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PCDD/F MEASUREMENT AT TWO 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, SO_x, NO_x 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 in suspended particles were monitored in central Taiwan (Mountain Lulin) and Thailand (Doi Ang Khang) using high volume ambient air samplers during the spring seasons in 2015. 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 and PSCF model using tracers to apportionment of PCDD/Fs in atmosphere.

Materials and methods

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-°N, 120.92-°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 Thailand, the sampling site is located at Thai-Myanmar border junction (99.05-°E 19.93-°N; 1,536 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 (2015/3/01-4/9), one sample was taken every day for 24 hours at Mt. Lulin 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-1000R). The HV-1000R 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 elsewhere8. 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 HNO3/ 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 2015, the back trajectory analyses using HYSPLIT at the altitudes of 3 km from the location of Lulin station in central Taiwan was also evaluated. 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 5.0), available from U.S. EPA (2014) 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 (2015/3/1-4/9), the PSCF was calculated using three-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 2010-2015 range from 0.91-31.26 fg I-TEQ m^{-3} and 9.61-46.2 μg m^{-3}, respectively (Fig. 2). 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, 10.4 – 8873 pg I-TEQ g-TSP^{-1} in 2013, 12.1 – 65.9 pg I-TEQ g-TSP^{-1} in 2014 and 7.08 – 52.4 pg I-TEQ g-TSP^{-1} in 2015. To analyze the effects of the Southeast Asia biomass burning event in Taiwan during the period of March, 2015, on the levels of ambient PCDD/F compounds, the atmospheric PCDD/F samples were also collected at source regions in northern Thailand during 2015/3/1-4/9. The atmospheric PCDD/F average concentrations measured in Thailand (Doi Ang Khang) during the sampling time were 8.16 ± 14.5 fg I-TEQ m^{-3}, and the TSP concentrations were 144±61.8 μg m^{-3}. The PCDD/F concentration at Mt. Lulin was lower than Doi Ang Khang. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (1 km resolution) data shows significant active fire detections occurred during 2015/3/1-4/9. Figure 3 shows that the highest value of atmospheric PCDD/F concentrations obtained from observations of Mt. Lulin occurred between 2015/3/19-3/21 and 2015/04/04-04/06. It's means that were two times higer concentration PCDD/Fs events. The PCDD/F concentration increased significantly from 0.83 fg I-TEQ m^{-3} to 1.41 fg I-TEQ m^{-3}, and decreased dramatically to 0.67 fg I-TEQ m^{-3} on 2015/03/19-03/21. Figure 4 shows that the atmospheric PCDD/F concentrations were range from 1.73-69.8 fg I-TEQ m^{-3} during the sampling time (2015/3/1-4/9) at Doi Ang Khang. Subsequently, a high concentration event occurred during 2015/3/15-3/18, which the atmospheric PCDD/F concentration was 69.8 fg I-TEQ m^{-3} at Doi Ang Khang. Figures 5 and 6 shows the PCDD/F congener distribution in ambient air measured at Doi Ang Khang and Mt. Lulin stations during biomass burning and normal periods in 2015. In this study, the high concentration event was used the higher than potassium 75th percentile for the definition. The PCDD/fish species were dominating the 1,2,3,4,6,7,8 HpCDD, OCDD, 2,3,7,8 TCDF, 1,2,3,7,8,9 HpCDF, OCDF at the Mt.Lulin and Doi Ang Khang. It was different in the figure 5 that PCDD of normal higher than biomass burning event time.There was a significant increased of PCDDs in biomass burning event at Mt.Lulin (Fig. 6). Figure 6 also shows the PCDD/F congener distributions in ambient air measured at Lulin station during biomass burning and normal periods in 2015, and the ratios of PCDDs/PCDFs during the normal and biomass burning periods at Lulin station were 1.47 and 2.89, respectively. That indicated the PCDFs contribution decreased slightly during the biomass burning event. Figure 7 shows the back trajectory statistics result. There were 35.5% back trajectory from northern areas of southeast Asia and 30.3% back trajectory from coastal areas of the Philippines. Based on the predicted results of PSCF, Figure 8 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° to 130° and latitude 15° to 25°, indicated that the major atmospheric PCDD/F emission source areas for Mt. Lulin were northern areas of southeast Asia and coastal areas of the Philippines, it's also the same with the back trajectory predicted.

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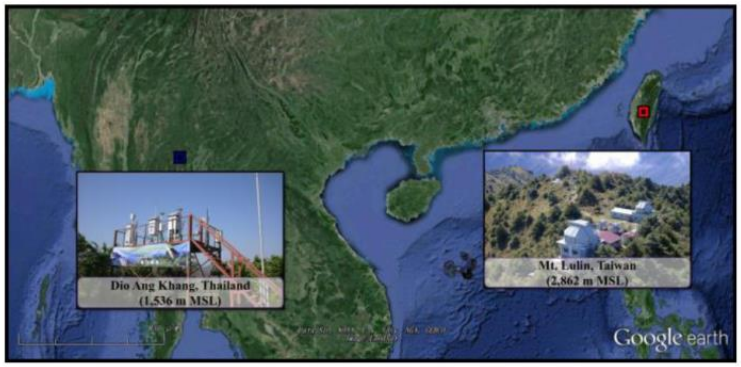

Fig. 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

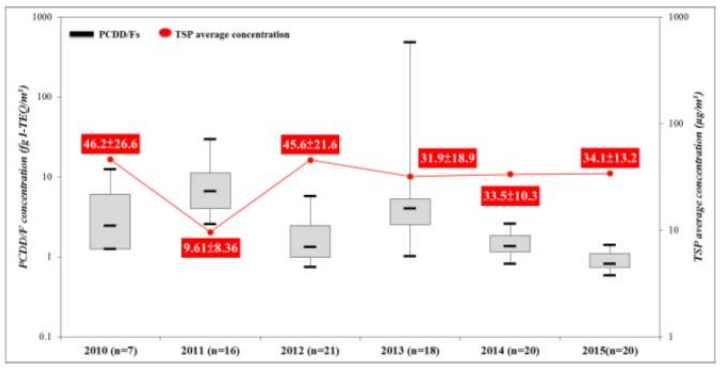

Fig. 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during 2010-2015.

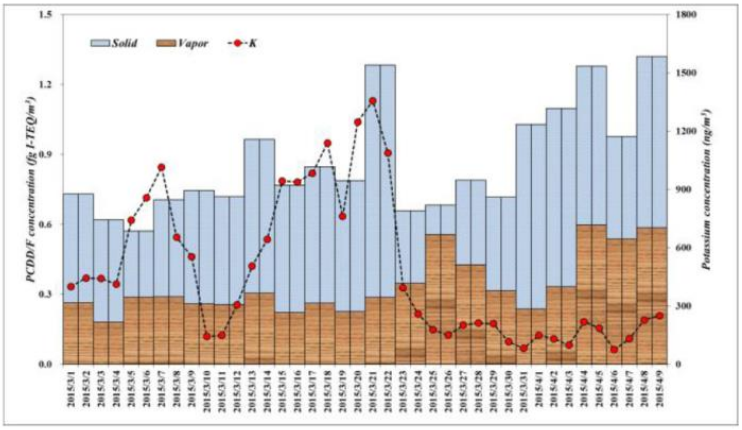

Fig. 3 Variation of atmospheric solid and vapor phase PCDD/F and Potassium concentrations measured in Mt. Lulin, Taiwan during March, 2015.

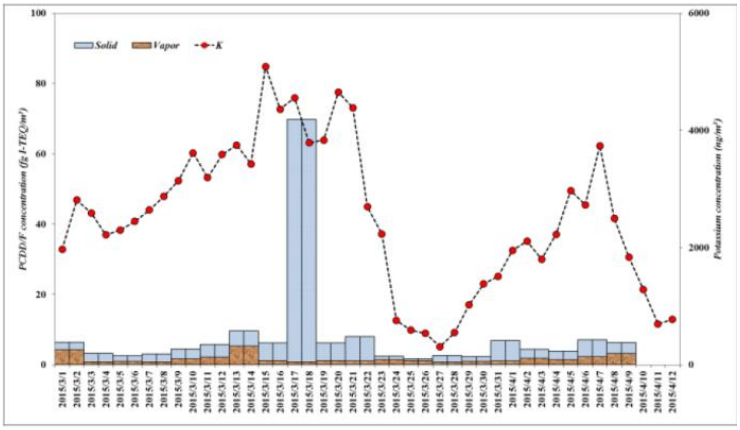

Fig. 4 Variation of atmospheric solid and vapor phase PCDD/F and Potassium concentrations measured in Doi Ang Khang, Thailand during March, 2015.

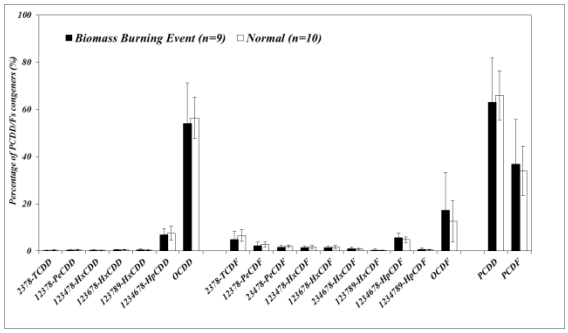

Fig. 5 Atmospheric PCDD/F congener distribution at Doi Ang Khang stations during March, 2015.

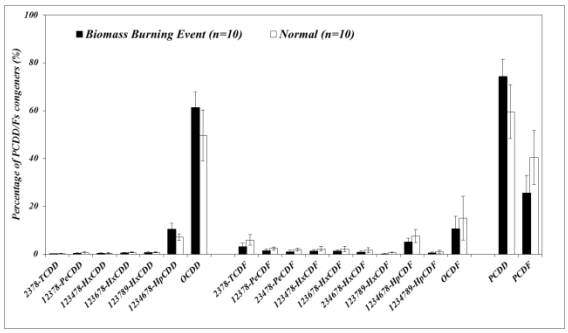

Fig. 6 Atmospheric PCDD/F congener distribution in ambient air at Lulin station during March, 2015.

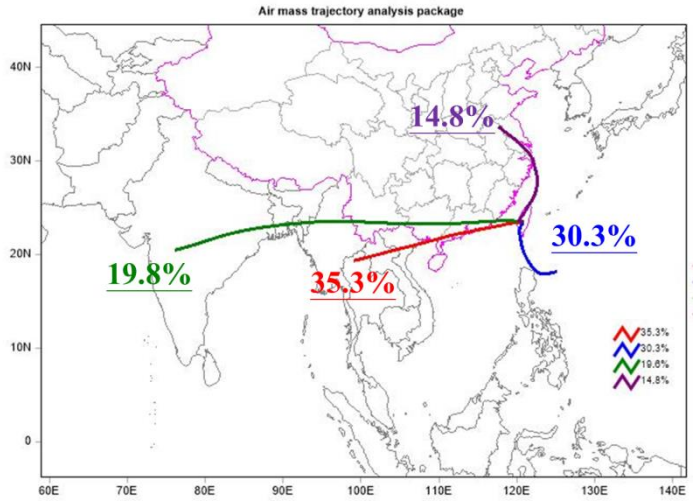

Fig.7 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during the sampling period.

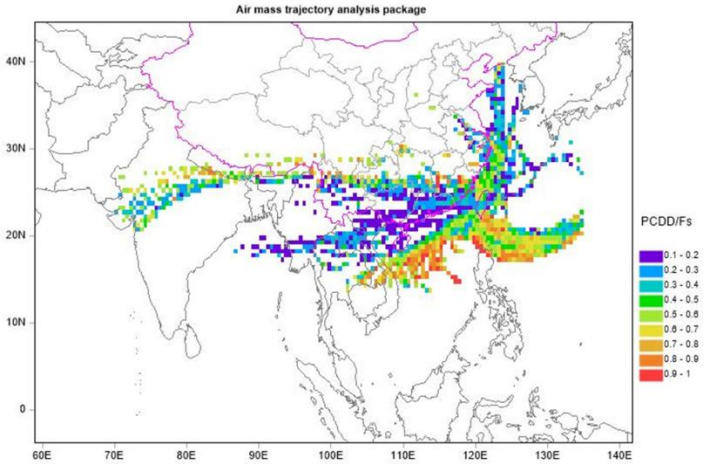

Fig.8 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during the sampling period.