# VARIATION OF PCDDs/PCDFs CONCENTRATION IN COOLING SYSTEM OF MUNICIPAL SOLID WASTE INCINERATORS

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**Introduction**

In commercial scale of municipal solid waste (MSW) incinerator, the cooling system is used to cool down the combustion gas prior to entering the air pollution control devices (APCD). This cooling system has been indicated as a source of PCDDs/PCDFs re-synthesis, so called *de novo* synthesis[1-4]. However, a few results have been reported the re-synthesis rate of PCDDs/PCDFs in cooling system due to the sampling difficulty at high flue gas temperature. Since the outlet temperature of 2nd combustion chamber is regulated to maintain above 850 °C in most of countries, the sampling at the inlet of cooling system is not easy. This study was carried out to investigate how much PCDDs/PCDFs are re-synthesized in cooling system, using the our developed sampling probe for high temperature, and thus to provide the relevant information for the proper control of PCDDs/PCDFs.

**Material and Methods**

The three medium- and large-scale MSW incinerators were selected in order to investigate enrichment of PCDDs/PCDFs in cooling system such as gas-tubular-type and water-tubular-type waste heat boiler (WHB) and water-spray-type cooling tower (Fig. 1). At each incinerators five samples were collected from the inlet and outlet of cooling system simultaneously. Since the temperature of the inlet of cooling system was as high as around 900 °C, the our developed sampling probe, which is consisted of water jacket, quartz nozzle and probe, was used for PCDDs/PCDFs sampling[5]. The PCDDs/PCDFs samples was divided into two phase samples, i.e., the particulate and the gaseous phase samples. Each phase samples were extracted and analyzed separately, according to the Korean Standard Testing Method for Dioxins and Furans[6]. The PCDDs/PCDFs concentration of each phase samples were analyzed by HRGC/HRMS (High Resolution Gas Chromatograph/High Resolution Mass Spectrometer: Micromass Co., Autospec Ultima) above 10,000 resolution with SP-2331 column of60m x 0.32mmID x 0.25μm. Operation conditions of the HRGC/HRMS during PCDDs/PCDFs analysis are given in Table 1. TEQ (Toxic Equivalents as 2,3,7,8-TCDD) values were calculated by using I-TEF(International-Toxicity Equivalency Factor).

940 °C 193 °C 120 °C

**Incinerator (30ton/day) → WHB → SDA/BF → Stack**

(a) Incineration process, having gas-tubular-type WHB

853 °C 259 °C 159 °C

**Incinerator (200ton/day) (SNCR) → WHB → SDA/BF → Stack**

(b) Incineration process, having water-tubular-type WHB

895 °C 383 °C 249 °C 293°C 196 °C

**Incinerator (100ton/day) → WST → Air Pre-heater → SDA/BF → SCR → Stack**

(c) Incineration process, having water-spray-type cooling system.

Fig. 1. Incineration process of MSW incinerator studied.

Table 1. GC/MS analytical condition for PCDDs/PCDFs

| Parameters | PCDDs/PCDFs |
|---|---|
| Injector | 250 °C |
| Column | SP-2331 (60 m x 0.32 mm ID x 0.2 μm) |
| Oven | 120 °C (3 min) → 10 °C/min to 200 °C (3min) → 3 °C/min to 265 °C (15min) |
| Carrier Gas | He, 2.5 ml/min |
| Ionization | EI, 36 eV |
| Ion Source | 270 °C |
| Resolution | > 10,000 |
| Monitoring | 4 Function, SIM (Selected Ion Monitoring) |

**Results and Discussion**

In gas-tubular-type WHB, the PCDDs/PCDFs concentrations of the particulate phase and the gaseous phase at the outlet of WHB were 23 times and 4 times higher than those at the inlet of WHB, respectively (Fig. 2). Relatively large amounts of PCDFs were re-synthesized at the outlet of cooling system in comparison to the PCDDs as shown that the ratios of PCDFs to PCDDs were 74 : 26 at the inlet and 82 : 18 at the outlet. Two major re-synthesized 2,3,7,8-substituted congeners were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, and their TEQ values were 42 % and 49 % of the total TEQ values at the inlet and the outlet, respectively.

In water tubular type WHB, PCDDs/PCDFs concentration at the outlet was 13.6 times higher than that at the inlet (Fig 3). Also, it was found that the PCDDs/PCDFs enrichment rate of the gaseous phase was much higher than those of particulate phase by representing that the outlet concentration was 53 times in gaseous phase and 10 times in particulate phase higher than the inlet concentrations. In this case, a severe re-synthesis of PCDDs/PCDFs was resulted from the poor cooling effect of WHB as showing the outlet temperature as high as 260°C. Although the ratios of

PCDFs to PCDDs at the outlet were a little lower than that at the inlet, the PCDFs concentration was four times or more higher than the PCDDs concentration at both the inlet and the outlet. Like the results of gas-tubular type WHB, two major 2,3,7,8-substituted congener re-synthesized were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, and their TEQ values to the total TEQ values were increased from 49 % at the inlet to 53 % at the outlet.

In water-spray-type cooling tower, the PCDDs/PCDFs concentrations of both the particulate phase and the gaseous phase were reduced after the flue gas passed through the water spray tower (Fig. 4). Especially, the particulate-phase PCDDs/PCDFs were removed up to 93.3 %, varying from 2.016 ng-TEQ/$Nm^3$ at the inlet to 0.135 ng-TEQ/$Nm^3$ at the outlet. It could be explained that as the particles were cooled down by spraying the water, they wereagglomerated and settled down the bottom of water spray tower, so the particulate phase PCDDs/PCDFs was removed from flue gas stream. Consequently, the PCDDs/PCDFs could be enriched in WHB-type cooling system, but reduced in water-spray-type cooling system. Although it has an advantage of reducing the PCDDs/PCDFs concentration, water-spray-type cooling system has disadvantages such as increasing the volume of flue gas and inability for recovering the waste heat.

**References:**

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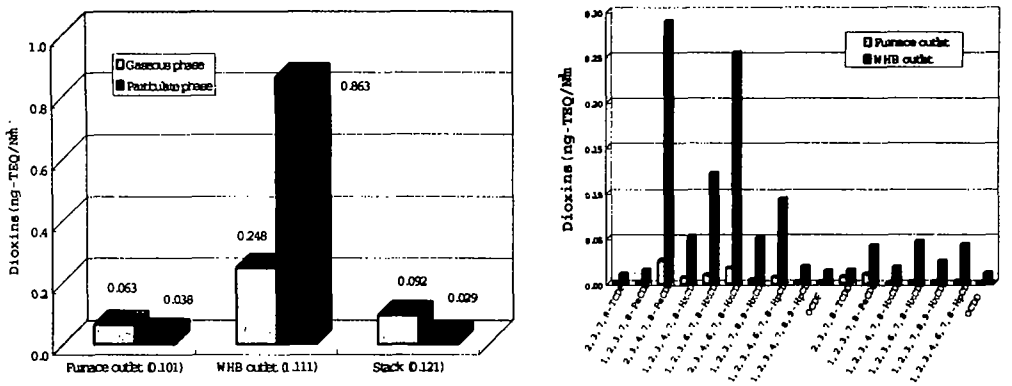


Fig. 2. PCDDs/PCDFs concentration variation and 2,3,7,8-congener profile at the gas-tubular-type WHB of MSW incinerator.

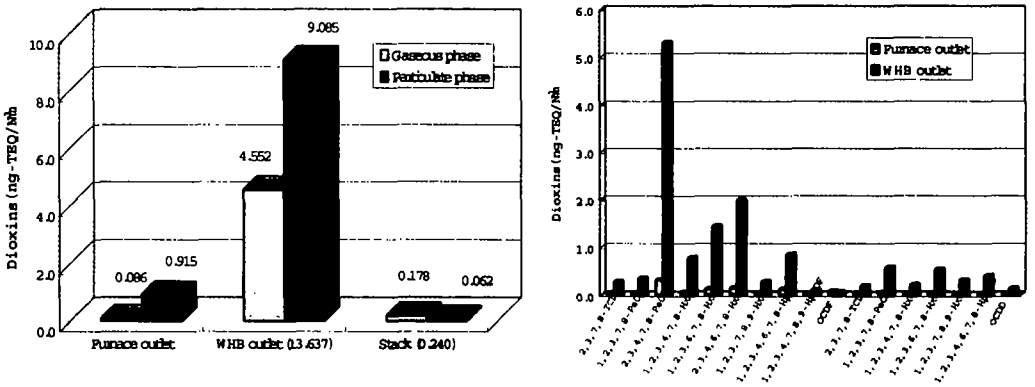


Fig. 3. PCDDs/PCDFs concentration variation and 2,3,7,8-congener profile at the water-tubular-type WHB of MSW incinerator.

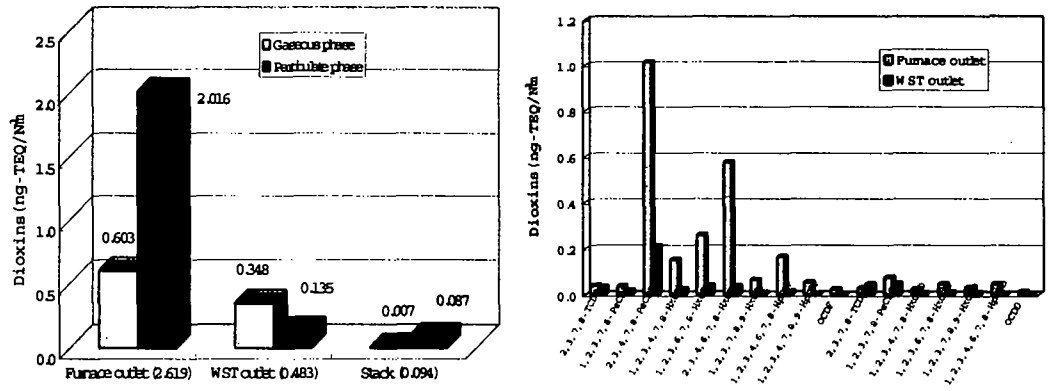


*Fig. 4. PCDDs/PCDFs concentration variation and 2,3,7,8-congener profile at the water-spray-type cooling system of MSW incinerator.*