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Temporal Variation of PCDDs, PCDFs and PCBs in Baikal Seals (*Pusa sibirica*)

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Abstract—This study investigated accumulation features and temporal trends of dioxins and related compounds (DRCs), such as PCDD/Fs, dioxin-like PCBs (DL-PCBs), and non dioxin-like PCBs (NDL-PCBs) in the blubber of Baikal seals collected in 1992 and 2005. PCBs including DL- and NDL-congeners were dominant. Concentrations of PCDD and PCB congeners in males were significantly higher than in females. However, such a trend was not observed for PCDFs. In males, age-dependent accumulations were observed for PCDD, mono-*ortho* PCB and NDL-PCB congeners. PCDFs and non-*ortho* PCBs showed no such trend, implying that exposure of seals to these contaminants has been decreasing in recent years. No decreasing temporal trend was observed for PCDDs, mono-*ortho* PCBs and NDL-PCBs, suggesting that Baikal seals are still exposed to relatively high levels of PCDDs and PCBs. TEQs of PCDDs and mono-*ortho* PCBs in seals collected in 2005 were within 62–77% of total TEQs. The TEQ levels in 40% of the specimens exceeded the threshold level for immunosuppression observed in harbor seals.

Keywords: PCDD/Fs, PCBs, temporal trend, Baikal seal (*Pusa sibirica*)

INTRODUCTION

Lake Baikal is exposed to considerable influx of anthropogenic pollutants, because of the rapidly developing industrial activities since the 1960s. Especially, input of organochlorine compounds (OCs), such as dioxins, PCBs, and DDTs, into Lake Baikal occurred heavily during the 1990s and possibly even now. High levels of OCs were detected in Baikal seals and water birds (Iwata *et al.*, 1995; Nakata *et al.*, 1995; Kunisue *et al.*, 2002), and hence, their toxic effects such as immunosuppression have been of great concern.

In Russia, production and use of certain harmful chemicals were banned since the late 1980s. However, still continuing illegal use of PCBs could be suspected because 500 tons of Sovol, a technical PCB was produced every year up to 1992 (Ivanov and Sandell, 1992). Furthermore, in Russia, PCB was used not only in closed systems like transformers and capacitors but also open systems such as plasticizers. Therefore, discharge of a large amounts of PCBs to the environment were noticed. On the other hand, no information on the present status of dioxins and related compounds (DRCs) such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like PCBs (DL-PCBs) in Lake Baikal is available. Previously, our study group elucidated contamination status of DRCs in Baikal seals collected in 1992 (Iwata *et al.*, 2004), and demonstrated that the DRC concentrations were higher than those in other seal species collected from various regions of the world and the TEQ levels exceeded the estimated threshold concentrations for immunosuppression reported in harbor seal (Ross *et al.*, 1995). From these facts, recent contamination and toxic impacts of PCDDs, PCDFs, and PCBs in Baikal seals are still of concern.

The objectives of this study are to understand the contamination status, accumulation features such as gender-difference, age-dependent variation and temporal trends of PCDDs, PCDFs and PCBs by analyzing blubber samples of Baikal seals collected in 1992 and 2005. In addition, the possible risk by PCDDs, PCDFs and PCBs to Baikal seals is also discussed.

MATERIALS AND METHODS

Baikal seals were collected by shooting from Lake Baikal in 1992 and 2005 under license from local government by shooting and were immediately dissected. Blubber samples of 10 males (age: 0.5–35.5) in 1992, and 10 males (age: 0.25–41.5) and 10 females (0.25–41.5) in 2005 were obtained and stored in Environmental Specimen Bank for Global Monitoring (*es*-BANK) of Ehime University (Tanabe, 2006) at –25°C until analysis.

The PCDD/Fs and DL-PCBs were analyzed following the method described previously (Tanabe *et al.*, 2004). Briefly, blubber samples (3 g) were ground with anhydrous sodium sulfate and extracted in a Soxhlet apparatus with dichloromethane (DCM). The extract was concentrated and an aliquot of the extract was used for lipid determination by gravimetric method. $^{13}C_{12}$-labeled PCDD/Fs and DL-PCBs were spiked into the remaining extract as internal standards (IS). Lipid in this solution was removed by gel permeation chromatography (GPC). The first fraction containing lipid was discarded, and the second fraction containing PCDD/Fs and DL-PCBs was collected, concentrated and passed through activated silica-gel packed in a glass column. PCDD/Fs and DL-PCBs were eluted with hexane. After concentration, the cleaned up extract was spiked onto activated alumina packed in a glass column. The first fraction eluted with hexane contained most of the mono-*ortho* PCBs, and the second fraction eluted with 50% DCM in hexane contained the remaining mono-*ortho* PCBs, non-*ortho* PCBs and PCDD/Fs. Then the second fraction was passed

Table 1. Concentrations (pg/g lipid wt.) of PCDDs, PCDFs and PCBs in the blubber of Baikal seals collected in 1992 and 2005.

	Samples collected in 2005 Male									
	Immature (n = 3)					Mature (n = 7)				
	Mean	±	SD	Median	Range	Mean	±	SD	Median	Range
ΣPCDDs	26	±	14	26	(12–40)	110	±	85	73	(17–230)[b,*]
ΣPCDFs	30	±	4.0	32	(25–32)	36	±	26	26	(18–93)
Σnon-*ortho* PCBs	1300	±	300	1300	(960–1600)	1300	±	570	1300	(760–2300)[b,*]
Σmono-*ortho* PCBs[a]	830	±	350	850	(480–1200)	2100	±	1200	2000	(640–3600)[b,**]
Σnon dioxin-like PCBs[a]	3400	±	1100	3800	(2100–4200)	15000	±	12000	9700	(2600–35000)[b,*]
ΣTEQ	260	±	98	250	(160–360)	500	±	300	410	(170–950)b*

	Samples collected in 2005 Female									
	Immature (n = 3)					Mature (n = 7)				
	Mean	±	SD	Median	Range	Mean	±	SD	Median	Range
ΣPCDDs	12	±	3.7	12	(8.8–16)	16	±	7.0	11	(9.8–26)
ΣPCDFs	24	±	1.4	25	(23–25)	27	±	8.4	25	(19–42)
Σnon-*ortho* PCBs	740	±	170	770	(550–900)	730	±	260	700	(460–1100)
Σmono-*ortho* PCBs[a]	420	±	100	430	(310–510)	450	±	180	380	(240–760)
Σnon dioxin-like PCBs[a]	2300	±	770	2000	(1700–3100)	3300	±	1800	3300	(980–6100)
ΣTEQ	140	±	35	150	(100–170)	150	±	60	120	(82–250)

[a]ng/g lipid wt.

[b]Concentrations in mature male were significantly higher than those in mature female. *$p < 0.05$; **$p < 0.01$.

Table 2. Relationships between age and concentrations of dioxins and related compounds and non dioxin-like PCBs in the blubber of Baikal seal collected in 2005.

	Male (n = 10)*				Female (n = 10)*			
	a	b	r^2	p	a	b	r^2	p
Dioxins and related compounds								
PCDDs								
2,3,7,8-T_4CDD	0.99	1.8	0.86	<0.001	0.0035	2.8	0.0023	0.89
1,2,3,7,8-P_5CDD	3.1	0.74	0.85	<0.001	0.069	6.7	0.090	0.40
1,2,3,4,7,8-H_6CDD	0.065	1.1	0.8	<0.001	0.0253	0.88	0.51	<0.05
1,2,3,6,7,8-H_6CDD	0.35	1.5	0.83	<0.001	0.052	1.6	0.40	<0.05
1,2,3,7,8,9-H_6CDD	0.041	0.42	0.81	<0.001	0.0072	0.32	0.35	0.071
PCDFs								
2,3,7,8-T_4CDF	0.27	12	0.23	0.16	0.068	14	0.059	0.50
1,2,3,7,8-P_5CDF	0.22	7.6	0.12	0.33	–0.021	8.0	0.018	0.71
2,3,4,7,8-P_5CDF	0.065	5.1	0.060	0.50	–0.011	4.0	0.019	0.70
Non-ortho PCBs								
3,3′,4,4′-T_4CB (#77)	1.7	88	0.16	0.26	0.43	20	0.38	0.057
3,4,4′,5-T_4CB (#81)	1.8	100	0.32	0.091	–0.017	66	0.00021	0.97
3,3′,4,4′,5-P_5CB (#126)	11	860	0.13	0.30	–2.0	640	0.020	0.70
3,3′,4,4′,5,5′-H_6CB (#169)	0.63	21	0.48	<0.05	0.31	20	0.29	0.11
Mono- *ortho* PCBs								
2,3,3′,4,4′-P_5CB (#105)	1700	99000	0.90	<0.0001	180	88000	0.0059	0.83
2,3,4,4′,5-P_5CB (#114)	1600	15000	0.90	<0.0001	31	12000	0.014	0.74
2,3′,4,4′,5-P5CB (#118)	44000	350000	0.91	<0.0001	340	260000	0.0034	0.87
2′,3,4,4′,5-P_5CB (#123)	110	6900	0.57	<0.05	100	4100	0.15	0.26
2,3,3′,4,4′,5-H_6CB (#156)	4300	39000	0.87	<0.0001	600	31000	0.19	0.20
2,3,3′,4,4′,5′-H_6CB (#157)	2300	6800	0.91	<0.0001	210	9000	0.26	0.13
2,3′,4,4′,5,5′-H_6CB (#167)	1500	11000	0.92	<0.0001	190	8400	0.23	0.16
2,3,3′,4,4′,5,5′-H_7CB (#189)	190	1600	0.87	<0.0001	69	1400	0.32	0.090

through activated carbon-dispersed silica gel packed in a glass column. The first fraction was eluted with 25% DCM in hexane to obtain the remaining mono-*ortho* PCBs and combined with the first fraction separated by alumina column. Non-*ortho* PCBs and PCDD/Fs were eluted with toluene as the second fraction. Both fractions were concentrated to near dryness. $^{13}C_{12}$-labeled CB-157 prepared in decane was added in the combined first fraction, and $^{13}C_{12}$-labeled 1234-T_4CDD and 123789-H_6CDD with decane were added in the second fraction. Identification and quantification were performed using a gas chromatograph (GC: Agilent 6890 series) with an auto injection system and a bench-topped double-focusing mass selective detector (MS: JEOL GC-Mate II) for mono-*ortho* PCBs and a high resolution MS (JEOL JMS-800D) for non-*ortho* PCBs and PCDD/Fs.

NDL-PCBs were analyzed as follow the method. Briefly, blubber samples (2 g) were ground with anhydrous sodium sulfate and extracted in a Soxhlet apparatus with diethyl ether/hexane (3:1). The extract was concentrated and $^{13}C_{12}$-labeled PCBs were spiked into an extract as internal standard. Lipid in this extract was removed by GPC. The second fraction of GPC including PCBs was concentrated and passed through the activated silica gel packed in a glass column. PCBs were eluted with 5% DCM in hexane, and this fraction was concentrated to

Table 2. (continued).

	Male (n = 10)*				Female (n = 10)*			
	a	b	r^2	p	a	b	r^2	p
Non dioxin-like PCBs								
2,4,4′-T_3CB (#28)	0.042	12	0.052	0.53	−0.078	11	0.43	<0.05
2,2′5,5′-T_4CB (#52)	0.21	18	0.19	0.21	0.0055	15	0.000095	0.98
2,2′4′,5-T_4CB (#49)	0.052	4.5	0.18	0.22	0.00055	3.9	0.000016	0.99
2,4,4′,5-T_4CB (#74)	3.5	92	0.67	<0.01	0.081	67	0.0020	0.90
2,2′,3,5′,6-P_5CB (#95)	0.23	8.2	0.27	0.13	0.041	7.3	0.012	0.76
2,2′,4,5,5′-P_5CB (#101)	11	240	0.51	<0.05	0.27	190	0.0014	0.92
2,2′,4,4′,5-P_5CB (#99)	67	87	0.73	<0.01	0.067	220	0.00011	0.98
2,3′,4,4′,6-P_5CB (#119)	2.5	11	0.68	<0.01	0.0052	5.0	0.00093	0.93
2,2′,3,4,5′-P_5CB (#87)	1.5	61	0.62	<0.01	0.068	43	0.0017	0.91
2,3,3′,4′,6-P_5CB (#110)	2.4	110	0.26	0.13	−0.30	80	0.018	0.71
2,2′,3′,4,5,6′-H_6CB (#149)	6.1	45	0.57	<0.05	0.32	50	0.018	0.71
2,2′,4,4′,5,5′-H_6CB (#153)	300	−170	0.85	<0.001	12	600	0.19	0.21
2,2′,3′,4,4′,5-H_6CB (#138)	73	260	0.63	<0.01	4.3	360	0.091	0.40
2,3,3′,4,4′,6-H_6CB (#158)	3.8	9.3	0.52	<0.05	0.17	16	0.058	0.50
2,2′,3,3′,4,4′-H_6CB (#128)	0.90	6.3	0.33	0.085	0.035	7.6	0.0076	0.81
2,2′,3,3′,5,5′,6-H_7CB (#178)	6.4	−2.2	0.87	<0.0001	0.66	14	0.31	0.096
2,2′,3,4′,5,5′,6-H_7CB (#187)	11	3.4	0.68	<0.01	1.6	30	0.29	0.11
2,2′,3,4,4′,5′,6-H_7CB (#183)	13	−7.3	0.83	<0.001	1.7	25	0.42	<0.05
2,2′,3,3′,4′,5,6-H_7CB (#177)	0.77	1.8	0.48	<0.05	0.11	3.2	0.14	0.29
2,2′,3,3′,4,4′,6-H_7CB (#171)	2.7	−1.6	0.85	<0.001	0.26	4.9	0.39	0.052
2,2′,3,4,4′,5,5′-H_7CB (#180)	70	−31	0.85	<0.001	8.7	120	0.42	<0.05
2,2′,3,3′,4,4′,5-H_7CB (#170)	27	4.9	0.83	<0.001	2.4	42	0.39	0.055
2,2′,3,3′,5,5′,6,6′-O_8CB (#202)	2.3	−5.0	0.82	<0.001	0.36	3.0	0.49	<0.05
2,2′,3,3′,4′,5,5′,6-O_8CB (#199)	7.4	−14	0.82	<0.001	1.3	7.4	0.55	<0.05
2,2′,3,3′,4,4′,5,5′-O_8CB (#194)	13	−26	0.75	<0.01	2.0	8.9	0.52	<0.05
2,3,3′,4,4′,5,5′,6-O_8CB (#205)	1.3	−1.9	0.71	<0.01	0.19	1.0	0.49	<0.05
2,2′,3,3′,4,5,5′,6,6′-N_9CB (#208)	1.3	−3.1	0.69	<0.01	0.25	1.1	0.55	<0.05
2,2′,3,3′,4,4′,5,5′,6-N_9CB (#206)	7.6	−15	0.63	<0.01	1.5	4.0	0.56	<0.05
2,2′,3,3′,4,4′,5,5′,6,6′-D_{10}CB (#209)	2.1	−4.7	0.55	<0.05	0.51	0.69	0.71	<0.01

*Concentration (pg/g lipid wt.) = $a \times$ age (year) + b.

H_7–O_8CDDs and H_6–O_8CDFs were not examined because concentrations of these congeners were below detection limit values in all the samples.

near dryness. Identification and quantification were performed using a GC (Agilent 6890 series)-MS (Agilent 5973N).

TEQs were calculated using the mammalian TEFs proposed by WHO in 1998 (Van den Berg *et al.*, 1998).

The decline of DRC and PCB levels in the blubber of Baikal seals were calculated using the following equation:

$$C_t = C_0 \times e^{-kt}$$

where C_0 and C_t are the concentrations of the first (1992) and the last (2005) investigation, respectively. k is the constant and t is the time interval (13 years) between the investigations. Half-life times ($t_{dec1/2}$) was defined as the duration in

Table 3. Comparison of DRCs concentrations (pg/g lipid wt.) in male blubber of Baikal seals collected in 1992 and 2005 and estimated half-lives of DRCs.

Congener	Samples collected in 2005				Samples collected in 1992				Half-life	
	Mean	±	SD	Range	Mean	±	SD	Range	k	$t_{1/2}$ (year)
Dioxins and related compounds										
PCDDs										
2,3,7,8-T_4CDD	18	±	17	(3.1–51)	26	±	19	(3.4–64)	0.0430	16.1
1,2,3,7,8-P_5CDD	53	±	55	(6.8–160)	65	±	51	(9.3–170)	0.0419	16.5
1,2,3,4,7,8-H_6CDD	2.2	±	1.2	(0.6–3.9)	4.1	±	2.3	(1.6–8.1)[b,*]	0.0496	14.0
1,2,3,6,7,8-H_6CDD	7.2	±	6.0	(1.4–19)	13	±	9.4	(3.2–31)	0.0643	10.8
1,2,3,7,8,9-H_6CDD	1.1	±	0.73	(0.36–2.3)	2.0	±	1.3	(0.67–4)	0.0487	14.2
PCDFs										
2,3,7,8-T_4CDF	17	±	8.9	(8–37)	49	±	27	(13–84)[b,**]	0.0812	8.50
1,2,3,7,8-P_5CDF	11	±	10	(3.7–39)	63	±	36	(27–130)[b,***]	0.135	5.12
2,3,4,7,8-P_5CDF	6.1	±	4.1	(2.6–16)	30	±	15	(12–56)[b,***]	0.139	4.99
Non-*ortho* PCBs										
3,3′,4,4′-T_4CB (#77)	120	±	68	(24–220)	220	±	440	(12–1500)	NC[c]	
3,4,4′,5-T_4CB (#81)	130	±	52	(54–220)	350	±	220	(110–730)[b,**]	0.0801	8.70
3,3′,4,4′,5-P_5CB (#126)	1000	±	460	(530–2100)	2300	±	1100	(920–4600)[b,**]	0.0578	12.0
3,3′,4,4′,5,5′-H_6CB (#169)	32	±	15	(13–62)	55	±	28	(17–110)[b,*]	0.0336	20.6
Mono-*ortho* PCBs[a]										
2,3,3′,4,4′-P_5CB (#105)	380	±	290	(110–840)	420	±	280	(72–900)	0.0221	31.4
2,3,4,4′,5-P_5CB (#114)	41	±	27	(13–91)	49	±	28	(11–87)	0.0210	33.0
2,3′,4,4′,5-P_5CB (#118)	1100	±	740	(300–2300)	1100	±	730	(230–2200)	0.0139	49.9
2′,3,4,4′,5-P_5CB (#123)	8.8	±	2.3	(6.1–12)	13	±	6.7	(4.4–24)	0.0189	36.7
2,3,3′,4,4′,5-H_6CB (#156)	110	±	71	(29–240)	140	±	86	(32–300)	0.0217	31.9
2,3,3′,4,4′,5′-H_6CB (#157)	45	±	38	(8.2–120)	46	±	33	(8.3–100)	0.0209	33.2
2,3′,4,4′,5,5′-H_6CB (#167)	36	±	25	(9.4–79)	52	±	36	(10–120)	0.0277	25.0
2,3,3′,4,4′,5,5′-H_7CB (#189)	4.8	±	3.4	(1.4–11)	9.2	±	6.6	(2.0–22)	0.0418	16.6

which initial concentrations decrease to half.

Mann-Whitney U test was used for gender-differences and temporal trends analysis. Regression analysis was carried out to examine the relationships between age and concentrations of PCDD/Fs and PCBs. A p value of less than 0.05 was considered to indicate statistical significance. These analyses were executed using Statcel 97 for Excel.

RESULTS AND DISCUSSION

Contamination status and gender difference

DRCs, except H_6-H_7CDFs and O_8CDD/Fs, were detected in all the blubber samples (Table 1). In the specimens collected during 2005, mono-*ortho* PCBs were dominant followed by non-*ortho* PCBs > PCDDs > PCDFs in males and in females the pattern was non-*ortho* PCBs > PCDFs > PCDDs. Concentrations of DL-PCBs were 4–5 orders of magnitude higher than those of PCDD/Fs. Concentrations of almost all the PCDD and DL-PCB congeners in male were significantly higher than those in females, suggesting excretion of these contaminants by parturition and lactation. On the other hand, no gender-difference was observed for PCDFs. This could be due to the lower transfer potency of PCDF congeners to pup by parturition and lactation compared with PCDDs and DL-

Table 3. (continued).

Congener	Samples collected in 2005				Samples collected in 1992				Half-life	
	Mean	±	SD	Range	Mean	±	SD	Range	*k*	$t_{1/2}$ (year)
Non dioxin-like PCBs[a]										
2,4,4′-T_3CB (#28)	13	±	2.7	(7.7–16)	21	±	9.5	(9.6–40)	0.0353	19.6
2,2′5,5′-T_4CB (#52)	21	±	7.9	(11–41)	27	±	7.6	(16–40)[b,*]	0.0172	40.3
2,2′4′,5-T_4CB (#49)	5.4	±	2.0	(2.8–10)	6.6	±	1.8	(4.1–9.3)	0.0197	35.2
2,4,4′,5-T_4CB (#74)	150	±	68	(70–250)	240	±	130	(62–410)	0.0312	22.2
2,2′,3,5′,6-P_5CB (#95)	12	±	7	(5.5–31)	18	±	8.6	(8.2–38)	0.0408	17.0
2,2′,4,5,5′-P_5CB (#101)	430	±	260	(190–1100)	600	±	400	(160–1500)	0.0200	34.7
2,2′,4,4′,5-P_5CB (#99)	1200	±	1200	(250–4200)	1200	±	1200	(160–4200)	0.0096	72.2
2,3′,4,4′,6-P_5CB (#119)	53	±	49	(14–170)	63	±	61	(11–210)	0.0116	59.7
2,2′,3,4,5′-P_5CB (#87)	86	±	31	(43–140)	200	±	180	(39–650)[b,*]	0.0373	18.6
2,3,3′,4′,6-P_5CB (#110)	150	±	76	(67–350)	220	±	130	(80–530)	0.0369	18.8
2,2′,3′,4,5,6′-H_6CB (#149)	150	±	130	(42–490)	210	±	190	(42–680)	0.0119	58.2
2,2′,4,4′,5,5′-H_6CB (#153)	4800	±	5100	(550–15000)	3800	±	3800	(370–12000)	0.00670	103
2,2′,3′,4,4′,5-H_6CB (#138)	1500	±	1500	(380–5300)	2000	±	2000	(260–6900)	0.0148	46.8
2,3,3′,4,4′,6-H_6CB (#158)	73	±	85	(18–300)	110	±	130	(16–460)	0.0248	27.9
2,2′,3,3′,4,4′-H_6CB (#128)	21	±	25	(6.3–92)	40	±	49	(7.4–170)[b,*]	0.0476	14.6
2,2′,3,3′,5,5′,6-H_7CB (#178)	100	±	110	(14–320)	100	±	100	(8.7–310)	0.0202	34.3
2,2′,3,4′,5,5′,6-H_7CB (#187)	180	±	200	(35–700)	250	±	290	(22–980)	0.0172	40.3
2,2′,3,4,4′,5′,6-H_7CB (#183)	220	±	240	(25–730)	260	±	270	(21–900)	0.0206	33.7
2,2′,3,3′,4′,5,6-H_7CB (#177)	15	±	18	(3.4–63)	25	±	33	(2.6–110)	0.0129	53.7
2,2′,3,3′,4,4′,6-H_7CB (#171)	44	±	48	(4.7–140)	45	±	47	(3.8–150)	0.0146	47.5
2,2′,3,4,4′,5,5′-H_7CB (#180)	1100	±	1200	(100–3300)	1200	±	1200	(86–3700)	0.0218	31.8
2,2′,3,3′,4,4′,5-H_7CB (#170)	450	±	460	(36–1300)	390	±	410	(28–1300)	0.00670	103
2,2′,3,3′,5,5′,6,6′-O_8CB (#202)	33	±	41	(2.7–120)	31	±	35	(1.9–110)	0.0292	23.7
2,2′,3,3′,4′,5,5′,6-O_8CB (#199)	110	±	130	(6.8–370)	110	±	120	(5.6–370)	0.0266	26.1
2,2′,3,3′,4,4′,5,5′-O_8CB (#194)	190	±	240	(7.1–610)	180	±	210	(8.6–650)	0.0404	17.2
2,3,3′,4,4′,5,5′,6-O_8CB (#205)	19	±	24	(0.71–63)	17	±	18	(0.9–56)	0.0415	16.7
2,2′,3,3′,4,5,5′,6,6′-N_9CB (#208)	19	±	25	(0.62–73)	19	±	23	(0.84–72)	0.0308	22.5
2,2′,3,3′,4,4′,5,5′,6-N_9CB (#206)	110	±	150	(2.4–380)	120	±	140	(4.5–430)	0.0523	13.3
2,2′,3,3′,4,4′,5,5′,6,6′-D_{10}CB (#209)	31	±	47	(0.45–120)	31	±	40	(1.1–110)	0.0428	16.2

[a]ng/g lipid wt.

[b]Concentration in Baikal seals collected in 1992 was higher than those collected in 2005. $*p < 0.05$; $**p < 0.01$; $***p < 0.001$.

[c]Not calculated because of higher median concentration in 2005 than in 1992 samples.

1,2,3,4,6,7,8-H_7CDD, O_8CDD, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,3,7,8,9-, 2,3,4,6,7,8-H_6CDF, 1,2,3,4,6,7,8-, 1,2,3,4,7,8,9-H_7CDF, and O_8CDF were not shown due to concentrations below detection limits.

PCBs and/or decline of recent exposure to PCDF congeners.

NDL-PCB levels were in the range of 2100–35000 ng/g lipid wt. in males and 980–6100 ng/g lipid wt. in females (Table 1). Concentrations of almost all the NDL-PCB congeners in males were significantly higher than those in females, suggesting elimination of these contaminants via lactation. However, no gender-difference was observed for high chlorinated congeners such as Cl_8–Cl_{10}, suggesting possible lower transfer rates of these contaminants to milk due to their large molecular size.

Age-dependent accumulation

When the relationships between age and concentrations of DRC congeners were examined in Baikal seals collected in 2005, no age-dependent accumulation

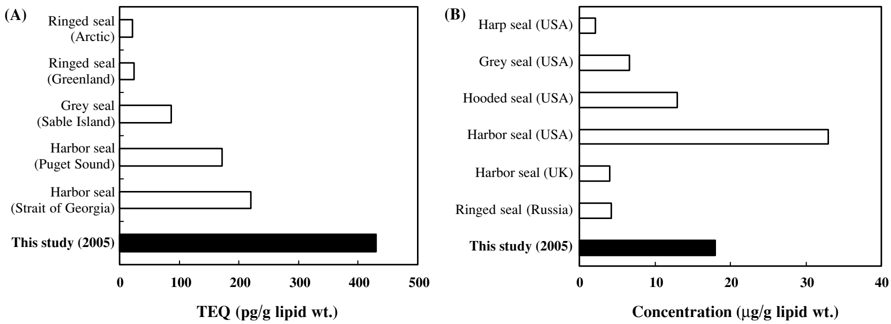

Fig. 1. Comparison of TEQ (A) and NDL-PCB (B) concentration in pinnipeds.

was observed for females (Table 2), suggesting that these contaminants are transferred from mother to pup via placenta and milk. On the other hand, significant age-dependent accumulation of all PCDD and mono-*ortho* PCB congeners was found for males (Table 2). However, concentrations of PCDFs and non-*ortho* PCBs in males did not increase with age (Table 2). This may indicate that the exposure of Baikal seals to PCDFs and non-*ortho* PCBs has been decreasing in recent years and/or these contaminants are more easily metabolized by Baikal seals than PCDDs and mono-*ortho* PCBs.

Significant age-dependent accumulation of almost all NDL-PCB congeners was found for males. However concentrations of CB-28, 49, 52, 95 and 128 in males did not increase with age, suggesting that these contaminants are more easily metabolized by Baikal seals. On the other hand, significant age-dependent accumulation of 8-10 chlorinated congeners was found in both males and females which may be due to their lower transfer rates to milk because of their large molecular size.

Temporal trend

Comparison of the data between 1992 and 2005 showed a significant decreasing trend of PCDFs and non-*ortho* PCBs except for CB-77 (Table 3), suggesting a decline of exposure to these compounds. But no such significant difference was observed for PCDDs, mono-*ortho* PCBs and NDL-PCBs (Table 3). When the half-lives of DRCs and NDL-PCBs were calculated using the data of 1992 and 2005 samples, longer half-lives for PCDDs, mono-*ortho* PCBs and NDL-PCBs than PCDFs and non-*ortho* PCBs were found, implying the presence of higher sources of the former compounds in and around Lake Baikal. It is likely that the sources of mono-*ortho* PCBs and NDL-PCBs are derived from Sovol, a technical PCB used in the Soviet Union, in which these compounds are abundant, but PCDD sources can not be clearly explained. As another possible reason why no decline of PCDD levels was noticed between 1992 and 2005 samples, it can be assumed that PCDD congeners may be more persistent than PCDF congeners in Baikal seals. Considering these observations, continuous investigations on DRCs in Baikal seals are needed to comprehend temporal trends and assessment of their risk.

Risk assessment

TEQ levels were significantly higher in males with the range of 160–950 pg TEQ/g lipid wt. in males and 82–250 pg TEQ/g lipid wt. in females (Table 1). DL-PCBs made the largest contribution to TEQs. TEQ and NDL-PCB levels observed in Baikal seals were relatively higher than those in seals from other areas (Fig. 1) (Nakata *et al.*, 1998; Addison *et al.*, 1999, 2005a, 2005b; Hobbs *et al.*, 2002; Ross *et al.*, 2004; Riget *et al.*, 2005; Hall and Thomas, 2007). In addition, TEQ levels in 40% of the specimens and NDL-PCBs in 10% of the specimens exceeded the immunosuppression value (TEQ: 209 pg/g lipid wt.; NDL-PCB: 16 μg/g lipid wt.) observed in harbor seals (Ross *et al.*, 1995; De Swart *et al.*, 1995). These results indicate that high levels of DRCs and NDL-PCBs present in Baikal seals may cause adverse effect such as immunosuppression. Especially, it can be expected that risk by PCBs are still at high.

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