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Bioaccumulation of Dioxins in the Benthic Fish from Hiroshima Bay

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Abstract—Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and non- and mono-*ortho*-chlorine-substituted polychlorinated biphenyls (no-PCBs and mo-PCBs) were measured in the benthic fish and sediment collected from Hiroshima Bay, Japan. Total TEQ in the sediment and the eleven fish species were 6.4 pg/g dry wt and 0.17–2.3 pg/g wet wt, respectively. In the fish samples, 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, 3,3′,4,4′,5-PeCB, and 2,3′,4,4′,5-PeCB accounted for more than 60% of TEQ of PCDDs, PCDFs, no-PCBs, and mo-PCBs, respectively, probably because they are predominant in the environment and/or have high TEF and accumulative properties. There were positive correlations between TEQ and the body lengths of fish for no-PCBs and mo-PCBs, but not for PCDDs and PCDFs. It is expected that the high bioaccumulative properties of PCBs led to the positive correlations between TEQ and body lengths. The BSAFs were high for the low chlorinated isomers of PCDD/Fs and high chlorinated isomers of no-PCBs. The difference in BSAF was small for mo-PCBs. To suggest the permissible level of dioxins in sediment for fish, it is necessary to take into account not only the total TEQ but also TEQ of individual isomers.

Keywords: dioxin, Hiroshima Bay, benthic fish, BSAF

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and non- and mono-*ortho*-chlorine-substituted polychlorinated biphenyls (no-PCBs and mo-PCBs) are mainly discharged into land and reach the marine environment. Because of the persistent and bioaccumulative properties of these chemicals, marine organisms, such as fish and invertebrates, accumulate these contaminants. In Japan, average human uptake of dioxin was estimated at 1.52–1.68 pg-TEQ/kg body weight/day; diet accounted for more than 90% of the total intake, and the estimates of intake through fish and shellfish accounted for approximately 45–70% of total dietary intake (Mato *et al.*, 2007). The investigation on the levels of dioxins in the benthic fish is important to evaluate the risk of

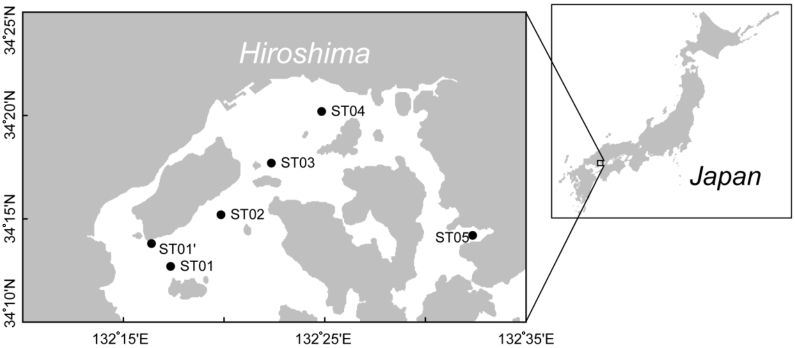

Fig. 1. Map showing sampling locations.

dioxins to human, and also, it is useful for clarifying the bioaccumulation of hydrophobic chemicals through benthic food web, because the isomers and congeners of dioxins have different biochemical and physicochemical properties. In the present study, we measured the concentrations of dioxins in the benthic fish and sediment collected from Hiroshima Bay, Japan and tried to clarify the differences in the bioaccumulation of different isomers.

MATERIALS AND METHODS

Sampling sites are shown in Fig. 1. The fish samples (Table 1) were collected from Hiroshima Bay between January 2002 and March 2005 by dragnet (ST01–ST04), the bottom gill net (ST01′), and fishing (ST05). The surface sediment sample (0–10 cm) was collected from ST04 in October 2003 by core sampler (ø10 cm). Concentrations of dioxins in the eleven fish species and the sediment were determined based on the methods reported by Ministry of the Environment, Government of Japan (2000, 2002).

The whole-body fish samples were homogenized and weighed (50 g). The dried sediment (25 g) was Soxhlet extracted in toluene for more than 16 h. Both fish and sediment extract were spiked with 13C-labeld internal standard, and shaken with 200 mL 1N-KOH/EtOH for 2 hrs (alkaline digestion) and then extracted two times with hexane. The hexane extracts were rinsed three times with distilled water, and washed with sulfuric acid until no color was visible in the sulfuric acid layer. The extracts were purified by the multi-layer silica gel dioxin column and the active carbon column. PCDDs, PCDFs, no-PCBs, and mo-PCBs were analyzed by high-resolution gas chromatography interfaced with high-resolution mass spectrometry.

The toxic equivalency (TEQ) value of each sample was calculated by using the toxic equivalency factors (TEF) provided by the World Health Organization (Van den Berg *et al.*, 2006).

The lipid content of the fish samples was determined gravimetrically from

Table 1. Details of fish samples collected from Hiroshima Bay, Japan.

Species	N (NP*)	BL (mm)	BW (g)	Station	Date
Platycephalus indicus	3	278 ± 50	198 ± 113	ST02, ST04	02/07/23, 02/10/15, 03/01/21
Apogon lineatus	1 (12)	61 ± 6	8.3 ± 2.9	ST01, ST02, ST03, ST04	02/07/23
Sillago japonica	3	192 ± 13	62.9 ± 9.0	ST04, ST05	03/04/15, 03/07/15
Repomucenus valenciennei	1 (8)	98 ± 11	11.5 ± 3.8	ST01, ST02, ST03, ST04	03/07/15
Acentrogobius pflaumi	1 (25)	45 ± 8	1.4 ± 0.8	ST01, ST02, ST03	02/10/15, 03/01/21, 03/04/14, 04/01/16
Amblychaeturichthys hexanema	1 (3)	129 ± 13	28.7 ± 6.9	ST04	03/07/15
Cryptocentrus filifer	1 (5)	98 ± 3	14.7 ± 1.6	ST04	02/7/23, 03/07/15
Pseudorhombus pentophthalmus	3	175 ± 9	105 ± 23	ST02, ST03, ST04	03/07/15, 03/10/20, 04/01/16
Pseudopleuronectes yokohamae	17	201 ± 43	231 ± 163	ST01′	04/06/14, 04/12/16, 05/03/04
Pleuronichthys cornutus	3	184 ± 23	172 ± 55	ST04	02/03/21, 03/01/21, 03/04/14
Cynoglossus robustus	1 (2)	185 , 165	39.0 , 25.6	ST03, ST04	03/10/20

*Number of samples pooled for analysis.

Table 2. Actual concentrations and TEQs of dioxins in the fish.

		Sediment	*P. indicus*	*A. lineatus*	*S. japonica*	*R. valenciennei*	*A. pflaumi*
TOC/lipid (%)		1.3	1.4	3.0	2.2	0.54	1.1
Actual concentration (sediment: pg/g dry wt; fish: pg/g wet wt)							
DXN	PCDDs	1,200	2.2	2.0	1.1	3.7	4.3
	PCDFs	150	1.7	1.9	2.2	0.75	1.2
	no-PCBs	91	36	36	65	4.2	2.5
	mo-PCBs	1,000	7,700	1,800	5,800	700	460
TEQ (sediment: pg/g dry wt; fish: pg/g wet wt)							
PCDD	2378	0.27	0.039	0.030	0.060	0.014	0.0018
	12378	0.97	0.13	0.18	0.12	0.017	0.12
	123478	0.19	0.00065	0.0057	0.0013	0.000077	0.0070
	123678	0.36	0.037	0.020	0.0036	0.0035	0.021
	123789	0.48	0.011	0.0049	0.0002	0.0029	0.0044
	1234678	0.76	0.0038	0.0022	0.00053	0.0023	0.0039
	12346789	0.22	0.00026	0.00023	0.00011	0.00071	0.00067
PCDF	2378	0.21	0.018	0.030	0.075	0.0050	0.0061
	12378	0.13	0.0069	0.0094	0.0032	0.0018	0.0046
	23478	0.96	0.13	0.26	0.21	0.067	0.15
	123478	0.36	0.019	0.0093	0.0029	0.0023	0.011
	123678	0.25	0.015	0.0083	0.0029	0.0024	0.0059
	123789	0.033	0.00092	0.00016	0.00071	0.0019	0.00032
	234678	0.37	0.019	0.013	0.0026	0.0040	0.0059
	1234678	0.14	0.00047	0.00055	0.00020	0.00051	0.00082
	1234789	0.020	0.000066	0.0000093	0.0000093	0.0000092	0.000018
	12346789	0.0036	0.0000016	0.0000020	0.0000020	0.0000055	0.0000063
no-PCB	33′44′	0.0080	0.0015	0.0023	0.0046	0.00019	0.000091
	344′5	0.0013	0.00058	0.00075	0.0013	0.000075	0.000036
	33′44′5	0.59	1.5	0.87	1.4	0.18	0.061
	33′44′55′	0.033	0.12	0.055	0.039	0.0072	0.026
mo-PCB	233′44′	0.0052	0.034	0.0083	0.023	0.0032	0.0024
	2344′5	0.00020	0.0023	0.00049	0.00098	0.00016	0.00013
	23′44′5	0.020	0.16	0.037	0.11	0.014	0.0088
	2′344′5	0.00051	0.0019	0.00072	0.0014	0.00033	0.00014
	233′44′5	0.0024	0.024	0.0036	0.016	0.0016	0.0014
	233′44′5′	0.00063	0.0053	0.0011	0.0037	0.00045	0.00037
	23′44′55′	0.0013	0.0075	0.0025	0.011	0.0012	0.00022
	233′44′55′	0.00039	0.0023	0.00051	0.0032	0.00032	0.00034
DXN	PCDDs	3.2	0.22	0.24	0.18	0.040	0.16
	PCDFs	2.5	0.21	0.33	0.30	0.085	0.19
	no-PCBs	0.63	1.6	0.93	1.4	0.19	0.087
	mo-PCBs	0.030	0.23	0.054	0.17	0.021	0.014
	Total	6.4	2.3	1.6	2.1	0.34	0.45

the Soxhlet extracts. Total organic carbon content of the sediment was determined using the CN analyzer.

RESULTS AND DISCUSSION

The actual concentrations and TEQ in the sediment and the fish samples were shown in Table 2. Concentrations of PCDDs, PCDFs, no-PCBs, and mo-PCBs and total TEQ in the sediment were 1,200, 150, 91, 1,000, and 6.4 pg/g dry wt, respectively. The ranges of those chemicals concentrations and TEQ in the eleven fish species were 1.1–4.6, 0.60–4.3, 2.5–80, 340–7,700, and 0.17–2.3 pg/g wet

Table 2. (continued).

		A. hexanema	*C. filifer*	*P. pentophthalmus*	*P. yokohamae*	*P. cornutus*	*C. robustus*
TOC/lipid(%)		1.7	1.4	1.4	2.6	2.2	0.38
Actual concentration (sediment: pg/g dry wt; fish: pg/g wet wt)							
DXN	PCDDs	4.6	2.7	3.9	0.94	3.6	2.6
	PCDFs	2.0	1.9	1.5	1.6	4.3	0.60
	no-PCBs	8.5	9.1	12	100	22	1.7
	mo-PCBs	520	2,000	2,800	6,100	790	340
TEQ (sediment: pg/g dry wt; fish: pg/g wet wt)							
PCDD	2378	0.025	0.018	0.039	0.070	0.048	0.00093
	12378	0.11	0.081	0.070	0.13	0.13	0.018
	123478	0.019	0.013	0.00061	0.00094	0.0032	0.000077
	123678	0.034	0.028	0.017	0.0098	0.013	0.0062
	123789	0.017	0.010	0.0079	0.0018	0.0057	0.0017
	1234678	0.0057	0.0054	0.0034	0.0014	0.0014	0.0020
	12346789	0.00061	0.00033	0.00073	0.000091	0.00013	0.00051
PCDF	2378	0.020	0.0084	0.028	0.060	0.036	0.0049
	12378	0.0067	0.0028	0.0088	0.0048	0.0063	0.0020
	23478	0.16	0.18	0.071	0.084	0.13	0.030
	123478	0.010	0.020	0.0088	0.0056	0.0055	0.0066
	123678	0.012	0.014	0.0091	0.0054	0.0053	0.0018
	123789	0.00016	0.0031	0.0012	0.0012	0.0046	0.00016
	234678	0.017	0.017	0.015	0.0092	0.011	0.0047
	1234678	0.00088	0.0011	0.00091	0.00012	0.00026	0.00041
	1234789	0.0000093	0.00015	0.000081	0.000078	0.0000093	0.00010
	12346789	0.0000049	0.0000039	0.0000038	0.0000040	0.0000020	0.0000059
no-PCB	33′44′	0.00055	0.00041	0.00027	0.0084	0.0016	0.000034
	344′5	0.00022	0.00020	0.00008	0.0021	0.00046	0.0000087
	33′44′5	0.13	0.29	0.57	1.3	0.33	0.061
	33′44′55′	0.032	0.041	0.091	0.040	0.048	0.022
mo-PCB	233′44′	0.0038	0.011	0.012	0.047	0.0038	0.0013
	2344′5	0.00016	0.00073	0.00061	0.0021	0.00019	0.000054
	23′44′5	0.0080	0.038	0.055	0.12	0.015	0.0075
	2′344′5	0.00029	0.00085	0.00077	0.0027	0.00027	0.000045
	233′44′5	0.0020	0.0048	0.0082	0.0067	0.0018	0.00028
	233′44′5′	0.00062	0.0012	0.0021	0.002	0.00054	0.00025
	23′44′55′	0.00032	0.0012	0.0028	0.0046	0.0012	0.00072
	233′44′55′	0.00048	0.0011	0.0017	0.00073	0.00073	0.000053
DXN	PCDDs	0.21	0.16	0.14	0.21	0.20	0.030
	PCDFs	0.23	0.25	0.14	0.17	0.19	0.050
	no-PCBs	0.16	0.33	0.66	1.3	0.38	0.083
	mo-PCBs	0.016	0.059	0.083	0.18	0.024	0.010
	Total	0.62	0.79	1.0	1.9	0.80	0.17

wt, respectively. Okumura *et al.* (2003) reported concentrations and TEQ of dioxins in the sediment and Japanese flounder (*Paralichthys olivaceus*) collected from Sendai Bay, Japan. PCDDs, PCDFs, and Co-PCBs concentrations and total TEQ in the sediment and the fish were 480, 53, 230, and 2.7 pg/g dry wt, and 2.8, 1.1, 1,300, and 1.5 pg/g wet wt, respectively. The results of the present study are similar to the results in Sendai Bay.

Profile of PCDDs and PCDFs isomers in the sediment and the fish are shown in Fig. 2 by a two-dimensional visualized method (Tanaka, 2004). Dominant PCDD isomers (more than 5% of total PCDD) were OCDD, 1,2,3,4,6,7,9-HpCDD, and 1,2,3,4,6,7,8-HpCDD in the sediment and OCDD, 1,3,6,8-TeCDD,

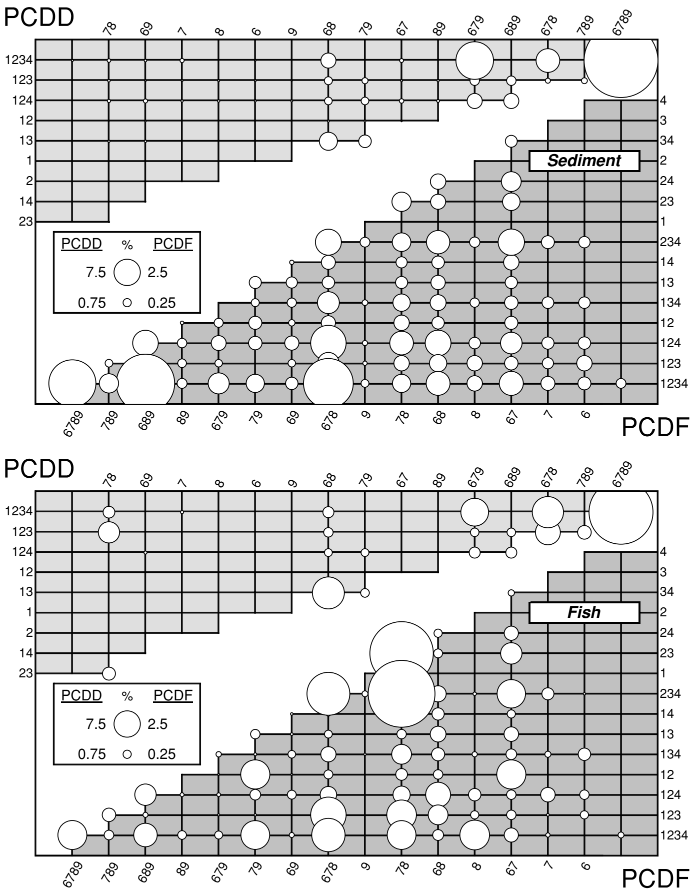

Fig. 2. Percentage of each isomer to total PCDD (the upper left of figure) or PCDF (the lower right of figure) concentration. Combination of the digits in the left and right vertical axes and the upper and lower positions in horizontal axes show the substitution positions of the chlorine atoms of each PCDD and PCDF isomer.

1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,9-HpCDD, and 1,2,3,6,7,8-HxCDD in the fish. Dominant PCDF isomers (more than 5% of total PCDF) were 1,2,3,4,6,8,9-HpCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF in the sediment and 2,3,4,7,8-PeCDF, 2,3,7,8-TeCDF, and 2,3,4,6,7,8-HxCDF in the fish. Compositions of PCDD isomers chlorinated in 1, 3, 6, 8 positions and of PCDD/F isomers chlorinated in 2, 3, 7, 8 positions in the fish were relatively higher than those in the sediment.

The ranges of TEQ of PCDDs, PCDFs, no-PCBs, and mo-PCBs in the fish samples were 0.030–0.24, 0.050–0.33, 0.083–1.6, and 0.010–0.23 pg/g wet wt, respectively (Table 2). 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, 3,3′,4,4′,5-PeCB, and 2,3′,4,4′,5-PeCB accounted for 60 ± 10%, 67 ± 11%, 87 ± 9%, and 65 ± 5%

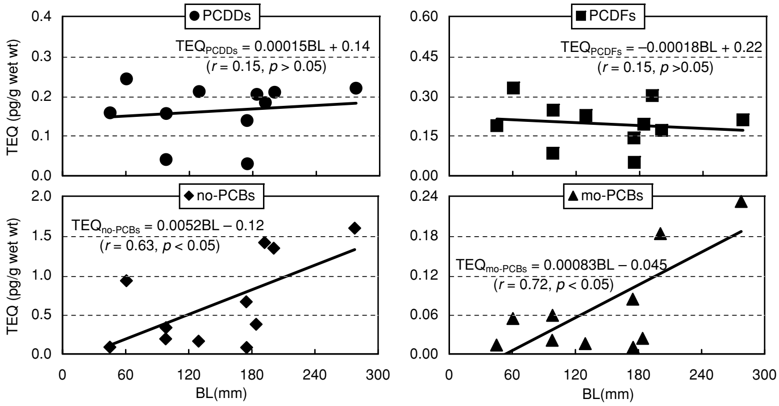

Fig. 3. Relationships between TEQ and body length of the fish.

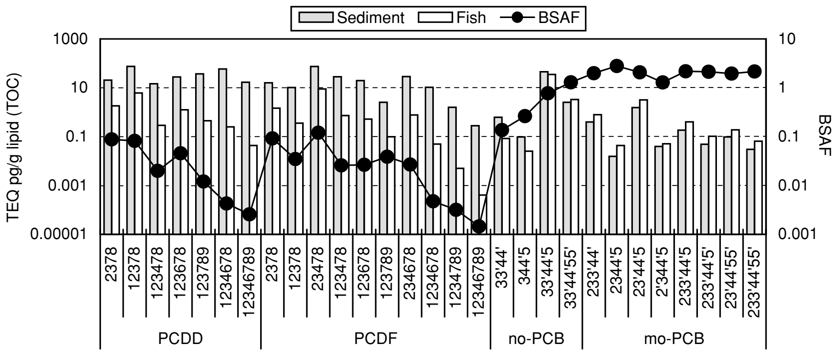

Fig. 4. TEQs of the fish (pg/g lipid wt) and the sediment (pg/g TOC) and BSAFs.

of TEQ of PCDDs, PCDFs, no-PCBs, and mo-PCBs, respectively. Pentachlorinated isomers were dominant among all dioxins, possibly because of their predominance in the environment and/or their high TEF and accumulative properties.

TEQ of PCDDs and PCDFs were not significantly correlated with body length of the fish samples (both $r = 0.15$; both $p > 0.05$) (Fig. 3). On the other hand, there were significant positive correlations between TEQ and body lengths for no-PCBs ($r = 0.63$; $p < 0.05$) and mo-PCBs ($r = 0.72$; $p < 0.05$) (Fig. 3). Okumura *et al*. (2004) reported that PCDD and PCDF concentrations did not correlate with body length, whereas no-PCB and mo-PCB concentrations were significantly correlated in Japanese flounder. The results of the present study are corresponding to the above results on Japanese flounder. Niimi (1996) examined the patterns of PCDDs, PCDFs, and PCBs in prey and predator species from Lake Ontario. Retention of PCB isomers was higher than those of PCDD/Fs in trouts which bioaccumulate PCBs through food chain. Generally, a large-size fish species has a long life, and is at the high trophic level in food chains. In the case of no-PCBs and mo-PCBs, it is expected that the high bioaccumulative properties led to the positive correlations between TEQ and the body lengths.

Biota-sediment accumulation factors (BSAFs) were calculated using the concentrations based on lipid weight of fish samples and the concentration based on total organic carbon (TOC) content in the sediment. The ranges of BSAF of PCDDs, PCDFs, no-PCBs, and mo-PCBs were 0.0026–0.086, 0.0016–0.12, 0.12–1.3, and 1.2–2.7, respectively (Fig. 4). BSAF tended to be high for the low chlorinated isomers of PCDD/Fs and for the high chlorinated isomers of no-PCBs. The difference in BSAF was small for mo-PCBs. Therefore, the major isomers contributing to TEQ in the sediment and the fish are different. To suggest the permissible level of dioxins in sediment for fish, it is necessary to take into account not only total TEQ but also TEQ of individual isomers which have high TEF and BSAF in the sediment, such as 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, and 3,3′,4,4′,5-PeCB.

REFERENCES

Mato, Y., N. Suzuki, N. Katatani, K. Kadokami, T. Nakano, S. Nakayama, H. Sekii, S. Komoto, S. Miyake and M. Morita (2007): Human intake of PCDDs, PCDFs, and dioxin like PCBs in Japan, 2001 and 2002. *Chemosphere*, **67**, S247–S255.

Ministry of the Environment, Government of Japan (2000): Daiokisin rui ni kakaru teisitu chosa manyuaru, 37 pp. (in Japanese).

Ministry of the Environment, Government of Japan (2002): Yasei seibutu no daiokisin rui tikuseki joukyou tou chosa manyuaru, 205 pp. (in Japanese).

Niimi, A. J. (1996): Evaluation of PCBs and PCDD/Fs retention by aquatic organisms. *Sci. Total. Environ.*, **192**, 123–150.

Okumura, Y., Y. Yamashita and S. Isagawa (2003): Sources of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs), and their bioaccumulation through the marine food web in Sendai Bay, Japan. *J. Environ. Monit.*, **5**, 610–618.

Okumura, Y., Y. Yamashita and S. Isagawa (2004): Concentrations of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, non-*ortho* polychlorinated biphenyls in Japanese flounder, with reference to relationship between body length and concentration. *J. Environ. Monit.*, **6**, 201–208.

Tanaka, H. (2004): Examination of the visual expressing method of PCB, PCDD, and PCDF concentrations. *Environ. Chem.*, **14**, 23–31 (in Japanese).

Van den Berg, M., L. S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker and R. E. Peterson (2006): The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.*, **93**, 223–241.

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