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Dechlorane-Related Compounds in Franciscana Dolphin (*Pontoporia blainvillei*) from Southeastern and Southern Coast of Brazil

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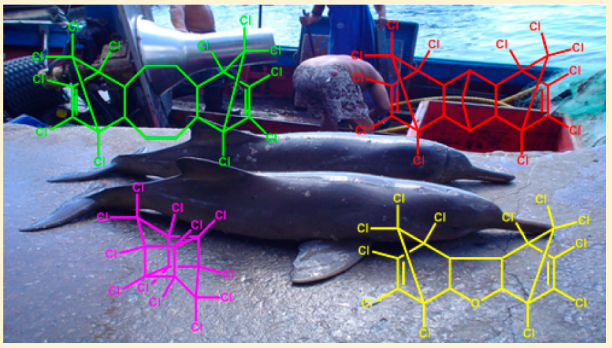
Supporting Information

ABSTRACT: Concentrations of Dechlorane (Dec) 603 (0.75 ng/g lipid weight (lw); mean) and Dec 602 (0.38 ng/g lw; mean) were quantified in more than 95% of the franciscana (*Pontoporia blainvillei*) dolphin samples, whereas the frequency of detection decreased to 75% for Dechlorane Plus (DP) (1.53 ng/g lw, mean). The presence of Chlordene Plus (CP) was also observed (0.13 ng/g lw, mean) in half of the samples. On the contrary, Dec 604, decachloropentacyclooctadecadiene ($aCl_{10}DP$), and undecachloropentacyclooctadecadiene ($aCl_{11}DP$) concentrations were below the limit of quantifications in all cases. To the best of our knowledge, this is the first article reporting the presence of Dec 603, Dec 602, and CP in mammals. For comparative purposes, levels of Mirex, polybrominated diphenyl ethers (PBDEs), and decabromodiphenylethane (DBDPE) are also reported. Considering geographic distribution evaluation together with the strong positive correlations found between DP and PBDEs ($r_s = 0.63$; $p < 0.01$), highly anthropogenic areas were identified as potential sources of these chemicals in this dolphin species. However, local sources for Dec 602, 603, Mirex, CP, and DBDPE were not found indicating that in this case historical use and/or atmospheric transport and deposition may play an important role in their fate.



INTRODUCTION

Dechloranes 602 (Dec 602; $C_{14}H_4Cl_{12}O$), 603 (Dec 603; $C_{17}H_8Cl_{12}$), 604 (Dec 604; $C_{13}H_4Br_4Cl_6$), and Dechlorane Plus (DP or Dec 605; $C_{18}H_{12}Cl_{12}$) have been used since the 1960s as additive halogenated flame retardants. Nevertheless, their production became important since the 1970s, when they were introduced as replacements of Mirex (also named Dechlorane; $C_{10}Cl_{12}$) in fire retardant applications. Although DP and DP analogues (Dec 602, 603, and 604) have been used for nearly 50 years, until recently (2006[1] for DP and 2010[2] for DP analogues) there was no evidence of their presence in the environment. The flame retardant performance characteristics of DP allow its use in electrical and electronic applications such as wires, cables, electronic circuits, as well as plastic roofing materials.[3] However, in some applications when DP does not meet specific voltage leakage and thermal standards, mixtures of Dec 602 and 604 have been used.[4]

Unfortunately, data related to DP production are scarce, or unavailable when it comes to the DP analogues. To date, only two DP manufacturing facilities have been identified: OxyChem in Niagara Falls (United States)[1] and Anpon Electrochemical Company in Huai'an (China).[5] DP is considered a high

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production volume chemical in the United States, included in the Domestic Substance List published by Environment Canada, and classified as a low production volume chemical in Europe, where it was proposed by the European Commission as a replacement for Deca-BDE, which suggested that its use will increase in coming years. Dechloranes 602, 603, and 604 were also patented by Hooker Chemicals (now Occidental Chemical Company, OxyChem)[6] in the United States. In addition, Dec 602 and 604 are included in the Environment Canada Nondomestic Substance List, thus international trade is recognized.

Dechloranes were designed and synthesized to minimize bioavailability of the chlorinated norbornene by increasing their molecular size over the classical organochlorine pesticides. Nevertheless, their presence in fish,[2,6,7] birds,[8−10] and humans[11] has been demonstrated. Trophic magnification factors (TMF) have also been studied reporting levels for DP isomers approximately five times higher than those of polybrominated diphenyl ethers (PBDEs).[12] Long range atmospheric transport of DP[13] has been reported as well, so it is logical that a recently published critical review[4] suggested that DP and its analogues may be candidates for Annex D evaluation under the Stockholm Convention (www.pops.int). The same study highlighted the need to obtain more monitoring and bioaccumulation information to help to elucidate their dispersion and potential impact in biota.

The franciscana dolphin (*Pontoporia blainvillei*) is a small cetacean that occurs only along the east coast of South America between Itaúnas (Espírito Santo State, Brazil, 18° 25́ S) and Golfo Nuevo (Chubut Province, Argentina, 42° 35́ S).[14] The species has been described to have great site fidelity,[15] and it does not appear to undergo large seasonal migrations. This dolphin is characteristically found in coastal habitats, generally turbid waters up to 30 m depth, with a decrease in population density as it moves away from the coast. The species occupies top trophic-levels, feeding mainly on shallow-water fish (sciaenids, engraulids, gadids, and carangids), cephalopods, and crustaceans.[16] However, the presence of many kinds of debris including discarded fishing gear such as pieces of nylon net, cellophane, and plastic fragments found in the stomachs of franciscanas was also reported.[16]

The franciscana dolphin is included in the Appendix II of the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), and listed as vulnerable in the International Union for Conservation of Nature and Nature Resources (IUCN) Red List of Threatened Species, being mortality from incidental entanglement in gill nets, by far the greatest threat to this species. Considering geographical distribution, habitat, and ecology characteristics described above, it is not difficult to propose others anthropogenic activities that could affect the species survival. Franciscana is subjected to pollution from several sources like the discharge of chemical contaminants from domestic, agricultural, and industrial wastewaters, boat traffic, tourism, and fishing operations, as demonstrated by the presence of heavy metals,[17] chlorinated pesticides, polychlorinated biphenyls (PCBs),[18,19] and also organobrominated,[20,21] perfluorochemicals[22] compounds, and pyrethroid insecticides[23] in specimens from Brazil, Uruguay, and Argentina. This demonstrates the potential use of these dolphins to assess environmental pollution.

In this work, the occurrence of some new halogenated norbornene flame retardants (Dec 602, 603, 604, DP, and Chlordene Plus (CP)) in dolphins from the Brazilian coast is reported. To the best of our knowledge, this is the first study on DP analogues in mammals. The presence of DP degradation products decachloropentacyclooctadecadiene (aCl_{10}DP) and undecachloropentacyclooctadecadiene (aCl_{11}DP) was also investigated. To establish comparisons and potential relations with other flame retardants, concentrations of polybrominated diphenyl ethers (PBDEs) and decabromodiphenylethane (DBDPE) were also measured. Sex, age, and geographic distribution differences were evaluated.

MATERIALS AND METHODS

Sample Collection. The franciscana distribution range was divided into four stocks, namely Franciscana Management Areas (FMAs).[14] FMA I included the coastal waters of Espírito Santo (ES) and Rio de Janeiro states; FMA II covers São Paulo (SP) to Santa Catarina (SC); FMA III is comprised of the coastal waters of Rio Grande do Sul (RS) and Uruguay; and FMA IV represents the coastal waters of Argentina (Figure 1). A total of 20 liver samples were either obtained from animals accidentally caught in gill nets or found stranded along the Southeastern and Southern coast of Brazil between 1994 and 2008. Samples covered all Brazilian FMAs. As in previous studies from the same area, dolphin sexuality maturity stage was determined from total length inside each FMAs.[21] Individuals were separated in three groups: juveniles (immature animals), male adults, and female adults (sexually mature individuals). After dissection, samples were lyophilized and preserved frozen at −20 °C until analysis.

Chemicals. Dec 602 (95%, CAS# 31107−44−5), Dec 603 (98%, CAS# 13560−92−4), and Dec 604 (98%, CAS# 34571−16−9) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). CP (CAS# 13560−91−3), aCl_{10}DP, aCl_{11}DP, and DP (CAS# 13560−89−9; *syn-DP* and *anti-DP* standards), were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). Mirex (CAS# 2385−85−5) was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). Two ^{13}C labeled polychlorinated biphenyls solutions (WP-LCS, containing among others $^{13}C_{12}$−CB-189) and (WP-ISS, containing $^{13}C_{12}$−CB-170) purchased from Wellington laboratories Inc. (Guelph, ON, Canada) were used as the surrogate and internal standards for all dechlorane related compounds. For DBDPE and PBDEs determinations, $^{12}C_{14}$-DBDPE, $^{13}C_{14}$-MDBDPE, BDE-CVS-E (five individual calibration solutions containing $^{12}C_{12}$−PBDEs and $^{13}C_{12}$−PBDEs), MBDE-MXE (containing $^{13}C_{12}$−BDE-3, −15, −28, −47, −99, −153, −154, −183, −197, −207 and −209, as surrogate standard), and BDE-CVS-EISS (containing $^{13}C_{12}$−BDE-138 as the internal standard) were obtained from Wellington laboratories Inc. (Guelph, ON, Canada). Other chemicals including: anhydrous sodium sulfate, sulfuric acid (95−97%), and organic trace analysis grade solvents (hexane, dichloromethane, ethyl acetate, and toluene) were purchased from Merck (Darmstadt, Germany).

Sample Preparation. DP, Dec 602, Dec 603, Dec 604, CP, aCl_{10}DP, aCl_{11}DP, Mirex, PBDEs, and DBDPE analyses were performed on extracts previously prepared for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and PCBs determination.[24] Prior to the extraction step, the samples were spiked with $^{13}C_{12}$ labeled surrogate standards (including WP-LCS and MBDE-MXE). Extractions were performed with an Accelerated Solvent Extraction system (ASE 100, Dionex, Sunnyvale, CA, USA) using hexane as solvent, at 100 °C, 1500 psi, 90% flush volume and three static cycles. Liver samples, ranging from 0.4 to 3.1 g were homogenized with 15 g of

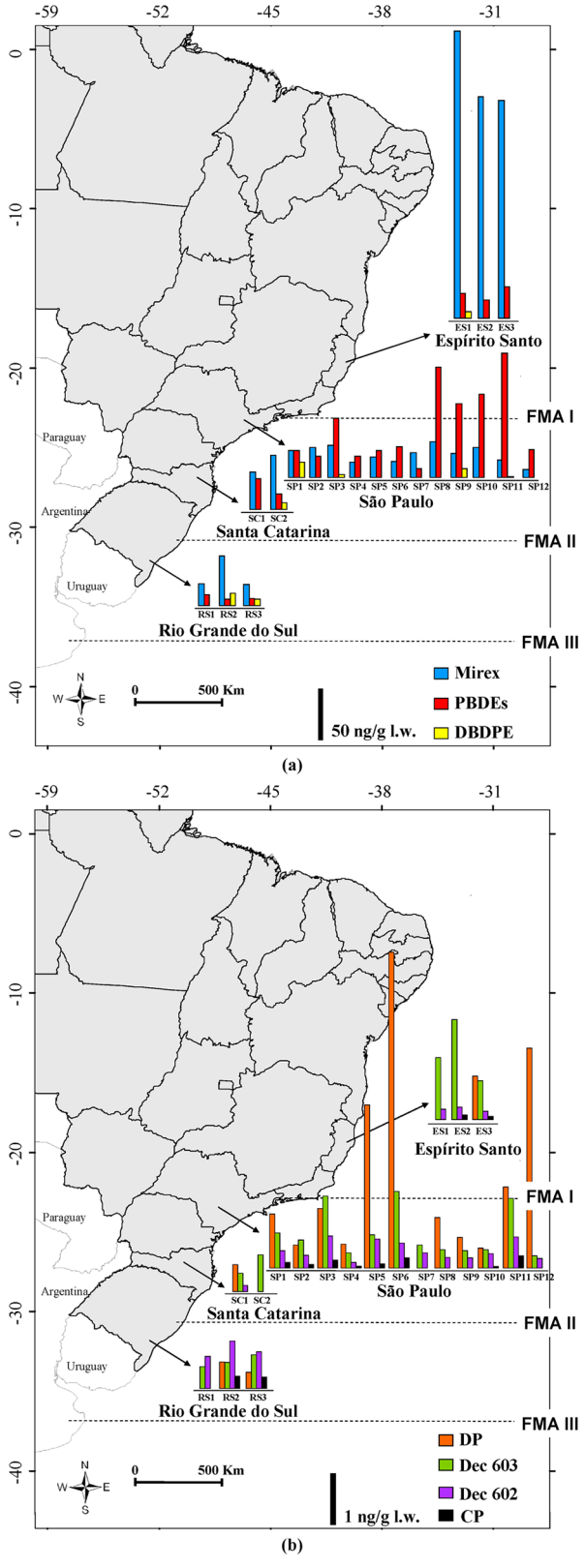

Figure 1. Distribution of (a) Mirex, PBDEs, DBDPE (b) DP, Dec 603, Dec 602, and CP concentrations (ng/g lw), measured in 20 franciscana dolphin liver samples from the Brazilian coast. Franciscana Management Areas (FMAs) were reproduced from Secchi et al., 2003.

anhydrous sodium sulfate and introduced into a 34 mL cell that were previously loaded by inserting two cellulose filters followed by 2 g of anhydrous sodium sulfate. The resulting extract was evaporated to constant weight for gravimetric lipid determination, and then redissolved in hexane. Sample purification consisted of two steps: a liquid extraction with 50 mL of concentrated sulfuric acid, followed by automatic purification using a Power Prep System (FMS, Inc., USA) with multilayer silica, alumina, and carbon columns. Two fractions were obtained: Fraction A, containing DBDPE, PCDD/Fs, and nonortho PCBs; Fraction B, containing dechlorane related compounds (Dec 602, Dec 603, Dec 604, CP, Mirex, and DP), PBDEs, and mono-ortho PCBs. Both fractions were concentrated to dryness under a flow of nitrogen, and redissolved in nonane spiked with the internal standards ($^{13}C_{12}$–PCDD/Fs for Fraction A; BDE-CVS-EISS and WP-ISS for Fraction B).

Chemical Analysis. DP and DP analogs were analyzed by high resolution gas chromatography coupled to high resolution mass spectrometry (MicroMass Autospec Ultima HRMS). The HRMS was operated in electron ionization mode (EI) at a resolution greater than 10 000 (10% valley). Chromatographic separation was carried out on an Agilent 6890 GC fitted with a 15 m DB-5-MS capillary column (0.25 mm i.d., 0.10 μm film thickness; J&W Scientific). Splitless injections of 1 μL were made onto an injector set isothermally at 280 °C. The initial oven temperature was set at 120 °C with a 1 min hold time, ramped at 20 °C/min to 240 °C, ramped at 5 °C/min to 275 °C, ramped at 40 °C/min to 320 °C, and held 4 min. The transfer line and source temperatures were set at 280 °C. Ions monitored were: 271.8102/273.8072 for Mirex, Dec 602 and CP; 262.8570/264.8540 for Dec 603; 417.7026/419.7006 for Dec 604; 201.8911/203.8881 for Dec aCl_{10}DP, and 237.8491/239.8462 for aCl_{11}DP. Because dechloranes eluted in the mono-ortho PCB fraction, $^{13}C_{12}$ PCB labeled ($^{13}C_{12}$–CB-189 as surrogate, and $^{13}C_{12}$–CB-170 as internal) standards were used to quantify target analytes. PBDEs and DBDPE were analyzed by low resolution mass spectrometry on an Agilent 5973 MSD operated in EI and in a Varian 320-MS-TQ operated in MS/MS mode, respectively. Complete details for both methods were previously reported.[25,26]

QC/QA. Criteria for quantification were: retention time and isotope ratio found within two seconds and 15% of the standard, and a signal-to-noise ratio greater than five. The average surrogate standard recoveries ranged from 56% to 98% (67 ± 11%; mean ± SD) for $^{13}C_{12}$–CB-189. The limits of detection (LODs) and quantification (LOQs) of the method were calculated as the concentration corresponding to a signal-to-noise ratio of 3 and 10, respectively. LODs and LOQs ranged between 0.002 and 0.181 ng/g lipid weight (lw) and between 0.006 and 0.603 ng/g lw for Dec 603 and Mirex. Injections of nonane, as instrumental blanks, were used to assess instrument contamination. Two procedural blanks of spiked sodium sulfate were treated as samples through the entire process. Concentrations of Mirex, CP, Dec 602, 603, 604, DP, Dec aCl_{10}DP, Dec aCl_{11}DP, PBDEs, and DBDPE in both procedural and instrumental blanks were below LODs.

Statistical Analysis. Statistical analysis was performed using SPSS Statistics software (version 17.0). Nonparametric statistical tests were used since data significantly deviated from a normal distribution (Shapiro-Wilk Test). Spearman's Rank Order correlations were run to determine interchemical relationships (Table S1 of the Supporting Information) and Mann–Whitney U test was used to investigate differences between pollutant levels among geographic locations and age/sex classes. To avoid the influence of maturity stage in female samples[20,27] caused by the maternal transfer of organohalogen compounds to offspring during reproductive process (gestation and lactation), adult female samples were not considered in the

statistical analysis. The level for significance was set at $p < 0.05$ for all tests. Concentrations were lipid normalized before statistical analysis and samples with values below LODs were considered as zero. No significant differences ($p > 0.05$) were observed between biological characteristics (lipid content and dolphin length) and sampling locations (ES, SP, SC, and RS states), which corroborates the representativeness of the sample.

For comparative purposes, chemical structures, physical/chemical properties, and environmental fate estimations (Tables S2 and S3 of the Supporting Information) were calculated with the EPI (Estimation Programs Interface)[28] *SuiteTM* v 4.10 (*KAOWIN*, *WSKOWWIN*, and *BCFBAF* software). Whole body (except liver) half-life data in juvenile rainbow and lake trout from Tomy et al 2004 and 2008 were also included.[29,30]

RESULTS AND DISCUSSION

Concentrations of Dechlorane Related Compounds, PBDEs, and DBDPE in Dolphins. Results for DP, Mirex, Dec 602, Dec 603, CP, PBDEs, and DBDPE in dolphin hepatic samples were listed in Table 1. All concentrations were expressed in ng/g lw. Dec 604, $aCl_{10}DP$, and $aCl_{11}DP$ were below detection limit in all of the samples and thus they are not included. Lipid content in the liver was 8.4 ± 1.8% (mean ± SD). No correlations were found between lipid values and any contaminant evaluated. Likewise, no differences were observed between geographic location and age/sex classes with the lipid content. Mirex (57.0−33.5 in the unit ng/g lw; mean - geomean, same for the following compounds) and PBDEs (36.4−26.0) resulted the major contaminants, following in decreasing order by DBDPE (7.29−5.60) and DP (1.53−0.98), Dec 603 (0.75−0.63), Dec 602 (0.38−0.32), and CP (0.13−0.11). Frequency of detection differed greatly between analytes: Mirex, PBDEs, and Dec 603 (100%) > Dec 602 (95%) > DP (75%) > CP (60%) > DBDPE (40%).

Zitko conducted a laboratory study in 1980 where the bioaccumulation of Dec 602, 603, and 604 was demonstrated in juvenile Atlantic salmon.[31] However, concentrations of DP analogs were not detected in wildlife until 30 years later.[6] To date, only three studies have reported the presence of Dec 602, 603, and 604 in wildlife biota: Laurentian Great Lakes lake trout,[6] eggs of peregrine falcons from Canada and Spain,[9] and oyster samples from Northern China.[32] However, to the best of our knowledge there are no previous studies on DP analogs (Dec 602, 603 and 604) in mammals. Dechlorane patterns in wildlife are ranked in literature as follows: Mirex > Dec 602 > DP > Dec 603 > CP in lake trout,[6] Mirex > Dec 602 > DP ≈ Dec 603 > Dec 604 in peregrine falcon eggs,[9] and DP ≈ Mirex ≫ Dec 602 and Dec 603 in oyster.[32] Relatively high DP levels were found in the latter study, albeit as authors suggested, they could be related to an unknown source of DP in the oyster's habitat, which is also reflected in the high DP values found in seawater samples from same area.[32] Caution should be exercised regarding interspecies and intersite comparisons; however, results from these studies are in agreement with the dolphin dechloranes pattern where Mirex was also detected at orders of magnitude higher than DP, Dec 603, and Dec 602. Even by accepting data gaps related to dechloranes production and use, it could be assumed that Mirex was produced in greater amounts compared to the other dechloranes. Nevertheless, given that Log K_{ow} greatly varies among dechloranes, differences in terms of bioaccumulation could be expected. As can be observed in Table S3 of the Supporting Information, Mirex presented the lowest log K_{ow} (7.01), followed by Dec 602 (8.05) > Dec 603 (11.2) ≈ DP (11.3) ≈ Dec 604 (11.5). This fact could explain the major contribution of Mirex to the dechlorane pattern in dolphins, and also in biota, because biomagnification potentials were described to dramatically decrease with log K_{ow} greater than 8.[12,30]

The Mirex concentrations measured in this present study (ranging from 7.63−275 ng/g lw) were similar to those previously reported in franciscana individuals from Rio Grande do Sul (22.4−119 ng/g lw, min−max)[18] and São Paulo (5−100 ng/g lw, min−max),[19] and could be related to its historical use in the covered area. In accordance to national implemented policies and the Stockholm Convention, Mirex was banned in most countries of South America, but its historical production and use as both pesticide and flame retardant have been recognized in Brazil.[19] No statistically significant correlations were found between hepatic Mirex levels and those obtained for the rest of contaminants (DP, Dec 602, Dec 603, CP, PBDEs, DBDPE).

Concentrations of DP in franciscana dolphins (1.53 ng/g lw, mean) are to the best of our knowledge the first data regarding its presence in cetaceans. Levels of DP were reported in aquatic biota,[2,6,7,12,32] bird eggs,[8−10] and even human[11] samples from North America, Europe, and Asia. Nevertheless, the present study represents the first evidence of DP bioacumulation in biota from the Southern Hemisphere. There are great difficulties when interspecies comparisons are performed, however these should be lower when levels are compared to other aquatic species. DP concentrations in franciscana dolphins, ranging from n.d. to 6.26 ng/g lw, were lower compared to those reported in oyster samples from China (250 ng/g lw)[32] where the extremely high levels of DP in a freshwater food web (up to 9630 ng/g lw) were attributed to e-recycling activities.[12] Conversely, DP concentrations in franciscana were in the range of those reported in the Great Lakes including zooplankton (0.55 ng/g lw), mussels (0.43 ng/g lw), walleye (0.76 ng/g lw), or goldeye (0.80 ng/g lw).[7]

Anti-DP fractions (f_{anti}) were calculated as the concentration of the anti isomer divided by sum of *syn*-DP and *anti*-DP concentrations. As discussed previously, two DP manufacturing plants have been identified to date, but unfortunately it is impossible to identify the origin of the DP in the liver of franciscana as commercial mixtures and products containing them are sold worldwide. In addition, although there have been some efforts to obtain data regarding DP isomer-specific thermal degradation, photodegradation, and water solubility that can be linked to species-specific bioaccumulation, biomagnifications, and/or biodegradation, they are scarce or unclear. For instance, Tomy et al., 2007, reported an *anti*-DP enrichment upon moving up the trophic chain in aquatic organism from Lake Ontario and Lake Winnipeg,[7] but an opposite behavior was found in the freshwater food web from a highly contaminated site in South China.[12] However, f_{anti} obtained in the present study (0.71 ± 0.16 (mean ± SD) closely resembles both technical products: OxyChem (f_{anti} = 0.69 ± 0.5; mean ± SD),[3] and Anpon (f_{anti} = 0.60)[5] mixtures.

Concentrations of Dec 602 and Dec 603 in franciscana dolphins were quite similar, but this is not in agreement with previous results in aquatic biota, where higher levels were reported in the former compare to the latter.[2,6,32] The Dec 602 estimated bioaccumulation factor (log BAF = 7.03) is higher than the one obtained for Dec 603 (Log BAF = 4.43) (Table S3

Table 1. Biological Data and Chemical Concentrations (ng/g Lipid Weight) in Franciscana (*Pontoporia blainvillei*) Liver Samples from Brazil[a]

sampling	code	type	sex	body length (cm)	lipid content (%)	PBDEs	DBDPE	Mirex	CP	Dec 602	Dec 603	*syn-DP*	*anti-DP*	DP	*Fanti*
Espírito	ES1	JUV	M	114	5.3	24.0	6.13	275.1	n.d.	0.20	1.22	n.d.	n.d.	n.d.	
Santo	ES2	AM	M	117	11.0	17.7	n.d.	211.8	0.10	0.24	1.99	n.d.	n.d.	n.d.	
	ES3	JUV	M	100	10.4	30.0	n.d.	208.6	0.06	0.16	0.77	0.39	0.47	0.86	0.55
	mean ± SD			110 ± 9	8.9 ± 3.1	23.9 ± 6.2		231.8 ± 37.5	0.08 ± 0.02	0.2 ± 0.04	1.33 ± 0.61				
	min−max			100−117	5.3−11	17.7−30.0		208.6−275.1	n.d. − 0.1	0.16−0.24	0.77−1.99				
São Paulo	SP1	AF	F	137	9.5	26.0	14.9	26.2	0.11	0.34	0.70	0.41	0.66	1.07	0.62
	SP2	JUV	F	108	11.3	20.1	n.d.	28.8	0.07	0.26	0.56	0.17	0.29	0.46	0.63
	SP3	JUV	F	95	8.7	56.8	2.85.	30.7	0.16	0.64	1.43	0.53	0.65	1.19	0.55
	SP4	JUV	F	109	9.5	20.5	n.d.	14.9	0.04	0.12	0.31	0.18	0.30	0.48	0.62
	SP5	JUV	F	90	10.1	26.1	n.d.	19.4	0.08	0.57	0.65	1.08	2.17	3.24	0.67
	SP6	AF	F	141	8.7	29.1	n.d.	15.6	0.20	0.50	1.52	1.37	4.89	6.26	0.78
	SP7	AM	M	116	10.2	8.50	n.d.	23.8	n.d.	0.30	0.46	n.d.	n.d.	n.d.	-
	SP8	JUV	M	94	6.3	105.4	n.d.	34.3	n.d.	0.21	0.37	0.42	0.58	1.00	0.58
	SP9	JUV	M	100	7.6	70.8	8.53	22.8	n.d.	0.20	0.35	0.18	0.42	0.60	0.70
	SP10	JUV	M	112	7.6	80.0	n.d.	28.7	0.03	0.29	0.36	0.16	0.23	0.39	0.59
	SP11	JUV	M	114	9.7	119.1	0.84	17.0	0.24	0.62	1.39	0.50	1.12	1.61	0.69
	SP12	n.a.	M	n.a.	7.4	26.3	n.d.	7.63	n.d.	0.20	0.25	1.30	3.07	4.36	0.70
	mean ± SD			111 ± 17	8.9 ± 1.4	49.1 ± 36.7	6.8 ± 6.3	22.47 ± 7.78	0.12 ± 0.08	0.35 ± 0.18	0.69 ± 0.47	0.57 ± 0.46	1.31 ± 1.49	1.88 ± 1.92	0.65 ± 0.07
	min−max			90 - 141	6.3 - 11.3	8.50 - 119.1	n.d. - 14.9	7.63 − 34.7	n.d. - 0.24	0.12 - 0.64	0.25 - 1.52	n.d. - 1.37	n.d. - 4.89	n.d. - 6.26	0.55 - 0.78
Santa	SC1	JUV	M	107	6.2	29.4	n.d.	35.4	n.d.	0.12	0.36	n.d.	0.54	0.54	1.00
Catarina	SC2	JUV	M	83	6.7	14.7	6.54	51.9	n.d.	n.d.	0.72	n.d.	n.d.	n.d.	
	Mean ± SD			95 ± 17	6.5 ± 0.3	22 ± 10.4		43.6 ± 11.6			0.54 ± 0.26				
	min−max			83−107	6.2−6.7	14.7−29.4		35.4−51.9			0.36−0.72				
Rio Grande	RS1	AM	M	129	5.5	10.8	n.d.	21.1	n.d.	0.63	0.43	n.d.	n.d.	n.d.	
do Sul	RS2	AM	M	134	8.9	6.31	11.9	47.3	0.24	0.94	0.52	n.d.	0.52	0.52	1.00
	RS3	n.a.	M	125	7.9	7.24	6.61	20.1	0.22	0.73	0.67	n.d.	0.32	0.32	1.00
	mean ± SD			129 ± 5	7.4 ± 1.8	8.1 ± 2.3	9.3 ± 3.8	29.5 ± 15.4	0.23 ± 0.01	0.77 ± 0.16	0.54 ± 0.12		0.42 ± 0.14	0.42 ± 0.14	1 ± 0
	min−max			125−134	5.5−8.9	6.31−10.8	n.d.−11.9	20.1−47.3	n.d.−0.24	0.63−0.94	0.43−0.67		n.d.−0.52	n.d.−0.52	1−1
TOTAL	Mean ± SD			112 ± 16	8.4 ± 1.8	36.4 ± 32.6	7.29 ± 4.54	57.0 ± 77.0	0.13 ± 0.08	0.38 ± 0.24	0.75 ± 0.49	0.56 ± 0.44	1.08 ± 1.31	1.53 ± 1.74	0.71 ± 0.16
	min−max			83−141	5.3−11.3	6.3−119.1	n.d.−14.9	7.63−275.1	n.d.−0.24	n.d.−0.94	0.25−1.99	n.d.−1.37	n.d.−4.89	n.d.−6.26	0.55−1.00

[a]n.a. = Data not available; n.d. = Not detected; JUV = juvenile; AM = adult male; AF = adult female.

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of the Supporting Information), which correlates well with results obtained in an vivo bioaccumulation study in Atlantic salmon,[31] and biota-sediment accumulation factors calculated in Great Lakes lake trout.[6] However, estimated biotransformation half-lifes also differ between Dec 602 (2752 day) and Dec 603 (138 000 day) (Table S1 of the Supporting Information) indicating that biotransformation and/or biomagnification rates should also be considered. As mentioned previously, there are many difficulties regarding interspecies and interlocation comparisons, however differences between Dec 602 and 603 levels among aquatic trophic levels reinforce the need of further research to investigate their behavior in biota. Concentrations of Dec 603 were reported as impurities in Aldrin and Dieldrin pesticides,[33] although contribution in no case exceed 1% of the commercial mixtures. Brazil recognized the production and use of these chemicals until 1998 after which they were banned (Administrative Rule 329, 1985, Ministry of Agriculture). Considering the presence of Aldrin and Dieldrin was reported in blubber and liver tissue from marine mammals,[27,34] the occurrence of Dec 603 in these dolphins could be associated to historical use and production of these pesticides.

Dec 604 was not found in any of the samples analyzed at levels above the quantification limits. This result is in agreement with those obtained in oyster samples collected in China.[32] In addition, Shen et al., 2010 evaluated the presence of Dec 604 in lake trout and whitefish from Lake Superior, Lake Huron, Lake Erie, and Lake Ontario, but it was only detected in Lake Ontario which, as authors suggest, is indicative of inputs resulting from its manufacturing in the Niagara area.[2] As mentioned in the introduction, Dec 604 was patented by Hooker chemicals.

Concentrations of CP were reported in tributary sediment samples of the Laurentian Great Lakes,[33] where CP had the lowest overall concentrations compared to the other dechloranes. However, the present study is the first evidence of its presence in biota. CP was measured in 40% of franciscana dolphin hepatic samples but at low levels compared to the other analytes. CP is also patented by OxyChem (patents 3392136 and 4388429) as a flame retardant, and it has also been described as an impurity (<1%) in Chlordane and Chlordene commercial mixtures.[33] Overall, distribution of Dec 602 and Dec 604 in the environment appears to be related to the use of consumer products, whereas Dec 603 and CP appear to be related to the use of organochlorine pesticides.[4] Thus, considering that concentrations of CP and Dec 603 in dolphin livers exhibited good correlation (r_s = 0.54, p < 0.01), and CP and Dec 602 were also (r_s = 0.62, p < 0.01), but no association was found between Dec 603 and 602, and the use of pesticides and flame retardants as potential sources of CP in this species would be implied.

The presence of DP dechlorination products ($aCl_{10}DP$ and $aCl_{11}DP$) was also evaluated in this cetacean. However, they were not detected in any of the samples analyzed. Concentrations of $aCl_{10}DP$ and $aCl_{11}DP$ have been reported in abiotic[4] and biotic[9,10] samples. Nevertheless, to date there is no evidence of their presence in aquatic food webs. As a result of their structural similarity to Mirex, concentrations of dechlorinated DP moieties in sediments from Niagara River and Lake Ontario[4] were attributed to DP photodegradation, but controversy exists related to their presence in biota. Concentrations of $aCl_{10}DP$ and $aCl_{11}DP$ in biological samples could be proposed to be of a metabolic origin, however, in a laboratory study conducted by Tomy et al. (2008) they were not detected in juvenile rainbow trout exposed to DP,[30] which suggested that bioaccumulation after abiotic DP degradation may also play an important role, particularly in wildlife samples. As mentioned earlier, although some of the dolphin samples contained relative high DP levels (up to 6.26 ng/g lw), concentrations of $aCl_{10}DP$ and $aCl_{11}DP$ were below LODs in all cases. These results may indicate that biological dechlorination of DP, or bioaccumulation of dechlorinated DP moieties may not occur in these dolphins and could reveal differences on the DP metabolic degradation mechanisms compared to PBDEs, whose biotransformation via debromination has been described to have an important role in biota.[29]

Concentrations of PBDEs (ranging from 6.31 to 119 ng/g lw; Tables 1 and Table S4 of the Supporting Information) were in the same range than those found for Mirex, and similar to those reported in previous studies (5.10−229 ng/g lw)[35] in the same species. A characteristic congener pattern was obtained in all samples, with BDE-47 being the major congener (accounting for 47 ± 9% of the total PBDEs; mean ± SD) followed by BDE-99 (17 ± 5%), BDE-209 (12 ± 17%), BDE-100 (12 ± 4%), BDE-154 (6 ± 3%), BDE-153 (4 ± 2%), BDE-28 (0.95 ± 0.95%), BDE-17 (0.18 ± 0.19%), BDE-206 (0.16 ± 0.46%), and BDE-207 (0.08 ± 0.24%). Strong positive correlations were found for BDE-154, BDE-153, BDE-100, BDE-99, and BDE-47 (r_s > 0.85, p < 0.01) indicating that penta-BDE technical mixtures were used in Southeastern and Southern Brazil. These congeners were detected in all samples, but the frequency of detection above the LOQs decreased to 60% and 15% for BDE-209 and nona-BDEs (BDE-206 and BDE-207), respectively. BDE-209, BDE-207, and BDE-206 made up a small fraction of total PBDEs; however, their presence in franciscana dolphins results of special interest. Good correlations (r_s > 0.66, p < 0.01) were also obtained for BDE-209, BDE-207, and BDE-206 and, excluding the other congeners, their contribution to total PBDEs revealed values of 94%, 4% and 2% (BDE-209, BDE-207, and BDE-206), which are well correlated with the pattern described for two Deca-BDE technical mixtures (Saytex 102E and Bromkal 82−0DE).[36]

Statistical tests also revealed a good correlation between DP and PBDEs (r_s = 0.63, p < 0.01), which indicated the use of PBDEs and DP technical mixtures in similar applications. This behavior was also found when DP isomer-specific associations were calculated, albeit lower statistically significance was obtained for *anti*-DP (r_s = 0.52, p < 0.05) compared to *syn*-DP (r_s = 0.68, p < 0.01). Furthermore, differences can be observed according to PBDEs congeners, as well. *syn*-DP correlated with BDE-154, BDE-153, BDE-100, BDE-99, and BDE-47 (r_s = 0.55, p < 0.02), whereas *anti*-DP is associated with BDE-209 and BDE-47 (r_s = 0.62 and r_s = 0.47, p < 0.02). Studies analyzing DP isomer-specific bioaccumulation are seldom reported, however, Wu et al., 2010 suggested that *syn*-DP may have bioaccumulation behavior similar to PBDEs, which is not the case for *anti*-DP.[12]

DBDPE was detected in eight samples including males and females from the four regions analyzed, at concentrations ranging from n.d. to 14.9 ng/g lw. DBDPE has been included in the list of potential flame retardant alternatives to the Deca-BDE formulation,[26] and as a consequence several studies have tried to evaluate Deca-BDE substitution degree by calculating DBDPE/BDE-209 ratios in abiotic samples. However, a similar approach should not be performed in biotic samples because it was reported that DBDPE has a lower bioavailability and/or bioaccumulation compared to BDE-209 in the mammal livers (exposed rats).[37] For comparative purpose, it could be said that

although DBDPE presented a lower frequency of detection (40%) compared to BDE-209 (70%), concentrations (7.29 ± 4.54 ng/g lw for DBDPE, and 8.54 ± 12.9 for BDE-209; mean ± SD) do not differ greatly.

Dechloranes, CP, PBDEs, and DBDPE Concentrations among Geographic Locations, and Age/Sex Classes. By trying to identify dechlorane potential sources, the influence of geographic distribution was evaluated. Spatial trends of DP, Dec 602, 603, CP, Mirex, PBDEs, and DBDPE are shown in Figure 1. No statistical differences were observed between sites and sample characteristics (lipid percentage and length). However, considering pollutant levels, statistically significant differences could be observed. As shown in Figure 1, individuals from Espírito Santo State presented higher Mirex concentrations ($p < 0.01$) than those found in other locations. Nevertheless, owing to the low number of samples obtained from ES State, this result has little statistical power and therefore do not allow us to suggest a plausible source of Mirex in the Northern range of the species distribution. Excluding samples from ES, levels of Mirex (7.63−51.9 ng/g lw, min−max) were in the same range as those previously reported in Rio Grande do Sul (22.4−119 ng/g lw, min−max)[18] and São Paulo (5−100 ng/g lw, min−max)[19] states. Statistical significance increased when individuals from São Paulo ($n = 12$) were compared to those obtained from the other states ($n = 8$). Samples from SP had higher DP and PBDEs levels ($p < 0.05$) than the rest of the samples. As mentioned previously, concentrations of both chemicals were also correlated ($p < 0.01$). Therefore, considering that PBDEs and DP were used in similar applications, their presence could be easily attributed to the high anthropogenic influence in the São Paulo State area. The estimated population in the states analyzed ranked as follows: 41.2 (SP) > 10.6 (RS) > 6.2 (SC) > 3.5 (ES) million people,[38] where SP is home to over 20% of the Brazilian population and contributing over a third of Brazil's Gross Domestic Product (GDP)[38] due to an important steadily growing industrial sector. No site differences were found for the remaining chemicals (Dec 602, 603, and CP), and consequently certain local sources could not be identified for these chemicals. This result must be viewed with caution for CP because its frequency of detection was low (60%). However, occurrence of Dec 603 and Dec 602 in samples from all states at similar levels confirms their presence in Brazil. Concentrations of dechloranes (including Dec 602 and Dec 603) were reported in air[4] and therefore atmospheric transport and/or deposition should not be disregarded; however, the relatively high temperatures of Brazilian waters may favor volatilization making deposition of pollutants from remote airborne sources less likely.[27]

The Mann-Whitney test showed no differences in the chemical content between female and male individuals. Only juvenile samples from the São Paolo State were considered. Marine mammals normally present no sex-related differences in the accumulation of pollutants, and this result is in agreement with previous studies of trace elements in the same species.[17]

Several studies have evaluated the bioaccumulation of pollutants from correlations between animal length and chemical concentrations. However, inter- and intra-FMA variations described elsewhere[23] resulting in the fact that animals collected in different areas presented similar body length but they are not necessary of the same age do not permit this comparison. To overcome this limitation, the variation of pollutants was investigated between juvenile (sexually immature) and adults (sexually mature) individuals. No statistical differences were found between Mirex, DP, Dec 602, Dec 603, and CP, for age classes. Although juvenile samples presented higher PBDEs ($p < 0.01$) levels than those found for adult males, this result is influenced by the fact that most juvenile samples (67%) were collected from the São Paulo State, which was identified as a potential source of PBDEs in franciscana dolphin hepatic samples. The effect of age in accumulation of pollutants has been studied at length in cetaceans, and both increasing[27] and decreasing[39] concentrations have been described; however, more research is needed to assess this influence on Dec 602, 603, and CP concentrations.

In summary, Dec 602, 603, DP, CP, PBDEs, and DBDPE were detected in franciscana specimens from the Southeastern and Southern coast of Brazil. To the best of our knowledge, this is the first study reporting the bioaccumulation of Dec 602, 603, and CP in mammals, and the first report presenting data of DP in cetaceans. Strong positive correlations between PBDEs and DP isomers revealed anthropogenic activities occurring in São Paulo State as potential sources of the chemicals in these individuals. However, although Dec 602, Dec 603, and CP were quantified in most of the samples, certain local sources could not be identified, suggesting that historical use of organochlorine pesticides containing these chemicals as impurities, and/or atmospheric transport and deposition may play an important role regarding their presence in Brazilian specimens.

Risk threshold levels for emerging Dechloranes are unknown; however, their presence in top trophic mammals arises high concern and strengthens the need of further research to complete gaps related to not only their toxicity and bioaccumulation potentials but also their presence and distribution in the environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results of Spearman correlation analysis; chemical structures; physical/chemical properties and environmental fate characteristics of chemicals analyzed; concentrations of PBDEs and box and whiskers diagrams for hepatic concentrations of Mirex, PBDEs, DBDPE, DP, Dec 603, Dec 602, and CP in liver samples of franciscana dolphins. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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