VARIATION OF AMBIENT PCDD/F CONCENTRATION IN NORTHERN TAIWAN DURING THE WINTER MONSOON EPISODE

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Abstract
In winter, Northeast monsoon episode originating in the mainland China make their way to populated area of East Asia, including Taiwan. Relevant epidemiological study reveals that suspended particles considerably influence respiratory health. Particularly, the contents of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) exist in suspended particles via long range transport have been investigated. In this study, the concentrations of total suspended particles and vapor/solid-phase PCDD/Fs are monitored at three sampling sites, one along the Northern coast of Taiwan, and the others in Taipei city and Northern Mountain, respectively. Before the winter monsoon season (2008/10/14-10/21), the atmospheric PCDD/F concentrations measured in northern Taiwan ranged from 0.901 to 11.4 fg I-TEQ/m^3. During the winter monsoon episode, an intensive observation program was carried out at the three stations in northern Taiwan since 2008/12/23 to 2009/1/14. Based on the results of the intensive observation program, the atmospheric PCDD/F concentrations (10.2~36.4 fg I-TEQ/m^3) measured in Taipei city during the normal periods were higher than that measured at other two background stations (2.35~22.5 fg I-TEQ/m^3). However, the atmospheric PCDD/F concentrations increased dramatically to 67.9 and 57.0 fg I-TEQ/m^3, respectively, at Northern coast and Northern Mountain during the Northeast monsoon episode (2009/1/9). Interestingly, the atmospheric PCDD/F concentrations measured at Northern Taiwan increased with decreasing temperature and relative humidity in ambient air during the Northeast monsoon episode.

Introduction
Polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) can be formed during combustion processes in the presence of carbon, oxygen, chlorine and metallic catalysts such as copper and iron. Oh et al.[1] have demonstrated that 70 to 80% of the PCDD/Fs in the atmosphere are bound to particles. Recently, relevant studies[2, 3] have indicated that approximately 972–51,200 fg I-TEQ/m^3 and 223–3,454 fg I-TEQ/m^3 PCDD/Fs were within the vicinity of electric waste processing facilities in the coastal provinces of Southeast China. Additionally, the results of our previous study[4] indicated that atmospheric PCDD/F concentrations increased 2.5 and 3.2 times in Northern Taiwan, during the Asian dust storm episode. Taiwan is an island in the subtropics, located off the southeast coast of Mainland China. In the winter and spring, Taiwan and the surrounding area is often under the influence of northeasterly monsoon winds originating in central Asia. The winter monsoon not only brings cold air but transports air pollutants and dust over long distances to Taiwan[5] and even to the Northwestern Pacific area. Recently, Prospero et al.[6], in a study of aerosols distributions in 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. Furthermore, they revealed that anthropogenic sulfate and nitrate concentrations in aerosols nearly doubled from 1981 to the mid-1990s, mainly due to increased emissions from China. A previous study[7] has likewise indicated that approximately 45% of total deposition of sulfate in Taiwan resulted from long-range transportation during the Northeast monsoon episode. In this study, the concentrations of particulate matters and seventeen 2, 3, 7, 8-substituted PCDD/F congeners were monitored with ambient air samplers at three sampling sites in northern Taiwan. The objective of this study is to evaluate the effects of the long-range transport episode on the partitioning of dioxin-like compounds between vapor and solid phases.

Materials and Methods
To measure PCDD/F concentrations and obtain vapor/solid partitioning of PCDD/Fs in ambient air during the periods of long range transport episodes, three sampling sites were set up based on the meteorological information and relative locations to the winter monsoon (Fig. 1). Sampling site A is located at radar station in Taipei county and near the coast of East China sea. Sampling site B is located at weather station (altitude: 820 m) on Yaming Mountain in Taipei city. Sampling site C is located at the campus of National Taiwan University in Taipei city. During the long-range transport episodes, one sample was taken everyday for 24 hours. Ambient air samples for the both 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 (8X10 inch) for collecting particle-bound compounds and polyurethane foam (PUF) plugs were used to retain PCDD/F compounds in the vapor phase. The total volume of the air sampled was > 800 m^3 for a typical sampling duration of 24 hours. Samples were brought back to the laboratory under refrigeration. The PUF and filter samples were than Soxhlet extracted with toluene for 24 hours, treated with concentrated sulfuric acid, and then passed through a series of clean-up columns containing sulfuric acid-silica gel, acidic aluminum oxide and celite/carbon. Finally, the dioxin congeners were analyzed using high resolution gas chromatography (HRGC) (Thermo Trace GC) /high resolution mass spectrometer (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W). The mass spectrometer was operated with a resolution greater than 10,000 under positive EI conditions, the data of seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed in the selected ion monitoring (SIM) mode.

Results and Discussion

Before the winter monsoon season (2008/10/14-10/21), the atmospheric PCDD/F concentration measured at Northern coast (Site A) and Northern mountain (Site B) in Taiwan range from 0.901 to 11.4 fg I-TEQ/m^3. The lower concentrations (0.901-3.80 fg I-TEQ/m^3) were measured at Site B. The results of our previous study [4] also indicated that the atmospheric PCDD/F concentrations measured in the urban area of Taiwan ranged from 20 to 110 fg I-TEQ/m^3. The low atmospheric PCDD/F concentration can be attributed to the lack of dioxin emissions and combustion sources within almost 10 km of the station at Site B. To further investigate the variation of atmospheric PCDD/F concentration during the winter monsoon episode, an intensive observation program was also carried out at the three stations in northern Taiwan since 2008/12/23 to 2009/1/14. During this period, the temperature and relative humidity in ambient observed at three sampling sites in northern Taiwan decreased sharply. Fig. 2 shows that the lowest daily temperature (3.8^oC) was observed at Site B on 2009/1/12. In the meantime, the daily average temperature and relative humidity observed in Taipei city (Site C) decreased to 12^oC and 58%, respectively. The winter monsoon not only brings cold air but transports air pollutants and dust over long distances to Taiwan. The PCDD/F measurement results indicated that there are four highly atmospheric PCDD/F events (2008/12/25, 2008/12/31, 2009/1/9 and 2009/1/12) during the Northeast monsoon period. Interestingly, the atmospheric PCDD/F concentrations measured at Northern Taiwan increased with decreasing temperature and relative humidity in ambient air during the Northeast monsoon episode. The highest atmospheric PCDD/F concentration (67.9 fg I-TEQ/m^3) was observed at Site A. However, the atmospheric PCDD/F concentration measured in urban area (Site C) was significantly lower than the background sites during the Northeast monsoon episode. Fig. 3 shows the PCDD/F concentrations in vapor/solid phases in northern Taiwan during the normal periods and Northeast monsoon episodes. The results indicated that the significant increases of solid-phase PCDD/Fs were observed at all three sampling sites in northern Taiwan especially in Northern mountain. During the normal periods, Fig. 4 shows that the quantities of PCDD/Fs adsorbed onto suspended particles was 370 pg I-TEQ/g-TSP in Taipei city (Site C) and 160 to 300 pg I-TEQ/g-TSP in background sites (Sites A and B). However, the particle-bound PCDD/Fs observed at Site B increased to 630 pg I-TEQ/g-TSP during the winter monsoon episode. During the winter monsoon episode, ambient temperatures observed at Site B were generally below 5^oC. Hence, the ambient air temperature affects the percentage of solid-phase PCDD/Fs. The results of the current study demonstrated that significant PCDD/F mass was adsorbed onto suspended particles measured in Northern Taiwan during the winter monsoon episode. We therefore conclude that the significant increase in solid-phase PCDD/Fs measured at northern Taiwan was attributable to the long-range transport of the effect of the Northeast monsoon episode.

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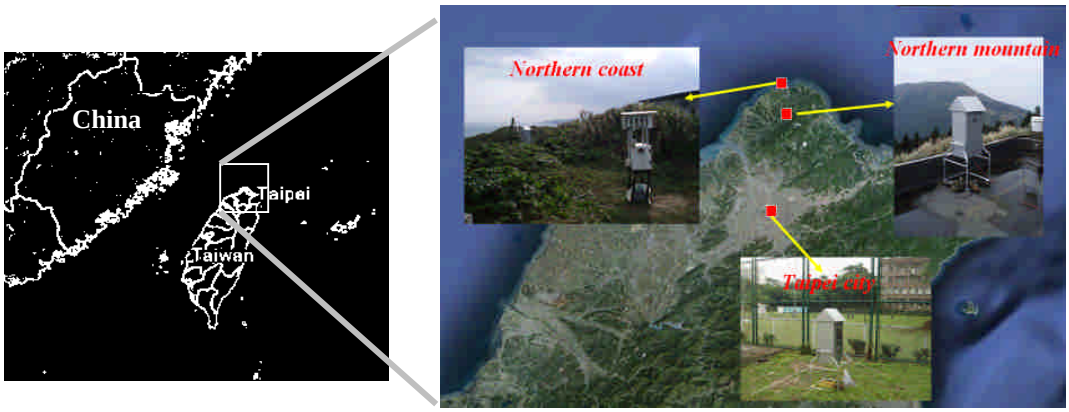

Fig. 1 Relative locations of three sampling sites (satellite image provided by http://maps.google.com).

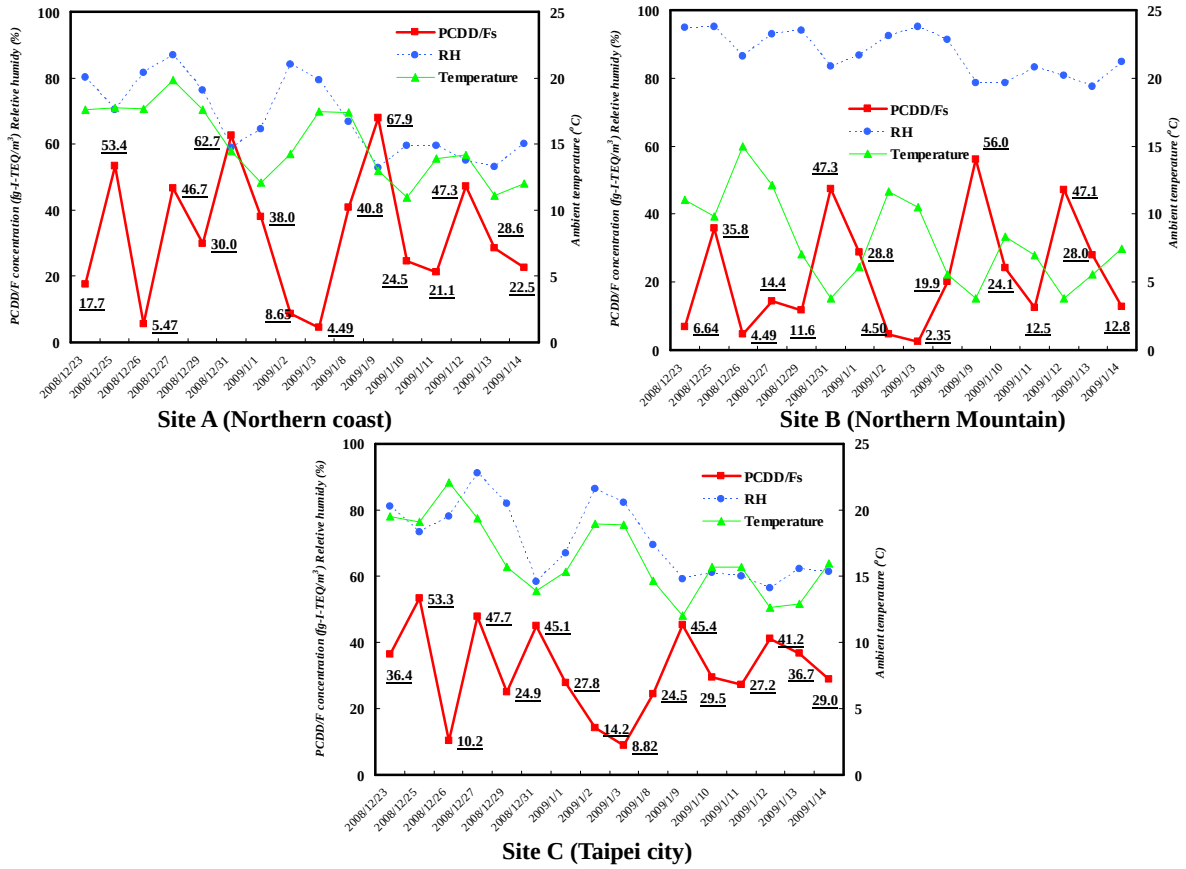

Fig. 2. Variation of atmospheric PCDD/F concentrations in Northern Taiwan during different periods.

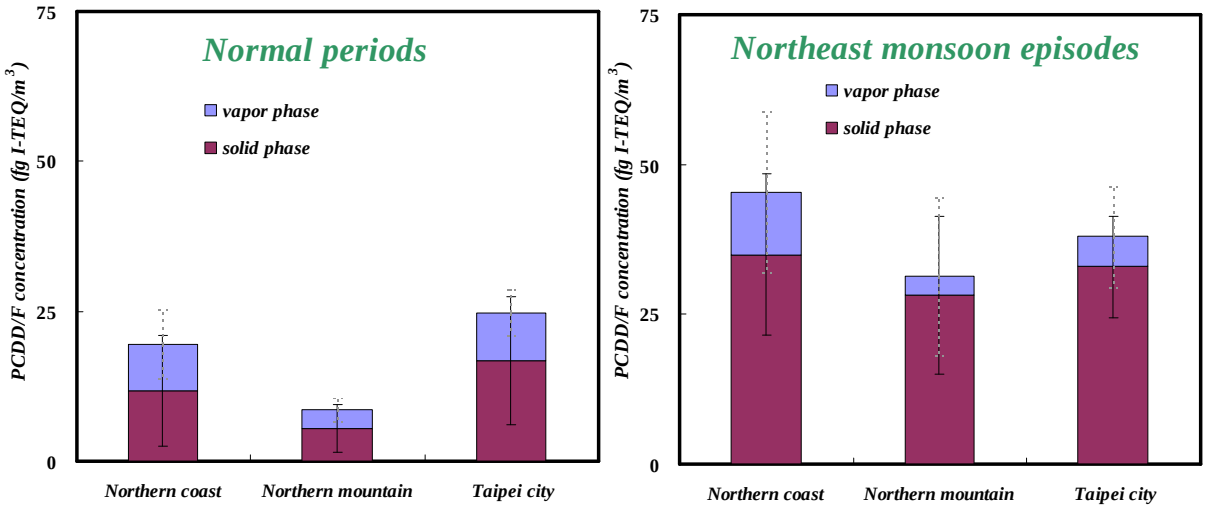

Fig. 3. Comparison of PCDD/F concentrations in vapor/solid phases in Northern Taiwan during the normal periods and Northeast monsoon episodes.

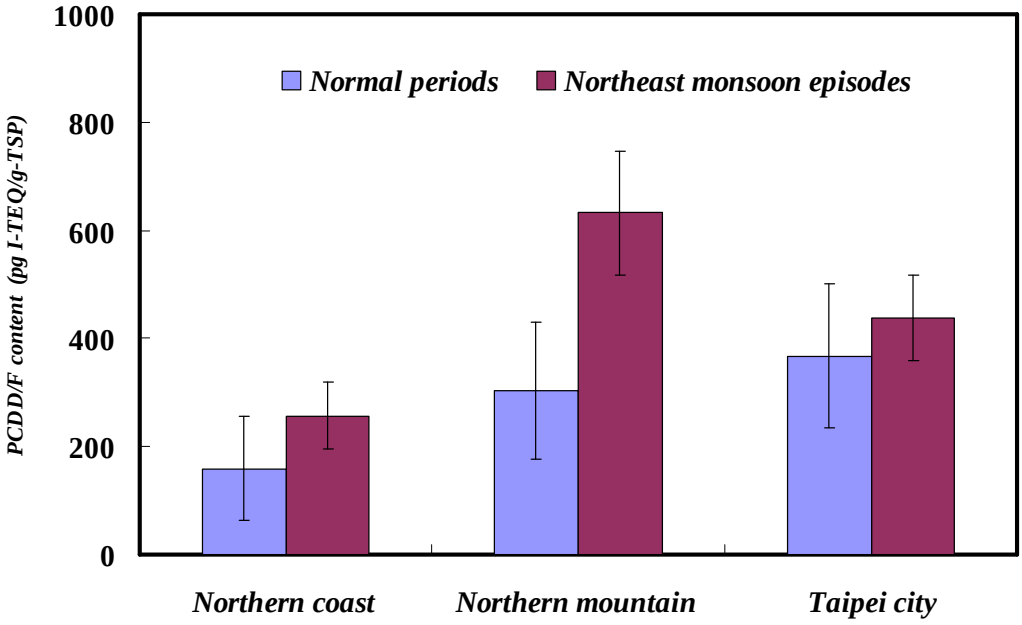

Fig. 4. Comparison of particle-bound PCDD/Fs in total suspended particle (TSP) in Northern Taiwan during the normal periods and Northeast monsoon episodes.