極端氣候與氣候變遷對台灣持久性有機污染物環境流布之影響

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ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent organic pollutants (POPs) that are formed and released unintentionally from anthropogenic sources. The high persistence of PCDD/Fs results in the concentrations of these contaminants in environment decreasing only very slowly. Two transport pathways, air and water, carry PCDD/Fs into all regions of the world. Recently, more frequent extreme weather events, such as storms and floods, have been projected to occur as a result of global warming. Extreme weather events have a documented impact on the remobilization and subsequent bioavailability of POPs. In this study, three specific episodes, namely winter monsoon, southeast biomass burning and tropical cyclone (typhoon) events, which influence the environmental fate and transport of PCDD/Fs in Taiwan, were evaluated based on a climate change scenario. During the winter (northeast) monsoon period, the temperature and relative humidity observed in northern Taiwan decreases sharply. During this time, the quantity of PCDD/Fs adsorbed onto suspended particles, as observed at background sites, was found to increase from 300±127 to 630±115 pg I-TEQ/g-TSP, which is even higher than that measured in Taipei City (438±80 pg I-TEQ/g-TSP). Hence, the winter monsoon not only brings cold air but also transports air pollutants and dust over long distances from mainland China to Taiwan. During the 2010 Southeast Asia biomass burning events (2010/3/22-3/28), the level of atmospheric PCDD/Fs were measured in central Taiwan (Mt. Lulin) and in the source region of northern Thailand (Chiang Mai); this revealed that the variations in atmospheric PCDD/F concentrations at these two sites followed a similar pattern. On 25 March 2010, the atmospheric PCDD/F concentration increased dramatically from 1.43 to 6.09 fg I-TEQ/m^3 at Mt. Lulin and from 7.64 to 12.1 fg I-TEQ/m^3 in northern Thailand. However, the atmospheric PCDD/F concentration decreased dramatically 1 day after the biomass burning event.

Key words: Dioxin, reservoir, biomass burning, extreme weather, long-range transport.

1. INTRODUCTION

Recently, the United Nations Environment Programme **(UNEP/AMAP, 2011)** proposed that the conceptual representation of key factors influencing the environmental fate and transport of PCDD/Fs under a climate change scenario include: (1) the strength of secondary re-volatilization sources, (2) wind fields and wind speed, (3) precipitation, (4) ocean currents, (5) the melting of polar ice caps and mountain glaciers, (6) the frequency of extreme events, (7) the degradation and transformation of POPs, (8) environmental partitioning and (9) biotic transport. Climate variation thus may lead to exposure to these chemicals via a variety of sources, processes and mechanisms. This has implications when evaluating the effectiveness of the Stockholm Convention because the measured levels of POPs will include a climate-induced component **(UNEP/AMAP, 2011)**. 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 northeast monsoon winds (October to March) that originates from central Asia. The northeast monsoon not only brings cold air but also transports airborne pollutants and dust over long distances from central Asia to Taiwan **(Hsu et al., 2009)** and even onwards into the South China Sea area **(Wang et al., 2011)**. In addition, the majority of environmental PCDD/F sources are related to anthropogenic activities, some natural processes generating PCDD/Fs in small amounts have been identified biomass burning **(Hung et al., 2010)**. More forest fires and biomass burning events are projected to occur as a result of global warming. During the past decade, Southeast Asia biomass burning has raised global concerns over its adverse effects on visibility, human health and global climate, due to the emission of particulate matter and other gaseous pollutants such as CO, SO_x, NO_x and volatile organic compounds including PCDD/Fs **(Gullett et al., 2006)**. In this study, three specific episodes, namely winter monsoon and southeast biomass burning events were explored in terms of their influence on the environmental fate and transport of PCDD/Fs in Taiwan under a climate change scenario.

2. EXPERIMENTAL

To measure PCDDs/PCDF concentrations and obtain vapor/solid partitioning of the PCDD/Fs in ambient air during the long range transport episodes, three sampling sites were set up in northern Taiwan based on meteorological information and their location relative to the Northeast winter monsoon (Fig. 1a). Sampling site A was located at radar station in Taipei County and near the East China Sea coast. Site B is located at a weather station (1,080 m above mean sea level) on Yang-Ming Mountain area of northern Taiwan. No significant PCDD/F emission sources existed in the vicinity of these two sampling stations. Sampling site C is located on the campus of National Taiwan University in Taipei City, which is situated in a volcanic basin in northern Taiwan and has a population of 2.6 million. During the winter monsoon episodes, one sample was taken every day, with each sample covering 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). In order to measure the long-range transport of PCDD/Fs, two high-altitude sampling sites were selected based on meteorological information and their location relative to biomass burning in Eastern Asia (Fig. 1b). In central Taiwan, the sampling station was located at the peak of Mt. Lulin (23.51-^{o}N, 120.92-^{o}E; 2,862 m above mean sea level). Chiang Mai, with an elevation of 310 m, is located in the mountainous northern Thailand. This city is a shipping center for agricultural products from the surrounding region, but also produces silver and wood articles, pottery, silk goods and cotton goods. The sampling site is located at Suthep Mountain under the jurisdiction of the Doi Suthep-Pui National Park Protection Unit (1,396 m above mean sea level). In central Taiwan, all PCDD/F samples were taken during regular sampling periods (February, March, April, June, October and December, 2010) and four to six samples were taken each month for the analysis of PCDD/Fs. During the special long range transport season (March 2010), one sample was taken every day at Mt. Lulin and Chiang Mai, with each sample covering 24 hours. For PCDD/Fs analysis, the ambient air and sediment samples were then spiked with known amounts of internal quantification standards according to USEPA method 23 and 1613, respectively. The detail information regarding the extraction and clean-up procedure of PCDD/F samples was provided elsewhere **(Chi et al., 2008 and 2009)**. Finally, the PCDD/F samples were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (Thermo DFS) equipped with a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W).

3. RESULTS AND DISCUSSION

3.1 Variation of ambient PCDD/F concentration in northern Taiwan during the winter monsoon episode

In winter, northeast monsoon episodes originating in the mainland China make their way to the populated areas of East Asia, including Taiwan. Before the northeast monsoon season (2008/10/14-10/21), the atmospheric PCDD/F concentration measured at the northern coast (Site A) and the northern mountain (Site B) sites in Taiwan ranged from 0.901 to 11.4 fg I-TEQ/m^3. During the period 2008/12/23 to 2009/1/14, the ambient temperature and relative humidity observed at three sampling sites in northern Taiwan decreased sharply. Fig. 2 shows that the lowest daily temperature (3.8^{o}C) was observed at Site B on 2009/1/12. At the same time, the daily average temperature and relative humidity observed in Taipei City (Site C) decreased to 12^{o}C and 58%, respectively. The winter monsoon not only brings cold air but also transports air pollutants and dust over long distances to Taiwan. The PCDD/F measurement results indicated that there were four atmospheric PCDD/F event peaks (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 the northern Taiwan sites increased with the decreasing temperature and relative humidity of the ambient air during the Northeast monsoon episodes. The highest atmospheric PCDD/F concentration (67.9 fg I-TEQ/m^3) was observed at Site A. Interestingly, the atmospheric PCDD/F concentrations measured at the urban area (Site C) were significantly lower than the background sites during the Northeast monsoon episodes. The backward trajectory analysis periods are shown in Fig. 3. Over Taiwan, the weather patterns are strongly affected by the monsoon circulation over East Asia. In general, the northeast monsoon prevails from late autumn to early spring, while the southwest monsoon prevails in late spring and early autumn **(Lin et al. 2004; 2007).** The backward trajectories (Fig. 3) calculated for northern Taiwan reveal that the air masses seem to have originated over the coast of mainland China during the northeast monsoon periods (2008/12/24~12/25, 2008/12/31~2009/1/1, 2009/1/8~1/9, 2009/1/11~1/13). Table 1 indicates that the atmospheric PCDD/F concentrations observed at background stations, namely Site A (10.4±7 fg I-TEQ/m^3) and Site B (18.9±11 fg I-TEQ/m^3), were lower than that observed at Site C (25.3±13 fg I-TEQ/m^3) during the non-northeast monsoon periods. However, significant increases in PCDD/F concentrations and decreases in ambient temperature and relative humidity were observed at three sampling stations during the northeast monsoon periods. Interestingly, the atmospheric PCDD/F concentrations observed at the background stations, namely Site A (39.1±13 fg I-TEQ/m^3) and Site B (48.4±14 fg I-TEQ/m^3), were even higher than that observed at Site C (38.0±10 fg I-TEQ/m^3) in urban area during the northeast monsoon periods. We therefore consider that the elevated atmospheric PCDD/F concentrations observed in northern Taiwan during the northeast monsoon periods are attributable to the transportation of anthropogenic emissions from mainland China.

3.2 Evaluation of long-range transport of PCDD/Fs during the Southeast Asia biomass burning event

To evaluate the effects of biomass burning on the atmospheric concentration variation of POPs, the atmospheric PCDD/Fs were monitored in central Taiwan (Mt. Lulin) and in northern Thailand (Chiang Mai) during a specific biomass burning season in 2010. During the regular sampling periods, the atmospheric PCDD/F and TSP concentrations measured at the Lulin station in 2010 were 0.232±0.02-4.12±0.3 fg I-TEQ/m^3 and 8.6±2.6-45.2±29 μg/m^3, respectively (Fig. 4). The lowest concentrations were measured during the summer season (23-30 June, 2010). Atmospheric PCDD/F concentrations measured at Mt. Lulin in central Taiwan were significantly lower than those measured at other background stations. The low atmospheric PCDD/F concentration can be attributed to the lack of dioxin emissions and combustion sources within almost 50 km of the station at Mt. Lulin. Nonetheless, much higher concentrations of atmospheric PCDD/Fs and TSPs were observed at the Lulin station during the spring season. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (1 km resolution) data shows significant active fires could be detected over the period 21st to the 25th March. The satellite data and air mass paths revealed that the air mass of the PCDD/F peak layer seems to have come from the biomass-burning regions during these episodes. An intensive observation program of atmospheric PCDD/Fs was carried out at the same time at Lulin station and in the source regions of northern Thailand. Fig. 5 shows the atmospheric PCDD/F concentrations measured in central Taiwan and the source regions in northern Thailand (2010/3/22-3/28) during the Southeast Asia biomass burning events. These results reveal that the variations in atmospheric PCDD/F concentrations at these two sites were quite similar. On 25 March 2010, the atmospheric PCDD/F concentration increased dramatically from 1.43 to 6.09 fg I-TEQ/m^3 at Mt. Lulin and from 7.64 to 12.1 fg I-TEQ/m^3 in northern Thailand. Interestingly however, the atmospheric PCDD/F concentration then decreased dramatically 1 day after the biomass burning event. To further investigate the impact of Southeast Asia biomass burning on East Asia, we conducted tracer simulations via WRF/Chem using tracers placed from 22nd to 27th March over the fire locations reported by the MODIS satellite. Fig. 6 depicts the horizontal distribution of the tracer concentration and wind field at the level of 700 hPa (around 3 km). At 08:00 UTC 25 March, the high concentration tracers were found to have been transported to Taiwan following the strong wind belts and this continued over the whole day. Then the tracer concentration gradually diluted after 26

March. Our modeling study fits very well with the sampling at Mt. Lulin. The simulation results confirm that the source of the high PCDD/F concentration is attributable to biomass burning in Indochina, specifically northern Thailand.

3.3 Sources of PCDD/Fs in a reservoir system in northern Taiwan during the tropical cyclone (typhoon) event

In general, the deposition fluxes of PCDD/Fs measured in reservoir systems are a useful way of evaluating the effectiveness of legislative actions on the inputs of contaminants. In order to quantify the relative PCDD/F deposition fluxes and to identify probable sources, a comprehensive and systematic investigation was conducted to measure atmospheric and sedimentary deposition in the Feitsui reservoir in northern Taiwan. As shown in Fig. 7, the atmospheric PCDD/F deposition flux measured at the meteorological station of the investigated reservoir ranged from 0.95 to 30.8 pg I-TEQ/m^2/day. The annual atmospheric PCDD/F input flux in the vicinity of the reservoir was 2.4 ng I-TEQ/m^2/year. However, a much higher deposition flux of atmospheric PCDD/Fs was observed during the northeast monsoon episode (December, 2008). In this work, we develop an objective method to classify the air mass following each frontal passage in northern Taiwan according to the amounts of long-range transported (LRT) dust and air pollutants **(Chi et a., 2011)**. The meteorological parameters observed near the coasts, such as temperature and winds, can be used to identify the time and intensity of the frontal passage. The air mass behind a front usually contains Asian continental air, while winds before the frontal passage tend to be weak and thus local emissions can then dominate the distribution of air pollutants. For contrast purposes, the analysis starts one day before the frontal passage and lasts for four days in order to cover the entire period of a typical frontal passage. Fig. 7 indicated that significant long range transport of pollutants occurred during the northeasterly monsoon period (January to May and October to December) in 2008.

To evaluate the anthropogenic pollution history and the impact of the specific events in northern Taiwan, PCDD/F concentrations and crust-derived elements were analyzed at 2 cm intervals in one dated sediment core collected at the reservoir being investigated. The total organic carbon (TOC) and water content at various depths of a sediment core collected from the lower reaches of the reservoir. The TOC content increases with depth and is thus higher at the bottom of the core. Relevant studies regarding the sedimentation rate in the Feitsui Reservoir **(Lo, 1994)** have indicated that the 20 cm modern sediment corresponds to a time span of 15 years (from June 1987 to August 2002), which yielded a mean sedimentation rate of 1.3 cm/year. In the present study, the core bottom (depth: 30–32 cm) contained root debris exhibiting a yellowish color, which distinguished it from the grayish sediments of the upper core. The bottom layer is apparently the old soil and marks the year in which the reservoir was filled (A.D. 1987). Therefore, the mean sedimentation rate was determined to be 1.5 cm/year. The representative age of the sediment core at various depths was estimated from the sedimentation rate. The results reveal that the PCDD/F concentrations ranged from 0.7 to 3.3 ng I-TEQ/kg. Based on the PCDD/F concentrations at different depths and the mean sedimentation rate, the annual input fluxes of PCDD/Fs into the reservoir can be calculated. As shown in Fig. 8, the PCDD/F input flux into sediment of the reservoir ranged from 8.1 to 20 ng I-TEQ m^2/year. The PCDD/F input flux (9.0 ng I-TEQ m^2/year) obtained from the surface sediment (depth: 0-2 cm) was significantly higher than the atmospheric PCDD/F deposition rate (2.4 ng I-TEQ m^2/year). The catchment area of the reservoir is around 330 km^2, which is 30 times greater than that of the reservoir area (10.2 km^2). Therefore, the PCDD/F input flux measured in the reservoir would seem to be the sum of the PCDD/F input flux in the reservoir and its catchment area. The higher PCDD/F input flux in the sediments as compared with atmospheric deposition thus probably reflect erosion in the lower reaches of the reservoir catchment area, especially during intensive typhoon events. Typhoon and flooding events may significantly contribute to the re-emission and redistribution of PCDD/Fs and other POPs originally stored in sediment and agricultural soils. Therefore, Fig. 8 compared the PCDD/F input flux in sediment with the variation in number of typhoon events and total rainfall during typhoon events in northern Taiwan over the past 20 years. The results indicated that, during intensive typhoon events (total rainfall >1,500 mm during typhoon events), which occurred in 1990, 2001, 2004 and 2005, there were significant increases in PCDD/F input flux observed at the corresponding depths of sediment core. The PCDD/F input flux was also related to the number of typhoon events in the area of the reservoir of interest. The level of crust-derived elements measured at depths of 24-26 cm (estimated year 1990), 12-14 cm (estimated year 2001), 6-8 cm (estimated year 2004) and 4-6 cm (estimated year 2005) in the sediment core were higher than those measured at other depths within the sediment core. These results suggest that the sharp increases in the input flux of PCDD/Fs and mineral-derived elements during 1990, 2001, 2004 and 2005 are likely to have resulted from a deep turbid layer that formed upstream after landslides and/or mud flows during the typhoon period. Therefore, intensive and consecutive tropical cyclones (typhoons) that result in heavy rainfall causes increased soil erosion; this resulted in a significantly higher PCDD/F input flux into the sediment of the reservoir, specifically in 1990, 2001, 2004 and 2005.

4. CONCLUSIONS

As climate change alters the primary and secondary release of PCDD/Fs, then the levels and patterns of exposure to these chemical of wildlife and humans will also change. We consider that the climate change will increase the airborne transport to downwind locations such as Taiwan from the main emission areas of the Asian continent. This is because there will be higher wind speeds and stronger air circulation, both of which are relevant on a regional scale to long-range transport. After primary release, PCDD/Fs circulate via environmental media until deposited in environmental reservoirs. Secondary release involves remobilization from these reservoirs.

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REFERENCES

Chi, K.H., Hsu, S.C., Wang, S.H., Chang, M.B., 2008. Increases in ambient PCDD/F and PCB concentrations in Northern Taiwan during an Asian dust storm episode. Science of the Total Environment 401, 100-108.

Chi, K.H., Liu, K.T., Chang, S.H., Chang, M.B., 2009. Atmospheric deposition of PCDD/Fs measured via automated and traditional samplers in Northern Taiwan. Chemosphere 77, 1184-1190.

Chi, K.H., Hsu, S.-C., Lin, C.-Y., Kao, S.J., Lee, T.Y., 2011. Deposition fluxes of PCDD/Fs in a reservoir system in northern Taiwan. Chemosphere 83, 745-752.

Gullett, B.K., Touati, A., Huwe, J., Hakk, H.E., 2006. PCDD and PCDF emissions from simulated sugarcane field burning. Environmental Science & Technology 40, 6228-6234.

Hsu, S.C., Liu, S.C., Huang, Y.T., Chou, C.C.K., Lung, S.C.C., Liu, T.H., Tu, J.Y., Tsai, F., 2009. Long-range southeastward transport of Asian biosmoke pollution: Signature detected by aerosol potassium in Northern Taiwan. Journal of Geophysical Research 114, D14301.

Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J.M., Leppänen, S., Bossi, R., Skov, H., 2010. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006. Science of the Total Environment 408, 2854-2873.

Lin, C.Y., Liu, S.C., Chou, C.C.K., Liu, T.H., Lee, C.T., Yuan, C.S., Shiu, C.J., Young, C.Y., 2004. Long-range transport of Asian dust and air pollutants to Taiwan. Terrestrial, Atmospheric and Oceanic Sciences 15, 759-784.

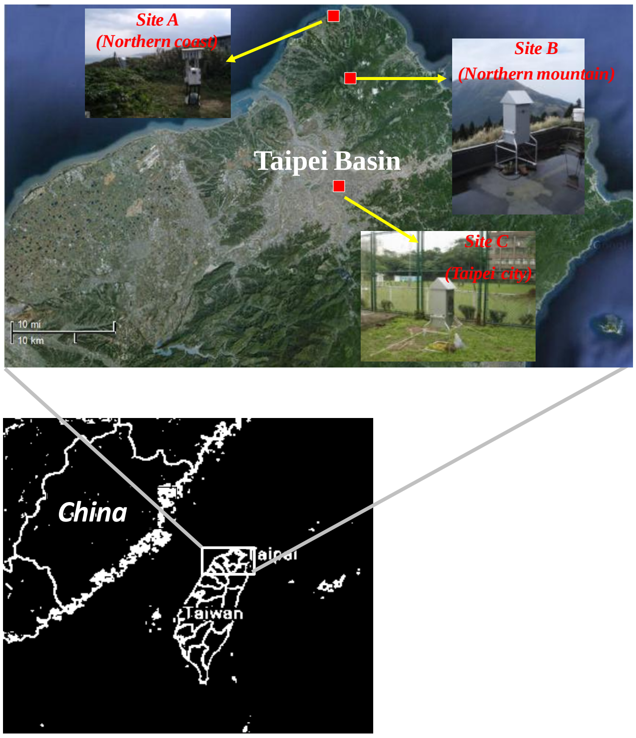
Lin, C.Y., Wang, Z., Chen, W.N., Chang, S.Y., Chou, C., Sugimoto, N., Zhao, X., 2007. Long-range transport of Asian dust and air pollutants to Taiwan: observed evidence and model simulation. Atmospheric Chemistry and Physics 7, 423-434.

Lo, K.F.A., 1994. Quantifying soil erosion for the Shihmen reservoir watershed, Taiwan. Agricultural Systems 45, 105-116.

UNEP/AMAP, 2011. Climate Change and POP s: Predicting the Impacts.Report of the UNE P/AMAP Expert Group. Secretariat of the Stockholm Convention, Geneva. 62.

Wang, S.-H., Tsay, S.-C., Lin, N.-H., Hsu, N.C., Bell, S.W., Li, C., Ji, Q., Jeong, M.-J., Hansell, R.A., Welton, E.J., Holben, B.N., Sheu, G.-R., Chu, Y.-C., Chang, S.-C., Liu, J.-J., Chiang, W.-L., 2011. First detailed observations of long-range transported dust over the northern South China Sea. Atmospheric Environment 45, 4804-4808.

(a)



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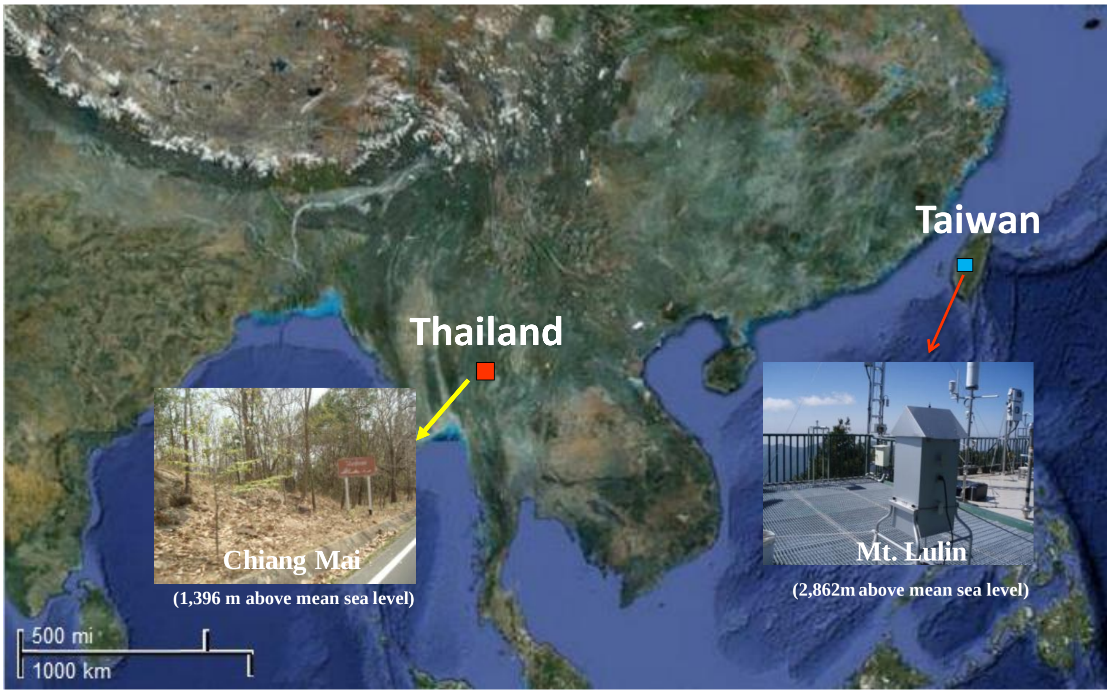

Fig. 1 Relative locations of (a) three sampling sites during the winter monsoon events and (b) two high-altitude sampling sites in Southeast Asia (satellite image provided by http://maps.google.com)

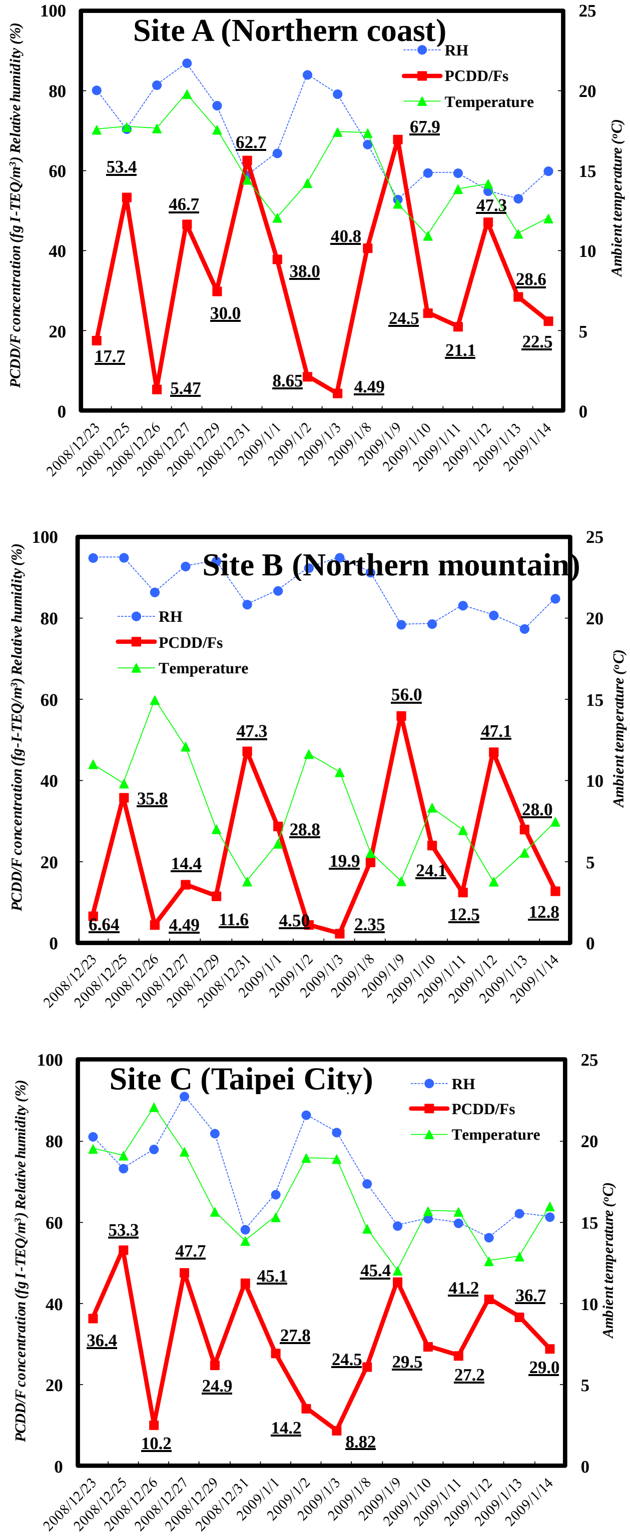

Fig. 2 Variation of atmospheric PCDD/F concentration, ambient temperature and relative humidity (RH) in northern Taiwan during different periods.

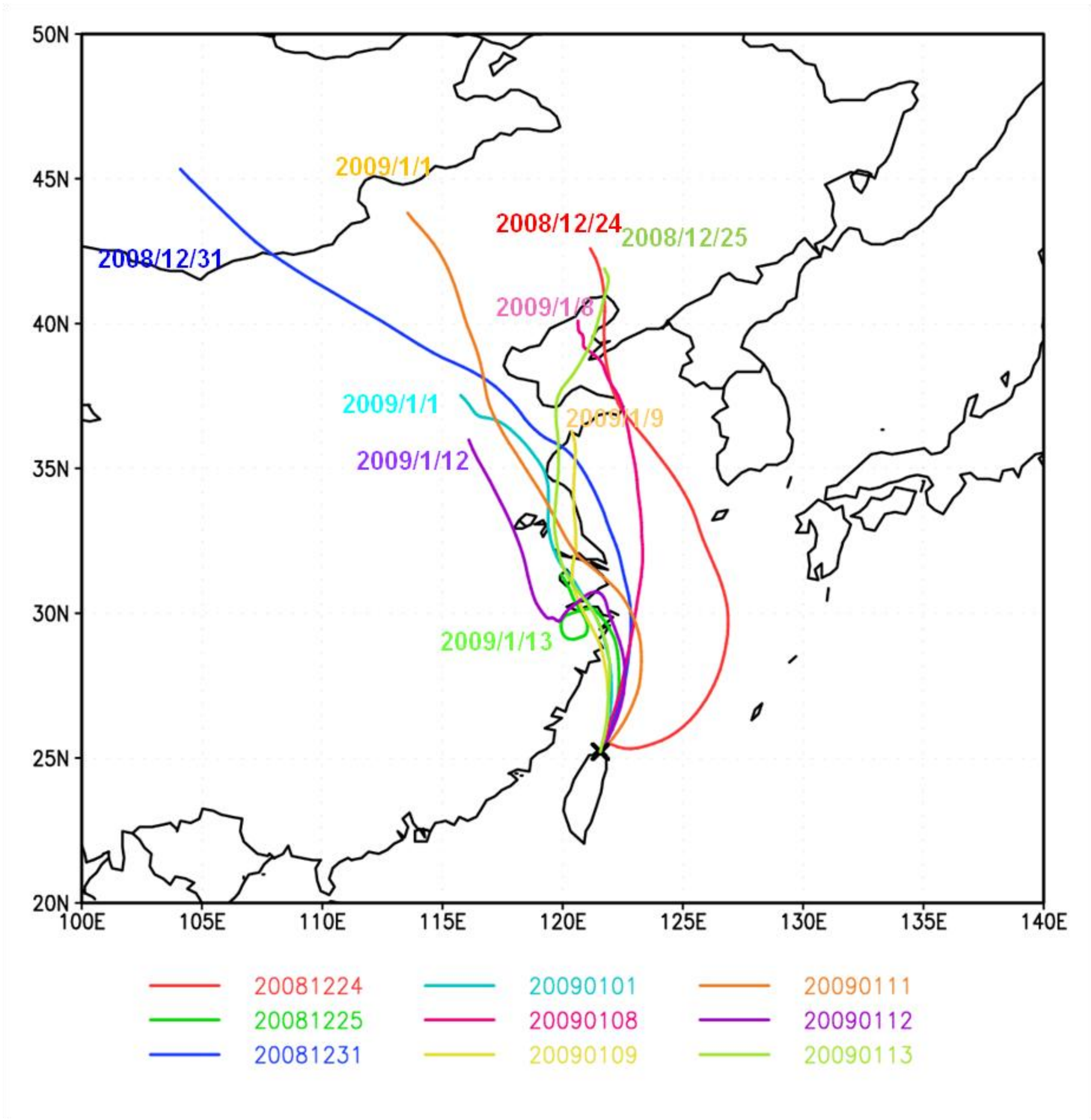

Fig. 3 Five-day backwards trajectory modeling of the atmospheric sampling stations in northern Taiwan during the winter monsoon period.

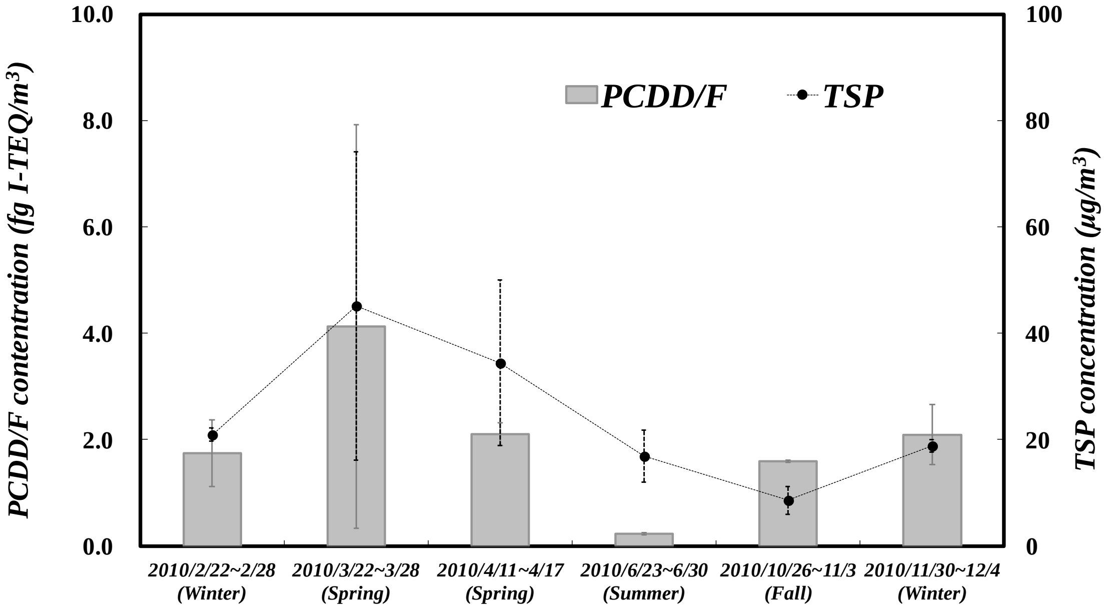

Fig. 4 Atmospheric PCDD/F and total suspended particle (TSP) concentrations measured at Lulin station during different periods.

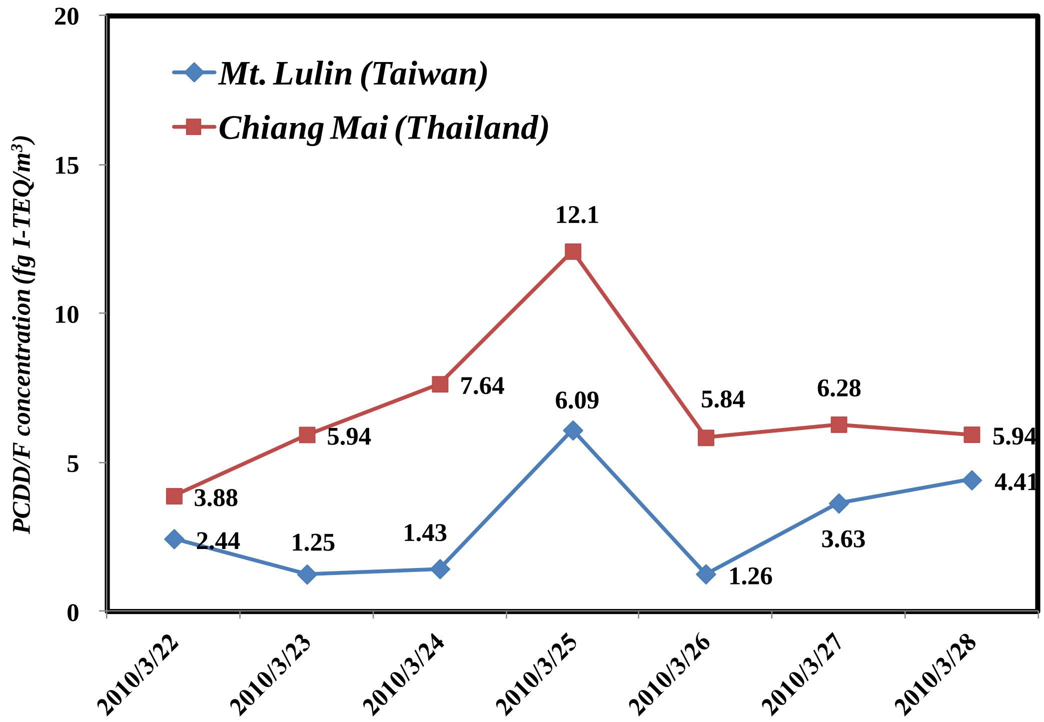

Fig. 5 Variation in atmospheric PCDD/F concentrations measured in Taiwan and Thailand during significant biomass burning events (2010/3/22-3/28).

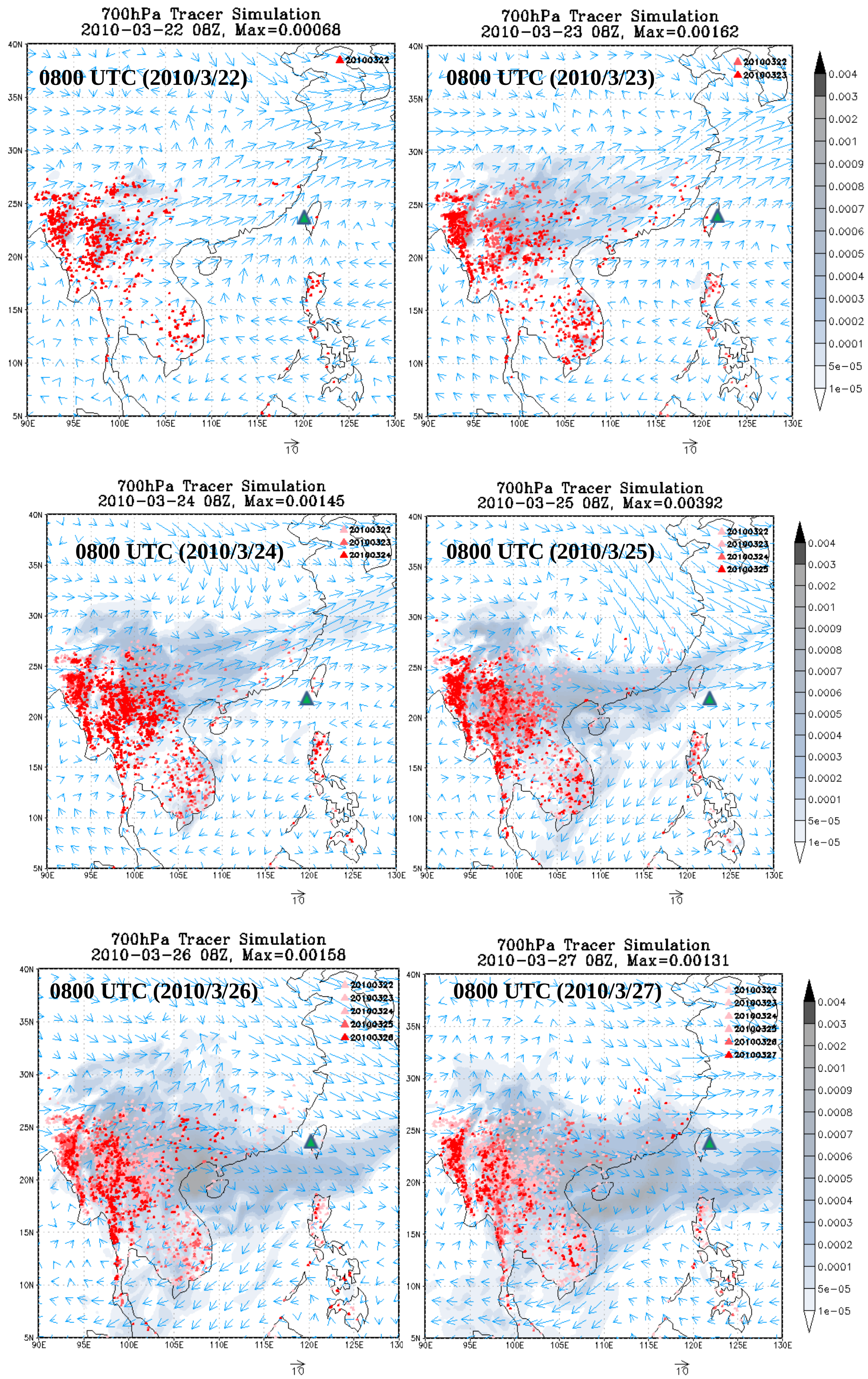

Fig. 6 Simulated distributions of tracer concentration (colored) and wind field at 700 hpa (08:00UTC 22 March 2010 to 0800 UTC 27 March 2010).

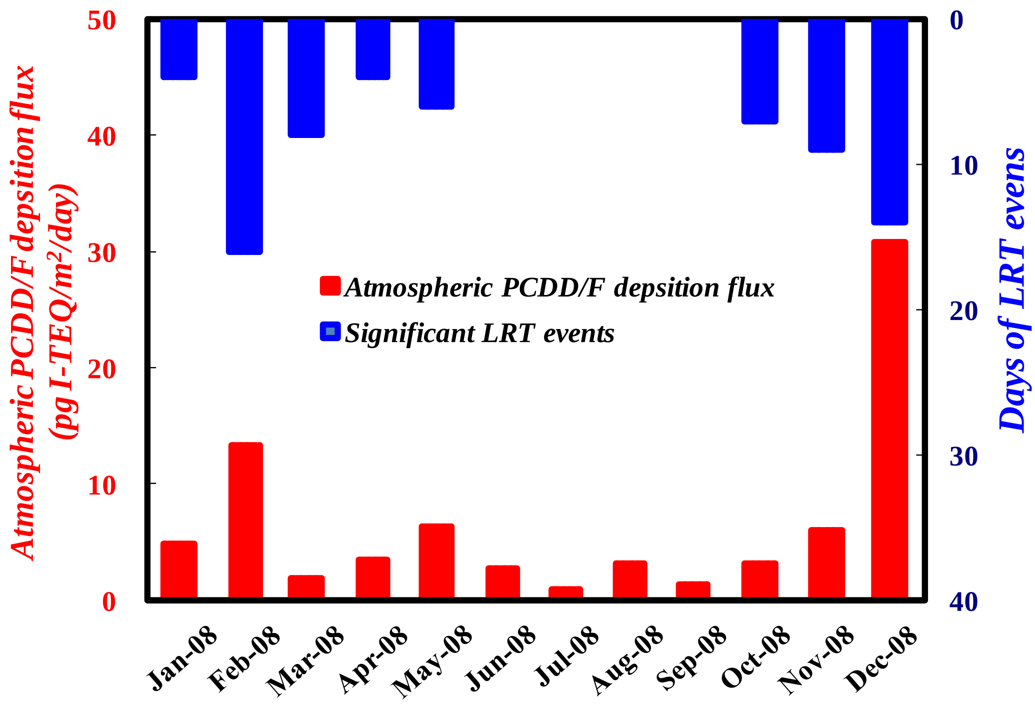

Fig. 7 Comparison of atmospheric PCDD/F deposition flux monthly variation measured in northern Taiwan in relation to the significant long-range pollutant transpiration events during 2008.

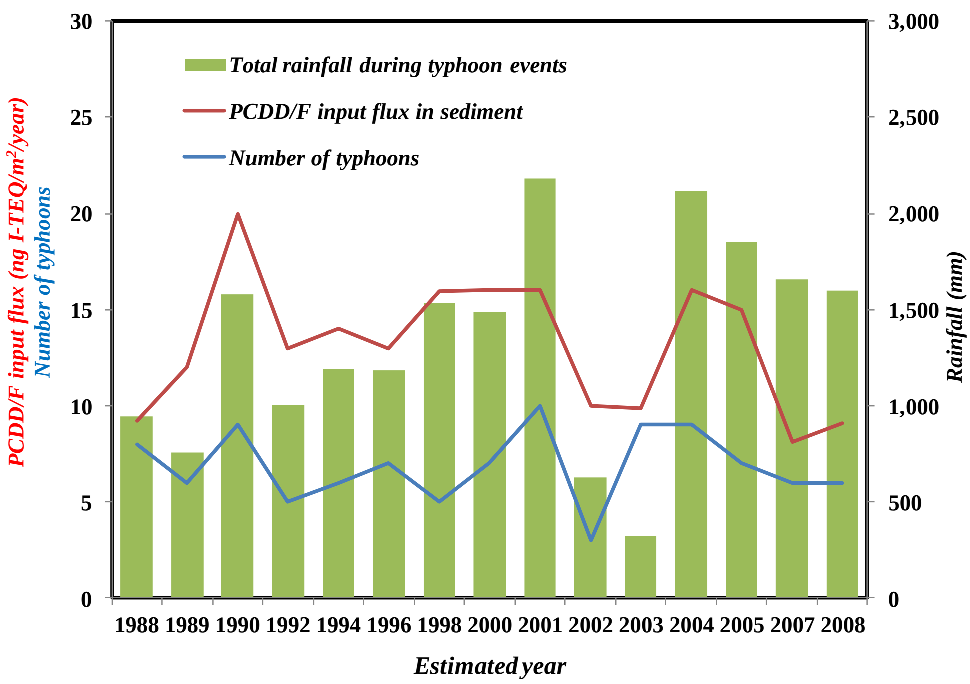

Fig. 8 Comparison of PCDD/F input flux in sediment in relation to the variation in total rainfall and number of typhoons during typhoon events in northern Taiwan.