

Supplementary Materials

Influence of Biomass Burning on the Levels of Atmospheric Polycyclic Aromatic Hydrocarbons and Their Nitro Derivatives in Chiang Mai, Thailand

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There are 7 pages, with 2 tables and 1 figure.

The 19 NPAHs were analyzed using HPLC with chemiluminescence (CL) detection. The system consists of five HPLC pumps (LC-20AD), a system controller (CBM-20A), a degasser (DGU-20A5), an auto sample injector (SIL-20AC), a column oven (CTO-20AC) (all from Shimadzu, Kyoto, Japan), and a CL detector (S-3400, Soma Optics Ltd., Tokyo, Japan). The NPAHs were purified using a clean-up column (Cosmosil π NAP, 50 mm \times 4.6 mm i.d. 5 μ m, Nacalai Tesque, Kyoto, Japan) with its guard column (10 mm \times 4.6 mm i.d.), and were then reduced to their amino derivatives by using a reduction column (NPPak-RS, 10 mm \times 4.0 mm i.d. JASCO, Tokyo, Japan) under 80°C. The mobile phase in the clean-up and reduction columns was acetate buffer (pH 5.5)–ethanol (5/95, v/v) at a flow rate of 0.2 mL/min. Only a fraction of the amino derivatives was trapped on the concentration column (Spheri-5 RP-18, 30 mm \times 4.6 mm i.d. 5 μ m, Perkin Elmer, MA, USA) by using a switching valve. The concentrated fraction was applied to two separation columns (Cosmosil 5C₁₈-MS-II, 150 mm \times 3.0 mm i.d. 5 μ m and Cosmosil 5C₁₈-AR-II, 250 mm \times 3.0 mm i.d. 5 μ m, both from Nacalai Tesque) in tandem. All columns, except for the reduction column, were maintained at 20°C. The mobile phase in the separation columns was a gradient elution of 10 mM imidazole buffer (pH 7.6) and acetonitrile at a flow rate of 0.5 mL/min. The eluted fraction from the separation columns was mixed with the CL reagents and detected by the CL detector. The CL reagent solutions were acetonitrile solutions containing 0.02 mM *bis*(2,4,6-trichlorophenyl)oxalate and 15 mM hydrogen peroxide at a flow rate of 0.5 mL/min.

The HPLC system was carried out by using the procedure described in a previous study with some modifications (Tang *et al.*, 2005). To improve selectivity for NPAHs, the clean-up column was changed from a basic column with octadecyl silica (ODS) to the column (π NAP) with naphthylethyl group bonded silica. Ethanol percentage in the mobile phase for the clean-up and reduction column increased with the change of the clean-up column. The combination of a monomeric ODS column (Cosmosil 5C₁₈-MS-II) and a polymeric ODS column (Cosmosil 5C₁₈-AR-II) enabled us to separate 2-NFR and 2-NP. To decrease acetonitrile consumption, we used the separation columns with smaller internal diameter than the previous paper and decreased the flow rates of the mobile phase for the separation columns and of the CL reagent.

PAH Analysis

The 10 PAHs were determined by using HPLC with fluorescence detection (HPLC-FL) without modification (Toriba *et al.*, 2003). The system consisted of two HPLC pumps (LC-10A), a fluorescence detector (RF-10A), a system controller (SCL-10A), a degasser (DGU-14A), an auto sample injector (SIL-10A) and a column oven (CTO-10AS) (all from Shimadzu). PAHs were separated by using a guard column (Inertsil ODS-P, 10 × 4.0 mm i.d., 5 μ m, GL Sciences, Tokyo, Japan) and an analytical column (Inertsil ODS-P, 250 × 4.6 mm i.d., 5 μ m, GL Sciences) with acetonitrile/water gradient and fluorescence detection.

LG Analysis

LG analysis was carried out according to a reported method with minor modifications (Hsu *et al.*, 2007). An adequate volume (10 μL) of the ethanol extract was evaporated to dryness, and then the residue was derivatized by adding 10 μL of pyridine, 10 μL of 1,4-dithioerythritol (5 mM), 20 μL of silylating agents and 50 μL of toluene. The reaction mixture was heated at 80°C for 60 min. After cooling, 10 μL of 1-phenyldodecane (0.1 mM) as a syringe spike was added to the derivatized solution. The derivatized samples were applied to gas chromatography coupled with mass spectrometry (GC-MS). The Agilent 6890N Network Gas Chromatograph was fitted with a DB-5MS column (30 m \times 250 μm i.d., 0.25 μm film thickness). The Agilent 5975B inert MSD mass spectrometer was operated in electron impact mode (EI). Helium was used as the carrier gas, at a flow rate 1.0 mL/min. The injector temperature was set at 250°C. The column temperature was programmed as follows: initial temperature of 70°C, hold for 1 min, ramp at 20.0°C/min to 300°C, hold for 2 min. The MS ion source temperature was set at 230°C. The derivatized LG was injected 1 μL , under splitless mode. LG quantification was performed in selected ion monitoring mode (SIM), with specific fragment ions at m/z 333.

PM₁₀ Monitoring at the Air Quality Monitoring (AQM) Stations

Ambient PM₁₀ concentrations have been monitored at the Air Quality Monitoring (AQM) stations set up by the Pollution Control Department (PCD) of Thailand. There are two AQM

stations in Chiang Mai which are located at Provincial Hall (suburban) and Yupparaj Wittayalai School (downtown). PM_{10} were measured with the tapered element oscillating microbalance (TEOM) detector which utilizes an inertial mass weighing principle. Locations of our sampling site and two AQM sites by PCD were shown in Fig. S1. Monthly average PM_{10} and average PM_{10} during the 7-day sampling period were shown in Table S1.

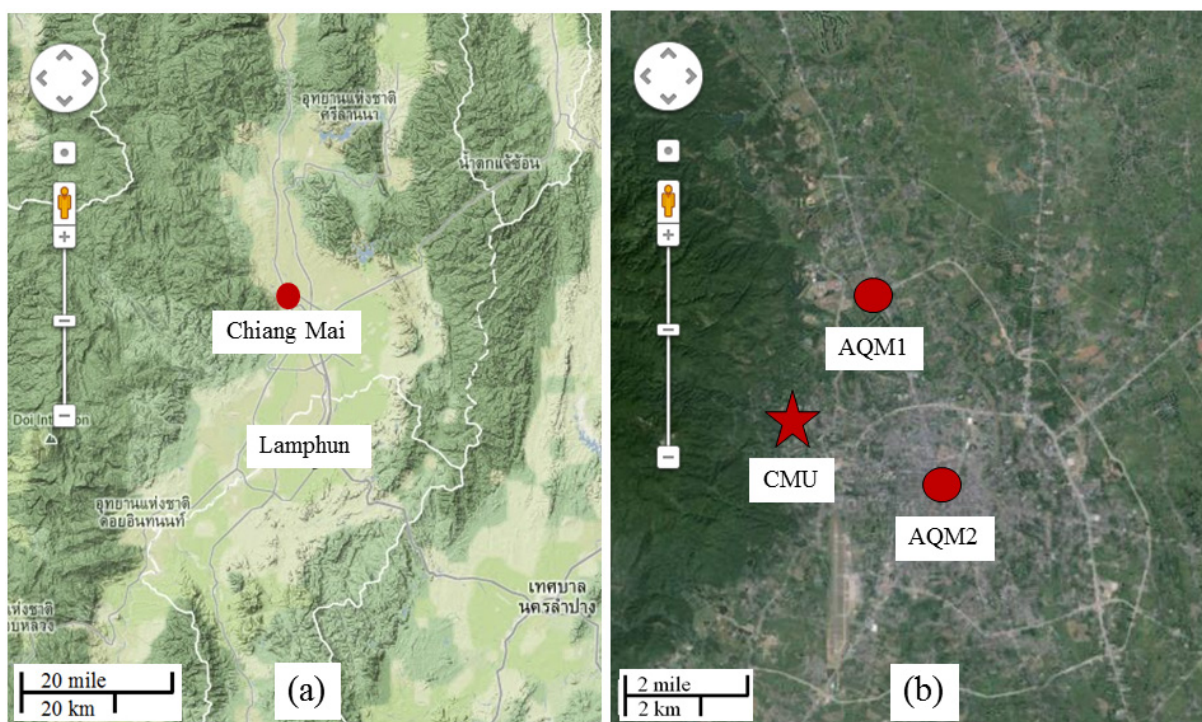


Fig. S1. Locations of (a) Chiang Mai-Lamphun basin and (b) the sampling site at Chiang Mai University (CMU) and the Air Quality Monitoring (AQM) sites (AQM1: suburban; AQM2: downtown) by PCD.

Table S1. Comparison between monthly PM₁₀ and average PM₁₀ during the 7-day sampling period in 2010 by PCD.

Month	Average PM ₁₀ concentration (µg/m ³)			
	Provincial Hall		Yupparaj Wittayalai School	
	Monthly ^a	The 7-day period ^b	Monthly ^a	The 7-day period ^b
February	67.4	91.4	77.6	102.3
March	111.6	101.1	120.2	111.1
April	102.0	62.2	106.6	66.6
May	35.4	19.6	40.8	25.8
August	17.7	16.6	23.1	23.6
September	18.7	18.6	23.6	22.5

^a Monthly PM₁₀ indicates average PM₁₀ concentration in each month.

^b The 7-day sampling period indicates average PM₁₀ concentrations during the period corresponding to our sampling days (Feb 24–March 2, March 24–30, April 24–30, May 17–23, Aug 21–27 and Sept 8–14).

Table S2. Comparison of total PAHs concentration between Chiang Mai and other cities in Southeast Asia.

City/Country	Location	Total concentration (ng/m ³)	Reference
Chiang Mai, Thailand	Suburban area	0.60–4.14	This study
Bangkok, Thailand	Roadside	10.1–28.2	Boonyatumanond <i>et al.</i> (2007)
Ho Chi Minh City, Vietnam	Urban area	7.6–8.7	Hein <i>et al.</i> (2007)
	Roadside	19.0	
Hanoi, Vietnam	Urban area (site I)	1.9–15.8	Pham <i>et al.</i> (2012)
	Roadside (site T)	6.1–10.6	