THE CHARACTERISTIC OF PCDD/F IN FINE PARTICLE FROM FLUE GAS AND SOURCE APPORTIONMENT VIA POSITIVE MATRIX FACTORIZATION IN TAIWAN

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Introduction

Dioxins (polychlorinated dibenzo-p-dioxin, PCDDs) and furans (polychlorinated dibenzofurans, PCDFs) and other pollutants as persistent organic pollutants which listed "hazardous air pollutants (Hazardous Air Pollutants, HAPs) substances. PCDD/Fs are formed and released unintentionally from anthropogenic sources. PCDD/Fs are ubiquitous in air, water, soil, sediment, plants, and are released as byproducts during various thermal processes of combustion, incineration, and metal smelting[1,2,3]. Municipal solid waste incinerators (MSWIs) have been historically associated with emissions of toxic chemicals, such as PCDD/Fs and heavy metals, among other pollutants[4]. Particularly, the contents of dioxin-like compounds and other pollutants exist in suspended particles. $PM_{2.5}$ (particle matter with an aerodynamic of less than or equal to 2.5 μm) is a crucial air pollutant on the basis of its adverse human health effects and degradation of visibility and the chemical composition of $PM_{2.5}$ is a key to fully understanding and assessing its impacts on climate, air quality[5]. Positive matrix factorization (PMF) has become a factor analytic (FA) model of choice for quantitative source apportionment of contaminants in many air quality monitoring studies[6,7]. In this study, the PCDD/Fs major emission sources such as industrial boiler, municipal waste incinerators (MWI), electric arc furnace (EAF), and the vicinity of stationary pollution sources have been investigated regarding the distribution of PCDD/Fs, trace metals, carbon, water-soluble ions in $PM_{2.5}$. The PMF model has been used in this study to analyze the source apportionment of PCDD/Fs. The objective of this study is to figure out the chemical profiles of stack gas and the vicinity atmosphere, moreover, estimate the relative contribution of various sources around the stationary pollution source regions.

Materials and methods

In this study, the flue gas samples were collected for analysis of PCDD/Fs from three stationary pollution sources and ambient air samples in the vicinity of the three investigated industries simultaneously duration of 24 hours during summer season 2015. We chose industrial boiler, MWI, and EAF is located in the industrial region of Taoyuan county, Taipei city, and Miaoli county, respectively. According to the direction of the monsoon, we set up the sampler at upwind and downwind site in the vicinity of stationary pollution sources (Figure 1). In addition, the atmospheric concentrations of seventeen 2, 3, 7, 8-substituted PCDD/Fs, trace metal content and water soluble ions in suspended particles were monitored in central Taiwan (Mountain Lulin) as the background site. The sampling procedures were performed following the main guideline of the Taiwan EPA NIEA A101.75C for flue gas collection, European Union EN-14907 $PM_{2.5}$ for ambient air collection. Both of stack gas and ambient air samples for both vapor phase and solid phase of dioxin-liked compounds were collected. The ambient sampling instruments consisted of HVS $PM_{2.5}$ sampler (Analitica), the 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. HVS $PM_{2.5}$ sampler (Analitica) was connected to a vacuum pump and 700 m³ of air mass was collected in 24 h at a sampling flow rate of 500 L/m³. In this study, the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed by high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (JEOL JMS-700). The quartz fiber filter was used to determine a range of elements (Al, Fe, Na, Mg, K, Ca, Sr, Ba, Ti, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sn, Sb, Tl, Pb, V, Cr, As, Y, Se, Zr, Ge, Rb, Cs, Ga, La, Ce, Nd) by inductively coupled plasma-mass spectrometry (ICP-MS)(NexIon 300X, Perkin-Elmer). The quartz fiber filter was used to analyze the water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) by ion chromatography (IC). Organic carbon (OC) and elemental carbon (EC) were measured with IMPROVE_A thermal/optical reflectance (TOR) protocol. Besides, the software Positive Matrix Factorization (PMF, version 5.0), available from U.S. EPA (2014) was used to identify and quantify sources that contribute to ambient PCDD/F concentrations in the vicinity of stationary pollution sources.

Results and discussion

The results showed that the highest concentration of TPM (3.73 mg/Nm³) and $PM_{2.5}$ (0.53±0.39 mg/Nm³) in industrial boiler flue gas, the highest concentration of dioxin was 0.206±0.107 ng I-TEQ/Nm³ in EAF

flue gas (Table 1). The distribution of dioxin species, industrial boiler flue gas and MWI flue gas had higher proportion of PCDDs than PCDFs, but EAF flue gas had higher proportion of PCDFs than PCDDs in $PM_{2.5}$ and vapor phase. In industrial boiler flue gas of $PM_{2.5}$, the main metal were Ca, Al, Fe, the highest water-soluble ions was SO_4^{2-} ,and OC/EC ratio was 0.78. In MWI and EAF flue gas of $PM_{2.5}$, the main metal were Ca and Zn respectively, the highest water-soluble ions were Cl^- and OC/EC ratios were greater than 2.0 (Figure 2). An OC/EC ratio greater than 2.0-2.2 has been used for identification and evaluation of secondary organic aerosols[8,9]. In the vicinity of stationary sources, the highest concentration of $PM_{2.5}$ was 35.1±4.75 μg/m^3 at site E (investigated EAF downwind site), the highest dioxin concentration was 31.1±16.3 fg I-TEQ/m^3 at site B (investigated industrial boiler downwind site) (Table 2). All the measurements indicated that the atmospheric PCDD/Fs measured in this study were all lower than the air quality standards for dioxins in Japan (0.6 pg-TEQ/m^3). The distribution of atmospheric PCDD/Fs species around the stationary sources were PCDFs in vapor phase, the main metal were Na, K and Ca, the highest concentrations of water-soluble ions were SO_4^{2-},and OC/EC ratios were greater than 2.0 that indicated the species generated from secondary aerosol (Figure 3). The result (Table 3) of PMF also showed that analysis of atmospheric dioxins in the vicinity of industrial boiler, around 23.7% dioxins were provided from industrial boiler investigated. In the vicinity of the MWI, around 8.3% from the incinerator investigated. In the vicinity of the EAF, around 52.2% from the EAF investigated. The results of this study has been initially completed the fingerprint characteristics of industrial boiler, MWI, EAF in Taiwan.

Acknowledgements

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Table 1. PCDD/Fs concentration in vapor and solid (PM and $PM_{2.5}$) phases measured at different stationary plant.

ΣPCDD/Fs (ng I-TEQ/Nm^3)	Vapor	PM	Vapor	$PM_{2.5}$
Industrial boiler	0.006	0.002	0.003±0.003	0.0005±0.0003
MWI	0.017±0.005	0.005±0.001	0.026±0.013	0.004±0.002
EAF	0.202±0.030	0.004±0.002	0.205±0.106	0.001±0.0003

Table 2. Atmospheric PCDD/Fs concentrations in vapor and solid (PM$_{2.5}$) phases measured at different sampling sites

Sampling Site	A (n=3)		B(n=3)	
	Vapor	PM$_{2.5}$	Vapor	PM$_{2.5}$
ΣPCDD/Fs (fg I-TEQ/m^3)	12.7±6.69	3.54±2.47	25.5±13.4	5.55±2.91
ΣPCDD/Fs (vapor+solid)	16.3±9.14		31.1±16.3	
Sampling Site	C (n=3)		D (n=3)	
	Vapor	PM$_{2.5}$	Vapor	PM$_{2.5}$
ΣPCDD/Fs (fg I-TEQ/m^3)	2.98±1.71	1.27±0.724	12.3±8.10	2.55±2.79
ΣPCDD/Fs (vapor+solid)	4.25±2.43		15.4±9.48	
Sampling Site	E (n=3)		F (n=3)	
	Vapor	PM$_{2.5}$	Vapor	PM$_{2.5}$
ΣPCDD/Fs (fg I-TEQ/m^3)	13.0±3.93	6.34±0.929	21.1±0.760	8.02±2.15
ΣPCDD/Fs (vapor+solid)	20.3±4.66		29.3±2.06	

Table 3. PCDD/Fs source apportionment with PMF analysis at different atmospheric ambient sampling regions.

Atmospheric ambient regions	Potential source	Correlation	Percentage (%)
Industrial boiler	Industrial boiler investigated	r=0.992	23.7
	Sintering plant	r=0.987	20.0
	Open burning	r=0.99	56.3
MWI	Open burning	r=0.92	28.5
	Secondary aluminum	r=0.97	25.6
	Incinerator investigated	r=0.92	8.3
	Industrial waste incinerator	r=0.99	37.6
EAF	Northeast monsoon event	r=0.96	13.1
	Open burning	r=0.98	34.7
	EAF investigated	r=0.99	52.2
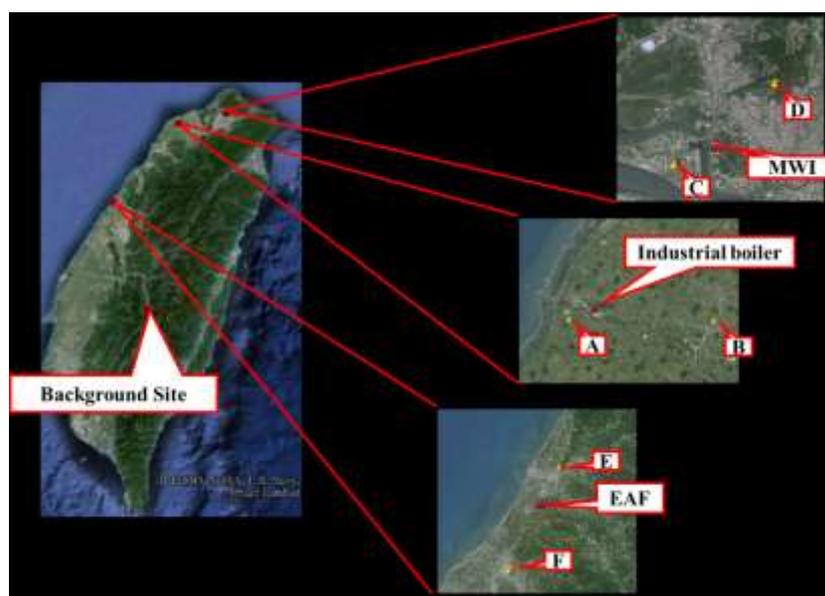
Figure 1.   Relative sampling locations in Taiwan.
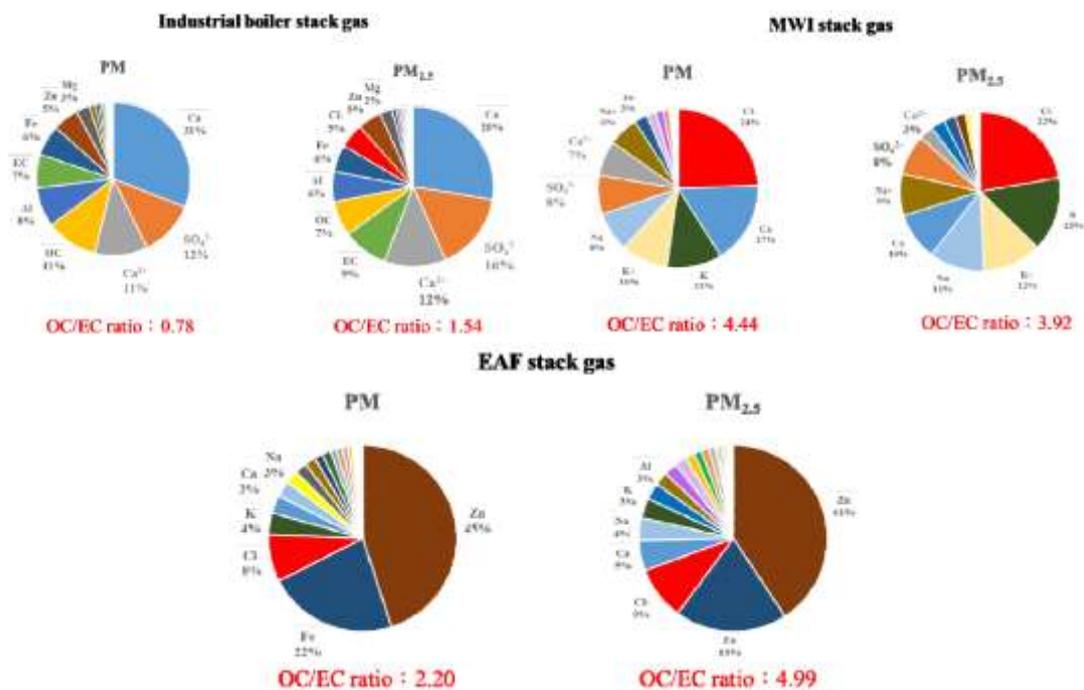
Figure 2.   The percentage of chemical species in PM$_{2.5}$ at different stationary stack gases.
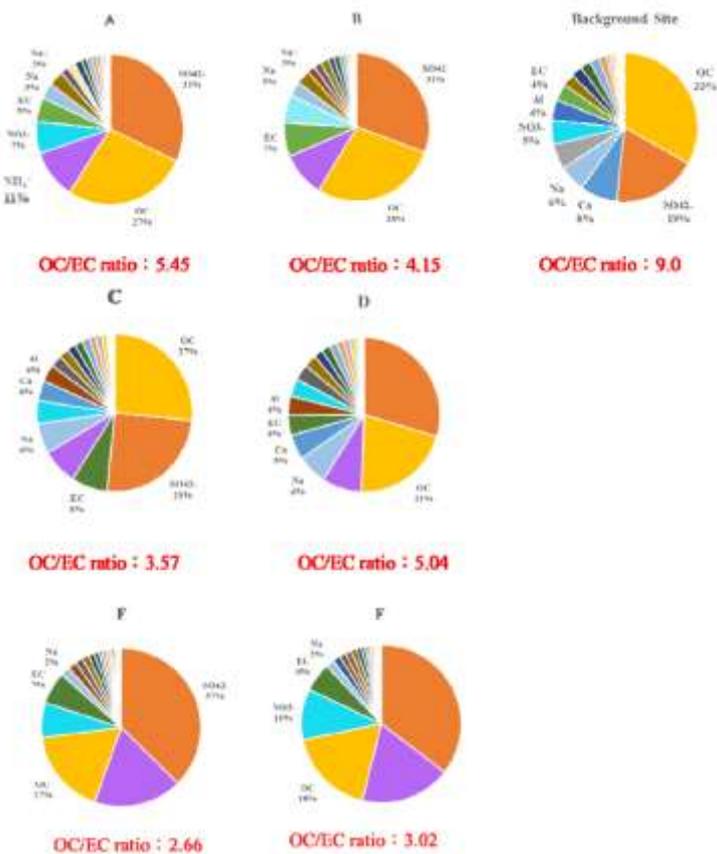
Figure 3.   The percentage of atmospheric chemical species in PM$_{2.5}$ in the vicinity of stationary

pollution sources.