Investigation on Plant Leaf as an Indicator of Air Pollution by PCDDs/DFs

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Introduction

Polychlorodibenzo-*p*-dioxin and polychlorodibenzofurans (PCDDs/DFs) are released into the atmosphere from various sources. Especially, combustion processes are known to be played an important role on the release of PCDDs/DFs into the environment. Therefore, it is important to know the PCDD/DF levels in ambient air, due to observe PCDDs/DFs in the environment. However, only limited data are currently available on ambient air concentrations, distribution and transport, due to high cost and the place to set up of continuous data aquisition through traditional methods of air sampling[1)]. Accumulation of lipophilic organic trace substances in plant leaves is attributed to uptake of PCDDs/DFs from the atmosphere[2-6)]. On the accumulation of 2,3,7,8-TCDD to plant leaf, Travis and Hattemer-Frey estimated 56% of the total 2,3,7,8-TCDD in plants originates from air-to-leaf vapor mass transfer[7)]. However, the relationshipa between PCDDs/DFs in plant leaf and ambient air have been scarcely studied. In the present study, we investigated the relationships between the levels of PCDDs/DFs in plant leaves and ambient air in Matsuyama city, Japan in order to evaluate plant leaf as an indicator of air pollution by PCDDs/DFs.

Experimental

Plant leaves and Air Samples

Samples were taken from cherry trees at the five locations in Matsuyama , Japan, during August to September, 1997. Plant leaves were collected at all directions of the tree and were combined as one sample.

The sampling points were set up at the five sites near by where the plant leaves were taken in Matsuyama, from on August to September, 1997. Polyurethane foam plug (PUF, Model HA, Achilles Co. Ltd., Japan, diameter 35mm, length 50mm, density 20$\pm$1.6kg/m^3) was used as an adsorbent for collection of PCDDs/DFs. Prior to use, PUF plugs were cleaned with acetone and toluene in a Soxhlet extractor (500mL) for 30 hours, respectively. Three dried PUF plugs were packed in a glass column (i.d. 35mm, length 160mm) and set into the stainless steel shelter to prevent from the rain. Air samples were taken over 5-6 days with two air pumps (Model AP-240Z, IWAKI Co. Ltd., Japan) and these six PUF plugs were combined as one sample.

Analysis

Plant leaves were washed with cleaned water and cut into as small as possible. PCDDs/DFs adsobed on plant leaves (20g on wet weight basis) and six PUF plugs from individual sampling site were Soxhlet-extracted with acetone and toluene (500mL) for 24 hours, respectively.The interfering substances in the extract was removed by sulfuric acid. Then, silica gel and activated carbon column chromatographies were carried out for purification and separation. The purified extract was concentrated to 100 μL before analysis by GC-MS. All samples were analyzed by HRGC-HRMS (JEOL SX102A-HP5890 II) equipped with a CHROMPACK CP-Cil 88 for Dioxins.

Results and Discussion

Concentrations and compositions of PCDDs/DFs in plant leaves

Table1 shows the concentrations of PCDDs/DFs in plant leaves from Matsuyama, Japan. The sampling locations in Matsuyama were selected from two mountain areas, urban areas and a rural area. The concentrations of PCDDs and PCDFs were in a wide range from 14.7 to 55.3 pg/g and from 22.5 to 46.2 pg/g, respectively. The mean concentrations of these compounds in the samples was urban area > mountain area ≒ rural area.

The predominant congeners of PCDDs and PCDFs in the all samples were consisted with lower chlorinated compounds. Moreover, the TEQ of PCDDs/DFs was also in a wide range from 0.58 to 2.46 pg/g. However, several researchers reported that predominant congener for PCDDs was contributed by high chlorinated compounds [1,8]. It could be estimated that the congener profiles in plant leaves may be affected by ambient air.

Concentrations and compositions of PCDDs/DFs in ambient air

Table2 shows the concentrations of PCDDs/DFs in ambient air from Matsuyama, Japan. The concentrations of PCDDs and PCDFs were in a wide range from 0.87 to 6.38 pg/g and from 1.74 to 6.49 pg/g, respectively. The mean concentrations of these compounds in the samples was in the order of urban area > rural area > mountain area. The order is strongly indicated the influence of municipal waste incinerator (MWI). In this study, PCDFs were detected higher than PCDDs from the all samples. Seike et al. also found high contribution of PCDFs to the total PCDD/DF concentrations [9].

The predominant congeners of PCDDs and PCDFs detected in all the samples were lower chlorinated compounds. The calculated TEQ of PCDDs/DFs was also in a wide range of 0.036 to 0.14 pg/g.

Relationships between Plant leaves and Ambient air

For highly lipophilic chemicals, the contamination mechanism of plant leaves via atomosphere is a more important than root uptake and translocation to the plant leaves[2-6]. The congener profiles of PCDDs/DFs detected from plant leaves and ambient air were similar in all cases and resemble to that type of typical, combution source patterns. As well as the congener pattern, a similar analogue patterns were observed in the plant leaves and ambient air. Therefore, above results indicated that the concentrations of PCDDs/DFs in plant leaves were reflected the ambient air . The comparison of plant leaves with air concentrations of PCDDs/DFs from the same sites show Figures1 and 2. According to the correlationships between the concentrations of PCDDs/DFs in plant leaves and those of ambient air, the correlation value for TEQ was higher than those for total PCDD/DF concentration. The reason to a above results could be the contribution of non-2,3,7,8 substituted congeners such as 1,3,6,8-, 1,3,7,9-TCDD, from other sources such as impurities of pesticides.

Table1. Concentrations (pg/g on wet weight basis) of PCDDs/DFs in Cherry Tree Leaves

Site	M1	U1	M2	R1	U2
Sampling Date	Aug.19,1997	Aug.23,1997	Sep.17,1997	Sep.17,1997	Sep.22,1997
PCDDs					
TeCDDs	15	19	2.9	10	13
PeCDDs	10	9.4	3.1	5.5	11
HxCDDs	8.9	15	3.6	5.7	9.9
HpCDDs	4.5	5.4	3.5	4.5	3.0
OCDD	6.9	6.5	1.6	1.8	1.3
Total PCDDs	45.3	55.3	14.7	27.5	38.2
PCDFs					
TeCDFs	14	14	9.1	11	16
PeCDFs	11	12	6.1	6.9	15
HxCDFs	6.4	9.9	4.5	4.3	8.4
HpCDFs	2.7	5.7	2.8	2.5	2.7
OCDF	3.4	4.6	-	3.6	-
Total PCDFs	37.5	46.2	22.5	28.3	42.1
Total PCDDs/DFs	82.8	101.5	37.2	55.8	80.3
I-TEQ	*1.00*	*2.46*	*0.58*	*0.65*	*1.24*

M: Mountain area, U: Urban area, R: Rural area

Table2. Concentrations (pg/m^3) of PCDDs/DFs in Ambient Air

Site	M1	U1	M2	R1	U2
Sampling Date	Aug.18-25,1997	Aug.23-28,1997	Sep.17-22,1997	Sep.17-22,1997	Sep.18-25,1997
PCDDs					
TeCDDs	0.45	2.5	0.36	1.2	0.88
PeCDDs	0.19	1.7	0.18	0.51	0.34
HxCDDs	0.23	1.3	0.20	0.44	0.37
HpCDDs	0.13	0.45	0.09	0.12	0.10
OCDD	0.07	0.43	0.04	0.06	N.D.
Total PCDDs	0.97	6.38	0.87	2.23	1.59
PCDFs					
TeCDFs	0.94	3.4	0.98	1.9	1.4
PeCDFs	0.41	1.8	0.47	0.84	0.55
HxCDFs	0.29	0.94	0.23	0.33	0.29
HpCDFs	0.10	0.35	0.10	0.11	0.15
OCDF	N.D.	N.D.	0.15	0.09	N.D.
Total PCDFs	1.74	6.49	1.93	3.27	2.39
Total PCDDs/DFs	2.71	12.87	2.80	5.50	3.98
I-TEQ	*0.061*	*0.140*	*0.036*	*0.050*	*0.073*

M: Mountain area, U: Urban area, R: Rural area

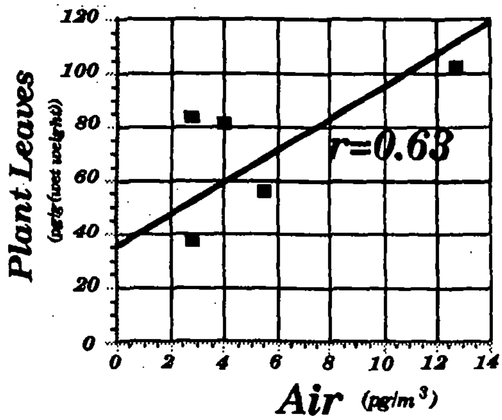

Fig.1 Correlationships between PCDD/DF Concentrations in Plant Leaves and Ambient Air.

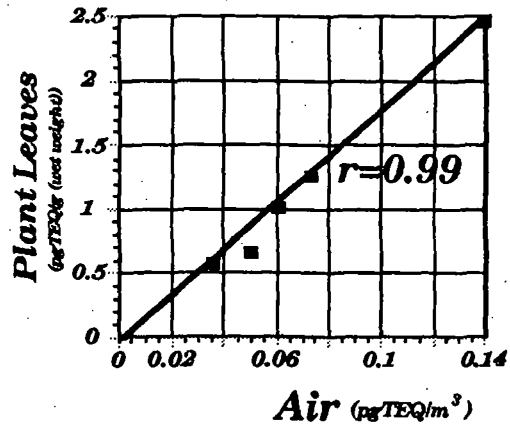

Fig.2 Correlationships between PCDD/DF TEQ in Plant Leaves and Ambient Air.

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