PCDD/F MEASUREMENT AT HIGH-ALTITUDE STATION IN EASTERN ASIA: EVALUATION OF LONG-RANGE TRANSPORT AND SOURCE APPORTIONMENT OF PCDD/FS DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT IN 2007-2016

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Introduction

Previous studies indicated that uncontrolled combustions including 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 have not been regulated[1]. Annual emissions of PCDD/Fs from the open burning of crop residues in China mainland were estimated to range 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 biomass. A previous study[3] indicated that 70 to 80% of PCDD/F concentrations in the atmosphere were essentially bound to particles. Positive Matrix Factorization (PMF) has become a factor analysis (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) using high volume ambient air samplers during the spring seasons in 2007-2016. 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 in 2007-2016. Moreover, speculate the relative contribution of various emission sources by applying PMF, PSCF and SRA model using tracers to apportionment of PCDD/Fs in atmosphere.

Materials and methods

To measure the long-range transport of PCDD/Fs, the high-altitude sampling sites was 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. No significant PCDD/F emission sources existed in the vicinity of the high-altitude station. During a special long range transport season (2007-2016, N=135), one sample was taken every day for 24 hours at Mt. Lulin 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 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). To identify the sources of the Southeast Asia biomass burning episode that occurred during spring seasons in 2007-2016, the backward 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 (2007-2016, N=135), the PSCF was calculated using three-day backward trajectories calculated using the HYSPLIT model. Moreover, speculate the relative contribution of various emission sources by applying the methods as SRA (Source Regional Apportionment, SRA) to apportionment of PCDD/Fs in atmosphere.

Results and discussion

During the regular sampling periods, the atmospheric PCDD/F, TSP and $PM_{2.5}$ average concentrations measured at Mt. Lulin station in spring 2007-2016 ranged from 0.91-31.2 fg I-TEQ m^{-3}, 9.61-55.6 μg m^{-3} and 14.7-17.8 μg m^{-3}, respectively (Fig. 2). In this study, the biomass burning event was defined as the day when potassium concentrations were higher than overall 75th percentile. The amounts of PCDD/Fs adsorbed onto suspended particles in each eventvaried. The particle-bound PCDD/Fs in each event was found to be 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. The atmospheric PCDD/F average concentrations measured in Taiwan (Mt.Lulin) during the sampling time were 1.19 ± 0.25 fg I-TEQ m^{-3}, and the $PM_{2.5}$ concentrations were 14.7 ± 8.07 μg m^{-3} in 2016. The dominant PCDD/F congeners were found to be 1,2,3,4,6,7,8 HpCDD, OCDD, 2,3,7,8 TCDF, 1,2,3,7,8,9 HpCDF and OCDF at Mt.Lulin station. The backward trajectory statistics result showed four possible pathways including 57.2% backward trajectory from northern areas of southeast Asia, 31.2% backward trajectory from coastal areas of the Philippines and 11.6% backward trajectory from coastal areas of the northeast China (Fig. 3). Based on the predicted results of PSCF, Figure 4 shows the maps of potential PCDD/F emission source regions for the Lulin station in combining with the MODIS-Global Fire points during the biomass burning period. The high PSCF values were located between longitude 60° to 110° and latitude 20° to 30°, indicating that the major atmospheric PCDD/F emission source areas for Mt. Lulin were northern areas of southeast Asia which corresponds to the prediction of backward trajectory analysis. To identify the sources of the Southeast Asia biomass burning episode that occurred during spring seasons in 2007-2016, the backward trajectory analyses using HYSPLIT at the altitudes of 3 km from the location of Lulin station in central Taiwan and PMF model were also evaluated. Combining the results of factor analysis receptor model (PMF) model and trajectory cluster analysis (PSCF) to quantify directional contributions for each source category. Figure 5 shows the SRA maps of backward trajectory regions for the Mt. Lulin station in 2015. In spring, PCDD/Fs contributed a higher percentage and the R3 (46% , Pan Pacific and Philippines) and R4 (35%, Indochina) was an important contributor (Table 1).

Acknowledgements

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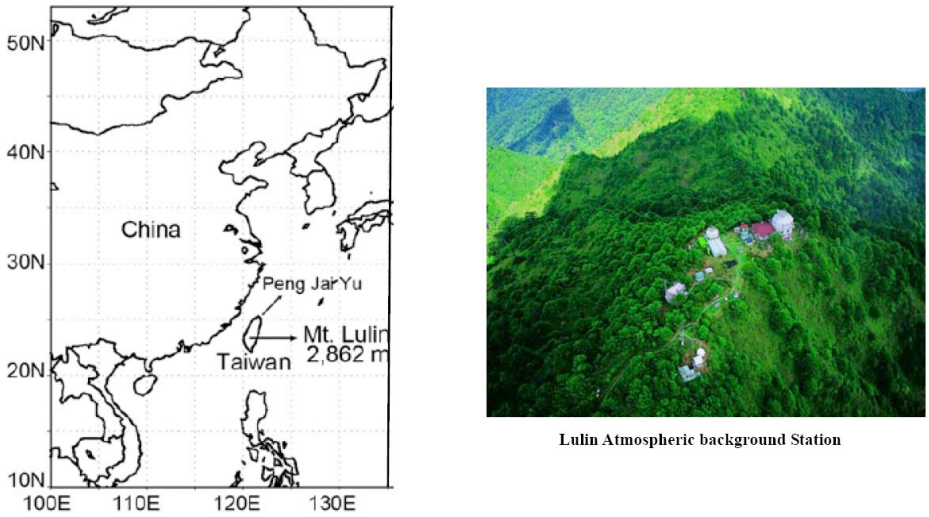

Fig. 1 Relative locations of the high-altitude sampling sites in Southeast Asia.

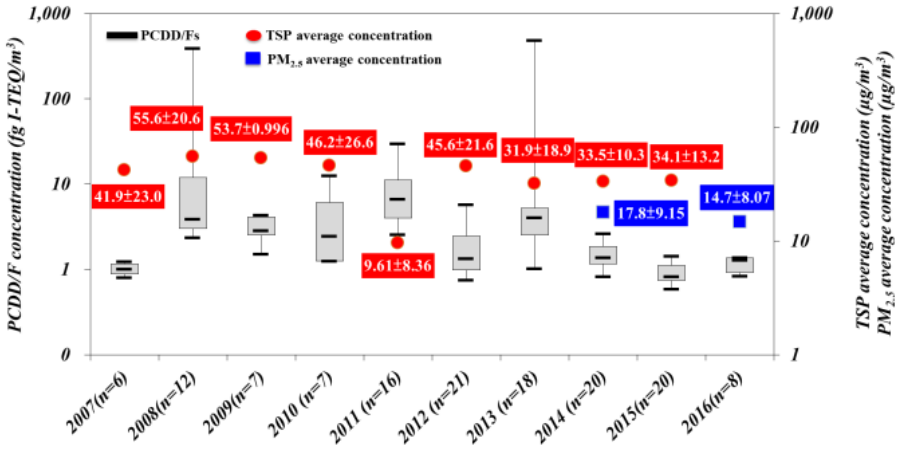

Fig. 2 Atmospheric PCDD/Fs , total suspended particles and fine particles measured at Lulin station during 2007-2016.

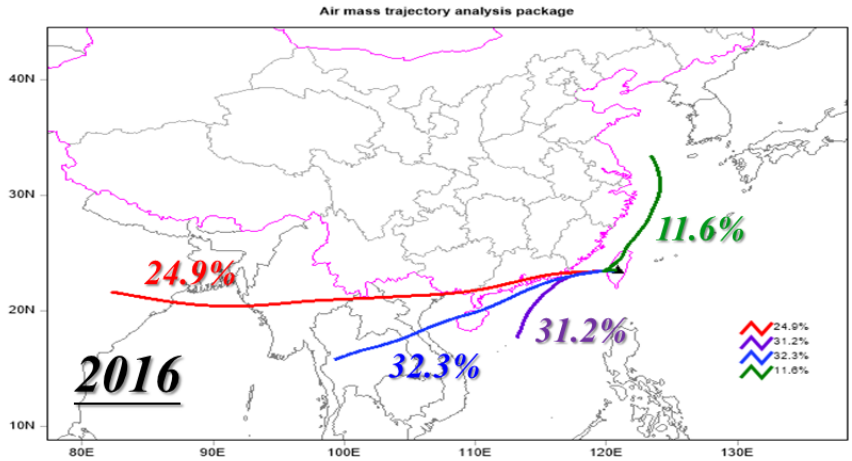

Fig.3 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during the sampling period (2016).

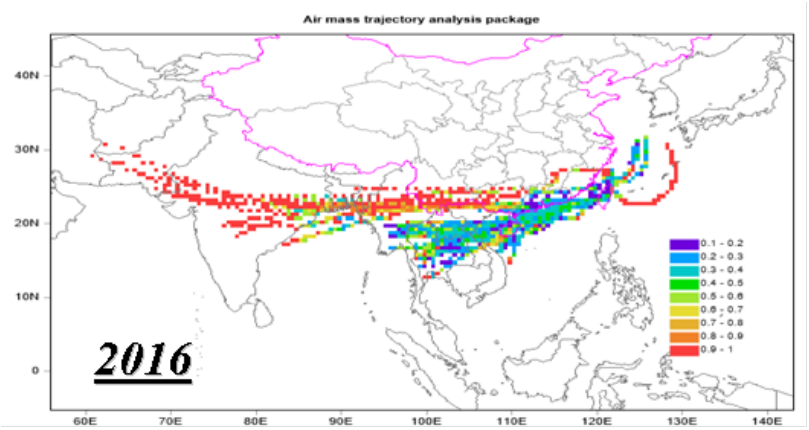

Fig.4 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during the sampling period (2016).

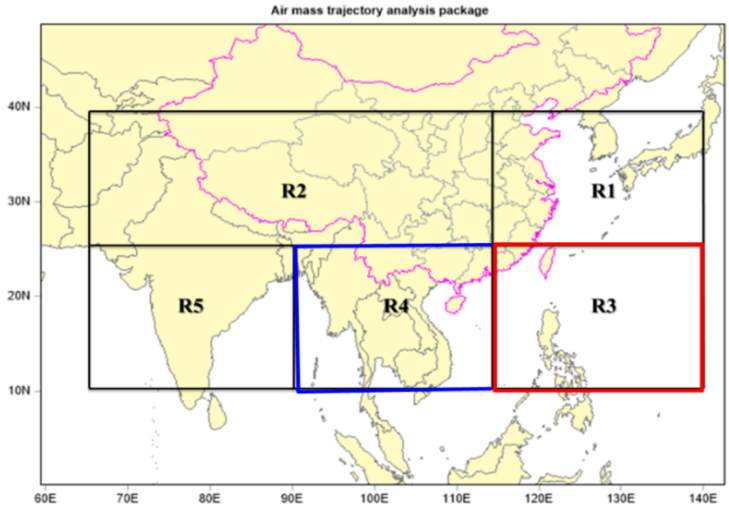

Fig.5 SRA maps of backward trajectory regions for the Mt. Lulin station during the sampling period (2015).

Table.1 Result of SRA for the Mt. Lulin station during the sampling period (2015).

Regional	Factor 1 Human Activities and Unknown	Factor 2 Biomass Burning	Factor 3 Open Burning	Total
R1 Japan, Korea, Northeast of China	2.21%	2.75%	4.28%	9%
R2 North China, Central China	1.21%	1.50%	2.34%	5%
R3 Pan Pacific and Philippines	10.9%	13.6%	21.2%	46%
R4 Indochina	8.31%	10.3%	16.1%	35%
R5 India Peninsula	1.23%	1.53%	2.38%	5%
Total	24%	30%	46%	100%