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# Atmospheric $PM_{2.5}$ and Depositions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Kaohsiung Area, Southern Taiwan

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## ABSTRACT

Kaohsiung County, in southern Taiwan, has both highly industrial and rural areas. In this study, the characteristics of PCDD/Fs in the ambient air of Kaohsiung (urban), Meinong (rural) and Xiaogang (heavy industrial zone) in 2014 and 2015 were modeled based on the prevailing meteorological conditions and the measured ambient air concentrations of $PM_{2.5}$, $PM_{10}$ and TSP. The yearly average $PM_{2.5}$ concentrations in the ambient air of the three areas were in the range of 23 to 31 μg $m^{-3}$, all above the National Air Quality Standard of Taiwan (15 μg $m^{-3}$). The simulated average concentrations of PCDD/Fs in the whole of Kaohsiung area in terms of toxicity equivalent were in the range of 0.034–0.053 pg $WHO_{2005}$-TEQ $m^{-3}$. The average total deposition fluxes of total-PCDD/Fs-$WHO_{2005}$-TEQ ranged between 155.4 and 276.6 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ with 1,2,3,7,8-PeCCD and 2,3,4,7,8-PeCDF being the dominant congeners in terms of PCDD/Fs $WHO_{2005}$-TEQ. Xiaogang area with highly industrial activities had the highest concentrations of $PM_{2.5}$ and PCDD/Fs and corresponding total-PCDD/Fs $WHO_{2005}$-TEQ deposition fluxes, while the Meinong in the rural site recorded the lowest. Average dry deposition velocities of total PCDD/Fs $WHO_{2005}$-TEQ for both 2014 and 2015 were 0.162, 0.148 and 0.161 cm $s^{-1}$ for Kaohsiung, Meinong and Xiaogang, respectively, while the average scavenging ratios of total PCDD/Fs $WHO_{2005}$-TEQ were 6232, 4701 and 6802, for Kaohsiung, Meinong and Xiaogang, respectively. The information provided in this work is useful for both further studies and environmental control strategies concerning atmospheric aerosols and dioxins.

***Keywords:*** PCDD/Fs; $PM_{2.5}$; $PM_{10}$; Dry deposition; Wet deposition.

## INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have received much public concern due to their ubiquitous nature caused by their stable, persistent, lipophilic and bio-accumulative properties as well as their ability to undergo global dispersion via long range transport (Wu *et al.*, 2009b; Chen *et al.*, 2010). PCDD/Fs are semi-volatile organic compounds (SOCs) and persistent organic pollutants (POPs), which are toxic to human health. PCDD/Fs can get into the human body via ingestion, inhalation and dermal contact (Shih *et al.*, 2009; Chen *et al.*, 2010). In the human body, they pose health risks to the human immune system, interfere with developmental, reproductive and regulatory hormones and even create the risk of cancer (Lin *et al.*, 2010; Chi *et al.*, 2011). They are chemically stable, which have low solubility in the water and have been shown to accumulate in the food chain (Shih *et al.*, 2009).

Combustion processes in nature, such as forest fires and volcanoes as well as anthropogenic activities are the main sources of the PCDD/Fs released into the environment (Chi *et al.*, 2011). Comparing to these two sources, anthropogenic activities are the most dominant sources contributing to the presence of PCDD/Fs in the environment, which include plenty of manufacturing processes of human products. The main sources of PCDD/Fs have been detected mostly

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coming from the emissions of waste combustion, chemical plants, thermal sources, metal smelting process, and vehicles (Schuhmacher *et al.*, 2000; Wang *et al.*, 2003; Lin *et al.*, 2007; Hsieh *et al.*, 2009; Chuang *et al.*, 2010, 2011).

PCDD/Fs are emitted in the atmosphere where they are transformed, degraded as well as transported from source to receptor sites (Chi *et al.*, 2009; Xu *et al.*, 2009; Fang *et al.*, 2011). In the atmosphere, the PCDD/Fs are partitioned between gas and particle phases a process which is dependent on their vapor pressures, ambient temperatures and other parameters (Wu *et al.*, 2009a; Wang *et al.*, 2010; Cheruiyot *et al.*, 2015). The PCDD/Fs can be degraded by chemical reactions controlled by the OH radicals as well as by the photochemical reactions (Chi *et al.*, 2009). Removal of PCDD/Fs from the atmosphere occurs via both dry and wet deposition (Giorgi, 1988; Chi *et al.*, 2009; Wu *et al.*, 2009a; Huang *et al.*, 2011a; Mi *et al.*, 2012).

Particulate matter is a kind of aerosol, which is defined as a suspension of a solid or liquid particle in a gas (Ghosh *et al.*, 2014). The composition of aerosols includes haze, smoke, fumes, mist and fog, dust and smog. Aerosols can be classified into three categories according to their aerodynamic diameters: TSP, $PM_{10}$, and $PM_{2.5}$ (Lu *et al.*, 2016). Aerodynamic diameters of TSP ranges from ~0 to 100 μm, while that of $PM_{10}$ ranges from ~0 to 10 μm, and that of $PM_{2.5}$ are from ~0 to 2.5 μm (Chow *et al.*, 2015). TSP, $PM_{10}$ and $PM_{2.5}$ have been found to contribute to low visibility and poor air quality (Chen *et al.*, 2014). The content of ambient particulate matters is conglomerate of many pollutant subclasses and it also comprises organic and inorganic species. The sources of particulate matter can be natural or anthropogenic (Kong *et al.*, 2014; Alghamdi *et al.*, 2015). Natural sources include volcanic eruptions, wood burning, and sea sprays, while anthropogenic sources include industries, automobiles and construction activities. In addition to the primary sources, there is the secondary aerosol formation in the environment. After gaseous pollutants through photochemical reaction produces freshly nucleated particles which called secondary aerosol formation. The studies show that the formation of secondary aerosol depending on their saturation ratio and environmental conditions. Ambient particulate matters can be removed from the atmosphere by either dry or wet deposition. Dry deposition occurs when the particles are affected by gravity and when inertial forces impact on surfaces, such as trees, buildings, ground and bodies of water, while wet deposition means that aerosols are incorporated into cloud droplets and removed with precipitation and also occurs when the particles located below a precipitation cloud become scavenged by impacting droplets.

The objectives of this study were to investigate concentrations of $PM_{2.5}$, $PM_{10}$, and the concentrations of PCDD/Fs. Additionally, the gas-particle partitioning and dry and wet deposition fluxes of atmospheric PCDD/Fs in southern Taiwan were also evaluated. This study was divided into three areas: one was industrial area, Xiaogang; the second one was nearby mountain area, Meinong; the other part was the rest of Kaohsiung City. To achieve these goals, samples were collected near municipal solid waste incinerators (MSWIs), electric arc furnaces and sinter plants in Xiaogang area for a period of four years. Collected samples were analyzed for specific 17 PCDD/Fs congeners to establish atmospheric concentration level, and then gaseous and particulate concentration could be calculated. Dry and wet deposition fluxes were simulated by model calculation during 2014 and 2015. Results of this study provides long-term data of PCDD/Fs in Taiwan and display helpful information of building up more comprehensive inventory for understanding the level of PCDD/Fs in Kaohsiung city as well as giving some useful data for further investigation.

## METHODS

### *Sampling Sites*

Samples used in this experiment were obtained from three areas in Kaohsiung County in South of Taiwan (Fig. 1). The sampling sites were chosen since there are few studies focusing on the difference in atmospheric deposition patterns in Kaohsiung County of Taiwan. Sampling period was from February 2010 to April 2013. This data was used to simulate the deposition and partition characteristics of PCDD/Fs for the year 2014 and 2015.

### *Meteorological Conditions and PM Concentration during the Sampling Periods*

The pollutant transmissions and deposition in the atmosphere are affected by the meteorological conditions, such as wind speed, rainfall intensity, $PM_{2.5}$, $PM_{10}$, and TSP concentrations and the atmospheric stability. In this study, the pertinent meteorological information and $PM_{10}$ concentrations for Kaohsiung, Meinong, and Xiaogang, respectively, for the year 2014 and 2015 were obtained from the nearby air quality monitoring stations. The meteorological conditions prevailing in the sampling areas over the whole simulated period of 2014–2015 are summarized in the Tables 1–3.

### *Sampling Procedures and Analysis*

Samples were collected, for a period of five days, using PS-1 sampler (Graseby Andersen, GA) according to the T09A method which was referred by the United States Environmental Protection Agency (US-EPA). The PS-1 sampler was used to collect both gas and particle-phase compounds. For all the samples the average volume of ambient air sampled was in the range of 630 to 1370 $m^3$. Particle-phase compounds were collected by quartz fiber filter, whereas the gas-phase was collected using polyurethane foam. To evaluate contamination during sampling, one field blank was taken during the individual sampling events for quality assurance purposes. Field blanks were loaded into the sampling system, but no air was drawn through them. They experienced the same handling, storage, and analysis procedures as the actual samples.

All the chemical analyses in this study were carried out in an accredited laboratory, Super Micro Mass Research and Technology Centre, in Cheng Shiu University which is certified by Taiwan EPA to analyze PCDD/Fs in Taiwan. High-resolution gas chromatograph/high-resolution mass


**Fig. 1.** Sampling sites at Kaohsiung, Meinong and Xiaogang.

**Table 1.** Meteorological data at Kaohsiung.

| Year unit | Month | Temperature °C | $PM_{10}$ (range) μg $m^{-3}$ | $PM_{2.5}$ (range) μg $m^{-3}$ | TSP μg $m^{-3}$ | Wind speed m $s^{-1}$ | Rainfall mm |
|---|---|---|---|---|---|---|---|
| 2014 | Jan. | 19.5 | 105 (64–121) | 54 (49–56) | 130 | 5.6 | 0.0 |
| | Feb. | 20.3 | 71 (43–83) | 36 (33–39) | 87.4 | 7.1 | 16.0 |
| | Mar. | 22.6 | 83 (45–98) | 40 (35–45) | 103 | 12.2 | 67.0 |
| | Apr. | 25.9 | 73 (39–87) | 35 (31–38) | 90.0 | 8.9 | 27.0 |
| | May | 27.8 | 44 (26–57) | 19 (14–21) | 54.4 | 6.1 | 199 |
| | June | 29.2 | 35 (21–46) | 12 (7–14) | 43.8 | 7.0 | 235 |
| | July | 30.3 | 36 (24–45) | 14 (8–17) | 44.9 | 12.8 | 310 |
| | Aug. | 29.1 | 30 (20–36) | 11 (7–14) | 36.6 | 7.2 | 902 |
| | Sep. | 29.5 | 42 (28–51) | 18 (13–22) | 52.3 | 10.6 | 172 |
| | Oct. | 27.2 | 82 (48–93) | 39 (34–44) | 102 | 6.6 | 0.0 |
| | Nov. | 25.2 | 88 (55–99) | 42 (37–49) | 109 | 5.3 | 1.5 |
| | Dec. | 20.2 | 101 (66–117) | 51 (47–54) | 126 | 6.1 | 13.5 |
| **Annual** | | **25.6** | **66 (30–105)** | **31 (11–54)** | **81.5** | **8.0** | 1940 |
| 2015 | Jan. | 19.9 | 98 (66–118) | 47 (42–52) | 121 | 6.9 | 6.0 |
| | Feb. | 20.8 | 90 (63–108) | 44 (41–49) | 112 | 6.7 | 38.0 |
| | Mar. | 23.6 | 77 (49–95) | 37 (33–42) | 96.0 | 6.5 | 0.0 |
| | Apr. | 26.2 | 59 (41–73) | 22 (18–26) | 73.3 | 7.9 | 7.0 |
| | May | 28.3 | 36 (25–46) | 13 (10–17) | 44.5 | 7.9 | 300 |
| | June | 30.6 | 30 (22–40) | 8 (6–11) | 37.0 | 6.8 | 10.0 |
| | July | 29.5 | 35 (27–43) | 12 (8–15) | 43.6 | 8.8 | 200 |
| | Aug. | 28.8 | 35 (28–43) | 12 (8–17) | 43.4 | 16.6 | 548 |
| | Sep. | 28.8 | 45 (32–53) | 19 (14–26) | 55.3 | 12.3 | 141 |
| | Oct. | 27.7 | 63 (42–78) | 28 (22–31) | 78.6 | 4.8 | 25.5 |
| | Nov. | 26.2 | 77 (53–89) | 33 (27–40) | 94.9 | 4.9 | 41.0 |
| | Dec. | 22.4 | 86 (55–104) | 39 (34–44) | 106 | 5.3 | 27.5 |
| **Annual** | | **26.1** | **61 (30–90)** | **26 (8–47)** | **75.5** | **8.0** | **1340** |

spectrometry (HRGC/HRMS) (Hewlett Packard 6970 Series, CA, USA) was used for PCDD/F analysis. Detailed analytical procedures and instrumental parameters of PCDD/Fs given in the previous work (Wang *et al.*, 2010). In summary, seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed and one field blank was incorporated for each sample. Additionally, $^{13}C_{12}$-2,3,7,8-substituted PCDD/Fs internal standards were spiked into samples to quantify for recoveries during analysis.

***Gas-Particle Partitioning***

Gaseous and particulate concentrations of PCDD/Fs were evaluated by the gas-particle partitioning multiplying the total concentrations of PCDD/Fs. The gas-particle

**Table 2.** Meteorological data at Meinong.

| Year unit | Month | Temperature °C | $PM_{10}$ (range) μg $m^{-3}$ | $PM_{2.5}$ (range) μg $m^{-3}$ | TSP μg $m^{-3}$ | Wind speed m $s^{-1}$ | Rainfall mm |
|---|---|---|---|---|---|---|---|
| 2014 | Jan. | 18.5 | 81 (46–122) | 43 (23–78) | 100 | 1.1 | 0.0 |
| | Feb. | 19.9 | 61 (37–87) | 32 (13–50) | 75.6 | 1.2 | 21.8 |
| | Mar. | 22.6 | 76 (28–109) | 38 (9–67) | 94.2 | 1.3 | 18.0 |
| | Apr. | 25.9 | 61 (34–91) | 26 (7–46) | 75.6 | 1.3 | 10.2 |
| | May | 27.3 | 28 (14–59) | 11 (1–29) | 34.7 | 1.1 | 129 |
| | June | 29.0 | 24 (14–34) | 8 (2–15) | 29.8 | 1.4 | 252 |
| | July | 30.1 | 27 (12–51) | 11 (3–28) | 33.5 | 1.4 | 509.2 |
| | Aug. | 28.6 | 21 (7–33) | 8 (0–16) | 26.0 | 1.3 | 581 |
| | Sep. | 29.4 | 31 (12–59) | 13 (0–37) | 38.4 | 1.3 | 190 |
| | Oct. | 27.1 | 69 (43–88) | 34 (20–51) | 85.6 | 1.1 | 14.0 |
| | Nov. | 25.0 | 65 (40–92) | 37 (24–54) | 80.6 | 1.0 | 0.6 |
| | Dec. | 19.5 | 74 (35–120) | 42 (19–72) | 91.8 | 1.0 | 17.8 |
| **Annual** | | **25.2** | **52 (21–81)** | **25 (8–43)** | **63.9** | **1.2** | 1740 |
| 2015 | Jan. | 19.6 | 79 (30–117) | 40 (13–63) | 98.0 | 1.1 | 2.2 |
| | Feb. | 21.1 | 74 (28–125) | 37 (11–74) | 91.8 | 1.1 | 14.2 |
| | Mar. | 23.9 | 66 (39–93) | 29 (10–47) | 81.8 | 1.3 | 2.4 |
| | Apr. | 26.5 | 47 (22–90) | 18 (4–30) | 58.3 | 1.4 | 12.4 |
| | May | 28.2 | 27 (6–49) | 12 (3–24) | 33.5 | 1.2 | 456 |
| | June | 30.7 | 25 (16–61) | 9 (4–13) | 31.0 | 1.4 | 37.8 |
| | July | 29.0 | 23 (5–41) | 11 (3–22) | 28.5 | 1.4 | 409 |
| | Aug. | 28.2 | 21 (7–56) | 11 (3–27) | 26.0 | 1.5 | 670 |
| | Sep. | 26.8 | 35 (10–55) | 20 (10–28) | 43.4 | 1.4 | 211 |
| | Oct. | 26.0 | 47 (13–82) | 27 (8–45) | 58.3 | 1.1 | 53.0 |
| | Nov. | 26.5 | 55 (32–79) | 32 (19–42) | 68.2 | 1.0 | 7.6 |
| | Dec. | 22.3 | 61 (19–111) | 35 (10–68) | 75.6 | 1.0 | 31.4 |
| **Annual** | | **25.7** | **47 (21–79)** | **23 (9–40)** | **57.9** | **1.2** | **1910** |

partitioning was simulated by an equation, proposed by several researchers, that successfully describes gas-particle partitioning constant (Yamasaki *et al.*, 1982; Pankow, 1987; Pankow and Bidleman, 1991, 1992):

$$Kp = \frac{F / TSP}{A} \quad (1)$$

$K_p$: gas-particle partitioning constant ($m^3$ $\mu g^{-1}$),
TSP: concentration of total suspended particulate material (μg $m^{-3}$),
F: particle phase concentration of PCDD/Fs (pg $m^{-3}$),
A: gaseous phase concentration of PCDD/Fs (pg $m^{-3}$).

Plotting log $K_p$ against the logarithm of the subcooled liquid vapor pressure ($P_L^o$), gives:

$$\log K_P = m_r \times \log P_L^o + b_r \quad (2)$$

$P_L^o$: subcooled liquid vapor pressure (Torr),
$m_r$: slope of a plot of log $K_p$ vs. log $P_L^o$
$b_r$: y-intercept in a plot of log $K_p$ vs. log $P_L^o$ (Lohmann and Jones, 1998).

Eitzer and Hites (1989) have correlated $P_L^o$ of PCDD/Fs with gas chromatographic retention indexes (GC-RI) on a non-polar (DB-5) GC-column using p,p'-DDT as a reference standard (Eitzer and Hites, 1989), and the correlation has been re-developed by (Hung *et al.*, 2002):

$$\log P_L^o = \frac{-1.34(RI)}{T} + 1.67\times10^{-3}(RI) - \frac{1320}{T} + 8.087 \quad (3)$$

RI: gas chromatographic retention indexes (GC-RI), referred to Donnelly and Hale (Hale *et al.*, 1985; Donnelly *et al.*, 1987),
T: ambient temperature (K) (Hung *et al.*, 2002)

A complete datasets on the gas-particle partitioning of PCDD/Fs in Taiwan have been reported by (Chao *et al.*, 2004). From their data, parameters for Eq. (1) were determined as $m_r = -1.29$ and $b_r = -7.2$ with $R^2 = 0.94$. In this study, those parameters are also used for estimating the partitioning constant ($K_p$) of PCDD/Fs.

***Dry Deposition Fluxes of PCDD/Fs***

The dry deposition fluxes of PCDD/Fs in the atmosphere is a combination of both gas-phase and the particle-phase fluxes, which is given by:

$$F_T = F_g + F_p, \quad (4)$$

$$C_T \times V_{d,T} = C_g \times V_{d,g} + C_p \times V_{d,p} \quad (5)$$

$F_T$: the summation of PCDD/F deposition fluxes from both gas and particle phases,
$F_g$: the PCDD/F deposition flux contributed by the gas phase (Wang *et al.*, 2010),

**Table 3.** Meteorological data at Xiaogang.

| Year unit | Month | Temperature °C | $PM_{10}$ (range) μg $m^{-3}$ | $PM_{2.5}$ (range) μg $m^{-3}$ | TSP μg $m^{-3}$ | Wind speed m $s^{-1}$ | Rainfall mm |
|---|---|---|---|---|---|---|---|
| 2014 | Jan. | 19.8 | 117 (72–196) | 51 (24–110) | 145 | 2.0 | 0.0 |
| | Feb. | 20.5 | 81 (46–118) | 34 (17–47) | 100 | 2.0 | 18.4 |
| | Mar. | 23.0 | 98 (44–174) | 36 (9–74) | 122 | 2.0 | 56.8 |
| | Apr. | 26.3 | 82 (44–120) | 31 (10–49) | 102 | 2.0 | 18.6 |
| | May | 28.3 | 48 (30–92) | 22 (6–43) | 59.5 | 1.9 | 167 |
| | June | 29.7 | 44 (29–73) | 15 (8–32) | 54.6 | 2.0 | 178 |
| | July | 30.8 | 39 (21–63) | 15 (5–29) | 48.4 | 2.4 | 297 |
| | Aug. | 29.4 | 35 (19–50) | 14 (6–26) | 43.4 | 2.1 | 876 |
| | Sep. | 29.5 | 47 (25–69) | 23 (7–37) | 58.3 | 2.1 | 203 |
| | Oct. | 27.3 | 86 (53–129) | 40 (27–58) | 107 | 1.9 | 0.4 |
| | Nov. | 25.2 | 92 (59–128) | 41 (23–65) | 114 | 1.8 | 2.2 |
| | Dec. | 20.0 | 106 (54–164) | 51 (25–87) | 131 | 1.8 | 10.4 |
| **Annual** | | **25.8** | **73 (35–117)** | **31 (14–51)** | **90.4** | **2.0** | 1830 |
| 2015 | Jan. | 19.8 | 103 (45–151) | 49 (15–78) | 128 | 1.9 | 7.0 |
| | Feb. | 20.8 | 100 (48–153) | 48 (19–86) | 124 | 2.0 | 40.6 |
| | Mar. | 23.6 | 87 (47–135) | 38 (11–62) | 108 | 2.1 | 0.4 |
| | Apr. | 26.1 | 62 (32–102) | 24 (12–43) | 76.9 | 2.3 | 11.2 |
| | May | 28.3 | 43 (28–76) | 15 (6–33) | 53.3 | 2.1 | 288 |
| | June | 30.7 | 42 (28–69) | 10 (5–15) | 52.1 | 2.4 | 24.6 |
| | July | 29.6 | 45 (30–65) | 14 (5–32) | 55.8 | 2.4 | 212 |
| | Aug. | 28.8 | 38 (21–82) | 15 (2–30) | 47.1 | 2.3 | 575 |
| | Sep. | 28.8 | 44 (26–67) | 22 (7–40) | 54.6 | 2.3 | 119. |
| | Oct. | 27.6 | 59 (28–108) | 31 (12–48) | 73.2 | 1.8 | 22.8 |
| | Nov. | 26.2 | 78 (56–105) | 36 (20–51) | 96.7 | 1.8 | 60.8 |
| | Dec. | 22.5 | 81 (39–133) | 44 (20–88) | 100 | 1.9 | 31.6 |
| **Annual** | | **26.0** | **65 (38–103)** | **29 (10–49)** | **80.8** | **2.1** | **1390** |

$F_p$: the PCDD/F deposition flux contributed by the particle phase,

$$F_T = C_T \times Vd_{,T}, \quad (6)$$

$$F_g = C_g \times V_{d,g} \text{ and } F_p = C_p \times V_{d,p} \quad (7)$$

$C_T$: the measured concentration of total PCDD/Fs in the ambient air,
$V_{d,T}$: the dry deposition velocity of total PCDD/Fs,
$C_g$: the calculated concentration of PCDD/Fs in the gas phase,
$V_{d,g}$: the dry deposition velocity of the gas-phase PCDD/Fs,
$C_p$: the calculated concentration of PCDD/Fs in the particle phase,
$V_{d,p}$: the dry deposition velocity of the particle-phase PCDD/Fs.

Dry deposition of particle-phase PCDD/Fs occurs mainly via the gravitational settling. The dry deposition velocities of particle-phase PCDD/Fs ($V_{d,p}$) can be simulated by Eqs. (5) and (7).

***Theory of Scavenging Ratios***

The wet deposition flux of PCDD/Fs is a combination of both vapor dissolution into the rain and the removal of suspended particulates by precipitation. The gas scavenging ratio, $S_g$, can be estimated by

$$S_g = RT/H \quad (8)$$

$S_g$: the gas scavenging ratio of PCDD/Fs (dimensionless),
$R$: the universal gas constant ($82.06 \times 10^{-6}$ $m^3$ atm $mol^{-1}$ $K^{-1}$),
$T$: ambient temperature (K),
$H$: Henry constant ($m^3$ atm $mol^{-1}$).

$$S_g = C_{rain,dis}./C_g \quad (9)$$

$C_{rain,\ dis}$: the dissolved-phase concentration of PCDD/Fs in the raindrop,
$C_g$: the concentration of PCDD/Fs in the gas phase.

The particle scavenging ratio, Sp, on the other hand, can be calculated by:

$$S_p = C_{rain,\ particle}/C_p \quad (10)$$

$S_p$: the particle scavenging ratio of PCDD/Fs (dimensionless),
$C_{rain,particle}$: the particle-phase concentration of PCDD/Fs in the raindrop,
$C_p$: the concentration of PCDD/Fs in the particle phase.

Total scavenging of precipitation ($S_{tot}$) is the sum of gas and particle scavenging, which can be calculated by:

$$S_{tot} = S_g(1 - \Phi) + S_p \times \Phi \quad (11)$$

$S_{tot}$: the total scavenging ratio of PCDD/Fs (dimensionless),
$\Phi$: the fraction of PCDD/Fs bound to particles.

Due to the lack of real measured data for the particle scavenging ratios of PCDD/Fs, the values used in this study

were referenced to those in Eitzer and Hites (1989) work.

### *Determination of Wet Deposition Fluxes of PCDD/Fs*

Wet deposition is the removal of particles in the atmosphere by precipitation (rainfall and cloud droplets) and precipitation scavenging accounts for the majority of removing SVOCs from the atmosphere by wet deposition (Huang *et al.*, 2011b). Wet deposition flux of SVOCs is a combination of both vapor dissolution into rain and removal of suspended particulates by precipitation (Bidleman, 1988; Koester and Hites, 1992).

The wet deposition flux of SVOCs can be evaluated as follows:

$$F_{w,T} = F_{w,dis} + F_{w,p} \quad (12)$$

$$F_{w,dis} = C_{rain,\ dis} \times Rainfall \quad (13)$$

$$F_{w,p} = C_{rain,\ particle} \times Rainfall \quad (14)$$

$F_{w,T}$: the wet deposition flux of SVOCs from both vapor dissolution into the rain and removal of suspended particulates by precipitation,
$F_{w,dis}$: the wet deposition flux contributed by vapor dissolution into rain,
$F_{w,p}$: the wet deposition flux contributed by removal of suspended particulates by precipitation,
Rainfall: monthly rainfall (m)

### *QA/QC*

The protocol for quality assurance/quality control (QA/QC) was rigorously followed. In this study, the recovery efficiency of all samples conformed to the relevant quality control requirements and the blank tests also show that no significant contamination. The field blank samples showed nondetection for most congeners except OCDF and OCDD which averaged at 0.00193 and 0.00206 pg $m^{-3}$, respectively. In this study the mean recoveries of standards for all $^{13}C_{12}$-2,3,7,8-substituted PCDD/Fs were in the range of 25–130% in comparison to the criteria recoveries of 70–130%. The MDLs for individual congeners ranged from 0.000438 to 0.00602 pg $m^{-3}$ while the MDLs for the total PCDD/Fs the range was from 0.0147 to 0.0406 pg $m^{-3}$.

## RESULTS AND DISCUSSION

### *Meteorological Conditions during Sampling Period*

The prevailing meteorological conditions influence the deposition and partitioning of PCDD/Fs in the atmosphere. The corresponding values for temperature, $PM_{2.5}$, $PM_{10}$, and TSP are as shown in Tables 1–3. During the sampling period the monthly average atmospheric temperatures at Kaohsiung, Meinong, and Xiaogang were in the range of 19.5–30.3°C, 18.5–30.1°C and 19.8–30.8°C for 2014, while for 2015 it was 19.9–30.6°C, 19.6–30.7°C and 19.8–30.7°C for 2015, respectively. The yearly average temperatures in 2014 were 25.8, 25.6 and 25.2°C for Kaohsiung, Meinong, and Xiaogang while for 2015 they were 26.1, 25.7 and 26.0°C, respectively with the highest temperature's being observed in June.

As for the prevailing wind speeds, the 2014 yearly average wind speeds at Kaohsiung, Meinong and Xiaogang were 8, 1.2 and 2 m $s^{-1}$ while for 2015 they were 8, 1.2 and 2.1 m $s^{-1}$ respectively. At Kaohsiung the annual average $PM_{2.5}$, $PM_{10}$ and TSP levels were 31.0, 66.0 and 81.5 μg $m^{-3}$ in 2014 while for 2015 the levels were 26.0, 61.0 and 75.5 μg $m^{-3}$ respectively. In 2014, the average annual $PM_{2.5}$, $PM_{10}$ and TSP levels at Meinong were 25.0, 52.0 and 63.9 μg $m^{-3}$, respectively while in 2015 the levels were 23.0, 47.0 and 57.9 μg $m^{-3}$ respectively. As for Xiaogang, the $PM_{2.5}$, $PM_{10}$ and TSP annual average levels were 31.0, 73.0 and 90.4 for 2014 and 29.0, 65.0 and 80.8 μg $m^{-3}$ for 2015, respectively. The yearly average of $PM_{2.5}$ concentrations were all above the National Air Quality Standard of 15.0 μg $m^{-3}$ for Taiwan.

In the whole period, January was the driest month while august was the month with highest rainfall intensity for all sampling sites. In 2014 Kaohsiung recorded the highest amount of annual rainfall (1940 mm) while in 2015 the highest rainfall amount was recorded at Meinong (1900 mm).

### *Simulated Ambient air PCDD/F Concentrations*

Fig. 2 shows regression line showing the correlation between $PM_{10}$ and the total simulated PCDD/Fs mass concentrations at Xiaogang. The correlation coefficient in this study was 0.98 which is similar to the study of Chandra Suryani *et al.* (2015) and Huang *et al.* (2011a) who reported correlation coefficients of 0.99 and 0.94, respectively. Fig. 3 shows the regression line of the correlation of $PM_{2.5}$ with total simulated PCDD/Fs mass concentrations. Currently in the world, $PM_{2.5}$ levels have attracted the attention of many. In this study, the correlation coefficient of $PM_{2.5}$ and total PCDD/Fs mass was 0.92 which was lower than that of $PM_{10}$ vs. total simulated PCDD/Fs. During sample collection, the mass of $PM_{10}$ is greater than that of $PM_{2.5}$ which makes it more precise and reliable to do regression with the total mass concentration of PCDD/Fs. The strong correlations support the simulation of PCDD/Fs concentration data for the period 2014 and 2015.

Fig. 4 shows the simulated PCDD/F-$WHO_{2005}$-TEQ concentrations and corresponding $PM_{10}$ and $PM_{2.5}$. The simulated ambient air mean total PCDD/F mass concentrations at Kaohsiung during 2014 and 2015 were in the range of 0.33–1.20, 0.33–1.13 pg $m^{-3}$, respectively, and averaged 0.75 and 0.69 pg $m^{-3}$, respectively, while in terms of concentrations of toxicity equivalent quantity were in the range of 0.021–0.077 and 0.021–0.072 pg $WHO_{2005}$-TEQ $m^{-3}$, respectively, and averaged 0.048 and 0.044 pg $WHO_{2005}$-TEQ $m^{-3}$, respectively for 2014 and 2015.

Moreover, in Meinong, simulated average total PCDD/F mass concentrations in 2014 and 2015 were in the range of 0.23–0.93, 0.23–0.91 pg $m^{-3}$, respectively, and averaged 0.580 and 0.530 pg $m^{-3}$, respectively, while in terms of concentrations of toxicity equivalent quantity were in the range of 0.014–0.059 pg $WHO_{2005}$-TEQ $m^{-3}$, 0.014–0.058, respectively, and averaged 0.037 and 0.034 pg $WHO_{2005}$-TEQ $m^{-3}$, respectively.

During 2014 and 2015, simulated ambient air mean total PCDD/F mass concentrations at Xiaogang were in the

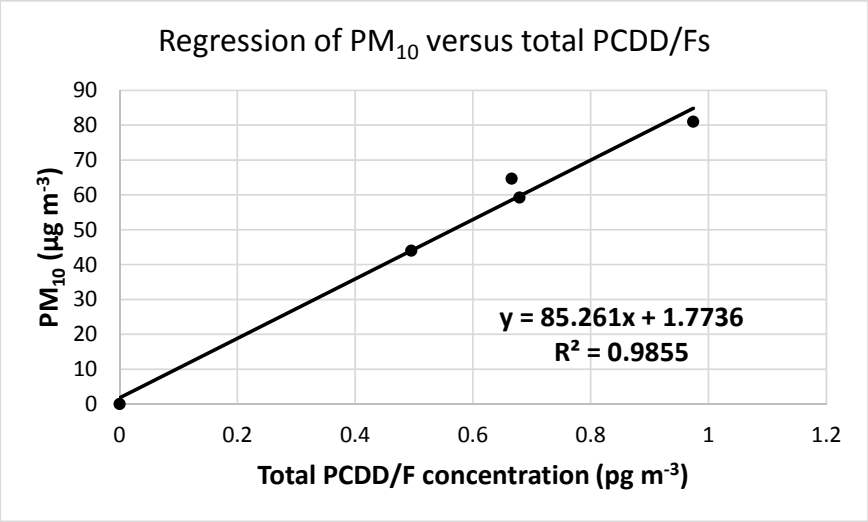


**Fig. 2.** Regression between $PM_{10}$ (µg $m^{-3}$) and total PCDD/F mass concentration (pg $m^{-3}$) during sampling period in Xiaogang.

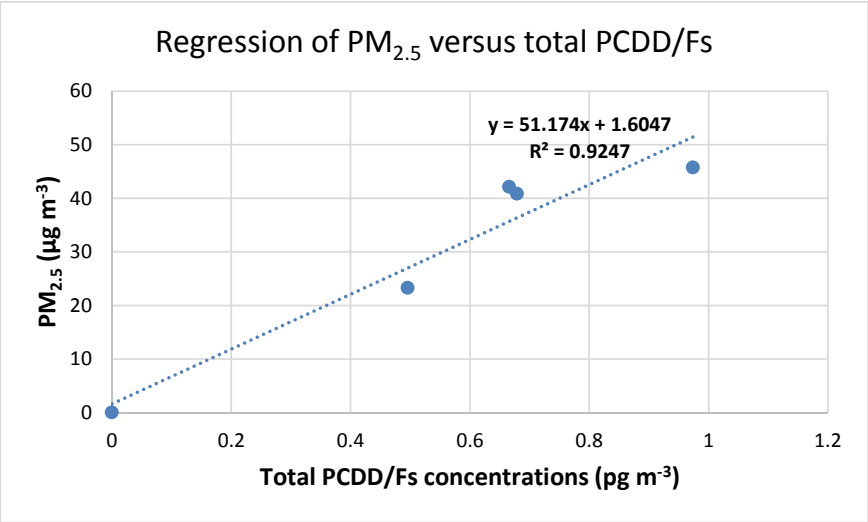


**Fig. 3.** Regression between $PM_{2.5}$ (µg $m^{-3}$) and total PCDD/F mass concentration (pg $m^{-3}$) during sampling period in Xiaogang.

range of 0.39–1.35, 0.42–1.19 pg $m^{-3}$, respectively, and averaged 0.83, 0.74 pg $m^{-3}$, respectively, while the concentrations in terms of toxicity equivalent quantity were in the range of 0.025–0.086, 0.027–0.076 pg $WHO_{2005}$-TEQ $m^{-3}$, respectively, and averaged 0.053 and 0.047 pg $WHO_{2005}$-TEQ $m^{-3}$, respectively.

Comparing the simulated monthly PCDD/F-$WHO_{2005}$-TEQ with the $PM_{10}$ and $PM_{2.5}$ levels in the ambient air shows that the concentrations were very much dependent on the levels of particulate matter. Therefore control of PM from the sources will subsequently lead to reductions in ambient dioxin levels.

### *Gas-Particle Partitioning of PCDD/Fs*

The average seasonal gas-particle partitioning of PCDD/Fs for the whole of Kaohsiung are presented in the Fig. 5. A closer look at the seasonal gas partition profiles for Kaohsiung, Meinong and Xiaogang shows that higher chlorinated PCDD/Fs are primarily in the particle phase every season. Because of larger molecular weight, higher chlorinated PCDD/Fs have a lower vapor pressure, making which tend to be associated with particles in the ambient air (Wu *et al.*, 2009a; Lin *et al.*, 2010; Huang *et al.*, 2011a, b). Additionally, gas phase of PCDD/Fs in winter shows higher partition comparing to the summer season, which is due to lower ambient air temperature in winter than in summer. From a previous study, particle phase of PCDD/Fs was found to increase with the reduction of temperature (Huang *et al.*, 2011a) and as temperature rose, particle phase of PCDD/Fs would probably evaporate to the gas phase. These phenomenon caused by vapor pressure and ambient air temperature has been reported as the main factor influencing the partition of SVOCs (Pankow, 1987).

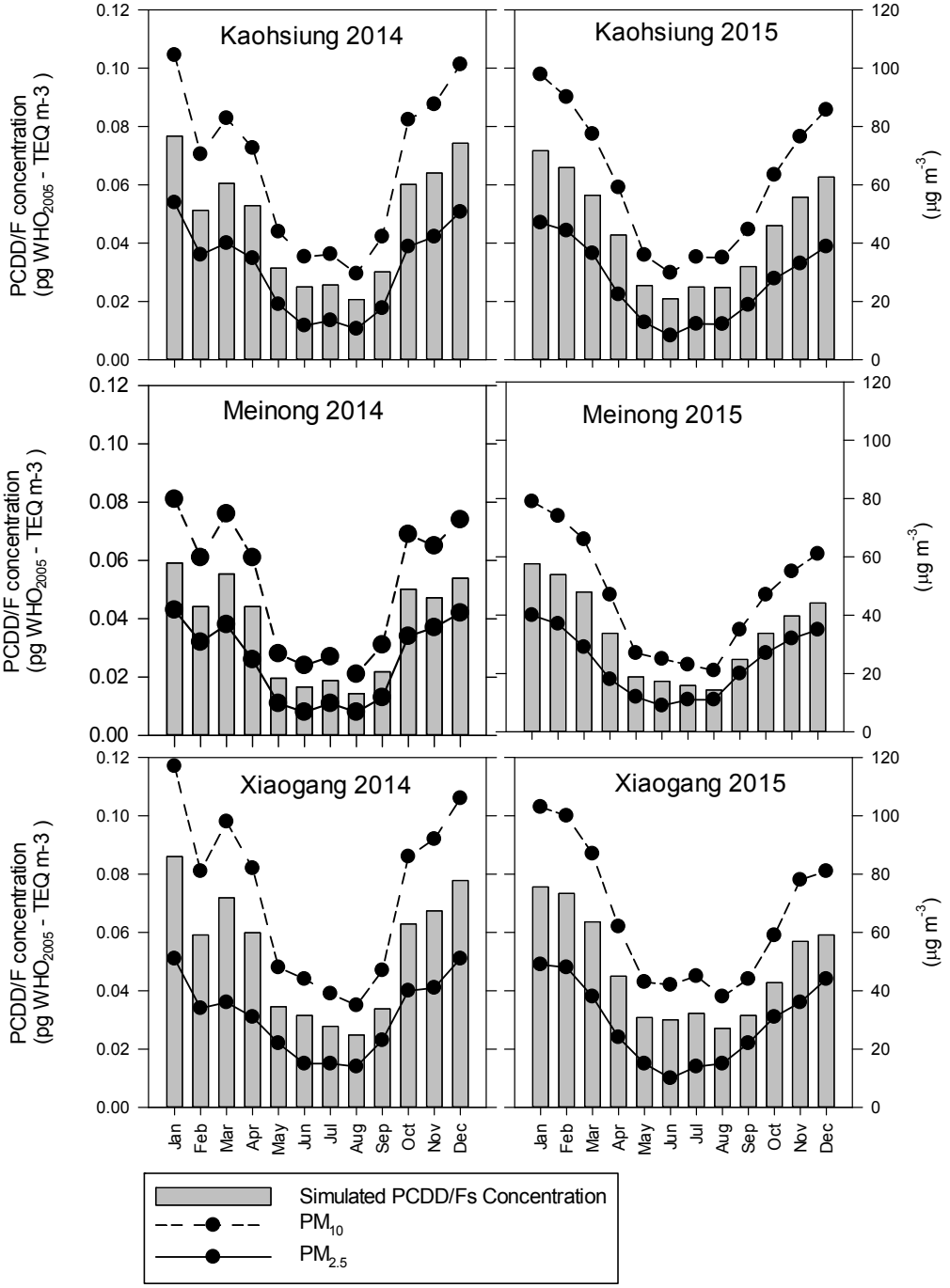


**Fig. 4.** Simulated PCDD/F-$WHO_{2005}$-TEQ concentration and corresponding $PM_{10}$ and $PM_{2.5}$ levels in the ambient air of Kaohsiung, Meinong and Xiaogang, respectively.

***Dry Deposition of PCDD/Fs***

Fig. 6 shows the monthly dry deposition fluxes for both 2014 and 2015 calculated for Kaohsiung, Meinong and Xiaogang. Monthly dry deposition fluxes of total PCDD/Fs $WHO_{2005}$-TEQ at Kaohsiung, ranged from 22.6 to 555 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 210.7 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 32.1 to 404 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 182 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. As for Meinong, monthly dry deposition flux of total PCDD/Fs $WHO_{2005}$-TEQ ranged from 9.70 to 418 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 148 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 7.80 to 373 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 129 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. At Xiaogang, monthly dry deposition flux of total PCDD/Fs $WHO_{2005}$-TEQ ranged from 22.1 to 632 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 234 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 31.1 to 469 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 190.8 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$.

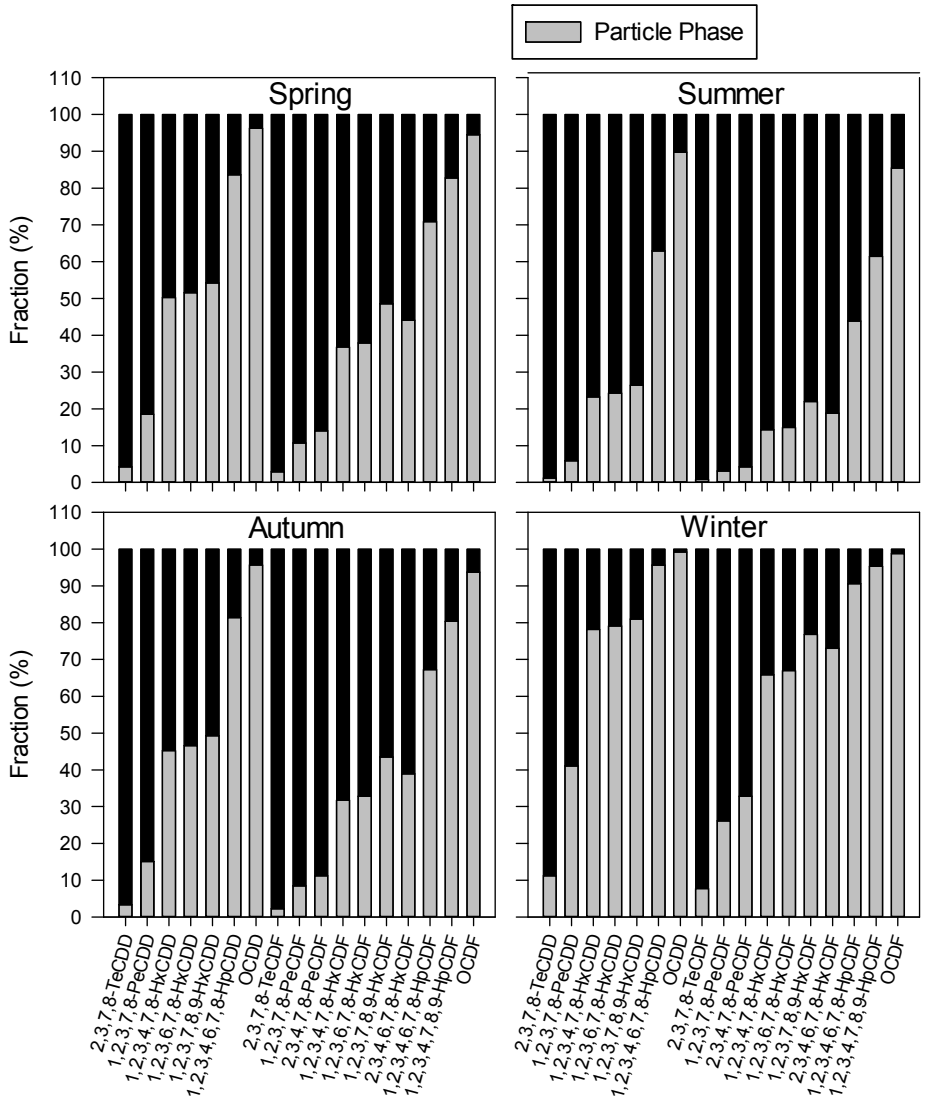


**Fig. 5.** Seasonal gas-particle partitioning of total PCDD/Fs mass concentration at Kaohsiung, Meinong and Xiaogang.

The highest dry deposition fluxes at Xiaogang was in January in both years as well as Kaohsiung and Meinong, while the lowest dry deposition fluxes were in August in both years at three areas. Dry deposition fluxes strongly depend on the days without rainfall, the more days without rainfall, higher dry deposition are, due to no scavenging of rainfall from the ambient air. Previous studies mentioned that the total dry deposition flux was found to increase as the ambient air temperature decreased (Shih *et al.*, 2006; Huang *et al.*, 2011a). When ambient air temperature decreased in the winter season, the particle amount of PCDD/Fs would increase and thus the total dry deposition flux was larger in January than in August. In June 2014 and 2015, the number of days without rain was the highest in the respective years. This meant that the dry deposition dominated the deposition in the month of June and contributed a higher fraction to the total deposition. On the other hand, the particulate concentration in the month of June was low which meant the amount of PCDD/Fs available in particulate phase was lower. Additionally, the higher temperatures encountered in the month of June possibly encouraged volatilization of dioxins from particulate surfaces. Therefore, dry deposition, which is largely dependent on particulate phase, was lowest in June compared to other months. When comparing the annual dry deposition flux of total PCDD/Fs $WHO_{2005}$-TEQ, the highest dry deposition was recorded at Xiaogang, followed by Kaohsiung, and then Meinong. Higher $PM_{10}$ concentrations at Xiaogang compared to Kaohsiung and Meinong were largely responsible for this observation. Table 4 further tabulates more values from other studies.

The dry deposition velocities were determined by using the annual total dry deposition fluxes divided by the average annual air concentrations. The resulting dry deposition velocities at Kaohsiung were determined as 0.167 cm $s^{-1}$ and 0.157 cm $s^{-1}$ for 2014 and 2015, respectively, and averaged at 0.162 cm $s^{-1}$. On the other hand, at Meinong, the calculated dry deposition velocities for 2014 and 2015 were 0.152 cm $s^{-1}$ and 0.144 cm $s^{-1}$ and averaged at 0.148 cm $s^{-1}$. At Xiaogang, the determined dry deposition velocities were 0.168 cm $s^{-1}$ and 0.154 cm $s^{-1}$ for 2014 and 2015, respectively and

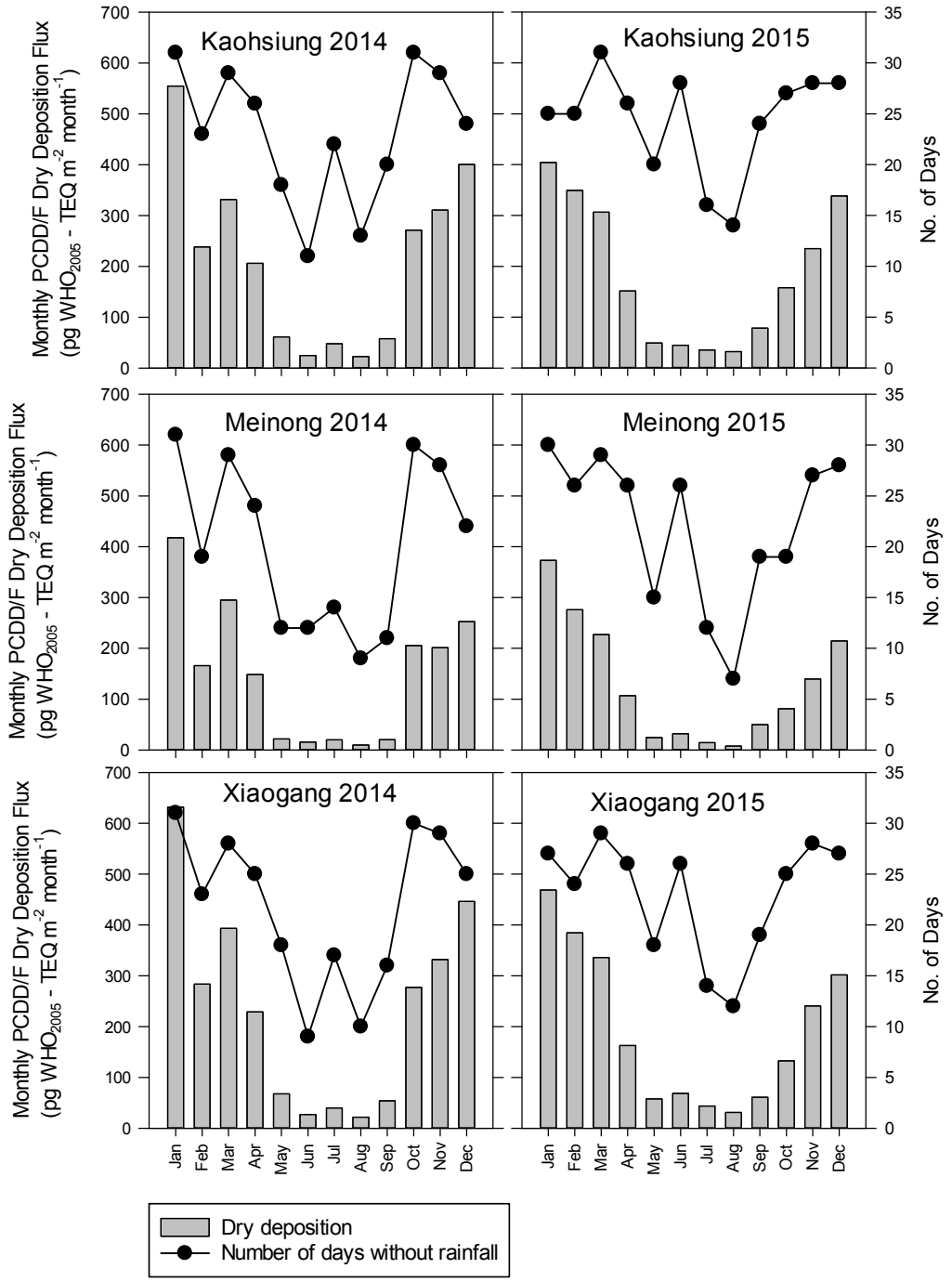


**Fig. 6.** Monthly Dry deposition flux of total PCDD/Fs-$WHO_{2005}$-TEQ at Kaohsiung, Meinong and Xiaogang, respectively.

averaged at 0.161 cm $s^{-1}$. These values were lower than those reported for Hengchun (0.280 cm $s^{-1}$) and Lulin (0.220 cm $s^{-1}$) in our previous study. The dry deposition depends majorly on particle phase but for Kaohsiung, Meinong, and Xioagang greater fraction of PCDD/Fs $WHO_{2005}$ TEQ was in the more toxic lower molecular congeners as shown in the later section.

### *Monthly Wet Deposition Flux of Total PCDD/Fs-$WHO_{2005}$-TEQ*

Wet deposition of PCDD/Fs is the removal of both particle-phase and vapor-phase PCDD/Fs from the atmosphere by rainfall or other precipitation. The calculated monthly wet deposition flux of total PCDD/Fs-$WHO_{2005}$-TEQ are presented in Fig. 7. Simulated monthly wet deposition fluxes of total PCDD/Fs $WHO_{2005}$-TEQ at Kaohsiung, Meinong and Xiaogang during 2014 and 2015 were shown in Fig. 2.

At Kaohsiung, the wet deposition fluxes ranged from 0.0 to 149 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 42.6 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 0.0 to 119 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 34.4 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. The

**Table 4.** Comparison for the dry deposition from previous studies and this study.

| Country | Location | Sampling Period | Total TEQ flux | Reference |
|---|---|---|---|---|
| Taiwan | Industrial | 2010–2011 | 12.4–20.6 pg I-TEQ $m^{-2}$ $day^{-1}$ | Mi *et al.* (2012) |
| | Urban | | 13.6–21.8 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Rural | | 14.3–26.1 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Urban | | 8.30–13.1 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Urban | 2009 | 3.72–56.8 pg I-TEQ $m^{-2}$ $day^{-1}$ | Wu *et al.* (2009a) |
| | Urban | 2006 | 3.07–18.9 pg I-TEQ $m^{-2}$ $day^{-1}$ | Shih *et al.* (2006) |
| | Coastal | 2013 | 1.87–4.24 pg I-TEQ $m^{-2}$ $day^{-1}$ | Chandra Suryani *et al.* (2015) |
| | Mountain | 2013 | 0.49–1.20 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Industrial | 2014 | 0.74–21.1 pg I-TEQ $m^{-2}$ $day^{-1}$ | This study |
| | Industrial | 2015 | 1.04–15.6 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Rural | 2014 | 0.32–13.9 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| | Rural | 2015 | 0.26–12.4 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| Korea | Urban | 2002 | 2.7–10.1 pg I-TEQ $m^{-2}$ $day^{-1}$ | Moon *et al.* (2005) |
| | Suburban | | 3.0–12.6 pg I-TEQ $m^{-2}$ $day^{-1}$ | |
| USA | Urban | 2003–2004 | 1.50 pg I-TEQ $m^{-2}$ $day^{-1}$ | Correa *et al.* (2006) |
| Japan | Urban | 1996–1998 | 36.0–51.0 pg I-TEQ $m^{-2}$ $day^{-1}$ | Ogura *et al.* (2001) |
| Italy | Industrial | 1998–1999 | 0–9.2 pg I-TEQ $m^{-2}$ $day^{-1}$ | Guerzoni *et al.* (2004) |

monthly wet deposition flux of total PCDD/Fs $WHO_{2005}$-TEQ for Meinong, ranged from 0.0 to 69.7 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 24.1 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 1.80 to 71.3 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 26.5 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. At Xiaogang, monthly wet deposition flux of total PCDD/Fs $WHO_{2005}$-TEQ ranged from 0.0 to 183 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 47.0 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ during 2014, while in 2015, those ranged from 0.5 to 140 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 42.9 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$.

The highest wet deposition fluxes were recorded in August for all the sampling areas since summer season has more rainfall amount compared to winter season which has less rainy days. By considering the annual total wet deposition and the annual total rainfall the concentrations in the rainfall were determined in terms of pg $WHO_{2005}$-TEQ $L^{-1}$. At Kaohsiung, the corresponding concentrations in the rainfall were 0.263 and 0.307 pg $WHO_{2005}$-TEQ $L^{-1}$ for 2014 and 2015, respectively. As for Meinong, the concentrations in the rainfall were 0.166 and 0.167 pg $WHO_{2005}$-TEQ $L^{-1}$ for 2014 and 2015 respectively. For 2014 and 2015 the concentrations of PCDD/Fs in the rainfall at Xiaogang were the highest at 0.308 and 0.369 pg $WHO_{2005}$-TEQ $L^{-1}$ respectively. These values were one order of magnitude higher than the average concentrations previously recorded for Hengchun (0.064 pg $WHO_{2005}$-TEQ $L^{-1}$) and Lulin (0.027 pg $WHO_{2005}$-TEQ $L^{-1}$) (Chandra Suryani *et al.*, 2015). Values of wet deposition from previous studies are tabulated in Table 5.

The corresponding scavenging ratios were estimated by dividing the total PCDD/Fs $WHO_{2005}$-TEQ concentrations in the rainfall by the concentration of total PCDD/Fs $WHO_{2005}$-TEQ in the ambient air. The corresponding scavenging ratios at Kaohsiung were 5490, and 6980 for 2014 and 2015, respectively and averaged at 6232. For Meinong the scavenging ratios were determined as 4490 and 4910 for 2014 and 2015 respectively and averaged at 4700. As for Xiaogang, the corresponding scavenging ratios calculate were 5820 and 7860 for 2014 and 2015 respectively with an average of 6840. The scavenging ratios at Kaohsiung Meinong, and Xiaogang were much lower than those reported for Hengchung (mean 8015) and Lulin (mean 13450) in our previous study (Chandra Suryani *et al.*, 2015).

### *Monthly Total (Wet + Dry) PCDD/Fs-$WHO_{2005}$-TEQ Deposition Fluxes and Contribution Fractions of Dry Deposition Flux to Total Deposition Fluxes*

Fig. 8 shows both the simulated monthly total (wet + dry) PCDD/Fs-$WHO_{2005}$-TEQ deposition fluxes and the contribution fractions of the dry deposition to the total (dry + wet) deposition fluxes of total-PCDD/Fs-$WHO_{2005}$-TEQ. Total deposition fluxes of PCDD/Fs are the summation of wet and dry deposition which includes both particle-bound and vapor-phase PCDD/Fs fluxes. In Kaohsiung, monthly total deposition fluxes of total PCDD/Fs ranged from 75.0 to 555 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 254 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ in 2014, while in 2015, those ranged from 46.4 to 400 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 220 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. Additionally, at Meinong, monthly total deposition fluxes of total PCDD/Fs ranged from 44.0 to 420 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 172 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ in 2014, while in 2015, those ranged from 36.3 to 376 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 155 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. Monthly total deposition fluxes of total PCDD/Fs at Xiaogang ranged from 33.3 to 640 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 280 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ in 2014, while in 2015, those ranged from 47.7 to 480 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ and averaged 230 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$.

For all the sites, the highest value occurred in winter season, especially in January, while the lowest one was probably in June during both years. These maximum and minimum values are similar to dry deposition fluxes but are opposite to wet deposition fluxes, which demonstrated the contributions of dry deposition fluxes, were much more than wet deposition fluxes during both years.

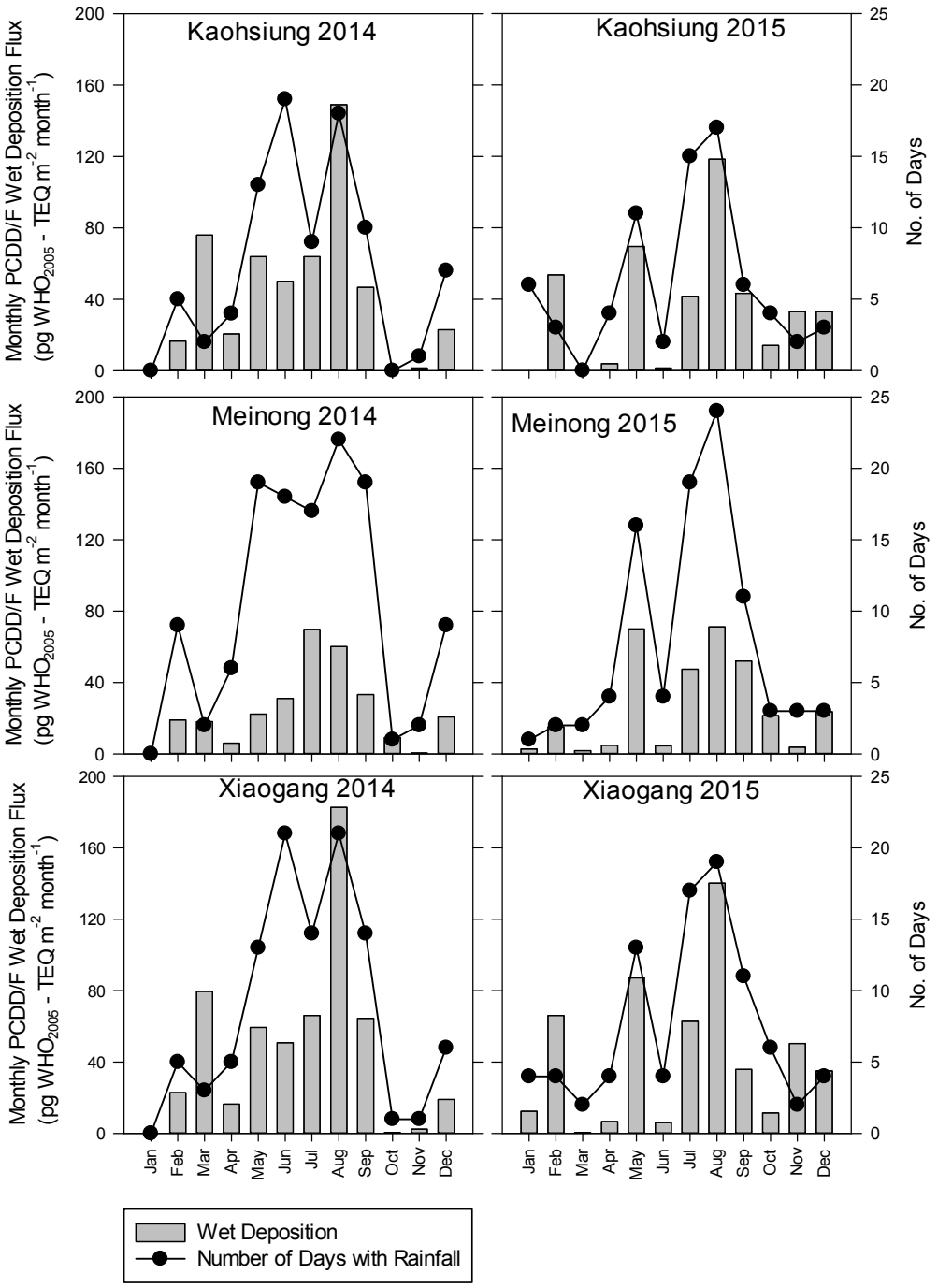


**Fig. 7.** Monthly wet deposition flux of total PCDD/Fs-$WHO_{2005}$-TEQ at Kaohsiung, Meinong, and Xiaogang, respectively.

### *Congener Profile for PCDD/Fs in Total Deposition Fluxes*

The congener profiles of PCDD/Fs $WHO_{2005}$-TEQ total deposition fluxes at three areas are shown in Fig. 9. The dominant congeners were 1,2,3,7,8-PeCCD which contributed between 17.2 and 18.2 and 2,3,4,7,8-PeCDF with a range of 20.6-21.5%, respectively. Following closely were 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF showing that PCDFs contributed highly to the toxicity of the PCDD/Fs.

## CONCLUSIONS

The results of this study illustrate that by using the $PM_{10}$ data, we can confidently predict the PCDD/F concentrations in different areas. These predictions can help provide information with less sampling work and lower costs. By using the methodology of this study, we can successfully determine the spatial and temporal trends of the PCDD/Fs and further evaluate the impact of atmospheric PCDD/F deposition over the time in the future. The results of this study can be summarized as follows:

**Table 5.** Comparison for the wet deposition from previous studies and this study.

| Country | Location | Sampling Period | Total TEQ flux | Reference |
|---|---|---|---|---|
| Taiwan | Industrial | 2014 | 0–183 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | This study |
| | Industrial | 2015 | 0.5–140 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | This study |
| | Rural | 2011 | 5–120 pg I-TEQ $m^{-2}$ $month^{-1}$ | Huang *et al.* (2011b) |
| | Coastal | 2013 | 0.8–30. pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | Chandra Suryani *et al.* (2015) |
| | Mountain | 2013 | 0.2–21.5 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | (Chandra Suryani *et al.*, 2015) |
| | Rural | 2014 | 0–69.7 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | This study |
| | Rural | 2015 | 1.8–71.3 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$ | This study |

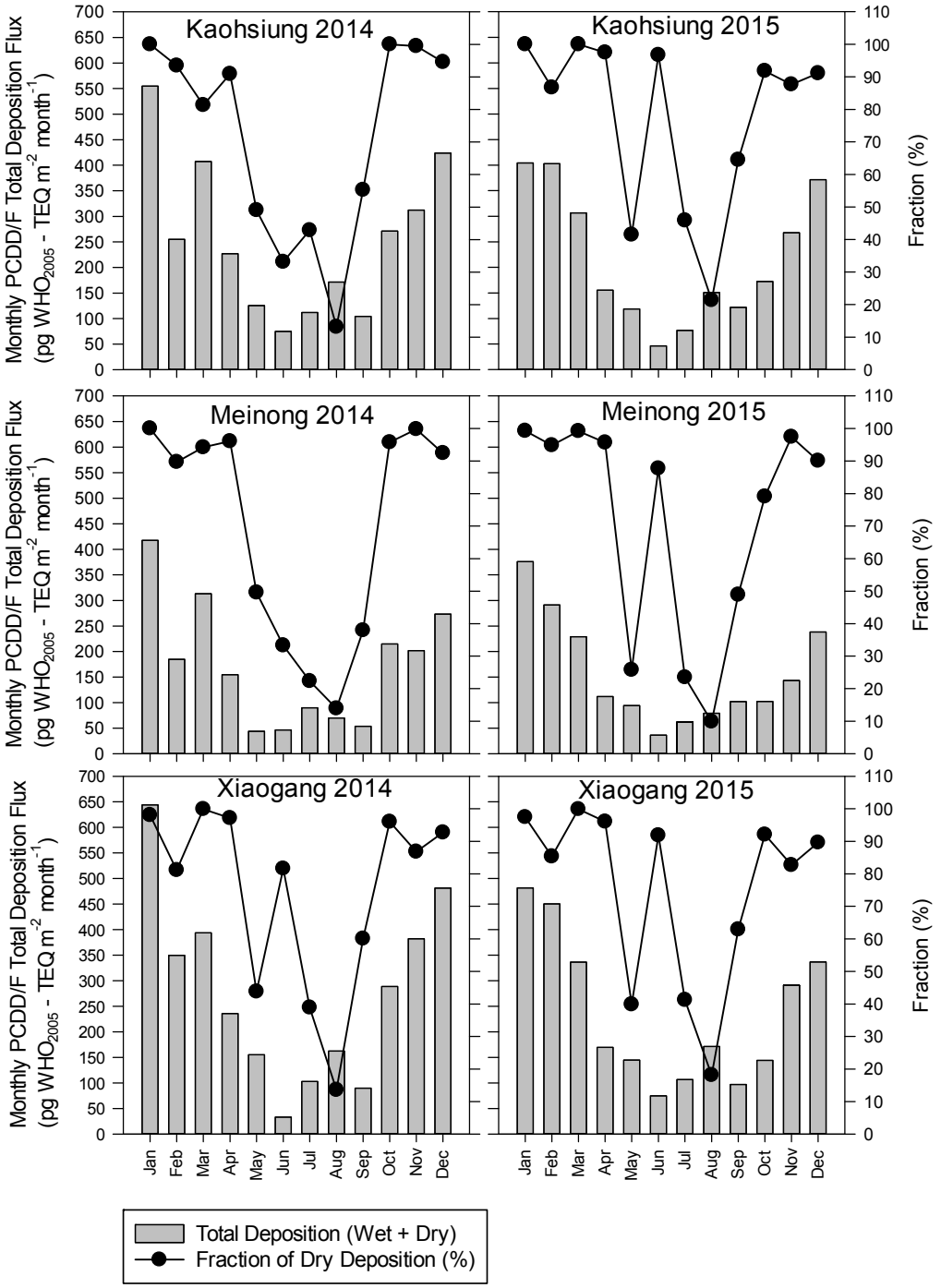


**Fig. 8.** Monthly Total (dry + wet) deposition flux of total PCDD/Fs-$WHO_{2005}$-TEQ and contribution fractions (%) of dry deposition to the total PCDD/F (dry + wet) deposition at Kaohsiung, Meinong, and Xiaogang, respectively.

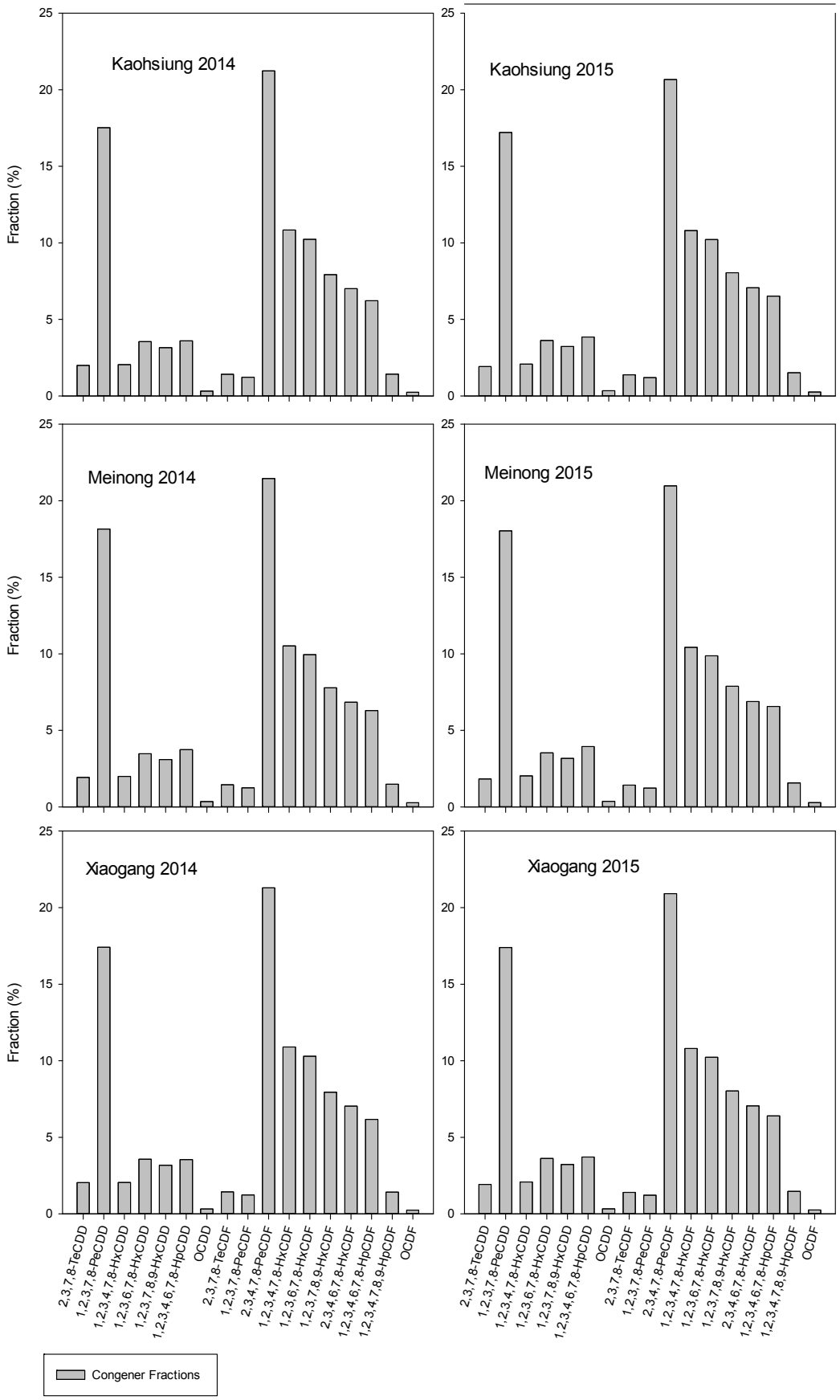


**Fig. 9.** Contribution fractions (%) of dry deposition to the total PCDD/F (dry + wet) deposition fluxes in the terms of $WHO_{2005}$-TEQ at Kaohsiung, Meinong, and Xiaogang, respectively.

1. There were good correlations between $PM_{10}$ and $PM_{2.5}$ with total simulated PCDD/Fs mass concentrations at Xiaogang with a correlation coefficient (r) of 0.98 for $PM_{10}$ and 0.92 for $PM_{2.5}$. The yearly average $PM_{2.5}$ concentrations in 2014 and 2015 in the three areas were 31 and 26 μg $m^{-3}$ for Kaohsiung, 25 and 23 μg $m^{-3}$ for Meinong and 31 and 29 μg $m^{-3}$ for Xiaogang, respectively. These levels were above the allowed 15 μg $m^{-3}$ by National Air Quality Standard of Taiwan.
2. The yearly average concentrations of total PCDD/Fs $WHO_{2005}$-TEQ in Kaohsiung area in terms of toxicity equivalent were in the range of 0.034–0.053 pg $WHO_{2005}$-TEQ $m^{-3}$ with the highest levels recorded at Xiaogang, while the lowest were observed at Meinong.
3. Generally, higher chlorinated PCDD/Fs were associated with particulate phase, while lower chlorinated congeners were dominantly in the gas phase. Additionally, during winter, lower chlorinated congeners increased in fraction in the particle phase but reduced in the summer due to the influence of temperature.
4. During 2014, the average dry deposition flux total PCDD/Fs $WHO_{2005}$-TEQ at Kaohsiung, Meinong, and Xiaogang were 211, 148 and 234 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$, respectively, while in 2015 the mean dry deposition fluxes were 182 129 and 191 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$, respectively. The corresponding average dry deposition velocities of total PCDD/Fs $WHO_{2005}$-TEQ for both 2014 and 2015 were 0.162, 0.148 and 0.161 cm $s^{-1}$ for Kaohsiung, Meinong and Xiaogang, respectively.
5. Considering the wet deposition flux of total PCDD/Fs-$WHO_{2005}$-TEQ, the monthly average ranged from 24.1 to 47.0 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$. The highest wet depositions were observed for Xiaogang. The corresponding total PCDD/Fs $WHO_{2005}$-TEQ concentrations in the rain of three modeled areas were in the range of 0.166–0.369 pg $WHO_{2005}$-TEQ $L^{-1}$; while the average scavenging ratios of total PCDD/Fs $WHO_{2005}$-TEQ were 6230, 4700 and 6840, for Kaohsiung, Meinong, and Xiaogang, respectively.
6. In terms of the average total deposition fluxes of total-PCDD/Fs-$WHO_{2005}$-TEQ in 2014 and 2015, Kaohsiung reported 253 and 216 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$, respectively, while for Meinong the levels were averaged at 172 and 155 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$, respectively. As for Xiaogang, the average total deposition fluxes of total PCDD/Fs-$WHO_{2005}$-TEQ were 277 and 234 pg $WHO_{2005}$-TEQ $m^{-2}$ $month^{-1}$, respectively; In terms of PCDD/Fs $WHO_{2005}$-TEQ, the dominant congeners were 1,2,3,7,8-PeCCD and 2,3,4,7,8-PeCDF.

## ACKNOWLEDGMENTS

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