Influence of Biomass Burning on Characterization of Atmospheric Polycyclic Aromatic Hydrocarbons and their Nitro Derivatives in Chiang Mai,Thailand

Ph.D. Dissertation

Influence of Biomass Burning on Characterization of Atmospheric Polycyclic Aromatic Hydrocarbons and their Nitro Derivatives in Chiang Mai, Thailand

タイ・チェンマイにおける大気中多環芳香族炭化水素とそのニトロ誘導体の特性解析とバイオマス燃焼の影響

Graduate School of Natural Science and Technology, Kanazawa University,
Kakuma-machi, Kanazawa 920-1192, Japan

THANYARAT CHUESAARD

Abstract

Chiang Mai and several other provinces in northern Thailand have been annually facing air pollution problems during the dry season. The levels of airborne particulate matter (PM) increase in the season and often exceed the standard level in Thailand. Biomass burning is expected as a main contributor to the high PM concentrations. PM contains many inorganic and organic hazardous compounds. Among them, polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are of great concern because of their toxicity (carcinogenicity or mutagenicity) to human. However, the contribution of biomass burning to PAHs and especially NPAHs remains unclear. This study reports atmospheric levels and distribution profiles of PAHs and NPAHs in Chiang Mai, Thailand. Ten PAHs, 19 NPAHs, and levoglucosan, a marker for biomass burning, were quantified in total suspended particulates collected in Chiang Mai during the dry, transition, and wet seasons in 2010. PAHs and NPAHs were analyzed by HPLC with florescence and chemiluminescence detections, respectively. In addition, LG was analyzed by GC-MS after derivatization with a silylating reagent. The concentrations of PAHs and NPAHs in the dry season were significantly higher than those in the wet season. The [Benzo[*a*]pyrene (BaP)]–[benzo[*ghi*]perylene (BghiPe)] ratio, as an indicator of traffic, and the correlations of PAHs and NPAHs with LG showed that biomass burning significantly contributes to air pollution in the dry season. We proposed 9-nitroanthracene (9-NA) as a marker of biomass burning and the [9-NA]–[1-nitropyrene (1-NP)] ratio as a new indicator for assessing the contribution of biomass burning. The analysis using the markers indicated that biomass burning was a major source of PAHs and NPAHs in the dry season, whereas vehicle exhaust was the main contributor in the wet season. The high carcinogenic risks in the dry season correlate with more harmful air conditions during this season. Thus, it is important to control biomass burning to reduce air-pollution-related health risks during the dry season in northern Thailand. These results should be useful in controlling and managing air pollution in Thailand.

1. Research problem, motivation and purpose

Chiang Mai and several other provinces in northern Thailand have been annually facing air pollution problems during the dry season. The causes are probably due to massive biomass burning (forest fires and agricultural burning), the geographical (basin) and meteorological conditions. During this period, the northern region is covered by particulate matter (PM) such as PM_{10} that is PM less than 10 μm in diameter. The daily average concentrations of PM_{10} often exceed the Thai ambient air quality standard of 120 $\mu g/m^3$. More importantly, many consecutive days with high PM_{10} level resulted in smog-related health threats to the residents from Feb to April every year. In addition, the highest incidence of lung cancer has been recognized in this region of Thailand.

One group of compounds with high mutagenic and carcinogenic properties found in ambient PM are polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs), which are ubiquitous environmental contaminants formed by the incomplete combustion of organic materials. In the dry season of northern Thailand, biomass burning was expected as a main contributor to the critical levels of air pollutants. However, the contribution of biomass burning to PAHs and especially NPAHs remains unclear.

The purpose of this study is to investigate the atmospheric levels and distribution profiles of PAHs and NPAHs in Chiang Mai, a representative city in northern Thailand, and to discuss the possible emission sources and health risks in the region. We used levoglucosan (1,6-Anhydro-β-D-glucose, LG), a marker of biomass burning, to support the estimation of the source of PAHs and NPAHs. The results are expected to facilitate air pollution management in northern Thailand.

2. Material and methods

PM samples were collected at the rooftop of a nine-story building at the Faculty of Science in Chiang Mai University. Total suspended particulates (TSP) were collected using quartz fiber filters and a high-volume air sampler at a flow rate of 700 L min^{-1} for 23 h. We collected samples for seven consecutive days during the dry season (Feb, March, April), the transition period (May), and the wet season (Aug, Sept) of 2010. The filter samples were ultrasonically extracted with dichloromethane and the concentrated extracts were subjected to HPLC for detecting PAHs and NPAHs. The structures and abbreviations of targeted 10 PAHs and 19 NPAHs in this research are shown in Fig. 1 and 2, respectively.

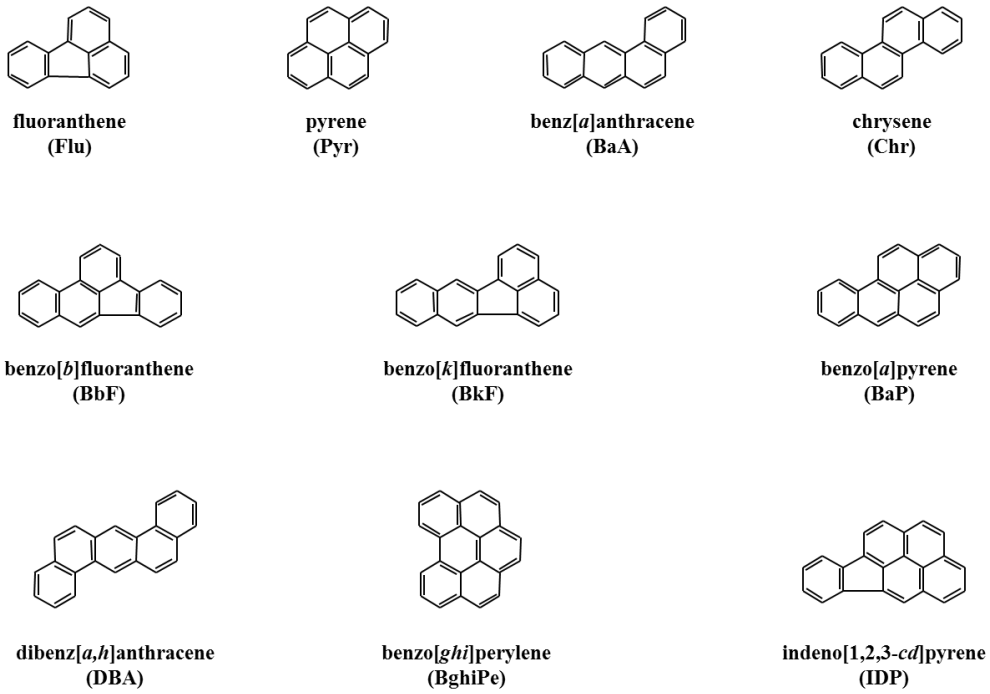

Fig. 1 The structures of targeted 10 PAHs in this research.

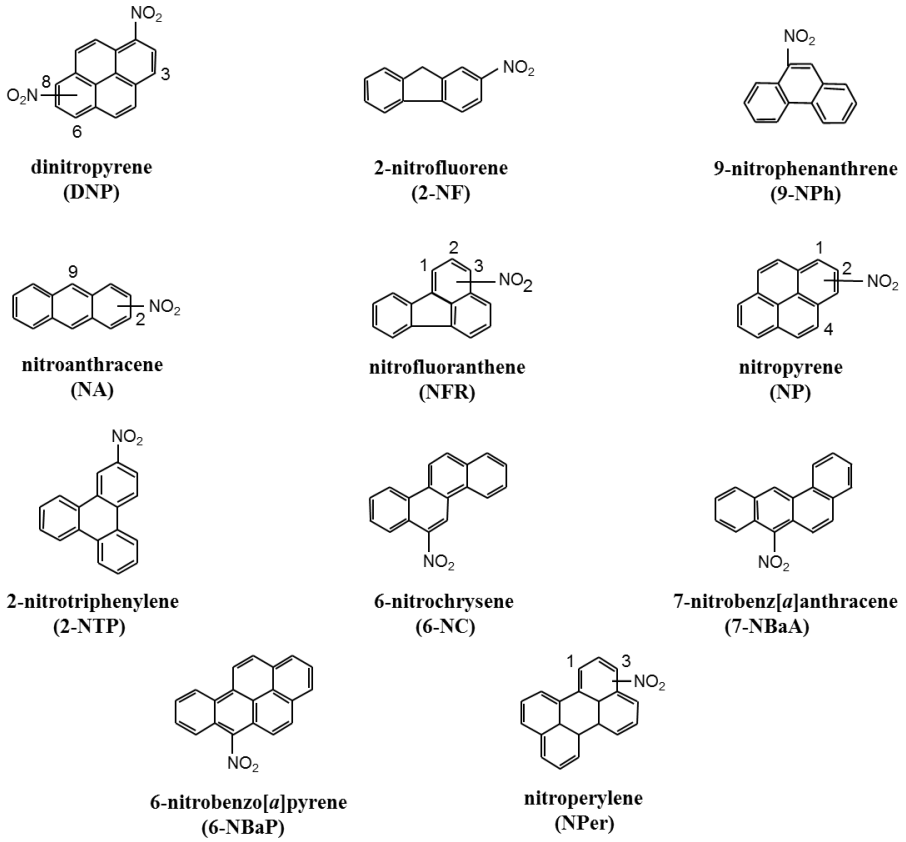

Fig. 2 The structures of targeted 19 NPAHs in this research.

3. Results and discussion

3.1. Ambient concentrations of PAHs

In this study, we focused on the 16 PAHs identified as priority pollutants by US EPA, and chose 10 PAHs in them as the analytes that have four to six rings and are distributed in the particle phase. As shown in Fig. 3, a clear seasonal variation in PAH concentrations was observed over the study period, with significantly higher concentrations in the dry season (Feb > March > April) than in the wet season (Aug and Sept).

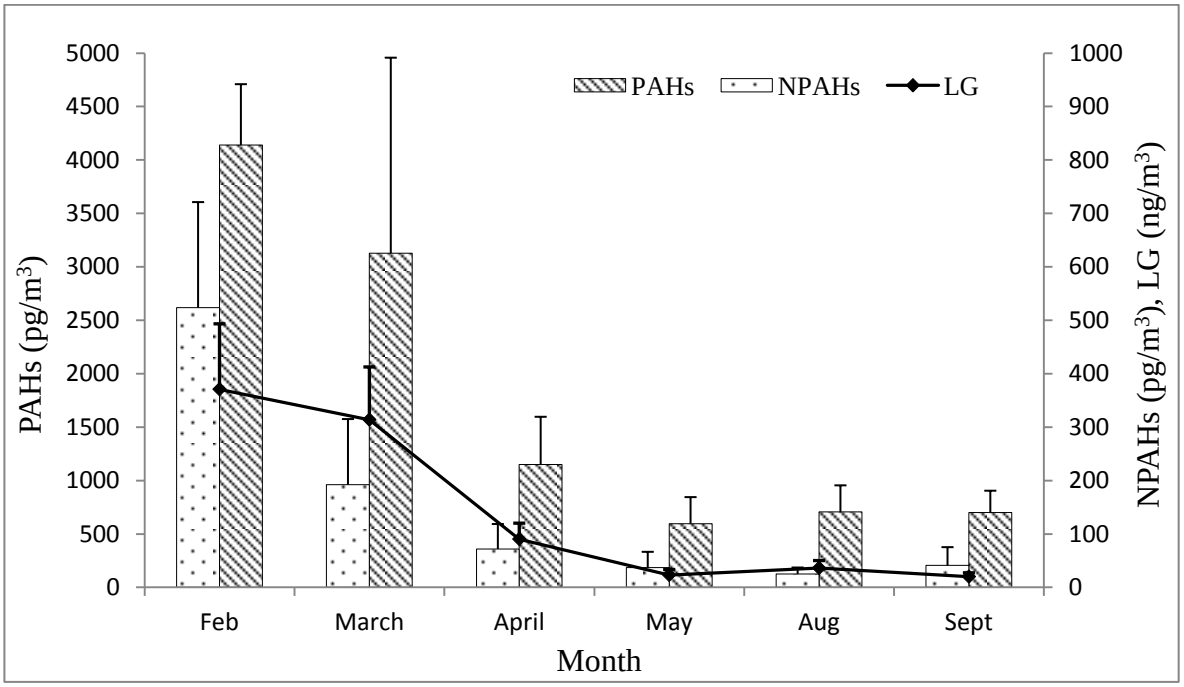

Fig. 3 Monthly concentrations (mean ± SD) of PAHs, NPAHs, and LG. Each bar represents the mean concentrations of the total PAHs or NPAHs; [PAHs] = [Flu] + [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [DBA] + [BghiPe] + [IDP], [NPAHs] = [1,3-DNP] + [1,6-DNP] + [1,8-DNP] + [9-NA] + [2-NFR] + [2-NP] + [4-NP] + [3-NFR] + [1-NP] + [6-NC] + [7-NBaA] + [3-NPer] + [6-NBaP]. The line plot connects the mean concentrations of LG.

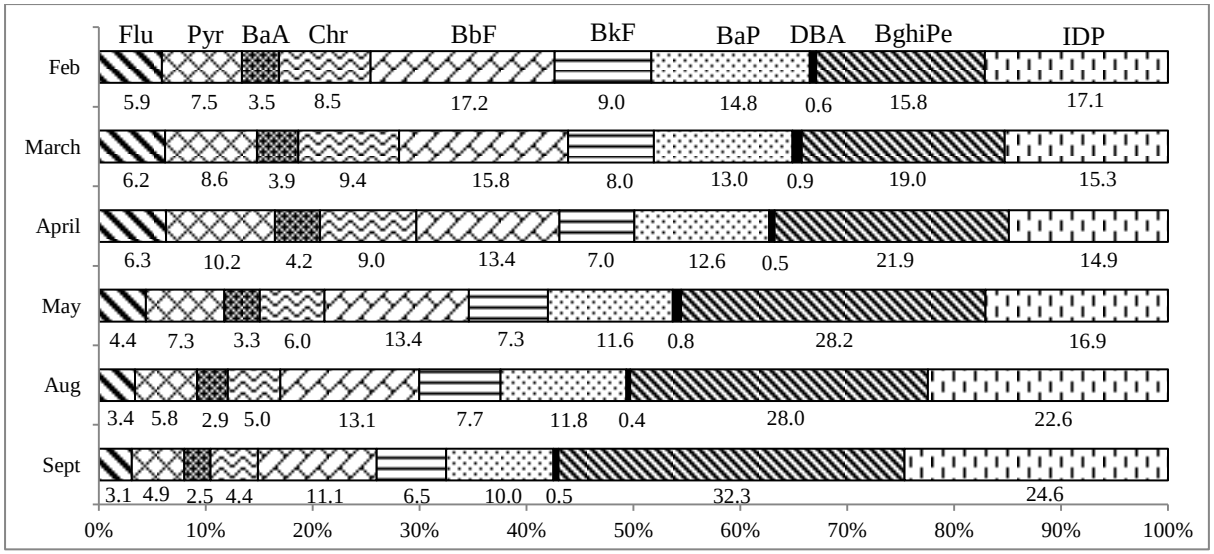

Fig. 4 Monthly composition profiles of PAHs. The numbers under the bars denote the percentage of each compound in the total concentration.

The proportion of each PAH to the total PAH concentrations was calculated monthly to show the seasonal variations in the PAH profiles (Fig. 4). The proportions of BaP as a tracer for biomass burning and BghiPe and IDP as tracers for vehicle exhaust were abundant. The increase in BaP in the dry season and that in BghiPe and IDP in the wet season suggest increased contribution of biomass burning in the dry season and vehicle exhaust in the wet season, respectively. The concentration ratios of PAHs are useful to identify the characteristic of combustion sources. The [BaP]/[BghiPe] value (<0.6) indicates the predominant contribution of traffic emissions. The ratios in the wet season (0.32–0.42) were within the range of the traffic emission indicators, whereas the increase in the ratio in the dry season (0.58–0.95) suggests the increased contribution of source(s) other than traffic emissions (Fig. 5).

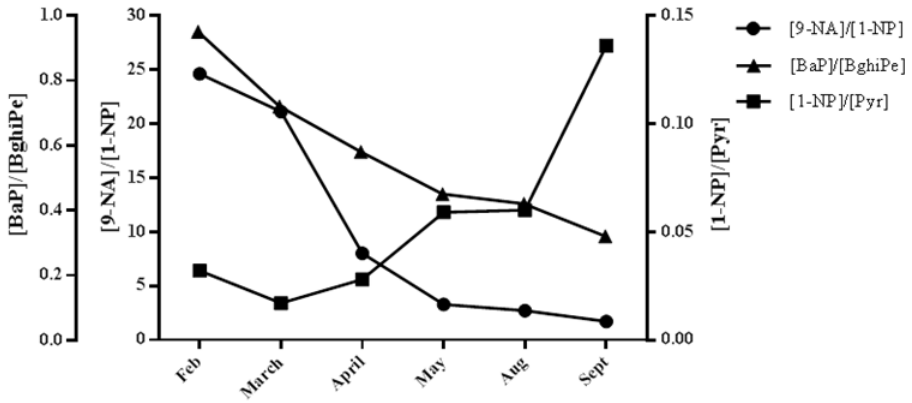

Fig. 5 Monthly diagnostic ratios of [9-NA]–[1-NP], [1-NP]–[Pyr], and [BaP]–[BghiPe].

3.2. Ambient concentrations of NPAHs

The total NPAH and PAH concentrations have similar trends, with significantly higher concentrations in the dry season than in the wet season (Fig. 3). Moreover, the total NPAH concentration was one order of magnitude lower than the total PAHs each month. The NPAH profiles in the dry and wet seasons are shown in Fig. 6. Overall, 9-NA, 2-NFR, and 2-NP were abundant in the determined 19 NPAHs in both seasons, accounting for 72.7%–90.9% of the total NPAH concentrations each month.

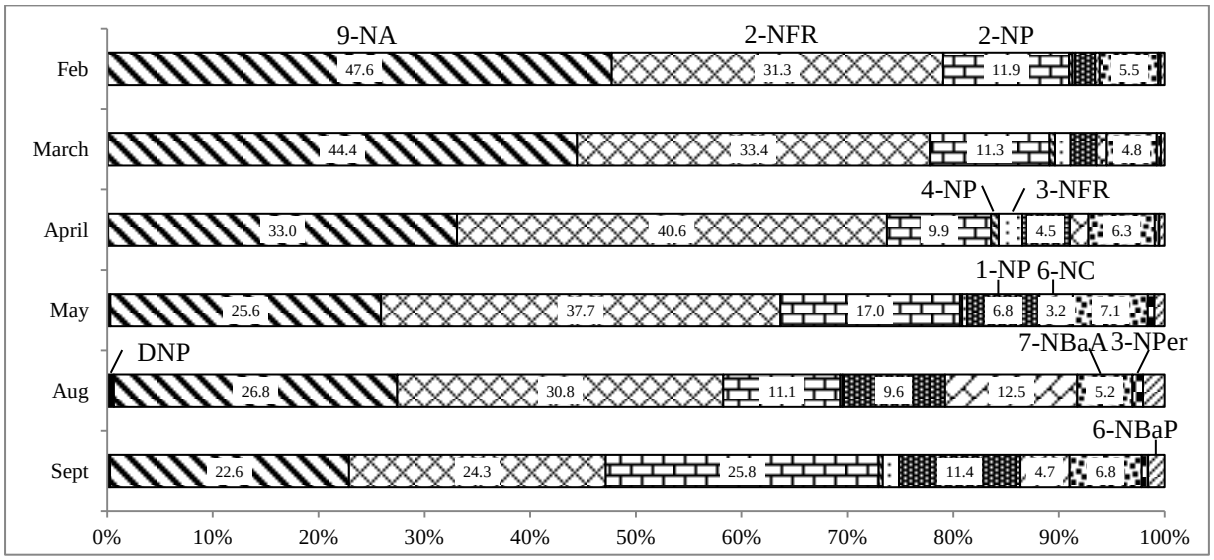

Fig. 6 Monthly composition profiles NPAHs. The numbers in the bars denote the percentage of each compound in the total concentration.

Among the NPAHs—except 2-NFR and 2-NP, which represent secondary formation of NPAHs in the atmosphere—9-NA was the most abundant. Although several reports have suggested the generation of 9-NA from diesel exhaust, the unexpected high concentrations of 9-NA in the dry season were obviously different from the distinct behavior of NPAHs derived from vehicle exhaust (Fig. 6). It seems likely that 9-NA can be produced by biomass burning. This hypothesis is supported by finding NPAHs emitted from wood combustion. Therefore, 9-NA is likely correlated with biomass burning, probably because of the low temperatures in biomass combustion and the high reactivity of PAH nitration. The combustion temperature in wood stoves (500–600°C) is much lower than in diesel engines (2700–3000°C). Anthracene (Ant) may be produced in higher levels in biomass combustion, and as a result, produce more 9-NA. From the investigation for the nitration reactivity of

PAHs, the most reactive positions in Ant are the meso positions (C-9 and C-10) and the relative reactivity of Ant (1,200) is higher than those of BaP (1,100), Pyr (27), Chr (6.3), BaA (4.5), phenanthrene (<2), and Flu (<0.4). The high nitration reactivity of Ant at position 9 may accelerate the preferential generation of 9-NA under the lower-temperature combustion of biomass relative to other sources.

3.3. PAH and NPAH correlation with LG

To identify the contribution of biomass burning to air pollutants, LG has been considered as an excellent tracer of biomass-burning sources. The strong correlation of PAHs and NPAHs with LG in the dry season and the poor correlation in the wet season suggest that biomass burning is the major contributor of PAHs and NPAHs (Table 1). In particular, among NPAHs, 9-NA showed the highest correlation coefficient with LG, suggesting the generation from biomass burning. The significant correlation among the individual and total PAHs and NPAHs and between PAHs and NPAHs in the dry season also suggests the existence of a common source (data not shown). Although the concentrations of NPAHs per weight unit for vehicle exhaust particulates are higher than those for biomass-burning particulates, massive biomass burning can be a major source of NPAHs.

Table 1 Correlation coefficients of PAHs and NPAHs with LG in the dry and wet seasons.

	Dry	Wet
Flu	0.812**	0.509
Pyr	0.838**	0.630*
BaA	0.869**	0.641*
Chr	0.877**	0.446
BbF	0.898**	0.464
BkF	0.895**	0.513
BaP	0.876**	0.606*
DBA	0.867**	−0.243
BghiPe	0.921**	0.292
IDP	0.915**	0.313
∑PAHs	0.910**	0.458
1,3-DNP	0.706**	0.236
1,6-DNP	0.738**	−0.142
1,8-DNP	0.539*	0.692**
9-NA	0.850**	0.152
2-NFR	0.802**	0.131
2-NP	0.801**	−0.026
4-NP	0.662**	−0.114
3-NFR	0.167	−0.090
1-NP	0.688**	−0.252
6-NC	0.490*	0.278
7-NBaA	0.605**	0.044
3-NPer	0.767**	0.185
6-NBaP	0.653**	−0.103
∑NPAHs	0.829**	0.084

** Correlation is significant at the 0.01 level (2-tailed),* Correlation is significant at the 0.05 level (2-tailed).

3.4. Evaluation of emission sources by diagnostic ratios using NPAHs

The concentration ratios of PAHs and NPAHs can be used to compare combustion sources. The [1-NP]–[Pyr] ratio for coal stove (0.001) was much smaller than that for diesel exhaust (0.36). As shown in Fig. 5, the [1-NP]/[Pyr] values in this study are lower in the dry season than in the wet season. This suggests that the contribution of vehicle exhaust in the dry season is low and increases with the wet season approaching.

Generation of large amounts of 9-NA from biomass burning was observed in this study. We proposed the [9-NA]–[1-NP] ratio as an indicator to distinguish biomass burning from vehicle exhaust. The transition of the ratio was clearly opposite to that of the [1-NP]–[Pyr] ratio (Fig. 5). The high [9-NA]/[1-NP] and low [1-NP]/[Pyr] values in Feb and March were strongly influenced by biomass burning, whereas the opposite pattern in Sept was strongly influenced by vehicle exhaust. The low [9-NA]/[1-NP] and high [1-NP]/[Pyr] values in Sept (1.70/0.136) were remarkably similar to those in Asian cities such as Kanazawa (0.08/0.141) and Hanoi (0.17/0.145), which are highly affected by vehicle exhaust. Chinese cities with predominant contributions from coal burning showed low [9-NA]/[1-NP] and [1-NP]/[Pyr] values, i.e., Fushun (3.67/0.013) and Shenyang (6.30/0.012). The profile of Chiang Mai with low [1-NP]/[Pyr] values in the dry season was clearly distinguished from coal burning using the [9-NA]/[1-NP] values. A [9-NA]/[1-NP] value of more than 10 should indicate strong contributions from biomass burning.

3.5. Carcinogenic risk

Carcinogenic risk was estimated using toxic equivalent factors (TEFs) according to the procedure by Albinet *et al.* (*Atmos. Environ.*, **42**, 43-54, 2003), and was calculated as shown in Eq. (1).

$$\text{Carcinogenic risk} = [\sum[\text{PAH}]i\ \text{TEF}_{\text{PAH}i} + \sum[\text{NPAH}]i\ \text{TEF}_{\text{NPAH}i}] \times \text{UR}_{\text{BaP}} \quad (1)$$

The carcinogenic risk calculated using eight PAHs and five NPAHs is shown in Fig. 7. The carcinogenic risks in Feb were 6.2 times higher than the average risk in the wet season, indicating more harmful air conditions in the dry season than in the wet season. The results suggest that it is important to control biomass burning to reduce air-pollution-related health risks during the dry season.

Although the atmospheric concentrations of NPAHs were lower than those of PAHs and the risks were calculated using only five NPAHs, the risk from NPAHs is 21% of the total

risk in Aug. Since the direct-acting mutagenicity of individual NPAHs, especially secondary NPAHs other than the five compounds, is not negligible, the risks would be higher than the presented values. Therefore, the determination of NPAHs levels in ambient air is important for assessing health risks.

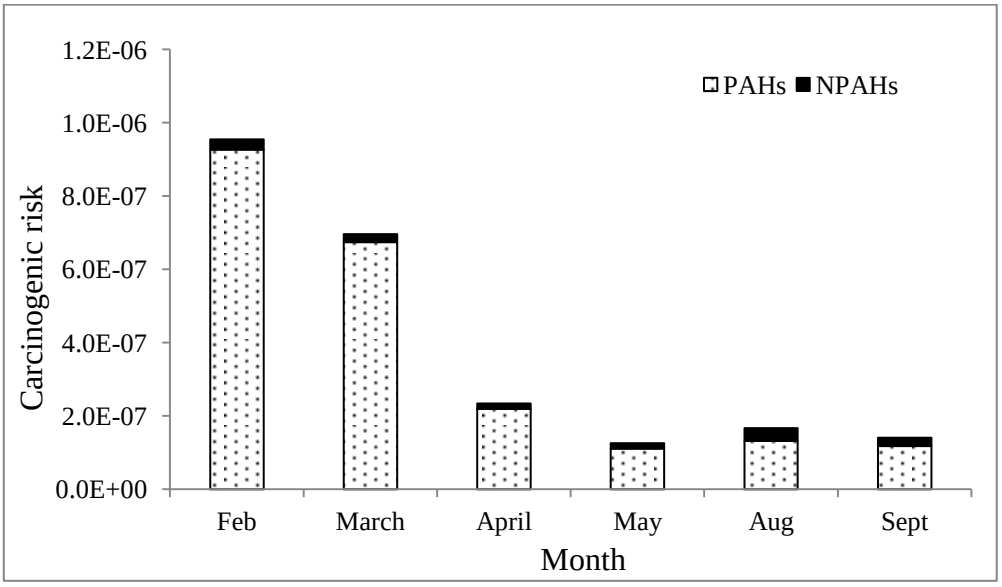

Fig. 7 Total carcinogenic risk calculated from the atmospheric concentrations of eight PAHs and five NPAHs; [8PAHs] = [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [DBA] + [BghiPe] + [IDP]; [5NPAHs] = [1-NP] + [4-NP] + [6-NC] + [1,6-DNP] + [1,8-DNP].

4. Conclusions

In recent years, high smog levels during the dry season have been affecting northern Thailand. Chiang Mai is a typical city which is located in the basin and is surrounded by mountain and appropriate to assess the air pollution in northern Thailand. The high PM concentrations in the dry season are due to massive biomass burning, stable meteorological conditions, and the basin geomorphology of the region. In addition to PAHs, this study reports for the first time the NPAH levels and distribution profiles of ambient air in Chiang Mai. The most severe PAH and NPAH contaminations occur in the dry season, and biomass burning is the major source of PAHs and NPAHs. 9-NA is the most abundant NPAH in the dry season, suggesting strong contribution from biomass burning. We propose 9-NA as a marker of biomass burning and the [9-NA]–[1-NP] ratio a suitable indicator for identifying the contribution of biomass burning. It is apparently important to control biomass burning to reduce air-pollution-related health risks during the dry season. These results should be useful in controlling and managing air pollution in Thailand.

学位論文審査結果の要旨

〔審査経過〕審査方針に従い、学位申請論文に対する各審査委員による面接と諮問を実施した。平成25年8月5日に口頭発表（最終試験）を行い、終了後に開催した論文審査委員会において協議の結果、以下のように判定した。

〔審査結果〕東南アジアの国々では、都市部で大気汚染が深刻化しており、タイ・チェンマイでは乾季の大規模な森林火災（バイオマス燃焼）によって発生する大気中の粒子状物質が大気環境の悪化を招いており、肺がんの患者数も増加している。健康影響を及ぼす粒子状物質中の有害な化学成分に対して、バイオマス燃焼の寄与についてほとんど研究が進んでいないのが実状である。本研究では、チェンマイ市内において大気中の粒子状物質を乾季と雨季に連続捕集し、発がん性／変異原性を有する多環芳香族炭化水素(PAH)、ニトロ多環芳香族炭化水素(NPAH)及びバイオマス燃焼のマーカー物質であるレボグルコサンを測定した。その結果、乾季のPAH及びNPAH濃度は、雨季の濃度に比べて著しく高く、レボグルコサンとの相関性が高いことから、乾季においてバイオマス燃焼が主要な発生源であることが明らかとなった。また、新たなバイオマス燃焼の指標として、[9-Nitroanthracene] - [1-Nitropyrene]比を提案し、その有用性を証明した。本研究は、タイにおける大気中の粒子状物質やPAH及びNPAHの発生に対するバイオマス燃焼の寄与を初めて明らかにし、それらの低減政策に対して有用な示唆を与える研究である。従って、審査委員会は学位申請論文が博士（学術）に値すると判定した。