Deposition of atmospheric dioxins to the surrogate surfaces to elucidate the uptake pathway by plant leaves and the application of a surrogate surface to long term monitoring

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Introduction

The uptake of atmospheric dioxins by plants is considered to be a key process in the food chain and acts as a bio-indicator for atmospheric pollution[1]. In order to simulate the transfer of dioxins from the atmosphere to plant leaves, some surrogate surfaces were investigated in previous experiments[2]. From our experiments, it was found that the deposition of gaseous phase dioxins was dominant uptake pathway to the plant leaves. Though it was noteworthy that plant leaves, like cabbage and potato, which were cultivated on contaminated soil by herbicides, show specific dioxin patterns, it was estimated that the dioxins uptake into the leaves occurred through the soil-bound deposition on plant leaves rather than through vaporization from the soil. There are still two possibilities for dioxins uptake. One is possibly that small soil particles are taken into leaves inside. The other possibility is that dioxins transfer to leaves through contact with the soil while soil particles remain on the leaves surface. Therefore, in this paper we attempted to check the possibility of the latter transfer process. We also aimed to apply another surrogate surface as an alternative for plant leaves to monitor dioxins in the atmosphere for a long time. A polyurethane filter, which surface was modified to increase the permeability to air, was investigated as a sorbent to monitor the atmospheric dioxins.

Materials and methods

Experiment 1

Sample preparation 1.1

Petri dishes (internal diameter of 9cm and height of 1cm) were coated inside with 0.02g of Hist paraffin dissolved in 1ml hexane. Two varieties of fly ash (1g each) and contaminated soils (1g each) were spread inside of the resulting Petri dishes separately and were kept at a constant temperature of 22°C for three weeks. Remaining fly ash and soils on the Petri dishes were blown off with nitrogen gas and removed with distilled water and then the coated paraffin inside the dishes were dissolved with hexane and the dishes were rinsed with dichloromethane and hexane.

Sample preparation 1.2

Petri dishes coated inside with 0.02g polystyrene dissolved in 1ml dichloromethane was tested in the same method as Sample preparation 1.1.

Experiment 2

Sample preparation 2.1

Two Petri dishes (26cm*2cm) were coated inside with Hist paraffin and were placed on the roof of the building for three weeks. After the samples were collected, the coated paraffin were dissolved with hexane and the dishes were rinsed with dichloromethane and hexane..

Sample preparation 2.2

Two Everlight Scott filters (10cm*30cm*0.5cm,HF-08, Bridgestone Kaseihin Seizo Co.) cleaned with Soxhlet extraction with acetone were placed on the roof of the same building as

in Sample preparation 2.1. for two weeks. One Scott filter was washed with distilled water and another was not treated. Then, the filters were Soxhlet extracted with acetone for 12 hours.
Clean up: All extracts were concentrated and internal standard of ^{13}C-dioxins were added. The extracts were washed with concentrated sulfuric acid and purified by three columns: first a silica gel column, next an $AgNO_3$-silica gel mixed column, and finally on a carbon charcoal column. Toluene fraction of the final column was used for dioxins analysis.
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
Transfer of particle-bound dioxins through contact from highly contaminated soil to a surrogate surface
Hist paraffin surfaces were used to simulate particle-bound dioxins transfer to leaves surface. Fly ashes, which contain dioxins at a relatively high concentration were used and compared to the control. As shown in Figure 1, a small amount of dioxins in the fly ashes were transferred to the Hist paraffin and the pattern of doxins in the Hist paraffin showed the same pattern as in the fly ashes. In the case of direct contact to the herbicides-contaminated soil, a high concentration of TCDDs was found to transfer to the Hist paraffin. The pattern of dioxins in the Hist paraffin was same as the original one in the soil mainly contaminated by Chlornitrofen (CNP). Main fraction of TCDDs were 1368- and 1379-tetra dioxin. The same tendency was observed in the experiments using polystyrene surfaces (Figure 2). Compared to the Hist paraffin, amounts of transferred dioxins were quite smaller less than 10pg, but the patterns in the fly ashes and CNP were reflected similarly. These surfaces are very flat and hard and they seem to have no possibility to take into the fly ashes and soil particles inside, so it was confirmed that dioxins were directly transferred to these surrogate surfaces. Theses results indicate the particle-bond dioxins deposited on the plant leaves might transfer to leaves while the particle remained on leaves surface.

Application of surrogate surfaces to monitor the long term atmospheric Dioxins level instead of plant leaves
Dioxins deposition on the Hist paraffin was tested outdoor and the same dioxins pattern in the Hist paraffin was observed as the fly ashes (Figure 3). As the dioxins patterns we investigated previously with mineral oil, polyurethane foam and ODS (polytetrafluoroethylene disk containing octadecyl silica particle) disk showed the gas phase pattern in the atmospheric dioxins[2], the result observed for the Hist paraffin seemed to be attributed to the paraffin's property that have not so much affinity to gas phase dioxins. Finally, amount of dioxins collected on the Hist paraffin surface was very small and limited. In this method it is difficult to monitor the atmospheric dioxins for a long time as an alternative for plant leaves. Therefore, the Scott filter (SF, mesh texture polyurethane foam made up by heating treatment) was investigated to apply to the long term dioxin monitoring, because it has very large surface area for adsorption. As can be seen in Figure 4, dioxins deposited on the SF filter were similar to the dioxins in leaves showing gas phase pattern in the atmosphere. The SF filter has various advantages that a good permeability to air, a large surface area, good stability to some solvent and low dioxins blank. In the preliminary test, we could trap the sufficient amount of dioxins enough to evaluate the TEQ values, so it was found that the SF filter could be an efficient passive sampler to monitor the atmospheric dioxins. In order to check the influence of particles attached on the filter, we compared the SF filter washed with water with one not washed with water after sampling. In a case of the SF filter washed with water, dioxins diminished 10% to 50% and TEQ decreased to an extent of 0-80% losing mainly highly chlorinated dioxins as in Table 1. Considering the TEQ value 0.65pgTEQ/m^3 measured in this site before, deposited dioxins amount on SF roughly corresponded to 10m^3 air.

References

1. Tojo T., Seike N., Matsuda M., Kawano M., Wakimoto T. (2000), Investigation on Cherry tree leaves as an indicator of air pollution by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, Journal of Environmental Chemistry, 10. 1, 13.
2. Kurokawa Y., Tobiishi K., Matsueda T., Sakuragi K. and Imato T.;(2003),Deposition of atmospheric PCDD/F to the surrogate surfaces to elucidate the uptake pathway by plant leaves, Organohalogen Compounds, 52, 446.

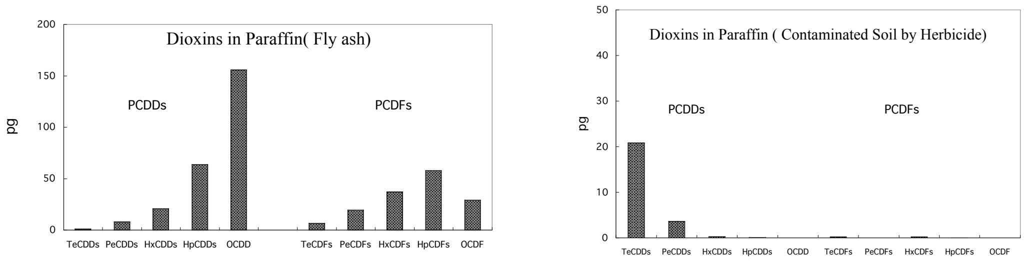

Figure 1 Dioxins transferred to Hist paraffin from Fly ash (left) and contaminated soil (right)

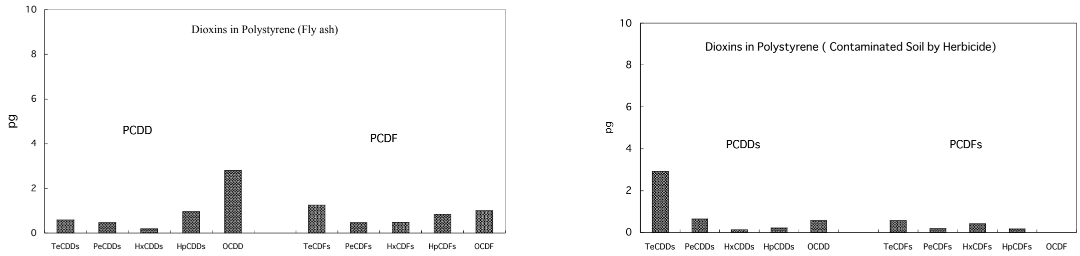

Figure 2 Dioxins transferred to Polystyrene from Fly ash (left) and contaminated soil (right)

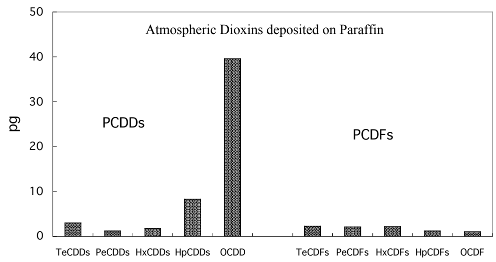

Figure 3 Dioxins deposited on Hist paraffin from the atmosphere

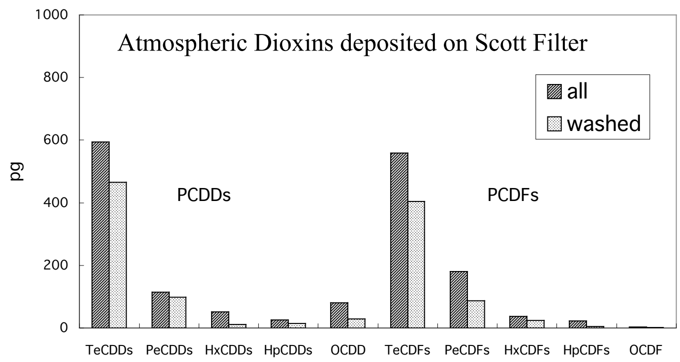

Figure 4 Dioxins deposited on Scott Filter from the atmosphere

Table 1 Dioxins deposited on Scott Filter (pg-TEQ)

	All	Washed	Loss(%)
TeCDDs	0.38	0.39	-3
PeCDDs	2.0	1.8	13
HxCDDs	0.36	0.28	21
HpCDDs	0.12	0.06	48
OCDD	0.01	0.00	64
total PCDDs	2.9	2.5	14
TeCDFs	0.56	0.37	33
PeCDFs	0.88	0.24	73
HxCDFs	0.86	0.42	52
HpCDFs	0.12	0.03	78
OCDF	0.00	0.00	67
total PCDFs	2.4	1.1	57
total PCDD/Fs	5.3	3.5	33