Air pollution by PCDDs, PCDFs and non-ortho coplanar PCBs in Japan using pine needle as a biomonitoring indicator

Osamu Aozasa, Masaru Ikeda, Teruyuki Nakao, Souichi Ohta and Hideaki Miyata
Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-01, Japan
Chin-Wan Huang
Department of Chemistry, Chung Yuan Christian University Chung-Li, Taiwan, 32039, Republic of China
Hui-Tuh Tsai
Department of Environmental Engineering and Health, China-Nan JR. College of Pharmacy, Taiwan, Republic of China

1. Introduction

The indeciduous pine tree grows in every areas except for Okinawa (the most southern prefecture) in Japan, and its needle has the lipophil cuticle on the surface. This suggests that the pine needle might be a useful biomonitoring indicator for air pollution by lipophilic substances. In fact, several researchers estimated air pollution by PCDDs and PCDFs using spruce needle as an indicator[1-3]. On the other hand, in recent years, toxic coplanar PCBs (Co-PCBs) having similar biological effects to PCDDs and PCDFs have been the subject of much concern in the environmental field. Therefore, PCDDs, PCDFs and Co-PCBs have been treated with so-called dioxin analogues.
In this study, we developed a suitable analytical method for dioxin analogues including Co-PCBs in pine needle, and surveyed their pollution levels in pine needle samples from various locations in Japan using the developed method, in order to estimate the air pollution at each location.

2. Experiment

1) Sample

About 1 kg of pine needle was collected in Osaka in January, 1995. The sample was lyophilized, cut into a length of ca. 3 cm, and then stirred well up. The specimen was used for investigation on analytical method. For survey study, samples of pine needle were collected at various locations in January to April, 1995. These samples were also treated with the method described above.

2) Examination on a suitable solvent for extraction

After spiking of internal standards (five $^{13}C_{12}$-PCDDs and five $^{13}C_{12}$-PCDFs, each 400 pg; three $^{13}C_{12}$-Co-PCBs, each 500 pg), 30 g of pine needle sample was homogenized with 300 ml of four kinds of extract solvent (see Fig. 1) by a ultramixture machine, and then extracted for 3 hrs. under reflux. After addition of silicagel (30 g), each extract was stirred, filtered and concentrated to less than 0.3 ml, followed by adjusting to a volume of 10 ml with n-hexane. The solution was purified on multi-layer and alumina columns, followed by HRGC-HRMS analysis according to our method described elsewhere[4].

3) Examination on extraction time

After spiking of internal standards, 30 g of sample was extracted with 300 ml of toluene for 1 hr. under reflux. After removing the extract, same amounts of internal standards and toluene were again added into the original sample and extracted for 1 hr. The trial was repeated more 6 times. Each extract was analyzed according to above method.

4) Examination on reproducibility of analytical data

After spiking of internal standards, each three 50 g of sample was extracted with 500 ml of toluene for 4 hr under reflux. Each extract was analyzed according to above method. The coefficient of variation for each dioxin analogue was calculated on the analytical data.

5) Survey on pollution levels of dioxin analogues in pine needle samples

Samples (each 50 g) from 11 prefectures (see Tables 1 and 2) were analyzed for dioxin analogues according to the analytical procedure in the term [4)] of Method.

3. Results and discussion

1) Extraction solvent

In published papers[1-3], methylene chloride was used as the extraction solvent for PCDDs and PCDFs in pine needle. As shown in Fig. 1, however, the extractive ability of the solvent was poorer than did toluene. The relative magnitude of extraction efficiency for PCDDs/PCDFs was arranged in order of toluene (100), methylene chloride (27), benzene (18) and hexane (12). Therefore, toluene was used as the extraction solvent in this study.

2) Extraction time

As shown in Fig. 2, it is revealed that a great part of extractive amounts of PCDDs and PCDFs was derived from a period of the first 1 hr extraction time. 99.9% of PCDDs and 100% of PCDFs were extracted for the extraction time of 3 hrs. The suitable extraction time was concluded to be 4 hrs.

3) Reproducibility

In the triple analysis, the coefficients of variation for PCDD and PCDF congeners were 3.7 to 10% and 2.4 to 5.1%, respectively, indicating the reproducibility of our method to be very excellent.

4) Pollution levels by dioxin analogues in pine needle samples

As shown in Tables 1 and 2, total actual concentration of Co-PCBs, PCDDs or PCDFs was in a wide range of 2.48 to 124 pg/g, 26.7 to 761 pg/g or 17.7 to 1166 pg/g, respectively. The major congener for Co-PCBs was 3,3'4,4'-TCB at all locations. However, the majors for PCDDs and PCDFs varied among the examined areas.

As well as the actual level, the TEQ level of Co-PCBs, PCDDs or PCDFs was also in a wide range of 0.04 to 5.40 pg/g, 0.02 to 4.57 pg/g or 0.43 to14.2 pg/g, respectively. The contamination level was remarkably high at urban and/or industrial areas such as Tiba, Kanagawa, Shizuoka, Nara, Osaka and Fukuoka. While the local areas with a small population density such as Hokkaido, Iwate, Tottori, Shimane and Oita showed the lower pollution level. Thus contamination tendency was also seen in a case of blue mussel survey for sea pollution[5]. For example, the ratios of total TEQ of Co-PCBs, PCDDs and PCDFs in blue mussel at Osaka versus Hokkaido were 14 and 37[5]. These values were almost same to that (15) in this study.

As shown in Fig. 3, there was a difference in the contributions of PCDDs, PCDFs and Co-PCBs to the total actual concentration among surveyed areas. The values were 1.7 to 28.0% for Co-PCBs, 30.4 to 85.9% for PCDDs and 12.3 to 63.2% for PCDFs, respectively. In Hokkaido and Fukuoka prefectures, a great part of the total was occupied by PCDDs with 86 and 79%, respectively. While more than 50% of the total was attributable to PCDFs in Tiba, Kanagawa and Shizuoka. In addition, the relatively high contribution of Co-PCBs was seen in Iwate, Osaka, Tottori and Oita. These results suggest that the contamination source might be different among tested locations.

Now, we are analyzing pine needle samples from other locations, and the data will be presented at this conference.

4. References

1) Reischl, A., M. Ressinger, H. Thoma and O. Hutzinger (1989): Accumulation of organic air constituents by plant surfaces-A sampling system for atmospheric polychlorodibenzo-p-dioxin (PCDD) and polychlorodibenzo-p-furan (PCDF), Chemosphere,18, 561-568.

2) Fiedler, H., C. Lau, K. Cooper, R. Andersson, S.-E. Kulp, C. Rappe, F. Howell and M. Bonner (1995): PCDD/PCDF in soil and pine needle samples in a rural area in the United States of America, Organohalogen Compounds, 24, 285-292.

3) Kohler, J., L. Peich, R. Dumler, H. Thoma and O. Vierle (1995): Monitoring of PCDD/F-levels with bioindicator plants, Organohalogen Compounds, 24, 205-208.

4) Lu, J.-R., H. Miyata, C.-W. Huang, H.-T. Tsai, V.-Z. Sheng, T. Nakao, Y. Mase, O. Aozasa and S. Ohta (1995): Contamination levels of PCDDs, PCDFs and non-ortho chlorine substituted coplanar PCBs in milkfish and crab from culture pond and coastal area near open-air incineration sites from metal reclamation in Wan-Li, Taiwan, Republic of China, Chemosphere, 31, 2959-2970.

5) Miyata, H., O. Aozasa, K. Yamamori, A. Fujiwara and Y. Yasuda (1994): Survey on pollution of dioxin and related compounds monitoring by blue mussel as a biological indicator at 24 coastal areas in Japan, Organohalogen Compounds, 20, 187 -190.

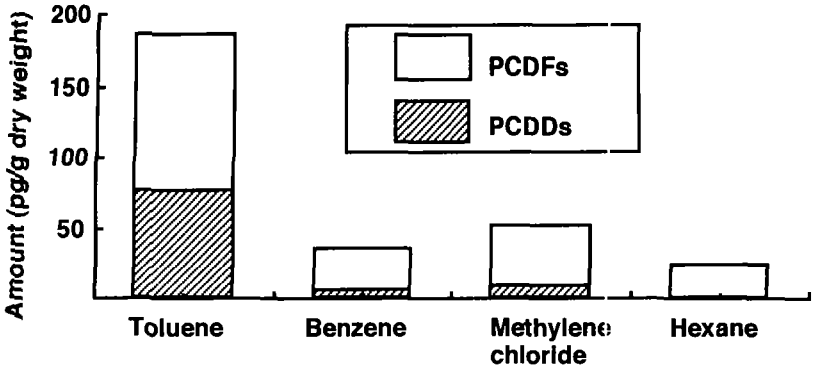

Fig. 1 Amounts of 2,3,7,8-PCDDs and 2,3,7,8-PCDFs in pine needle extracted with various solvents

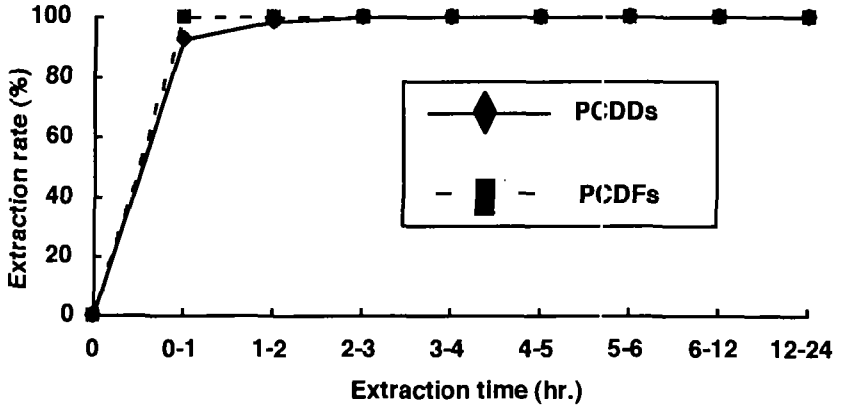

Fig. 2 Extraction rates of 2,3,7,8-PCDDs and 2,3,7,8-PCDFs in pine needle

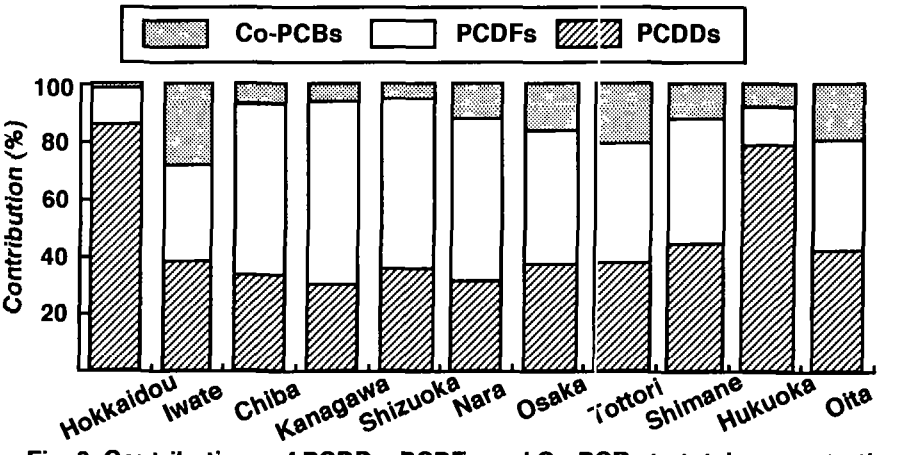

Fig. 3 Contributions of PCDDs, PCDFs and Co-PCBs to total concentration in pine needle from 11 locations

Table 1 Acutual (pg/g) and TEQ (pg/g) concentrations Co-PCBs of and PCDDs in pine needle samples

Compound	Sampling location										
	Hokkaido	Iwate	Chiba	Kanagawa	Shizuoka	Nara	Osaka	Tottori	Shimane	Fukuoka	Oita
3,3',4,4'-TCB	2.28	16.1	73.1	79.6	35.9	110	115	34.1	45.2	69.7	51.0
3,3',4,4',5-PeCB	0.12	2.52	42.0	29.1	11.2	25.9	23.80	4.30	6.32	10.2	7.28
3,3',4,4',5,5'-HxCB	0.08	0.90	9.44	9.36	2.87	5.93	5.43	0.09	0.61	0.63	0.45
Total Co-PCBs	2.48	19.4	124	118	49.9	142	144	38.5	52.1	80.5	58.8
Total TEQ	0.04	0.46	5.40	4.17	1.62	3.99	3.80	0.78	1.11	1.75	1.26
2,3,7,8-TCDD	0.06	0.26	0.22	0.13	0.03	0.99	1.29	N.D.	6.95	0.04	0.18
others	2.80	3.17	199	210	25.0	30.6	6.28	40.0	113	45.6	39.1
1,2,3,7,8-PeCDD	N.D.	0.48	1.91	1.25	0.93	0.62	2.94	N.D.	1.57	0.70	0.76
others	2.91	1.33	151	90.8	28.9	39.4	65.3	13.9	28.5	22.8	20.8
1,2,3,4,7,8-HxCDD	4.82	0.96	1.03	1.44	0.64	0.55	4.82	N.D.	1.31	5.78	0.67
1,2,3,6,7,8-HxCDD	N.D.	0.50	1.72	1.91	0.91	0.90	4.67	N.D.	2.68	0.26	0.93
1,2,3,7,8,9-HxCDD	N.D.	1.09	N.D.	N.D.	0.48	0.47	4.39	N.D.	1.92	N.D.	0.10
others	4.29	1.22	89.0	78.4	26.5	43.0	68.5	6.87	21.2	14.2	11.3
1,2,3,4,6,7,8-HpCDD	11.7	3.06	23.3	37.6	34.3	42.2	31.8	1.86	2.21	25.4	4.77
others	18.2	1.19	36.8	46.9	28.4	62.6	30.2	2.05	4.37	32.9	6.74
OCDD	78.7	13.5	92.2	91.8	196	143	108	5.40	10.5	614	40.7
Total PCDDs	124	26.7	597	560	343	364	329	70.2	195	761	126
Total TEQ	0.74	0.80	1.78	1.56	1.24	2.06	4.57	0.02	8.36	1.86	0.82

Table 2 Acutual (pg/g) and TEQ (pg/g) concentrations of PCDFs in pine needle samples

Compound	Sampling location										
	Hokkaido	Iwate	Chiba	Kanagawa	Shizuoka	Nara	Osaka	Tottori	Shimane	Fukuoka	Oita
2,3,7,8-TCDF	1.78	0.82	11.9	12.0	2.30	3.83	9.78	0.98	2.27	1.90	1.90
others	7.05	5.31	433	432	118	187	20.8	38.2	106	75.9	71.7
1,2,3,7,8-PeCDF	0.78	N.D.	18.8	14.2	0.51	0.17	14.0	N.D.	9.29	N.D.	0.11
2,3,4,7,8-PeCDF	0.78	0.95	13.5	12.9	7.03	5.86	13.5	0.53	4.96	N.D.	N.D.
others	4.68	3.93	324	252	115	112	133	10.1	39.9	18.7	19.9
1,2,3,4,7,8-HxCDF	N.D.	0.81	10.3	18.0	8.92	4.47	12.1	0.74	3.00	0.61	1.31
1,2,3,6,7,8-HxCDF	0.62	1.50	15.9	24.6	12.3	7.87	12.71	0.99	3.44	0.81	1.85
1,2,3,7,8,9-HxCDF	N.D.	1.33	N.D.	N.D.	N.D.	N.D.	2.62	N.D.	1.82	N.D.	N.D.
2,3,4,6,7,8-HxCDF	N.D.	N.D.	20.5	36.2	23.2	14.3	15.7	0.71	2.99	0.37	1.72
others	0.75	1.22	118	166	90.3	87.8	64.5	5.64	10.6	5.88	6.39
1,2,3,4,6,7,8-HpCDF	0.72	2.44	64.2	100	162	131	64.4	8.50	5.01	5.26	7.22
1,2,3,6,7,8,9-HpCDF	0.13	1.03	1.06	9.32	N.D.	N.D.	3.33	N.D.	0.09	N.D.	N.D.
others	0.17	N.D.	13.0	46.3	N.D.	57.5	20.1	N.D.	0.61	1.25	N.D.
OCDF	0.27	3.93	8.14	42.3	35.4	51.6	15.7	10.8	0.05	12.7	1.28
Total PCDFs	17.7	23.3	1052	1166	575	663	403	77.3	190	123	113
Total TEQ	0.68	0.96	14.2	17.4	9.86	7.35	13.4	0.70	4.35	0.43	0.76
Sum total[a)]	144	69.5	1773	1844	967	1169	875	186	437	965	298
Sum total TEQ[b)]	1.45	2.22	21.4	23.1	12.7	13.4	21.8	1.50	13.8	4.04	2.84

a) : Sum total concentrations of PCDDs, PCDFs and Co-PCBs
b) : Sum total TEQ of PCDDs, PCDFs and Co-PCBs