

APPLICATION OF A LONG-TERM STACK SAMPLING SYSTEM FOR EVALUATING PCDD/F EMISSIONS DURING START-UP PERIOD OF AN MWI IN TAIWAN

Chang SH, Hung PC, Chang MB*

Graduate Institute of Environmental Engineering, National Central University, 300, Jhongda Road, Jhongli City, Taiwan (R.O.C.)

Introduction

In Taiwan, 24 large-scale municipal waste incinerators (MWIs) are in operation. Stringent emission standard has been promulgated for PCDD/Fs ($0.1 \text{ ng I-TEQ/Nm}^3$) from large-scale MWIs in Taiwan since 2003. "Activated carbon injection + bag filter" (ACI+BF) technology is applied in 23 MWIs for controlling PCDD/F emissions while one MWI adopts SCR system for PCDD/F removal (or destruction). Annual PCDD/F emission from 24 large-scale MWIs based on normal operation is significantly reduced from $2.53 \text{ g I-TEQ/year}$ in 2002 to $1.33 \text{ g I-TEQ/year}$ in 2011. However, $2.70 \text{ g I-TEQ/year}$ of PCDD/F emission is discharged from these MWIs during start-up period in 2011. Literature indicates that PCDD/F concentration at boiler outlet during start-up period is 15 times of that during normal operating condition. The emission concentration of PCDD/Fs at stack is higher than 1 ng I-TEQ/Nm^3 , even though 99.6% of PCDD/F removal efficiency is achieved by APCDs.^[1] The Adsorption MEthod for SAMpling (AMESA[®]) developed in accordance with EN1948 manual sampling method has been adopted in some facilities of Europe, Korea, Japan etc. for long-term PCDD/F stack sampling.^[2,3,4] However, the study on emission characteristics of PCDD/Fs during start-up period is relatively few. In this study, a long-term stack sampling system is applied to evaluate the characteristics of PCDD/F emission during the start-up period of an MWI located in northern Taiwan.

Materials and methods

The sampling system developed in this study is a continuous semi-VOC sampler based on the criteria of U.S. EPA Method 23.^[5] The continuous sampler includes stack probe (Pitot tube, temperature sensor of flue gas and temperature control of stack probe), filter (quartz filter, temperature control of filter holder), cooler and XAD-2 adsorbent (cool water supply, temperature sensor before XAD-2 adsorbent), water collection (1 large water container and 4 impingers), and control unit (pump, data recorder, temperature and flow rate controller). This continuous sampler can be stably operated for 1 week. The scheme of continuous sampler is shown in Figure 1.

The capacity of the MWI investigated in this study is 600 ton/day with 2 stoker furnaces and 110.2 GWh of electricity was generated in 2012. This study focuses on the characteristics of PCDD/F emission during start-up period of this MWI. Two samplings were conducted in 2011 and 2012, respectively. The sampling started on the 2nd day after start-up. Solid- and gaseous samples were treated with extraction and clean-up procedures, and then analyzed with high resolution gas chromatography (HRGC) (Thermo Trace GC)/high resolution mass spectrometry (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS ($60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$, J&W). Sampling recoveries of gaseous samples adsorbed by XAD-2 resin are all between 75% and 95%, which is within the acceptable 70 -130% range set by the U.S. EPA in Method 23. In this study, AEC (average PCDD/F emission concentration) indicates average concentration of PCDD/Fs with n-days sampling. nst-m of Sampling No. indicates the mth time continuous sampling in the nth investigation.

Results and discussion

Figures 1 and 2 show the results of the 1st and 2nd long-term samplings during the start-up period of the MWI investigated in this study, respectively. In first investigation, AEC of 1st-1 with 2-days sampling is $0.525 \text{ ng I-TEQ/Nm}^3$ and higher than emission standard of large-scale MWI in Taiwan. However, the PCDD/F emission decreased gradually as the operation of MWI is stabilized. 12 days after start-up, PCDD/F emission is lower than $0.1 \text{ ng I-TEQ/Nm}^3$, and $0.0556 \text{ ng I-TEQ/Nm}^3$ of AEC of PCDD/Fs is obtained at 14.5 days after start-up. Regarding to second investigation, AEC of PCDD/Fs with 2-day continuous sampling (Sampling No. 2nd-1) is $1.45 \text{ ng I-TEQ/Nm}^3$. Interestingly, it is significantly higher than $0.525 \text{ ng I-TEQ/Nm}^3$ of Sampling No. 1st-1. It

may be attributed to the high uncertainty during start-up period of this MWI with complex waste composition, unstable operating state (such as unstable temperature distribution), memory effect (PCDD/Fs may be formed on fly ash accumulated in pipe). By the way, Wang et al. (2007) compare two different start-up processes of MWI and indicate that PCDD/F concentrations at boiler outlet may differ by 15 times between two start-up processes.^[1] Moreover, previous study indicates that a relatively high PCDD/F concentration (96.9 ng I-TEQ/Nm³) was measured in an MWI of Taiwan during 18 hours' start-up period.^[6] Therefore, PCDD/F emission during start-up process is unstable. By the way, PCDD/F emission investigated during 2nd start-up period decreased rapidly with increasing operating time as well. About 9th day after start-up MWI, AEC of Sampling No. 2nd-6 is measured as 0.0521 ng I-TEQ/Nm³ which is lower than 0.1 ng I-TEQ/Nm³ of emission limit.

On the other hand, literature indicates that memory effect may exist in AMESA and further shows higher HpCDD and OCDD distributions compared manual sampling.^[7] For better understanding the characteristics of continuous sampling system, a manual sampling based on USEPA Method 23 is carried out on the 2nd day of Sampling No. 1st-1. TEQ concentration of manual sampling is 0.0629 ng I-TEQ/Nm³, which is not significantly different from the AEC of Sampling NO. 1st-1. Mass distributions of PCDD/F congeners between continuous and manual samplings are not significantly different either. However, the sampling time with 1st-1 is two days (48 hours) and may not be long enough for memory effect compared with 168 hours of sampling time carried out in literature.^[7] However, the ratio between gas- and solid-phase congeners (G/S ratio) found with continuous sampling is significantly different from the manual sampling. For manual sampling, G/S ratios of 17 toxic PCDD/Fs are commonly lower than that with continuous sampling (Figure 3). Interestingly, G/S ratio is significantly decreased with increasing chlorinated level of PCDD/F congeners, especially for continuous sampling. It may be attributed to different boiling points between low and highly Cl-substituted congeners. Boiling points of PCDD/F congeners are commonly increased with increasing chlorine-substituted level. Compared with manual sampling, higher G/S ratios with continuous sampling may be attributed to the desorption of PCDD/Fs from fine particles collected by filter over a long period of sampling time.

This study sets up a continuous semi-VOC sampler in an MWI and clarifies the average emission concentration (AEC) of PCDD/Fs during start-up period. The results indicate that PCDD/F emission concentrations are significantly different between two start-up processes due to complex waste composition and unstable operating condition. Nevertheless, PCDD/F concentrations at 1st and 2nd investigations are lower than the emission limit (0.1 ng I-TEQ/Nm³) starting from the 12th and 9th day after start-up, respectively. On the other hand, higher gas/solid ratios of PCDD/Fs are found with the continuous sampling possibly due to desorption of PCDD/Fs from fine particles during continuous sampling.

Acknowledgements

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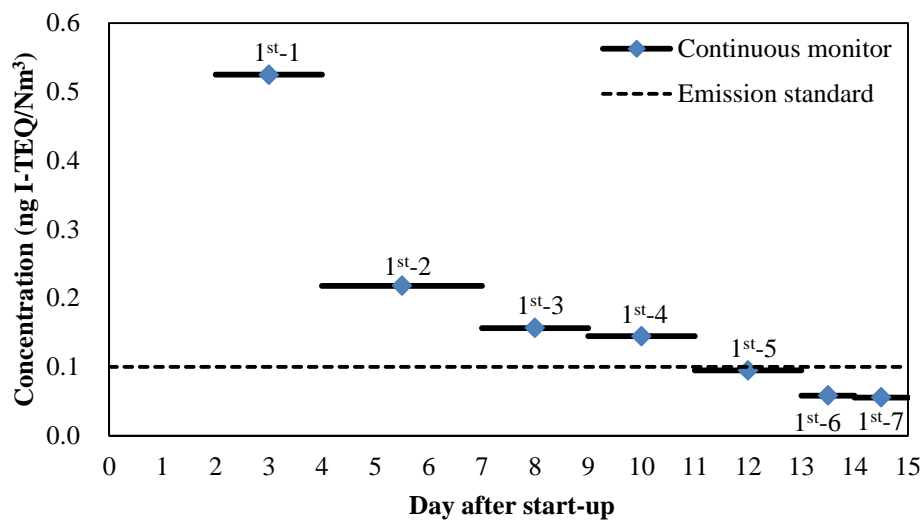


Figure 1 PCDD/F emission during start-up period of the MWI investigated (1st investigation).

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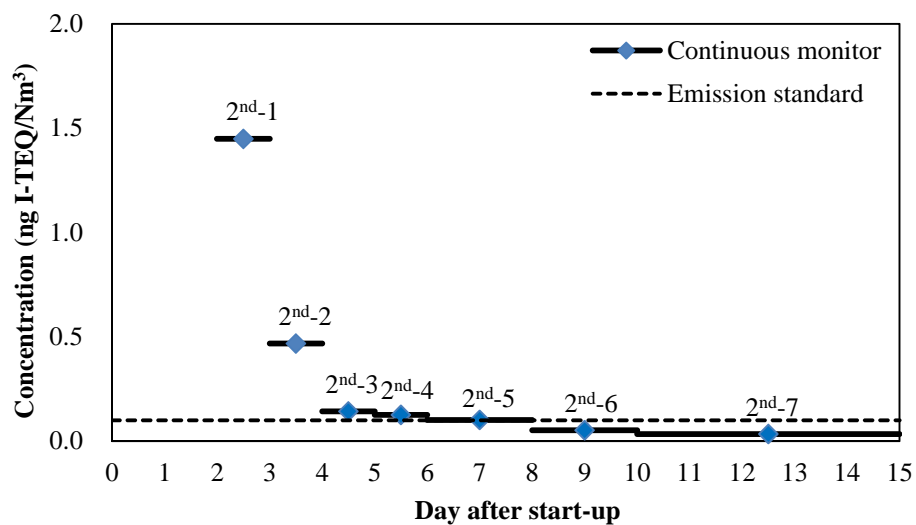


Figure 2 PCDD/F emission during start-up period of the MWI investigated (2nd investigation).

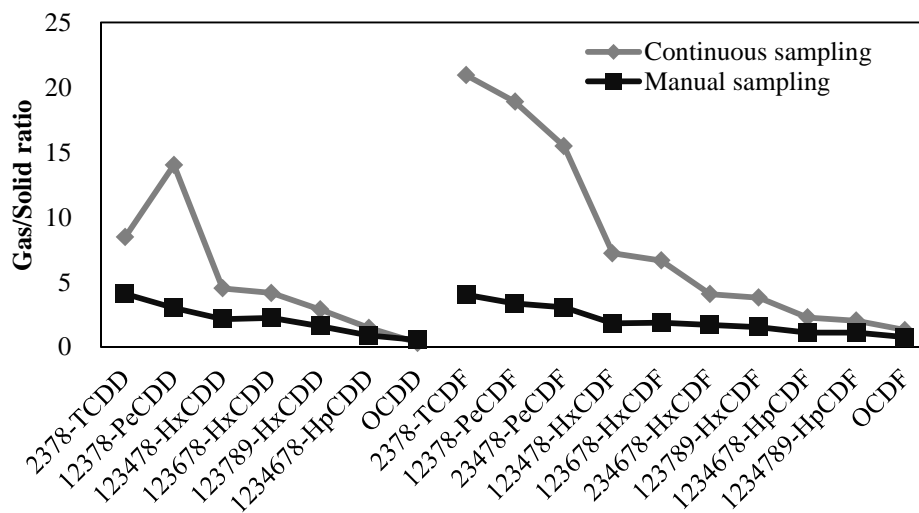


Figure 3. G/S ratios of 17 toxic PCDD/Fs with continuous and manual sampling, respectively.