

ENVIRONMENTAL LEVELS - POSTERS

CONCENTRATION AND DISTRIBUTION OF PCDD/DFs IN ENVIRONMENTAL SAMPLES NEAR A PAPER MILL

Jong-Guk Kim, Kyoung-Soo Kim, Jin-Soo Park, Tea-Seop Chung

Department of Environmental Engineering Chonbuk National University, 664-14 Duckjin-Dong
Duckjin-Gu Chonju Chonbuk, 561-756 Korea

Introduction

The main emission sources of PCDD/DFs are combustion process, bleaching of pulp and chemical process (pesticide etc). While entering soil and water through dry/wet deposition from combustion process, PCDD/DFs are specially accumulated in land and water bodies, and then finally exposed to human. Nevertheless, the study of PCDD/DFs has focused only on MSWI, and as the result of that, any study on environmental PCDD/DFs is scarcely done in Korea.

With respect to the above information, this study was meant to focus on the levels of PCDD/DFs, and also the relation between emission source and environmental sample. The levels and isomer distribution of PCDD/DFs were studied in an incinerator of a paper mill, environmental samples such as soil, vegetable, fish and sediment were also collected for study.

Materials and Method

Samples

From October 1998 to December 1999, soil, sediment, vegetable and fish samples were collected in the vicinity of a paper mill. The vegetable represents the scallion. Sample information is shown in Table 1 below.

Table.1 Sample Information

	Incinerator	Soil	Vegetable	Sediment	Fish
Number of Samples	3	4	3	4	5
Quantity of Samples	3~3.7Nm ³	10g	300~400g	30g	20~40g

Extraction from samples

Collected samples were separated as form of samples and then were spiked with the ¹³C₁₂-labelled internal standards. Fish samples were finely homogenised and digested in 1N-KOH solution. Soil and sediment were extracted using ASE system (1500psi, 150 , solvent was toluene, 2cycles). Vegetables were extracted with soxhlet extractor and samples of incinerator used - both liquid-liquid extraction and soxhlet extraction.

Samples Clean-up

Clean-up procedures were modified from the method of EPA 1613. After extraction, the samples were treated concentrated sulfuric acid. Crude extract from every sample was further purified in silica-gel column and then basic alumina column, and finally, in activated carbon-impregnated silica-gel column chromatography.

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Quantification

Determination of PCDD/DFs was performed by HRGC/HRMS on a Autospec Ultima mass spectrometer at a resolution of 10,000 in selected ion mode. Isomeric specific separation of PCDD/DFs were carried out on a SP-2331 capillary column. TEQs were calculated using I-TEFs for PCDD/DFs.

Results and Discussion

Concentration

Table 2 summarizes the concentration of PCDD/DFs in incinerator and environmental samples. TEQ concentration of incinerator ranged from 6.5 to 76.6 pgTEQ/Nm³, much lower than MSWI (1~466pgTEQ/Nm³) in Korea¹). In case of environmental sample, TEQ concentration of soil (0.25 ~ 7.03pgTEQ/g) was the highest but, that of sediment (0.06 ~ 0.42pgTEQ/g) was low. Compared with previous study, PCDD/DFs level of sediment was much lower because percentage loss ignition (%LOI) was lower than that of soil by 2~3 times. LOI of sediment was 0.9~1.6% but that of soil was 2.2~7.9%. That is consistent Hites.etc²), who suggested, after deposition, vapor-phase and dissolved-phase PCDD/DFs movement into soil or sediment is controlled by the equilibrium sorption/desorption processes between the soil or sediment compartments.

TEQ level of fish was a little higher than that of other samples but that of vegetable was the lowest 0.020 ~0.027pgTEQ/g. This is the reason why one-year-vegetable is exposed to emissions for short-term, while PCDD/DFs of fish are accumulated through food-chain. In addition, difference of dioxin levels among fish samples may depend on the species, probably due to their fat content or habit of diet, if the difference of sampling date or site is ignored.

Table.2 Concentration of PCDD/DFs in Incinerator and Environmental Samples (pg/g)

	Number	PCDDs	PCDFs	TEQ
Incinerator	3	66.8~404.4 pg/Nm ³	64.9~3158 pg/Nm ³	6.5~76.6 pg/Nm ³
Soil	4	2.9 ~ 73.8	1.8 ~ 44.5	0.25 ~ 7.03
Vegetable	3	0.41 ~ 1.04	0.63 ~ 0.84	0.020 ~ 0.027
Sediment	4	1.99 ~ 14.3	0.88 ~ 6.24	0.06 ~ 0.42
Fish	5	0.37 ~ 7.18	8.18 ~ 18.01	0.51 ~ 1.46

Concentration of 2,3,7,8-substitued isomer

1. Soil and Vegetable

Fig.1 show the concentration of soil and vegetable samples. Generally PCDD/DFs enter soil and vegetable through dry/wet deposition, while soil would reflect cumulative deposition, vegetable broadly reflects air concentration. Compared vegetable with soil, 1,2,3,7,8,9-HxCDF and OCDF level of vegetable was higher than those of soil. It is the common fact that the concentrations of contaminants near the soil surface would be important to determine pollution of vegetation. But in this study, PCDD/DFs concentration in vegetable was unrelated to PCDD/DFs level in soil, which is consistent with the relatively low vapor pressure of OCDD/F. Since the liposolubility of PCDD/DFs, those chemicals would not be taken up and translocated by vegetables.

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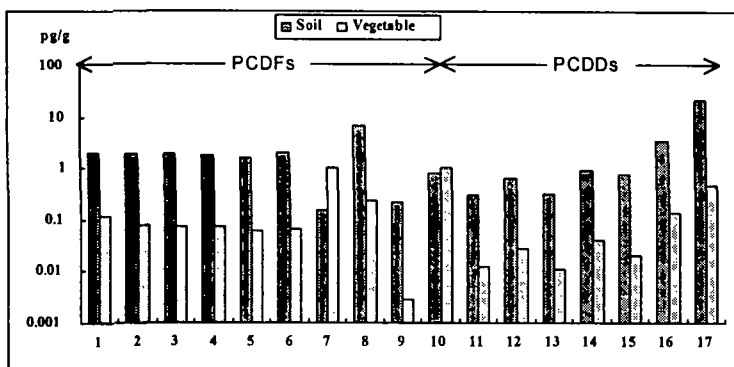


Fig. 1 Concentration of Soil and Vegetable

2. Fish and Sediment

Fish and Sediment concentration is shown Fig. 2. The Fish data were dominated 1,2,3,4,6,7,8-HpCDF, 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF isomers. Isomer pattern is similar with other studies except that 1,2,3,4,6,7,8-HpCDF was highly detected³. For the PCDDs, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD and OCDD were predominantly detected. 1,2,3,4,6,7,8-HpCDF was highly detected in the Furans. But 1,2,3,4,7,8,9-HpCDF and OCDF were not detected. Other studies mentioned that these isomer were not detected⁴. When the number of chlorine atoms increased, the predominance of 2,3,7,8-substituted isomers vanished. In the TEQ concentration, 2,3,4,7,8-HpCDF and 1,2,3,7,8-PeCDF were predominant⁵. Two isomers occupied 44.9 ~ 67.5% of the total TEQ concentration.

For the Sediment, 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD were highly detected. In the PCDDs, the more number of chlorine atoms increases, the more concentration are augment⁶

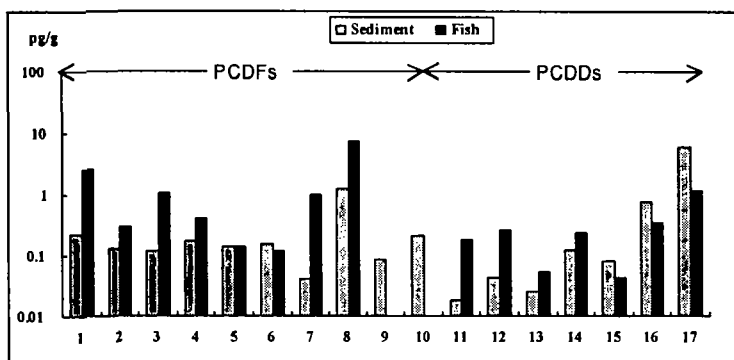


Fig. 2 Concentration of Sediment and Fish

Isomer Distribution

Isomer distribution of environmental samples and incinerator is shown Fig.3. The PCDD/DFs isomer composition was similar for all samples except fish. The value of 1,2,3,4,6,7,8-HpCDF and 2,3,7,8-TCDF remarkable high in PCDFs, OCDD and 1,2,3,4,6,7,8-HpCDD dominated in PCDDs. In this study, 2,3,7,8-TCDF was higher than OCDF in environmental samples near paper mill

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incinerator, while 1,2,3,4,6,7,8-HpTCF, OCDF, 1,2,3,4,6,7,8-HpCDD, OCDD were the dominating isomer in MSWI. Generally one would expect relative PCDD/DFs isomer concentrations in sinks to be similar to those of the emissions, however this is usually not the case. Isomer distribution of environmental samples contaminated through atmosphere deposition was similar to that of emission source in this study but that of fish was a wide difference.

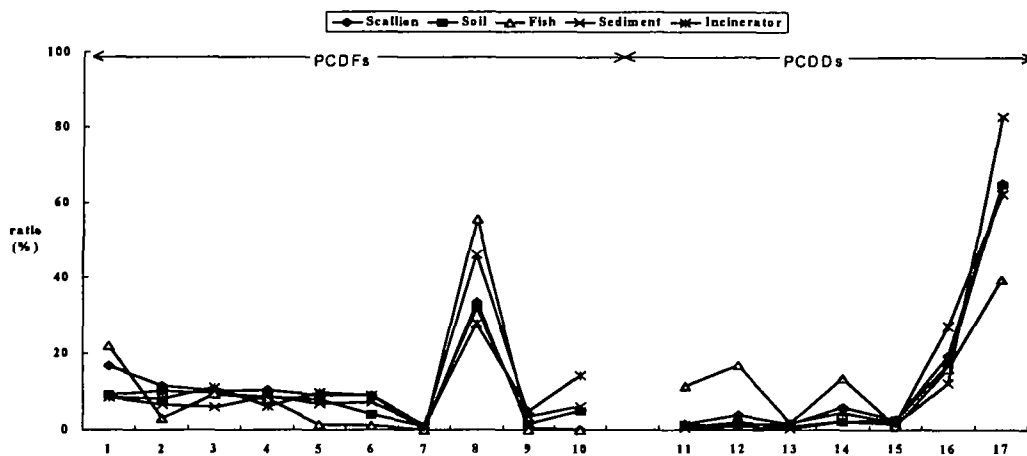


Fig.3 Isomer Distribution of Environmental samples and Incinerator

Acknowledgments

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Reference

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