

## Concentration of PCDDs/PCDFs and coplanar PCBs in human skin lipids

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### Introduction

PCDDs, PCDFs and coplanar PCBs (Co-PCBs) accumulate in the human body because of their highly lipophilic properties. Many scientists have determined the concentrations of PCDDs, PCDFs and Co-PCBs in several human tissue samples including the adipose tissue<sup>1</sup>, blood<sup>2</sup>) and breast milk<sup>3</sup>). Oshiro reported that organohalogen compounds such as dieldrin could be detected in the skin surface lipids<sup>4</sup>). Ohgami *et al.* also measured the levels of PCBs and PCQs in skin surface lipids of patients with Yusho<sup>5</sup>). Such kinds of investigations would provide very important information for the elimination of these lipophilic chemicals from the human body. On the other hand, studies concerning the excretion of dioxin-like chemicals through the skin surface have not been reported and very limited information about the role of skin for their excretion is available. To evaluate the role of skin, we have analyzed totally 8 samples of the human skin surface lipids for PCDDs,PCDFs and Co-PCBs and compared their levels with those in the blood.

### Methods

Skin surface lipids samples were collected from 8 male volunteers in Fukuoka, Japan, in August and September, 1994. The skin samples which were collected in both periods, were analyzed separately and the blood samples were collected at a later period and analyzed. The range of age was 21 -73 years old and the average age was 47 years. All samples (face skin lipid) were collected using a cotton pad with 70% alcohol. The time of collection was early in the morning before washing the face, which was washed the previous night. The face skin was wiped for 10 consecutive days. The cotton pads which were used for wiping the face surface, were extracted with a mixed solvent of n-hexane and acetone(2:1) using an ultra sonic generator. The extracts were washed with distilled water, and then dried with anhydrous sodium sulfate. Each extract was then concentrated to dryness, and the lipid

weight was determined gravimetrically. The extract was purified on a AgNO<sub>3</sub>-silica gel column and charcoal column.

Ten kinds of <sup>13</sup>C-labeled PCDDs/PCDFs and three kinds of <sup>13</sup>C-labeled Co-PCBs were added as internal standards for checking recoveries of PCDDs/PCDFs and Co-PCBs through the whole analytical procedure. The PCDDs/PCDFs and Co-PCBs were analyzed by the HRGC/HRMS technique using a Finnigan MAT-95 mass spectrometer (Finnigan MAT-95, Germany) directly interfaced with a Varian Model 3400 gas chromatograph. All target compounds were measured with an SP-2331 capillary column (0.32mmX60m; film thickness, 0.25μm). The mass resolution (5 % valley) was 7000 to 8000.

## Results and discussion

The mean weight of the skin lipids collected from the same volunteers was 0.268 g (collected in August) and 0.219 g (collected in September), respectively. Concentrations of PCDDs, PCDFs and Co-PCBs in the skin surface lipid (16 samples) and blood (8 samples) were determined and the results are summarized in Table 1 and 2 on a lipid basis. The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) toxic equivalent (TEQ) of PCDDs and PCDFs were calculated using I-TEF and those of the Co-PCBs were calculated using the data reported by WHO<sup>6</sup>. The respective mean TEQ concentrations of PCDDs, PCDFs and Co-PCBs were 7.8, 7.5, and 13.7 pg/g for the skin surface lipids and 10.4, 10.4, and 15.2 pg/g for the blood samples, respectively. In the blood, only 2,3,7,8-substituted isomers were detected. However, in the skin surface lipids, we detected not only 2,3,7,8-substituted isomers but also non-2,3,7,8-substituted ones which are generally not detectable in human tissue samples, except for stool samples<sup>7</sup>. At present, we have no idea to explain the existence of non-2,3,7,8-substituted isomers in the skin surface lipid. As shown in Fig.1, among the PCDDs, OCDD showed the highest concentration in the skin surface lipids and, in general, their levels seemed to increase in proportion to the grade of chlorination. In PCDFs, Hep-CDF indicated the highest level in the skin lipids but in the blood sample, Pe-CDF was the most abundant congener (Fig.2). The congener pattern of tetra to hexa for both PCDD/PCDF congeners showed no clear difference between the skin lipids and blood (skin<blood). However, the concentrations of hepta- and octa-PCDD in the skin surface lipids were much higher than those in the blood. As shown in Fig.3, the greatest concentration was seen in 3,3',4,4',5-PeCB, the most toxic congener in Co-PCBs for the blood, but the 3,3',4,4'-TeCB levels in the skin surface lipids was about 20 times higher than that found in the blood. Fig.4 shows the percent TEQ distribution in the skin lipids and blood and about 50 % of the mean TEQ level was attributable to Co-PCBs for both samples.

## Conclusions

Levels of PCDDs/PCDFs and coplanar PCBs have been measured in human skin surface lipids and blood. The average concentrations of PCDDs, PCDFs and coplanar PCBs in skin surface lipids was 7.8, 7.5 and 13.7 TEQ pg/g and those in the blood was 10.4, 10.4 and 15.2 TEQ pg/g on a lipid basis, respectively.

The isomer profile of skin surface lipids was quite different from that of human samples such as adipose tissue, blood and breast milk. Especially, the existence of non-2,3,7,8-substituted isomers in the skin surface lipid is remarkable.

## References

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**Table 1 Concentration of PCDDs,PCDFs and Co-PCBs in skin surface lipid(pg/g lipid basis)**

| Congener            | S-1    | S-2   | S-3    | S-4    | S-5    | S-6    | S-7    | S-8   | Min   | Max    | Mean   | SD     |
|---------------------|--------|-------|--------|--------|--------|--------|--------|-------|-------|--------|--------|--------|
| 2,3,7,8-TCDD        | 0.7    | 1.8   | 0.7    | 1.6    | 2.4    | 1.7    | 1.0    | 0.8   | 0.7   | 2.4    | 1.3    | 0.6    |
| 1,2,3,7,8-PeCDD     | 3.0    | 3.8   | 6.0    | 6.8    | 7.2    | 5.6    | 4.2    | 5.5   | 3.0   | 7.2    | 5.3    | 1.5    |
| 1,2,3,4,7,8-HxCDD   | 0.8    | 1.6   | 2.3    | 1.4    | 1.2    | 1.2    | 0.8    | 1.0   | 0.8   | 2.3    | 1.3    | 0.5    |
| 1,2,3,6,7,8-HxCDD   | 6.4    | 21.7  | 18.2   | 15.2   | 13.9   | 12.3   | 9.7    | 8.2   | 6.4   | 21.7   | 13.2   | 5.2    |
| 1,2,3,7,8,9-HxCDD   | 0.9    | 3.8   | <0.6   | 2.0    | 3.8    | <0.8   | 2.4    | 3.4   | ND    | 3.8    | 2.1    | 1.6    |
| 1,2,3,4,6,7,8-HpCDD | 21.7   | 22.7  | 225.1  | 32.8   | 77.4   | 158.9  | 72.2   | 41.3  | 21.7  | 225.1  | 81.5   | 73.4   |
| OCDD                | 362.1  | 246.5 | 2284.6 | 1620.6 | 2418.5 | 1769.6 | 1586.8 | 541.5 | 246.5 | 2418.5 | 1353.8 | 859.2  |
| 2,3,7,8-TCDF        | 3.0    | 2.6   | 1.6    | 3.6    | 3.4    | 2.1    | 1.6    | 3.2   | 1.6   | 3.6    | 2.6    | 0.8    |
| 1,2,3,7,8-PeCDF     | 4.2    | 1.3   | 4.3    | 2.2    | 6.1    | 4.3    | 1.3    | 3.4   | 1.3   | 6.1    | 3.4    | 1.7    |
| 2,3,4,7,8-PeCDF     | 9.6    | 16.7  | 6.3    | 10.1   | 13.3   | 7.3    | 9.7    | 12.8  | 6.3   | 16.7   | 10.7   | 3.4    |
| 1,2,3,4,7,8-HxCDF   | 3.3    | 4.7   | 3.8    | 5.1    | 6.7    | 3.4    | 3.0    | 2.7   | 2.7   | 6.7    | 4.1    | 1.3    |
| 1,2,3,6,7,8-HxCDF   | 3.4    | 4.4   | 4.3    | 4.7    | 5.0    | 5.1    | 1.6    | 3.0   | 1.6   | 5.1    | 3.9    | 1.2    |
| 1,2,3,7,8,9-HxCDF   | <1.2   | <1.0  | <0.8   | 1.6    | 6.6    | <1.0   | <1.0   | <0.6  | ND    | 6.6    | 1.2    | 2.2    |
| 2,3,4,6,7,8-HxCDF   | 2.6    | 3.4   | <0.8   | 1.5    | 5.8    | 1.4    | 3.0    | 4.9   | ND    | 5.8    | 2.8    | 1.9    |
| 1,2,3,4,6,7,8-HpCDF | 7.6    | 6.0   | 59.8   | 9.7    | 64.2   | 54.0   | 8.1    | 9.4   | 6.0   | 84.2   | 29.8   | 31.2   |
| 1,2,3,4,7,8,9-HpCDF | <1.0   | <1.1  | <0.5   | <1.1   | <2.0   | <1.1   | <0.8   | <0.9  | ND    | -      | -      | -      |
| OCDF                | NA     | NA    | NA     | NA     | NA     | NA     | NA     | NA    | -     | -      | -      | -      |
| 3,3',4,4'-TeCB      | 1556.5 | 117.6 | 416.9  | 61.3   | 688.1  | 353.8  | 180.1  | 83.6  | 61.3  | 1556.5 | 432.2  | 501.1  |
| 3,3',4,4',5-PeCB    | 123.7  | 75.8  | 221.0  | 88.3   | 165.3  | 162.5  | 69.0   | 150.0 | 69.0  | 221.0  | 131.9  | 52.7   |
| 3,3',4,4',5,5'-HxCB | 25.1   | 29.0  | 22.4   | 34.4   | 58.9   | 19.3   | 33.3   | 47.7  | 19.3  | 58.9   | 33.8   | 13.4   |
| Total PCDD          | 395.4  | 301.9 | 2537.0 | 1680.4 | 2524.4 | 1949.3 | 1677.2 | 601.6 | 301.9 | 2537.0 | 1458.4 | 913.3  |
| Total PCDF          | 41.0   | 51.3  | 404.4  | 78.8   | 753.2  | 391.3  | 64.5   | 59.6  | 41.0  | 753.2  | 230.5  | 261.1  |
| Total PCDD/PCDF     | 436.4  | 353.2 | 2941.4 | 1759.2 | 3277.7 | 2340.6 | 1741.8 | 661.2 | 353.2 | 3277.7 | 1688.9 | 1129.7 |
| Total Coplanar PCB  | 1705.2 | 222.4 | 660.4  | 184.0  | 912.3  | 535.6  | 282.4  | 281.2 | 184.0 | 1705.2 | 598.0  | 513.4  |
| PCDD-TEQ            | 3.6    | 6.9   | 10.3   | 8.8    | 11.1   | 9.2    | 6.7    | 5.7   | 3.6   | 11.1   | 7.8    | 2.5    |
| PCDF-TEQ            | 6.3    | 10.0  | 5.2    | 6.9    | 11.2   | 5.9    | 6.0    | 8.1   | 5.2   | 11.2   | 7.5    | 2.1    |
| Co-PCBs TEQ         | 13.4   | 7.9   | 22.5   | 9.2    | 17.5   | 16.6   | 7.3    | 15.5  | 7.3   | 22.5   | 13.7   | 5.3    |
| TEQ(International)  | 23.3   | 24.8  | 38.1   | 24.9   | 39.7   | 31.8   | 20.1   | 29.4  | 20.1  | 39.7   | 29.0   | 7.1    |

NA: not available

ND: not detectable

**Table 2 Concentration of PCDDs,PCDFs and Co-PCBs in blood lipid(pg/g lipid basis)**

| Congener            | B-1   | B-2   | B-3   | B-4    | B-5   | B-6   | B-7   | B-8   | Min   | Max    | Mean  | SD    |
|---------------------|-------|-------|-------|--------|-------|-------|-------|-------|-------|--------|-------|-------|
| 2,3,7,8-TCDD        | 1.0   | 1.8   | 4.5   | 2.8    | 1.6   | 1.5   | 1.5   | 2.1   | 1.0   | 4.5    | 2.1   | 1.1   |
| 1,2,3,7,8-PeCDD     | 5.7   | 10.1  | 11.7  | 8.7    | 9.3   | 9.9   | 5.9   | 7.2   | 5.7   | 11.7   | 8.6   | 2.1   |
| 1,2,3,4,7,8-HxCDD   | <1.7  | 3.0   | 3.8   | 3.0    | 1.3   | 0.9   | 1.3   | 7.1   | ND    | 7.1    | 2.6   | 2.2   |
| 1,2,3,6,7,8-HxCDD   | 8.6   | 66.7  | 22.4  | 35.1   | 23.1  | 12.7  | 18.9  | 22.6  | 8.6   | 66.7   | 26.2  | 18.1  |
| 1,2,3,7,8,9-HxCDD   | 2.8   | 14.2  | <3.3  | 3.4    | 2.8   | 7.5   | <1.2  | 5.5   | ND    | 14.2   | 4.5   | 4.7   |
| 1,2,3,4,6,7,8-HpCDD | 23.4  | 51.1  | 59.5  | 47.2   | 11.2  | 9.6   | 9.0   | 16.9  | 9.0   | 59.5   | 28.5  | 20.8  |
| OCDD                | 170.1 | 693.0 | 611.9 | 986.9  | 344.4 | 150.4 | 179.7 | 325.5 | 150.4 | 986.9  | 432.7 | 302.1 |
| 2,3,7,8-TCDF        | 0.9   | 1.2   | 1.5   | 1.6    | 1.8   | 1.0   | 1.2   | 1.3   | 0.9   | 1.8    | 1.3   | 0.3   |
| 1,2,3,7,8-PeCDF     | 1.2   | 1.9   | 3.7   | 1.7    | 2.8   | 1.4   | 1.8   | 1.5   | 1.2   | 3.7    | 2.0   | 0.9   |
| 2,3,4,7,8-PeCDF     | 14.4  | 32.1  | 14.0  | 18.9   | 15.1  | 14.7  | 13.9  | 13.8  | 13.8  | 32.1   | 17.1  | 6.3   |
| 1,2,3,4,7,8-HxCDF   | 5.0   | 19.1  | 7.3   | 4.0    | 7.0   | 7.5   | 5.8   | 7.8   | 4.0   | 19.1   | 8.0   | 4.7   |
| 1,2,3,6,7,8-HxCDF   | 1.7   | 12.0  | 14.8  | 4.1    | 5.8   | 2.7   | 2.9   | 4.4   | 1.7   | 14.8   | 6.1   | 4.8   |
| 1,2,3,7,8,9-HxCDF   | <1.5  | 3.6   | <1.3  | 2.5    | <0.5  | <1.6  | <0.5  | <2.6  | ND    | 3.6    | 0.8   | 1.4   |
| 2,3,4,6,7,8-HxCDF   | <1.5  | 2.5   | <1.3  | 3.8    | <0.5  | <1.6  | <0.5  | <2.6  | ND    | 3.8    | 0.8   | 1.5   |
| 1,2,3,4,6,7,8-HpCDF | 6.0   | 8.4   | 8.9   | 6.4    | 11.6  | 8.0   | 3.5   | 5.1   | 3.5   | 11.6   | 7.2   | 2.5   |
| 1,2,3,4,7,8,9-HpCDF | <1.9  | <2.0  | <1.5  | <1.2   | <0.5  | <2.3  | <0.8  | <2.5  | ND    | -      | -     | -     |
| OCDF                | NA    | NA    | NA    | NA     | NA    | NA    | NA    | NA    | -     | -      | -     | -     |
| 3,3',4,4'-TeCB      | 10.8  | 19.1  | 18.2  | 20.6   | 27.9  | 8.5   | 14.1  | 18.5  | 8.5   | 27.9   | 17.2  | 6.1   |
| 3,3',4,4',5-PeCB    | 65.6  | 134.6 | 221.4 | 191.6  | 128.8 | 82.0  | 121.2 | 213.2 | 65.6  | 221.4  | 144.8 | 58.4  |
| 3,3',4,4',5,5'-HxCB | 51.0  | 66.9  | 55.6  | 88.6   | 102.9 | 52.9  | 70.4  | 73.9  | 51.0  | 102.9  | 70.3  | 18.2  |
| Total PCDD          | 211.6 | 839.8 | 713.8 | 1087.0 | 393.7 | 192.5 | 216.3 | 386.9 | 192.5 | 1087.0 | 505.2 | 335.5 |
| Total PCDF          | 35.8  | 80.7  | 74.7  | 63.1   | 62.6  | 41.7  | 41.1  | 43.8  | 35.8  | 80.7   | 55.4  | 17.1  |
| Total PCDD/PCDF     | 247.4 | 920.6 | 788.5 | 1150.1 | 456.3 | 234.2 | 257.5 | 430.6 | 234.2 | 1150.1 | 560.6 | 349.1 |
| Total Coplanar PCB  | 127.4 | 220.6 | 295.2 | 300.8  | 259.6 | 143.4 | 205.8 | 305.7 | 127.4 | 305.7  | 232.3 | 70.2  |
| PCDD-TEQ            | 5.4   | 16.4  | 14.2  | 12.7   | 9.5   | 8.8   | 6.8   | 9.7   | 5.4   | 16.4   | 10.4  | 3.7   |
| PCDF-TEQ            | 8.1   | 20.1  | 9.6   | 11.2   | 9.3   | 8.6   | 8.1   | 8.4   | 8.1   | 20.1   | 10.4  | 4.0   |
| Co-PCBs TEQ         | 7.1   | 14.1  | 22.7  | 20.1   | 13.9  | 8.7   | 12.8  | 22.1  | 7.1   | 22.7   | 15.2  | 5.9   |
| TEQ(International)  | 20.5  | 50.6  | 46.5  | 44.0   | 32.7  | 26.2  | 27.6  | 40.2  | 20.5  | 50.6   | 36.0  | 10.8  |

NA: not available

ND: not detectable

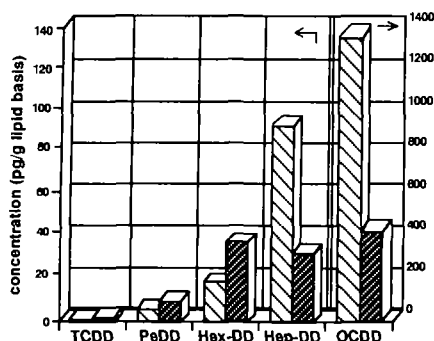


Fig. 1 Congener pattern of PCDDs in the skin lipid and blood □:skin lipid ▨:blood

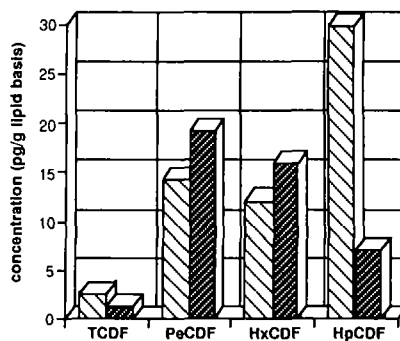


Fig. 2 Congener pattern of PCDFs in the skin lipid and blood □:skin lipid ▨:blood

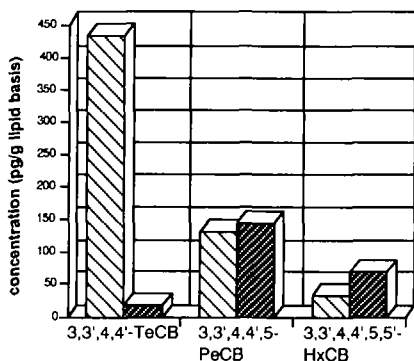


Fig. 3 Congener pattern of Co-PCBs in the skin lipid and blood □:skin lipid ▨:blood

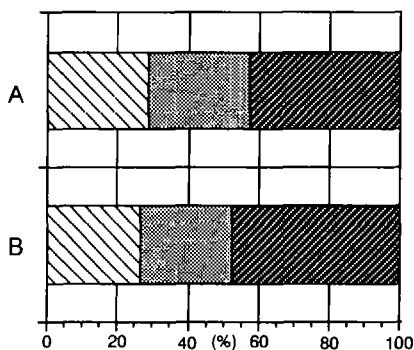


Fig. 4 Percentage TEQ contribution in the skin lipid and blood A:skin lipid B:blood □:PCDDs ▨:PCDFs ▩:Co-PCBs

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