THE DISTRIBUTION AND SOURCE APPORTIONMENT OF STATIONARY SOURCE FLUE GAS AND ATMOSPHERIC PCDD/FS IN TAIWAN

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Introduction

Polychlorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofurans PCDF (PCDFs) which known as dioxin is one of the persistent organic pollutants (POPs) announced by United Nations Environment Programme (UNEP). Although most of these dioxin species were had low toxicity, it was long half-life and easy to diffuse in the atmospheric. PCDD/Fs were by dry and wet deposition and landing in the topsoil and finally through the food chain to enter the human body.

Epidemiological studies have indicated that there are significant correlation between the exposure to fine particulate matter ($PM_{2.5}$) and adverse effects on human health¹⁻⁵. According to the results of the studies in Taiwan, there were correlation between monthly $PM_{2.5}$ concentrations and all cause, cardiovascular diseases, cerebrovascular disease, respiratory diseases, and pneumonia, and other studies also indicated that there were significant correlation between $PM_{2.5}$ and the rate for medical of asthma, arrhythmia, and myocardial infarction⁶⁻⁸. Another study also indicated that the mortality of all-cause mortality (1.18%), cardiovascular disease (1.03%), myocardial infarction (1.22%), stroke (1.76%), and respiratory deaths (1.71%) increased for each 10 µg/m³ increase in the $PM_{2.5}$ concentrations⁹. The fine particles can retain deep in the lungs for long time, and can cause some inflammations¹⁰, while some chemical in the $PM_{2.5}$ can enhance these effects. This study aims to investigate the source apportionment of PCDD/Fs in $PM_{2.5}$ from stationary emission sources in Taiwan.

Materials and methods

During the sampling periods, the flue gas samples were collected from major Taiwanese stationary sources including coal-fired boiler (CFB), municipal waste incinerator (MWI) and electric arc furnace (EAF) were set up. According to the direction of the monsoon, set up the ambient air sampler at upwind and downwind station in the vicinity of stationary pollution sources. To measure the background concentration of PCDD/Fs in PM_{2.5}, the high-altitude background sampling site was selected based on the meteorological information in Central Taiwan (Fig. 1). During CFB flue gas sampling periods (2015/6/12-18), the prevalent winds in the area came from southwest. The ambient sampling site C1 and C2 were located about 3 km from the coal-fired boiler. During the MWI flue gas sampling periods (2015/8/15-20), the prevalent winds in the area also came from southwest. The ambient sampling site M1 and M2 were located about 3 km from the plant. During the EAF flue gas sampling periods (2015/9/19-24), the dominant winds in the area came from northeast. The ambient sampling site E1 and E2 were located about 8 km from the plant. On the other hand, the background sampling station is located at the peak of Mt. Lulin (23.51-°N, 120.92-°E; 2,862 m above mean sea level). Its high elevation means it is generally free from local pollution.

The sampling procedures of stack gases of different facilities were performed following the main guideline of the Taiwan EPA NIEA A212.10B for flue gas collection¹¹. The sampling method of fine particle in flue gas was estimating the flue gas in a fixed flow rate, minimizing the error at the sampling condition, and collecting $PM_{2.5}$ by the cyclone splitter. The PCDD/F compounds were collected using adsorbent tube (XAD-2) and quartz fiber filters.During each sampling periods, one sample was taken every 24 hours in the meantime. Ambient air samples for both vapor phase and particle phase ($PM_{2.5}$) of dioxin compounds were collected using high volume sampling trains (Analitica HVS-PM_{2.5}). The Analitica HVS-PM_{2.5} samplers were equipped with Whatman quartz fiber filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs were used for retaining PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 700 m³ for a typical sampling duration of 1 day. The distributions of water-soluble ions, trace metals, PCDD/Fs and carbon in PM_{2.5} in the vicinity of each emission sources were also analyzed. The PCDD/F content in PM_{2.5} was used to predict the Relative Risk (RR) of cancer (from Taiwan Cancer Registry database), and disease specific death rate at different regions. Finally, source apportionment of atmosphere PCDD/Fs was done using Positive Matrix Factorization (PMF) model.

Results and discussion:

The highest concentration of $PM_{2.5}$ was 0.53 ± 0.39 mg/Nm³ measured in flue gas of CFB, however the highest PCDD/F concentration was 0.206 ± 0.107 ng I-TEQ/Nm³, measured in flue gas of EAF. Higher proportion of

PCDDs over PCDFs were observed in the flue gases of CFB and MWI whereas higher proportion of PCDFs was found in PM_{2.5} and vapor phase in EAF (Fig. 2). In the vicinity of stationary emission sources, the measurements indicated that the mass concentrations of PM_{2.5} were 10.2 ± 1.71 , 12.2 ± 2.08 , 10.1 ± 2.65 , 11.3 ± 3.73 , 29.5 ± 4.29 , and $35.1\pm4.75 \ \mu g/m^3$ at site C1, C2, M1, M2, E1, and E2, respectively. The PM_{2.5} measured at downwind sites were higher than upwind sites. In addition, the concentration of PM_{2.5} was $4.26\pm1.59 \ \mu g/m^3$ at Mt.Lulin (background site). The highest concentration of PM_{2.5} was $35.1\pm4.75 \ \mu g/m^3$ at site E2 (downwind of EAF site). All measurements showed that atmospheric PM_{2.5} concentrations were lower than the air quality standards for PM_{2.5} in Taiwan ($35\mu g/m^3$), except site E2. It may be affected by particulate matter emitted from EAF. The highest dioxin concentration (vapor +solid) was $31.1\pm16.3 \ fg I-TEQ/m^3$ at site C2 (CFB downwind site), average concentration (vapor+solid) was $0.50\pm0.12 \ fg I-TEQ/m^3$ at background site.

For the PM_{2.5} measured in flue gas of CFB, the main metal elements were Ca, Al, Fe; the dominant water-soluble ion was SO₄²⁻, and OC/EC ratio was around 0.78 (Fig. 3). Regarding the PM_{2.5} in flue gas of MWI and EAF, the main metal were Ca and Zn, respectively, Cl⁻ was the major water-soluble ion, and OC/EC ratios were greater than 2.0. According to the principal component analysis (PCA), the Factor 1 and Factor 2 were with 44.8% and 21.5% variance in atmospheric PCDD/Fs of PM_{2.5} (Fig. 4a), and 32.5% and 28.1% variance in atmospheric and emission source PCDD/Fs of PM_{2.5} (Fig. 4b). Fig. 4 also showed the Group 1 and Group 2 were separated to different distribution. That indicated that Group 1 and Group 2 were affected by different emission sources. Group 1 and Group 2 were similar with ambient samples, background samples, respectively in Fig. 4a. On the other hand, Group 1 represented source emission samples when Group 2 were consisted of ambient samples (Fig. 4b). PMF analysis found that the sources of PCDD/Fs were 14.6% from EAF (r=0.81), 52.6% from CFB (r=0.74), 18.0% from traffic (r=0.85) and 14.8% from MWI (r=0.76) (Fig. 5). Furthermore, the high PM_{2.5} concentrations exposure group (Site E2) showed significantly higher health relative risk for all causes of death for both males and females than low PM_{2.5} exposure group (Site M1).

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References:

1. Corbett, J. J., Winebrake, J. J., Green, E. H., Kasibhatla, P., Eyring, V., & Lauer, A. (2007). Mortality from ship emissions: a global assessment. *Environmental science & technology*, 41(24), 8512-8518.

2. Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Speizer, F. E. (1993). An association between air pollution and mortality in six US cities. *New England journal of medicine*, 329(24), 1753-1759.

3. Perez, L., Medina-Ramón, M., Kunzli, N., Alastuey, A., Pey, J., Pérez, N., Sunyer, J. (2009). Size fractionate particulate matter, vehicle traffic, and case-specific daily mortality in Barcelona, Spain. *Environmental science* & *technology*, 43(13), 4707-4714.

4. Pope III, C. A., & Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of the air & waste management association*, 56(6), 709-742.

5. Samoli, E., Stafoggia, M., Rodopoulou, S., Ostro, B., Alessandrini, E., Basagaña, X., Karanasiou, A. (2014). Which specific causes of death are associated with short term exposure to fine and coarse particles in Southern Europe? Results from the MED-PARTICLES project. *Environment International*, 67, 54-61.

6. Bell, M. L., Levy, J. K., & Lin, Z. (2007). The effect of sandstorms and air pollution on cause-specific hospital admissions in Taipei, Taiwan. *Occupational and environmental medicine*.

7. Hsieh, Y.-L., Yang, Y.-H., Wu, T.-N., & Yang, C.-Y. (2010). Air pollution and hospital admissions for myocardial infarction in a subtropical city: Taipei, Taiwan. *Journal of Toxicology and Environmental Health*, Part A, 73(11), 757-765.

8. Tsai, S.-S., Chiu, H.-F., Wu, T.-N., & Yang, C.-Y. (2009). Air pollution and emergency room visits for cardiac arrhythmia in a subtropical city: Taipei, Taiwan. *Inhalation toxicology*, 21(13), 1113-1118.

9. Dai L, Zanobetti A, Koutrakis P, Schwartz JD. (2014). Associations of fine particulate matter species with mortality in the United States: a multicity time-series analysis. *Environ Health Perspect*, 122 837 842

10. Slezakova, K., Morais, S., & do Carmo Pereira, M. (2013). Atmospheric nanoparticles and their impacts on public health: InTech.

11. Chi K.-H., Chang M.-B., Chang S.-H. (2008). Measurement of atmospheric PCDD/F and PCB distributions in the vicinity area of Waelz plant during different operating stages. *Science of The Total Environment*, 391(25), 114-123



Fig. 1 Locations of stationary source and atmospheric PCDD/Fs sampling sites in Taiwan.



Fig.2 The distribution of PCDD/F congeners measured in stack gases at different facilities.



Fig.3 The percentage of chemical species in $PM_{2.5}$ measured in stack gases at different facilities.



Fig.4 Score plot from principal component analysis of PCDD/Fs at (a) the vicinity of stationary pollution and (b) compared with emissions.



Fig.5 Source apportionment of atmospheric PCDD/Fs at the vicinity of stationary pollution in Taiwan by using PMF.