Emissions of PCDD/Fs in flue gas from a medical waste incinerator in Shanghai

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Abstract: Emission characteristics of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and 17 congeners from a medical waste incineration plants in Shanghai, China were investigated. Results showed that the dioxin concentration ranged from 5.0 to 23.3 ng I-TEQ (Toxic Equivalent Quantity) Nm⁻³ under normal combustion concentration. The high dioxin incidence area was found in the boiler outlet and the bag filter inlet, and over 95% of the dioxins were present in the gaseous state. Polychlorinated dibenzofurans (PCDFs) accounted for a higher proportion of the total amount of PCDD/Fs than polychlorinated dibenzo-p-dioxins (PCDDs).

1. Introduction
The amount of medical waste has rapidly increased in China in recent years, from 450,000 metric tons in 2007 [1] to more than 600,000 metric tons in 2014 [2] and the largest amount of medical waste is generated in Shanghai [2]. Medical waste is currently being managed by incineration. There were 157 incineration plants in operation in China by the end of 2012 [3]. The flue gas generated by these medical waste incinerators has attracted increasing attention due to formation of large quantity of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), commonly known as dioxins. Dioxins are potentially toxic chemicals with serious health hazard even at extremely low doses. The majority of dioxins tend to travel long distances before falling to earth with rainfall or settling as particles [4]. Additionally, dioxins are extremely persistent with an estimated half-life of 7-11 years in humans [5]. Due to a high chlorine content and poor burning condition, incineration of medical waste emits a large amount of PCDD/Fs [6,7]. Thus, many countries have developed strict emission standards, which require further treatment of the exhaust gas before releasing to the atmosphere. In China, the emission standard of PCDD/Fs is 0.5 ng I-TEQ Nm⁻³ [8] and in Shanghai, 0.1 ng I-TEQ Nm⁻³ [9]. The European Union (EU) legal limit is 0.1 ng I-TEQ Nm⁻³ [10], and the U.S. limits are 0.4 ng I-TEQ Nm⁻³ for existing units and 0.2 ng I-TEQ Nm⁻³ for new units, respectively [4,11], which are much more stringent than the Chinese standard. The average PCDD/Fs emission in flue gas of 41 medical waste incinerators from China is 7.51 ng I-TEQ Nm⁻³, which far exceeds the national emission standard. The largest emissions from two incinerators are 67.52 ng I-TEQ Nm⁻³ and 59.20 ng I-TEQ Nm⁻³, 100 times more than the limit. Only 43.9% of the medical waste incinerators meets the national requirement of 0.5 ng I-TEQ Nm⁻³ and 14.63% are within the limit of 0.1 ng I-TEQ Nm⁻³ [3].

Formation mechanism of PCDD/Fs during waste incineration is very complex and is affected by many factors, such as temperature, chlorine content, precursors in the feed of a combustion process, oxygen availability, residence time, and feed processing [6,12,13,14]. In addition, there are very limited
studies focusing on the current PCDD/Fs emissions in flue gas from medical waste incineration, especially for the 17 congeners which are considered to be the most harmful to human health among 75 polychlorinated dibenzo-p-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs) congeners from the combustion processes. Thus, there is a critical need to study the presence of PCDD/Fs congeners, and their species and characteristics in flue gas from the full-scale medical waste incinerators. Therefore, the overall goal of this study was to examine the presence and distribution of PCDD/Fs from a commercial-scale medical waste incineration facility in Shanghai.

2. Materials and Methods

2.1 Full-scale medical waste incinerator

This research was conducted using a full-scale medical waste incinerator in Shanghai, China. The incinerator plant has a capacity of 72 metric ton/day and operates 300 days/year. The incinerator has a two-stage combustion system consisting of a rotary kiln of 4.3 m diameter. The post-combustion system has a retention time of more than 2 sec at 1100 °C to insure the complete destruction of hazardous organic compounds present in the medical waste. Pipes and accessories from the boiler outlet to the bag inlet are the high risk areas for the formation of PCDD/Fs in the plant, and 95% of PCDD/Fs (TEQ) was found to be in the gas phase. The original air pollution control system installed in the plant was retrofitted with rapid cooling tower to prevent the formation of PCDD/Fs, dry-type reactor, traditional ACI (Activated Carbon Injection Technology), bag filter, and wet scrubbing tower, to ensure that the flue gas meets the emission standards. Combustion conditions of the medical waste incineration plant are shown in Table 1.

2.2 Sampling and Analyses

Flue gas samples were taken from four sampling points ((1) the post-combustion chamber outlet; (2) the high temperature point in the waste heat boiler (entrance point); (3) the waste heat boiler outlet; (4) the bag filter inlet.) The emission of PCDD/Fs in flue gas was measured simultaneously at four sampling points.

Samples collected were analyzed by the Belgian SGS company and the analytical method they used was US EPA Method 23 (US EPA1995). Identification and quantification of PCDD/Fs were performed by HRGC/HRMS using a 7890 Series gas chromatograph (Agilent, USA) and AutoSpec Premier (Waters).

Table 1 Combustion conditions of the medical waste incineration plant

| Parameter                              | Value            |
|----------------------------------------|------------------|
| Medical waste amount                   | 2400–2500 kg/h   |
| Temperature of rotary kiln head        | 870–890 °C       |
| Temperature of kiln                    | 1020–1050 °C     |
| Temperature of post-combustion chamber outlet | 1050 °C          |
| Temperature of quench tower inlet     | 170–176 °C       |
| Temperature of quench tower outlet    | 185 °C           |

3. Results and Discussion

3.1 Presence, species and characteristics of PCDD/Fs

The concentrations of PCDD/Fs in flue gas at the four sampling points are shown in Figure 1.
The total dioxin emission ranged from 5.0 to 23.3 ng I-TEQ Nm\(^{-3}\) under normal operation conditions. Under unfavorable combustion conditions, significant amount of dust deposition took place in the pipeline, which resulted drastic increase in the dioxin concentration to 149.04 ng I-TEQ Nm\(^{-3}\) at the bag entrance. As evident from the figure, the concentration of PCDD/Fs in flue gas increased from the high temperature zone of the boiler to the boiler outlet, and it further increased significantly at the entrance of the bag and reached as high as 149.04 ng I-TEQ Nm\(^{-3}\). However, PCDD/Fs concentration decreased from the post-combustion chamber outlet to the boiler inlet. The concentration of PCDD/Fs from the boiler inlet to the boiler outlet increased by nearly two folds and from the boiler outlet to the bag entrance by 19 folds. For effective emission control, reformation of PCDD/Fs should be prevented from the boiler outlet to the bag entrance (quench tower) or in the air pollution control system. Considering the temperature of the boiler outlet of about 230–280°C and the temperature at the inlet of the bag of 180°C, it could be speculated that dioxins were likely to be formed in large amount at temperatures between 180–280°C through de novo synthesis. De novo synthesis is known to occur in a relatively low temperature range of 200-400 °C \([15-16]\). De novo process proceeds through burn off of smaller, relatively innocuous chemical molecules with simultaneous oxidation and chlorination at a relatively low temperature in presence of oxygen \([12,13]\).

The decrease in dioxins concentration from the post-combustion chamber outlet to the boiler inlet could be explained by another heterogeneous pathway. The medical waste was found to contain metals, which were incorporated into the fly ash (2176 mg/kg in this study). Fly ash was carried over to the cooler (250-400°C) post-combustion zone of the incineration system \([12]\); hence, dioxins existed mainly in the fly ash rather than in the flue gas.

Figure 2 shows the concentration and distribution of 17 PCDD/F congeners at four sampling points. In general, furans constituted a large proportion of contaminant in the flue gas. At the entrance of the bag, the concentrations of 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, OCDF, and OCDD were 30.13 ng I-TEQ Nm\(^{-3}\), 15.65 ng I-TEQ Nm\(^{-3}\), 34.57 ng I-TEQ Nm\(^{-3}\), and 25.44 ng I-TEQ Nm\(^{-3}\), respectively, and are higher than other congeners. Gao et al. (2009) \([10]\) and Węgiel et al. (2014) \([17]\) also reported similar pattern that the PCDD/Fs in stack gas from medical waste incinerators were usually characterized by higher fractions of OCDF, 1,2,3,4,6,7,8-HpCDF, OCDD, and 1,2,3,4,6,7,8-HpCDD. The mechanism of PCDFs formation is different from that of PCDD\(_{18,19}\) \([18,19]\) and formation of different amount of PCDDs and PCDFs is influenced by precursor concentration and chlorine content \([4,14,20]\). Wang et al. (2003) \([14]\) reported that chlorine content with a threshold value of 0.8-1.1% in the waste was the most important factor. The authors reported that when the chlorine content was below the
threshold value, the formation of PCDDs dominated and the formation of PCDFs dominated above the threshold value. In this study, the chlorine content was 2-4% (above the threshold value); thus PCDFs were the dominant species.

![Figure 2. Concentrations of PCDD/F congeners at four sampling points](image)

At the entrance of the bag, with the increasing chlorine content (substituted number of chlorine atom in congeners), the concentration of congeners grew faster. Concentrations of highly chlorinated congeners were higher than that of low chlorinated congeners. Karademir et al. (2004) [21] also reported similar findings for a hazardous waste incinerator using fixed-bed activated carbon filter.

At the post-combustion chamber outlet, furans constituted the main component of flue gas accounting for 82.2% of the total concentration of the contaminants. The concentrations of 1,2,3,4,6,7,8-HpCDF, OCDF, and OCDD were higher in the 17 congeners, and were 7.35 ng I-TEQ Nm⁻³, 8.29 ng I-TEQ Nm⁻³, 2.60 ng I-TEQ Nm⁻³, respectively. The total concentration of dioxins in the flue gas was 25.28 ng I-TEQ Nm⁻³. The total dioxin TEQ was 0.74 ng I-TEQ Nm⁻³, mainly caused by 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF, which contributed 28.2%, 10.5%, 13.2%, 16.6%, and 9.9%, respectively, of the total dioxin TEQ.

At the exit of the boiler, furans also constituted the main component of the flue gas, which accounted for 67.6% of the total concentration. The concentrations of 1,2,3,4,6,7,8-HpCDF, OCDF, and OCDD were higher in the 17 congeners and were 0.97 ng I-TEQ Nm⁻³, 1.46 ng I-TEQ Nm⁻³, and 1.42 ng I-TEQ Nm⁻³, respectively. The total concentration of dioxins in the flue gas was 7.36 ng I-TEQ Nm⁻³. The total dioxin TEQ was 0.53 ng I-TEQ Nm⁻³, and 2,3,4,7,8-PeCDF had the highest contribution (45.2%) to the total dioxin TEQ.

PCDFs had a higher contribution to the total dioxin amount at all sampling points, indicating that chlorine content played a crucial role in the formation of PCDD/Fs [12,14]. For the samples at the bag filter entrance, high chlorine content or high molecular weight congeners were dominant. The de novo synthesis reactions were the main mechanism leading to high molecular weight PCDF congeners formation. The results further strengthened that de novo synthesis was the main formation mechanism at high dioxin incidence area of our tests - from the boiler outlet to the bag entrance. Gao et al. (2009) [10] and Gunes et al. (2015) [22] also reported that the de novo synthesis of PCDD/Fs was dominant in the medical waste incineration.

3.2 Gas/particle partitioning

The differences in physical and chemical attributes of PCDD/F congeners have an important role in assessing their following removal by carbon adsorption. Since activated carbon can effectively remove
gas-phase dioxins [21] and it is inefficient in removing particle-bound dioxins, the partitioning of these compounds plays a significant role. Figure 3(a and b) shows the distribution of 17 congeners in the flue gas before and after ACI-bag filter. Both before and after the bag filtration, the gaseous fraction of dioxins was much higher than particle bound dioxins indicating that dioxins were mainly in the gas phase.

At the entrance of the bag, the total toxic equivalent concentrations of dioxins in solid and gas phases were 0.23 ng I-TEQ Nm⁻³ and 149.04 ng I-TEQ Nm⁻³, respectively. Dioxins were mainly in the gas phase, accounting for 99.8% of the total TEQ. PCDD compounds constituted 18.9% of the total dioxin TEQ, and PCDF had the highest contribution (81.1%) to the total dioxin TEQ. The concentrations of 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF were higher in the 17 congeners existing in gas phase, and were 0.33 ng I-TEQ Nm⁻³, 3.01 ng I-TEQ Nm⁻³, 6.18 ng I-TEQ Nm⁻³, 6.02 ng I-TEQ Nm⁻³, 8.13 ng I-TEQ Nm⁻³, respectively.

At the exit of the bag, the total toxic equivalent concentrations of dioxins in solid and gas phase were 0.15 ng I-TEQ Nm⁻³ and 2.13 ng I-TEQ Nm⁻³, respectively. Dioxins were also mainly present in the gas phase, accounting for 93.3% of the total TEQ. PCDF had the highest contribution (79.7%) to the total dioxin TEQ, and PCDD compounds constituted 20.3% of the total dioxin TEQ. The concentrations of 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF were higher in the 17 congeners present in the gas phase, and were 0.78 ng I-TEQ Nm⁻³, 0.16 ng I-TEQ Nm⁻³, 0.23 ng I-TEQ Nm⁻³, 0.20 ng I-TEQ Nm⁻³, and 0.32 ng I-TEQ Nm⁻³, respectively.

Figure 3. Gas/particle partitioning of PCDD/F congeners before ACI-bag filter (1) and after ACI-bag filter (2)

4. Conclusions
In this study, emission characteristics of PCD from a medical waste incineration plant were investigated.
Under normal combustion concentration, the dioxin concentration range was in 5.0-23.3 ng-ITEQ Nm\(^{-3}\). When the combustion condition was not ideal and the pipeline was seriously dusted, the dioxin concentration at the entrance of the bag increased up to 56.6 ng-ITEQ Nm\(^{-3}\). Sampling and analysis results at different parts of process showed that the high dioxin incidence area was from boiler outlet to bag filter inlet and over 95% of the dioxins were present in the gas state. De novo synthesis, which is known to occur in a relatively low temperature window of 200-400°C, was the main formation mechanism at the high dioxin incidence area of the tests. PCDFs accounted for a higher proportion of the total amount of PCDD/Fs than PCDDs.

The efficiency of the traditional air pollution control in our aimed plant was 97.5%, which met the Chinese emission standard of dioxins (0.5 ng-ITEQ Nm\(^{-3}\)). However, nowadays in Shanghai, the new emission standard of 0.1 ng-ITEQ Nm\(^{-3}\) is much stricter. Thus, there is an urgent need for a more efficient PCDD/Fs removal method.

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