EVALUATION OF ATMOSPHERIC PCDD/F COMPOUNDS IN TSP AND $PM_{2.5}$: MEASUREMENT AND THE RELATIVE HEALTH RISK IN TAIWAN

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Introduction

The standard of $PM_{2.5}$ (fine particles, diameters <2.5 μm) was established in 1997 by the US EPA to protect public health. The standard has been strengthened in 2012 and currently set at 35 μg/m^3 for 24 hrs and 15 μg/m^3 for annual average in the U.S. Epidemiological and toxicological studies have demonstrated that increased particulate matter (PM) cause increased cardiovascular mortality and morbidity, and this PM toxicity may increase as the particle size decreases. According to the epidemiological studies in Taiwan, National Mortality Registry data were used to investigate the risk of $PM_{2.5}$, and the studies indicated that the associations of total mortality and cardio-respiratory mortality with monthly $PM_{2.5}$ concentrations were more consistent in Taipei city. Each 10 μg/m^3 elevation in $PM_{2.5}$ air pollution was associated with approximately 4%, 6%, 8% increased risk of all-cause, cardiopulmonary, and lung cancer mortality, respectively[1]. For these cardiovascular causes of death, a 10 μg/m^3 elevation in $PM_{2.5}$ was associated with 8% to 18% increases in mortality risk, with comparable or larger risks being observed for smokers relative to nonsmokers[2]. Recently, Taiwan government set the limit of ambient $PM_{2.5}$ for different air quality monitoring network and will be enforced starting from 14th May 2012. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are announced as one of the sixty-five environmental hormones in Environment Agency of Japan, and they are regulated as one of the twenty-one persistent organic pollutants (POPs) under the Stockholm Convention in 2009. PCDD/Fs are formed and released unintentionally from anthropogenic sources. Particularly, the contents of dioxin-like compounds exist in suspended particles. In United States, hazardous air pollutants (HAPs) have caused much public concerns due to serious health effects they may cause. Due to their toxicity, endocrine disturbing effect, carcinogenicity and bioaccumulation, PCDD/F content in $PM_{2.5}$ have raised great public concern worldwide. Thus, we need to build up the database of $PM_{2.5}$ including characteristics of PCDD/F content in Taiwan.

Materials and methods

In this study, the ambient air samples were collected for the analysis of PCDD/Fs and DL-PCBs from five locations over duration of 24 hrs during winter and summer season 2012-2013, using both TSP and $PM_{2.5}$ samplers. Locations with diverse characteristic such as urban (campus of National Taiwan University), traffic-affected zones (Taipei city) and sub-urban (campus of National Yang Ming University) in northern Taiwan, two industrial area were also selected in central Taiwan (Figure 1). The sampling procedures were performed following the main guidelines of the Taiwan-EPA NIEA A809.11B, US-EPA $PM_{2.5}$-Federal Reference Method, and European Union EN-14907 $PM_{2.5}$. The sampling instruments consisted of a HVS TSP sampler (Shibata, HV-700), FRM $PM_{2.5}$ sampler (PQ-200), and HVS $PM_{2.5}$ sampler (Analitica). Ambient air samples for both vapor phase and solid phase of dioxin-liked compounds were collected. 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. The main difference between these devices refers to the size of the particles that can reach the filter surface. The TSP sampler allows trapping the whole particulate, while in the $PM_{2.5}$ system only particles with a size below 2.5 μm can be collected. The HVS TSP sampler (Shibata, HV-700) and HVS $PM_{2.5}$ sampler (Analitica) was connected to a vacuum pump and 700 m^3 of air mass was collected in 24 h at a sampling flow rate of 500 L/m^3. The FRM $PM_{2.5}$ sampler (PQ-200) were taken every 24 h and collected operating the instrument at an average ambient airflow of 16.7 L/m^3. The PUF and filter samples were than Soxhlet extracted with toluene for 24 hrs, treated with concentrated sulfuric acid, and then passed through a series of clean-up columns containing sulfuric acid-silica gel, acidic aluminum oxide and celite/carbon. In this study, the seventeen 2,3,7,8-substituted PCDD/F congeners and 12 DL-PCBs were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (JEOL

JMS-700) equipped with a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W). In addition, The software Positive Matrix Factorization (PMF, version 3.0), available from U.S. EPA (2012) was used to identify and quantify sources that contribute to ambient PCDD/F concentrations in Taipei city.

Results and discussion

Table 1 indicated the daily average TSP and $PM_{2.5}$ concentrations measured at different area in this study, the significantly higher TSP (185±33.1 μg/m^3) and $PM_{2.5}$ (25.8 ± 4.74 μg/m^3) concentrations were measured at traffic-affected zone and urban station, respectively. In addition, the results measured at urban station indicated that the $PM_{2.5}$ mass concentration followed by Taiwan NIEA A205.11C $PM_{2.5}$ method was 24.6±4.01 μg/m^3, and 25.0 ± 4.42 μg/m^3 followed by European Union EN-14907 $PM_{2.5}$ method. According to the methods of EN-14907 and Taiwan NIEA A205.11C, the relative difference between those two $PM_{2.5}$ mass sampling methods was about 5%. For the PCDD/F analysis, Fig. 2 demonstrated that the PCDD/Fs concentrations of TSP samples were 28.2±3.51, 12.4±7.22, 10.9±8.11, 321±108, and 57.6±45.4 fg WHO-TEQ/m^3 at urban, suburban, traffic-affected zone, western industrial area, and central industrial area, respectively. Furthermore, 23.7±3.01, 9.37±7.86, 8.34±6.22, 275±84.2, 47.7±37.2fg WHO-TEQ/ m^3 for $PM_{2.5}$ samples were measured at urban, suburban, traffic-affected zone, western industrial area, and central industrial area, respectively. In addition, the distribution of vapor/solid-phase PCDD/F concentrations in TSP and $PM_{2.5}$ samples were also illustrated in Fig. 2. Over 60% atmospheric PCDD/Fs were distributed in solid phase. Comparing the results between the $PM_{2.5}$ and TSP samples, the PCDD/F concentrations in $PM_{2.5}$ samples account for 58% to 74% of TSP samples. Hence, the fine particles contained higher levels of PCDD/Fs than coarse particles. The PCDD/F content in $PM_{2.5}$ and TSP were also illustrated in Fig. 3. The results showed that the fine particles contained with higher levels of PCDD/Fs than coarse particles. Especially for the western industrial area, the total quantity of PCDD/Fs in $PM_{2.5}$ and TSP were higher than other station. Yoichi et al.(1998)[5] investigated the particle size distribution of PCDD/Fs in atmospheric and indicated that over 50% of PCDD/Fs were found on small particles with the diameters less than 1.1μm, and providing over 47% of the total TEQs. In this study, the lifetime average daily dose (LADD) and excess cancer risk (ECR) were also evaluated at different sites in Taiwan (Table 2). For PCDD/F concentration of $PM_{2.5}$ samples, the results indicated that the western industrial area (0.275 pg WHO-TEQ/m^3) were much higher than the central industrial area (0.048 pg WHO-TEQ/m^3), urban station (0.024 pg WHO-TEQ/m^3), suburban station (0.009 pg WHO-TEQ/m^3), and traffic-affected zone (0.008 pg WHO-TEQ/m^3). The results of LADD and ECR in the western industrial area (0.059 pg WHO-TEQ/day/kg and 5.89×10^{-6}, respectively) and the central industrial area (0.010 pg WHO-TEQ/day/kg and 1.02×10^{-6}, respectively) were higher than that for urban station (0.005 pg WHO-TEQ/day/kg and 5.08×10^{-7}, respectively), suburban station (0.002 pg WHO-TEQ/day/kg and 2.01×10^{-7}, respectively), and traffic-affected zone (0.002 pg WHO-TEQ/day/kg and 1.79×10^{-7}, respectively). The ECR values of the western industrial area and the central industrial area were higher than 10^{-6}. The results also indicated that the residents living around of the industrial area had high health relative risk. Wang et al. (2003)[6] also indicated that the LADD and ECR of residents living at the nearby of the industrial area were higher than urban area, residential area, and rural area in Taiwan. In addition, Table 3 indicated that the health relative risk of the all cause (Relative risk=1.200, CI=1.118-1.289, P<0.0001) and liver cancer (Relative risk=1.567, CI=1.162-2.113, P=0.0032) in high PCDD/F exposure group were significant higher than low PCDD/F exposure group. The high mass concentration of $PM_{2.5}$ is not necessarily to have high health relative risk, so the chemical content and toxicity of $PM_{2.5}$ must to be investigated. According to the statistical results of PMF analysis (Fig. 4), the major contributors of atmospheric PCDD/Fs for TSP and $PM_{2.5}$ samples observed at urban in Taipei, Taiwan were IWI (9.6% for TSP; 22.5% for $PM_{2.5}$), MSWI (47.4% for TSP; 57.2% for $PM_{2.5}$), crematorium (18.2% for TSP; 4.5% for $PM_{2.5}$), long-range transport (24.7% for TSP; 15.7% for $PM_{2.5}$), respectively. Our results indicated that fine particles contain larger amounts of PCDD/Fs than coarse particles and potentially had a more serious impact on air quality and public health. When the potential health risk by the inhalation of $PM_{2.5}$ is going to be investigated, the PCDD/Fs associated with $PM_{2.5}$ should be seriously taken into account.

Acknowledgements

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Table 1. Daily average concentration ($\mu g/m^3$) of TSP and $PM_{2.5}$ measured at different areas.

	Urban (n=12)	Suburban (n=6)	Traffic-affected zone (n=6)	Western industrial area (n=4)	Central industrial area (n=4)
TSP ($\mu g/m^3$)	133 ± 26.7	137 ± 28.3	185 ± 33.1	113 ± 20.8	101 ± 41.0
$PM_{2.5EU}$ ($\mu g/m^3$)	25.8 ± 4.74	12.7 ± 3.75	14.1 ± 8.85	19.2 ± 4.14	15.2 ± 3.38

Table 2. PCDD/F concentration, the lifetime average daily dose (LADD), and excess cancer risks (ECR) at different areas.

		Urban	Suburban	Traffic-affected zone	Central industrial area	Western industrial area
PCDD/F concentration (pg WHO-TEQ/m^3)	$PM_{2.5}$	0.024	0.009	0.008	0.048	0.275
LADD (pg WHO-TEQ/day/kg)	$PM_{2.5}$	0.005	0.002	0.002	0.010	0.059
ECR	$PM_{2.5}$	5.08×10^{-7}	2.01×10^{-7}	1.79×10^{-7}	1.02×10^{-6}	5.89×10^{-6}

Table 3. The health relative risk of high exposure group and low exposure group in $PM_{2.5}$ and PCDD/Fs.

	$PM_{2.5}$			PCDD/Fs		
	Relative Risk	95% CI	*p-value*	Relative Risk	95% CI	*p-value*
All cause	0.925	0.889-0.964	0.0002	1.2	1.118-1.289	<0.0001
Cardiovascular	1.111	0.966-1.279	0.1405	1.024	0.770-1.363	0.868
Pneumonia	0.662	0.544-0.806	<0.0001	1.081	0.789-1.483	0.627
All cancer	0.893	0.829-0.962	0.0027	1.064	0.929-1.218	0.3708
Lung cancer	0.877	0.750-1.049	0.1607	1.146	0.853-1.540	0.3656
Liver cancer	1.206	1.013-1.434	0.035	1.567	1.162-2.113	0.0032
Colon cancer	0.893	0.709-1.126	0.3395	1.027	0.668-1.579	0.9042

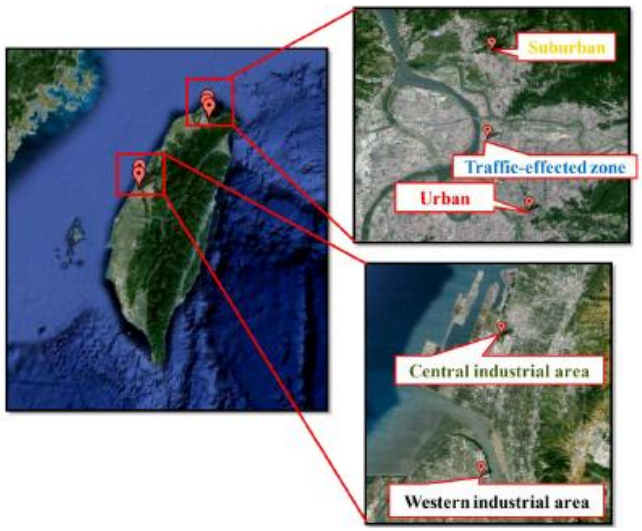

Figure 1. Relative sampling locations in Taiwan.

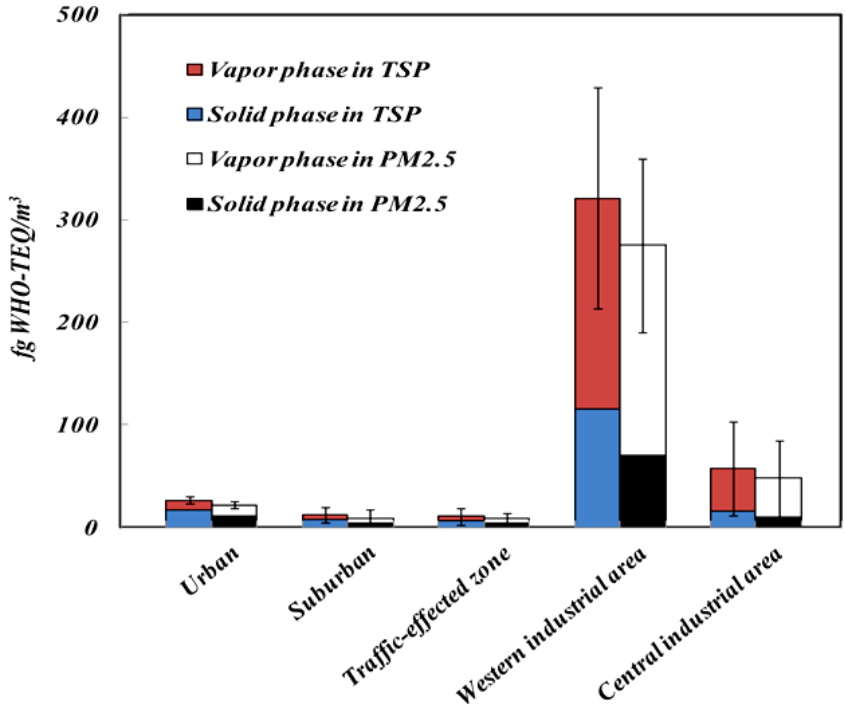

Figure 2. Atmospheric PCDD/F concentrations of TSP and $PM_{2.5}$ samples in solid phase and vapor phase.

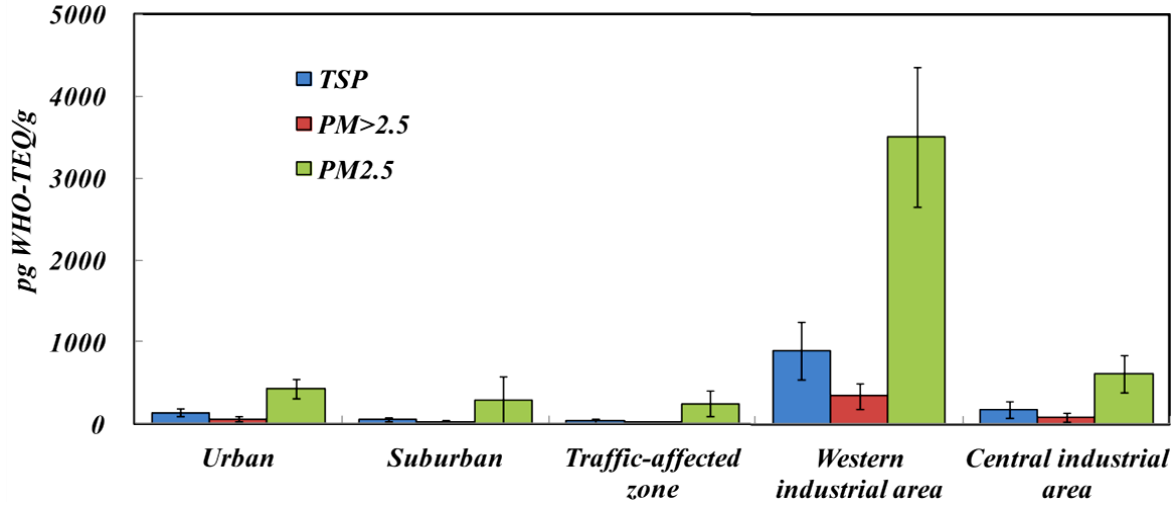

Figure 3. The total quantity of PCDD/Fs in $PM_{2.5}$ and TSP.

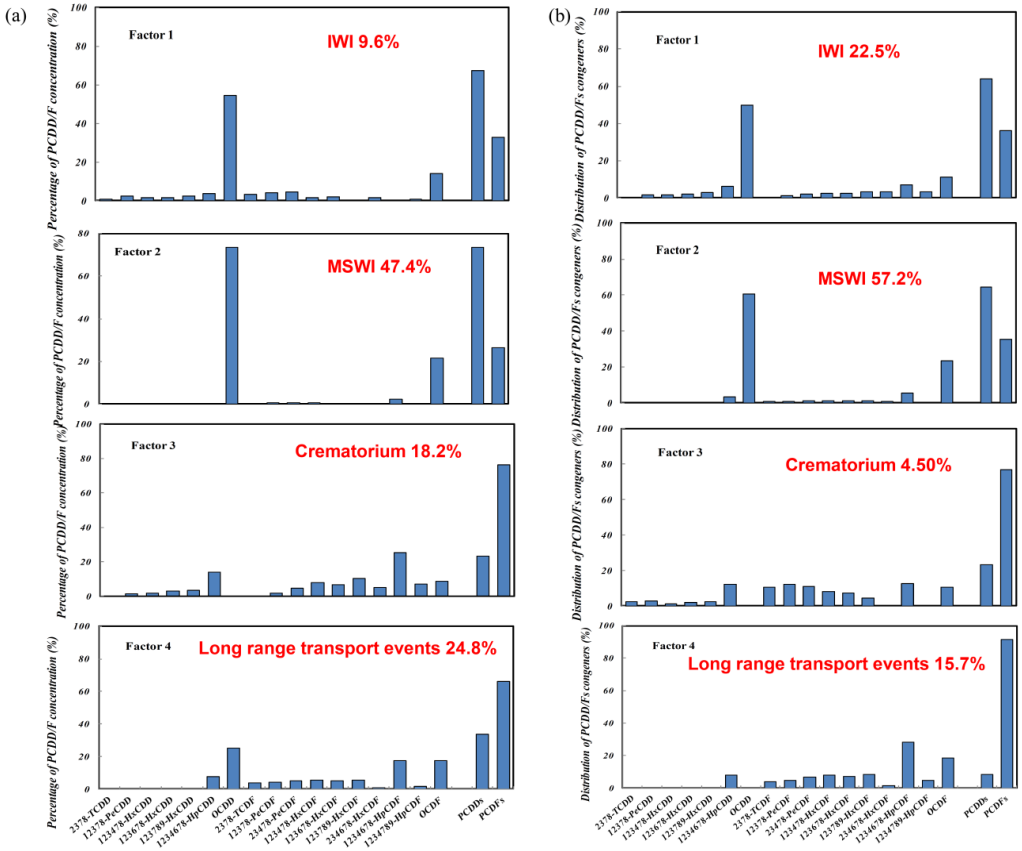

Figure 4. Distribution of PCDD/Fs congener with PMF in (a) TSP and (b) $PM_{2.5}$ in Taipei.