar, 2007; Kajiwara et al., 2002).

Among the different size-classes (adults, juveniles and calves), significant differences were only found between adult males and both juveniles and calves for PCBs, and between adult females and juveniles for HCB. The small number of calves analyzed and the high variability of POPs levels in juveniles have probably influenced the results and concealed other differences. Except for Dieldrin, which was not found in all samples, levels of organochlorines in males increased with age (Fig. 2), whereas in females some compounds increased (PCBs, DDTs, for example) with age and others remained constant (HCB and Dieldrin) (Fig. 2). Kajiwara et al. (2004) found similar results in franciscana from southeastern Brazil.

The transference from mother to offspring by lactation is an important process of "excretion" of organochlorine compounds (Ridgway and Michelle, 1995). This process is related to contaminant's properties such as log $K_{ow}$ values, molecular size, water solubility and protein-specific binding capability, since the transfer between blubber and milk involves diffusion through a largely aqueous microlayer (the mammary gland) (Sormo et al., 2003).

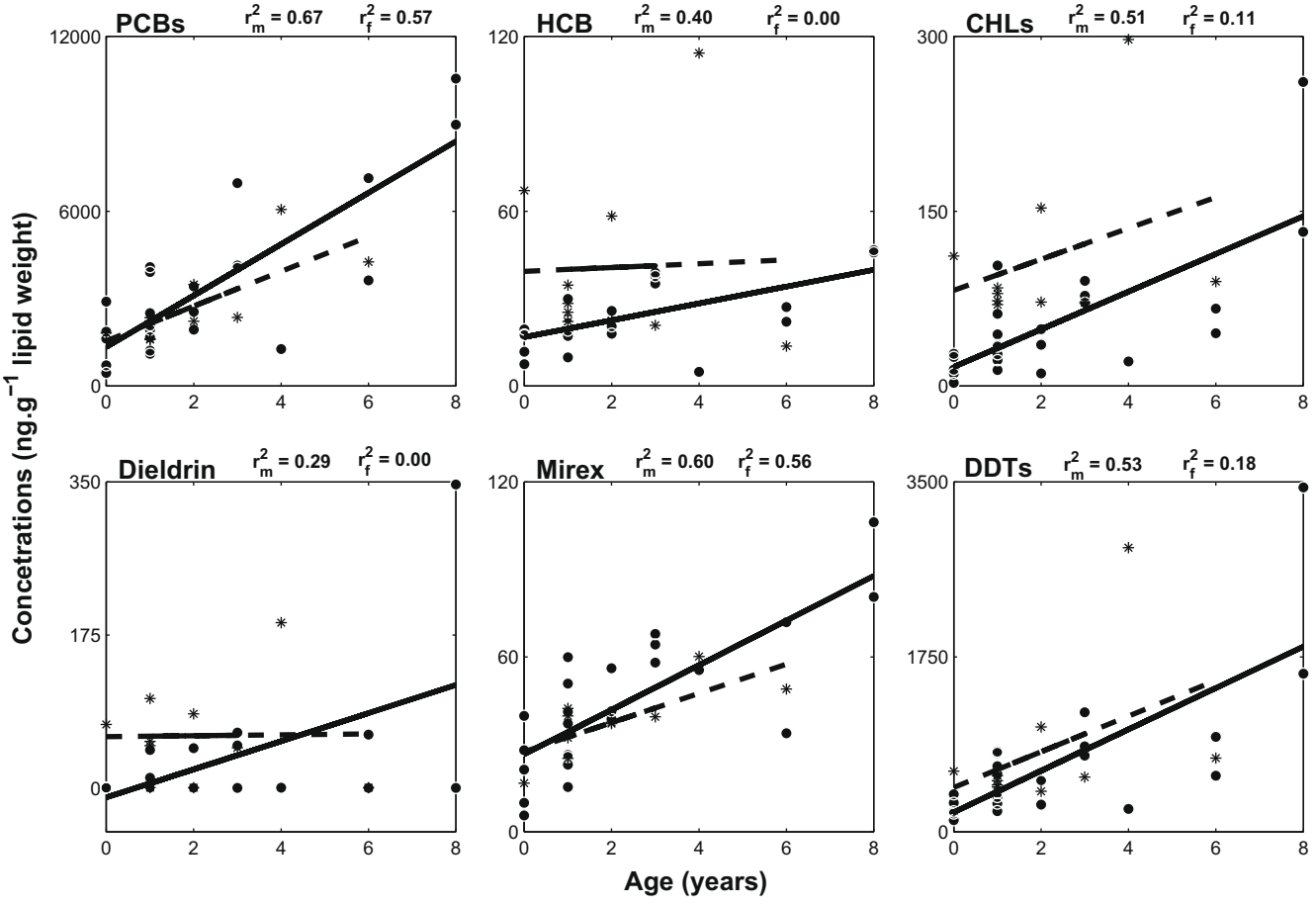


**Fig. 2.** Variation of POPs with age in male ($n$ = 24) and female ($n$ = 10) franciscana (● males; ∗ females; - - - linear regression for females; —— linear regression for males).

As a result, less lipophilic compounds, such as Dieldrin ($K_{ow} \approx 4$), will be preferably "excreted" from the mother, in comparison to more lipophilic ones (DDTs $K_{ow} \approx 6$ and PCBs $K_{ow} \approx 5$–8). However, compounds with relatively higher $K_{ow}$, such as HCB and CHLs ($K_{ow} \approx 5$ and 6, respectively), seem also to be more efficiently transferred. HCB is a smaller molecule and CHLs are more soluble in water (56 $\mu g\,L^{-1}$) than DDTs (1.2–5.5 $\mu g\,L^{-1}$) and PCBs (0.01–0.0001 $\mu g\,L^{-1}$).

### 3.3. Temporal trends of OC levels

Time-related trends of OCs in *P. blainvillei* are showed in Table 1 and illustrated in Fig. 3. Mean concentrations of Dieldrin and HCB decreased significantly over the period 1994/95–2003/04 ($p < 0.05$). Levels of CHLs and DDTs also seem to have decreased, but not significantly ($p < 0.1$), while PCBs and Mirex levels did not differ over the period of study or even showed a slightly increase (PCB levels from 1994 to 2000).

Dieldrin levels showed the most accentuate decrease during the period of study. This negative trend is consistent with the chemical history of use. Although there are no data regarding its use/production in Brazil, its precursor, Aldrin (that is readily metabolized to Dieldrin by both plants and animals) was formulated from 1977 to 1990 by Shell Company and, between 1961 and 1982, 10,600 tons were imported (PNUMA, 2002). Recently this amount decreased to 300 tons (1995) and 0.02 tons (1998) (MDIC, 2009). Same history of use has HCB, whose importations showed a accentuate decrease: with 834 tons imported in 1965, 4 tons during 1989–1996 and only 72 kg between 1997 and 2004 (MDIC, 2009). CHLs were not widespread used within the South America and the last importation to Brazil was 15 tons between 1989 and 1996 (MDIC, 2009), what explains their low levels and apparently decreased in the last decade. On the other hand, the steady levels of Mirex could be a result of its high stability since has not been used recently in the region (PNUMA, 2002).

Even slightly, DDTs levels also decreased over 1994–2004 indicating the effect of restrictions in their use. This effect can be better observed when data from 2004 are compared to data from 1979 (O'Shea et al., 1981). Even though O'Shea et al. (1981) used packed columns – which is known to underestimate DDTs concentrations by 30–40% – they found levels in 1979 much higher (~95%) than those found in 2004.

Although several studies show a decrease in PCBs levels (e.g. Aguilar and Borrel, 2005; Borrel and Aguilar, 2007; Dietz et al., 2004), the suggested steady state of PCBs levels presented here has also been reported in some previous studies using marine mammals as bioindicators (Aono et al., 1997; Hobbs et al., 2001; Kajiwara et al., 2002; Tanabe et al., 2003). This discrepancy is apparently due to: (1) there is faster declining trend in the regions where contamination was initially high and close to the source of contamination (Aguilar and Borrel, 2005), which it could be the explanation for PCBs decreasing levels in some areas (e.g. Borrel and Aguilar, 2007); (2) any decline in the environment input of persistent organochlorines is detected later in organisms situated in the top of the trophic web than those feeding at low trophic levels (Tanabe et al., 2003). Besides, the stable levels found in *P. blainvillei* samples could be due to recent environmental inputs caused by releases from remaining stocks of PCB-containing equipments – the total stock of PCBs in Brazil has been estimated to be about 130,000 tons; 10% of the total worldwide production – and environmental recycling. Breivik et al. (2007) suggested that levels of PCBs in marine biota are unlikely to decline before 2010–2030, since it is estimated the only a small fraction (about one third) of the total PCB released in the environment has reached the oceans (Tanabe, 1988).

To provide further insights into organochlorine trends the composition of DDTs and PCBs was also examined. The proportion of *p,p′*-DDE to total DDTs increased slightly during the period of study (from 0.75 to 0.79). These values confirm that the southwestern Atlantic is a "weathered" system where no significant new inputs of DDTs have occurred during the last decade. Also, the decrease in the DDTs/PCBs ratio, about 75% over 1994–2004, support that DDTs concentrations decreased faster than PCBs. This suggests the existence of a steady source of PCBs in the Southern Brazilian ecosystem, possibly from the remaining stocks of equipment containing PCBs (e.g. old capacitors and transformers). Both more recalcitrant and less persistent PCBs, as well as more toxic congeners (*ortho* PCBs), did not show any difference during the sampling period.

### 3.4. Comparison with other studies

POPs residues detected in *P. blainvillei* were compared with levels reported in small cetaceans from other regions. Geographical

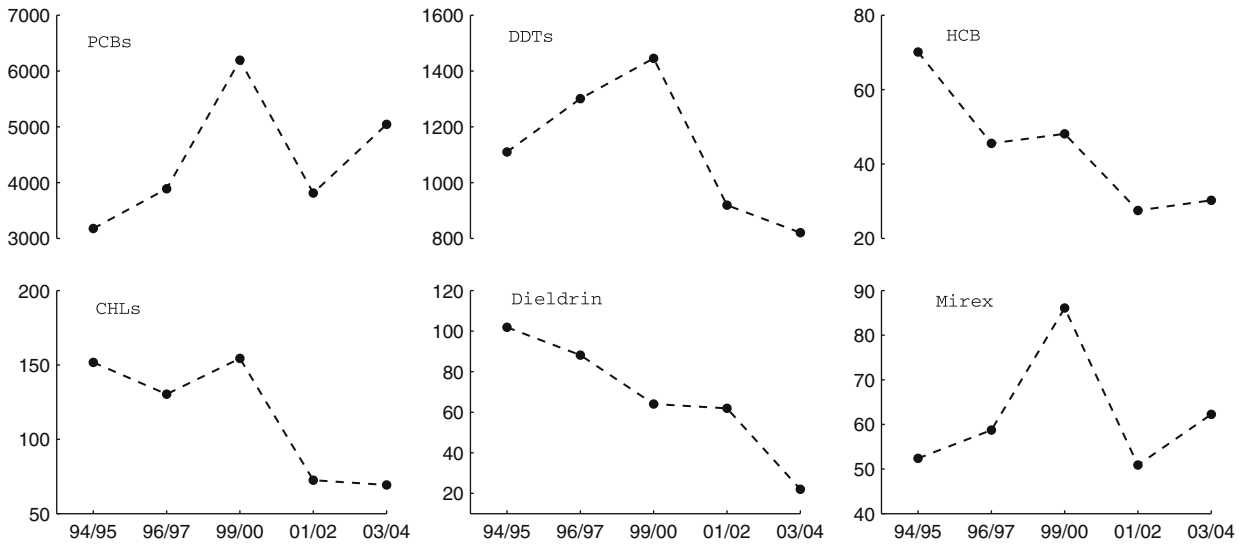


**Fig. 3.** Concentration ng $g^{-1}$ lw of PCBs and chlorinated pesticides in *Pontoporia blainvillei* over the last decade.

comparisons are necessarily limited because of the numerous sources of variability across the studies. Therefore, only a few specific comparisons are discussed here, together with general trends.

On the global scale, concentrations in franciscana are much lower than those from the Northern Hemisphere (e.g. Borrel and Aguilar, 2007; Kajiwara et al., 2002), except for *Sousa chineses* from India (Kajiwara et al., 2006) and *Grampus griseus* from Italy (Storelli and Marcotrigiano, 2000). Within the Southern Hemisphere, concentrations of PCBs were higher than those found in Australian and African cetaceans (de Kock et al., 1994; Law et al., 2003) and DDTs were lower than levels reported in Africa and slightly higher than concentrations found in Australia (de Kock et al., 1994; Law et al., 2003). In comparison with another franciscana population from southeastern Brazil (Kajiwara et al., 2004), the levels were very similar for PCBs, CHLs and HCB, but lower for DDTs.

## 4. Conclusions

Overall organochlorines concentrations in blubber of *P. blainvillei* were lower than levels from the literature; however the possibility of adverse effects cannot be discarded. About temporal trends, levels of chlorinated pesticides showed a slightly decreased in the last 10 years. Since the use of these compounds has been prohibited only in the mid-eighties it is expected more significant decreasing in the next years. Among pesticides, Mirex levels were an exception and, like PCBs, showed no variation during the last decade. Among the South America countries, Uruguay is the only countries where Mirex was not prohibited, suggesting a possible source of this compound to the region (PNUMA, 2002). The steady PCBs levels could be due to recent input from remaining stocks, so efforts should be done to identify and discontinue these contamination sources. Furthermore, continuing investigations should be conducted in order to follow the future trends of POPs in this region.

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