OCCURRENCE OF DIOXINS, FURANS AND DIOXIN-LIKE PCBs IN ARCTIC AND ANTARCTIC WILDLIFE

Kurunthachalam Senthil Kumar[1], Kurunthachalam Kannan[2], John Paul Giesy[2], Simonetta Corsolini[3], Thomas Evans[4], Junko Nakanishi[1] and Shigeki Masunaga[1]

[1] Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan
[2]National Food Safety and Toxicology Center, Michigan State University, East Lansing, MI 48824, USA
[3] Dipartimento di Scienze Ambientali, Universita di Siena, I-53100 Siena, Italy
[4] U.S. Fish and Wildlife Service, Anchorage, Alaska, USA

Introduction

Planar chlorinated hydrocarbons (PCHs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (dioxin-like PCBs), are ubiquitous contaminants in aquatic ecosystems. Consequently, PCDDs, PCDFs and dioxin-like PCBs have been detected in freshwater and marine organisms throughout the northern hemisphere[(1)]. Concentrations in the marine environment of the southern hemisphere are generally lower and it is believed that atmospheric transport accounts for most of these materials transported to the southern oceans[(2)]. Oceans were major sinks and final destination for persistent pollutants, which are transported from continental areas by atmospheric and or by oceanic currents. Furthermore, global distillation or fractionation by condensation in cold polar waters has been proposed as a mechanism whereby the polar regions may become sinks for some PCHs. Penguins in Antarctic have been reported to contain detectable levels of environmental contaminants such as PCBs and DDE in their fat and eggs [(3-5)]. Very little is known on the accumulation of dioxins, furans and dioxin-like PCBs in polar animals. In this study, dioxins, furans and dioxin-like PCBs were measured in wildlife samples from polar regions.

Materials and Methods

Sample collection and handling

Samples of polar bear livers were collected from the tissues archived by the U.S. Fish and Wildlife Service, Anchorage, Alaska. Antarctic organisms- skua eggs, penguin eggs, fish (*Trematomus pennelli*), weddell seal liver and krill whole body were collected during the Xth (1994-1995) and XIth (1995-1996) Expeditions in Terra Nova Bay in Antarctica in the framework of the Italian National Program of Researchers in Antarctica (PNRA). Samples were collected during the months of October to February 1994-96.

Analysis of dioxin, furan and dioxin-like PCB congeners

Prior to chemical analysis, samples were freeze-dried. Moisture content was determined and extracted with Soxhlet apparatus for 10-15 h in dichloromethane. Details of the analytical procedures are reported previously [(6-8)]. Identification and quantification of 2,3,7,8-substituted congeners of PCDD/DFs and dioxin-like PCBs were performed by a high-resolution gas chromatography (HRGC) (Hewlett Packard 6890 Series) coupled with a high-resolution mass spectrometer (HRMS) (Micromass Autospec- Ultima).

Results and Discussion

PCDD/DF and dioxin-like PCB congeners in Antarctic

Of the planar compounds monitored in wildlife of the Antarctic, weddell seal contained only two PCDD congeners, 123678-HxCDD and OCDD and one PCDF congener, 23478-PeCDF with a total concentration of 8.3 pg/g fat wt (Table 1). Similarly krill contained only 123789-HxCDD and OCDD congeners. Among PCDFs, 12378-PeCDF, 123478-HxCDF, 123678-HxCDF and 1234789-HpCDF were found at detected levels with a total of 27 pg/g fat wt in krill (Table 1). Fish species showed a slightly different pattern with 1234678-HpCDD and OCDD and 2378-TCDF, 23478-PeCDF, 123789-HxCDF, 1234678-HpCDF and OCDF at detectable levels with a total concentration of 12 pg/g fat wt (Table 1). Further, eggs of penguins contained greater concentrations of PCDD/DFs than seal, fish and krill with predominant congeners being 1234678-HpCDD and OCDD in all the samples. Notably, except for 123789-HxCDF all other PCDFs congeners were present in all penguin eggs. Especially, 2378-TCDF, 23478-PeCDF and hexa-chlorinated PCDFs were found at great concentrations. Collectively, the mean and range concentrations of PCDD/DFs in penguin eggs were 83 and 17-390 pg/g fat wt, respectively (Table 1). Eggs of southern polar skua contained higher levels of PCDD/DFs when compared to penguin eggs with a mean and ranges of 130 and 86-210 pg/g fat wt (Table 1). Interestingly, all PCDD and PCDF congeners were detected in skua eggs. The most prevalent congeners among PCDD and PCDF homologues were 12378-PeCDD, 123478-HxCDD, 123678-HxCDD and OCDD and 2378-TCDF, 23478-PeCDF, and all of the hexa-CDF congeners. PCDD homologues were slightly higher in seal, and much higher in krill. Whereas, PCDF homologues were predominant in fish tissue, penguin and skua eggs. The differences in concentrations between two bird species may be due to different feeding habit and ecology. Besides, specific elimination or metabolic capacity of PCDDs also may be expected in penguins. Few earlier studies have reported total PCB concentrations in penguins [3-6].

Table 1. Concentrations of PCDD/DFs (pg/g fat weight) in Antarctic and Arctic wildlife samples.

Congener	WSL*	Krill	Fish	Penguins (*n*=6)	SPS** (*n*=4)	Polar bear (*n*=5)	Blank
PCDDs							
2,3,7,8-D	<0.01	<0.01	<0.01	1.0a (<0.01-6.0)	1.3a (<0.01-3.6)	0.2a (<0.01-0.9)	ND
1,2,3,7,8-D	<0.01	<0.01	<0.01	7.8 (<0.01-46)	15 (10-33)	1.5 (<0.01-3.1)	ND
1,2,3,4,7,8-D	<0.01	<0.01	<0.01	1.9 (<0.01-11)	5.7 (4.7-9.2)	1.1 (<0.01-2.6)	ND
1,2,3,6,7,8-D	0.95	<0.01	<0.01	5.2 (<0.01-30)	16 (12-26)	2.2 (<0.01-5.0)	ND
1,2,3,7,8,9-D	<0.01	0.2	<0.01	0.2 (<0.01-0.1)	0.3 (<0.01-0.7)	0.08 (<0.01-0.2)	ND
1,2,3,4,6,7,8-D	<0.01	<0.01	0.7	2.0 (<0.01-8.3)	1.9 (<0.01-6.0)	0.9 (<0.01-3.7)	<0.01
OCDD	4.2	24	3.4	3.3 (<0.01-7.3)	5.5 (2-11)	5.1 (2.0-11)	<0.01
PCDFs							
2,3,7,8-F	<0.01	<0.01	5.4	18 (4.2-66)	13 (7.5-20)	0.3 (<0.01-1.3)	ND
1,2,3,7,8-F	<0.01	0.80	<0.01	4.2 (<0.01-19)	4.5 (2.2-8.1)	0.3 (<0.01-0.7)	ND
2,3,4,7,8-F	3.2	<0.01	1.6	23 (2.7-110)	41 (30-62)	13 (2.6-42)	ND
1,2,3,4,7,8-F	<0.01	0.9	<0.01	4.3 (0.9-20)	6.1 (<0.01-13)	0.8 (<0.01-2.5)	ND
1,2,3,6,7,8-F	<0.01	0.8	<0.01	3.6 (0.4-19)	5.8 (4.1-13)	0.1 (<0.01-0.5)	ND
2,3,4,6,7,8-F	<0.01	<0.01	<0.01	6.4 (0.9-32)	8.5 (5.9-10)	1.8 (<0.01-9.0)	ND
1,2,3,7,8,9-F	<0.01	<0.01	0.2	0.02 (<0.01-0.1)	0.6 (<0.01-14)	0.4 (<0.01-0.9)	ND
1,2,3,4,6,7,8-F	<0.01	<0.01	0.5	0.8 (0.2-2.4)	0.8 (0.4-1.2)	0.3 (<0.01-0.9)	<0.01
1,2,3,4,7,8,9-F	<0.01	0.8	<0.01	0.5 (<0.01-2.7)	0.8 (<0.01-1.1)	0.1 (<0.01-0.5)	<0.01
OCDF	<0.01	<0.01	0.42	0.6 (0.4-1.5)	0.8 (<0.01-1.8)	1.3 (<0.01-1.6)	<0.01
Sum of PCDDs	5.1	24	4.1	21 (1.2-110)	46 (24-83)	11 (3.8-19)	<0.01
Sum of PCDFs	3.2	3.2	8.2	62 (12-280)	82 (62-130)	18 (4.2-54)	<0.01

Detection limits = <0.01 (pg/g);ND= not detected; *, **, respectively, weddell seal and Southern polar skua; a mean values were derived from detected congeners (less than detection limits=0)

Greater concentrations of dioxin-like PCBs were observed in all the samples analyzed from the Antarctic. Eggs of southern polar skua showed great concentrations of dioxin-like PCBs of 1400 (800-1900 ng/g) followed by penguins 270 (17-1500), Weddell seal 57 ng/g, fish 7.7 and krill 0.9 ng/g fat wt (Table 2). All 4 non-*ortho* copanar PCBs were detected in all the samples although at 4- to 200- times lower than mono-*ortho* PCB concentrations. The predominant non-*ortho* congeners were IUPAC Nos. 126 and 77 found in all the samples. IUPAC Nos. 105, 157/167 were predominant in seals, IUPAC 105 and 118 were higher in krill and fish. In the eggs of penguins and skua IUPAC Nos. 105, 118, 156 and 167 were the most predominant congeners. Among two di-*ortho* PCBs IUPAC 170 was higher only in seal, whereas, IUPAC 180 was predominant in other wildlife samples (Table 2).

Table 2. Concentrations of dioxin-like PCBs (ng/g fat weight) in Antarctic and Arctic wildlife samples.

PCBs[1]	WSL*	Krill	Fish	Penguins (n=6)	SPS** (n=4)	Polar bear (n=5)	Blank
81	0.002	0.003	0.001	0.02 (0.01-0.03)	0.01 (0.01-0.01)	0.0003 (<0.001-0.001)	ND
77	0.02	0.05	0.04	0.6 (0.2-2.0)	0.8 (0.5-1.1)	0.02 (0.01-0.05)	ND
126	0.1	0.04	0.05	0.7 (0.1-2.8)	1.5 (1.2-1.7)	0.1 (0.04-0.2)	ND
169	0.004	0.003	0.01	0.7 (0.1-3.1)	2.0 (1.9-2.2)	0.3 (0.1-0.6)	ND
105	10	0.1	0.1	16 (0.5-90)	25 (18-45)	32 (6.3-86)	ND
114	1.8	<0.1	<0.1	0.4 (<0.1-2.4)	3.6 (1.9-5.2)	3.2 (1.8-4.2)	ND
118	0.1	0.4	1.8	7.7 (0.4-19)	140 (150-240)	79 (1.6-250)	ND
123	0.1	0.03	0.03	<0.1	3.0 (1.6-5.2)	<0.01	ND
156	1.0	<0.1	0.5	15 (0.5-82)	30 (29-53)	92 (62-120)	ND
157	7.7	<0.1	0.1	2.3 (0.1-13)	6.6 (4.5-9.5)	71 (46-89)	ND
167	8.8	<0.1	<0.1	11 (0.3-63)	30 (21-43)	2.1 (<0.1-6.8)	ND
189	0.2	<0.1	<0.1	7.5 (3.0-17)	7.1 (4.4-11)	41 (4.7-72)	ND
170	27	0.1	1.7	66 (2.1-370)	150 (140-190)	910 (600-1400)	ND
180	<0.1	0.2	3.4	160 (3.4-790)	950 (430-1500)	1300 (890-1900)	ND
Non-*ortho*	0.2	0.1	0.1	1.9 (0.4-7.9)	4.3 (4.0-4.6)	0.4 (0.1-0.8)	ND
Mono-*ortho*	30	0.5	2.5	60 (11-290)	320 (230-410)	320 (170-580)	ND
Di-*ortho*	27	0.3	5.1	210 (6.0-1200)	1100 (570-1600)	2200 (1500-3300)	ND

Detection limits for non-*ortho* and mono-*ortho* PCBs, respectively 0.001 (ng/g) and 0.1 (ng/g).
[1]IUPAC numbers, *, **, respectively, weddell seal and Southern polar skua

PCDD/DF and dioxin-like PCB congeners in Arctic

Concentrations of PCDD/DFs in polar bears ranged from 7.9-65 pg/g, fat wt with the mean value of 29 pg/g fat wt (Table 1). PCDD homologues were prevalent in three individuals and PCDF congeners were high in two individuals. 12378-PeCDD, 123678-HxCDD and OCDD were the predominant PCDD congeners while 23478-PeCDF, 123478-HxCDF and OCDF were the predominant PCDF congeners. Elevated concentrations of dioxin-like PCBs, 2500 (1700-3600) ng/g fat weight, were noticed in polar bear liver when compared with Antarctic wildlife samples (Table 2). Non-*ortho* coplanar PCBs were 0.0006 to 0.029% of the sum of dioxin-like PCBs. The mono-*ortho* PCBs were the second highest at 9.2 to 21 % of sum of dioxin-like PCBs. This feature is somewhat different from Antarctic wildlife samples.

TEQ estimation

Toxic equivalencies (TEQ) were estimated by applying WHO-TEFs proposed in 1998 using fish [fish, krill], birds [penguins and skua] and mammals [seal and polar bear] TEFs, respectively. The estimated TEQ concentrations in the animals were in the following order; krill (0.33 pg/g), fish (1.4 pg/g), weddell seal liver/fat (23 pg/g), polar bear liver 120 (84-190 pg/g) penguin egg 150

(30-650 pg/g) and skua egg 270 (220-350 pg/g) pgTEQ/g on a fat wt basis (Fig. 1). In both Arctic and Antarctic environments, 2378-TCDF, 23478-PeCDF, 12378-PeCDD, 2378-TCDD, and homologues of hexa-chlorinated PCDD/DFs greatly contributed to TEQs.

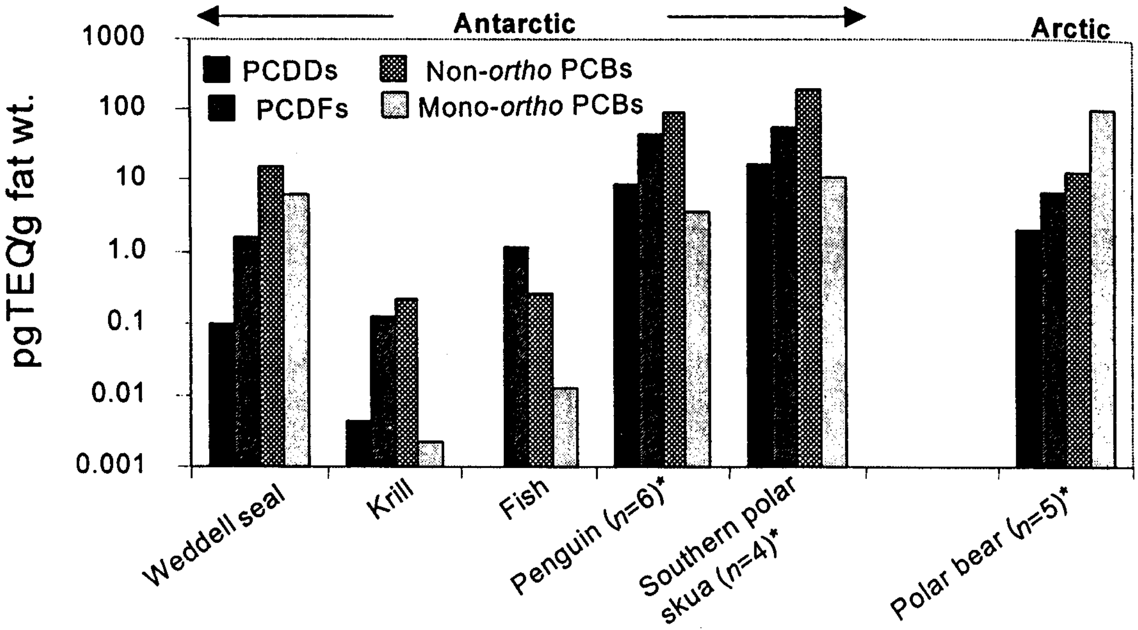

Figure 1. Toxic equivalency in Antarctic and Arctic animals (*mean value).

Acknowledgements
This study was supported by Grant-in-Aid for the Development of Innovative Technology, Ministry of Education, Culture, Sports, Science and Technology, Japan and Japan Society for the Promotion of Science (JSPS) Fellowship awarded to Dr. K. Senthil Kumar (ID P00165).

References

(1) Muir, D.C.G. and Norstrom, R.J. (1991) Tech Rep Can Fish Aquatic Sci. 1774, 820-826.
(2) Hannah, D.J., Jones, P.D., Buckland, S.J., van Maanen, B.T., Letham, S.V., van Helden, A. and Donoghue, M. (1993) Organohalogen Compounds 12, 333-335.
(3) Subramanian, A.N., Tanabe, S., Hidaka, H. and Tatsukawa, R. (1986) Environ. Pollut. 40, 173-189
(4) Van den Brink, N. W., van Franeker, J.A. and de Ruiter-Dijkman, E.M. (1998) Environ Toxicol Chem. 17, 702-709.
(5) Corsolini, S., Kannan, K., Evans, T., Focardi, S. and Giesy, J.P. (2000) Organohalogen Compounds 46, 314-317.
(6) Iseki, N., Hayama, S-I., Masunaga, S. and Nakanishi, J. (2000) J. Environ Chem. 10, 817-831.
(7) Senthil Kumar, K., Kannan, K., Paramasivan, O.N., Shanmugasundaram, V.P., Nakanishi, J. and Masunaga, S. (2001a) Environ Sci Technol. (in press)
(8) Senthil Kumar, K., Iseki, N., Hayama, S., Nakanishi, J. and Masunaga, S. (2001b) Arch Environ Contam Toxicol. (in press)