# PARTICLE SIZE DISTRIBUTIONS OF PCDD/Fs IN FLY ASH

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## Introduction

PCDD/Fs have been considered as the most hazardous chemicals for human beings and these compounds known to be formed during incineration processes as well as natural processes. It has been estimated that up to 50% of the known dioxin sources in the environment may be derived from waste combustion. Fly ash has a catalytic potential for PCDD/Fs generation in actual combustion therefore, many studies are conducted to identify the PCDD/Fs formation mechanism on fly ash. The particle size distributions of PCDD/Fs in fly ash will be helpful to understand this formation mechanism. The emitted fly ash particles to atmosphere can affect human health. It is known that the particle size below 2.5 μm can have a critical effect on human health, and the PCDD/Fs levels are high in fine fly ash particles. However, only a few studies are conducted with particle size and most previous studies were confined to the coarse particle size in fly ash,
Therefore, in this study, we are intended to investigate the PCDD/Fs distribution in fine fly ash particles. Using continuous splitt fractionation, we have been able to separate fine fly ash particles and analyzed PCDD/Fs levels in each size fraction..

## Methods and Materials

Size fractionation of Fly ash sample was obtained by using sieve and continuous SPLITT fractionation. The separating method using SPLITT was described elsewhere. (M.H.Moon et al,2001).Sample preparation was completed according to the US EPA method 1613. Before mass analysis, $^{13}C_{12}$-labelled PCDD/Fs-recovery standards (1 ng) were added. PCDD/Fs were analyzed via HRGC/HRMS (HP 6890 series II/JMS 700T) with a DB-5MS column (60 m length, 0.25 mm i.d., 0.25 μm film thickness).

## Results and Discussions

*The weight fraction and PCDD/Fs concentration with particle size*

The weight fraction of each particle size was obtained by dividing with the total weight and presented in Table 1. .In rough fractionation of particle size with using sieve, most of particles in fly ash are less than 53μm. The large variation of size distribution of fly ash particles was reported as sample types and reporters but, in most cases, the weight fraction of fine particle was higher than that of coarse particle. However, they focused their studies to the minimum particle size around 50 μm. Therefore, it is difficult to evaluate the size distribution below 50μm. In this case, which was intended to separate particle size below 53 μm with split fractionation, the size of more than 70% of particle was less than 5 μm. The largest mass fraction was ranged between 2.5 μm and 5 μm. The mass fraction of water was similar with that of particle size <53μm.

The measured PCDD/Fs concentrations with particle size are ranged between 0.101 ~ 1.118 ng-TEQ/g (9.277 ~ 79.1 ng/g). As the Table 1 was shown, PCDD/Fs levels in fine particles were higher than those of coarse particles, which was consistent with other previous reports. Chang and Chung reported the PCDD/Fs concentration was increased as the particle size decreased in fly ash particle. The highest PCDD/Fs level was observed in the range of particle size 1 ~ 5 μm which was similar with the result of mass percentage. These results indicate there are a large fraction of fine particles containing high levels of PCDD/Fs in Korean MSWI fly ash, which affect human health seriously. Therefore, a more careful management is needed in this range of particle size.

Table 1. Mass percentage and PCDD/Fs concentration with particle size

| Sample | range (um) | mass (%) | PCDD/Fs conc | |
|---|---|---|---|---|
| | | | TEQ (ng-TEQ/g) | total (ng/g) |
| *6a | >53 | 17.8 | 0.257 | 57.252 |
| *6b | <53 | 82.2 | - | - |
| 1b** | 20-53 | 5.1 | 0.101 | 9.277 |
| 2b** | 10-20 | 12.2 | 0.115 | 20.905 |
| 3b** | 5-10 | 21.0 | 0.455 | 48.158 |
| 4b** | 2.5-5 | 46.5 | 1.114 | 79.100 |
| 5b** | 1-2.5 | 11.4 | 1.118 | 76.765 |
| 5a** | <1 | 3.9 | 0.678 | 47.698 |

* ; separating particle size using sieve

** ; separating particle size below 53 um using splitt

*PCDD/Fs homologue pattern with particle size*

To compare PCDD/F-homologue patterns of each particle size, all data were normalized to the total sum of [PCDDs]+[PCDFs] =1 and presented in Figure 1. As the Figure 1 was shown, a large variation of PCDD/Fs homologue pattern was observed among the particle size samples. Therefore, principal component analysis (PCA) was used to evaluate similarities or differences of PCDD/F-homologue patterns in each sample..

The result of PCA was presented in Figure 2 and the two significant components account for 87%(69% + 18%) of the variation in this plot. As the Figure was shown, the axis of principal component 2 divided all particle size samples into two groups except one sample ( >53μm). From the PCA results, as the value of p[2] increase, the lower chlorinated dioxins are dominant. In the reverse case, the lower chlorinated furans are dominant. Compared to other samples. less chlorinated dioxins were dominant in group 1 which was clustered with samples larger than 10 μm, while less chlorinated furans were dominant in group 2 which was clustered mainly with samples smaller than 10 μm. As the Figure 2 was shown, there existed larger fraction of OCDD in particles over 53μm, which was considered quite characteristic pattern. However, the fraction of other dioxins is still dominant except for that of OCDD. Therefore, the particle size sample above 53μm can be clustered into group 1. From these results, remarkable homologue patterns were observed as related with particle size ; low chlorinated furans are dominant in fine particles (smaller than

10μm), while low chlorinated dioxins in coarse particles (larger than 10μm). However, the different PCDD/Fs homologue patterns were reported. Clement and Karasek (1982) was reported that the OCDD level was skewing in the small particles and TCDD level was skewing in large particles. In another their study, the dioxin levels were decreased with increasing particle size regardless of homologue types. From these results, these different homologue patterns suggest the possibility of different PCDD/Fs behavior of fly ash type due to a different incineration condition, incinerator type and etc. Therefore, further investigations using a lot of fly ash samples are needed to verify a characteristic homologue patterns with particle size.

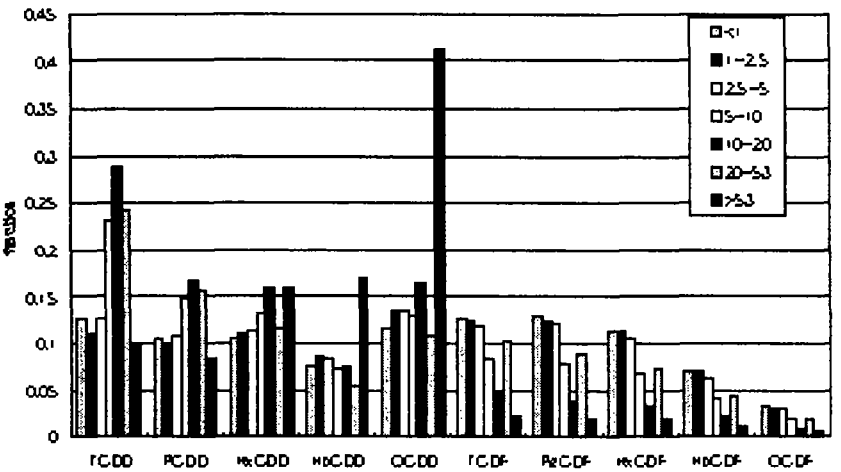


Figure 1 The PCDD/Fs homologue patterns with respect to particle size

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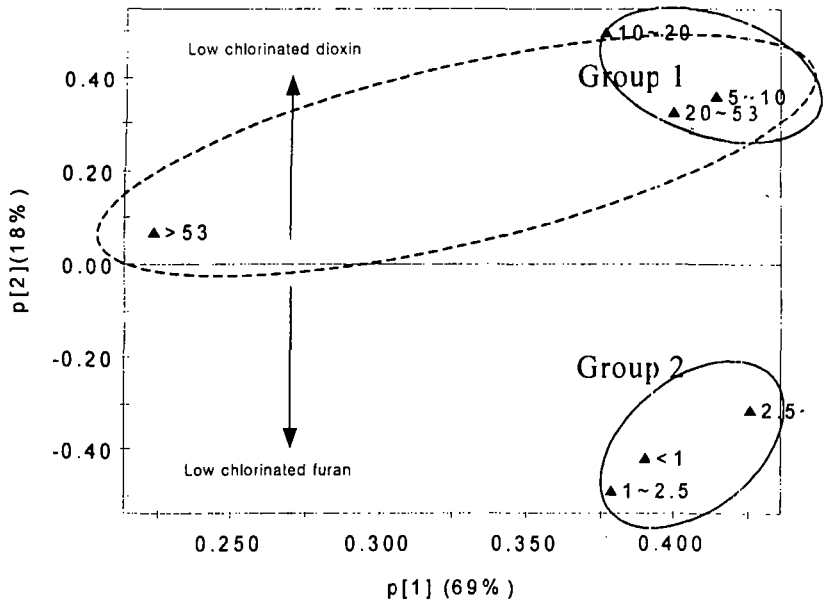


Figure 2. The PCA results of PCDD/Fs homologue patterns with particle size