# PCDD/F MEASUREMENT AT THREE HIGH-ALTITUDE STATIONS IN EASTERN ASIA: EVALUATION OF LONG-RANGE TRANSPORT OF PCDD/FS DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT

Chi KH[1*], Chen YF[1], Lin CY[2], Sheu GR[3], Lin NH[3]

[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]Department of Atmospheric Sciences, National Central University, Chungli 320, Taiwan.

## Introduction

Limited data suggest that field burning of agricultural crops can result in formation and emission of PCDD/Fs[1]. The year 2000 draft United States inventory of PCDD/F sources indicates that about 6% of the estimated total annual emissions come from forest fires[2]. It is further unclear whether PCDD/F emissions are mainly from combustion of the biomass itself, or simply due to the volatilization of compounds on the biomass surface that had previously been ''scrubbed'' from the atmosphere[3]. In recent years, Eastern Asia biomass burning has caused global concerns due to its adverse effects on visibility, human health and global climate by emitting particulate matter and other gaseous pollutants such as CO, $SO_x$, $NO_x$ and VOCs. A previous study[3] also indicated that the PCDD/F emission factor via biomass burning ranged from 15 to 25 ng TEQ/kg burned. The mass-specific emissions are about 20 times higher than the concentration of the extracted biomass, suggesting that PCDD/F emissions are not simply a result of vaporization of cuticle-bound PCDD/F but are formed predominantly during the biomass combustion. Relevant epidemiological study[4] reveals that suspended particle considerably influences respiratory health. A previous study[5] indicated that around 70 to 80% PCDD/F concentrations in the atmosphere were essentially bound to particles. The solid-phase PCDD/Fs are brought into the atmosphere through wind blowing, and eventually settle to water bodies or other receptors in the environment via either dry or wet deposition mechanism. To our knowledge, few studies have been conducted toward examining the relationship between the Eastern Asia biomass burning and the concentrations of atmospheric PCDD/Fs. In this study, the concentrations of particulate matter and seventeen 2, 3, 7, 8-substituted PCDD/F were monitored in central Taiwan (Mountain Lulin), northern Vietnam (Son La) and Thailand (Chiang Mai) using high volume ambient air samplers during 2010 and 2011. The objective of this study is to evaluate the effects of Southeast Asia biomass burning on the atmospheric concentration variation of dioxin compounds.

## Materials and methods

In order to measure the long-range transport of PCDD/Fs, three high-altitude sampling sites were selected based on the meteorological information and location relative to the biomass burning in Eastern Asia (Fig. 1). In central Taiwan, the sampling station is located at the peak of Mt. Lulin (23.51-$^{o}$N, 120.92-$^{o}$E; 2,862 m above mean sea level). Its high elevation means it is generally free from local pollution. Mt. Lulin generally lies in the free troposphere (especially during the winter months) and is free from boundary layer pollution. Frontal mechanisms, which frequently occur in winter and spring of Taiwan, have been reported to be able to transport pollutants from the boundary layer to the free troposphere. Chiang Mai, with an elevation of 310 m, is located in the mountainous northern Thailand. This city is a shipping center for agricultural products of the surrounding region, but also produces silver and wood articles, pottery, and silk 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). It is located to the west of Chiang Mai, about 20 km away. Fires, which were several hundred meters away from the site, were occasionally observed during the experiment. In northern Vietnam, the sampling station is located at the National hydro-meteorological service of Vietnam, northeastern regional hydro-meteorological observatory(103.91-°E 21.32-°N; 660 m above mean sea level) in Son La province. No significant PCDD/F emission sources existed in the vicinity of these three high-altitude stations. In central Taiwan, all PCDD/F samples were taken during the regular sampling periods (Febuary, March, April, June, Octobor, December, 2010 and March 2011) for the analysis of PCDD/Fs with 4 to 6 samples taken each month. During a special long range transport season (2010/3/22-3/28 2011/3/19-3/30), one sample was taken everyday

for 24 hours at Mt. Lulin, Son La and Chiang Mai in the meantime. Ambient air samples for both vapor phase and particle phase of dioxin-liked compounds were collected using high volume sampling trains (Shibata HV-1000F). The HV-1000F samplers were equipped with Whatman quartz fiber filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs were used for retaining PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 1,000 $m^3$ for a typical sampling duration of 1 day. The PUF and filter samples were than Soxhlet extracted with toluene for 24 hrs, 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. The detailed information regarding the extraction and clean-up procedure of PCDD/F samples is provided elsewhere[6]. In this study, only the seventeen 2,3,7,8-substituted PCDD/F congeners 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).

**Results and discussion**

During the regular sampling periods, the atmospheric PCDD/F and TSP concentrations measured at Lulin station in 2010 and 2011 range from 0.232±0.02-6.76±4.6 fg I-TEQ/$m^3$ and 8.6±2.6-54.2±29 μg/$m^3$, respectively (Fig. 2). The lowest concentrations were measured during the summer season (23-30 June, 2010). Atmospheric PCDD/F concentrations measured at Lulin Mountain 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 Lulin Mountain. However, a significant increase of PCDF compounds in ambient air is measured during the spring, and the highest concentration of atmospheric PCDD/Fs and TSPs was observed at Lulin station during the spring season. In addition, the average concentrations of CO, ozone and $PM_{10}$ measured at Lulin station in 2010 are about 144±67 ppb, 33±15 ppb and 11.2±10 μg/$m^3$, respectively. The background concentrations of CO, ozone and $PM_{10}$ are estimated 82 ppb, 28 ppb and 6.0 μg/$m^3$, respectively. Especially in March, the concentrations of above three pollutants (CO: 215±92 ppb, ozone:51±17 ppb and $PM_{10}$: 25±15 μg/$m^3$,) show twice higher than their background values. These results imply that the higher atmospheric PCDD/F and TSP concentrations observed at Lulin station in the spring could be attributed to the effects of long-range transport of Southeast Asia biomass burning. Based on meteorological data, the southwest and west winds predominated since March at Lulin Mountain. To analyze the effects of the Southeast Asia biomass burning event in Taiwan during the period of March, 2010 and 2011, on the levels of ambient PCDD/F compounds, the atmospheric PCDD/F samples were also collected at the source regions in northern Thailand on 2010/3/22-3/28 and northern Vietnam on 2011/3/19-3/30. The five-day back trajectory analyses are calculated using HYSPLIT at the altitudes of 3 km from the location of Lulin station in central Taiwan for the events of March 2010 and 2011, respectively, suggested that the air masses in central Taiwan originated from Indochina on those periods at a lower elevation than the trace layer. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (1 km resolution) data shows significant active fire detections occurred during 2010/3/24-3/25, 2011/3/20-3/21 and 2011/3/27-3/28. At Mt. Lulin,our measurements indicated that the CO and ozone concentration observed at Lulin station during the Southeast biomass burning events (2010/3/24-3/25, 2011/3/20-3/21 and 2011/3/27-3/28) ranged from 105-298 ppb and 33-82 ppb, respectively. The satellite data and air mass paths revealed that the air masses of the PCDD/F peak layer possibly came from biomass-burning regions for these episodes. An intensive observation program was carried out at the same time at Lulin station. Figures 3 and 4 show the atmospheric PCDD/F concentrations measured in Taiwan and the source regions in northern Thailand (2010/3/22-3/28) and northern Vietnam (2011/3/19-3/30) during biomass burning events and reveal that the variations of atmospheric PCDD/F concentrations at these three sites were quite similar. The highest PCDD/F content (579 pg I-TEQ/g-TSP) was measured in northern Vietnam during the burning event (2011/3/27-3/28). In the same period, PCDD/F contents in suspended particles of around 399 pg I-TEQ/g-TSP were measured at Mt. Lulin. Interestingly,, the atmospheric PCDD/F concentration decreased dramatically 2 days after those biomass burning event. Backward trajectories calculated for Mt. Lulin and Son La showed similar paths during (2011/3/27-3/28), implying that the higher PCDD/F concentrations measured at Mt. Lulin originated from the source regions of biomass buring in northern Vietnam. Figure 5 shows the PCDD/F congener distributions in ambient air measured at Lulin station during the regular sampling periods. The results indicate that PCDFs account for 41~53% of total PCDD/Fs. The distribution of PCDD/F congeners measured at Lulin station is quite different from those measured at urban

and industrial area in Taiwan with high PCDF distribution (>60%) conducted[7]. However, Figure 6 shows that the PCDFs account for 65% of the total PCDD/Fs measured during the Southeast Asia biomass burning event (March, 2010 and 2011). Interestingly, Figure 6 also shows that the distribution of PCDD/F congener observed in the source regions of biomass burning in northern Thailand and Vietnam was similar to the measurement at Mt. Lulin in Taiwan during the significant biomass burning event. Gullett et al.[8] indicated that raw biomass is dominated by PCDDs, particularly OCDD, whereas the emissions are dominated by PCDFs, primarily PeCDFs. These observations suggest that the emissions are not simply a result of target volatilization and dechlorination, but represent in situ formation. Hence, the measurements conducted in this study demonstrate that the increase in PCDF compounds could be attributed the long-range transport of the Southeast Asia biomass burning event.

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**References:**

1. Meyer C, Mueller J, Beer T, Marney D, Bradbury G. (2004) *Organohalogen Compd. 66*, 913-19.
2. US EPA, Sources of dioxin-like compounds in the United States. (2001) Draft (external) Final Report; EPA/600/P-00/001Cb.
3. Gullett B K, Touati A. (2003) *Atmos. Environ.* 37, 803-13.
4. Husar R B et al. (2001) *J. Geophys. Res.* 106, 18317.
5. Dockery D W, Pope C A, Xu X, Spengler J D, Ware J H, Fay M E, Ferris B G, Speizer F E. (1993) *New England Journal Medicine* 329, 1753.
6. Chi KH, Lin TY, Ou Yang CH, Wang JL, Lin NH, Sheu GR, Lee CT. (2010) *Environ. Sci. Technol.* 44, 2954-60.
7. Chang M B, Chi K H, Chang S H, Chen Y W. (2004) *Atmos. Environ.* 38, 2535-44.
8. Gullett B K, Touati A, Huwe J, Hakk H. (2006) *Environ. Sci. Technol.* 40, 6228-34.

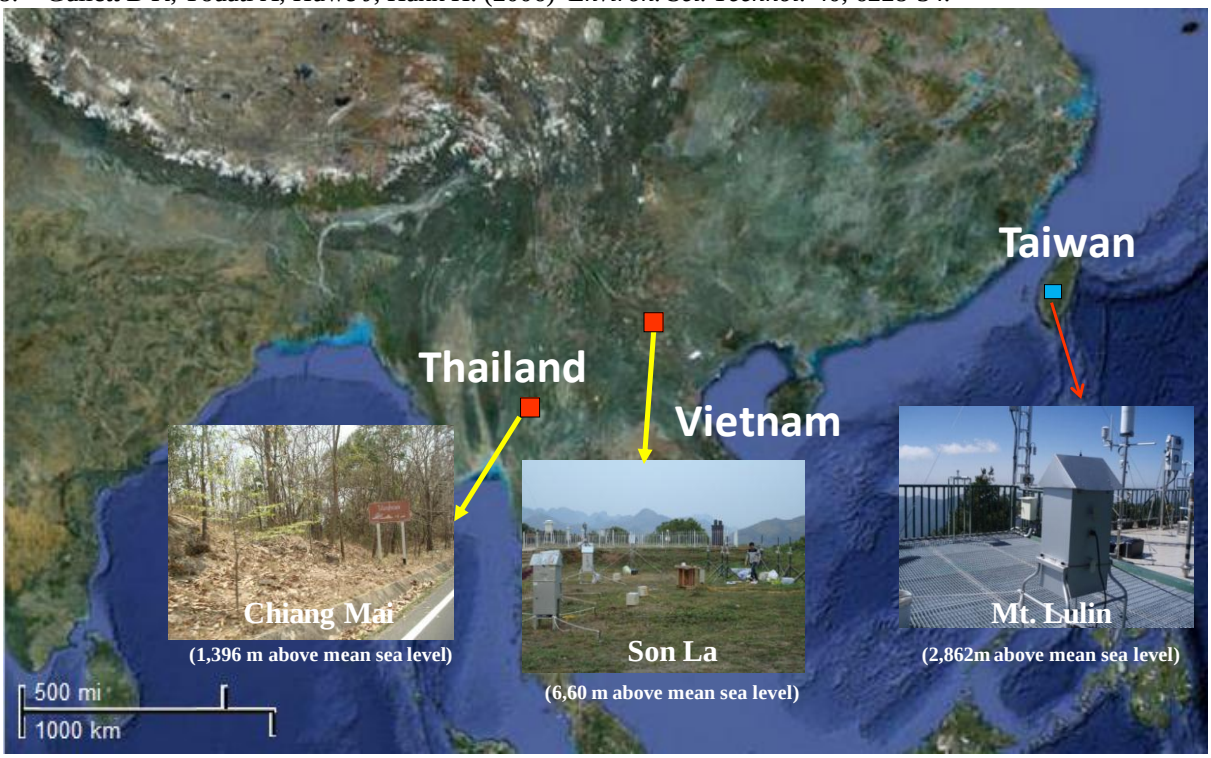


Figure 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

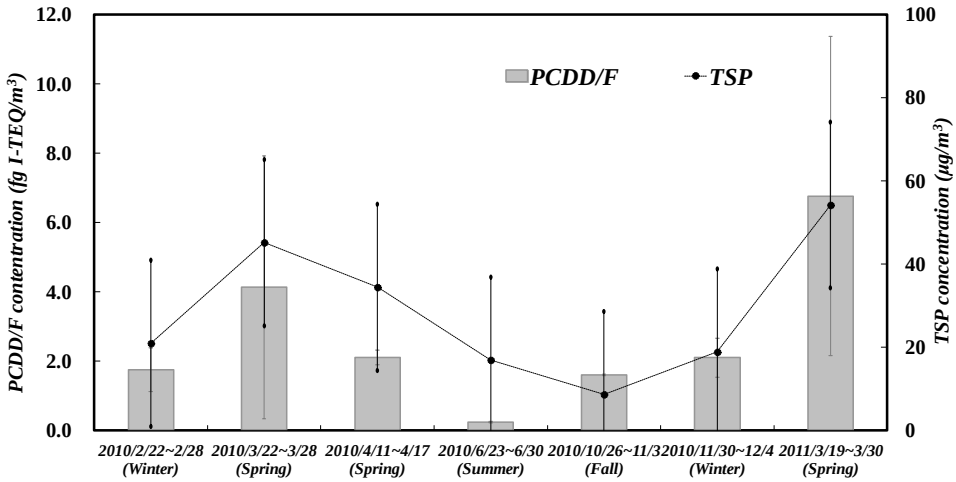


Figure 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during different periods.

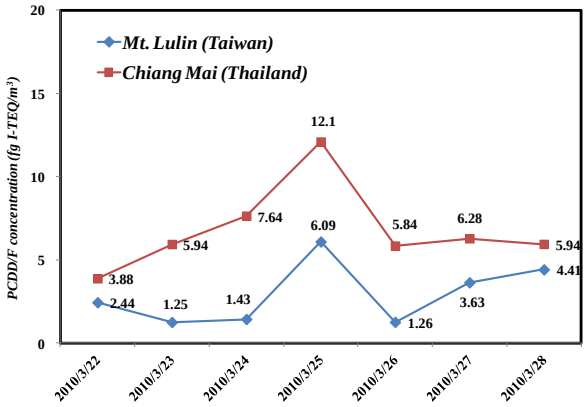


Figure 3 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Thailand during significant biomass burning event (2010/3/22-3/28).

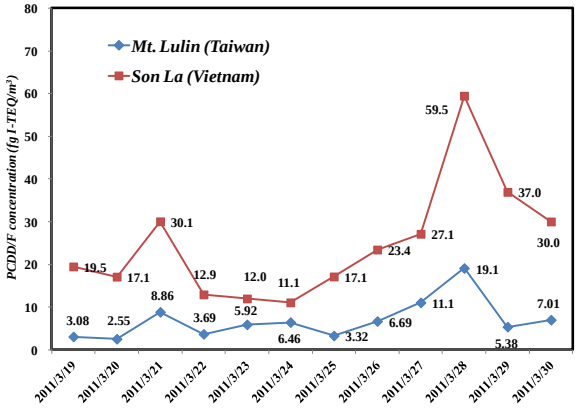


Figure 4 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Vietnam during significant biomass burning event and northern Vietnam (2011/3/19-3/30).

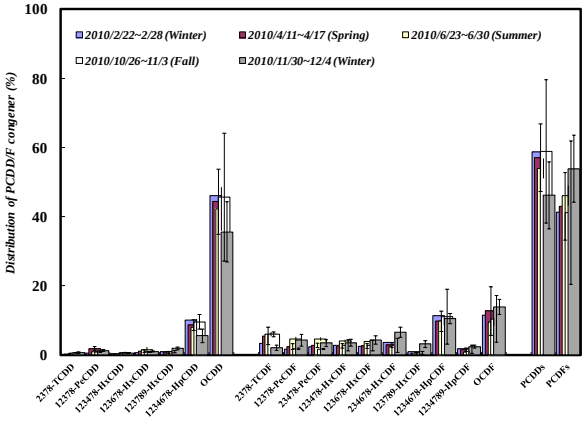


Figure 5 PCDD/F congener distribution in ambient air at Lulin station during regular sampling periods.

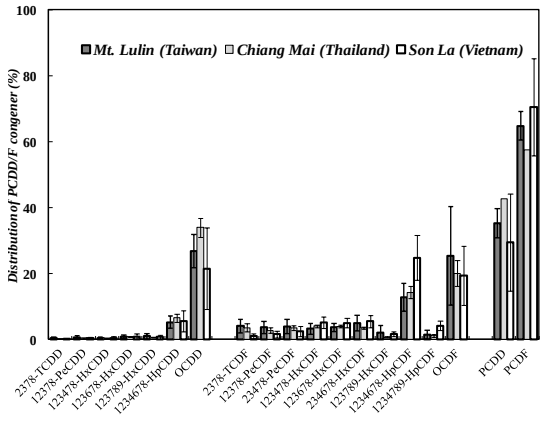


Figure 6 PCDD/F congener distribution in ambient air in central Taiwan, northern Thailand and Vietnam during Southeast Asia biomass burning event.