Levels of PCDDs and PCDFs in Fish and Shrimp from Lake Kasumigaura

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INTRODUCTION

In this study, various fish and shrimp species were subjected to the determination of PCDDs and PCDFs to characterize the environmental fates of and human health effects caused by these compounds in Lake Kasumigaura. Lake Kasumigaura, the second largest lake in Japan, is located in a mainly agricultural area. Congener specific analysis was performed including non-2,3,7,8-substituted isomers and the most toxic 2,3,7,8-substituted isomers. Biota-sediment accumulation factors (BSAF) were also calculated.

EXPERIMENT

Samples of shrimp, pond smelt and piscivorous chub were collected from Lake Kasumigaura in Nov. 1994, were kept frozen until preparation.

A homogenized sample (30g) was spiked with a mixture of ^{13}C-PCDD/F internal standards and digested with 300ml of 1N ethanolic KOH solution for 2 hrs at room temperature. The saponified sample was extracted with 300ml of *n* -hexane and treated with concentrated sulfuric acid. The clean-up was performed using silica gel, alumina and activated carbon impregnated silica gel column chromatography. The final extracts were analyzed using a high resolution gas chromatography/high resolution mass spectrometry (HRGC:HP 5890 series Ⅱ, HRMS: VG Autospec-Ultima). A DB-5 60m column (J&W Scientific) was used for the separation of most congeners except for some 2,3,7,8-substituted isomers which were separated using a DB-17 60m column. MS was performed in the EI mode at a resolution of 10000.

RESULTS AND DISCUSSION

The isomers detected in samples are listed in Table 1. Table 2 shows the recoveries of

^{13}C-internal standards, levels of major isomers of PCDD/Fs in fish on a wet weight basis and the biota-sediment accumulation factors.

TCDFs and TCDDs

Most of the TCDF isomers are detected in shrimp and fish samples. The total TCDF level is 10.15pg/g for shrimp, 6.0pg/g for pond smelt and 5.34pg/g for piscivorous chub. Four peaks of TCDDs are assigned in these samples. That of 1368-TCDD is the largest among those of all TCDD isomers detected.

PeCDFs and PeCDDs

The total PeCDF levels are 6.24pg/g, 4.42pg/g and 5.57pg/g for shrimp, pond smelt and piscivorous chub, respectively. Levels of non 2,3,7,8-substituted isomers are higher than those of 2,3,7,8-substituted isomers in all samples. The level of total PeCDDs is 1.80pg/g for shrimp, 2.09pg/g for pond smelt and 2.30pg/g for piscivorous chub.

HxCDFs and HxCDDs

For shrimp, pond smelt and piscivorous chub the total HxCDF and total HxCDD level ranges 1.29~1.58pg/g and 1.75~2.33pg/g, respectively. Levels of non 2,3,7,8-substituted isomers are higher than those of 2,3,7,8-substituted isomers in shrimp, whereas those of 2,3,7,8-substituted isomers are higher than those of non 2,3,7,8-substituted isomers in pond smelt and piscivorous chub.

TEQs

The I-TEQ levels in shrimp, pond smelt and piscivorous chub range from 0.83 to 2.64pg/g which are close to the reported values for coastal fish in Japan[1]. The level of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD contribute the greatest to the total TEQ levels in all samples. These two isomers make up 65% of the total TEQs for shrimp and pond smelt and 62% for piscivorous chub. Relatively high amounts of 23478-PeCDF in our samples were consistent with the results previously reported[1),2)].

Biota-sediment accumulation factors

Biota-sediment accumulation factors (BSAF) were calculated for major isomers of PCDD/Fs and for three samples. BSAF is defined as the ratio of the chemical concentration in an organism (pg/g wet weight) to that in sediment (pg/g dry weight)[3)].

BSAFs of piscivorous chub are the highest for most 2,3,7,8-substituted isomers, compared with BSAFs of shrimp and pond smelt. A tendency in which BSAFs of 2,3,7,8-substituted isomers are higher than those of non 2,3,7,8-substituted isomers, including tetra- and hexa-dioxins and furans, is observed. This tendency is most marked for piscivorous chub, but is not observed for shrimp. This suggest that more 2,3,7,8-substituted isomers are accumulated in fish of higher tropic levels in the food chain compared to the non 2,3,7,8-substituted isomers. However, the BASF of 1368-TCDD is exceptionally high in pond smelt. It is concluded that the high 1368-TCDD level in the sediment resulted in the highest total PCDD/F level being detected in the pond smelt among the three species tested. The 1368-TCDD is thought to originate from the herbicide CNP (chlornitrofen)[4)], which was heavily used in the Lake Kasumigaura basin.

Figure 1 shows the relationship between BSAFs of 2,3,7,8-substituted isomers and the number of substituted chlorine atoms of PCDD/Fs. BSAFs of 2,3,7,8-substituted isomers are related to the numbers of chlorine atoms. Figure 1 shows that the average BSAFs for TCDD/Fs are on the order of 0.1 to 1.0, whereas BSAFs for OCDD/Fs are less than 0.001. These data clearly demonstrate a decrease in BSAF for highly chlorinated congeners compared with less chlorinated ones.

In conclusion, 1) total PCDD/F levels in species tested range from 25.7pg/g to 43.9pg/g, 2) non-2,3,7,8-substituted isomers account for more than 50% of the total PCDD/Fs, 3) TEQs range from 0.83pg/g to 2.64pg/g, 4) BSAFs are markedly high for 2,3,7,8-substituted isomers, 5) BSAF is strongly related to the species level in the food chain.

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Table 1. Isomers found in shrimp, pond smelt and piscivorous chub

TCDF	1368-, 1468-, 2468-, 1247/1347/1346/1246-, 1367/1348/1379/1248-, 1268/1467/1468-, 1369/1237-, 2467/1238/1236/1469/1678/1234-, 1278-, 1267/1349-, 2348/2378/2347/ 2346/1249/1279-, 2367-, 3467/1269-
PeCDF	13468/12468-, 13678-, 12368/12478/13467/13478/12467-, 23468/12469/12347/12346-, 12378-, 12367-, 12678/12379-, 23478/12489/12679/12369-, 23467-
HxCDF	123468-, 134678/124678-, 134679-, 124679-, 124689-, 123467/123478-, 123678-, 234678-
HpCDF	1234678-, 12346789-, 1234689-, 1234789-
TCDD	1368-, 1379-, 1369-, 1247/1248/1378/1469-, 2378-
PeCDD	12468/12479-, 12368-, 12478-, 12379-, 12467/12489-, 12347-, 12378-
HxCDD	124679/124689-, 123468-, 123679/123689-, 123478-, 123678-, 123467/123789-
HpCDD	1234679-, 1234678-

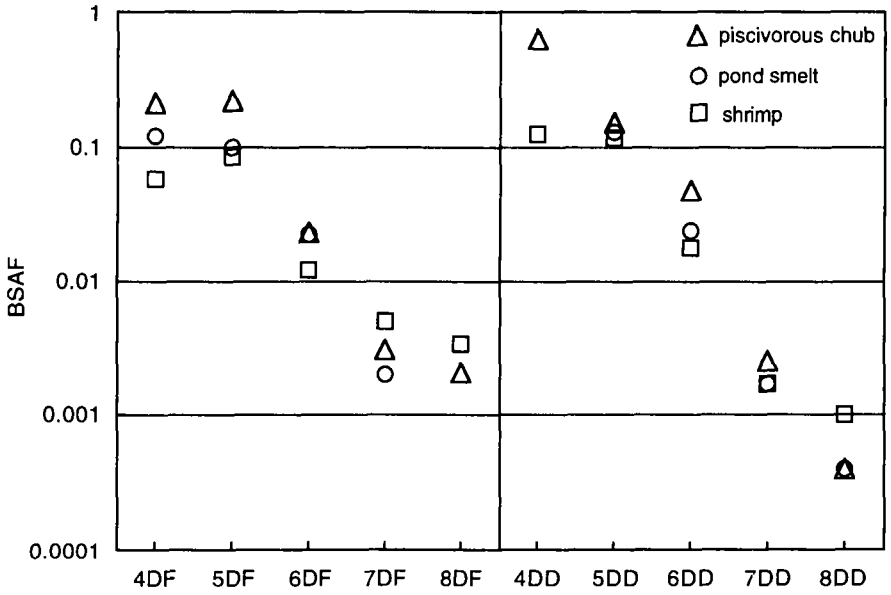

Figure 1. BSAFs of 2,3,7,8-substituted isomers for each homologue group

Table 2. Concentrations of PCDDs and PCDFs and biota-sediment accumulation factors (BSAF) for samples of shrimp, pond smelt and piscivorous chub

Compound	[A] Recovery (%)	Level of PCDD/Fs				[C] BSAF		
		shrimp	pond smelt	piscivorous chub	[B] sediment	shrimp	pond smelt	piscivorous chub
TCDF 2378	76.3±3.1	0.71	1.49	2.70	4.19	0.169	0.356	0.644
1368		0.93	0.48	0.48	2.77	0.336	0.173	0.173
1247/1347		1.62	0.60	0.24	7.99	0.203	0.075	0.030
1367/1348		1.05	0.71	0.17	7.38	0.142	0.096	0.023
1369/1237		0.98	0.36	0.10	6.51	0.151	0.055	0.015
2367		0.96	0.69	0.85	6.22	0.154	0.111	0.137
3467/1269		0.92	0.11	0.11	5.87	0.157	0.019	0.019
others		2.98	1.56	0.69	59.99	0.050	0.026	0.012
Total TCDFs		10.15	6.00	5.34	100.92			
PeCDF 12378	91.3±5.2	0.41	0.41	0.91	4.70	0.087	0.087	0.194
23478	98.7±7.0	0.63	0.81	1.75	5.25	0.120	0.154	0.333
13468/12468		0.73	1.04	0.34	12.16	0.060	0.086	0.028
12367		0.37	0.33	0.31	3.74	0.099	0.088	0.083
others		4.10	1.83	2.26	57.95	0.071	0.032	0.039
Total PeCDFs		6.24	4.42	5.57	83.80			
HxCDF 123478	81.3±8.5	0.14	0.30	0.24	9.09	0.015	0.033	0.026
123678	92.2±6.0	0.16	0.21	0.26	8.31	0.019	0.025	0.031
234678	86.6±7.0	0.16	0.34	0.39	11.61	0.014	0.029	0.034
123789	81.0±11.0	n.d.	n.d.	n.d.	0.87			
others		0.83	0.58	0.69	76.42	0.011	0.008	0.009
Total HxCDFs		1.29	1.43	1.58	106.30			
HpCDF 1234678	80.3±8.5	0.25	0.14	0.18	73.27	0.003	0.002	0.002
1234789	74.9±8.3	0.11	n.d.	0.05	7.55	0.015		0.007
others		0.15	0.09	0.15	68.68	0.002	0.001	0.002
Total HpCDFs		0.51	0.23	0.38	149.50			
OCDF		0.26	n.d.	0.12	76.54	0.003		0.002
TCDD 2378	68.4±3.5	0.08	n.d.	0.40	0.63	0.127		0.635
1368		1.39	24.14	5.12	264.07	0.005	0.091	0.019
others		1.14	1.29	0.23	151.70	0.008	0.009	0.002
Total TCDDs		2.61	25.43	5.75	416.40			
PeCDD 12378	93.9±5.8	0.43	0.47	1.50	3.59	0.120	0.131	0.418
12468/12479		0.25	0.36	0.09	22.15	0.011	0.016	0.004
others		1.12	1.26	0.71	79.96	0.014	0.016	0.009
Total PeCDDs		1.80	2.09	2.30	105.70			
HxCDD 123478	93.3±9.6	0.13	0.16	0.49	6.78	0.019	0.024	0.072
123678	93.9±8.1	0.43	0.61	1.15	12.58	0.034	0.048	0.091
123789		0.16	0.20	0.31	11.97	0.013	0.017	0.026
others		1.61	0.78	0.05	256.77	0.006	0.003	0.0002
Total HxCDDs		2.33	1.75	2.00	288.10			
HpCDD 1234678	80.8±7.4	0.56	0.57	0.78	325.75	0.002	0.002	0.002
others		0.99	0.54	0.29	702.65	0.001	0.001	0.0004
Total HxCDDs		1.55	1.11	1.07	1028.40			
OCDD	80.7±8.5	3.84	1.47	1.68	4190.70	0.001	0.0004	0.0004
Total PCDFs/PCDDs		30.83	43.93	25.73				
I-TEQ (pg/g)		0.83	1.00	2.64				

[A] Recovery: Mean value ± S.D., N.D.=<0.01

[B] Sediment: Reference 3)

[C] BSAF= Cf/Cs, Cf: Concentrations of PCDD/Fs in fish (pg/g, w. w.)
Cs: Concentrations of PCDD/Fs in sediment (pg/g, d.w.)