PCDD/F MEASUREMENT AT HIGH-ALTITUDE STATION IN EASTERN ASIA: EVALUATION OF PCDD/FS IN TSP AND $PM_{2.5}$ VIA LONG-RANGE TRANSPORT AND SOURCE APPORTIONMENT DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT IN 2014

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Introduction

The source of aerosols can be divided into primary aerosols and secondary aerosols. Moreover, atmospheric particulate matter, such as TSP (total suspended particulate matter) and $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) were the sources of air pollution. Particulate air pollution includes solid and vapor phase pollution directly emitted into the atmospheric. On the other hand, 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]. A previous study[2] showed that the PCDD/F emission factor via biomass burning which contributes between 0.5% and 68% in developing countries. Annual emissions of PCDD/Fs from the open burning of crop residues in China mainland were estimated to be ranging from 1.38 to 1.52 g I-TEQ/year between 1997 and 2004, which contributed to approximately 10%-20% of the total PCDD/F emissions in China mainland. Another 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 region. 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 and $PM_{2.5}$ were monitored in receptor region (Mountain Lulin in Taiwan) and source region (Doi Ang Khang in Thailand) using high volume ambient air samplers with cascade impactor during the spring seasons in 2014. The objective of this study is to evaluate the particulate in TSP and $PM_{2.5}$ 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 2014. 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, 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-ºN, 120.92-ºE; 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 station is located at Doi Ang Khang (19.93-ºN, 99.05-ºE; 1,536 m above mean sea level) Thai-Myanmar border junction. No significant PCDD/F emission sources existed in the vicinity of the high-altitude station. During a special long range transport season (N=40), 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) for TSP and cascade impactor to collect $PM_{2.5}$. 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). For metal analysis, total suspended particles (TSPs) and fine particles ($PM_{2.5}$) 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 different sources of TSP and $PM_{2.5}$ in Southeast Asia biomass burning episode that occurred during spring seasons in 2014, 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 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 in TSP and $PM_{2.5}$ at Lulin station. Moreover, to identify the likely source regions of PCDD/Fs at the Lulin station during the biomass burning period (2014, March, N=40), the PSCF was calculated using three-day backward trajectories calculated using the HYSPLIT model. Furthermore, 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 average mass concentration of TSP, $PM_{2.5}$ and PCDD/F in different phases distribution at Mt. Lulin station in spring 2014 range from12.1-65.9 μg/m^3, 4.67-49.0 μg/m^3 and 0.92-15.7 fg I-TEQ/m^3, respectively (Fig. 2a and Fig. 3a). Otherwise, the average mass concentration of TSP, $PM_{2.5}$ and PCDD/F in different phases distribution at Doi Ang Khang station range from76.7-414 μg/m^3, 47.6-237 μg/m^3 and 3.78-28.0 fg I-TEQ/m^3, respectively (Fig. 2b and Fig. 3b). In this study, the high concentration event was used the higher than potassium 75th percentile for the definition. Fig. 3 showed that variation of atmospheric TSP, $PM_{2.5}$ and vapor phase PCDD/F concentrations measured in Mt. Lulin, (Taiwan) and Doi Ang Khan (Thailand). The result indicted that biomass burning event occurred and atmospheric PCDD/Fs in TSP was major for solid phase. Otherwise, PCDD/Fs in $PM_{2.5}$ was major for vapor phase. It's probably due to the emission source were different. The proportion of PCDD/F in $PM_{2.5}$ and TSP were also different. As Fig. 3 showed that PCDD/F in $PM_{2.5}$ was higher than in TSP. Tracer for biomass burning were using potassium to identify potential source. Correlation of TSP and potassium was 0.85 at receptor region. Composition of metal were major for Al, Fe, Na, Mg, K and Ca at receptor region (Mt.Lulin). Moreover, the composition of metal at source region (Doi Ang Khang) as the same as receptor region (Mt.Lulin) was major for Al, Fe, Na, Mg, K and Ca. In addition, it's also major for Ti and Mn.
The backward trajectory statistics result showed three possible pathways including 14.9% backward trajectory from Central India, 34.5% backward trajectory from coastal areas of southeast Asia and 50.6% backward trajectory from Bengal, Southern China and Indochina (Fig. 4). Based on the predicted results of PSCF, Fig. 5 shows the maps of potential PCDD/F emission source regions for the Lulin station in TSP and $PM_{2.5}$ during the biomass burning period. The PSCF values range from 0.3-0.7 and 0.7-1.0 in TSP were located between Bengal, Southern China and Indochina; North India and Southern China, respectively. On the other hand, The PSCF values range from 0.3-0.7 and 0.7-1.0 in $PM_{2.5}$ were located at Indochina; North India, respectively. It's indicating that the major atmospheric PCDD/F in TSP emission source areas for Mt. Lulin were northern areas of southeast Asia which corresponds to the prediction of backward trajectory analysis. To identify the different sources of the Southeast Asia biomass burning episode in TSP and $PM_{2.5}$ that occurred during spring seasons in 2014, 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. In spring, the SRA result of PCDD/Fs in TSP and $PM_{2.5}$ (Fig. 6) indicated that the higher cotribution were provided by R3 (69.3% for TSP, 39.4% for $PM_{2.5}$, Southern China, Indochina), R2 (13.9% for TSP, Central China) and R5 (24.2% for $PM_{2.5}$, Central India). The main source contribution region of PCDD/F in TSP measured at Mt. Lulin was Southern China and Indochina, but PCDD/F in $PM_{2.5}$ mostly provided from Southern China, Indochina and Centrial India.

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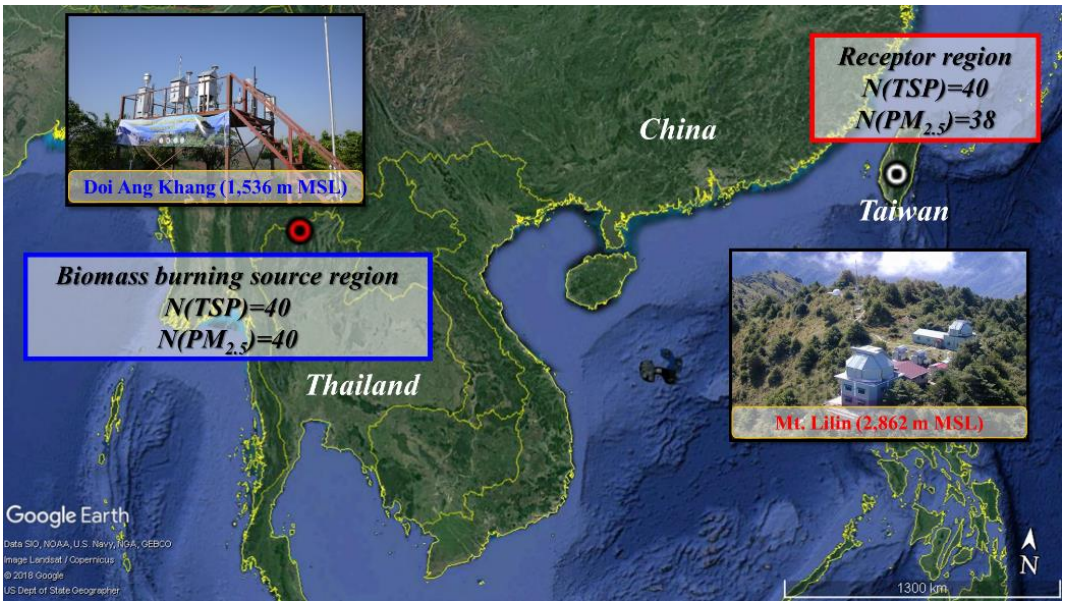

Fig. 1 Relative locations of the high-altitude sampling sites in Southeast Asia during 2014/03/01~04/12.

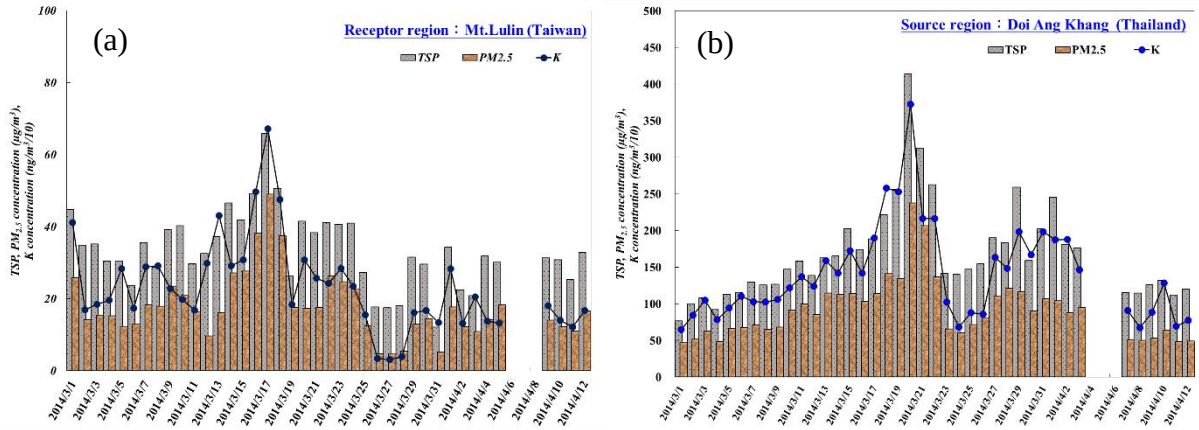

Fig. 2 Atmospheric PCDD/Fs, Potassium, total suspended particles and fine particles measured at Lulin and Doi Ang Khang station during 2014/03/01~04/12.

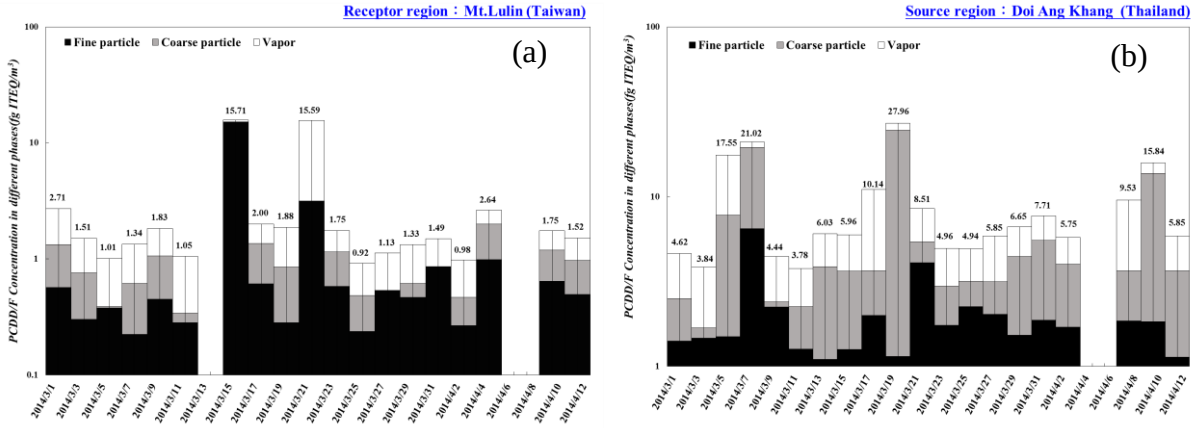

Fig. 3 Atmospheric PCDD/F concentrations in different phases measured in Mt. Lulin, (Taiwan) and Doi Ang Khang (Thailand) during 2014/03/01~04/12.

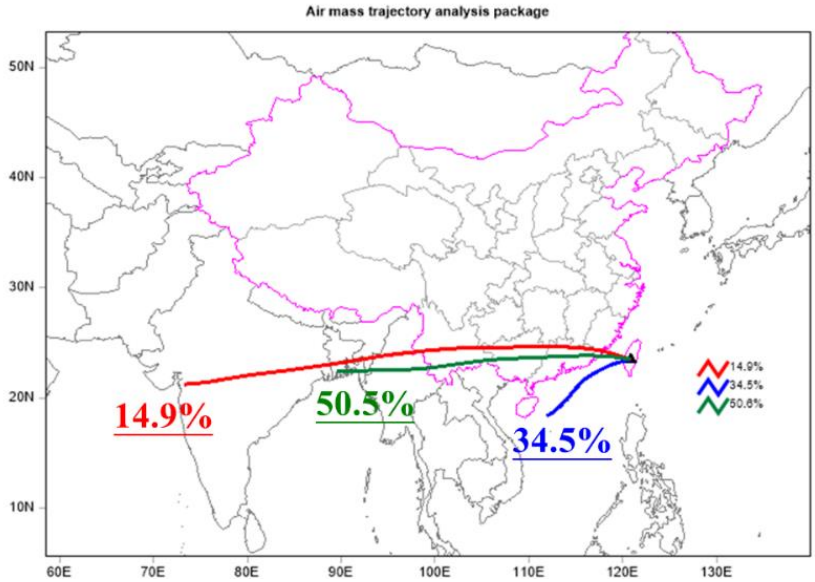

Fig. 4 Maps of potential PCDD/Fs source regions for the Mt. Lulin station during 2014/3/1~4/12.

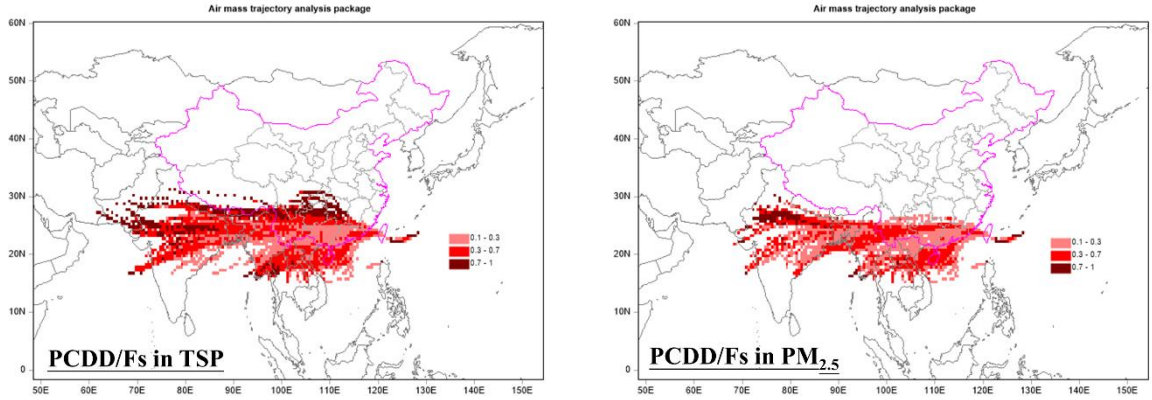

Fig. 5 PSCF value of potential PCDD/Fs in TSP and $PM_{2.5}$ source regions for the Mt. Lulin station.

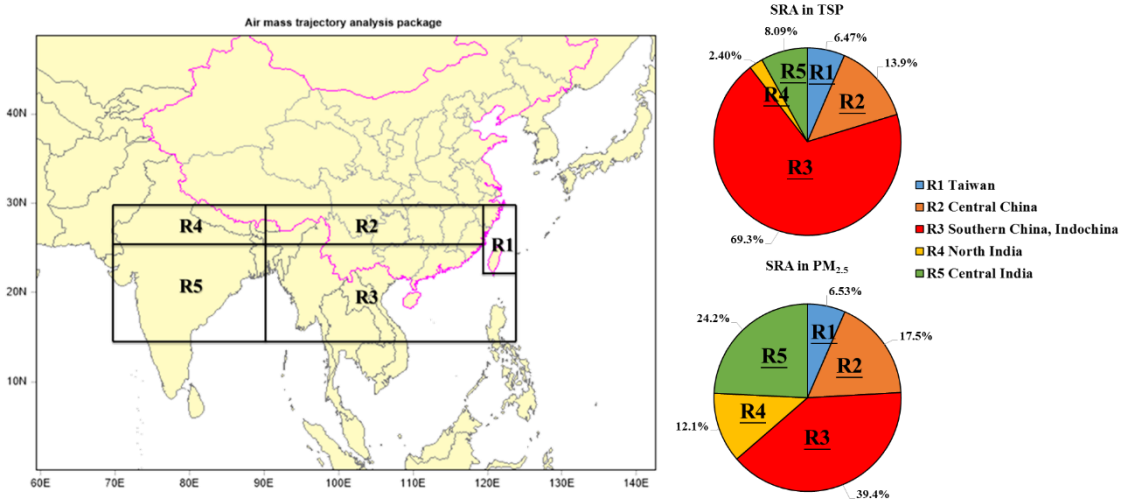

Fig. 6 Result of SRA in atmosphere PCDD/F distributed in TSP and $PM_{2.5}$ for the Mt. Lulin station during the sampling period (2014)