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Emission characteristics of PCDD/Fs in stack gas from municipal solid waste incineration plants in Northern China

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HIGHLIGHTS

- Emission factors of PCDD/Fs in stack gas from MSWIs were evaluated.
- The indicatory compounds of PCDD/Fs in stack gas were pointed out.
- 1,2,3,7,8,9-H6CDF and 1,2,3,4,7,8-H6CDF can be used as TEQ indicators.
- PCDD/Fs formation mechanisms were discussed through the PMF model.

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ABSTRACT

Emission characteristics including congener's profile, gas emissions and toxic equivalent concentration (TEQ) indicators of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in 57 stack gas samples from 6 municipal solid waste incinerators (MSWIs) in Northern China were investigated by gas chromatography-high resolution mass spectrometry (HRGC-HRMS). Additionally, PCDD/Fs formation mechanisms from the MSWIs were briefly discussed. Results revealed that the concentrations and equivalent concentrations of PCDD/Fs emissions in stack gas from 6 MSWIs were in the range of 0.11–2.53 ng Nm^{-3} and 0.007–0.059 ng TEQ Nm^{-3}, respectively. The emission factors of PCDD/Fs from 6 MSWIs varied from 0.027 to 0.225 μg I-TEQ $tonne^{-1}$, with a mean value of 0.17 μg I-TEQ $tonne^{-1}$ waste, which was estimated to an annual emission of 234.96 mg I-TEQ of PCDD/Fs from 6 MSWIs to the atmosphere. O8CDD, O8CDF and 1,2,3,4,6,7,8-H7CDD were the indicatory compounds of PCDD/Fs to apportion the sources of PCDD/Fs in environmental medium especially in ambient environment of MSWIs. 1,2,3,7,8,9-H6CDF and 1,2,3,4,7,8-H6CDF can be used as TEQ indicators for monitoring PCDD/Fs emission. Based on the positive matrix factorization (PMF) model, eight factors were extracted by the PMF analysis. Formation of low-chlorinated PCDDs (1,2,3,7,8-P5CDD, 1,2,3,4,7,8-H6CDD, 1,2,3,6,7,8-H6CDD and 1,2,3,7,8,9-H6CDD) possessed strong correlation, and the chlorophenols maybe the important precursors of low-chlorinated PCDDs, which were generated within the low chlorinated content. Penta- and hexa-PCDFs formation in stack gas from MSWI may block catalytic sites for PCDFs formation from carbon. Meanwhile, possible formation mechanisms of high-chlorinated PCDDs (hepta- and octa-PCDDs) and high-chlorinated PCDFs (hepta- and octa-PCDFs) were respectively dependent.

1. Introduction

Municipal solid waste (MSW) incineration in China has boosted more than twelvefold in the past decade, in response to rapid increase in MSW generation. By 2015, the capacity of MSW incineration in China has reached 0.23 million tonnes d^{-1}, which is one third of the total capacity around the world (Lu et al., 2017). MSW incinerators (MSWIs) are regarded as key sources of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran (PCDD/Fs) emissions, and the emissions of PCDD/Fs has drawn increasing attention due to its high toxicity, stability, persistence,

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lipophilicity and bioaccumulation properties (Wania and Mackay, 1996; Lee et al., 2016; Xue et al., 2017; Tang et al., 2017; Zhu et al., 2016). As continuous public criticisms and even recurrent anti-incineration protests are caused by the concern on the PCDD/Fs emissions in recent years, tracing the PCDD/Fs emissions from MSWI is a job of great importance to MSW management.

Extensive researches concentrated on the subject of emission characteristics and formation mechanisms of PCDD/Fs from MSW incinerators (Hatanaka et al., 2001; Lonati et al., 2007; Wu et al., 2011; Nzihou et al., 2012; Ma et al., 2013; Vallejo et al., 2015; Zhu et al., 2018). Emission characteristics of PCDD/Fs from MSW incinerators could intuitively reflect the combustion condition, air pollution control devices (APCD) and emission levels. In the past decades, the related researches were gradually reported in China. Bie et al. (2007) investigated the congener concentration distribution of PCDD/Fs in the flue gas and fly ash from MSWIs by applying a twin internal fluidized bed incinerator in Harbin. Ni et al. (2009) analyzed the congener's distribution characteristics from the various MSWIs using principal component analysis and hierarchical cluster analysis, whilst calculating and estimating the emission factors and gas emission of PCDD/Fs in the stack gas. Moreover, Gao et al. (2009) and Li et al. (2017) had conducted detailed research into gas emission estimation, TEQ indicators and factor composition of PCDD/Fs, but they only focused on the stack gas from medical waste incinerators (MWIs). The related emission information of PCDD/Fs from MSWIs in China should be taken into consideration. Meanwhile, the emission control of PCDD/Fs in the stack gas from MSWI continued to be improved by the Ministry of Environmental Protection of China in the recent years (China MEP, 2016). Therefore, more detailed information about emission characteristics of PCDD/Fs from MSWIs would be essential to the control of pollutants and the reduction of risk to public health.

Efficient PCDD/Fs control method could be taken through understanding the formation mechanisms. PCDD/Fs are mainly generated in the post-furnace by de novo synthesis or precursor synthesis (Stieglitz, 1998; Chang and Huang, 2000; Gan et al., 2003; Wang et al., 2003). Numerous highly chlorinated PCDD/F congeners could be produced at the temperature from 250 to 400 °C in the occurrence of de novo synthesis, whilst the formation rate of PCDD congeners is significantly lower than the PCDF congeners (Yamamoto et al., 1989). When the temperature between 250 and 650 °C, the formation of PCDFs would be more easer, especially for the low chlorinated congeners by precursor syntheses (Nakahata and Mulholland, 2000). The chlorination of less chlorinated congeners produced in the gas phase (Wikström and Marklund, 2000), whilst dechlorination of highly chlorinated congeners produced by de novo synthesis (Iino et al., 2000). More detailed information about the correlation of the formation mechanisms among the PCDD congeners or PCDF congeners are still limited. Positive matrix factorization (PMF) model is a powerful and widely useful factorization method for source apportionment which needs little source profile data (Wang et al., 2016, 2017; Wu et al., 2017). This model has been widely applied in the source apportionment of air pollutants, such as PM2.5, PAHs and organic aerosols (Jaeckels et al., 2007; Lee et al., 2008; Wang et al., 2016; Kong et al., 2018). Moreover, PMF model could also be used to analyze the congeners profile, factor composition and congener's formation mechanisms of PCDD/Fs in stack gas from MWIs which is reported by Li et al. (2017).

In order to investigate emission characteristics and possible formation mechanisms of PCDD/Fs in stack gases from municipal solid waste incinerators in China, stack gas samples from 6 MSWIs were collected. The objectives of this paper are: (1) to investigate the congener distribution characteristics of PCDD/Fs from 6 MSWIs, and determine the indicatory PCDD/Fs of the MSWI source; (2) to investigate the emission factors of PCDD/Fs; (3) to obtain the TEQ indicators of PCDD/Fs by correlation analysis; (4) to investigate factor composition and formation mechanisms of PCDD/Fs congeners based on the PMF model.

2. Materials and methods

2.1. Site description and sample collection

Stack gas samples were collected from 6 MSWIs (see Table 1), which were located in Northern China, in the year of 2016. These MSWIs use the same type of APCD, i.e., the combination of selective non-catalytic reduction (SNCR), semi-dry spraying, actived carbon injection, and bag filter. All the stack gas samples were collected and determined by the third party testing organization commissioned by the 6 MSWIs plants. PCDD/Fs were sampled isokinetically using the isostack sampler, which consist of glass fiber filter, resin (amberlite XAD-2, Supleco) and 5 impingers (2 water, 2 empties and 1 silica gel), and a sampling time of 120–180 min, according to the national standard coded as HJ 77.2–2008. Before the sampling of flue gas, $13C_{12}$-labelled with 100 ng mL^{-1} in nonane, as sampling standards, was spiked into the resin. Samples were collected three times at the sampling site and the average value was determined. Finally, 57 stack gas samples were collected.

2.2. Extraction and analysis

PCDD/Fs sampling, cleanup, determination and congener analysis were all conducted in accordance with the national standard method coded as HJ 77.2–2008. Stack gas samples were transferred into Soxhlet with toluene for 24 h, and then subsequently washed with sulfuric acid until there was no color remaining. Clean-up procedures were performed with a multi-layer silica gel column and an alumina column. The final clean extract was collected stepwise, and concentrated with a nitrogen stream. Injection standards (10 μL) were spiked into micro-vials, and the extracts were re-dissolved in 1 mL of decane for PCDD/Fs analysis.

The purified extract was performed on high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS). For HRGC, a Hewlett–Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph equipped with a capillary GC column Rtx-2330 (Restec) (60 m × 0.25 mm × 0.1 μm) was used for PCDD/Fs analysis. Samples (1 μL) were injected in splitless mode at an injector temperature of 280 °C. The temperature program was set as follows: initial column temperature 90 °C (held for 1.5 min), the temperature was then programmed at 25 °C min^{-1} to 180 °C, finally ramped at 3 °C min^{-1} to 260 °C (held for 25 min) (Zhang et al., 2013). For HRMS, an Autospec Premiermass spectrometer with a positive electron impact source was employed. The ion source was operated at 250 °C with the electron energy of 37 eV, ionization current of 0.5 mA and ion accelerating voltage of 8 kV, and the mass spectrometer was tuned to a mass resolution of 10,000. All data were acquired in the selected ion monitoring mode (SIM). International toxic equivalents (I-TEQ) values for PCDD/Fs were calculated by using international-toxicity equivalency factor (I-TEF). All data was normalized by 11% of O_2 content.

2.3. Positive matrix factorization (PMF) model

PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices (US EPA, 2014), which was suitable for environmental data because it accounts for variable uncertainties and constraints all values to be positive, as in real environmental problems (Wang et al., 2016). In the present study, a 17 × 57 dataset (17 individual PCDD/Fs and 57 stack gas samples) were introduced into PMF 5.0 model to distinguish