# EMISSION CHARACTERISTICS OF PCDD/Fs FROM A SMALL WASTE INCINERATOR IN CHINA

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**Introduction**

PCDDs (Polychlorinated Dibenzo-*p*-dioxins) and PCDFs (Polychlorinated Dibenzofurans) are commonly known as dioxins that could originate from different sources, including waste incinerations, forest fires, vehicles and even cigarette smoking. According to the different level of chlorination and positioning of chlorine atoms, there exist different kinds of congeners. After PCDD/Fs were discovered in the flue gases and fly ash of municipal waste incinerators (MSWs) in 1977 [1], much work has been conducted to investigate the possible routes and mechanism leading to the formation of PCDD/Fs in MSWs due to their toxicological effects and associated adverse health implications.

To date, a large number of research on PCDD/F emissions has tended to focus on large-scale incinerators. However, only a few studies were carried out on PCDD/Fs emissions from small waste incinerators (SWIs) (capacity < 0.5 t/h). In Japan, Nakao et al. [2] stressed that great importance should be attached to SWIs because of the high amounts of PCDD/F emissions during incineration of waste with chlorine- containing plastics or copper. In Taiwan, Chen [3] reported that 11 SWIs emitted 121 μg of PCDDs/DFs per ton of waste, approximately 200 times higher than that emitted from 21 large MWIs. The high value may reflect old age or inadequate air pollution control devices (APCDs) of the SWIs. Many SWIs lack effective controls on air pollutants owing to irregular waste feeding, uncontrolled combustion, and insufficient gas cooling systems or APCDs [4].

To the best of our knowledge, there is no previous analysis of PCDD/Fs characteristics from different components constituting the dioxin inputs and outputs from a SWI. In this study, PCDD/F concentrations in different samples (urban solid waste, fly ash, bottom ash, slag and waste water) of the selected SWI were measured and compared. The corresponding congener profiles of 2,3,7,8-substituted PCDD/Fs were also presented and compared.

**Materials and methods**

The investigation was carried out in a small waste incinerator (SWI) in the south of China. The kiln-type SWI operated for no longer 8h per day without any air pollution control device and treated residential waste generated from not only sub districts but also market places. The assessment of PCDD/Fs characterization in a SWI includes the analysis of the different components which constitute the dioxin input and output. So on the input side, the two urban solid waste (USW) samples were collected from a sub district and a market place, respectively. On the output side, the stack fly ash, bottom ash, slag and waste water samples were collected thrice in the corresponding sampling points from the SWI. The average value was determined from the three PCDD/F values.

Samples were pretreated prior to the congener-specific analysis of PCDD/Fs. The samples were extracted by Soxhlet extraction with 250 mL toluene for about 24 h, and then were concentrated by a rotary evaporator. Then, the $^{13}C_{12}$-labeled PCDD/Fs internal standards were spiked into the extracts. The clean-up procedure for PCDD/Fs analysis was performed with two columns: sulfuric acid/multi-layer silica gel column and basic alumina/florisil column. Prior to injection, $^{13}C_{12}$-labeled PCDD/Fs injection internal standards were added to the corresponding fractions for calculation of the recovery rate.

Analysis was carried out by using high resolution gas chromatograph coupled with high resolution mass spectrometer (HRGC/HRMS).

**Results and discussion:**

Table 1 Characterization of PCDD/Fs concentrations in different samples

| PCDD/PCDFs | Stack Fly ash(ng/g) | Bottom ash (ng/g) | Slag (ng/kg) | Waste water (ng/L) | USW1 (ng/kg ) | USW2 (ng/kg) |
|---|---|---|---|---|---|---|
| 2378-TCDD | 0.26 | 0.01 | 0 | 0.37 | 0 | 0.17 |
| 12378-PeCDD | 1.49 | 0.04 | 0 | 0.89 | 0 | 0 |
| 123478-HxCDD | 3.22 | 0.06 | 0 | 1.05 | 0 | 0 |
| 123678-HxCDD | 7.27 | 0.15 | 0 | 2.94 | 0 | 0 |
| 123789-HxCDD | 5.88 | 0.11 | 0 | 1.86 | 0 | 0 |
| 1234678-HpCDD | 14.72 | 0.98 | 17.40 | 14.51 | 0 | 0 |
| OCDD | 33.67 | 1.58 | 30.30 | 52.54 | 2.39 | 36.8 |
| 2378-TCDF | 2.01 | 0.13 | 7.89 | 5.68 | 49.30 | 5.04 |
| 12378-PeCDF | 1.95 | 0.14 | 0 | 4.98 | 17.30 | 1.41 |
| 23478-PeCDF | 4.63 | 0.34 | 0 | 10.56 | 1.11 | 2.13 |
| 123478-HxCDF | 3.99 | 0.29 | 0 | 7.31 | 2.36 | 0.44 |
| 123678-HxCDF | 3.32 | 0.26 | 0 | 6.82 | 0.49 | 0.65 |
| 234678-HxCDF | 4.68 | 0.32 | 0 | 9.95 | 0.91 | 0 |
| 123789-HxCDF | 1.03 | 0.08 | 0 | 1.70 | 0 | 0 |
| 1234678-HpCDF | 13.90 | 0.79 | 0 | 23.16 | 0 | 0.15 |
| 1234789-HpCDF | 1.07 | 0.07 | 0 | 1.44 | 1.56 | 0 |
| OCDF | 2.95 | 0.39 | 0 | 5.28 | 0 | 0 |
| PCDDs | 66.51 | 2.92 | 47.70 | 74.16 | 2.39 | 36.97 |
| PCDFs | 39.52 | 2.81 | 7.89 | 76.88 | 73.03 | 9.82 |
| PCDDs/PCDFs ratio | 1.68 | 1.04 | 6.05 | 0.96 | 0.03 | 3.76 |
| Total PCDD/Fs | 106.02 | 5.73 | 55.59 | 151.04 | 75.42 | 46.79 |
| PCDDs (I-TEQ) | 2.82 | 0.08 | 0.37 | 1.60 | 0.07 | 0.20 |
| PCDFs (I-TEQ) | 4.07 | 0.29 | 0.79 | 8.93 | 3.10 | 1.75 |
| PCDDs/PCDFs (I-TEQ) ratio | 0.69 | 0.28 | 0.47 | 0.18 | 0.02 | 0.12 |
| Total PCDD/Fs (I-TEQ) | 6.90 | 0.37 | 1.16 | 10.53 | 3.17 | 1.95 |

USW1: urban solid waste collected from a sub district; USW2: urban solid waste collected from a market place.

Table 1 shows the concentrations and I-TEQs of PCDD/Fs of urban solid waste, stack fly ash, bottom ash, slag, and waste water samples. It is not so surprising to see that the PCDD/Fs concentration of stack fly ash (mean value=6.90 ng I-TEQ/g) was much higher than those concentrations found in bottom ash (mean value=0.37 ng I-TEQ/g), slag (mean value=1.16 ng I-TEQ/kg). The bottom ash and slag met the environmental quality standards for soil (less than 1 ng I-TEQ/g ) in Japan Ministry of the Environment. So the bottom ash and slag can be applied for construction blocks. However, a high amount of PCDD/Fs was transferred into the stack fly ash, indicating that the SWI can not control PCDD/Fs emissions without any gas cooling facility and APCD. These results indicate that SWIs emit much higher dioxin concentrations than do large MWIs, attributed to these factors: poorly performing combustion chambers, inadequate APCDs, irregular waste inputs, open gates during waste feeds, and discontinuous waste combustion [4]. Compared with the output samples, the input samples (USW) presented much low PCDD/Fs levels, indicating that a large number of PCDD/Fs were produced in the process of incinerating waste in the SWI.

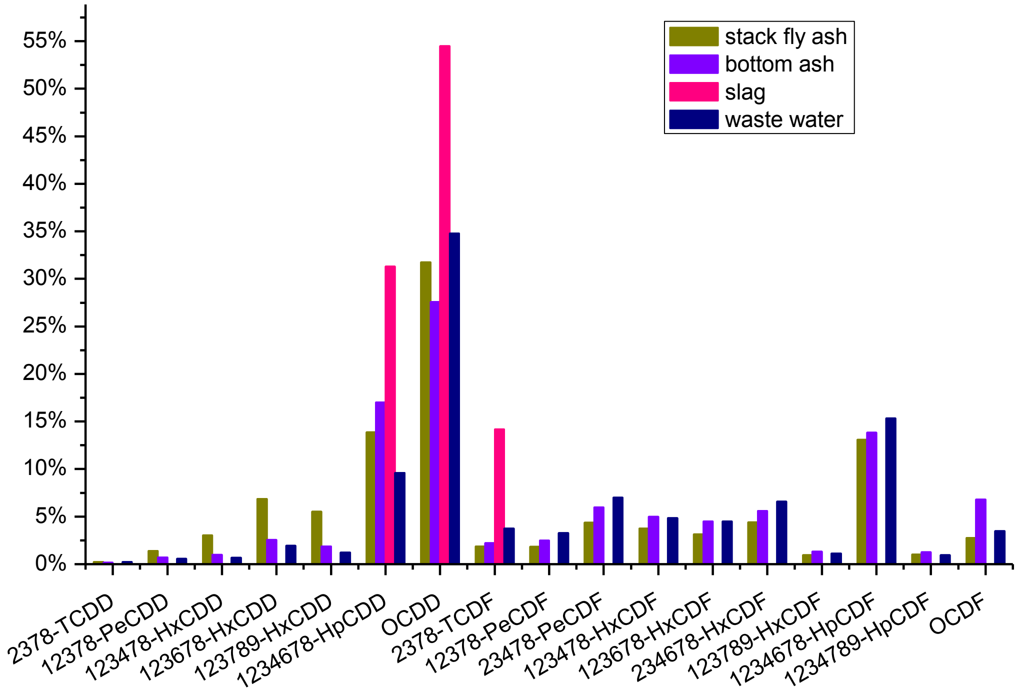


Figure 1. Congener profiles of PCDD/Fs in the output samples (stack fly ash, bottom ash, slag and waste water samples).

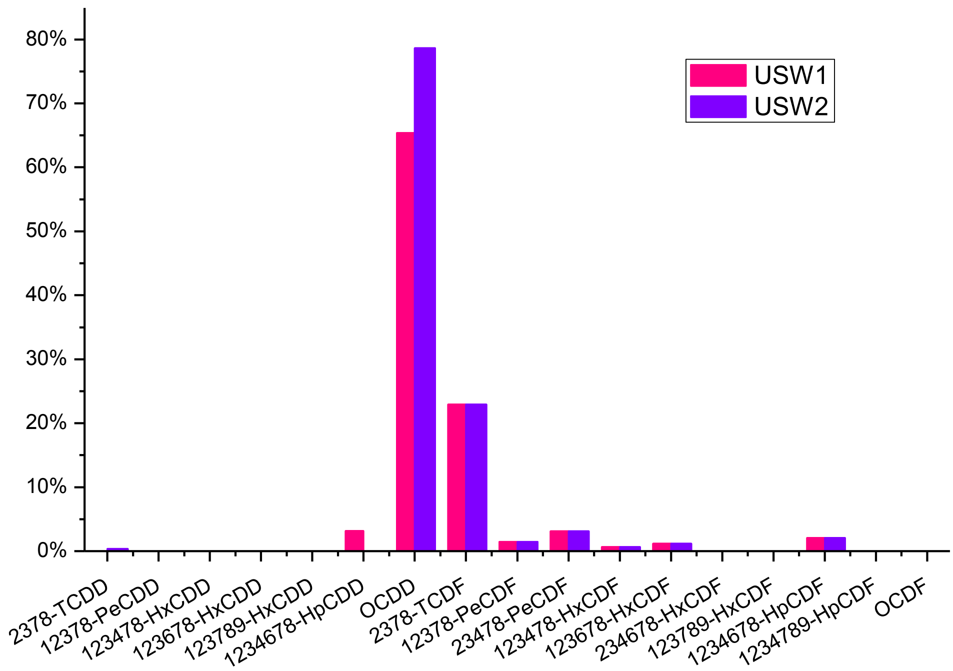


Figure 2. Congener profiles of PCDD/Fs in the input samples (urban solid waste samples).

As shown in Figure 1, large similarities could be presented in congener profiles. It can be observed that as the chlorinated-level increases, the concentration of the 2,3,7,8,-PCDD congener increases, but the concentration of the 2,3,7,8,-PCDF congener presents irregularities. For PCDDs, the most dominant congener is OCDD, followed by 1,2,3,4,6,7,8-HpCDD and for PCDFs, 1,2,3,4,6,7,8-HpCDF was the major congener. As shown in Figure 2, remarkable differences could be found compared with those output congener profiles in Figure 1. The USW concentration congener profiles are clearly dominated by a high content of OCDD followed by 2,3,7,8-TCDF. The fraction of OCDD and 2,3,7,8-TCDF reaches around 90% of the total PCDD/Fs, which is similar to the profile reported by Abad et al [5].

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