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

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Introduction

Previous studies indicated that uncontrolled combustions including those from forest fires, open burning of agricultural residues, house fires, and backyard household waste combustion have been identified as a large potential source of PCDD/Fs but has not been regulated[1]. Annual emissions of PCDD/Fs from the open burning of crop residues in China mainland were estimated to be ranging from 1.38×10^3 to 1.52×10^3 g I-TEQ per annum between 1997 and 2004, which contributed to approximately 10%-20% of the total PCDD/F emissions in China mainland. In recent years, Eastern Asia biomass burning has caused global concerns due to its adverse effects on visibility, human health and global climate by increasing particulate matter levels and other gaseous pollutants such as CO, SOx, NOx and VOCs. A previous study[2] also indicated that the PCDD/F emission factor via biomass burning ranged from 15 to 25 ng TEQ/kg burned. A previous study[3] indicated that around 70 to 80% PCDD/F concentrations in the atmosphere were essentially bound to particles. Positive matrix factorization (PMF) has become a factor analytic (FA) model of choice for quantitative source apportionment of contaminant species in many air quality monitoring studies[4,5]. In addition, the Potential Source Contribution Function (PSCF) computations identify potential source regions and the preferred pathways of pollutant species to a receptor site. Many studies have employed PSCF to give spatial renderings of contaminant species such as inorganic components of aerosols[6,7]. In this study, the atmospheric concentrations of seventeen 2, 3, 7, 8-substituted PCDD/Fs, trace metal content and water soluble ions in suspended particles were monitored in central Taiwan (Mountain Lulin), northern Vietnam (Son La), and Thailand (Doi Ang Khang) using high volume ambient air samplers during the spring seasons in 2013. The objective of this study is to evaluate the effects of Southeast Asia biomass burning on the atmospheric concentration variation of dioxin compounds and assess the potential for long-range transport of PCDD/Fs. Moreover, speculate the relative contribution of various emission sources by applying PMF, PSCF and WRF/Chem model using tracers to apportionment of PCDD/Fs in atmosphere.

Materials and methods

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, and is able to investigate the impact of long-range transported air pollutants in the free troposphere in East Asia. In northern Vietnam, the sampling site 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. In northern Thailand, the sampling site is located at Thai-Myanmar border junction (99.05-°E 19.93-°N; 1536 m above mean sea level).No significant PCDD/F emission sources existed in the vicinity of these three high-altitude stations. During a special long range transport season (2013/2/22-4/8), one sample was taken every day for 24 hours at Mt. Lulin, Son La and Doi Ang Khang in the meantime. Ambient air samples for both vapor phase and particle phase of dioxin 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 900 m^3 for a typical sampling duration of 1 day. The detailed information regarding the extraction and clean-up procedure of PCDD/F samples is provided elsewhere[8]. 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 (MARSX press, CEM Corporation, Matthews, NC, USA). Digested solutions were analyzed for several trace major metals 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 during spring seasons in 2013, 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 software Positive Matrix Factorization (PMF, version 3.0), available from U.S. EPA (2012) was used to identify and quantify sources that contribute to ambient PCDD/F concentrations at Lulin station. To identify the likely source regions of PCDD/Fs at the Lulin station during the biomass burning period (2013/2/22-3/31), the PSCF was calculated using five-day backward trajectories calculated using the HYSPLIT model.

Results and discussion

During the regular sampling periods, the atmospheric PCDD/F and TSP average concentrations measured at Mt. Lulin station in spring 2011-2013 range from 1.07-6.99 fg I-TEQ m^{-3} and 13.8-59.8 μg m^{-3}, respectively (Fig. 2). The concentration of the atmospheric PCDD/F increased during the event period, but the TSP concentration had no clear trend. Therefore, the amounts of PCDD/Fs adsorbed onto suspended particles in each event are varied. The particle-bound PCDD/Fs in each event range from 86.3- 9252 pg I-TEQ g-TSP^{-1} in 2011, 9.82-103 pg I-TEQ g-TSP^{-1} in 2012, and 10.4 – 8873 pg I-TEQ g-TSP^{-1} in 2013. Comparison with the concentrations Chi et al.(2013)[9] measured at the background stations in Taiwan during 2008-2009, which ranged from 16.0 to 152 pg I-TEQ g-TSP^{-1}, the concentrations observed in this study were significantly higher, that indicated the impact on background Lulin station during Southeast Asia biomass burning event. To analyze the effects of the Southeast Asia biomass burning event in Taiwan during the period of March, 2013, on the levels of ambient PCDD/F compounds, the atmospheric PCDD/F samples were also collected at source regions in northern Thailand during 2013/2/22-4/8 and northern Vietnam during 2013/2/24-4/8. The atmospheric PCDD/F average concentrations measured at Thailand (Doi Ang Khang) and Vietnam (Son La) during the sampling time were 8.87 ± 12.4 and 19.8 ± 10.1 fg I-TEQ m^{-3}, respectively, and the TSP concentrations were 105±63.1 and 147±76.8 μg m^{-3}, respectively. The PCDD/F concentration at Son La was 2 times higher than Doi Ang Khang, while the TSP concentration at Son La was 1.4 times higher than Doi Ang Khang. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (1 km resolution) data shows significant active fire detections occurred during 2013/3/12-4/10. Figure 3 shows that the highest value of atmospheric PCDD/F concentrations obtained from observations at Son La occurred between 2013/3/5-3/8. The PCDD/F concentration increased significantly from 9.74 fg I-TEQ m^{-3} to 44.9 fg I-TEQ m^{-3}, and decreased dramatically to 6.87 fg I-TEQ m^{-3}, and the dioxin predominately distributed in solid phase (83.5%). Investigating the association between concentration of atmospheric PCDD/Fs and non-sea-salt potassium ions during the sampling time, and the results showed a positive correlation (R^2=0.63). In addition, the relationship between the solid-phase PCDD/Fs and non-sea-salt potassium ions also showed a positive correlation (R^2=0.71). In contrast, Figure 4 shows that the atmospheric PCDD/F concentrations were 1.89-8.96 fg I-TEQ m^{-3} during the sampling time (2013/2/22-3/8) at Doi Ang Khang, and the partitioning of solid-phase PCDD/Fs were around 38%. Subsequently, a high concentration event occurred during 2013/3/12-3/13, which the atmospheric PCDD/F concentration was 58.0 fg I-TEQ m^{-3}, and partitioning of solid-phase PCDD/Fs were only 29.9% at Doi Ang Khang. There were significant differences between the partitioning of solid-phase PCDD/Fs in significant biomass burning events at Son La and Doi Ang Khang, which may be due to the different sources of PCDD/F emission. In addition, the atmospheric PCDD/F concentrations were 3.13-12.3 fg I-TEQ m^{-3} during the period after high concentration event (2013/3/14-3/30) at Doi Ang Khang. During that period, the average partitioning of solid-phase PCDD/Fs was 84% which had significant differences with the preceding sampling time, and this may be due to the meteorological condition or other factors. Figure 5 shows the PCDD/F congener distribution in ambient air measured at Son La and Doi Ang Khang stations during event and non-event periods in 2013. The PCDD/PCDF ratios during the non-event and event periods in Son La were 2.02 and 1.59, respectively, indicated that the distribution of PCDFs increased significantly during the biomass burning event. Whereas, the PCDD/PCDF ratios during the non-event and event periods in Doi Ang Khang were 2.62 and 3.75, respectively, which were contrary to the observations in Son La, indicated that the average proportions of PCDDs increased during the biomass burning event. However, the

PCDD/PCDF ratio during the high concentration event (2013/3/12-3/13) was 1.36, demonstrated the proportion of PCDFs was increased. Gullett et al.[2] indicated that the quantity and composition of the numerous organic compounds released from biomass burning depend on various factors, such as the fuel composition, burn rate, the topography and morphology of the terrain and the weather conditions, and this may explained the differences in PCDD/F congener distribution in Son La and Doi Ang Khang during the biomass burning events. Regarding the atmospheric PCDD/F measurements conducted at Mt. Lulin in Taiwan, the results indicated that the atmospheric PCDD/F concentration increased dramatically from 7.71 to 484 fg I-TEQ/m^3 (2013/3/18-3/20). The trace gas (CO) of biomass burning also significantly increased to 345 ppb during the same period. However, the atmospheric PCDD/F concentration decreased dramatically to 1.02 fg I-TEQ/m^3 1 days after the biomass burning event. Figure 6 shows the PCDD/F congener distributions in ambient air measured at Lulin station during event and non-event periods in 2013, and the PCDD/PCDF ratios during the non-event and event periods at Lulin station were 5.90 and 4.45, respectively, indicated the PCDFs contribution increased slightly during the biomass burning event. Analyzing the atmospheric PCDD/F samples (n=18) at Lulin station during the biomass burning period in 2013 by PMF model, the results found that the average contributions of the three factors to the atmospheric PCDD/F concentrations were 72% for biomass burning, 5.4% for open burning and 22% for domestic wastes incineration. Based on the predicted results of PSCF, Figure 7 shows the maps of potential PCDD/F emission source regions for the Lulin station and combined with the MODIS-Global Fire points during the biomass burning period. The high PSCF values were between longitude 100.10° to 121.07° and latitude 18.2° to 24.25°, indicated that the major atmospheric PCDD/F emission source areas for Mt. Lulin were northern area of southeast Asia and coastal areas of southeast China.

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References:

1. Zhang Q, Huang J, Yu G. (2008); *Environmental Pollution* .151: 39-46
2. Gullett BK, Touati A. (2003); *Atmos. Environ.* 37: 803-13
3. Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG, Speizer FE. (1993); *New England Journal Medicine*. 329: 1753
4. Larsen 3rd, RK, Baker, JE. (2003); *Environ. Sci. Technol.* 37: 1873-81
5. Polissar, AV, Hopke, PK, Paatero, P, Malm, WC, Sisler, JF. (1998); *Journal of Geophysical Research* 103: 19045-57
6. Zeng, Y, Hopke, PK. (1989); *Atmos. Environ.* 23 : 1499-509
7. Ara Begum, B, Kim, E, Jeong, C, Lee, D, Hopke, PK. (2005); *Atmos. Environ.* 39: 3719-24.
8. Chi KH, Lin TY, Ou Yang CH, Wang JL, Lin NH, Sheu GR, Lee CT. (2010); *Environ. Sci. Technol.* 44: 2954-60
9. Chi KH, Lin CY, Wang SH, Lin NH, Sheu GR, Lee CT. (2013); *Atmos. Environ.* 78: 203-10

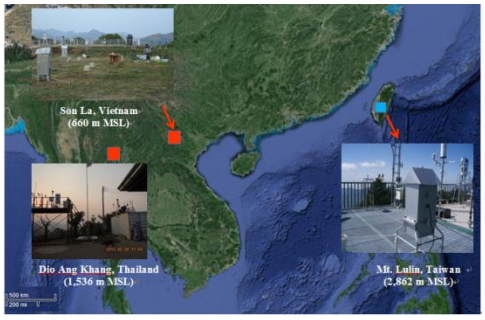

Fig. 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

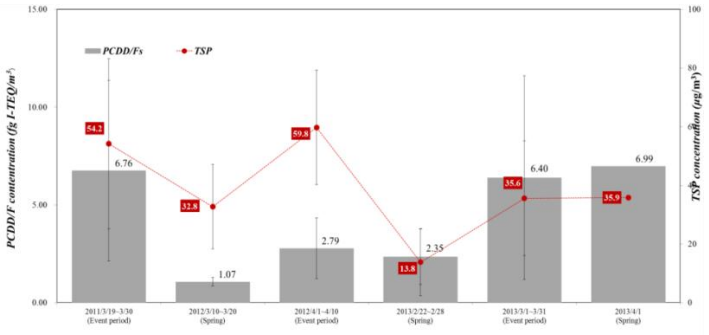

Fig. 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during different periods.

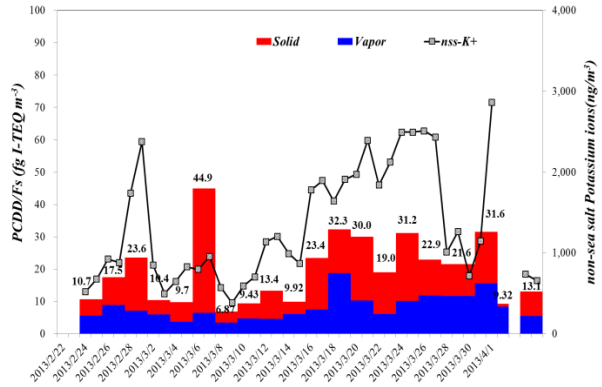

Fig. 3 Variation of atmospheric PCDD/F and Potassium concentrations measured in Son La, Vietnam during March, 2013.

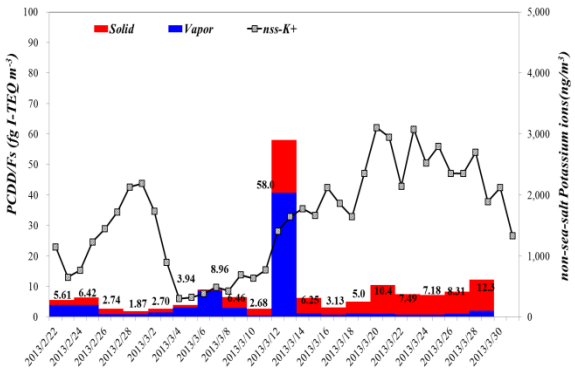

Fig. 4 Variation of atmospheric PCDD/F and Potassium concentrations measured in Doi Ang Khang, Thailand during March, 2013.

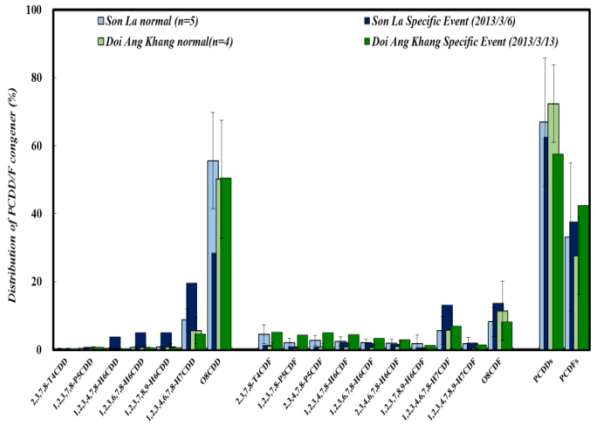

Fig. 5 Atmospheric PCDD/F congener distribution at Son La and Doi Ang Khang stations during March, 2013.

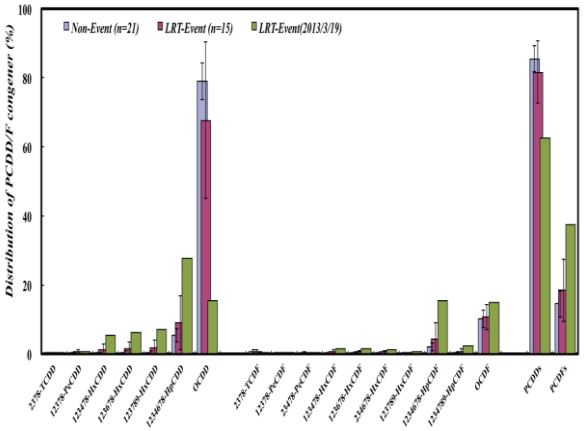

Fig. 6 PCDD/F congener distribution in ambient air at Lulin station during March, 2013.

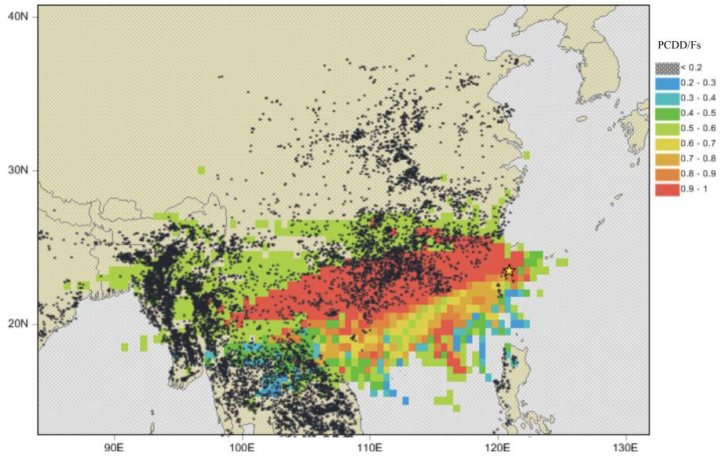

Fig.7 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during the biomass burning period combined with the MODIS-Global Fire points (black dots).