ISOMER PROFILE OF PCDDs, PCDFs AND DIOXIN-LIKE PCBs IN SEDIMENT FROM KAHOKUGATA LAGOON AND INFLOWNG RIVERS, JAPAN

Kakimoto H.[1], Oka H.[1, 2], Noguchi K.[1], Tsukabayashi H.[1], Tang N.[2], Toriba A.[2], Kizu R.[3], Hayakawa K.[2]
[1]Ishikawa Prefectural Institute of Public Health and Environmental Science, Kanazawa, 920-1154 Japan;
[2]Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, 920-1192 Japan;
[3]Faculty of Pharmaceutical Sciences, Doshisha Women's College of Liberal Arts, Kyotanabe, 610-0395 Japan

Abstract

Sediment samples were collected in Kahokugata Lagoon and inflowing rivers, central Japan. We determined the concentrations of dioxins (PCDDs, PCDFs and dioxin-like PCBs) of the sediment samples. The highest TEQ concentration (77 pg-TEQ/g-dry) was observed at a site located on the east side catchment drain of the lagoon. The homologue and isomer compositions of PCDD/DFs indicated that all the sediment samples are strongly influenced by now-banned chlorinated herbicides, such as chloronitrofen (CNP) and pentachlorophenol (PCP). The ratio of OCDD to PCDDs+PCDFs was higher in the northern part of the lagoon and lower in the southern part of the lagoon. This result indicated that PCP contamination was greater in the northern part of the lagoon than in the other parts. We found an outstandingly high ratio of dioxin-like PCBs (DL-PCBs) to the total dioxins at a sampling site located in the downstream of a river flowing into the east side catchment drain. On the other hand, the unusual isomer compositions of PCDFs caused by the discharge from a dye plant, which was previously observed in water samples, were much reduced in the present sediment samples.

Introduction

Kahokugata Lagoon is located 8 km north of central Kanazawa, which is the capitol city of Ishikawa Prefecture, central Honshu Island, Japan. Kahokugata Lagoon used to be brackish but is now a small (4.1km^2) freshwater lagoon with an average depth of 2.2 m. It was reclaimed since the early 1960s and the present size of the lagoon is only about 25% of the original size. Paddy fields surround the lagoon and many rivers empty into it. The ratio of the present lagoon's surface to entire watershed is the smallest (only 1.5%) of the main lagoons in Japan[1)]; therefore, persistent chemicals were thought to concentrate in sediment in the lagoon. In our previous study, we showed that water samples collected in the lagoon and inflowing rivers contained comparatively high levels of dioxins and the concentrations tended to be higher in spring and summer, the periods of plowing, planting and rice growing[2)]. Dioxins contained in chlorinated herbicides (CNP and PCP) as impurities still exist in soil of paddy fields[3, 4)] and are released into rivers with a large volume of water for irrigation during the above seasons.

In the present study, we collected surface sediment samples from the lagoon and rivers flowing into the lagoon and determined the dioxin concentrations of the sediment samples to compare the spatial distributions of concentration and homologue/isomer composition with those of the water samples. We also examined whether the peculiar isomers previously discharged from a dye manufacturing plant were still present in the sediment samples.

Materials and Methods

Surface sediment samples were collected at eleven sites (Fig. 1) including six sites in Kahokugata Lagoon (Nos. 1, 2, 4, 5, 10 and 11) and five sites in rivers that flow into the lagoon (Nos. 3, 6, 7, 8 and 9) using an Ekman barge sediment container in May 2005, busy farming season.

Sediment samples were pretreated according to procedures of the Ministry of the Environment, Japan with minor modifications. The samples were air-dried at room temperature for a week and after complete dehydration, they were screened with 2 mm mesh strainers. The screened samples (ca. 60 g) were soxhlet extracted for 24 hr in toluene. The crude extract was treated with H_2SO_4 and was loaded onto a multi-layered silica gel column. After these treatments, PCDD/DFs and DL-PCBs were fractionated with an active carbon-dispersed silica gel reversible column. The PCDD/DFs and DL-PCBs fraction were finally concentrated and 1 μL of each was injected into a high resolution GC/MS (HP-6890; Agilent + MS-700D; JEOL). PCDD/DFs and DL-PCBs were analyzed by the SIM method with a mass-resolution higher than 10,000.

All the isomers in the SIM chromatograms were identified and quantified with software "DIOK Ver.2" (JEOL). The recovery rates of clean-up spikes (^{13}C-labelled toxic isomers of dioxins added before the above clean up procedures) were calculated with software "DIOK Ver.2".

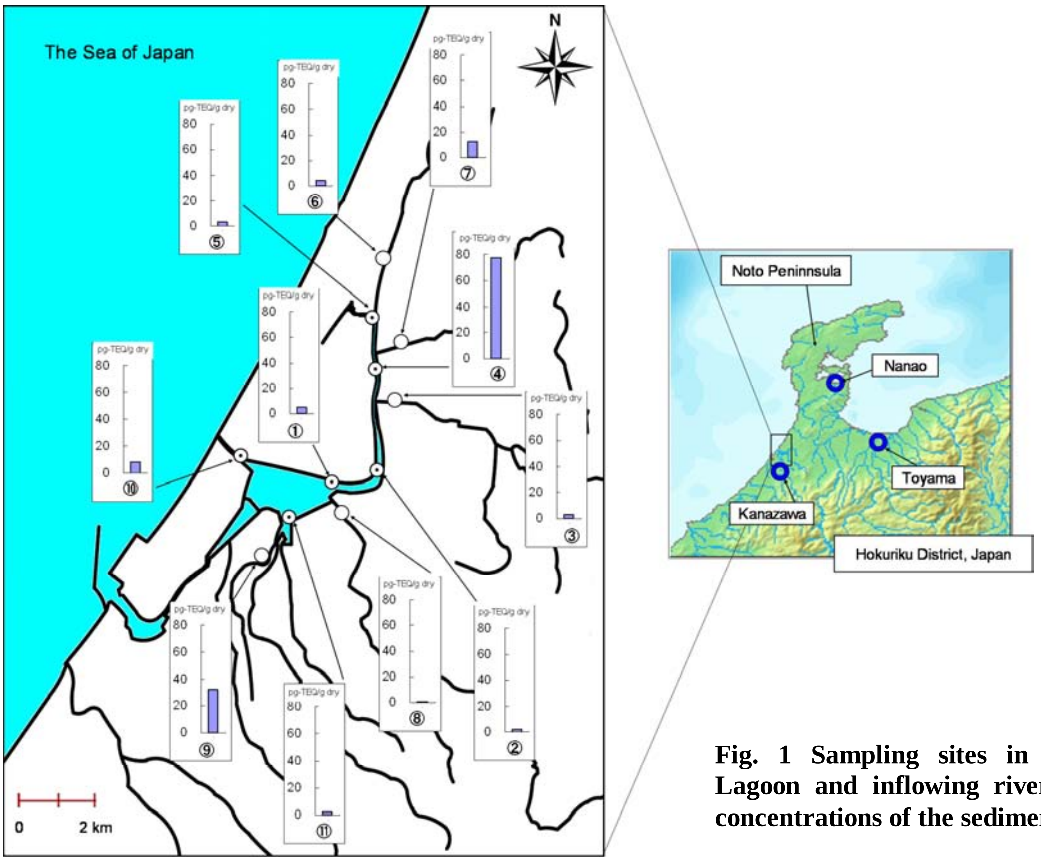

Fig. 1 Sampling sites in Kahokugata Lagoon and inflowing rivers and TEQ concentrations of the sediment samples.

Results and Discussion

Dioxin Concentration

The dioxin concentration of the surface sediment samples ranged from 0.55 to 77 pg-TEQ/g-dry (Fig. 1). The highest concentration was obtained at a site located in the east side catchment drain (No.4). The concentrations at the other sampling sites were much lower than the concentration at site No. 4. The concentrations of the sediment samples from the mouth of Unoke River (No. 5) and Kanazawa Race Track (No. 11) were only 3.0 and 2.5 pg-TEQ/g-dry, although the concentrations of the water samples collected at these two sites were high enough to exceed the Japanese environmental standard as we previously reported[2)].

Contributions of toxic isomers to the TEQ

The largest and the second largest contributor to the TEQ in the sediment samples were 1,2,3,7,8-PeCDD (26%) and 1,2,3,4,6,7,8-HpCDD (16%), respectively (Table 1). This result agreed with our previous study in water samples[2)]. However, the isomers that made the third contribution to the TEQ in the sediment samples were 2,3,4,7,8-PeCDF (8.5%), though that was 1,2,3,6,7,8-HxCDD (8.1%) in water samples. This difference indicates that the main sources of dioxins in the sediment samples were a little different from those in the water samples. Because 2,3,4,7,8-PeCDF is the largest contributor to the TEQ in combustion-origin samples[5)], dioxins that were emitted from many sources related to combustion are thought to be deposited on the lagoon's surface and finally accumulate in sediment of the lagoon.

PCDDs+PCDFs occupied more than 90% of the TEQ at most of the sampling sites. However, the contribution ratio of DL-PCBs to the TEQ was peculiarly high at site No. 3 (41%) and No. 4 (15%) (Fig. 2). Especially, the TEQ concentration of DL-PCBs was 12 pg-TEQ/g-dry at site No. 4 and was about six times higher than those obtained in the sediments from Lake Suwa, Japan[6)]. Site Nos. 3 is located at the east side catchment drain and site No. 4 is located at the lower reach of a river flowing into the east side catchment drain.

Homologue Composition of PCDD/DFs

The concentration ratio of TeCDDs to PCDDs+PCDFs was higher (52－59%) at sites Nos. 3, 8, 9 and 11, while the concentration ratio of OCDD to PCDDs+PCDFs was higher (50－69%) at site Nos. 4, 5, 6 and 7 (Fig. 3). These results mean that the sediment samples of the northern part of Kahokugata Lagoon and its associated rivers were more contaminated with PCP than the other parts of the lagoon. We previously reported that the

OCDD/(PCDDs+PCDFs) ratios of water samples were higher in the northern part of the lagoon[2]. Thus, the spatial distributions of dioxin concentrations in the water and sediment samples were not similar but the spatial distribution of homologue composition of PCDD/DFs in the sediment samples were almost the same as those in the water samples. The differences in the ratios of TeCDDs and of OCDD to PCDDs+PCDFs between the sampling sites might be due to differences in the integrated amounts of the herbicides applied in different regions.

Table 1. Contribution ratios (%) of toxic dioxin isomers to the TEQ in the sediment (the present study) and the water (our previous study) samples.

Toxic Isomer	Sediment Samples (n=11) mean	S.D.	Water Samples (n=12) mean	S.D.	Toxic Isomer		Sediment Samples (n=11) mean	S.D.	Water Samples (n=12) mean	S.D.
2,3,7,8-TeCDD	4.8	± 3.7	2.4	± 2.7	#81	3,4,4',5-TeCB	0.0	± 0.0	0.0	± 0.0
1,2,3,7,8-PeCDD	26.2	± 3.6	24.1	± 4.1	#77	3,3',4,4'-TeCB	0.1	± 0.1	0.0	± 0.0
1,2,3,4,7,8-HxCDD	3.2	± 0.7	3.8	± 0.7	#126	3,3',4,4',5-PeCB	3.6	± 3.2	1.8	± 1.9
1,2,3,6,7,8-HxCDD	6.8	± 1.5	8.1	± 1.4	#169	3,3',4,4',5,5'-HxCB	0.1	± 0.1	0.0	± 0.0
1,2,3,7,8,9-HxCDD	7.4	± 2.3	8.0	± 2.0	#123	2',3,4,4',5-PeCB	0.0	± 0.0	0.0	± 0.0
1,2,3,4,6,7,8-HpCDD	16.0	± 6.4	21.8	± 4.7	#118	2,3',4,4',5-PeCB	1.4	± 3.1	0.2	± 0.3
OCDD	2.7	± 1.9	3.9	± 0.9	#105	2,3,3',4,4'-PeCB	0.5	± 1.0	0.1	± 0.1
					#114	2,3,4,4',5-PeCB	0.1	± 0.2	0.0	± 0.0
2,3,7,8-TeCDF	0.7	± 0.3	0.7	± 0.5	#167	2,3',4,4',5,5'-HxCB	0.0	± 0.0	0.0	± 0.0
1,2,3,4,8/1,2,3,7,8-PeCDF	1.0	± 0.5	0.7	± 0.4	#156	2,3,3',4,4',5-HxCB	1.7	± 4.6	0.1	± 0.2
2,3,4,7,8-PeCDF	8.5	± 5.3	6.6	± 4.5	#157	2,3,3',4,4',5'-HxCB	0.3	± 0.7	0.0	± 0.1
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	4.1	± 1.6	4.9	± 2.8	#189	2,3,3',4,4',5,5'-HpCB	0.0	± 0.0	0.0	± 0.0
1,2,3,6,7,8-HxCDF	2.9	± 1.4	2.7	± 1.0						
1,2,3,7,8,9-HxCDF	0.5	± 0.3	0.2	± 0.2						
2,3,4,6,7,8-HxCDF	4.1	± 1.7	4.3	± 1.7						
1,2,3,4,6,7,8-HpCDF	2.6	± 1.1	4.7	± 4.6						
1,2,3,4,7,8,9-HpCDF	0.5	± 0.2	0.5	± 0.2						
OCDF	0.1	± 0.0	0.2	± 0.2						

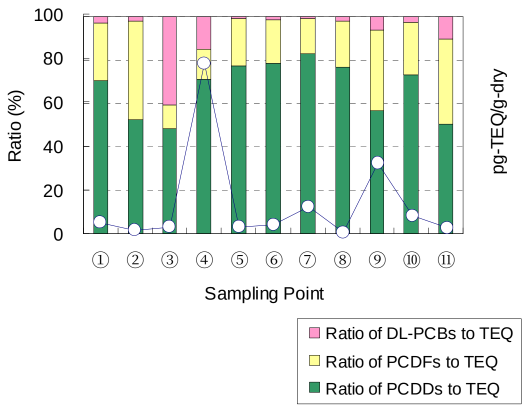

Fig. 2 Contribution ratios (%) of PCDDs, PCDFs and DL-PCBs to the TEQ of the sediment samples.

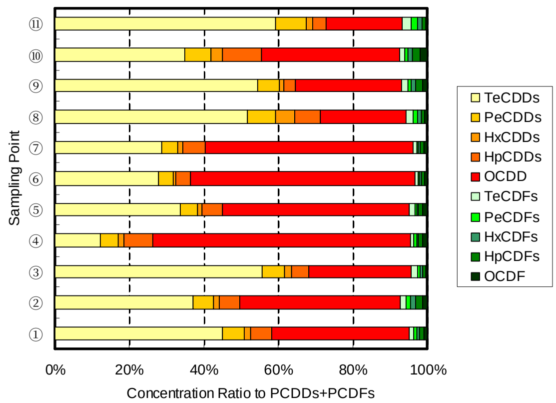

Fig. 3 Homologue profiles of PCDDs and PCDFs (Concentration ratios (%) of each homologue to PCDDs+PCDFs) of the sediment samples.

The Main Isomer Composition

Table 2 shows the concentration ratios of main isomers of PCDD/DFs and DL-PCBs to the total dioxins of all the samples. Although the ratios of every homologue and isomer to the total dioxins are different between the sampling sites, the ratio of each isomer to their homologue did not vary so largely between the samples. For example, the ratios of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD to the total dioxins ranged widely (4.4% - 36% for 1,3,6,8-TeCDD and 2.1% - 12% for 1,3,7,9-TeCDD), but the ratios of these isomers to TeCDDs were 71% ± 5.7% (RSD = 0.080) and 29% ± 4.6% (RSD = 0.16), respectively.

The ratios of DL-PCBs to the total dioxins at site Nos. 3 and 4 were very high (84% and 46%, respectively). Because the concentration ratio of DL-PCBs to the total dioxins is, in general, very low in most sediment samples (e.g. 0.56% for the average of seven sediment samples from a river in Korea[7]), the above two samples might be exceptionally contaminated by commercial PCBs. Among the DL-PCB compounds, the concentration ratio of #118 to the total dioxins was the largest (48%), and was followed by #105 (15%) and #156 (14%) in the sediment sample of site No. 3. The above order of DL-PCB isomers agrees well with the results of previous studies on sediment polluted by commercial PCBs[6, 8)].

In our previous study, we reported that the ratios of 1,3,6,8-TeCDF and 1,3,6,7,8-PeCDF, which are non-toxic and usually present at very low level in the environmental samples, to their homologue were remarkably high because of discharge from a dye manufacturing plant a little upstream of the site No. 6. However, the above two isomers were not predominant in the sediment sample of site No. 6 in the present study (Table 2). But the 1,3,6,7,8-PeCDF/PeCDFs ratio was fairly high (8.2%) at site No. 5, which is about 1.7 km downstream of site No. 6. Because the above isomers were more prominent in the dissolved part of the dyeing wastewater than in the suspended part[2)] and because there is no other source (dye manufacturing plant) between site Nos. 5 and 6, dioxins contained in the dyeing discharge might still remain in water at site No. 6 and some of these dioxins might have gradually sank to the surface of sediment while flowing downstream.

Table 2. Concentration ratio (%) of the main isomers of PCDD/DFs and DL-PCBs to the total Dioxins in the sediment samples. (%)

Homologue/Isomer		Sediment Sample Nos.																						mean ± S.D.
		①		②		③		④		⑤		⑥		⑦		⑧		⑨		⑩		⑪		
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	b ± b
TeCDD	Total TeCDDs	42.3		36.2		9.1		6.6		33.3		27.6		28.4		48.1		46.8		31.8		47.2		
	1,3,6,8-	30.1	(71.2)	23.6	(65.2)	6.7	(73.6)	4.4	(65.9)	23.4	(70.3)	17.9	(64.8)	19.6	(69.1)	33.7	(70.0)	32.2	(68.8)	27.0	(85.0)	35.6	(75.4)	(70.9) ± (5.7)
	1,3,7,9-	11.3	(26.7)	11.6	(32.1)	2.4	(26.4)	2.1	(31.4)	9.1	(27.4)	8.9	(32.3)	9.3	(32.8)	12.4	(25.8)	11.3	(24.2)	12.0	(37.7)	10.5	(22.3)	(29.0) ± (4.6)
	2,3,7,8-	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	0.0	(0.1)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)	(0.0) ± (0.0)
	1,2,3,4/1,2,4,6/1,2,4,9/1,2,3,8-	0.3	(0.7)	0.3	(0.8)	0.1	(0.6)	0.2	(2.7)	0.2	(0.7)	0.3	(1.0)	0.2	(0.8)	0.3	(0.6)	0.4	(0.8)	0.6	(2.0)	0.3	(0.6)	(1.0) ± (0.7)
PeCDD	Total PeCDDs	5.5		5.3		1.0		2.7		4.5		3.7		4.3		6.9		5.1		6.4		6.5		
	1,2,4,6,8/1,2,4,7,9-	0.8	(14.7)	0.8	(14.7)	0.2	(16.8)	0.4	(13.7)	0.7	(14.4)	0.5	(14.0)	0.6	(13.7)	1.3	(18.9)	0.7	(14.3)	0.8	(12.6)	1.1	(16.5)	(14.9) ± (1.8)
	1,2,3,6,8-	3.4	(61.8)	3.3	(61.5)	0.6	(59.1)	1.7	(63.4)	2.8	(62.2)	2.3	(63.4)	2.7	(62.7)	3.2	(47.0)	2.7	(53.4)	4.1	(64.5)	4.0	(62.6)	(60.1) ± (5.3)
	1,2,3,7,9-	1.1	(19.8)	1.1	(19.8)	0.2	(17.7)	0.5	(19.5)	0.9	(20.1)	0.7	(20.0)	0.8	(19.0)	1.1	(16.4)	0.8	(16.1)	1.3	(20.0)	1.1	(17.7)	(18.7) ± (1.5)
	1,2,3,7,8-	0.0	(0.7)	0.0	(0.7)	0.0	(1.0)	0.0	(0.9)	0.0	(0.7)	0.0	(0.7)	0.0	(1.0)	0.1	(1.3)	0.0	(0.7)	0.0	(0.8)	0.0	(0.6)	(0.8) ± (0.2)
HxCDD	Total HxCDDs	1.5		1.4		0.3		0.8		1.1		0.9		1.5		4.7		0.9		2.8		1.3		
	1,2,3,4,6,8/1,2,4,6,7,9/1,2,4,6,8,9-	0.7	(47.9)	0.6	(43.4)	0.2	(53.0)	0.3	(41.0)	0.5	(44.1)	0.4	(42.0)	0.6	(41.5)	2.2	(46.6)	0.6	(62.1)	1.2	(44.4)	0.6	(46.9)	(46.6) ± (6.2)
	1,2,3,6,7,9/1,2,3,6,8,9-	0.4	(29.7)	0.5	(31.4)	0.1	(28.5)	0.3	(33.3)	0.4	(32.6)	0.3	(34.3)	0.5	(33.1)	1.4	(30.0)	0.2	(23.7)	0.9	(32.1)	0.4	(34.0)	(31.2) ± (3.1)
	1,2,3,4,7,8-	0.1	(3.8)	0.1	(4.1)	0.0	(2.7)	0.0	(4.4)	0.0	(3.3)	0.0	(3.4)	0.1	(3.9)	0.1	(1.6)	0.0	(4.2)	0.1	(3.0)	0.0	(3.0)	(3.4) ± (0.8)
	1,2,3,6,7,8-	0.1	(6.9)	0.1	(8.3)	0.0	(5.3)	0.1	(9.1)	0.1	(7.9)	0.1	(8.5)	0.1	(8.5)	0.1	(2.9)	0.1	(8.9)	0.2	(5.5)	0.1	(8.2)	(7.3) ± (1.9)
	1,2,3,7,8,9-	0.1	(8.3)	0.1	(7.9)	0.0	(7.9)	0.1	(8.7)	0.1	(8.3)	0.1	(8.3)	0.1	(9.2)	0.3	(6.1)	0.1	(6.1)	0.2	(6.9)	0.1	(4.6)	(7.5) ± (1.4)
HpCDD	Total HpCDDs	5.4		5.3		0.7		4.2		5.5		3.7		5.9		6.4		2.9		9.5		2.8		
	1,2,3,4,6,7,9-	2.8	(52.2)	2.7	(50.2)	0.4	(54.2)	2.0	(48.4)	2.8	(51.0)	1.9	(51.8)	2.7	(46.4)	3.7	(58.6)	1.4	(50.0)	5.4	(56.6)	1.6	(56.8)	(52.4) ± (3.8)
	1,2,3,4,6,7,8-	2.6	(47.8)	2.7	(49.8)	0.3	(45.8)	2.1	(50.2)	2.7	(49.0)	1.8	(48.2)	3.2	(53.6)	2.6	(41.4)	1.4	(48.9)	4.1	(43.4)	1.2	(43.2)	(47.4) ± (3.6)
OCDD	1,2,3,4,6,7,8,9-	34.7		42.0		4.5		37.4		49.3		59.3		55.2		21.4		24.3		33.7		16.4		
PCDDs		89.3		90.2		15.6		51.6		93.8		95.2		95.3		87.5		80.0		84.1		74.3		
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	b ± b
TeCDF	Total TeCDFs	1.0		1.4		0.3		0.6		1.2		1.0		1.0		1.8		1.6		1.2		1.9		
	1,3,6,8-	0.0	(1.0)	0.0	(1.0)	0.0	(1.1)	0.0	(0.8)	0.0	(2.0)	0.0	(1.0)	0.0	(0.9)	0.0	(2.1)	0.0	(1.3)	0.0	(0.9)	0.0	(1.5)	(1.2) ± (0.5)
	1,3,7,8/1,3,7,9-	0.0	(1.2)	0.0	(1.5)	0.0	(1.1)	0.0	(0.7)	0.0	(2.3)	0.0	(1.0)	0.0	(0.8)	0.1	(2.9)	0.0	(1.1)	0.0	(1.0)	0.0	(1.4)	(1.4) ± (0.7)
	2,4,6,8-	0.8	(76.1)	0.9	(63.4)	0.2	(74.1)	0.5	(83.8)	1.0	(79.7)	0.8	(83.1)	0.8	(79.1)	0.7	(40.3)	1.0	(64.2)	0.9	(74.4)	1.2	(60.8)	(70.8) ± (12.9)
	1,2,7,8-	0.0	(1.1)	0.0	(1.1)	0.0	(1.3)	0.0	(0.8)	0.0	(0.4)	0.0	(0.5)	0.0	(0.7)	0.0	(1.3)	0.0	(1.2)	0.0	(1.3)	0.0	(1.8)	(1.0) ± (0.4)
	2,4,6,7-	0.0	(2.5)	0.0	(3.4)	0.0	(2.3)	0.0	(1.8)	0.0	(1.7)	0.0	(1.9)	0.0	(2.1)	0.1	(5.1)	0.1	(3.5)	0.0	(2.4)	0.1	(3.2)	(2.7) ± (1.0)
	2,3,7,8-	0.0	(1.1)	0.0	(1.0)	0.0	(0.9)	0.0	(0.7)	0.0	(0.4)	0.0	(0.3)	0.0	(0.7)	0.0	(1.5)	0.0	(1.0)	0.0	(1.3)	0.0	(1.2)	(0.9) ± (0.4)
PeCDF	Total PeCDFs	0.7		1.1		0.1		0.3		0.5		0.4		0.5		1.0		0.8		0.8		1.3		
	1,2,4,6,8-	0.1	(18.9)	0.1	(10.8)	0.0	(17.5)	0.1	(24.7)	0.1	(22.4)	0.1	(24.9)	0.1	(22.8)	0.1	(7.5)	0.1	(16.9)	0.1	(17.7)	0.2	(16.9)	(18.3) ± (5.5)
	1,3,6,7,8-	0.0	(2.2)	0.0	(3.0)	0.0	(1.4)	0.0	(3.4)	0.0	(8.2)	0.0	(4.0)	0.0	(1.6)	0.0	(2.9)	0.0	(2.7)	0.0	(1.7)	0.0	(2.1)	(3.0) ± (1.9)
	1,2,3,6,8/1,3,4,7,8-	0.0	(6.1)	0.1	(5.2)	0.0	(4.9)	0.0	(4.2)	0.0	(3.9)	0.0	(4.0)	0.0	(4.8)	0.1	(9.3)	0.1	(7.7)	0.0	(5.7)	0.1	(7.0)	(5.7) ± (1.7)
	1,2,3,4,8/1,2,3,7,8-	0.0	(3.9)	0.1	(4.7)	0.0	(4.8)	0.0	(3.1)	0.0	(3.2)	0.0	(3.1)	0.0	(3.8)	0.1	(5.5)	0.0	(4.6)	0.0	(4.9)	0.1	(5.3)	(4.3) ± (0.9)
	2,3,4,6,8-	0.2	(34.9)	0.3	(22.9)	0.0	(35.4)	0.1	(41.9)	0.2	(37.1)	0.2	(40.6)	0.2	(38.5)	0.1	(11.6)	0.2	(26.8)	0.3	(31.6)	0.3	(21.9)	(31.2) ± (9.4)
	2,3,4,7,8-	0.0	(3.5)	0.1	(6.4)	0.0	(2.9)	0.0	(2.4)	0.0	(2.1)	0.0	(2.7)	0.0	(2.9)	0.0	(3.8)	0.0	(3.8)	0.0	(3.0)	0.1	(4.5)	(3.5) ± (1.2)
HxCDF	Total HxCDFs	0.7		1.3		0.1		0.3		0.6		0.4		0.5		0.9		1.0		1.0		0.9		
	1,2,3,4,6,8-	0.1	(12.3)	0.1	(9.5)	0.0	(11.9)	0.0	(13.1)	0.1	(12.8)	0.1	(12.5)	0.1	(12.6)	0.1	(8.9)	0.1	(12.6)	0.1	(10.6)	0.1	(11.9)	(11.7) ± (1.4)
	1,2,4,6,7,8-	0.1	(20.7)	0.2	(14.6)	0.0	(17.7)	0.1	(24.5)	0.1	(23.8)	0.1	(24.6)	0.1	(22.1)	0.1	(15.0)	0.2	(15.1)	0.3	(24.9)	0.2	(22.4)	(20.5) ± (4.1)
	1,2,3,4,7,8/1,2,3,4,7,9-	0.1	(8.2)	0.1	(9.1)	0.0	(8.6)	0.0	(7.1)	0.0	(8.2)	0.0	(8.2)	0.0	(7.6)	0.1	(10.1)	0.1	(9.5)	0.1	(8.4)	0.1	(9.6)	(8.6) ± (0.9)
	1,2,3,6,7,8-	0.0	(7.1)	0.1	(8.6)	0.0	(4.0)	0.0	(5.8)	0.0	(5.2)	0.0	(5.0)	0.0	(5.1)	0.1	(6.7)	0.1	(5.7)	0.1	(6.5)	0.1	(6.6)	(6.0) ± (1.3)
	1,2,4,6,8,9-	0.1	(16.4)	0.1	(10.2)	0.0	(22.7)	0.1	(25.6)	0.2	(26.2)	0.1	(28.9)	0.1	(26.0)	0.1	(8.7)	0.1	(10.0)	0.2	(18.7)	0.1	(13.7)	(18.8) ± (7.5)
	1,2,3,7,8,9-	0.0	(1.7)	0.0	(0.6)	0.0	(1.3)	0.0	(0.7)	0.0	(1.9)	0.0	(0.5)	0.0	(1.3)	0.0	(0.8)	0.0	(0.9)	0.0	(1.3)	0.0	(0.5)	(1.1) ± (0.5)
	2,3,4,6,7,8-	0.1	(9.6)	0.1	(10.8)	0.0	(8.7)	0.0	(7.4)	0.0	(7.0)	0.0	(5.9)	0.0	(7.5)	0.1	(13.4)	0.1	(8.3)	0.1	(7.5)	0.1	(10.4)	(8.8) ± (2.1)
HpCDF	Total HpCDFs	1.1		2.0		0.1		0.7		1.2		0.8		0.9		1.0		1.6		1.9		0.8		
	1,2,3,4,6,7,8-	0.4	(34.2)	0.9	(46.1)	0.0	(28.4)	0.2	(30.6)	0.4	(32.8)	0.3	(30.8)	0.3	(30.1)	0.4	(44.2)	0.5	(32.0)	0.6	(32.3)	0.3	(38.1)	(34.5) ± (5.8)
	1,2,3,4,6,8,9-	0.6	(51.1)	0.7	(36.3)	0.1	(57.5)	0.4	(58.8)	0.7	(55.7)	0.5	(58.1)	0.6	(58.9)	0.4	(38.6)	0.8	(53.5)	1.0	(53.9)	0.4	(47.3)	(51.8) ± (7.9)
	1,2,3,4,7,8,9-	0.1	(6.1)	0.1	(5.7)	0.0	(7.5)	0.0	(5.2)	0.1	(5.6)	0.0	(5.8)	0.1	(5.5)	0.1	(6.2)	0.1	(6.2)	0.1	(6.3)	0.1	(8.1)	(6.2) ± (0.9)
OCDF	1,2,3,4,6,7,8,9-	1.0		1.1		0.1		0.7		1.1		0.8		0.9		0.6		1.1		1.9		0.5		
PCDFs		4.5		6.9		0.7		2.5		4.6		3.4		3.8		5.3		6.1		6.7		5.3		
		a	c	a	c	a	c	a	c	a	c	a	c	a	c	a	c	a	c	a	c	a	c	c ± c
DL-PCB	#81 3,4,4',5-TeCB	0.0	(0.5)	0.0	(0.6)	0.0	(0.0)	0.1	(0.2)	0.0	(0.4)	0.0	(0.4)	0.0	(0.5)	0.0	(0.6)	0.0	(0.3)	0.0	(0.3)	0.1	(0.4)	(0.4) ± (0.2)
	#77 3,3',4,4'-TeCB	0.7	(11.3)	0.2	(6.5)	0.2	(0.3)	2.9	(6.3)	0.1	(7.6)	0.1	(5.9)	0.0	(4.8)	0.6	(8.3)	1.0	(7.0)	0.7	(7.7)	1.5	(7.3)	(6.6) ± (2.7)
	#126 3,3',4,4',5-PeCB	0.0	(0.5)	0.0	(1.1)	0.0	(0.0)	0.1	(0.2)	0.0	(0.7)	0.0	(0.6)	0.0	(1.3)	0.1	(0.7)	0.1	(0.4)	0.0	(0.4)	0.1	(0.6)	(0.6) ± (0.4)
	#169 3,3',4,4',5,5'-HxCB	0.0	(0.1)	0.0	(0.5)	0.0	(0.0)	0.0	(0.0)	0.0	(0.1)	0.0	(0.2)	0.0	(0.4)	0.0	(0.3)	0.0	(0.1)	0.0	(0.1)	0.0	(0.2)	(0.2) ± (0.1)
	#123 2',3,4,4',5-PeCB	0.1	(0.8)	0.0	(0.7)	0.2	(0.3)	0.4	(0.9)	0.0	(0.9)	0.0	(0.7)	0.0	(0.8)	0.0	(0.6)	0.1	(0.7)	0.1	(0.6)	0.2	(1.2)	(0.8) ± (0.2)
	#118 2,3',4,4',5-PeCB	3.3	(62.5)	1.6	(55.4)	47.5	(56.8)	21.5	(46.9)	0.8	(51.8)	0.8	(54.4)	0.6	(56.0)	4.0	(56.0)	7.9	(57.0)	6.2	(67.7)	11.3	(55.2)	(55.4) ± (5.0)
	#105 2,3,3',4,4'-PeCB	1.5	(23.6)	0.6	(22.4)	15.4	(18.4)	12.8	(28.0)	0.4	(23.8)	0.3	(22.9)	0.2	(22.7)	1.6	(22.3)	2.9	(20.6)	1.2	(12.5)	4.4	(21.4)	(21.7) ± (3.8)
	#114 2,3,4,4',5-PeCB	0.1	(1.6)	0.0	(1.3)	0.5	(0.6)	0.8	(1.7)	0.0	(1.2)	0.0	(1.5)	0.0	(1.3)	0.1	(0.9)	0.2	(1.2)	0.0	(0.4)	0.3	(1.6)	(1.2) ± (0.4)
	#167 2,3',4,4',5,5'-HxCB	0.1	(1.9)	0.1	(2.8)	3.2	(3.9)	1.5	(3.2)	0.0	(2.8)	0.0	(2.8)	0.0	(2.6)	0.2	(2.3)	0.4	(3.0)	0.2	(2.4)	0.5	(2.5)	(2.7) ± (0.5)
	#156 2,3,3',4,4',5-HxCB	0.3	(5.1)	0.2	(6.5)	13.8	(16.5)	4.1	(9.0)	0.1	(8.1)	0.1	(7.8)	0.1	(6.8)	0.4	(5.4)	1.0	(7.1)	0.5	(6.0)	1.5	(7.3)	(7.8) ± (3.1)
	#157 2,3,3',4,4',5'-HxCB	0.1	(1.5)	0.0	(1.6)	2.2	(2.7)	0.3	(0.8)	0.0	(1.8)	0.0	(2.1)	0.0	(2.1)	0.1	(1.7)	0.3	(2.1)	0.1	(1.3)	0.4	(1.9)	(1.8) ± (0.5)
	#189 2,3,3',4,4',5,5'-HpCB	0.0	(0.5)	0.0	(0.8)	0.5	(0.6)	1.3	(2.9)	0.0	(0.7)	0.0	(0.7)	0.0	(0.7)	0.1	(0.7)	0.1	(0.6)	0.0	(0.5)	0.1	(0.5)	(0.9) ± (0.7)
DL-PCBs		6.2		2.8		83.7		45.9		1.6		1.4		1.0		7.2		13.9		9.2		20.4		

a, The ratios of each homologue and main isomers of PCDD/DFs, and of each compound of DL-PCBs are expressed as percents of the total dioxins.
b, The ratios of the main isomers of PCDD/DFs are also expressed as percents of their homologues (tetra-hepta CDD/DFs) with parentheses.
c, The ratio of each compound of DL-PCBs is also expressed as percent of the DL-PCBs with parentheses.

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