Spatial and Temporal Variation of PM$_{2.5}$ and Atmospheric PCDD/Fs in Northern Taiwan during Winter Monsoon and Local Pollution Episodes

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ABSTRACT

Winter monsoonal air masses traveling from Inner Mongolia to downwind nations can transport cold temperature and air pollutants. This study investigated the effects of the long-range transport (LRT) of air pollutants by northeastern monsoons and local pollution (LP) episodes on atmospheric PM$_{2.5}$, polychlorinated dibenzo-p-dioxin (PCDD), and polychlorinated dibenzofuran (PCDF) concentrations in northern Taiwan during the winters of 2014 and 2015. Air samples were collected in rural (Rural Site 1 was mountainous; Rural Site 2 was coastal) and urban (Urban Site 1 was urban; Urban Site 2 was suburban) areas in northern Taiwan as well as at a background site (Lulin Mountain) in central Taiwan. Atmospheric PCDD/F concentrations measured at different sites ranged from 11.0 ± 2.70 to 39.7 ± 22.7 fg international toxicity equivalency quantity (I-TEQ) m$^{-3}$ in 2014 and 7.99 ± 5.58 to 17.5 ± 12.3 fg I-TEQ m$^{-3}$ in 2015. During LRT and LP, the proportion of PCDFs was higher than that of PCDDs. Rural Site 1 (122 pg I-TEQ g$^{-1}$) and Urban Site 2 (82.4 pg I-TEQ g$^{-1}$) had the highest PCDD/F content in PM$_{2.5}$ during LRT and LP, respectively. The proportion of PCDD increased when neither event occurred. Principal component analysis revealed relationships between the component variance of PCDD/Fs and the sampling site altitude. The results of potential source contribution function (PSCF) suggested that the cold-air masses reaching Taiwan via LRT were most likely arriving from northern China, with pollutants collected along their routes. Wind speed and direction and geographical factors affected the accumulation of air pollutants in the atmosphere during LP.

Keywords: PM$_{2.5}$; Dioxin; North eastern monsoon; Long-range transport.

INTRODUCTION

PCDDs and PCDFs are airborne persistent organic pollutants that are semi-volatile with low vapor pressure. PCDD/Fs can exist in both particulate and vapor phases simultaneously (Zhu et al., 2017). PCDD/Fs are released into the environment through industrial processes such as burning, incineration, and metal smelting (Lohmann and Jones, 1998; Finocchio et al., 2006; Kulkarni et al., 2008; Cheruiyot et al., 2016; Wei et al., 2016). Among 210 PCDD/F congeners, the 17 congeners which possess chlorine substitution in the 2, 3, 7, and 8 positions, are toxic to the human endocrine system. They can cause health problems and increase the risk of cancers (Kulkarni et al., 2008; Degrendele et al., 2014). Characterized by a long half-life, PCDD/Fs tend to persist in the environment; in addition, because of their susceptibility to seasonal weather changes, they undergo atmospheric long-range transport (LRT), which can lead to cross-border pollution (Degrendele et al., 2014). For example, prevailing monsoons that are active at high speeds from a single general direction transfer pollutants via atmospheric transport from their emission sources to Taiwan, thereby increase pollutant concentration in downwind regions (Cheng et al., 2008; Chi et al., 2013b). Moreover, poor atmospheric dispersion and certain geographical factors may lower the mixing-layer height, make pollutants accumulate in the atmosphere and cause local pollution (LP) (Cheng et al., 2008; Choi et al., 2008). The coastal regions of China have highly developed economic and intense industrial activity. Therefore, these regions experience generally higher atmospheric concentrations of PCDD/Fs than the inland regions. For example, Tianjin (91.4 fg I-TEQ m$^{-3}$; (Ding et al., 2013), Jiangsu (81.4–1224 fg I-TEQ m$^{-3}$; (Sun et al., 2017), Shanghai (143.2–497.1 fg I-TEQ m$^{-3}$; (Li et al., 2008), Beijing (35.0–751 fg I-TEQ m$^{-3}$; (Zhou et al., 2014), and Hong Kong (69.8–152 fg WHO-TEQ m$^{-3}$; (Choi et al., 2008) have higher atmospheric PCDD/F concentrations than that of Sichuan (40–1930 fg I-TEQ m$^{-3}$; (Chen et al., 2011) and Harbin (51.2–61.9 fg WHO-TEQ m$^{-3}$; (Meng et al., 2016). Moreover, compared with the coastal and inland regions of China, northern Taiwan has lower atmospheric PCDD/F concentrations (e.g., 10.4–48.4 fg I-TEQ m$^{-3}$ (Chi et al.,

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As an island nation located to the southeast of China, Taiwan experiences northeastern monsoons and continental air masses in winter. During this season, cold air from northern China flows to the downwind regions such as Taiwan, Hong Kong, and Korea, carrying pollutants from emission sources located on this transport route (Cheng et al., 2008; Choi et al., 2008; Hsu et al., 2009; Min et al., 2013). A few days before monsoons and cold-air masses reach Taiwan, they were weakened due to the effect of the island (Chi et al., 2013a). This leads to poor atmospheric dispersion, rapid accumulation of locally emitted pollutants in the atmosphere, and heavy LP (Kuo et al., 2008). This study explored the effect of LRT and LP on the atmospheric environment of Taiwan. Air sampling was conducted in urban and rural areas in northern and central Taiwan by using a high-volume sampler in order to observe atmospheric conditions and variations of seventeen 2,3,7,8-substituted PCDD/Fs that are associated with PM$_{2.5}$.

METHODS

Sampling Sites

To investigate the variation of PCDD/F concentration and the characteristics of PCDD/F species, continuous observation of atmospheric PCDD/Fs was performed at five sampling sites, namely Rural Site 1, Rural Site 2, Urban Site 1, Urban Site 2, and Background Site (Fig. 1), during the northeastern monsoon period in 2014 and 2015. Rural Site 1 is in Yangmingshan National Park in northern Taiwan (121°33′47″E 25°12′50″N; 1080 m above mean sea level) and close to a weather station; 18 samples were collected at this site during December 7–9, 2014, and October 26–November 10, 2015. Rural Site 2 was at Fuguei Cape at the northernmost tip of Taiwan (121°32′16″E 25°17′51″N; 17 m above mean sea level) and close to the eastern coast. During winter monsoons, Fuguei Cape is the first area in Taiwan to be exposed to LRT (Chou et al., 2017), whose air-current trajectory covers northern China, Japan, and Korea (Min et al., 2013; Wang et al., 2016b). At this site, 18 samples were collected over the same period as at Rural Site 1.

The emission sources of PCDD/Fs in Taipei city are such as municipal waste incinerators, crematoria and traffic tailpipe emissions (Chang et al., 2003; Ho et al., 2016). Moreover, Taipei is a basin and thus is liable to the accumulation of air pollutants. Hence, a school in an urban area of Taipei and a university in a suburban area located at the north of the city were selected as Urban Site 1 and Urban Site 2 (121°30′57″E 25°07′22″N; 70 m above mean sea level), respectively. Urban Site 1 is near the traffic emission and Urban site 2 is close to suburban area. Seven samples were collected at Urban Site 2 site during October 28–November 10, 2015. The final sampling location, Background Site, was on Lulin Mountain in central Taiwan (120°52′25″E 23°28′07″N; 2862 m above mean sea level); far from residential areas and with no major anthropogenic sources of air pollutants in its vicinity, the mountain is exposed to negligible air pollution from human activities. Three samples were collected at Background Site during December 2–4, 2014.

![Fig. 1. Locations of five ambient air sampling stations selected in this study.](image-url)
Sample Collection and Analysis

From December 2014 to November 2015, high-volume sampler (Analitica PM2.5-HVS) was used to collect PCDD/Fs samples, in both particle and vapor phases, and PM2.5 samples at the aforementioned five sampling sites over a period of 24–48 h. In total, 49 samples were obtained. In accordance with the European Committee for Standardization standard for PM2.5 (EN 14907), the sampling of PM2.5 was conducted at a flow rate of 500 L min⁻¹. All PM2.5 samples were 700–1400 m³ in volume. The PM2.5-HVS captures PM2.5 and particle-phase PCDD/Fs on quartz fiber filters (ADVANTEC®, http://www.advantec.tw/, QR-100, Ø150 mm) and captures vapor-phase PCDD/Fs on polyurethane foam (TISCH, https://tisch-env.com/, TE-1123-4, diameter: 8.5 cm, height: 3 inch, density: 0.022 g cm⁻³). Before sampling, the quartz fiber filters were baked at 900°C for 5 h, conditioned at a constant humidity of 45% ± 5% and a temperature variation of < 3°C for at least 24 h, and weighed on a scale with a sensitivity of 0.1 mg.

For PCDD/F analysis, the vapor and particle-phase samples were spiked with known amounts of internal quantification standards according to USEPA Method 23. The polyurethane foam and filter samples were separately extracted with toluene for 24 hours and analyzed, respectively. The extraction and clean-up of the PCDD/F samples have been described elsewhere (Chang et al., 2003; Chi et al., 2008). Finally, the dioxin congeners were analyzed through high-resolution gas chromatography (Thermo Trace GC) and high-resolution mass spectrometry (Thermo DFS) by using a fused-silica capillary column (60 m × 0.25 mm × 0.25 mm; J&W DB-5 MS). The spectrometer was operated at a resolution of more than 10,000 under positive electron impact conditions, and datasets for the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed in the selected-ion monitoring mode. For quality control, a laboratory blank and matrix spike sample (2.0–20 pg µL⁻¹ PCDD/Fs) were analyzed after every eight samples. Method detection limits (0.02–0.10 fg m⁻³) were determined from the blanks and quantified at three times the standard deviation of the concentration in the blanks. In this study, the PCDD/F concentrations of all laboratory blank samples were < 1.15 pg. The mean recoveries of standards for all 13C12-2,3,7,8–substituted PCDD/Fs ranged from 48% to 111% and were all therefore within the acceptable 40%–130% range specified in USEPA Method 23. International toxic equivalent factors (I-TEFs) were adopted to compare the potential toxicity of each PCDD/F congener in a mixture with the well-studied and understood toxicity of TCDD, the most toxic member of the group (U.S.EPA, 1989). The I-TEF of each congener present in a mixture was multiplied by the respective mass concentration, and the products were then summed to obtain the 2,3,7,8-TCDD international toxic equivalence (I-TEQ) of the mixture.

Potential Source Contribution Function

PSCF combines data of air-mass back trajectories with that of pollutants in a receptor area to locate a potential source area of pollution; it is a probability function denoting the conditional probability that a given source area emits pollution. The PSCF values for grid cells in the domain of interest are estimated by counting the trajectory segment endpoints that terminate within the cells, as expressed in Eq. (1):

$$PSCF_{ij} = \frac{M_i}{N_j}$$

where $i$ is the longitude of a cell, $j$ the latitude of the cell, $N_j$ the number of endpoints that pass through the $ij$-th cell, and $M_i$ the number of endpoints that pass through the same cell when the concentration of an air pollutant surpasses an arbitrarily set criterion (which in this study was the 75th percentile of PCDD/F concentration from the 2015 sampling results). Next, the PSCF model was used in combination with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model to calculate air-mass back trajectories and to retrospectively analyze the trajectories at each sampling site on the basis of its longitude, latitude, and altitude.

Multivariate Data Analysis

Principal component analysis (PCA), a multivariate statistical analysis technique that is used to reduce mass data into common factors and retain the variability between the data, was conducted using SPSS Statistics V. 20. In this analysis, common factors with an eigenvalue of > 1 were chosen as principal components and varimax rotation was used resulting in 4 and 3 eligible principal components (PCs) in two analyses of two sets of data respectively. When performing PCA with the sample size smaller than the number of variables, (n < 17 in the case of PCDD/F), the KMO value cannot be calculated. However, some studies showed that principal component extraction can still be performed using PCA without KMO calculation (Larsen and Baker, 2003; Cincinelli et al., 2007; Luo et al., 2008; Qin et al., 2012; Ngo et al., 2017). Therefore, in this research, although, the small sample size made it ineligible to perform Bartlett’s test and KMO value calculation, the PCA still showed suitable principal components.

RESULTS AND DISCUSSION

In total, 49 samples were obtained at the five sampling sites during the winters of 2014 and 2015. Table 1 presents PM2.5 and PCDD/F concentrations and meteorological monitoring data collected over the study period. The mean PM2.5 concentrations in 2014 at Rural Site 1, Rural Site 2, Urban Site 1, and Background Site were 17.3 ± 15.6, 19.6 ± 5.63, 21.4 ± 12.9, and 5.12 ± 0.60 µg m⁻³, respectively, whereas that in 2015 at Rural Site 1, Rural Site 2, and Urban Site 2 were 13.9 ± 10.2, 20.5 ± 13.5, and 18.7 ± 15.9 µg m⁻³, respectively. The Gas/Particle ratio (G/P ratio) of PCDD/Fs were less than 1 in 2014 sampling period indicating that the proportion of PCDD/Fs in particle phase was higher than that of gas phase. However, the G/P ratio were higher than 1 in 2015 sampling period. The temperature and humidity in 2014 were lower than in 2015, but the
PM$_{2.5}$ concentrations were higher. The PM$_{2.5}$ concentrations at Rural Site 1 and Background Site were notably lower than those of the other sampling sites, largely because they were at higher altitudes and therefore away from anthropogenic sources of air pollution. This finding is consistent with that of Hueglin et al. (2005), which was undertaken in Switzerland. Moreover, throughout the two-year period, the mean concentrations of PM$_{2.5}$ at all sampling sites in northern Taipei was $17.7 \pm 13 \, \mu g \, m^{-3}$, lower than that reported by recent relevant studies: $29.3–102.2 \, \mu g \, m^{-3}$ in central Taiwan (Cheng et al., 2008), $43.2 \pm 20 \, \mu g \, m^{-3}$ in southern Taiwan (Cheng et al., 2014), $90.3 \pm 55$ and $95.5 \pm 42 \, \mu g \, m^{-3}$ in Shanghai (Feng et al., 2009), 106–131 $\mu g \, m^{-3}$ in Hebei (Chen et al., 2017; Xing et al., 2017) and 60.7 $\pm$ 20 and 187 $\pm$ 48 $\mu g \, m^{-3}$ in India (Panda et al., 2015).

**Variation of Atmospheric PCDD/F Concentrations and Congener Distribution in 2014**

Fig. 2 presents the PM$_{2.5}$ concentrations and the concentrations of particle- and vapor-phase PCDD/Fs at all sampling sites in 2014. The mean toxic equivalency (TEQ) of PCDD/Fs was $29.9 \pm 20.0 \, fg \, I$-TEQ $m^{-3}$ ($12.9–51.9 \, fg \, I$-TEQ $m^{-3}$) at Rural Site 1 and $28.9 \pm 9.7 \, fg \, I$-TEQ $m^{-3}$ (range: $17.0–34.8 \, fg \, I$-TEQ $m^{-3}$) at Rural Site 2. The mean PCDD/F concentration was $39.7 \pm 22.7 \, fg \, I$-TEQ $m^{-3}$ (range: $14.8–59.4 \, fg \, I$-TEQ $m^{-3}$) at Urban Site 1 and $11.0 \pm 5.1 \, fg \, I$-TEQ $m^{-3}$ at Background Site. These results showed that the PM$_{2.5}$ concentrations and the TEQ of PCDD/Fs at Rural Site 1 were equivalent to those at Rural Site 2. Moreover, the PM$_{2.5}$ concentrations and particle-phase PCDD/F concentrations were highest at Urban Site 1, indicating substantial toxic emissions from incineration, burning objects during religious activities, and the dense traffic in metropolitan Taipei (Ho et al., 2016). By contrast, Background Site, which was located far from areas of human activities, had the lowest PM$_{2.5}$ concentration and PCDD/F concentration. Lower levels of PM$_{2.5}$ concentrations and PCDD/F concentrations associated with such geographical locations were also reported in China (Ding et al., 2013), the United States (Cleverly et al., 2007), and Portugal (Cleverly et al., 2007; Coutinho et al., 2007; Ding et al., 2013). PCDD/F concentration levels recorded at all the other sampling sites were lower than those reported in Portugal (49.8 $fg$ I-TEQ $m^{-3}$), northeastern China (51.2–61.9 $fg$ WHO-TEQ $m^{-3}$), northern China (170–205 $fg$ WHO-TEQ $m^{-3}$) and southern China (81.4–1224 $fg$ I-TEQ $m^{-3}$) but similar to those reported in Argentina (39 $\pm$ 76 $fg$ I-TEQ $m^{-3}$) and Taiwan (34–53 $fg$ I-TEQ $m^{-3}$) (Coutinho et al., 2015; Cappelletti et al., 2016; Ho et al., 2016; Lee et al., 2016; Meng et al., 2016; Sun et al., 2017; Xing et al., 2017).

As can be seen in Table 1, background is the only site with D/F ratio larger than 1, while that ratio at both rural and urban areas we found to be less than 1. This suggested that human activities (possibly burning processes) had influenced the partitioning of PCDD/F in these areas. Lulin Mountain was chosen as background site because of its high altitude and being located inside national park where no human industrial and burning activities are allowed.

### Table 1. PM$_{2.5}$, ambient PCDD/F concentration and meteorological data observed during winter season in 2014 and 2015.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling period</th>
<th>PM$_{2.5}$ concentration (μg m$^{-3}$)</th>
<th>Total PCDD/Fs (fg I-TEQ m$^{-3}$)</th>
<th>Ambient temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Total Rainfall (mm)</th>
<th>GP Ratio</th>
<th>G/P ratio</th>
<th>TEQ of PCDD/Fs (μg m$^{-3}$)</th>
<th>G/P ratio: The ratio of ambient PCDD/F gas/particle phase.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural 1</td>
<td>2014/12/02–2015/01/11 (n = 15)</td>
<td>17.3 (± 15.6)</td>
<td>29.9 (± 20.0)</td>
<td>12 (± 2)</td>
<td>93 (± 7)</td>
<td>2014/12/02 (n = 3)</td>
<td>10.6</td>
<td>1.72 (± 0.32)</td>
<td>0.40 (± 0.26)</td>
<td>0.40 (± 0.26)</td>
</tr>
<tr>
<td>Rural 2</td>
<td>2014/12/02–2015/01/11 (n = 15)</td>
<td>13.9 (± 10.2)</td>
<td>7.99 (± 5.58)</td>
<td>19 (± 2)</td>
<td>71 (± 13)</td>
<td>2014/12/04 (n = 3)</td>
<td>25.4</td>
<td>1.06 (± 0.21)</td>
<td>0.58 (± 0.24)</td>
<td>0.58 (± 0.24)</td>
</tr>
<tr>
<td>Urban 1</td>
<td>2014/12/02–2015/01/11 (n = 15)</td>
<td>16.4 (± 13.9)</td>
<td>16.4 (± 13.9)</td>
<td>23 (± 1)</td>
<td>86 (± 3)</td>
<td>2014/12/02 (n = 3)</td>
<td>6.60</td>
<td>2.05 (± 0.88)</td>
<td>1.10 (± 0.88)</td>
<td>1.10 (± 0.88)</td>
</tr>
<tr>
<td>Urban 2</td>
<td>2014/12/02–2015/01/11 (n = 15)</td>
<td>21.4 (± 12.9)</td>
<td>17.5 (± 12.3)</td>
<td>25 (± 2)</td>
<td>73 (± 3)</td>
<td>2014/12/02 (n = 3)</td>
<td>25.4</td>
<td>0.60 (± 0.21)</td>
<td>0.58 (± 0.24)</td>
<td>0.58 (± 0.24)</td>
</tr>
<tr>
<td>Background</td>
<td>2014/12/02–2015/01/11 (n = 15)</td>
<td>10.6</td>
<td>19.6 (± 5.63)</td>
<td>16 (± 3)</td>
<td>96 (± 4)</td>
<td>2014/12/08 (n = 3)</td>
<td>10.6</td>
<td>5.12 (± 0.60)</td>
<td>1.98 (± 0.40)</td>
<td>1.98 (± 0.40)</td>
</tr>
</tbody>
</table>

*Chi et al., Aerosol and Air Quality Research, 17: 3151–3165, 2017*
The pollutant concentrations in general and PCDDF concentrations in particular are generally small. Being located at the altitude of almost 3,000 meter, the pollution collected at Lulin Mountain mostly originated from long range transport event as shown in previous research (Chi et al., 2010; Lee et al., 2011; Chi et al., 2016). The sources of pollution in Lulin Mountain are different from that at the urban area of Taiwan lead to the different in the PCDD/F profile and D/F ratio.

Fig. 3 depicts the profile of PCDD/F species at all sampling sites in 2014. Dominant PCDD/F species were 1,2,3,4,6,7,8-HpCDF (19.8%), OCDF (17.7%), and OCDD (13.2%) at Rural Site 1 and 1,2,3,4,6,7,8-HpCDF (19.1%), OCDF (17.6%), and OCDF (16.5%) at Rural Site 2 (Figs. 3(a) and 3(b)). Other PCDD/F congeners at both sites constituted less than 10% of all pollutant species. Dominant PCDD/F species at Urban Site 1 were OCDD (20.9%), 1,2,3,4,6,7,8-HpCDF (16.8%), OCDF (12.0%), and 1,2,3,4,6,7,8-HpCDD (10.4%) (Fig. 3(c)), which accounted for more than 50% of the PCDD/F species. The profile of these species was similar to that found in other research at urban cities as Buenos Aires in southern American and Harbin in Asia (Cappelletti et al., 2016; Meng et al., 2016). OCDD (43.0%) was the only dominant PCDD/F species at Background Site (Fig. 3(d)), whereas PCDF accounted for more than 60% of all PCDD/F species at Rural Site 1, Rural Site 2, and Urban Site 1. The proportion of PCDF was noticeably higher than that of PCDD at Background Site, indicating that higher PCDF proportions are associated with closer proximity to industrial and human activities (Min et al., 2013; Wang et al., 2016a). The variability of PCDD/Fs was found that in background site, although PM2.5 concentrations were relatively low, however, high PCDD/F content of was found in the solid phase (Chi et al., 2013b). This phenomenon can be explained by the decrease of vapor pressure at low temperature (Zhu et al., 2017). Comparing with rural and urban sampling sites, the higher levels of PM2.5 attached PCDD/Fs were found at Background Site. Other study also found that in background site, although PM2.5 concentrations were relatively low, however, high PCDD/F content of was found in the solid phase (Chi et al., 2010). Moreover, the results revealed a negative relationship between PCDD/PCDF ratio and PM2.5 concentration (Fig. 4(c)). The PCDD/PCDF ratio varied depending on PM2.5 concentration; the proportion of PCDFs correlated positively with PM2.5 concentration, which affected the profile of PCDD/F species in air. For example, higher proportions of PCDFs are typically seen in urban and suburban areas, where industrial or human activities are concentrated (Coutinho et al., 2015).

**Variation of Atmospheric PCDD/F Concentrations and Congener Distribution in 2015**

In this study, the hourly PM$_{2.5}$ concentrations (together with meteorological information) obtained from Taiwan Environmental Protection Administration (EPA) Wanli...
station was used to classify samples as polluted, possibly-polluted, or baseline data by AGAGE statistical method (O’Doherty et al., 2001). Samples with concentration smaller than that of the median of the total samples were considered as samples of “clean incidence”. The root mean square (σ) of those samples of “clean incidence” was calculated (Table S1). The PM$_{2.5}$ measurements higher than 3σ were classified as polluted measurements, when those lower than 2σ were defined as baseline data. The measurements with PM$_{2.5}$ concentration values between 2σ and 3σ were classified as possibly-polluted data. The possibly-polluted data were grouped as polluted event if the time between polluted and possibly-polluted data was less than 1 to 3 hour. Moreover, wind direction was used to determine the LRT of polluted data. If the prevailing wind direction in winter ranged from 0° to 90°, the polluted data was defined as transport-polluted event (LRT). Otherwise, polluted data outside the range of LRT wind direction were considered as local-polluted event (LP).

Due to small sample size of the 2014 sampling campaign, AGAGE method was only applied to the 2015 data. Over the study period, LRT occurred during October 27–30, November 2–3, and November 9–10 in 2015. LP incidence occurred on November 7 and 8, 2015 (Fig. 5). In 2015, the mean TEQ of PCDD/F was 7.99 ± 5.58 fg I-TEQ m$^{-3}$ (range: 2.15–21.6 fg I-TEQ m$^{-3}$) at Rural Site 1, 16.4 ± 13.9 fg I-TEQ m$^{-3}$ (range: 2.57–49.4 fg I-TEQ m$^{-3}$) at Rural Site 2, and 17.5 ± 12.3 fg I-TEQ m$^{-3}$ (range: 6.79–37.7 fg I-TEQ m$^{-3}$) at Urban Site 2. Northeastern monsoons descended firstly on Rural Site 2, located at the northernmost tip of Taiwan at a low altitude. Thus, when LRT occurred, the concentrations of PM$_{2.5}$ and PCDD/F were the highest at Rural Site 2, followed sequentially by Urban Site 2 and Rural Site 1 (Fig. 5). On the other hand, during the normal period (when neither LRT nor LP occurred), more toxic emissions were found at Urban Site 2 than in the rural sites. Finally, the concentrations of PM$_{2.5}$ and PCDD/Fs during LP (when pollutants accumulated) were the highest.
Fig. 4. Correlation between (a) PM$_{2.5}$ and PCDD/F concentration, (b) ambient air temperature and PM$_{2.5}$ bounded PCDD/Fs (c) PM$_{2.5}$ and PCDD/PCDF ratio during 2014 sampling campaign.

at Urban Site 1, followed sequentially by Rural Site 2 and Rural Site 1. High concentrations of air pollutants due to LP were also reported by Cheng et al. (2014).

Fig. 6 depicts the profile of PCDD/F species, based on the mass concentration of PCDD/Fs, at all the sampling sites in 2015. The dominant PCDD/F congener at Rural Site 1 during LRT, LP, and the normal period was OCDD (30.3%–41.6%), with the proportion of PCDFs (57.2% during LRT, 61.1% during LP, and 51.6% during the normal period) higher than that of PCDDs (Fig. 6(a)). At Rural Site 2, the dominant PCDD/F congener during LRT, LP, and the normal period was OCDD (17.9%–43.4%), with PCDFs dominating during LRT (54.2%) and LP (70.3%) and PCDD dominating during the normal period (47.6%) (Fig. 6(b)). On the other hand, the dominant PCDD/F congener at Urban Site 2 during LRT, LP, and the normal period was OCDD (26.1%–52.5%), with higher proportion of PCDDs than that of PCDFs during LRT (50.8%) and the normal period (59.9%), when PCDFs dominated during LP (60.2%). The results indicated that OCDD was the dominant PCDD/F congener at all three sampling sites during LRT, LP, and the normal period, which corresponded with findings of Coutinho et al. (2007) and Zhang et al. (2015). Moreover, the proportion of PCDFs was higher than that of PCDDs at all sites during LRT and LP and increased substantially during LP, largely because of emissions from industrial activity and pollutant accumulation (Lee et al., 2004).

The correlation between PM$_{2.5}$ and ambient PCDD/Fs during were examined by the Spearman correlation during 2015 sampling campaign (Table 3 and Fig. 7). In Fig. 7, the relationships between PM$_{2.5}$ concentrations, PCDD/F concentrations, and PCDD/F content variations in PM$_{2.5}$ during LRT, LP, and the normal period were presented. PCDD/F concentrations positively correlated with the TEQ of PCDD/Fs (Fig. 7(a)). The TEQ of PCDD/Fs increased with PM$_{2.5}$ concentrations during LRT and LP and decreased correspondingly during the normal period. On the other hand, PM$_{2.5}$ concentrations negatively correlated with the PCDD/PCDF ratio but positively with the proportion of PCDFs (Fig. 7(b)). Moreover, the PCDD/PCDF ratio exceeded 1 at rural and urban sampling sites, which corresponded with the findings of Coutinho et al. (2015), indicating that PCDFs originate from human activities that
can be categorized as a neighbouring pollution source. In summary, the TEQ of PCDD/Fs correlated positively with the log PCDD/PCDF ratio (Fig. 7(c)), indicating that the proportion of PCDFs increased with the TEQ of PCDD/Fs during LRT and LP and the proportion of PCDDs increased as the TEQ of PCDD/Fs decreased during the normal

Fig. 5. Variation of atmospheric PM$_{2.5}$, vapor/particle-phase PCDD/F concentration, ambient temperature and relative humidity measured in northern Taiwan during 2015 sampling campaign.
period. The correlations between ambient temperature and PCDD/F content in PM$_{2.5}$ during 2014 and 2015 were also different (Fig. S1). Because of higher ambient temperature in the 2015 sampling period, the PCDD/F content in PM$_{2.5}$ was also lower.

Overall, PCDD/F concentrations positively correlated with PM$_{2.5}$ concentrations but PCDD/F concentration, contrariwise, negatively correlated with temperature. The negative relationship between particle phase PCDD/F concentration and temperature can be attributed to the fact that low temperatures facilitate the adsorption and condensation of PCDD/Fs (Tang et al., 2017). The proportion of solid phase PCDD/Fs ranged from 50.9% to 86.8% in Taiwan during 2014 sampling campaign, this value is higher than the value of 47 ± 5% found in Vietnam, where the temperature during sampling period was higher than that of our study (Thuan et al., 2013). Moreover, PM$_{2.5}$ concentration correlated negatively with the PCDD/PCDF ratio but positively with the proportion of PCDFs indicated that increased proportions of PCDFs during LRT and LP (when PM$_{2.5}$ concentration rise) were due to human activities (Lee et al., 2007).

**LRT, LP, and Spatial Variation of PCDD/Fs in Northern Taiwan**

This study conducted a PCA on the data of the percentage of PCDD/F raw concentration of that were obtained during northeastern monsoons in 2014 (Fig. 8 and Table S2). Factor 1 (51.1% of the variance) correlated with 1,2,3,4,7,8-HCDD ($r = 0.96$), OCDD ($r = 0.89$), 2,3,7,8-TCDD ($r = 0.87$), and 1,2,3,7,8,9-HCDD ($r = 0.84$), and anticorrelated with 1,2,3,4,7,8-HxCDF ($r = -0.93$), 1,2,3,6,7,8-HxCDF ($r = -0.95$), 2,3,4,6,7,8-HxCDF ($r = -0.92$) and 1,2,3,4,6,7,8-HpCDF ($r = -0.97$). Factor 2 (15.4% of the variance) correlated with 1,2,3,7,8-PCDF and anticorrelated with 1,2,3,4,6,7,8-HpCDD ($r = -0.95$), 2,3,4,6,7,8-HxCDF ($r = -0.92$) and 1,2,3,4,6,7,8-HpCDF ($r = -0.97$). The score plot shown in Fig. 8 grouped the sampling sites into three groups 1, 2 and 3, corresponding to rural, urban and background, respectively. Group 1 was similar to group 2 in terms of the PCDD/F species profile, probably because both groups are susceptible to the considerable effect of the LRT of pollutants by northeastern monsoons. However, according to the high background scores, PCDDs with significantly low F1 loadings (<−0.4) would be the indicators of absence of local pollution. The profile of PCDD/F species in group 2 did not completely overlap with that in group 1, indicating that there might be other sources in urban areas (group 2) rather than just LRT. Group 3, which was at a high altitude, experienced fewer anthropogenic emissions.

In order to increase the sample size of PCA method, another PCA was also performed using the profile of PCDD/F species at all sampling sites in both two saping periods, 2014 and 2015 (Fig. 9 and Table S3). Factor 1 (37.6% of the variance) correlated with 2,3,4,6,7,8-HxCDF
Fig. 7. Correlation between (a) PM$_{2.5}$ and PCDD/F concentration, (b) PM$_{2.5}$ and PCDD/PCDF ratio (c) PCDD/PCDF ratio and PCDD/F (d) ambient air temperature and PM$_{2.5}$ bounded PCDD/Fs concentration during 2015 sampling campaign.

Table 3. Spearman correlation coefficients between PM$_{2.5}$ and ambient PCDD/Fs concentration during 2015 sampling campaign.

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th>PM$_{2.5}$</th>
<th>PCDD/F Content</th>
<th>log PCDD/PCDF ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRT</td>
<td>1.00</td>
<td>0.24</td>
<td>0.50</td>
<td>-0.01</td>
</tr>
<tr>
<td>LP</td>
<td>1.00</td>
<td>0.80</td>
<td>0.90</td>
<td>-0.03</td>
</tr>
<tr>
<td>Normal</td>
<td>1.00</td>
<td>0.57</td>
<td>0.20</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

*: significant correlations ($p < 0.05$).
**: significant correlations ($p < 0.01$).

Bold numbers were shown in Fig. 7.
Fig. 8. Principal Component Analysis of PCDD/F samples collected from different sampling sites in 2014 sampling campaign.

Fig. 9. Principal Component Analysis of atmospheric PCDD/F samples measured at different sampling sites in 2014 and 2015.

Air Mass Trajectories of PCDD/Fs in Northern Taiwan
Figs. 10(a)–10(c) shows the air-mass source trajectories and PSCF values of PCDD/Fs collected in northern Taiwan during 2015. Air masses with higher PSCF values originated from coastal cities of northern and eastern China (> 0.7) and Taiwan (> 0.5). Accordingly, PCDD/Fs might have travelled from somewhere in northern China to the coastal regions of northern and southern China to Taiwan, suggesting that these pollutants resulted in transboundary pollution because of air-mass transport (Chen et al., 2015; Yang et al., 2017), causing an increase of PCDD/F concentration on the island. A similar phenomenon was also observed before in Korea (Lee et al., 2007; Ghim et al., 2017). PCDD/Fs might also have been brought by air currents from the Pacific Ocean, which are active in the east of Taiwan. Several days before northeastern monsoons descended on Taiwan, the prevailing winds typically blew eastward at low speeds across the island, leading to poor atmospheric dispersion and accumulation of local anthropogenic emissions because of geographical factors and the low mixing-layer height in domestic urban areas (Chi et al., 2014). Moreover, the prevailing wind in Taiwan blowing eastward in the run-up to northeastern monsoons was also reported during the winters of 2005 and 2014 (Cheng et al., 2008; Chuang et al., 2016).

CONCLUSIONS
This study analyzed the concentrations of PM$_{2.5}$ and PCDD/Fs in five sampling sites in Taiwan during 2014–
Fig. 10. PSCF result of atmospheric PCDD/Fs at (a) Rural 1, (b) Rural 2, (c) Urban 2 station during 2015 sampling campaign.
2015. The findings are as follows. First, during the LRT and LP events, the concentrations of PM$_{2.5}$ and PCDD/Fs increased significantly; their variation differed across sampling sites and pollution days. Secondly, significant increases in PCDD/F concentrations were associated with temperature, PM$_{2.5}$ concentrations, and the proportions of PCDD/F congeners. Finally, during LRT, the PCDD/F concentration at the low-altitude Rural Site 2 was higher than at urban sampling sites; in particular, the results from the HYSPLIT model and PSCF suggested that air masses with higher PCDD/F concentrations originated largely from northern China. However, during LP, PCDD/F concentrations at urban sampling sites were higher than at Rural Site 2, suggesting that poor atmospheric dispersion across Taiwan during the winter caused local pollutants to accumulate. The findings of this study serve as a reference for further research exploring the effect of LRT and LP on environmental well-being and human health.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


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