PCDD/F MEASUREMENT AT A HIGH-ALTITUDE STATION IN CENTRAL TAIWAN: EVALUATION OF POPS VIA LONG RANGE TRANSPORT

Chi KH [1], Sheu, G R [2], Lin NH [2], Lee CT [3], Chang MB [3],
[1] Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan; [2] Department of Atmospheric Sciences, National Central University, Chungli 320, Taiwan. [3] Graduate Institute of Environmental Engineering, National Central University, Chungli 320 Taiwan.

Abstract
Recent biomass burning in eastern Asia has raised global concerns over its adverse effects on visibility, human health and global climate. The concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), total suspended particles (TSP) and other trace pollutants were monitored at Lulin atmospheric background station in central Taiwan at March, June, September and November 2008. The atmospheric PCDD/F and gaseous mercury concentrations measured at Lulin station ranged from 0.71-3.4 fg I-TEQ/m^3 and 1.2-1.8 ng/m^3, respectively, during the regular sampling periods. However, significantly higher concentrations of PCDD/Fs and non sea-salt SO_4^{2-}, NH_4^+ and NO_3^- ions were measured during the spring season. These high concentrations could be the result of long-range transport of the products of Eastern Asia biomass (forest fired) burning. During the Eastern Asia biomass burning event (18-24 March, 2008), an intensive observation program was also carried out at the same station. The results of this observation program indicated that the atmospheric PCDD/F concentration increased dramatically from 2.3 to 390 fg I-TEQ/m^3 (19 March, 2008). The trace pollutant (K^+) of biomass burning also significantly increased from 0.12 to 0.62 μg/m^3 during the same period, while the particle-bound PCDD/Fs in the TSP increased from 29 to 109 pg I-TEQ/g-TSP at Lulin station during the burning event. We conclude that there was a significant increase in the PCDD/F concentration in ambient air at a high-altitude background station in central Taiwan during the Eastern Asia biomass burning event.

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 bounded 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 using high volume ambient air samplers at Lulin background station. The objective of this study is to evaluate the effects of Eastern 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, a high-altitude sampling site was selected based on the meteorological information and location relative to the biomass burning in Eastern Asia (Fig. 1). 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). Mt. Lulin is part of the Central Mountain Range and is located inside Jade Mountain National Park. Its high elevation

means it is generally free from local pollution. Mt. Lulin is surrounded by other mountainous areas of relatively low altitude, and only Mt. Jade (3,954 m above mean sea level), situated to the northeast and several kilometers away, is higher than this site. This site 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. In this study, all PCDD/F samples were taken during the regular sampling periods (March, June, September and November, 2008) for the analysis of PCDD/Fs with 6 to 11 samples taken each month. During a special long range transport event (2008/3/18-3/24), one sample was taken everyday for 24 hours. 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 1,200 m^3 for a typical sampling duration of 1 day. For PCDD/Fs analysis, the dioxin-liked congeners are analyzed with high resolution gas chromatography (HRGC)/high resolution mass spectrometer (HRMS) (Thermo DFS) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 0.25μm, J&W). In addition, total atmospheric mercury was also sampled by drawing ambient air through two gold-coated quartz sand traps in series, for 24 hours during the regular sampling periods.

Results and Discussion

During the regular sampling periods, Fig. 2 shows that the atmospheric PCDD/F and mercury concentrations measured at Lulin station range from 0.71 to 3.4 fg I-TEQ/m^3 and 1.2 to 1.8 ng/m^3, respectively. Low PCDD/F and mercury concentration (Fig. 2) is attributed to the lack of emission and combustion sources within nearly 50 km of the vicinity area at Lulin Mountain. The lowest concentration of those pollutants was measured at summer season (2008/6/10-6/16). Compared with another study[6], the atmospheric PCDD/F concentrations measured at Lulin mountain is significantly lower than that measured at the primeval forest of Demark (6.15~24.0 fg I-TEQ/m^3). However, the highest concentrations of atmospheric PCDD/Fs, mercury and TSPs were observed at Lulin station during the spring season. Fig. 3 shows the concentrations of water-soluble ions in PM_{10} particles measured at Lulin station during the regular sampling periods. Significantly higher concentrations of non sea-salt SO_4^{2-}, NH_4^+ and NO_3^- ions were observed during the spring season (March 2008). A previous study[7] indicated that concentrations of chemical species were found to be elevated in the spring months, owing to the emissions from south/southeast Asia and peak biomass burning (forest fire) activities. Therefore, we consider that the higher PCDD/F concentration observed at Lulin station in spring may be attributed to the effect of Eastern Asian biomass burning via long-range transport. Fig. 4 shows the intensive hotspot/fire in Southeast Asia area in March 2008. The results of five-day atmospheric backward trajectories of Lulin station calculated using the HYSPLIT model in March 2008 (Fig. 5) also demonstrated that the air mass originating from biomass burning areas potentially carry pollutants to the Lulin station during 2008/3/18 to 2008/3/24. Therefore, the intensive observation program is carried out at the same time at Lulin station. Based on the observation of Taiwan EPA, the average concentrations of CO and ozone measured in ambient air at Lulin station were 0.12 ppm and 34 ppb, respectively. However, the CO and ozone concentration observed at Lulin station during the Eastern biomass burning event ranged from 0.19-0.25 ppm and 71-53 ppb, respectively (Table 1). In the meantime, the atmospheric PCDD/F concentration increases dramatically from 2.3 to 390 fg I-TEQ/m^3 (2008/3/19) at Lulin station during Eastern Asian biomass burning event. Interestingly, the atmospheric PCDD/F concentration decreases dramatically two day after the Eastern Asian biomass burning event. The non sea-salt ions analysis results (Fig. 6) also indicate that the NO_3^- and K^+ concentrations in PM_{10} aerosol observed at Lulin stations during the regular sampling periods were 0.043~0.73 and 0.01~0.12 μg/m^3, respectively. However, the NO_3^- and K^+ concentrations measured in atmospheric aerosol significantly increase to 1.4 and 0.62 μg/m^3, respectively, during the Eastern Asian biomass burning event. Additionally, Fig. 7 shows the particle-bound PCDD/Fs relative to the TSP at Lulin station during the Eastern Asian biomass burning event and regular sampling periods. During the regular sampling periods, the quantities of PCDD/Fs adsorbed onto suspended particles ranged from 22 to 65 pg I-TEQ/g-TSP. During the biomass burning event, the mass of PCDD/Fs adsorbed onto suspended particles increased to 109 pg I-TEQ/g-TSP. Apparently, the atmospheric particles from long-range transport cause large variations in PCDD/F and other trace pollutant concentrations. Fig. 8 shows PCDD/F congener distributions in ambient air measured at Lulin station. The PCDFs account for

35% of total PCDD/Fs measured before the Eastern Asian biomass burning event. However, the distribution of PCDFs increases to 67% during the biomass burning event (2008/3/19-3/21). Interestingly, the distribution of PCDFs decreases to 55% after the biomass burning event (2008/3/22-3/24).

Acknowledgements

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Table 1 PCDD/F concentrations measured at Lulin station during Asian biomass burning event.

Sampling period	2008/3/18	2008/3/19	2008/3/20	2008/3/21	2008/3/22	2008/3/23	2008/3/24
Ambient temperature (^{o}C)	8.9	7.2	7.0	8.4	7.8	5.5	3.3
Rainfall (mm)	0.0	0.0	0.0	0.0	0.0	38.0	3.4
CO (ppm)*	0.25	0.23	0.20	0.23	0.22	0.21	0.19
Ozone (ppb)*	71	62	53	56	53	59	59
TSPs (μg m^{-3})	89	53	78	77	82	59	61
PCDD/F concentration (fg-ITEQ m^{-3})	2.3	390	26	13	7.9	4.1	3.3

*** Data provided by Taiwan EPA**.

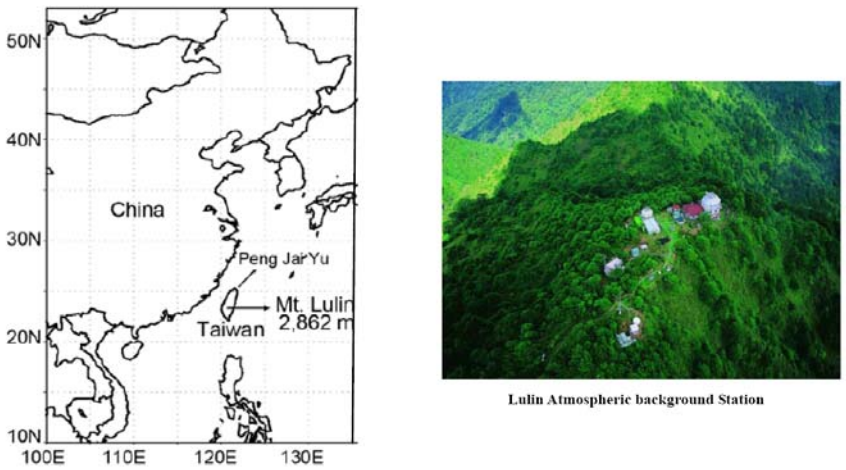

Figure 1 Relative locations of high-altitude sampling site.

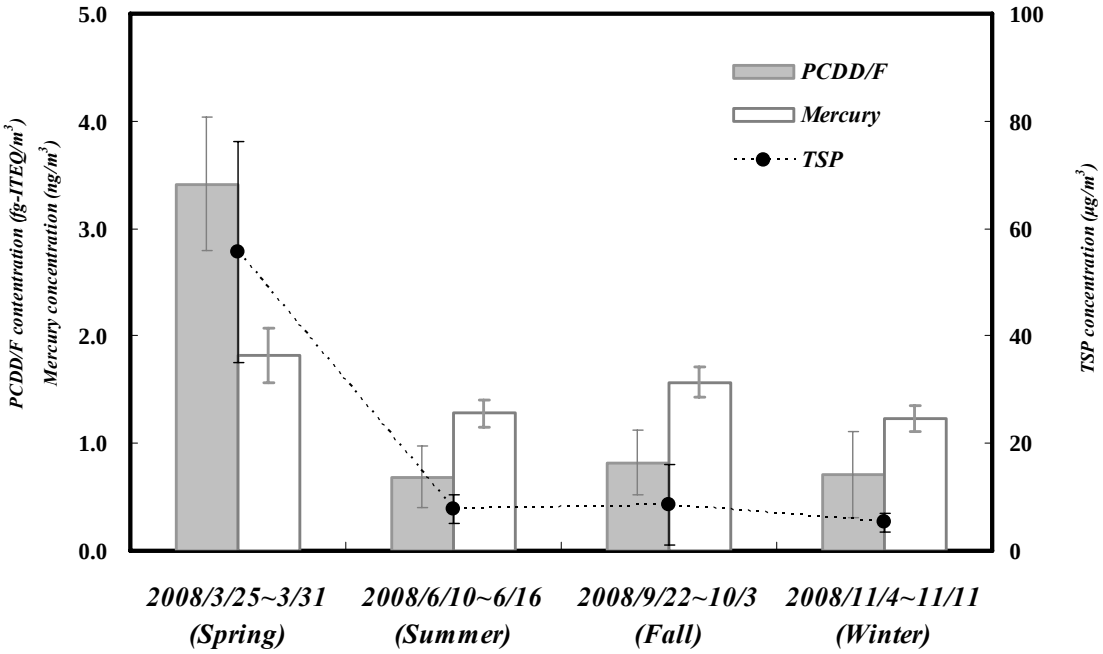

Figure 2 Atmospheric PCDD/F, mercury and total suspended particle (TSP) concentrations measured at Lulin station during different periods.

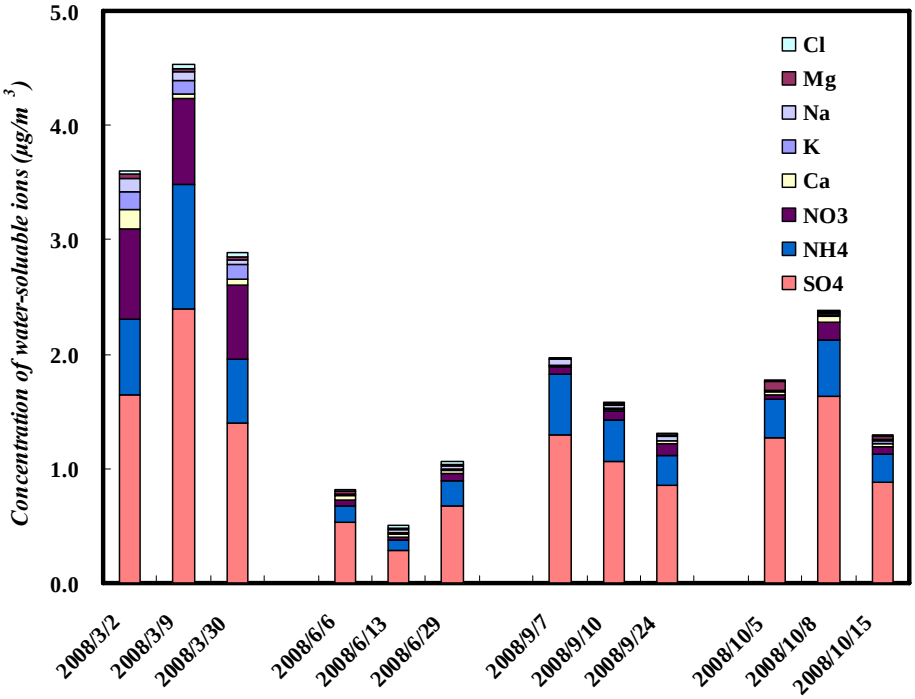

Figure 3 Concentrations of water-soluble ions in PM_{10} particles measured at Lulin station during different periods.

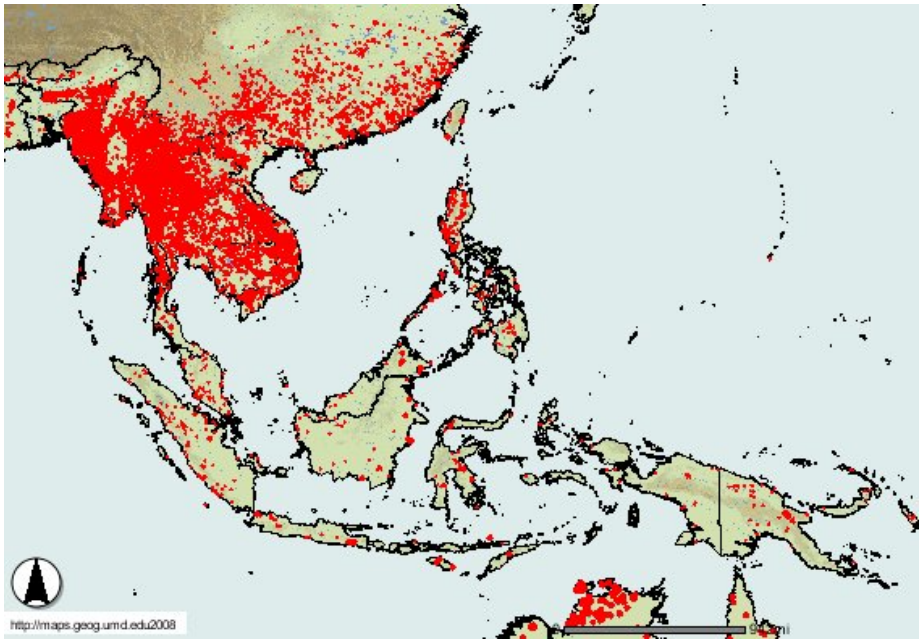

Figure 4 Active hotspot/fire observation by MODIS during Asian biomass burning event (March 2008) (http://maps.geog.umd.edu/firms/shapes.htm).

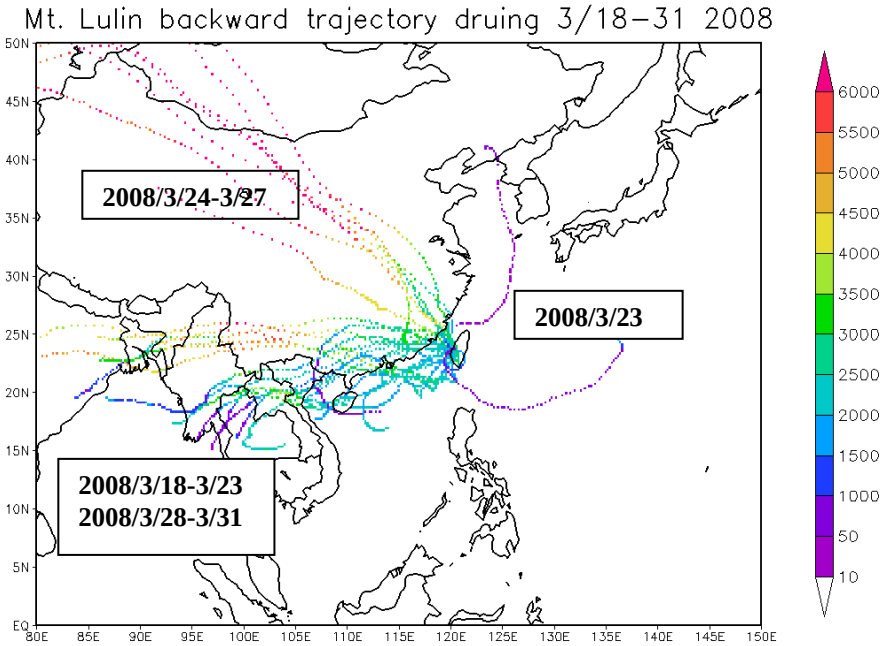

Figure 5 Five-day backward trajectories of Lulin station during Asian biomass burning event.

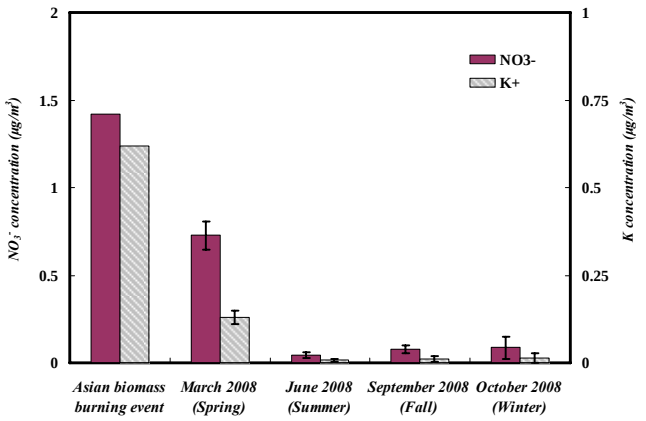

Figure 6 Concentrations of trace pollutant of biomass burning in PM_{10} particles measured at Lulin station.

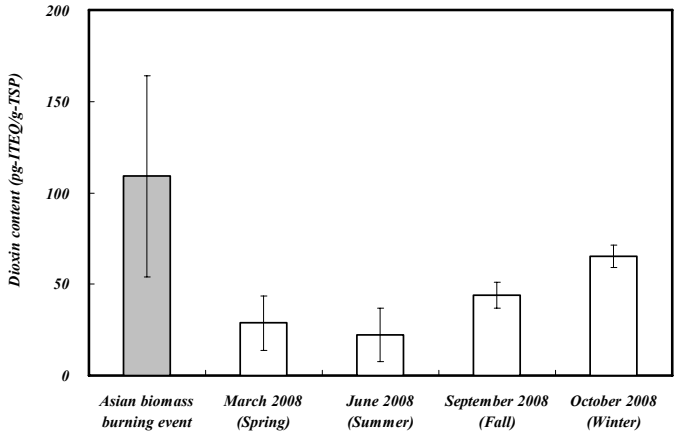

Figure 7 Comparison of particle-bound PCDD/Fs in total suspended particle (TSP) at Lulin station during different sampling periods.

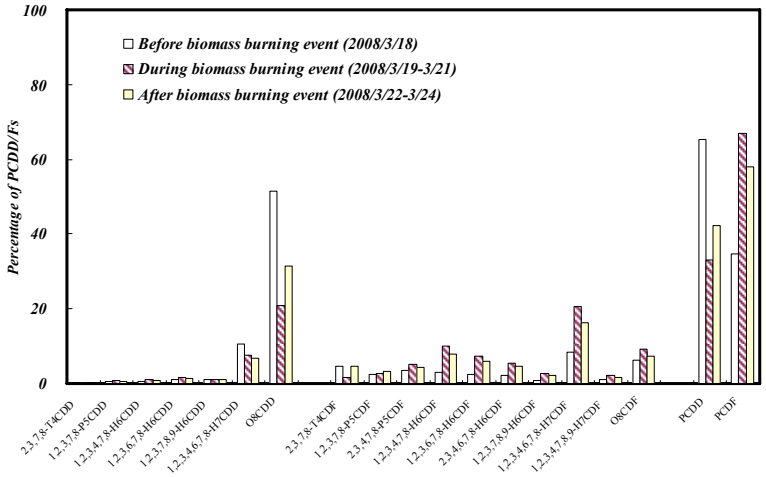

Figure 8 PCDD/F congener distribution in ambient air at Lulin station during Eastern Asia biomass burning event.