DEPOSITION OF ATMOSPHERIC PCDD/F TO THE SURROGATE SURFACES TO ELUCIDATE THE UPTAKE PATHWAY BY PLANT LEAVES

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Introduction

The uptake of atmospheric PCDD/Fs by plants has an important role in the food chain and acts as a biomonitor for atmospheric pollution. Several plants (potato, cabbage, radish[1,2] and cherry tree leaves[3]) have been used to investigate and evaluate the level of PCDD/Fs in Japan. A pattern of PCDD/Fs found in the leaves were similar to vapor phase patterns of PCDD/Fs taken in a polyurethane foam plug test using a high volume air sampler. As these gaseous patterns were not observed in European and American studies, these results relate strongly to the atmospheric PCDD/Fs in Japan. It is important to understand the uptake pathway to plant leaves in Japan. Welsch-Pausch, Mclachlan and Umlauf[4] have reported that dry gaseous deposition is the principal pathway of Cl4-Cl6 DD/F to Welsh ray grass leaves and the particle-bound deposition is also an important role for the uptake of congeners with 6 and more chlorine atoms. As the uptake process is estimated to be governed by the various properties of plant leaves surfaces, we used hydrophobic surrogate surfaces as a model surface of the plant leaves to simplify the pathway of PCDD/Fs from the atmosphere to plants leaves. In this paper, in order to evaluate the transfer of PCDD/Fs to leaves from gaseous and particle-bound PCDD/Fs deposited on the leaves surface, we investigated the deposition velocities and the transfer pattern of PCDD/Fs to the surrogate surface. We also investigated the transfer of PCDD/Fs from fly ash to the surrogate surface by placing the surrogate membrane on and above fly ash.

Materials and methods

Sample preparation 1.1 Petri dishes (an internal diameter of 15.5cm and height of 3cm) were coated inside with 0.2g of mineral oil dissolved in 2ml hexane. Two petri dishes were attached downward on a protective plastic plate and exposed to the environment for two weeks on the roof of the building (sample A). A petri dish was attached on the plate in the same way as the sample A and an air was blown to the surface of the petri dish from down side at a speed of 0.6m/s for the same period as the sample A (sample B). After the sample was collected, the dishes were rinsed with dichloromethane and hexane, and these rinsed solvents were mixed and filtered. Filtrate was extracted ultrasonically by toluene and hexane.

Sample preparation 1.2 Two polyurethane foams (a diameter of 8.6cm, height of 5cm) and a C18 disk (polytetrafluoroethylene disk containing octadecyl silica particle, a diameter of 9cm) were also placed on the roof of the building for three weeks. The samples were Soxhlet extracted with toluene for 12 hours.

Sample preparation 1.3 Atmospheric PCDD/Fs was collected by a low-volume air sampler. (ca 10 l/min, for 11days) Filter and polyurethane foam were Soxhlet extracted with toluene and acetone,

respectivery.

Sample preparation 2.1 Two varieties of fly ashes (1g) were spread inside the beakers (diameter of 11cm and height of 20cm), and C18 disks were placed on fly ash directly. The beakers were covered with glass lids large enough to allow for air exchange, and were kept on the roof for 3weeks. Remaining fly ashes on the C18 disks were blown off with nitrogen gas and the C18 disks were washed with distilled water. Then, these disks were Sohxlet extracted with toluene for 12 hours.

Sample preparation 2.2 A C18 disk was placed above the fly ash (3g) at a distance of 1.1cm and was kept at a constant temperature of 22°C for three weeks.

Clean up: All extracts were concentrated and internal standard of ^{13}C-PCDD/Fs was added. The extracts were washed with concentrated sulfuric acid and purified in 3 steps: first a silica gel column, next $AgNO_3$-silica gel mixed column, and finally on a carbon charcoal column. Toluene fraction was used for PCDD/Fs and non-*ortho* PCBs.

GC/MS analysis: This fraction was dried and redissolved in nonane. The samples were analyzed using GC/MS with a resolution of 10,000.

Results and Discussion

Deposition of atmospheric PCDD/Fs to surrogate surfaces:

Table 1 shows the deposition amounts of PCDD/Fs on the mineral oil in samples A and B. In sample B, we set up the condition, where an air current was applied at a fixed speed, in order to maintain a steady flow. The pattern of PCDD/Fs in the sample B showed the same gaseous pattern as A (Fig.1). This indicates the large partition of gaseous PCDD/Fs to mineral oil (Fig.1). The contribution of particle-bound PCDD/Fs may be smaller than that of gaseous ones. As far as TEQ, in the sample B the TEQ was almost twice as large as in the sample A. This was accompanied by an increase of the particle-bound PCDD/Fs (congeners of higher chlorinated DD/Fs). In order to calculate the deposition velocities of atmospheric PCDD/Fs on mineral oil, a PCDD/Fs concentration in the atmosphere was measured by low-volume air sampler (Fig.2). Deposition velocities of PCDD/Fs were in the range from 0.01 to 0.49cm/s in sample A and from 0.03 to 0.69cm/s in sample B, respectively (Table 1). Deposition velocities of TeCDDs were about 20 times larger than those of OCDDs in the case of sample B. The higher velocities of Cl4-Cl5 DD/Fs reported by Koester and Hites[5] were estimated to be due to the fact that partition of gaseous Cl4-Cl5 DD/Fs is higher than that of the other PCDD/Fs. Deposition velocities of PCDD/Fs on polyurethane foams and a C18 disk are also listed on Table 1. The three surrogates surfaces (mineral oil layer, polyurethane foam and C18 disk) used in this study reveal the uptake patterns of PCDD/Fs to be the same as gaseous patterns studied previously in plant leaves in Japan. These results suggest that gaseous depositions of PCDD/Fs dominantly influence the patterns of PCDD/Fs in plant leaves. These may be attributable to the larger fraction of lower chlorinated DD/Fs found in the atmosphere in Japan. Since the deposition velocities of the particle-bond PCDD/Fs, which are responsible for higher TEQ, are slower on plant leaves, only lower chlorinated DD/Fs may be appropriate as a biomonitor of the atmospheric PCDD/Fs.

Transfer of PCDD/Fs to C18 disk from fly ashes

C18 disks placed on fly ashes were used to simulate PCDD/Fs transfer from particle-bound PCDD/Fs to a leaf surface. Fly ashes, which contain PCDD/Fs at a relatively high concentration were used and compared to the control. As shown in Fig.3, 3-15% of PCDD/Fs in the fly ash were transferred to the C18 disk, and the transfer percentages increased with decreasing chlorine number of PCDD/Fs. We also measured the PCDD/Fs transfer to another C18 disk, placed above

the fly ash at a distance of 1.1cm. In this situation, no significant amounts of PCDD/Fs were transferred to the C18 disk through the air gap. The transfer mechanism of PCDD/Fs to the C18 disk placed directly on the fly ashes is not clear, but these preliminary results suggest that the particle-bound PCDD/Fs deposited on leaves surfaces have some capability of transfer into the leaves.

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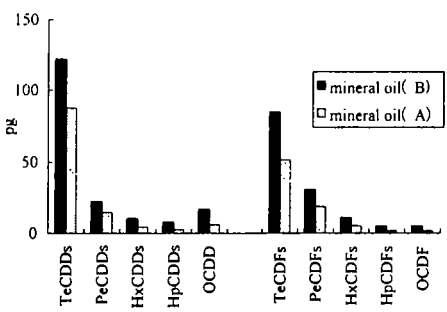

Fig.1 PCDD/Fs homologue profile of deposition on mineral oil layer ((B):applied current)

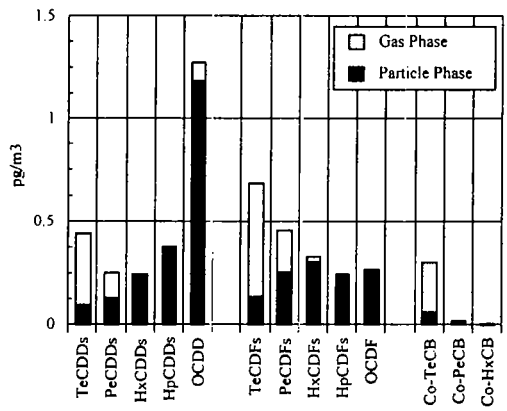

Fig. 2 PCDD/Fs homologues profile in air sample (low-volume air sampler)

Table 1 Deposition amounts and calculated deposition velocitie of PCDD/Fs on surrogate surfaces

	Mineral oil (A) pg	Mineral oil (A) TEQ pg	Mineral oil (B) pg	Mineral oil (B) TEQ pg	Ratio (B/A)	Ratio of TEQ (B/A)	Deposition velocities for Mineral Oil (A) (cm/s)	Deposition velocities for Mineral Oil (B) (cm/s)	Deposition velocities for Urethane foam (cm/s)	Deposition velocities for C18disk (cm/s)
TeCDDs	87.6	0.104	122.9	0.044	1.40	0.43	0.49	0.69	0.42	0.10
PeCDDs	14.3	0.258	22.0	0.468	1.54	1.82	0.14	0.21	0.25	0.11
HxCDDs	3.9	0.060	10.2	0.187	2.59	3.14	0.04	0.10	0.14	0.10
HpCDDs	2.8	0.011	7.8	0.039	2.78	3.67	0.02	0.05	0.12	0.04
OCDD	6.1	0.001	17.2	0.002	2.82	2.82	0.01	0.03	0.07	0.03
Total PCDDs	115	0.432	180	0.740	1.57	1.71	0.11	0.17	0.16	0.06
TeCDFs	51.8	0.037	84.7	0.074	1 64	2.02	0.19	0.31	0.20	0.10
PeCDFs	18.6	0.241	31.2	0.692	1 68	2.87	0.10	0.17	0.20	0.11
HxCDFs	5.1	0.207	10.9	0.498	2.13	2.41	0.04	0.08	0.10	0.07
HpCDFs	2.0	0.013	5.4	0.036	2.73	2.81	0.02	0.05	0.08	0.10
OCDF	1.9	0.000	5.4	0.001	2.79	2.79	0.02	0.05	0.06	0.09
Total PCDFs	79	0.497	138	1.301	1.73	2.62	0.10	0.17	0.15	0.10
Co-TeCB	56.4	0.006	54.6	0.005	0.97	0.97	0.45	0.44	0.34	1.57
Co-PeCB	5.6	0.555	6.6	0.656	1.18	1.18	0.68	0.80	0.50	1.83
Co-HxCB	0.7	0.007	0.8	0.008	1.18	1.18	0.26	0.31	0.53	0.71
Total Co-PCB	63	0.568	62	0.669	0.99	1.18	0.46	0.46	0.35	1.57

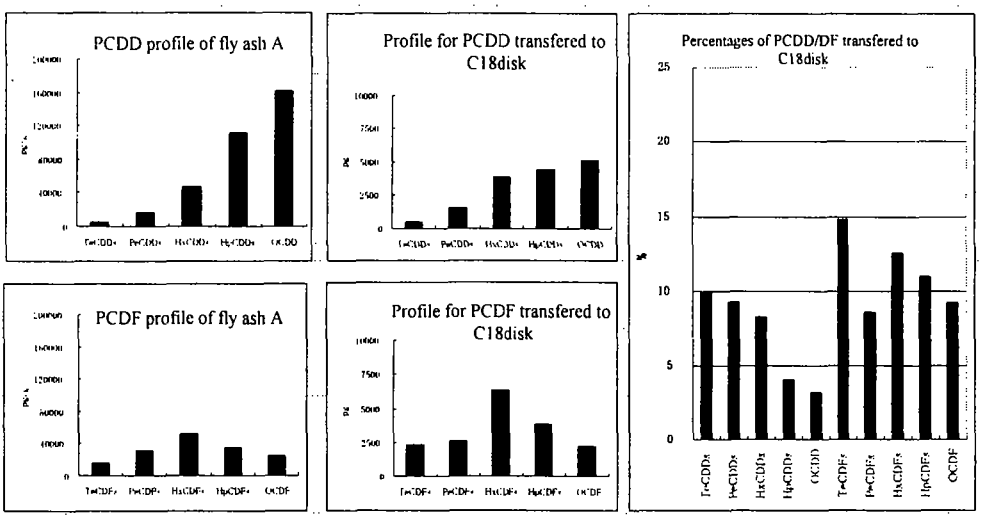

Fig.3 Homologue profiles for PCDD/Fs in fly ash, PCDD/Fs transfered to C18 disk and transfer percentages