# EVALUATION OF ATMOSPHERIC PCDD/FS IN THE BACKGROUND AREA AND REMOTE ISLAND SURROUNDING TAIWAN

Chi KH[1], Lin CY[2], Chang MB[3] , Lin NH[4], Shen GR[4]

[1] Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei 112, Taiwan; [2] Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan; [3] Graduate Institute of Environmental Engineering, National Central University, Chungli 320, Taiwan,[4] Department of Atmospheric Sciences, National Central University, Chungli 320, Taiwan

**Introduction**

PCDD/Fs are classified as persistent organic pollutants (POPs). They are unwanted by-products of various combustion processes that can be emitted directly into the atmosphere if not properly treated. In this study, no significant PCDD/F emission sources were existed in the vicinity of the six sampling stations investigated. However, Taiwan is an island located in the subtropics, off the southeast coast of mainland China. In the winter and spring, Taiwan and its surrounding areas are often influenced by northeasterly winter monsoon winds originating from central Asia. The winter monsoon not only brings cold air but also transports airborne pollutants and dust over long distances from central Asia to Taiwan[1] and even to the Northwestern Pacific area. Recently, **Prospero et al.**[2], in a study of aerosol distribution on Midway Island from 1981 to 2000, observed that pollutants such as sulfate and nitrate in aerosols increased concurrently with mineral dust during spring and winter. To date, no comprehensive measurements of the seasonal variations in PCDD/F concentrations in ambient air have been documented from the area outside the influence of pollutants and the remote islands surrounding Taiwan during 2008 and 2009. This study was initiated to address this important issue.

**Materials and methods**

In this study, six sampling sites (labeled A to F) were chosen based on meteorological conditions and locations relative to the winter monsoon circulation (Fig. 1). Of the stations in Taiwan Island, Site A was located at a weather station (121°33'47"E 25°12'50"N; 1,080 m above mean sea level) on Yaming Mountain in northern Taiwan near the East China Sea. Site B was located at the National Museum of Marine Biology and Aquarium (120°42'00"E 22°03'21"N; 3 m above mean sea level) in Pingtung County in southern Taiwan near the coast of the South China Sea. For the remote island stations, Site C was chosen at a weather station on Pengjiayu Island (122°04'20"E, 25°37'55"N; 3 m above mean sea level) in the East China Sea northeast of Taipei County, about 60 km from Taiwan. The island has an area of 1.14 $km^2$ and a maximum altitude of 165 m. The only inhabitants are the weather station and army staff. Site D was located at a weather station on Lanyu Island (121°33'55"E, 22°2'20"N; 300 m above mean sea level) in the Pacific Ocean, 80 km southeast of Taiwan. Lanyu Island has an area of around 48.5 $km^2$ and a population of 3300. Site E was located at an air quality monitoring station (119°56'59"E, 26°09'36"N; 50 m above mean sea level) on Matsu Island, in the Taiwan Straight 210 km northwest of Taiwan and 10 km from mainland China. Site F was located at a weather station on Dongsha Island (116°43'42"E, 20°42'6"N; 5 m above mean sea level), in the northern South China Sea about 440 km from Taiwan. In this study, all PCDD/F and TSP samples were taken at 24 to 48 hr intervals at the six stations during different seasons in 2008 and 2009 for the analysis of PCDD/Fs. Ambient air samples for both the vapor and solid phases of PCDD/F compounds were collected using high-volume sampling trains (Shibata HV-1000F). The HV-1000F samplers were equipped with Whatman quartz fiber filters (8 × 10 inch) for collecting particle-bound compounds and polyurethane foam (PUF) plugs were used to retain PCDD/F compounds in the vapor phase. For PCDD/F analysis, the ambient air samples were spiked with known amounts of internal quantification standards according to USEPA method 23. Finally, the dioxin congeners were analyzed using high resolution gas chromatography (HRGC) (Thermo Trace GC) and high resolution mass spectrometry (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25 μm, J&W).

**Results and discussion:**

Measurements (Table 1) indicated that the average atmospheric PCDD/F and TSP concentrations at Site A were 1.87~10.2 fg I-TEQ/$m^3$ and 6.95~40.2 μg/$m^3$, respectively, in northern Taiwan. The lowest concentrations were measured during the summer season (15-18 July, 2008). In southern Taiwan, Table 1 shows that the

atmospheric PCDD/F and TSP concentrations measured at Site B were in the ranges 1.95~3.74 fg I-TEQ/$m^3$ and 27.1~41.7 μg/$m^3$, respectively, during the summer season. In other Asian countries (such as Korea and Japan) [3,4], the atmospheric PCDD/F concentrations in urban areas have been shown to range from 28 to 120 fg I-TEQ/$m^3$, similar to another of our previous study[5] that measured atmospheric PCDD/F concentrations in the urban area of Taiwan to be in the range 20 to 110 fg I-TEQ/$m^3$. The atmospheric PCDD/F concentrations measured at Sites A and B in Taiwan were considerably lower than those measured in other countries. Table 1 also shows the particle-bound PCDD/Fs measured in the TSP fraction at the six stations during different sampling periods. In Taiwan, the quantities of PCDD/Fs adsorbed onto suspended particles ranged from 43.0 to 132 pg I-TEQ/g-TSP. Our previous study[5] indicated that the amounts of PCDD/Fs bound to suspended particles measured in rural areas of Taiwan were around 260 pg I-TEQ/g-TSP, significantly higher than those measured in this study. However, the highest concentration of atmospheric PCDD/Fs was observed at Site A (northern Taiwan) during the winter season (2009/2/16~2/26). The results of atmospheric PCDD/F and TSP concentrations measured at four sampling sites on remote Islands are shown in Table 1. The average PCDD/F concentrations were 1.74~10.8 fg I-TEQ/$m^3$, 3.54 fg I-TEQ/$m^3$, 7.75~65.2 fg I-TEQ/$m^3$ and 1.24~1.67 fg I-TEQ/$m^3$, respectively, at Sites C (Pengjiayu Island), D (Lanyu Island), E (Matsu Island) and F (Dongsha Island). The quantities of PCDD/Fs adsorbed onto suspended particles were 15.1~120 pg I-TEQ/g-TSP, 42.4 pg I-TEQ/g-TSP , 37.3~620 pg I-TEQ/g-TSP and 1.37~6.27 pg I-TEQ/g-TSP at Sites C, D, E and F, respectively. Equivalent studies at a background station[6,7] found atmospheric PCDD/F concentrations of 6.15-24.0 fg I-TEQ/$m^3$ in a primary forest in Denmark and 1.48-6.57 fg I-TEQ/$m^3$ in a regional park of the Simbruini Mountains in Italy. Atmospheric PCDD/F concentrations measured at all the remote islands except Site E were significantly lower than those measured at other background stations. The significantly lower PCDD/F concentrations (1.24~1.67 fg I-TEQ/$m^3$) and contents in suspended particles (1.37~6.27 pg I-TEQ/g-TSP) measured at Dongsha Island (Site F) in the South China Sea can be attributed to the lack of any combustion sources within almost 300 km of this island. In order to identify the sources of PCDD/F emissions and to examine how transport paths could affect the atmospheric PCDD/F concentration at the atmospheric sampling stations in Taiwan and on the remote islands surrounding Taiwan, the HYSPLIT (Hybrid Single-Particle Lagrangian-Integrated Trajectory) model[11] was used to trace the origins of the air masses. The backward trajectory analysis periods are shown in Fig. 2. Over Taiwan, the weather patterns are strongly affected by the monsoon circulation over East Asia. In general, the northeasterly monsoon prevails from late autumn to early spring while the southwesterly monsoon prevails in late spring and early autumn[8]. The backward trajectories (Fig. 2) calculated for Sites B, D and F showed similar transport routes, implying that the lower PCDD/F concentrations measured at those three stations all originated from the South China Sea and Pacific Ocean in summer. Interestingly, the backward trajectories calculated for Site E (Matsu Island) showed different paths during the autumn and summer seasons. During the summer season (2009/7/14~7/20), the air masses at Site E mostly came from Taiwan Island. However, the trajectories revealed that the air masses may have originated over the coast of mainland China during the autumn (2008/10/30~11/4). The highest concentration of atmospheric PCDD/Fs was observed at Site E (Matsu Island), where the quantities of PCDD/Fs adsorbed onto suspended particles reached 620 pg I-TEQ/g-TSP. Recently, similar studies have found pollutant levels of approximately 972–51,200 fg I-TEQ/$m^3$ and 223–3,454 fg I-TEQ/$m^3$ PCDD/Fs in the vicinity of electric waste processing facilities in the coastal provinces of Southeast China[9,10]. Sampling Site E was located in the Taiwan Strait about 210 km from Taiwan but only 10 km from mainland China. We therefore consider that the elevated atmospheric PCDD/F concentrations observed at Site E in the autumn and winter (Dec. to Feb.) could be attributed to the transport of anthropogenic emissions from mainland China. At Sites A and C, the northeasterly monsoon prevailed 16 February to 26 February 2009. Fig. 3 shows the atmospheric PCDD/F concentration measured at Sites A and C during this period and reveals that the variations of atmospheric PCDD/F concentrations at these two sites were quite similar. In addition, Table 1 indicates that the highest PCDD/F content (132 pg I-TEQ/g-TSP) was measured in northern Taiwan during the winter season (2009/2/16~2/26). In the same period, PCDD/F contents in suspended particles of around 120 pg I-TEQ/g-TSP were measured at Site C. Backward trajectories calculated for Sites A and C (Fig. 2) showed similar paths during 2009/2/16~2/26, implying that the higher PCDD/F concentrations measured at Sites A and C originated from the coastal area of mainland China. Sampling results shows the PCDD/F congener distributions in ambient air measured at different stations. The results indicate that PCDFs account for 48~54% of total PCDD/Fs in northern and southern Taiwan during the summer season. On the remote islands, PCDFs account for about 42~60% of total PCDD/Fs in ambient air during the summer. Significantly lower fractions of

PCDFs (42~45%) were observed at Site F (Dongsha Island). The highest fraction of PCDFs (78%) was observed during the winter (2008/10/9~10/21) at Site E (Matsu Island). In addition, high fractions of PCDFs were also observed during the winter (2009/2/16~2/26) at Site A (71%) and Site C (65%). Inspection of atmospheric PCDD/F concentrations at all sampling sites revealed that the highest PCDD/F concentrations in ambient air coincided with the highest PCDF fractions. Similar study[11] has indicated that the distributions of PCDF congeners observed in the emission gases from waste burning and industrial process are all higher than 70%. We consider that the high fraction of PCDFs observed at Sites A, C and E during the winter season probably originated as anthropogenic emissions from mainland China.

**Acknowledgements:**
The authors gratefully acknowledge the financial support provided by the Environmental Protection Administration (EPA-97-FA11-03-A018 and EPA-98-FA11-03-D020) and National Science Council (NSC 98-2111-M-001 -015 -MY3) of the Republic of China.

**References:**

1. Hsu SC, Liu SC, HuangYT, Chou CCK, Lung SCC, Liu TH, Tu JY, Tsai F. (2009); *J Geophys Res.* 114: D14301
2. Prospero JM, Savoie DL, Arimoto RA. (2003); *J Geophys Res.* 108, 4019
3. Makiya K. (1999); *Organohalogen Compounds* 43, 217-220
4. Lee SJ, Park H, Choi SD, Lee JM, Chang YS. (2007); *Atmos Environ.* 41: 5876–5886
5. Chi KH, Hsu SC, Wang SH, Chang MB. (2008); *Sci Total Environ.* 401(1): 100-108
6. Hovmand MF, Vikelsøe J, Andersen HV. (2007); *Atmos Environ.* 41: 2400-2411
7. Menichini E, Lacovella N, Monfredini F, Turrio-Baldassarri, L. (2007); *Chemosphere* 69: 422-434
8. Lin CY, Liu SC, Chou CCK, Huang SJ, Liu CM, Kuo CH, Young CY. (2005); *Atmos Environ.* 39: 6066-6076
9. Li H, Yu L, Sheng G, Fu J, Peng PA, (2007); *Environ. Sci. Technol*. 41: 5641-5646
10. Li YM, Zhang QH, Jiang G., (2007); *Organohalogen Compd.* 69: 1421-1423
11. Chang SH, Yeh JW, Chein, HM, Hsu LY, Chi KH, Chang MB. (2008); *Environ Sci Technol*. 42: 5727–5733

Table 1 PCDD/F concentrations and particle-bound PCDD/Fs in total suspended particles (TSP) measured in Taiwan and on remote islands surrounding Taiwan.

| *Location* | *Sampling period* | *Ambient temperature (°C)* | *TSPs (μg/m³)* | *PCDD/F concentration (fg I-TEQ/m³)** | *PCDD/F content in TSP (pg I-TEQ/g-TSP)* |
|---|---|---|---|---|---|
| ***Site A (Northern Taiwan)*** | 2008/7/15~7/18 (n=3) | 22.6 (±1.8) | 6.95 (±1.2) | **1.11~2.46 (1.87 ±0.69)** | **43.0 (±6.1)** |
| | 2009/2/16~2/26 (n=6) | 16.3 (±3.8) | 26.1 (±18) | **1.36~24.1 (10.2 ±8.8)** | **132 (±73)** |
| | 2009/3/26~4/5 (n=6) | 12.1 (±3.7) | 40.2 (±16) | **1.03~7.53 (5.44±2.7)** | **66.5 (±21)** |
| ***Site B (Southern Taiwan)*** | 2008/8/29~9/6 (n=5) | 27.5 (±0.81) | 27.1 (±8.5) | **2.03~5.59 (3.74 ±1.4)** | **50.8 (±15)** |
| | 2008/8/29~9/6 (n=5) | 28.7 (±0.24) | 41.7 (±9.6) | **1.07~4.07 (1.95 ±1.0)** | **54.2 (±7.0)** |
| ***Site C (Pengjiayu Island)*** | 2008/10/9~10/21 (n=7) | 25.0 (±1.2) | 47.7 (±19) | **0.428~3.80 (1.74 ±1.2)** | **15.1 (±12)** |
| | 2009/2/16~2/26 (n=6) | 18.3 (±2.6) | 49.1 (±35) | **0.606~23.9 (10.8 ±8.8)** | **120 (±76)** |
| ***Site D (Lanyu Island)*** | 2008/8/31~9/6 (n=4) | 32.1 (±2.7) | 30.5(±16) | **2.19~4.79 (3.54 ±1.1)** | **42.4 (±24)** |
| ***Site E (Matsu Island)*** | 2008/10/30~11/4 (n=3) | 22.4(±0.76) | 38.7 (±1.9) | **49.1~78.7 (65.2±15)** | **620 (±154)** |
| | 2009/7/14~7/20 (n=4) | 29.1 (±0.20) | 50.6 (±5.6) | **3.47~28.8 (7.75 ±3.7)** | **37.3 (±23)** |
| ***Site F (Dongsha Island)*** | 2008/8/4~8/11 (n=5) | 27.9(±0.80) | 44.0 (±17) | **0.577~3.47 (1.24 ±1.2)** | **1.37 (±0.8)** |
| | 2009/8/6~8/12 (n=4) | 28.1 (±1.0) | 83.6 (±15) | **1.49~1.88(1.67±0.20)** | **6.27 (±1.7)** |

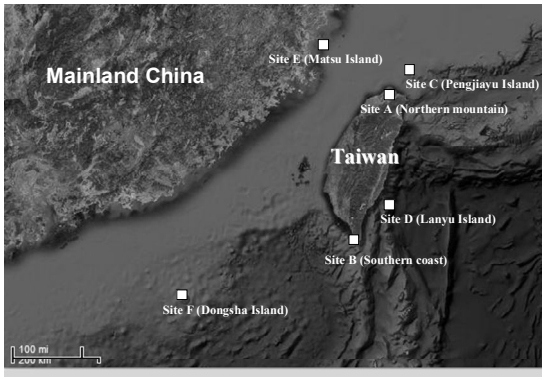


Fig. 1 Relative locations of costal and remote island sampling sites.

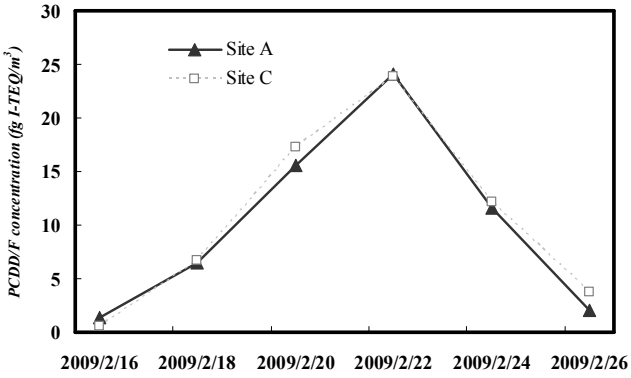


Fig. 3 Variation of atmospheric PCDD/F concentrations measured at Site A (Northern Taiwan) and Site C (Pengjiayu Island).

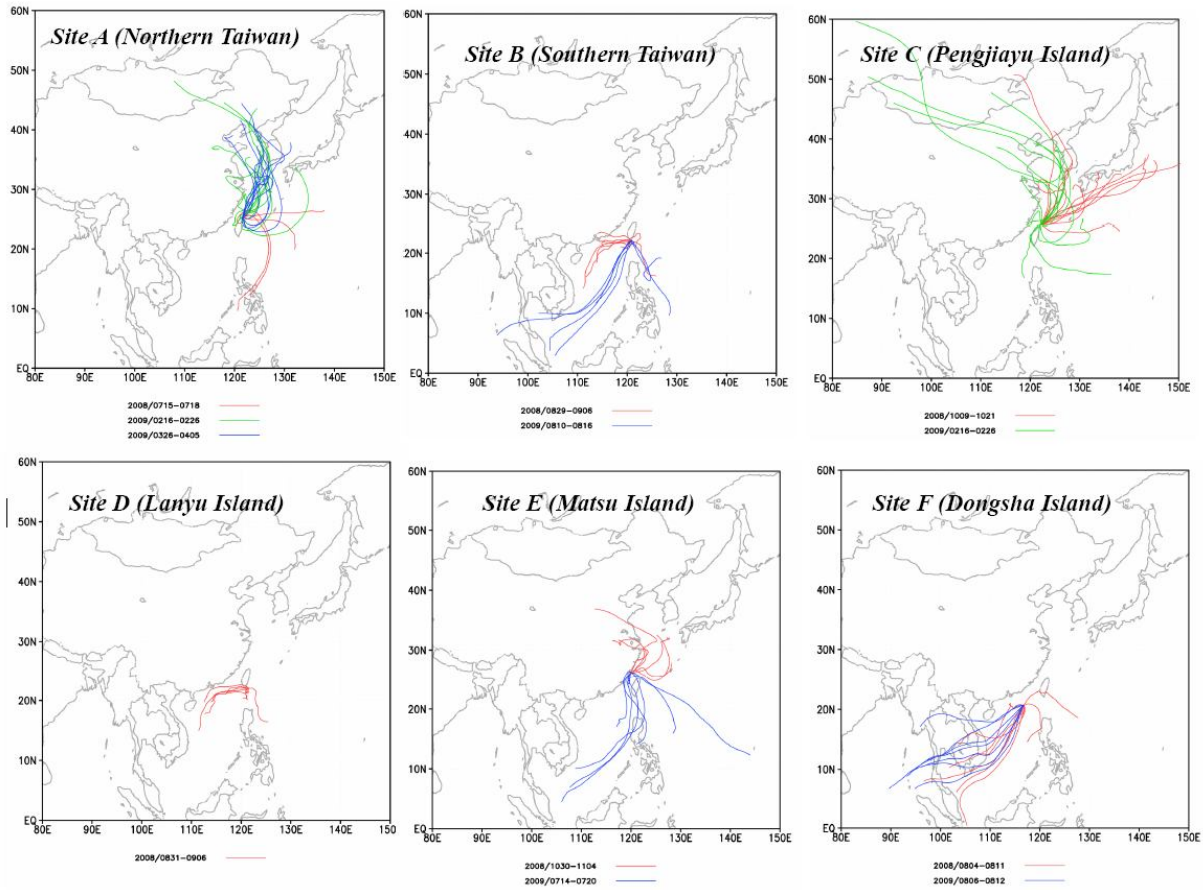


Fig. 2 Three-day backwards trajectory modeling of atmospheric sampling stations in Taiwan and on remote islands surrounding Taiwan during different sampling periods.