COMPARISON OF ATMOSPHERIC PCDD/Fs AND PCBs BETWEEN TSP AND $PM_{2.5}$ AEROSOL IN NORTHERN TAIWAN

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Introduction

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[1]. 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[2]. On the other hand, for the cardiovascular causes of death, a 10 μg/m^3 in $PM_{2.5}$ was associated with 8% to 18% increases in mortality risk, and larger risks being observed for smokers relative to nonsmokers[3]. Airborne particulate matter (PM) is the focus of public interest since ambient $PM_{2.5}$ (fine particles, diameters <2.5 μm) concentrations have been significantly related to health effects by epidemiological studies. US EPA has set up standard for fine PM ($PM_{2.5}$) in addition to PM_{10} in 1997. In 2006, they revised the criteria by lowering the standard for $PM_{2.5}$. 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. Dioxins 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. Dioxins 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. People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects. Due to their toxicity, endocrine disturbing effect, carcinogenicity and bioaccumulation, dioxins 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 dioxin content in Taiwan.

Materials and methods

Taipei is the administrative capital city of Taiwan. Ambient air samples were collected for the analysis of PCDD/Fs and DL-PCBs from three locations over duration of 24 h on November 7–13th 2012, December 10–13th 2012 and December 24–26th 2012, using both TSP and $PM_{2.5}$ samplers. Locations with diverse characteristic such as urban (National Taiwan University), traffic-affected zones (Datong station) and vicinity (National Yang Ming University) of the municipal solid waste incinerator (MWI) were selected (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 (#77, #81, #105, #114, #118, #123, #126, #156, #157, #167, #169 and #189) were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (Waters AutoSpec-Ultima and JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W).

Results and discussion

The measurements indicated that mean concentrations were 134 ± 18.5 μg/m^3 for TSP and 25.0 ± 4.40 μg/m^3 for $PM_{2.5}$ at urban station in Taipei city. According to the methods of EN-14907 and US-EPA FRM, the difference was about 1.60% in $PM_{2.5}$. The ratio of the U.S. EPA FRM and FEM $PM_{2.5}$ was about 0.77. According to NIEA A809.11B and EN-14907, the total PCDD/Fs and DL-PCBs concentrations (mean TEQ values) were 30.7 ± 5.26 fg WHO-TEQ / m^3 for the TSP samples and 25.5 ± 4.74 fg WHO-TEQ / m^3 for the $PM_{2.5}$ samples (Table 1). The mean DL-PCBs concentrations (mean TEQ values) were 2.40 ± 0.88 fg WHO-TEQ / m^3 for the TSP samples and 1.75 ± 0.64 fg WHO-TEQ / m^3 for the $PM_{2.5}$ samples (Table 1). Comparing the results for the $PM_{2.5}$ and TSP samples, the total TEQs PCDD/Fs and DL-PCBs concentrations in the $PM_{2.5}$ samples were about 61.0% of the TSP samples, indicating that the fine particles contained higher levels of PCDD/Fs than coarse particles. The ratio of PCDDs/PCDFs is often used as a unique fingerprint for PCDD/F sources. The ratio of ΣPCDD/ΣPCDF from chemical reaction formation is greater than 1, while de novo synthesis during combustion processes normally shows a ratio of ΣPCDD/ΣPCDF less than 1. In this study, the ratio of ΣPCDD/ΣPCDF was about 0.65. The total quantity of PCDD/Fs and DL-PCBs adsorbed onto suspended particles was 456 ± 129 pg WHO-TEQ/g-$PM_{2.5}$, and 67.6 ± 42.8 pg WHO-TEQ/g-$PM_{>2.5}$, respectively. The results indicated that the total quantity of PCDD/Fs and DL-PCBs in $PM_{2.5}$ was 6-fold more than $PM_{>2.5}$ (Table 2). Congener profiles of PCDD/Fs and DL-PCBs in air samples in Taipei city were illustrated in Figure 2 and Figure 3, respectively. Generally, the concentrations of PCDF homologues in both the TSP and $PM_{2.5}$ samples were higher than the PCDD homologues with the same degree of chlorination. The dominant congeners for TSP were octachlorinated dibenzo*p*-dioxin (OCDD) (43.5%), octachlorinated dibenzo-*p*-furans (OCDF) (16.0%), 1,2,3,4,6,7,8-heptachlorinated dibenzo-*p*-furans (HpCDF) (9.00%), and all these together accounted for more than 67.5% of total PCDD/Fs concentration and these are all highly chlorinated PCDD/Fs. For the PCDD/Fs in $PM_{2.5}$, the dominant congeners were OCDD(49.8%), OCDF(14.4%), 1,2,3,4,6,7,8-HpCDF(7.79%). OCDD had the lowest toxic potency (toxic equivalency factor proposed WHO, WHO_{2005}-TEF=0.0003), thus significantly lowering the total PCDD/Fs WHO-TEQ concentration. The most abundant congener patterns of DL-PCBs for TSP in the ambient air were PCB 118 (48.6%) followed by PCB 105 (24.3%) and PCB 77(15.2%). The most dominant contributor to the total TEQ of DL-PCBs was PCB 126 (88.0%) for TSP and PCB 126 (86.0%) for $PM_{2.5}$. The total PCDD/Fs and DL-PCBs concentrations for TSP and $PM_{2.5}$ had similarly trend in this present study. Vapor-solid partitioning of PCDD/Fs and DL-PCBs in Taipei were shown in Figure 4. In general, the concentration of solid phase PCDD/Fs accounted for 61.0% and 46.7% of the total PCDD/Fs concentration for TSP and $PM_{2.5}$ respectively. The concentration of solid phase DL-PCBs accounted for 24.2% and 12.1% of the total concentration for TSP and $PM_{2.5}$ respectively. Most of the DL-PCBs were in the vapor phase. For PCDD/Fs, Yoichi et al.(1998)[4] indicated that about 50% of the total PCDD/Fs were found on small particles with less than 1.1 μm, and providing over 47% of the total TEQs. According to the study[5], airborne particles was fractionated into four different size (<1.5, 1.5–2.5, 2.5–5.0, >5.0 μm), and found that more than 60% of particles were smaller than 5.0 μm, and the particles contained more than 86% of the total PCDD/Fs in solid phase. However, Ward et al. (2006)[6] indicated that the particles collected in the smoke impaired Missoula valley, by using the FRM $PM_{2.5}$ sampler (PQ-200), was not composed of significant amounts of PCDD/Fs during the smoke events. For PCBs, Wenliang et al.(2010)[7] indicated that size distribution of particle-bound PCBs showed that higher chlorinated CBs tended to the fine particles. And about the different between TSP and $PM_{2.5}$, the study indicated that total PCDD/Fs and TEQs concentrations in the $PM_{2.5}$ samples were about 66.8%-108% of the TSP samples, and the results showed that fine particles contained higher levels of PCDD/Fs than coarse particles[8]. Thus, PCDD/Fs and PCBs in ambient air tended to partition more to the fine particles. This had similarly trend in the present study. The results obtained in this study indicated that PCDD/Fs and DL-PCBs levels found using the TSP and $PM_{2.5}$ sampling systems were comparable, thus, we can to build up the database of $PM_{2.5}$ including characteristics of

dioxin content in Taiwan. 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 dioxins associated with $PM_{2.5}$ should be seriously taken into account.

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Table 1 PCDD/Fs and DL-PCBs (fg WHO-TEQ/m^3)

Sample concentration	NIEA A809.11B		EN-14907		$PM_{2.5}$/TSP Ratio
	Vapor (n=8)	TSP(n=8)	Vapor (n=8)	$PM_{2.5}$(n=8)	
PCDDs	4.41 ± 2.55	6.44 ± 2.27	5.35 ± 2.39	3.97 ± 1.57	0.63
PCDFs	6.76 ± 1.72	10.7 ± 3.66	7.38 ± 0.79	7.05 ± 2.96	0.65
ΣPCDD/Fs	11.2 ± 3.35	17.1 ± 4.44	12.7 ± 2.48	11.0 ± 3.60	0.64
ΣDL-PCBs	1.82 ± 0.61	0.57 ± 0.33	1.53 ± 0.58	0.21 ± 0.09	0.33
Total WHO- TEQ	13.0 ± 3.22	17.7 ± 4.68	14.3 ± 2.40	11.2 ± 3.62	0.63
ΣPCDDs/ΣPCDFs Ratio	0.68	0.60	0.73	0.57	
Total WHO- TEQ(Vapor + Solid)	30.7 ± 5.26		25.5 ± 4.74		

Table 2 Mass concentrations

	Concentration (n=8)
TSP(μg/m^3)	134 ± 18.5
$PM_{2.5}$(μg/m^3)	25.0 ± 4.40
pg WHO-TEQ/g ($PM_{>2.5}$)	67.6 ± 42.8
pg WHO-TEQ/g ($PM_{2.5}$)	456 ± 129

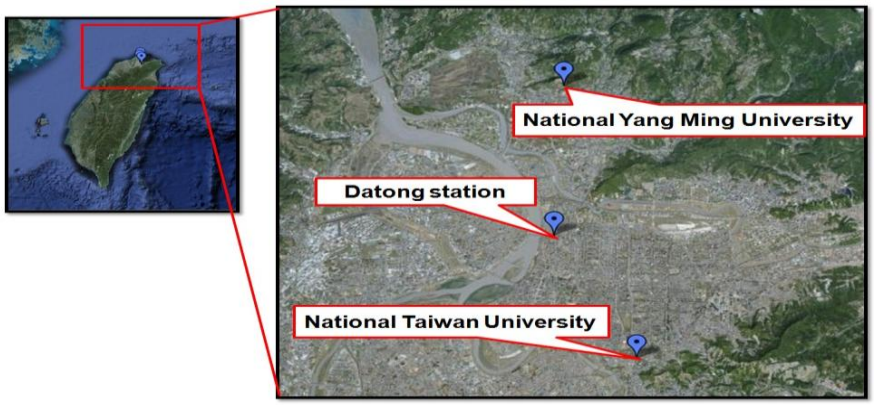

Figure 1 Relative locations of three sampling sites in Taipei Taiwan

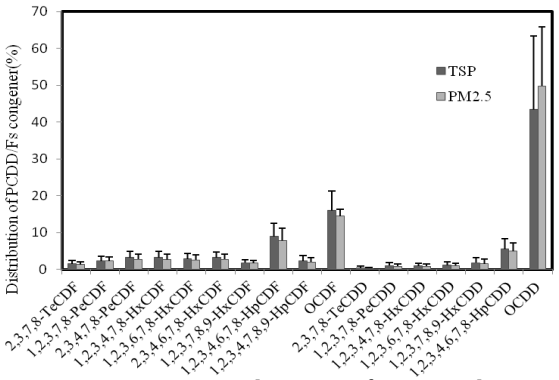

Figure 2 Distribution of atmospheric PCDD/F congener in TSP and $PM_{2.5}$ measurements.

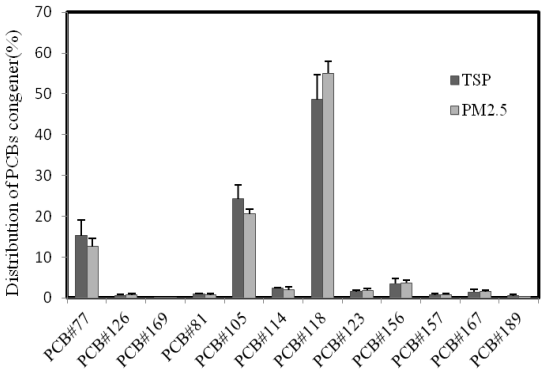

Figure 3 Distribution of atmospheric DL-PCB congener in TSP and $PM_{2.5}$ measurements.

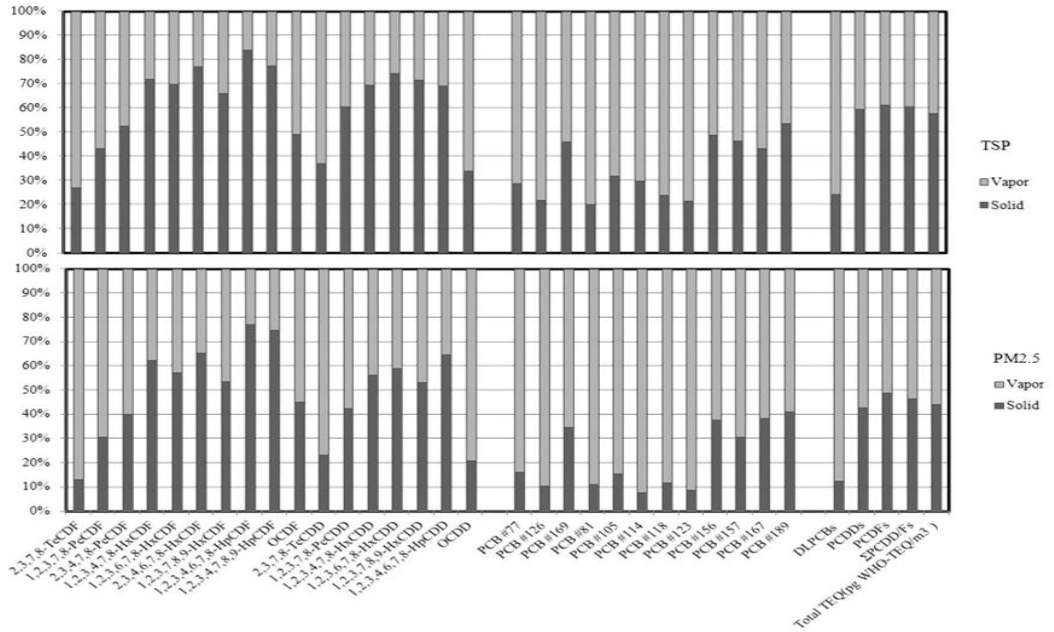

Figure 4 Comparison of vapor/solid phase partitioning of PCDD/F and PCB congeners in ambient air between TSP and $PM_{2.5}$ measurements.