DIOXINS AND RELATED COMPOUNDS IN BAIKAL SEALS (*PUSA SIBIRICA*): LEVELS, PATTERNS AND TEMPORAL TRENDS

Imaeda D[1], Kunisue T[1], Iwata H[1], Tsydenova O[1], Takahashi S[1], Amano M[2], Petrov EA[3], Batoev VB[4], Tanabe S[1]

[1]Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan; [2]Department of Animal Sciences, Teikyo University of Science and Technology, 2525 Yatsusawa Uenohara-shi, Yamanashi 409-0193, Japan; [3]The Eastern-Siberian Scientific and Production Fisheries Center, "VOSTSIBRYBCENTER", Ulan-Ude, Buryatia 670034, Russia; [4]Baikal Institute of Nature Management, Siberian Branch of Russian Academy of Sciences, Ulan-Ude, Buryatia 670047, Russia

Abstract

This study determined concentrations of dioxins and related compounds (DRCs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (co-PCBs) in the blubber of Baikal seals collected in 2005. DRCs were detected in all the samples and mono-*ortho* PCBs were dominant, followed by non-*ortho* PCBs > PCDDs > PCDFs in males, and non-*ortho* PCBs > PCDFs > PCDDs in females. Concentrations of PCDDs and co-PCBs in males were significantly higher than those in females, while levels of PCDFs were not significantly different. In addition, age-dependent accumulation of PCDDs and mono-*ortho* PCBs was observed in males, but there was no such trend for PCDFs and non-*ortho* PCBs. When the concentrations of DRCs in 2005 were compared with those in 1992, a significant decreasing trend was observed for PCDFs and non-*ortho* PCBs, but not PCDDs and mono-*ortho* PCBs. TEQs in Baikal seals were higher than those in seals from other areas and the levels in 40% of the specimens exceeded the estimated threshold level for immune suppression observed in harbour seals, implying that Baikal seals may be still at high risk from DRCs.

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 has been occurring heavily during the 1990s and possibly even now. High levels of OCs were detected in Baikal seals and water birds,[1-3] and hence, their toxic effects such as immunosuppression have been of great concern.

In Russia, however, the production and use of technical DDT and PCBs were regulated in 1974 and 1990s, respectively. Therefore, it seems that OCs input into Lake Baikal has been recently decreasing. In a recent study, significant decline of PCBs and DDTs levels in Baikal seal was found between 1992 to 2003.[4] On the other hand, no information on the present status of DRCs in Lake Baikal is available. Previously, our study group elucidated contamination status of DRCs in Baikal seals collected in 1992,[2] and demonstrated that the DRC concentrations were higher than those in other seal species collected from various regions and the TEQ levels exceeded the estimated threshold level for immune suppression reported in harbour seal.[2] Recent contamination and toxic impacts of DRCs in Baikal seals are still of concern.

The objective of this study is to understand recent contamination status and temporal trends of DRCs in the blubber of Baikal seals collected in 1992 and 2005.

Materials and Methods

Baikal seals were collected from Lake Baikal in 1992 and 2005 under licence 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 [5] at -25 °C until analysis.

Analysis of DRCs in the blubber samples was conducted using the method reported previously.[6] Identification and quantification were performed using HRGC-HRMS. TEQs were calculated using the mammalian TEFs proposed by WHO in 1998.[7]

The decline of DRC levels in the blubber of Baikal seals was 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 which initial concentrations decrease to half.

Results and Discussion

Contamination Status: DRCs, except H_6-H_7CDFs and O_8CDD/DFs, were detected in all the blubber samples (Table 1). Mono-*ortho* PCBs were dominant, followed by non-*ortho* PCBs > PCDDs > PCDFs in males and non-*ortho* PCBs > PCDFs > PCDDs in females collected in 2005, respectively. Concentrations of co-PCBs were 4-5 orders of magnitude higher than those of PCDD/DFs.

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

	1992		2005			
	Male (*n* =10)		Male (*n* =10)		Female (*n* =10)	
	Mean ± SD	(Range)	Mean ± SD	(Range)	Mean ± SD	(Range)
age (year)	13 ± 12	(0.5-35.5)	17 ± 16	(0.25-41.5)	17 ± 16	(0.25-41.5)
lipid (%)	90 ± 2.8	(86-94)	89 ± 1.6	(87-91)	91 ± 2.2	(86-93)
ΣPCDDs	110 ± 84	(18-280)	82 ± 80 [a,**]	(12-230)	15 ± 6.2	(8.8-26)
ΣPCDFs	140 ± 74	(52-270)	34 ± 22	(18-93)	26 ± 7.1	(19-42)
ΣNon-*ortho* PCBs	2900 ± 1600	(1100-6600)	1300 ± 490 [a,**]	(760-2300)	730 ± 230	(460-1100)
ΣMono-*ortho* PCBs [b]	1900 ± 1200	(370-3800)	1700 ± 1200 [a,***]	(480-3600)	440 ± 160	(240-760)
ΣTEQs	620 ± 360	(170-1100)	430 ± 270 [a,**]	(160-950)	150 ± 52	(82-250)

[a] Concentrations in males from 2005 were significantly higher than those in females. *p < 0.05, **p < 0.01, ***p <0.001

[b] ng/g lipid wt.

TEQ levels were in the range of 160-950 pg TEQ/g lipid wt. in males and 82-250 pg TEQ/g lipid wt. in females, and significantly higher TEQs in males (Table 1). TEQ levels observed in Baikal seals were relatively higher than those in seals from other areas. In addition, TEQs in 40% of the specimens exceeded the immunosuppression value (209 pg TEQ/g lipid wt.) [8] observed in harbour seal, implying that Baikal seals may be still at high risk by DRCs.

Accumulation Features: Concentrations of almost all the PCDD and co-PCB congeners in males were significantly higher than those in females, suggesting that these contaminants transfer from mother to pup via placenta and milk. This trend was consistent with the results reported previously in other pinnipeds.[9] On the other hand, no sex-difference was observed for PCDFs. This could be due to lower transfer potency of PCDF congeners to pup via lactation compared with PCDDs and co-PCBs and/or decline of recent exposure to PCDF congeners.

When relationships between age and concentrations of DRC congeners were examined in Baikal seals collected in 2005, no age-dependent accumulation of these congeners was observed for females (Table 2),

suggesting that these contaminants transfer 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, and this result was consistent with the data obtained in 1992 samples (Table 2). However, concentrations of PCDFs and non-*ortho* PCBs in males of 2005 did not increase with age, whereas significant age-dependent accumulation of these compounds was observed in 1992 samples (Table 2). This result 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. The strength of regression coefficient between age and concentrations of PCDF and non-*ortho* PCB congeners obtained from 1992 male samples was also weaker than those for PCDDs and mono-*ortho* PCBs (Table 2).

Table 2. Relationships between age and concentrations of DRCs in the blubber of Baikal seals.

Congener	1992				2005							
	Male (n =10)*				Male (n =10)*				Female (n =10)*			
	a	b	r^2	p	a	b	r^2	p	a	b	r^2	p
PCDDs												
2,3,7,8-T_4CDD	1.53	6.59	0.87	*<0.0001*	0.99	1.8	0.86	*<0.001*	0.0035	2.8	0.0023	*0.89*
1,2,3,7,8-P_5CDD	4.03	13.2	0.84	*<0.001*	3.1	0.74	0.85	*<0.001*	0.069	6.7	0.090	*0.40*
1,2,3,4,7,8-H_6CDD	0.174	1.84	0.81	*<0.0001*	0.065	1.1	0.8	*<0.001*	0.0253	0.88	0.51	*0.020*
1,2,3,6,7,8-H_6CDD	0.686	4.14	0.77	*<0.0001*	0.35	1.5	0.83	*<0.001*	0.052	1.6	0.40	*0.049*
1,2,3,7,8,9-H_6CDD	0.095	0.718	0.75	*0.0012*	0.041	0.42	0.81	*<0.001*	0.0072	0.32	0.35	*0.071*
PCDFs												
2,3,7,8-T_4CDF	1.5	30	0.43	*0.040*	0.27	12	0.23	*0.16*	0.068	14	0.059	*0.50*
1,2,3,7,8-P_5CDF	2.0	38	0.43	*0.038*	0.22	7.6	0.12	*0.33*	-0.021	8.0	0.018	*0.71*
2,3,4,7,8-P_5CDF	0.74	20	0.34	*0.077*	0.065	5.1	0.060	*0.50*	-0.011	4.0	0.019	*0.70*
1,2,3,4,7,8-H_6CDF	0.054	0.39	0.63	*0.0064*		N.C.			0.0020	-0.0039	0.11	*0.35*
1,2,3,6,7,8-H_6CDF	0.027	0.24	0.55	*0.014*		N.C.				N.C.		
Non-*ortho* PCBs												
3,3',4,4'-T_4CB (#77)	27	-130	0.51	*0.020*	1.7	88	0.16	*0.26*	0.43	20	0.38	*0.057*
3,4,4',5-T_4CB (#81)	11	210	0.37	*0.064*	1.8	100	0.32	*0.091*	-0.017	66	0.00021	*0.97*
3,3',4,4',5-P_5CB (#126)	79	1300	0.70	*0.0024*	11	860	0.13	*0.30*	-2.0	640	0.020	*0.70*
3,3',4,4',5,5'-H_6CB (#169)	2.3	26	0.88	*<0.0001*	0.63	21	0.48	*0.027*	0.31	20	0.29	*0.11*
Mono-*ortho* PCBs												
2,3,3',4,4'-P_5CB (#105)	23000	120000	0.95	*<0.0001*	1700	99000	0.90	*<0.0001*	180	88000	0.0059	*0.83*
2,3,4,4',5-P_5CB (#114)	2100	22000	0.82	*<0.001*	1600	15000	0.90	*<0.0001*	31	12000	0.014	*0.74*
2,3',4,4',5-P_5CB (#118)	59000	380000	0.91	*<0.0001*	44000	350000	0.91	*<0.0001*	340	260000	0.0034	*0.87*
2',3,4,4',5-P_5CB (#123)	450	7000	0.64	*0.0053*	110	6900	0.57	*0.012*	100	4100	0.15	*0.26*
2,3,3',4,4',5-H_6CB (#156)	6700	52000	0.87	*<0.0001*	4300	39000	0.87	*<0.0001*	600	31000	0.19	*0.20*
2,3,3',4,4',5'-H_6CB (#157)	2500	13000	0.86	*<0.001*	2300	6800	0.91	*<0.0001*	210	9000	0.26	*0.13*
2,3',4,4',5,5'-H_6CB (#167)	3000	14000	0.90	*<0.0001*	1500	11000	0.92	*<0.0001*	190	8400	0.23	*0.16*
2,3,3',4,4',5,5'-H_7CB (#189)	470	3000	0.74	*0.0014*	190	1600	0.87	*<0.0001*	69	1400	0.32	*0.090*

*Concentration (pg/g lipid wt.) = a × age (years) + b.

N.C.: Not calculated due to concentrations below detection limits.

1,2,3,4,6,7,8-H_7CDD, O_8CDD, 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 N.C. in all the samples.

Temporal Trends: In comparison with the data between 1992 and 2005, a significant decreasing trend was observed for PCDFs and non-*ortho* PCBs except PCB 77 (Table 3), suggesting the decline of exposure to these compounds. But no significant difference was observed for PCDDs and mono-*ortho* PCBs (Table 3). When half-lives for DRCs were calculated using data of 1992 and 2005 samples, longer half-lives for PCDDs ($t_{dec1/2}$ range: 17-46 years) and mono-*ortho* PCBs ($t_{dec1/2}$ range: 16-92 years) than PCDFs ($t_{dec1/2}$ range: 7.2-11 years) and non-*ortho* PCBs ($t_{dec1/2}$ range: 11-19 years) were found (Table 3), implying greater sources of PCDDs and mono-*ortho* PCBs are present in or around Lake Baikal. It is likely that the source of mono-*ortho* PCBs are derived from technical PCB products, 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 is possible 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 assess their risk.

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.

Congeners	1992 (n =10)	2005 (n =10)	Half-life Time	
	Mean ± SD	Mean ± SD	k	$t_{dec1/2}$ (year)
PCDDs				
2,3,7,8-T_4CDD	26 ± 19	18 ± 17	0.028	27
1,2,3,7,8-P_5CDD	65 ± 51	53 ± 55	0.016	46
1,2,3,4,7,8-H_6CDD	4.1 ± 2.3 [a,*]	2.2 ± 1.2	0.048	17
1,2,3,6,7,8-H_6CDD	13 ± 9.4	7.2 ± 6.0	0.046	17
1,2,3,7,8,9-H_6CDD	2 ± 1.3	1.1 ± 0.73	0.046	17
PCDFs				
2,3,7,8-T_4CDF	49 ± 27 [a,**]	17 ± 8.9	0.081	11
1,2,3,7,8-P_5CDF	63 ± 36 [a,***]	11 ± 10	0.13	7.2
2,3,4,7,8-P_5CDF	30 ± 15 [a,***]	6.1 ± 4.1	0.12	7.7
Non-*ortho* PCBs				
3,3',4,4'-T_4CB (#77)	220 ± 440	120 ± 68	0.047	17
3,4,4',5-T_4CB (#81)	350 ± 220 [a,**]	130 ± 52	0.076	11
3,3',4,4',5-P_5CB (#126)	2300 ± 1100 [a,**]	1000 ± 460	0.064	13
3,3',4,4',5,5'-H_6CB (#169)	55 ± 28 [a,*]	32 ± 15	0.042	19
Mono-*ortho* PCBs				
2,3,3',4,4'-P_5CB (#105)	420000 ± 280000	380000 ± 290000	0.0077	92
2,3,4,4',5-P_5CB (#114)	49000 ± 28000	41000 ± 27000	0.014	53
2,3',4,4',5-P_5CB (#118)	1100000 ± 730000	1100000 ± 740000	N.C.	
2',3,4,4',5-P_5CB (#123)	13000 ± 6700	8800 ± 2300	0.030	25
2,3,3',4,4',5-H_6CB (#156)	140000 ± 86000	110000 ± 71000	0.019	39
2,3,3',4,4',5'-H_6CB (#157)	46000 ± 33000	45000 ± 38000	N.C.	
2,3',4,4',5,5'-H_6CB (#167)	52000 ± 36000	36000 ± 25000	0.029	27
2,3,3',4,4',5,5'-H_7CB (#189)	9200 ± 6600	4800 ± 3400	0.050	16

[a] Concentrations in Baikal seals collected in 1992 were higher than those collected in 2005. $*p < 0.05$, $**p < 0.01$, $***p < 0.001$

N.C.: Not calculated due to no decrease between 1992 and 2005.

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.

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