TIME TRENDS OF PCDD/F AND COPLANAR PCB CONCENTRATIONS IN JAPANESE HUMAN ADIPOSE TISSUE - COMPARISON OF 1970-71, 1994-96 AND 2000

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar biphenyls (Co-PCBs) are ubiquitous and persistent environmental contaminants. Humans are exposed to PCDD/F and coplanar PCB compounds, through environmental/background, occupational or accidental exposure, and background exposures may result in disease even if the incidence is low (1,2). Sediment core monitoring has shown a gradual decrease in the concentrations of PCDD/Fs and coplanar PCBs in Tokyo Bay over the last 30 years (3). However, a decreasing trend of concentrations of these compounds in Japanese people seemed less certain and there is no available data to measure a time trend for human adipose tissue. The objectives of the present study were to determine the concentrations of PCDD/Fs and coplanar PCBs in adipose tissue of Japanese adult collected in 1970-71, 1994-96 and 2000, and to assess the temporal trends of the concentrations of these compounds and toxic equivalents (TEQs).

Materials and Methods

Human adipose tissues from the Kanto area in Japan were collected in 1970-71, 1994-96 and 2000 and frozen at –20℃ until analysis. 1 to 3g of the fat samples were homogenized with sodium sulfate and extracted with dichloromethane in a Soxhlet apparatus for 6hrs. The extract was transferred to a separation funnel with hexane. ^{13}C-labeled internal spikes were added. Samples were cleaned-up and analyzed according to published methods. Briefly, the extracts were treated with sulfuric acid and further clean up was made using silica gel and a active carbon column. Instrumental analysis was performed on a HRGC-HRMS (HP6890-JMS 700D, JEOL co.) with SIM mode. The HRMS was operated in electron impact mode at a resolution R>10,000 (10% valley). A gas chromatograph equipped with capillary columns CP-8CB-MS for the mass spectrometric detector was used. After data acquisition, the selected ion chromatograms were integrated and calculated using a DioK data system (JEOL co.).

Results and Discussion

Data for PCDD/Fs are presented in Table 1. Most of the 2378-substituted PCDD/Fs were detected in all the samples. Average concentrations of PCDD/Fs indicated that total dioxin level have decreased during the last 30 years. Significant declines were seen in TCDD, 123678-HxCDD, HpCDD, OCDD, TCDF, and 1234678-HpCDF during 1970-2000, especially HpCDD and OCDD which decreased more than 97%. PCP used in Japan contained highly chlorinated congeners such as OCDD, HpCDDs, OCDF and HpCDFs as impurities and these congener levels declined gradually up to the early 80s. The present results of temporal trends of highly chlorinated PCDD/Fs agreed well with sediment core data (3). Concentrations of PCDD/Fs in human adipose tissue may have dropped during the last several years, but the trend is unclear

because of small sample numbers (Table 1).

Temporal trends for TEQs using WHO-TEF $_{1998}$ seemed to increase from the late 80s to the mid-90s when compared to 1970-75. This may indicate changes of sources; the domestic ban on PCP and PCBs in the 1970s and an increase in other source such as unidentified or small-scale incinerations. However, we have no information on unique source identifications and there is still a lack of data on 80s Japanese exposure. In addition, the increase of TEQ during the 70s and 80s is not explained. In other countries such as Germany, a similar drastic TEQ reduction of 50-70% was reported for human blood during 1980-1999, as well as in other European countries and the USA (1).

The mean concentration of mono-*ortho* PCB was decreased by 68%, from 92.6 ng/g in 1970-71 to 29.6 ng/g in 2000 and a decrease in non-*ortho* PCBs concentration was also found to be 62% from 367 pg/g in 1970-71 to 140 pg/g in 2000. As seen in Table 2, the concentrations of most of the coplanar PCB congeners decreased significantly during 1970-2000. This also agreed well with the decline in concentrations of non-*ortho* PCBs in the Tokyo Bay sediment core to be

Table 1. Concentrations of PCDD/Fs and TEQs in 1970-71, 1994-96 and 2000 in Japanese human adipose tissue.

Periods	1970-71	(n=20)	1994-96	(n=15)	2000	(n=10)
Congener	Mean (SD)	CV%	Mean (SD)	CV%	Mean (SD)	CV%
2378-TCDD	3.3 (1.0)	31	2.5 (1.5)	59	0.9 (0.5)	56
12378-PeCDD	9.7 (4.2)	44	10.9 (5.4)	49	4.4 (3.0)	69
123478-HxCDD	7.7 (3.8)	49	2.9 (3.6)	121	1.9 (1.3)	67
123678-HxCDD	26.5 (10.1)	38	52.6 (32.3)	61	14.2 (8.3)	58
123789-HxCDD	6.9 (2.6)	38	5.5 (3.6)	65	1.4 (1.1)	82
1234678-HpCDD	233.4 (128.2)	55	13.7 (7.2)	53	5.5 (4.9)	90
OCDD	4503.3 (2360.0)	52	297.0 (260.0)	88	123.9 (194.1)	157
2378-TCDF	2.7 (1.6)	58	0.9 (0.8)	86	0.4 (0.3)	69
12378-PeCDF	1.3 (0.9)	66	0.9 (0.9)	95	0.3 (0.2)	70
23478-PeCDF	18.5 (6.3)	34	18.7 (10.2)	54	8.1 (5.0)	61
123478-HxCDF	10.1 (3.1)	30	8.8 (4.1)	47	2.4 (1.8)	76
123678-HxCDF	7.1 (2.6)	37	10.7 (5.1)	47	2.7 (1.9)	71
123789-HxCDF	0.3 (0.2)	63	0.1 (0.1)	215	0.1 (0.1)	104
234678-HxCDF	2.9 (0.7)	23	3.9 (1.7)	44	1.8 (1.4)	78
1234678-HpCDF	11.6 (4.3)	37	5.3 (2.5)	47	2.1 (1.7)	80
1234789-HpCDF	1.2 (1.1)	94	0.3 (0.2)	91	0.2 (0.2)	77
OCDF	5.5 (6.6)	119	0.1 (0.3)	238	0.4 (0.2)	50
PCDD/Fs	4852.0 (2453.4)	51	434.6 (339.4)	78	170.7 (217.0)	127
TEQ (WHO, 1998)	31.6 (9.2)	29	31.5 (16.1)	51	11.9 (7.4)	62

Table 2. Concentrations of coplanar PCBs and TEQs in 1970-71 and 2000 in Japanese human adipose tissue.

Periods Congener	1970-71 Mean (SD)	(n=20) CV%	2000 Mean (SD)	(n=10) CV%
2',3,4,4',5 (123)	2427 (1606)	66	630 (508)	81
2,3',4,4',5 (118)	53663 (33501)	62	12080 (9602)	79
2,3,4,4',5 (114)	2266 (1166)	51	1155 (686)	59
2,3,3',4,4' (105)	11746 (8772)	49	2147 (1803)	84
2,3',4,4',5,5' (167)	3560 (2065)	58	1887 (970)	51
2,3,3',4,4',5 (156)	10269 (5864)	57	8942 (4021)	45
2,3,3',4,4',5' (157)	1914 (1016)	53	1675 (851)	51
2,3,3',4,4',5,5' (189)	701 (563)	80	1138 (519)	46
mono-*ortho* PCBs	92546 (52823)	57	29653 (16203)	55
Congener	48 (27)	56	5 (2)	53
3,4,4',5 (81)	67 (52)	77	3 (2)	67
3,3',4,4',5 (126)	202 (146)	72	72 (60)	84
3,3',4,4',5,5' (169)	50 (25)	50	61 (25)	41
non-*ortho* PCBs	367 (217)	59	140 (78)	56
Coplanar-PCBs	92914 (53040)	62	29793 (16261)	55
TEQ (WHO, 1998)	35.4 (21.9)	62	15.3 (8.2)	54

66.8%, from 2200 pg/g to 730pg/g dry wt during 1970-1992 (3). Research on human milk in the Osaka area demonstrated that total PCB concentrations decreased 77% from 1.43 ppm in 1973 to 0.33 ppm in 1996 (4). Environmental concentrations of total PCBs decreased gradually in Japan from the early 1970s to the late 1980s. However, congener data on PCB 169 and 189 concentrations acquired in the present study do not show a decrease or an increase during the last 30 years. Concentrations of PCB 169 in dated sediments also did not decrease during 1970-1992 (3). One of the major sources of coplanar PCBs, such as congener PCB 169, was suspected to be emissions from municipal solid waste incineration (5). De novo synthesis of coplanar PCB congeners was observed in the combustion of municipal solid wastes (6). Further work on the characterization of the dynamics of sources of coplanar PCBs as well as those of PCDD/Fs is needed for precise estimation of human exposure in Japan. Time trends for TEQs of co-PCBs with other Japanese studies, there are significant decreases in PCB-TEQs during 1970s – middle of 1990s. However, temporal trends for the last 5 years are still not clear. Furthermore, there are dozens of tons of banned-PCB formulations in closed systems still operating or being kept in Japan, and their possible improper leakage to the environment is a matter of concern. Therefore, there is a need for research on the source characterization and for continuous monitoring of short-term temporal trends on background exposure to coplanar PCBs as well as to PCDD/F.

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