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Polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polychlorinated biphenyls in polar bear, penguin and south polar skua

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"Capsule": *Coplanar PCBs are the major contributors to dioxin-like toxicity to eggs of penguins and polar skua.*

Abstract

Concentrations of 2378-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (DFs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (dioxin-like PCBs) were measured in livers of polar bears from the Alaskan Arctic and in eggs of Adelie penguin and south polar skua and weddell seal liver, fish and krill from Antarctica. This is one of the first reports to document the concentrations of PCDDs/DFs in polar bear livers from Alaska, and in penguin and skua eggs from Antarctica. Concentrations of total PCDD/DFs in livers of polar bears ranged from 8 to 66 (mean: 26) pg/g, on a lipid weight basis. Concentrations of total PCDD/DFs in Antarctic samples were in the increasing order on a lipid weight basis; weddell seal liver (8.9 pg/g) < fish (11–17 pg/g) < krill (27 pg/g) < penguin eggs (mean: 23 pg/g) < south polar skua eggs (mean: 181 pg/g). Concentrations of dioxin-like PCBs (including two di-*ortho* congeners) in polar bear livers were in the range of 1080–3930 ng/g, lipid wt. Concentrations of dioxin-like PCBs in Antarctic samples were in the following order on a lipid weight basis; south polar skua eggs (mean: 1440 ng/g) > > penguin eggs (30 ng/g) > seal liver (57 ng/g) > fishes (6.2 ng/g) > krill (0.9 ng/g). Concentrations of 2378-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) calculated based on the WHO TEFs were higher in the eggs of polar skua (mean: 344; range: 220–650 pg/g, lipid wt.) from Antarctica than in polar bear livers from Alaska (mean: 120; range: 69–192 pg/g). In general, concentrations of PCDFs were greater than those of PCDDs in polar organisms. 23478-PeCDF is one of the dominant congener found in several samples. Concentrations of TEQs in polar bear livers and skua eggs were close to those that may cause adverse health effects. Dioxin-like PCBs, particularly, non-*ortho* coplanar PCBs were the major contributors to TEQ concentrations in penguin and skua eggs whereas mono-*ortho* PCBs accounted for a major portion of TEQs in polar bear livers.

Keywords: Antarctic; Arctic; PCBs; PCDD/DF; Polar bear; Penguin; South Polar skua

1. Introduction

Chlorinated hydrocarbons such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are ubiquitous contaminants in the environment. Due to their persistence and semi-volatility, PCDDs, PCDFs and PCBs are transported to remote marine environments by atmospheric transport (Baker and Hites, 1999; Lohmann et al., 1999; Ogura et al., 2001). Of particular concern is the deposition of chlorinated hydrocarbons transported from continental areas to polar regions (Muir et al., 1992; Wania and Mackay, 1993). Exposure to PCDD/DFs and dioxin-like PCBs is of concern because of their toxicity, which include endocrine disruption, hypovitaminosis A, hypothyroidism, carcinogenicity, neurotoxicity and reproductive effects in humans and wildlife (Giesy et al., 1994; Van den Berg et al., 1998). A common mechanism of action involves

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binding with the cytosolic *Ah*-receptor, which mediates many of these responses. Sources and toxic effects of PCDDs, PCDFs and dioxin-like PCBs have been discussed in detail elsewhere (Safe, 1990; Van den Berg et al., 1998; Giesy and Kannan, 1998).

The Arctic and the Antarctic are both remote, polar regions. The former is a perennial frozen sea surrounded by continents and the latter is a snow covered continent surrounded by oceans. The Southern Ocean isolates Antarctica from other oceans. Therefore, volatile contaminants can reach Antarctica primarily via the transport of air mass (Tanabe et al., 1983; Wania and Mackay, 1993). On the other hand, the Arctic is surrounded by continents in the northern Hemisphere, which is urbanized and industrialized (Muir and Norstrom, 1991). Due to the differences in geographical features, and ecosystem characteristics, organisms inhabiting the Arctic and the Antarctic are exposed to different levels and patterns of organochlorine compounds. Comparison of concentrations of organochlorines in both the poles would provide information on the extend of contamination in these remote areas of the globe. Since marine species living in the polar regions have greater lipid content then temperate or tropical species, they are prone to high accumulation of organochlorines.

While a few earlier studies have reported the occurrence of PCBs and DDT in polar organisms including penguins (Risebrough et al., 1976; Ballschmiter et al., 1981; Subramanian et al., 1986; Focardi et al., 1995; Van den Brink et al., 1998), polar bears (Norstrom et al., 1998) and Arctic and Antarctic seals (Bignert et al., 1989; Norstrom et al., 1990; Oehme et al., 1995a,b), only a few investigators have reported PCDD/DF concentrations. For example, prior to this study, concentrations of PCDDs/DFs in livers of polar bears from Alaskan Arctic, eggs of penguins and south polar skua have not been reported. The objectives of this study were to determine the concentrations and accumulation patterns of seventeen 2378-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and non-, mono- and di-*ortho* PCBs (14 congeners; collectively referred here as 'dioxin-like PCBs') in Arctic and Antarctic organisms and to estimate 2378-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of PCDDs, PCDFs and dioxin-like PCBs in polar organisms.

2. Materials and methods

2.1. Sample collection

As a part of an on-going study to document contaminant levels in polar bears in Alaska, native subsistence hunters collected polar bear livers from northern and western Alaska for the US Fish and Wildlife Service, Anchorage, Alaska. Polar bears were collected from 1993 to 2000 at Barrow, Gambell, Little Diomede and Prudhoe Bay of Alaskan coast. Bears from Barrow and Prudhoe Bay are from the south Beaufort Sea population and those from Little Diomede and Gambell are from Chuckchi/Bering Sea populations. Ages of some polar bears were analyzed by counting cementum growth layers in vestegal premolar teeth. Eggs of south polar skua (*Catharacta maccormicki*) and Adelie penguin (*Pygoscelis adeliae*), liver of an adult female weddell seal (*Leptonichotes weddelli*) were collected during the X, XI (1995–1996) and XIII (1998–1999) Expeditions in Terra Nova Bay in Antarctica in the framework of the Italian Antarctic Research Program (PNRA) during the austral summer months. Two species of fishes (*Trematomus pennelli, Chionodrodraco hamatus*) and krill (*Euphausta superba*) were collected in 1994–1995. Adelie penguin eggs (unhatched) and weddell seal liver were collected from Edmonson Point (74°20′56.7″ S and 165°08′10.03″ E) in 1995–1996. Polar skua eggs were collected in 1998–1999. Details of the samples are shown in Tables 1 and 2.

2.2. Analysis of dioxin, furan and dioxin-like PCB congeners

Prior to analysis, samples were freeze-dried. Moisture content was determined and samples were extracted using a Soxhlet apparatus for 10–15 h in dichloromethane. Details of the analytical procedure have been reported previously (Senthil Kumar et al., 2001a,b). Briefly, after the extraction, samples were concentrated to 10 ml using a Kuderna-Danish (K-D) concentrator and the solvent transferred to *n*-hexane. Lipid content was determined gravimetrically from an aliquot of the extract. Seventeen ^{13}C-labeled 2378-substituted tetra-, penta-, hexa-, hepta-, and octa-CDD and CDF congeners and fourteen dioxin-like PCBs (IUPAC Nos. 81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, 170, 180 and 189) were spiked into hexane extracts prior to sulfuric acid treatment. The hexane layer was rinsed twice with hexane-washed water, and dried by passing through anhydrous sodium sulfate in a glass funnel. The solution was concentrated to 2 ml and sequentially subjected to silica gel, alumina and silica gel-impregnated activated carbon column chromatography. Extracts were passed through activated silica gel (activated at 130 °C for 31/2 h) packed in a glass column (Wakogel, silica gel 60; 2 g) and eluted with 130 ml of hexane, which contained PCDD/DFs and dioxin-like PCBs. The hexane extract was K-D concentrated and passed through activated alumina (190 °C for 3 h) column (Merck-Alumina oxide, activity grade 1; 5g) and eluted with 30 ml of 2% dichloromethane in hexane as the first fraction, which contained several *ortho*-substituted PCBs. The second fraction eluted with 30 ml of 50%

Table 1
The details of Antarctic wildlife samples and concentrations of 2378-PCDD/DFs (pg/g), dioxin-like PCBs (ng/g) and TEQs (pg/g)

n Lipid (%)	Lipid wt. basis						Wet wt. Basis (mean)					
	Fish-1	Fish-2	Krill	Weddell seal	Adelie penguin	South polar skua	Fish-1	Fish-2	Krill	Weddell seal	Adelie penguin	South polar skua
	6[a]	*2*[a]	*52*[a]	*1*	*5*	*5*	*6*[a]	*2*[a]	*52*[a]	*1*	*5*	*5*
	2	8.2	3.2	2.7	10.5 (7.7–12.8)	9.1 (4.5–13.9)	2	8.2	3.2	2.7	10.5 (7.7–12.8)	9.1 (4.5–13.9)
PCDD/DFs												
2,3,7,8-D	<0.01	<0.01	<0.01	<0.01	0.1 (<0.01–0.2)	2.3 (<0.01–6.0)	<0.001	<0.001	<0.001	<0.001	0.005	0.19
1,2,3,7,8-D	<0.01	<0.01	<0.01	<0.01	0.2 (<0.01–0.5)	21 (1–46)	<0.001	<0.001	<0.001	<0.001	0.02	1.89
1,2,3,4,7,8-D	<0.01	<0.01	0.20	<0.01	<0.01	6.8 (4.0–11)	<0.001	<0.001	0.02	<0.001	0.01	0.61
1,2,3,6,7,8-D	<0.01	<0.01	<0.01	0.95	0.2 (<0.01–0.4)	19 (12–30)	<0.001	<0.001	<0.001	0.002	0.03	1.7
1,2,3,7,8,9-D	0.09	0.01	0.21	<0.01	0.02 (<0.01–0.1)	0.4 (<0.01–0.8)	0.002	0.001	0.004	<0.001	0.001	0.04
1,2,3,4,6,7,8-D	0.68	0.20	<0.01	<0.01	0.7 (<0.01–2.1)	3.2 (<0.01–8.3)	0.01	0.02	<0.001	<0.001	0.06	0.28
OCDD	3.4	0.77	24	4.2	2.5 (<0.1–7.3)	5.8 (2.1–11)	0.07	0.06	0.75	0.11	0.23	0.40
2,3,7,8-F	5.6	11	<0.01	<0.01	8.7 (4.2–15)	24 (7.5–66)	0.11	0.90	<0.001	<0.001	1.0	2.1
1,2,3,7,8-F	<0.01	1.2	0.80	<0.01	1.3 (<0.01–2.9)	7.4 (2.2–19)	<0.001	0.10	0.03	<0.001	0.15	0.56
2,3,4,7,8-F	<0.01	2.8	<0.01	3.2	4.7 (2.7–8.1)	56 (30–114)	<0.001	0.23	<0.001	0.11	0.58	5.1
1,2,3,4,7,8-F	<0.01	0.76	0.87	0.60	1.3 (0.9–1.9)	8.9 (<0.01–20)	<0.001	0.06	<0.001	0.02	0.17	0.84
1,2,3,6,7,8-F	<0.01	0.38	0.79	<0.01	0.6 (0.4–0.9)	8.4 (4.1–19)	<0.001	0.03	0.02	<0.001	0.06	0.73
2,3,4,6,7,8-F	<0.01	<0.01	<0.01	<0.01	1.3 (0.9–1.9)	13 (5.9–32)	<0.001	<0.001	<0.001	<0.001	0.13	1.1
1,2,3,7,8,9-F	0.14	<0.01	<0.01	<0.01	0.03 (<0.01–0.1)	0.5 (<0.01–1.2)	0.003	<0.001	<0.001	<0.001	0.004	0.05
1,2,3,4,6,7,8-F	0.54	0.26	<0.01	<0.01	0.5 (0.3–0.6)	1.1 (0.4–2.4)	0.01	0.02	<0.001	<0.001	0.05	0.09
1,2,3,4,7,8,9-F	<0.01	<0.01	0.77	<0.01	0.1 (<0.01–0.2)	1.3 (<0.01–2.7)	<0.001	<0.001	0.02	<0.001	0.01	0.12
OCDF	0.42	<0.01	<0.01	<0.01	0.4 (<0.01–0.7)	0.9 (0.1–1.8)	0.01	<0.001	0.00	<0.001	0.04	0.09
Dioxin-like PCBs												
Non-ortho PCBs												
81	<0.001	<0.001	0.003	0.002	0.01 (0.01–0.02)	0.01 (0.01–0.03)	<0.0001	<0.0001	0.0001	0.0001	0.001	0.001
77	0.04	0.05	0.05	0.02	0.3 (0.2–0.4)	1.0 (0.5–2.0)	0.001	0.004	0.001	0.001	0.03	0.09
126	0.05	0.05	0.04	0.15	0.2 (0.1–0.4)	1.7 (1.2–2.8)	0.001	0.004	0.001	0.004	0.02	0.16
169	0.01	0.03	0.003	0.004	0.2 (0.1–0.3)	2.2 (1.9–3.1)	0.0002	0.002	0.0001	0.0001	0.02	0.20
Mono-ortho PCBs												
105	<0.1	0.37	0.09	10	1.1 (0.8–1.7)	45 (18–90)	<0.001	0.03	0.003	0.28	0.11	4.2
114	<0.1	<0.1	<0.1	1.8	<0.1	3.7 (1.9–5.2)	0.0002	<0.003	0.001	0.05	<0.1	0.31
118	1.81	<0.1	0.35	50	5.5 (0.4–12)	160 (19–241)	0.04	<0.2	0.01	1.35	0.77	22.1
123	<0.1	<0.1	0.03	<0.1	<0.1	2.7 (0.1–5.2)	<0.001	<0.01	0.001	<0.01	<0.1	0.27
156	0.50	0.32	<0.1	1.0	1.2 (0.5–2.3)	49 (29–82)	0.01	0.03	0.001	0.03	0.13	4.57
157	<0.1	<0.1	<0.1	7.7	0.2 (0.1–0.4)	7.9 (4.5–13)	<0.001	<0.005	0.0005	0.21	0.02	0.72
167	<0.1	<0.1	<0.1	8.8	0.7 (0.4–1.3)	36 (21–63)	<0.001	<0.01	0.0005	0.24	0.07	3.3
189	<0.1	<0.1	<0.1	0.2	5.6 (3.0–11)	9.0 (4.4–17)	<0.01	<0.01	0.001	0.01	0.58	0.83
Di-ortho PCBs												
170	1.7	1.3	0.10	27	5.3 (2.1–11)	200 (135–370)	0.03	0.10	0.003	0.73	0.56	18
180	3.4	2.1	0.21	NA	9.7 (3.4–19)	920 (430–1500)	0.07	0.17	0.007	NA[b]	1.02	84

Table 1 (*continued*)

	Lipid wt. basis						Wet wt. Basis (mean)					
	Fish-1	Fish-2	Krill	Weddell seal	Adelie penguin	South polar skua	Fish-1	Fish-2	Krill	Weddell seal	Adelie penguin	South polar skua
n	6[a]	2[a]	52[a]	1	5	5	6[a]	2[a]	52[a]	1	5	5
Lipid (%)	2	8.2	3.2	2.7	10.5 (7.7–12.8)	9.1 (4.5–13.9)	2	8.2	3.2	2.7	10.5 (7.7–12.8)	9.1 (4.5–13.9)
PCDDs	4.1	1.0	24	5.1	3.7 (<0.1–11)	59 (19–113)	0.08	0.08	0.77	0.11	0.4	5.1
PCDFs	6.7	16	3.2	3.8	19 (9.4–32)	122 (50–278)	0.14	1.3	0.07	0.12	2.2	11
PCDD/DFs	11	17	27	8.9	23 (9.4–43)	181 (69–391)	0.22	1.4	0.85	0.23	2.6	16
NO PCBs[c]	0.10	0.13	0.09	0.2	0.7 (0.41–1.1)	4.9 (3.6–7.9)	0.002	0.01	0.003	0.005	0.08	0.45
MO PCBs[c]	2.3	0.7	0.47	80	14 (5.2–28.7)	313 (110–516)	0.05	0.06	0.02	2.2	1.7	36
DO PCBs[c]	5.1	3.4	0.31	27	15 (5.5–30)	1120 (565–1870)	0.1	0.3	0.0	0.7	1.6	102
PCBs	7.5	4.7	0.88	106	30 (11–60)	1440 (679–2390)	0.15	0.35	0.03	2.9	3.3	139
TEQs	0.60	2.4	0.58	23	51	344	0.01	0.20	0.02	0.65	5.9	32

[a] Number of individuals pooled.
[b] NA, not analyzed; values in parentheses indicate range.
[c] Denotes Non-, Mono- and Di-*ortho* PCBs, respectively.

dichloromethane in hexane contained PCDD/DFs and dioxin-like PCBs, which was purged under a gentle stream of nitrogen to 0.5 ml and passed through silica gel impregnated activated carbon column (0.5 g) to further separate mono- and di-*ortho* PCBs from non-*ortho* PCBs and PCDD/DFs. The first fraction eluted with 25 ml of 25% dichloromethane in hexane contained mono- and di-*ortho* PCBs. The second fraction eluted with 250 ml toluene contained non-*ortho* PCBs and PCDD/DFs. Sample extracts were analyzed by a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). Procedural blanks ($n=3$) were analyzed to check for interferences. HpCDD and HpCDF were detected in blanks at concentrations approximately <0.01 pg/g, and OCDD at approximately 0.1 pg/g. The values obtained for HpCDD, OCDD and HpCDF were not corrected for the blank concentrations.

2.3. Identification and quantification

Identification and quantification of 2378-substituted congeners of PCDD/DFs and dioxin-like PCBs were performed using a HRGC (Hewlett Packard 6890 Series) coupled with a HRMS (Micromass Autospec-Ultima). The HRMS was operated in an electron impact, selected ion monitoring mode at a resolution $R>10{,}000$ (10% valley). Separation was achieved using a DB-5 (J&W Scientific; 0.25mm i.d.×60 m length) and a DB-17 column (J&W Scientific; 0.25 mm i.d.×60 m length). Details of the oven temperature program are given elsewhere (Senthil Kumar et al., 2001b). Prior to injection, ^{13}C-labeled 1234-TeCDD and 123789-HxCDD were added as injection recovery standard. Mean recovery of spiked internal standard through the whole analytical procedure was 74% (range: 60–95%) and the reported concentrations were not corrected for the surrogate recoveries. PCDD/DFs, dioxin-like PCBs and TEQ concentrations are reported as pg/g on a lipid weight basis unless otherwise specified. Concentrations of dioxin-like PCBs refer to the sum of four non- and eight mono- and two di-*ortho* substituted PCB congeners. However, for TEQ estimation, only non- and mono-*ortho* PCBs were considered because TEF values were not proposed for two di-*ortho* PCBs, 170 and 180 (Van den Berg et al., 1998). PCB congeners are represented by the IUPAC numbers.

3. Results

3.1. Antarctic species

Concentration of total PCDDs/DFs in the liver of adult female weddell seal was (8.9 pg/g, lipid wt.) the lowest among the samples analyzed (Table 1).

Table 2
The details of Alaskan Arctic polar bear samples and concentrations of 2378-PCDD/DFs (pg/g), dioxin-like PCBs (ng/g) and TEQs (pg/g)

Lipid wt. basis

Sample I.D	2372LF	2372LK	2367LC	2368LF	12216LB	990083LD	940090LB	940149LB	990671LC	950086LB
Village[a]	LD	LD	Barr	LD	Barr	Barr	Gamb	LD	PB	Gamb
Year	2000	2000	2000	2000	1993	1999	1994	1994	1999	1995
Sex[b]	U	F	M	M	M	M	M	F	F	M
Age	NA	NA	NA	NA	21	NA	30	17	14	4
Growth stage[c]	C	A	A	A	A	A	A	A	A	S
Lipid (%)	12.1	7.3	9.8	11.9	7.7	6.9	9.2	11.6	6.4	7.9
PCDD/DFs										
2,3,7,8-D	0.88	<0.01	<0.01	<0.01	<0.01	1.7	<0.01	<0.01	5.4	1.1
1,2,3,7,8-D	0.91	1.7	1.7	3.1	<0.01	<0.01	<0.01	<0.01	6.0	2.1
1,2,3,4,7,8-D	<0.01	1.8	0.73	<0.01	<0.01	<0.01	<0.01	<0.01	1.5	<0.01
1,2,3,6,7,8-D	<0.01	3.3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	4.6	2.7
1,2,3,7,8,9-D	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01
1,2,3,4,6,7,8-D	<0.01	<0.01	3.7	0.8	<0.01	4.0	0.70	<0.01	<0.01	<0.01
OCDD	1.9	5.0	11	2.0	5.7	12	1.2	1.7	2.8	2.5
2,3,7,8-F	0.69	<0.01	0.60	0.4	<0.01	0.78	0.47	1.3	0.53	0.8
1,2,3,7,8-F	0.11	0.68	<0.01	<0.01	0.65	<0.01	0.15	<0.01	<0.01	<0.01
2,3,4,7,8-F	6.1	9.7	6.7	48	<0.01	11	8.9	6.9	12	13
1,2,3,4,7,8-F	<0.01	0.54	<0.01	2.4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1,2,3,6,7,8-F	0.17	<0.01	0.49	<0.01	<0.01	<0.01	0.46	0.43	0.60	<0.01
2,3,4,6,7,8-F	0.19	<0.01	<0.01	9.0	<0.01	<0.01	<0.01	0.49	0.49	4.3
1,2,3,7,8,9-F	0.30	0.75	<0.01	<0.01	<0.01	<0.01	1.6	<0.01	<0.01	<0.01
1,2,3,4,6,7,8-F	0.28	<0.01	0.89	0.4	<0.01	<0.01	0.32	0.23	<0.01	<0.01
1,2,3,4,7,8,9-F	<0.01	0.55	<0.01	<0.01	<0.01	<0.01	3.0	0.72	1.1	<0.01
OCDF	0.30	1.6	0.52	<0.01	1.3	0.66	1.1	0.42	<0.01	0.38
Dioxin-like PCBs										
Non-ortho PCBs										
81	<0.001	0.001	<0.001	<0.001	<0.001	0.001	0.001	0.001	0.002	0.001
77	0.01	0.03	0.01	0.05	0.02	0.1	0.1	0.1	0.2	0.2
126	0.04	0.1	0.1	0.2	0.1	0.4	0.2	0.2	0.3	0.3
169	0.1	0.2	0.2	0.6	0.5	0.4	0.1	0.1	0.1	0.2
Mono-ortho PCBs										
105	14	40	17	86	6.3	21	35	44	55	69
114	3.6	4.2	2.3	3.9	1.8	1.4	2.2	3.3	4.2	2.1
118	42	79	49	246	17	30	108	92	118	133
123	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
156	83	104	62	115	96	115	83	47	50	74
157	63	46	74	89	85	115	62	17	20	35
167	1.0	1.3	<0.1	6.8	1.2	0.63	0.87	1.3	1.6	3.2
189	4.7	67	25	37	72	<0.1	<0.1	<0.1	<0.1	<0.1
Di-ortho PCBs										
170	601	648	1065	863	1390	1470	539	234	355	356
180	893	1130	1180	1230	1890	2200	929	645	935	859

Wet wt. basis

Sample I.D	2372LF	2372LK	2367LC	2368LF	12216LB	990083LD	940090LB	940149LB	990671LC	950086LB
Village[a]	LD	LD	Barr	LD	Barr	Barr	Gamb	LD	PB	Gamb
Year	2000	2000	2000	2000	1993	1999	1994	1994	1999	1995
Sex[b]	U	F	M	M	M	M	M	F	F	M
Age	NA	NA	NA	NA	21	NA	30	17	14	4
Growth stage[c]	C	A	A	A	A	A	A	A	A	S
Lipid (%)	12.1	7.3	9.8	11.9	7.7	6.9	9.2	11.6	6.4	7.9
PCDD/DFs										
2,3,7,8-D	0.11	<0.001	<0.001	<0.001	<0.001	0.11	<0.001	<0.001	0.34	0.09
1,2,3,7,8-D	0.11	0.13	0.16	0.4	<0.001	<0.001	<0.001	<0.001	0.38	0.16
1,2,3,4,7,8-D	<0.001	0.13	0.07	<0.001	<0.001	<0.001	<0.001	<0.001	0.10	<0.001
1,2,3,6,7,8-D	<0.001	0.24	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.29	0.21
1,2,3,7,8,9-D	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,2,3,4,6,7,8-D	<0.001	<0.001	0.36	0.10	<0.001	0.28	0.06	<0.001	<0.001	<0.001
OCDD	0.23	0.37	1.1	0.23	0.43	0.86	0.12	0.20	0.18	0.19
2,3,7,8-F	0.08	<0.001	0.06	0.05	<0.001	0.05	0.04	0.15	0.03	0.06
1,2,3,7,8-F	0.01	0.05	<0.001	<0.001	0.05	<0.001	0.01	<0.001	<0.001	<0.001
2,3,4,7,8-F	0.74	0.71	0.65	5.7	<0.001	0.75	0.82	0.81	0.76	1.0
1,2,3,4,7,8-F	<0.001	0.04	<0.001	0.28	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1,2,3,6,7,8-F	0.02	<0.001	0.05	<0.001	<0.001	<0.001	0.04	0.05	0.04	<0.001
2,3,4,6,7,8-F	0.02	<0.001	<0.001	1.1	<0.001	<0.001	<0.001	0.06	0.03	0.34
1,2,3,7,8,9-F	0.04	0.06	<0.001	<0.001	<0.001	<0.001	0.15	<0.001	<0.001	<0.001
1,2,3,4,6,7,8-F	0.03	<0.001	0.09	0.05	<0.001	<0.001	0.03	0.03	<0.001	<0.001
1,2,3,4,7,8,9-F	<0.001	0.04	<0.001	<0.001	<0.001	<0.001	0.28	0.08	0.07	<0.001
OCDF	0.04	0.12	0.05	<0.001	0.10	0.05	0.10	0.05	<0.001	0.03
Dioxin-like PCBs										
Non-ortho PCBs										
81	<0.0001	0.0001	<0.0001	<0.0001	<0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
77	0.001	0.002	0.001	0.01	0.001	0.005	0.01	0.01	0.01	0.02
126	0.005	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02
169	0.01	0.01	0.02	0.07	0.04	0.02	0.01	0.01	0.01	0.02
Mono-ortho PCBs										
105	1.6	2.9	1.7	10	0.49	1.5	3.3	5.1	3.5	5.4
114	0.4	0.30	0.22	0.46	0.14	0.10	0.20	0.38	0.27	0.2
118	5.1	5.8	4.8	29	1.3	2.1	10	11	7.5	11
123	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
156	10.1	7.6	6.1	14	7.4	8.0	7.7	5.4	3.2	5.8
157	7.6	3.3	7.3	11	6.5	<0.01	<0.01	<0.01	2.9	<0.01
167	0.1	0.1	<0.01	0.8	0.1	<0.01	0.1	0.2	0.1	0.3
189	0.6	4.9	2.5	4.5	5.5	<0.01	<0.01	<0.01	<0.01	<0.01
Di-ortho PCBs										
170	0	0	0	0	0	0	0	0	0	0
180	0	0	0	0	0	0	0	0	0	0

Table 2 (*continued*)

	Lipid wt. basis										Wet wt. basis									
PCDDs	3.7	12	17	6	6	18	2	2	20	8	0.4	0.9	1.7	0.7	0.4	1.3	0.2	0.2	1.3	0.7
PCDFs	8.2	14	9	60	2	12	16	10	15	18	1.0	1.0	0.9	7.2	0.2	0.9	1.5	1.2	0.9	1.4
PCDD/DFs	12	26	26	66	8	30	18	12	35	26	1.4	1.9	2.6	7.9	0.6	2.1	1.7	1.4	2	2
NO PCBs[c]	0.1	0.3	0.3	0.8	0.6	0.8	0.4	0.4	0.5	0.7	0.02	0.02	0.03	0.09	0.05	0.05	0.04	0.05	0.03	0.1
MO PCBs[c]	211	341	230	583	280	284	292	204	249	317	26	25	22	69	21	12	21	22	17	22
DO PCBs[c]	1490	1778	2250	2093	3280	3670	1470	879	1290	1220	0	0	0	0	0	0	0	0	0	0
PCBs	1660	2120	2480	2670	3561	3930	1760	1080	1540	1530	26	25	23	69	22	12	21	22	17	22
TEQ	87	112	94	192	118	165	115	69	99	114	11	8.2	9.2	23	9.0	7.7	7.8	7.1	7.1	7.6

[a] LD, Barr, Gamb and PB, represent Little Diomede (Long:168 W 54 00, Lat:65 N 46 15), Barrow (Long:156 W 47 15, Lat:71 N 17 30), Gambell (Long:171 W 45 00, Lat:63 N 47 00) and Prudhoe Bay (Long:152 W 11 50, Lat:58 N 11 15), respectively.
[b] U, F and M indicates unidentified, female and male, respectively.
[c] C, A and S, represents, cub (<3 years), adult (>5 years) and sub-adult (3–4 years), respectively; NA, Not analyzed; ND, Not detected.

123678-HxCDD, OCDD, 23478-PeCDF and 123478-HxCDF were the four congeners found in weddell seal liver. Concentrations of PCDDs/DFs in krill and fish were 2–3 fold greater than those in seal liver. While the concentrations of ΣPCDDs were greater than those of ΣPCDFs in krill, fishes contained greater proportions of PCDFs. OCDD accounted for 88% of the ΣPCDD/DF concentrations of 24 pg/g, lipid wt., in krill. PCDF congeners such as 12378-PeCDF, 123478-HxCDF, 123678-HxCDF and 1234789-HpCDF were also found in krill at detectable concentrations. 2378-TCDF, 23478-PeCDF and OCDD were the major congeners in Antarctic fishes (Table 1).

Concentrations of ΣPCDDs/DFs in the eggs of Adelie penguins ranged from 9.4 to 43 pg/g, lipid wt. (Table 1). Concentrations of PCDFs were greater than those of PCDDs in the eggs of Adelie penguins. Except 123789-HxCDF and 123478 HxCDD, all the other 2378-substituted PCDFs were present in penguin eggs. Especially, PCDF congeners 2378-TCDF, 23478-PeCDF and hexa-chlorinated PCDFs were predominant in penguin eggs. This profile of PCDD/DF is different from those observed for weddell seal and krill. Among the samples analyzed, eggs of south polar skua contained the highest concentrations of ΣPCDDs/DFs of 69-391 (mean: 181) pg/g, lipid wt. (Table 1). Similar to that observed for penguin eggs, all PCDD and PCDF congeners were detected in skua. Concentrations of PCDFs were greater than those of PCDDs in the eggs of skua. 12378-PeCDD, 123478-HxCDD, 123678-HxCDD, OCDD, 2378-TCDF, 23478-PeCDF, and hexa-CDFs were the major congeners found in skua eggs.

Dioxin-like PCBs were also found in Antarctic samples. Skua eggs contained the greatest concentrations (679-2390 ng/g, lipid wt.) of dioxin-like PCBs (Table 1). Concentrations of dioxin-like PCBs in penguin eggs (mean: 30; range, 11–60 ng/g), weddell seal liver (57 ng/g), fishes (4.7–7.7 ng/g) and krill (0.9 ng/g) were 10–100 times less than those found in the eggs of polar skua. Non-*ortho* coplanar PCBs were detected in most of the Antarctic samples (Table 1). Among mono and di-*ortho* PCB congeners, pentachlorobiphenyls 105 and 118 and heptachlorobiphenyl 180 were prevalent in several Antarctic samples. In particular, chlorobiphenyls 105, 157, 167 and 170 in seal liver, 105 and 118 in krill, and 118, 170 and 180 in fish were the predominant ones. Among the PCB congeners analyzed in the eggs of penguin and south polar skua, chlorobiphenyls 105, 118, 170 and 180 predominated.

3.2. Arctic species (polar bear)

Concentrations of PCDD/DFs in livers of polar bears from Alaskan Arctic ranged between 8 and 66 (mean: 26) pg/g, lipid wt (Table 2). Concentrations of PCDFs were, in general, greater than those of PCDDs (Fig. 1).

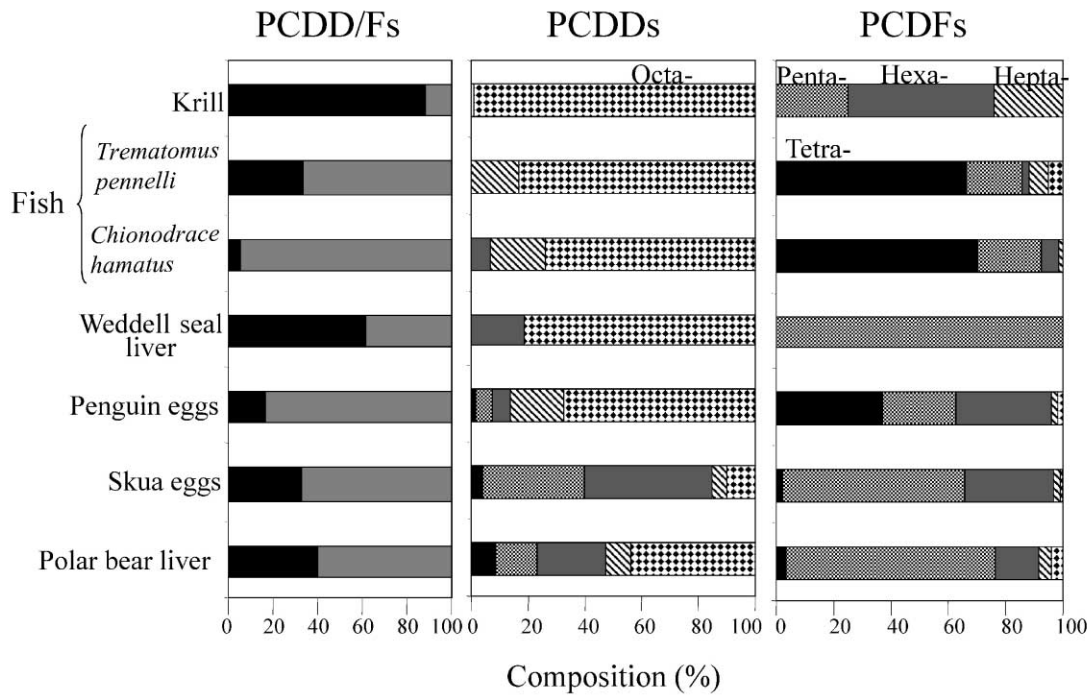

Fig. 1. Compositions of PCDD/DF homologues in Arctic and Antarctic organisms.

However, individuals from Prudhoe Bay and Barrow, particularly those collected in 1999 and 2000 contained greater concentrations of PCDDs than of PCDFs. 23478-PeCDF is the most abundant congener in polar bear livers. Furthermore, 2378-TCDD, 12378-PeCDD, 123678-HxCDD, OCDD, 23478-PeCDF, 123478-HxCDF and OCDF were also found in polar bear livers (Table 2). Mean concentration of 14 dioxin-like PCBs in polar bear livers was 2230 ng/g (Table 2). Non-*ortho* coplanar PCBs, 77, 126 and 169, were detected in the livers of all the polar bears. Among the non-*ortho* PCBs, CB-169 was the most abundant congener in some samples while a few individuals contained great concentrations of CB-126. Heptachlorinated, di-*ortho* PCBs congeners 170 and 180 were the most abundant congeners in polar bear livers contributing 79–93% of the dioxin-like PCB concentrations. Concentrations of PCDDs/DFs and dioxin-like PCBs were greater in adult polar bear livers than in sub-adults or cubs (data not shown). No significant differences in PCDD/DF concentrations were observed between male and female polar bears. In general, males recorded slightly greater levels than females (data not shown). However, due to the small sample size, age and gender related differences suggest trends but may not be representative of all polar bears (Table 2).

3.3. Dioxin-like toxic equivalents (TEQs)

Concentrations of 2378-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of PCDDs, PCDFs and dioxin-like PCBs were estimated by applying WHO-TEFs for fish (fish, krill), birds (penguins and skua) and mammals (seal and polar bear; Van den Berg et al., 1998). Di-*ortho* PCBs were not included in the estimation of TEQs as TEF values for these congeners are not presently available. The concentrations of TEQs were in the following increasing order; krill (0.58 pg/g, lipid wt.) < fishes (0.6–2.4 pg/g) < weddell seal liver (23 pg/g) < penguin eggs (28–pg/g) < polar bear liver (69–192 pg/g) < skua eggs (220–650 pg/g). Only in krill and fishes, PCDDs or PCDFs contributed to a significant portion of the TEQ concentrations (Fig. 2). Contribution of PCDDs to $\sum$TEQs was greater in krill whereas the contribution of PCDFs was greater in fishes. In most of the samples, particularly those at the higher trophic level in the food chain, such as polar bears, penguins, skua and weddell seal, non- and mono-*ortho* PCBs were the significant contributors to TEQ concentrations accounting for greater than 75% of the ΣTEQs (Fig. 2). Among PCDD/DF congeners, 2378-TCDF, 23478-PeCDF, 12378-PeCDD and 2378-TCDD were the major contributors to TEQ concentrations. Of the dioxin-like PCBs, CB-126 accounted for a significant portion of the TEQ concentrations.

4. Discussion

Samples of weddell seal liver, fishes and krill from Antarctica contained low, but detectable concentrations of PCDDs/DFs and PCBs. Occurrence of

PCDF congeners such as 2378-TCDF, 12378- and 23478-PeCDF at concentrations of 3.7–6.1 pg/g, lipid wt., has been reported in the blubber of crabeater seals (*Lobodon carcinophagus*) collected in 1986 in Antarctica (Bignert et al., 1989). However, PCDD congeners were not found at quantifiable concentrations in crabeater seals. Earlier studies had relatively high detection limits, which resulted in the lack of detection of several PCDD/DF congeners. In this study, rigorous sample clean-up lends to a considerable pre-concentration (almost a million fold) and high resolution mass spectrometry detection permitted a better detection limit and therefore, the identification of several congeners. This underlines the fact that methods with very low detection limits and blank values are needed to attain reliable results for samples from remote areas such as the Arctic and the Antarctic. OCDD accounted for 50% of the ΣPCDD/DF concentrations of 8.9 pg/g, lipid wt., followed by 23478-PeCDF, 123678-HxCDD and 123478-HxCDF. OCDD, HpCDD and OCDF were the predominant congeners found in the blubber of Antarctic fur seals (*Arctocephalus gazella*; Oehme et al., 1995a,b). Several studies have reported the occurrence of PCDD/DF congeners in seal blubber from the Arctic (Bignert et al., 1989; Norstrom et al., 1990). Compared to the concentrations found in Arctic ringed seal blubber (6–42 pg/g, lipid wt.; Norstrom et al., 1990), the concentration in weddell liver was less. The differences in PCDD/DF contamination between the Arctic and the Antarctic might be explained by differences in industrial and incineration activities in the northern and southern hemispheres (Oehme et al., 1995a,b). More than 80% of the industrialized regions, which act as source areas for PCDDs/DFs and PCBs are situated in the northern hemisphere. Atmospheric transport is assumed to be the main dispersion mechanism (Ogura et al., 2001). The slow inter-hemispheric air exchange (about 1-2 years) reduces the atmospheric transport of compounds from northern to southern hemisphere. Concentrations of PCDDs/DFs in seals were less than those found in fish or krill. This suggests that seals can metabolize PCDD/DF congeners (Tanabe et al., 1983; Addison et al., 1999); the seal analyzed in this study was an adult female, which might have excreted PCDD/DFs through lactation.

The major source of PCDDs/DFs in Antarctic organisms is expected to be atmospheric transport from other continents (Bennington et al., 1975; Ballschmiter et al., 1981). Occurrence of PCDDs/DFs at the concentrations of 0.12–1.8 pg/m^3 for PCDDs and $<$0.02–2.8 pg/m^3 for PCDFs has been reported in some specific sites of Antarctic air (Lugar et al., 1996). The air monitoring data suggested the presence of additional combustion related sources of PCDDs/DFs in the Antarctic. Profiles of PCDD/DF congeners in Antarctic organisms varied considerably, suggesting the presence of multiple sources. Furthermore, this can be explained by the differences in the tissues analyzed, trophic status, food habits, and metabolism. While weddell seal and krill contained OCDD as the predominant congener, TCDF or 23478-PeCDF predominated in fishes, penguin eggs and skua eggs. Indeed, concentrations of PCDDs were greater than those of PCDFs in weddell seal and krill while PCDF concentrations were greater than those of PCDDs in fishes, penguin eggs and skua eggs. Almost all the 2378-substituted congeners of PCDDs/DFs were found in penguin and skua eggs except 123789-HxCDD and 123789-HxCDF. 2378-TCDF is the most predominant congener present in penguin eggs whereas 23478-PeCDF was predominant in polar skua eggs. Concentrations of PCDD/DF congeners in penguin eggs were 10–100 fold less than those found in polar skua eggs. South polar skua spend about 4–5 months in Antarctica, then migrate through the southern Ocean and are not uncommon in the northern Pacific and northern Atlantic Oceans during the southern winter (Focardi et al., 1995). Therefore, great concentrations of PCDD/DFs and PCBs in skua may suggest exposure in wintering grounds. Total PCB concentration of up to 10,400 ng/g, wet wt., has been reported in livers of skua from Antarctica (Corsolini et al., 2000). This is greater than those reported for fish-eating water birds in the Great Lakes (Kannan et al., 2001). The endemic nature of Adelie penguins in Antarctic reflects local exposures. Furthermore, feeding habits of these two species cannot be excluded to account for the concentration differences. South polar skuas are predatory on other birds and feed on carcasses while Adelie penguins feed almost exclusively on fish and krill in the water column.

Earlier studies have reported the occurrence of PCDDs and PCDFs in tissues of polar bear fat (Norstrom et al., 1990) and milk (Oehme et al., 1995b) from the Canadian and Norwegian Arctic. This is the first study to report concentrations of PCDDs/DFs in the livers of polar bear from the Alaskan Arctic. TCDD and OCDD were the major congeners detected in the livers of polar bears in the Canadian Arctic (Norstrom et al., 1990). In this study, 23478-PeCDF was found to be the major congener in polar bear liver followed in order by OCDD and 123678-HxCDD. Only four of the 10 polar bear livers analyzed in this study contained TCDD at concentrations ranging from 0.9 to 5.4 pg/g, lipid wt. 23478-PeCDF was not found in Canadian seals (Norstrom et al., 1990), but were detected in Norwegian seals (Bignert et al., 1989) and polar bears from Alaska (this study). This suggests that 23478-PeCDF is unevenly distributed in the Arctic. Commercial PCBs have been proposed as an important source for 23478-PeCDF in the environment (Wakimoto et al., 1988), but it is also present in combustion sources (Rappe et al., 1987). Besides, opportunistic feeding of bears in local dumps of Barrow cannot be ignored. 1234678-HpCDD was the most predominant congener in the milk of polar bears from the Norwegian Arctic (Oehme et al., 1995b) and in the blubber of Antarctic fur seal (Oehme et al., 1995a).

Concentrations of PCDDs and PCDFs generally increased with the age of polar bears. Polar bear cubs (<3 years) had lowest concentrations followed by subadults (3–4 years) and adults (>5 years; Table 2). Although the small sample size (six males and four females) precluded from rigorous analysis of age, sex, time and location specific differences in contamination levels, the available data suggested that polar bears collected in Barrow, Alaska, in 2000 (66 pg/g, lipid wt.) contained slightly higher concentrations of PCDDs/DFs than those collected in 1993 (8 pg/g, lipid wt.). There appears a shift in PCDD and PCDF profiles from 1993 to 2000. Ratios of PCDDs to PCDFs in adult male polar bears from Barrow during 1993, 1999 and 2000 were 0.88, 1.5, and 2.4, respectively. Similarly, PCDD to PCDF ratios in adult female polar bears collected from Little Diomede in 1994 was 0.15 whereas those collected in 2000 was 1.1. The shift in favor of PCDD concentrations was attributed to an increase in the concentrations of 12378-PeCDD and 123678-HxCDD congeners. Great concentrations of 12378-PeCDD and 123678-HxCDD have been attributed to chlorophenol related sources. The geographical variation in the concentrations of PCDDs/DFs in polar bears from four villages was not different (Table 2) although the concentrations in polar bears from Little Diomede were generally greater than those from Gambell, Barrow and Prudhoe Bay.

The estimated ΣTEQs (sum of TEQs contributed by PCBs, PCDDs and PCDFs) of PCBs, PCDDs and PCDFs in polar bears ranged from 69 to 192 pg/g (mean: 117 pg/g). Non- and mono-*ortho* PCBs accounted for 86–96% (mean: 92%) of the total TEQs in polar bear livers (Fig. 2). Threshold concentrations for TEQs in livers of aquatic mammals to elicit physiological effects has been estimated to range from 160 to 1400 (mean: 520) pg/g (Kannan et al., 2000). The mean TEQ concentration in polar bear livers was approximately 4-fold less than mean threshold value of 520 pg/g, lipid wt. It should be noted that this estimate does not include safety factors that are generally applied for inter-species comparisons. Estimated ΣTEQs in the milk of polar bears from the Norwegian Arctic were from 2.3 to 6.9 pg/ml (mean: 4.2) (Oehme et al., 1995b). Non-*ortho* coplanar PCB congeners accounted for greater than 75% of the ΣTEQs in the milk of polar bears. However, mono-*ortho* PCBs were not analyzed in the study of polar bear milk. In this study, mono-*ortho* PCB congeners, particularly congeners 156, 157 and 118 contributed to a greater portion of TEQ concentrations in polar bear livers. Similar to that observed for polar bears, great contribution of non- and mono-*ortho* PCBs to ΣTEQs has been reported in coastal marine mammals. For instance, mono- and non-*ortho* PCBs accounted for 75 to 99% of the ΣTEQs in striped dolphins from the Mediterranean Sea (Kannan et al., 1993; Jimenez et al., 2000). PCDD/DFs contributed only 5% of the total TEQ concentrations of 85 pg/g, lipid wt., in the blubber of gray seals from Sable Island, Canada (Addison et al., 1999). These results suggest that PCBs are the major contributors to dioxin-like toxicity in marine mammals from remote marine locations.

No threshold egg TEQ concentrations are available for direct comparison with TEQs calculated in south

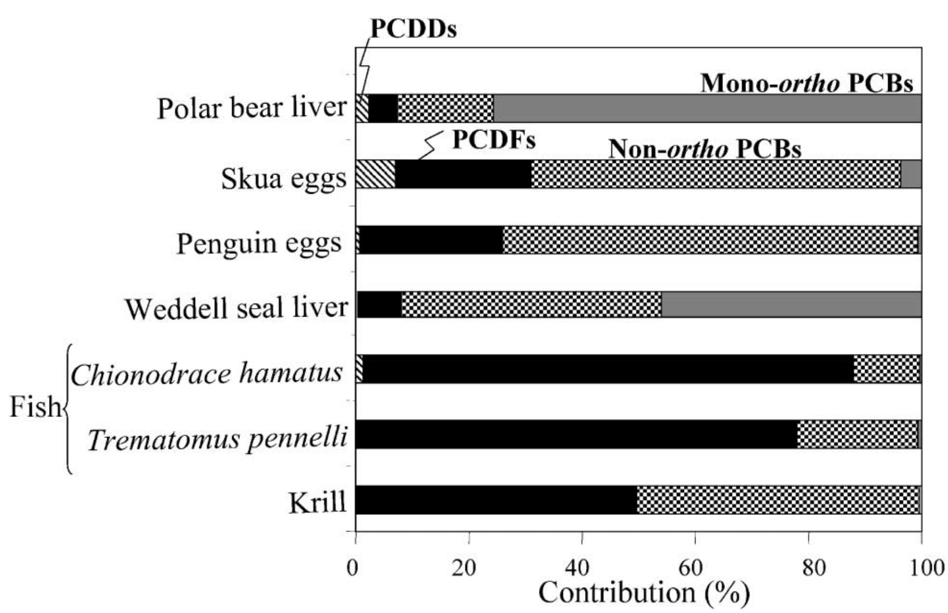

Fig. 2. Toxic equivalencies (TEQs) contribution by PCDD/DFs and dioxin-like PCBs (pg TEQ/g lipid wt.) in Arctic and Antarctic animals.

polar skua or penguin eggs. Although several studies have reported threshold values for TEQs in bird eggs (which vary widely depending upon the species, toxicity end point used, etc.), we compared the results reported for bald eagle eggs (Elliott et al., 1996). It should be noted that the comparison is to get an approximate estimate for possible adverse effects of dioxin-like compounds in skua and penguin eggs. The no-observed-effect-level (NOEL) for TEQs in bald eagle eggs was 100 pg/g and low-observed-effect-level (LOEL) was 210 pg/g on a wet weight basis (Elliott et al., 1996). Mean TEQ concentration in penguin eggs, on a wet weight basis, was 5.6 pg/g. This value is approximately18-fold less than the LOEL reported for bald eagle eggs. Similarly, mean TEQ concentration in skua eggs on a wet weight basis was 32 pg/g (Table 1). This value is only three-fold less than the LOEL for TEQs reported for bald eagle eggs. The margin of safety of three is not great enough to protect skua considering the wide variation in sensitivity that exists among bird species. Furthermore, a toxicity reference value of 70 pg TCDD/g egg was derived for American kestrel eggs (Kemler et al., 2000). Mean concentration of TEQs in skua eggs was only two-fold less than the toxicity threshold value reported for American kestrel eggs.

To our knowledge, this is the first report of PCDDs/DFs in the livers of Alaskan polar bears, eggs of penguins and south polar skua and other biota from Antarctica. Concentrations of TEQs in the eggs of polar skua are close to those that may cause adverse effects. Similarly, polar bears from Alaska contained noticeable concentrations of PCDDs/DFs. In general, 23478 PeCDD was the predominant congener in several samples. Non-*ortho* coplanar PCBs are the major contributors to TEQs in organisms from these remote marine locations.

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