PCDD/F MEASUREMENT AT TWO HIGH-ALTITUDE STATIONS IN EASTERN ASIA: EVALUATION OF LONG-RANGE TRANSPORT OF PCDD/Fs AND TRACE METALS DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT

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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), and northern Vietnam (Son La) using high volume ambient air samplers during 2010 to 2012. 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, two 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. 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 collected on Febuary, March, April, June, Octobor, December, 2010, March 2011 and March, April,2012 for the analysis of PCDD/Fs with 4 to 10 samples taken each month. During a special long range transport season (2010/3/22-3/28 2011/3/19-3/30 and 2012/3/10-3/20, 4/1-4/9), one sample was taken everyday for 24 hours at Mt. Lulin, and Son La 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). For metal analysis, total suspended particles (TSPs) collected by quartz fiber filters in ambient air were digested in an acid mixture of concentrated HNO_3/HF (4 ml/2 ml) using an ultra-high-throughput microwave digestion system (MARSXpress, CEM Corporation, Matthews, NC, USA). Digested solutions were analyzed for five major metals (Al, Fe, Na, Mg and Ca) using inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2100DV, Perkin-Elmer™ Instruments, USA). To identify the sources of the Southeast Asia biomass burning episode that occurred on March 2010, the back trajectory analyses using HYSPLIT at the altitudes of 3 km from the location of Lulin station in central Taiwan was also evaluated. Furthermore, we employed the WRF/Chem (Ver.3.0) modeling system with a tracer module to identify the long-range transport associated with biomass burning over Indochina in our case study. The tracers were assigned to the fire locations derived from MODIS satellite data over Indochina ranging from 5 to 25˚N and 90 to 110˚E. The Yonsei University (YSU)[7] planetary boundary layer scheme was selected in this study. The horizontal resolution for our simulations was 27 km and the grid box had 200 × 200 points in both the east-west and north-south directions. There were 35 vertical levels and the lowest level was about 20 m above the surface.

Results and discussion

During the regular sampling periods, the atmospheric PCDD/F and TSP concentrations measured at Lulin station in 2010 to 2012 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. The 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 to 2012, on the levels of ambient PCDD/F compounds, the atmospheric PCDD/F samples were also collected at the source regions in northern Vietnam on 2011/3/19-3/30 and 2012/3/13-3/22, 4/1-4/10. 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, 2011/3/27-3/28, 2012/313-319 and 2012/4/1-4/5.To further investigate the impact of Southeast Asia biomass burning on East Asia, we conducted tracer simulations via WRF/Chem using tracers placed during 2012/4/1-4/5 over the fire locations reported by the MODIS satellite. The simulated tracers were placed at the first level above the surface at each fire location with a concentration of 10,000 units per day (416.67 units/hr). The meteorological initial and boundary conditions for WRF/Chem were obtained from NCEP-FNL datasets at 6-hour intervals. The results depicts the horizontal distribution of the tracer concentration and wind field at the level of 700 hPa (around 3 km). The relatively strong wind belt (wind speed >10 m/s) at 700 hPa ranges from 20 to 30° N and merged into a higher-latitude strong-wind belt over East Asia's marginal seas. At 08:00 UTC 6 April, 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 8 April. 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 Vietnam. An intensive observation program was carried out at the same time at Lulin station. Figures 3 and 4 show the variation of atmospheric PCDD/Fs and potassium concentration in aerosol measured in Taiwan Mt. Lulin(2012/3/10-3/20, 4/1-4/10) and the source regions northern Vietnam (2012/3/13-3/22,4/1-4/10) during biomass burning events and reveal that the variations of atmospheric PCDD/F concentrations at these 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. We considered that the higher PCDD/F concentrations measured at Mt. Lulin originated from the source regions of biomass burning 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[8]. However, Figure 6 shows that the PCDFs account for 40% of the total PCDD/Fs measured during the Southeast Asia biomass burning event (March, 2010, 2011 and 2012). Gullett et al.[9] 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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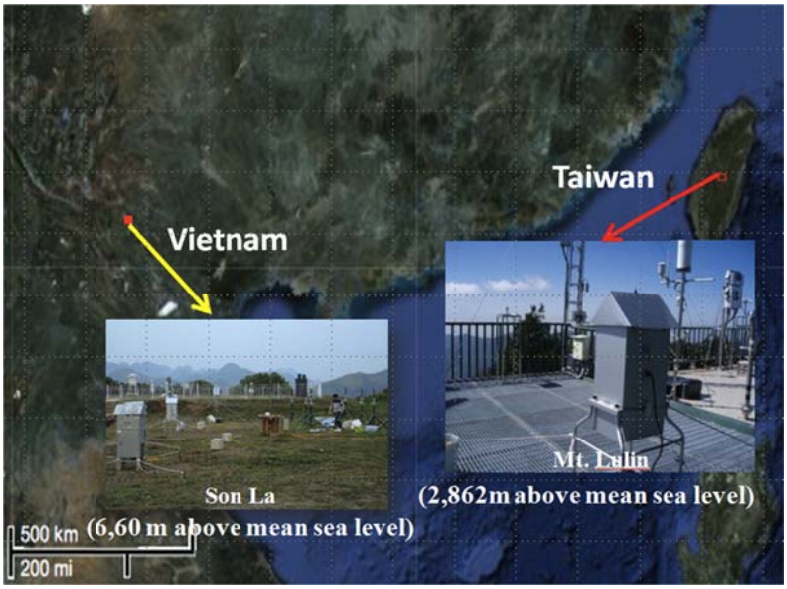

Figure 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

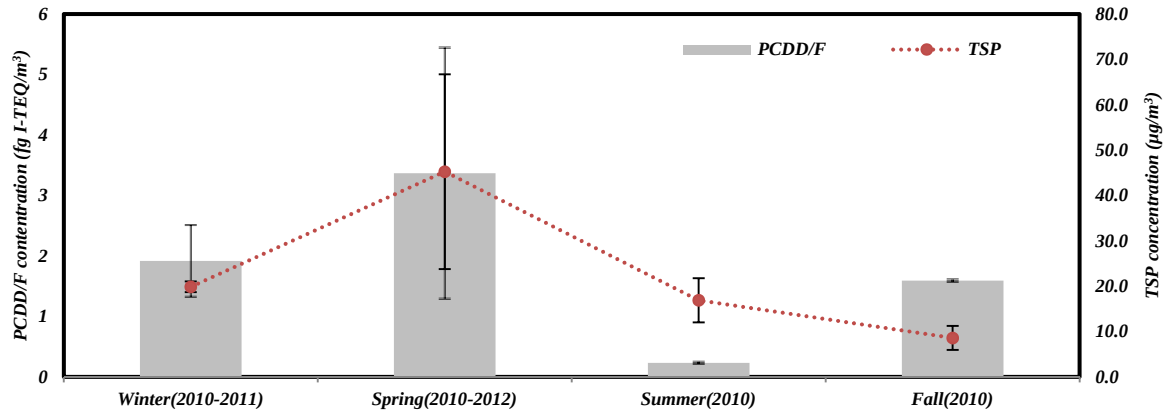

Figure 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during different periods.

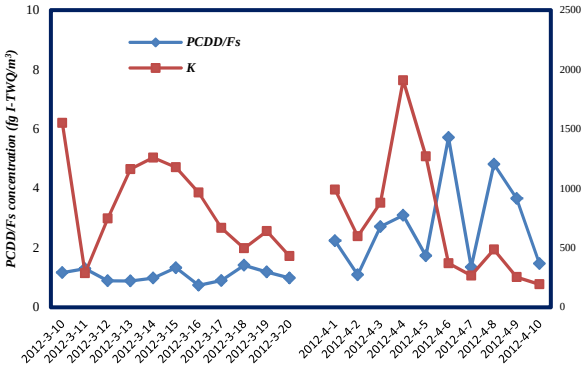

Figure 3 Variation of atmospheric PCDD/Fs and potassium concentration in aerosol measured in Taiwan Mt. Lulin during spring, 2012.#

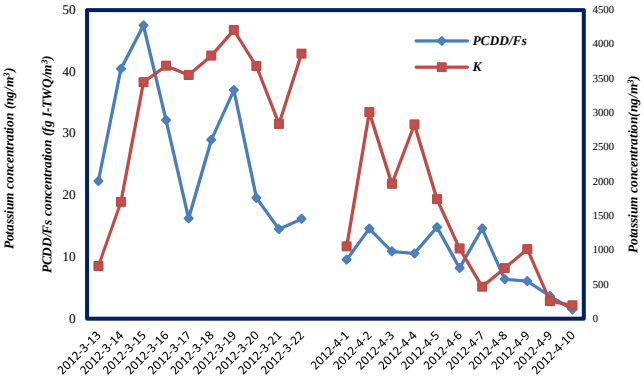

Figure 4 Variation of atmospheric PCDD/Fs and potassium concentrations in aerosol measured in northern Vietnam during spring, 2012.

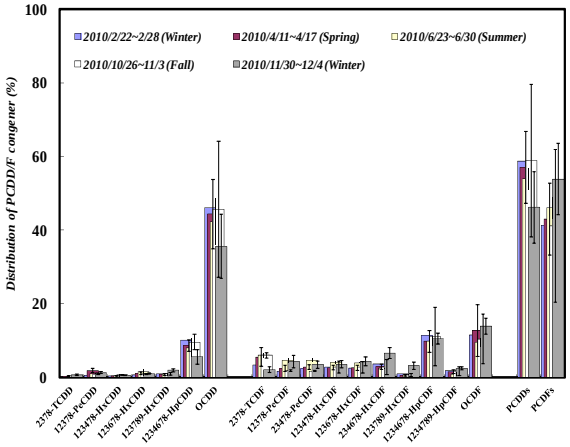

Figure 5 PCDD/Fs congener distribution in ambient air at Lulin station during regular sampling perio

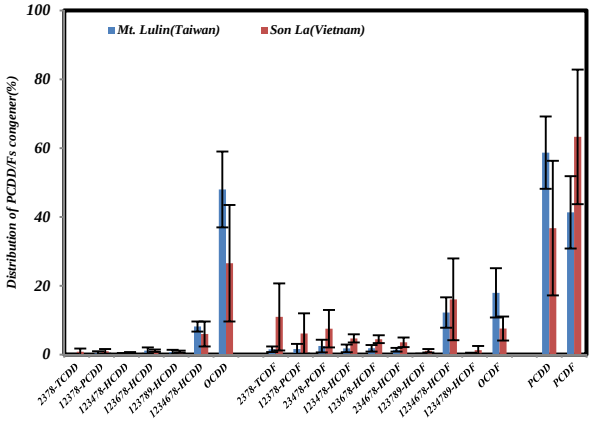

Figure 6 PCDD/F congener distribution in ambient air in central Taiwan and Vietnam during Southeast Asia biomass burning event.