CHAPTER 2

EXPERIMENT

2.1 Apparatus and chemicals

2.1.1 Instrument

1) Gas chromatograph-mass spectrometer, manufactured by Hewlett Packard, U.S.A. consisting of

a) Gas chromatograph, Agilent 6890

b) Mass spectrometer, Hewlett Packard 5973 Mass selective Detector

c) Auto injector, Agilent 7683

d) Data processing system with MSD ChemStation software D.01.02.16, Agilent Technologies, 1989-2004

2) HP – 5MS, 5% phenyl- 95% dimethyl polysiloxane, 30 m, 0.25 mm I.D., 0.25 µm film thickness, Alltech, U.S.A.

2.1.2 Equipment and Apparatus

1) AIRmetric MiniVol^{TM} Air sampler consisting of

a) Pump

b) Pre-separator and Cassete Filter Holder

c) Quatz fiber filter, Whatman$^{®}$47 mm, P/N 1851A047

d) 7 day Timer with battery back up

e) Sealed lead-acid batteries, 12 AH capacity (24 hours sampling duration)

f) 1amp built in charger adapter

g) Digital manometer, DIG 1135

2) Microbalance weight, Mettler Toledo, MX5, Swizerland

3) Analytical balance, AB 304-S, Mettler Toledo, Switzerland

4) Analytical balance, BB3, Mettler Toledo, Switzerland

5) Ultrasonicator, Transonic Digital, Elma, Germany

6) Rotary evaporator, Buchi Labortechnik AG, Switzerland, consisting of

a) Water bath, B480

b) Air pump, KNF laboport

c) Cooling device, NESLAB, U.S.A.

7) General packet radio service, GPSmap60CSx, Garmin, Taiwan

8) Moisture analyzer, MA50, Sartorius, Germany

9) Oven, 100-800, Memmert, Germany

10) Micropipettes with various volume ranges; 100 to 1000 µl and 1 to 10 ml (Brand, German)

11) 30 ml V-shaped flask

12) 1.5 ml amber screw bottle

13) Syringe filters

14) Parafilm

15) Beakers

16) Volumetric flasks

17) Desiccators

18) Vertex (Vortex-Genie 2, USA)

19) Petri dish plastic cover with aluminum foil

20) Nylon filter 0.45 µm

21) Filter paper, Whatman No.42, Whatman, England

2.1.3 Chemicals

1) Acetonitrile, HPLC grade, Merck, Germany

2) Mixed standard containing 16 priority PAHs at 1000 µg/ml Acetonitrile, Restex, USA

3) Internal standards (D_{10}-acenaphthene and D_{12}-pyrylene) Supelco, USA

4) Standard reference material (SRM), Urban dust 1649b, NIST, USA

2.2 Experimental framework

The framework of the overall experiments performed in this study is shown in Figure 2.1.

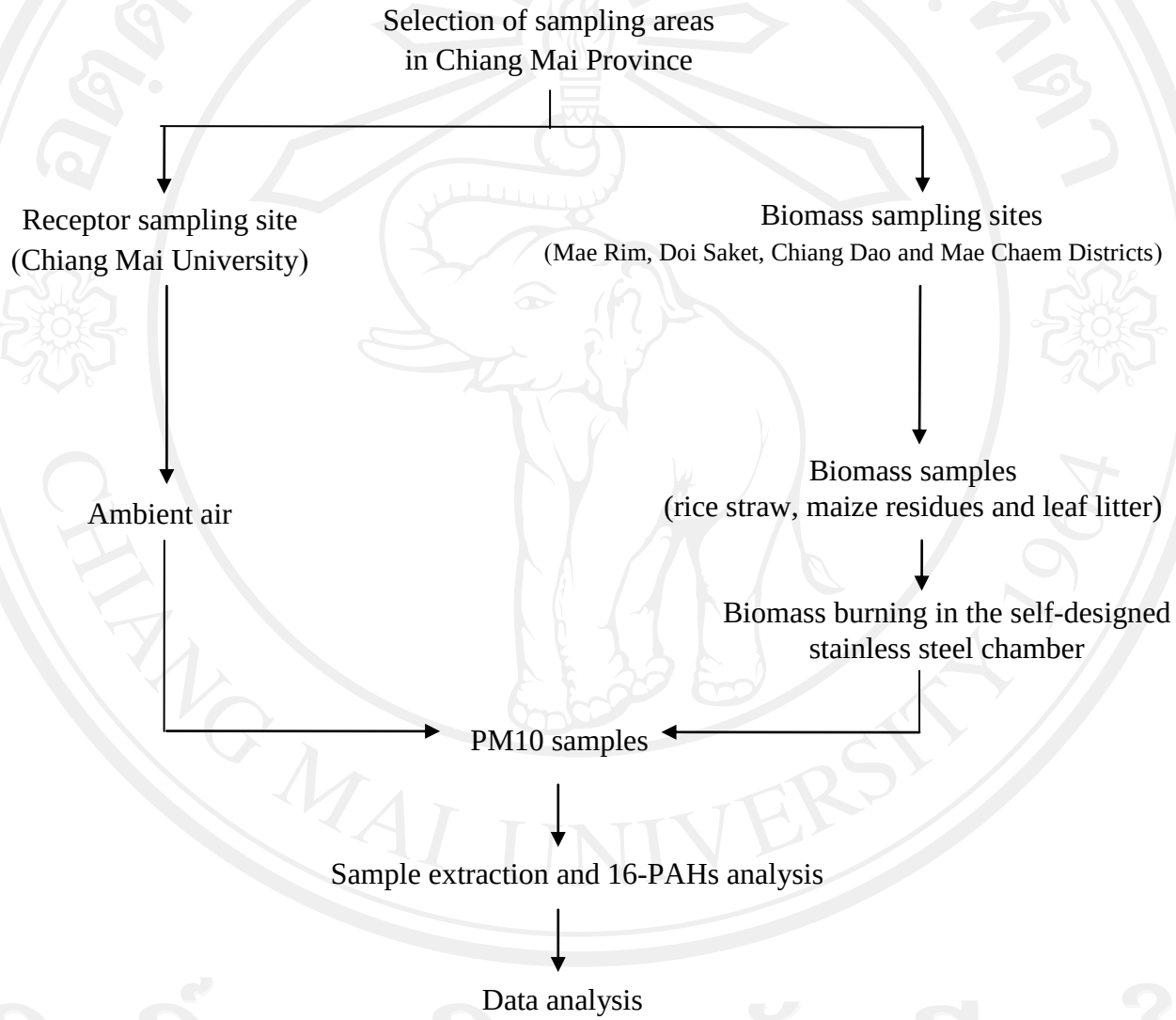


Figure 2.1 Diagram of experimental framework

2.3 Site description and collecting method for biomass samples

2.3.1 Sampling sites for biomass residues

Open burning in particular forest fire and burning in agricultural area is frequently found in northern part of Thailand (Kim Oanh, *et al.*, 2011; Office of Chiang Mai Agriculture, 2010; FIRMS). Three types of biomass, those were identified as being widely burnt in Chiang Mai Province, were selected. They were rice straw (sticky rice), maize residue, and leaf litter (mixed deciduous forest). They were selected from 4 districts in Chiang Mai Province where frequent open burning was detected. Biomass residues including straw of sticky rice, maize residue, and leaf litter were collected from 4 districts of Chiang Mai Province namely Chiang Dao, Mae Rim, Doi Saket and Mae Chaem. The information of these districts is given in Table 2.1. The samples were collected on November of 2010.

Table 2.1 General information of selected districts for biomass sampling

Districts	Details
Chiang Dao (CD)	
	
Location	Northern part of Chiang Mai (Coordinates: 18°52′13″N 99°8′12″E)
Total area	2165.8 km^2
Forest area	1777.5 km^2 (82%)
Crop area	89.8 km^2 (4%)
Rice field area	36.0 km^2 (2%)
Population No.	81,853 persons
Population density	37.8 persons/km^2
Number of sub districts	7 sub-districts
Number of villages	91 villages
Over view	Rural farming area, mainly rice fields and crop in the valley

Table 2.1 General information for each site (continued)

Districts	Details
Mea Rim (MR)	
	
Location	Central part of Chiang Mai (Coordinates: 18°54′50″N 98°56′42″E)
Total area	454.2 km^2
Forest area	272.4 km^2 (60%)
Crop area	25.5 km^2 (6%)
Rice field area	37.2 km^2 (8%)
Population No.	82,943 persons
Population density	182.7 persons/km^2
Number of sub districts	11 sub-districts
Number of villages	91 villages
Over view	Tourist area and agricultural area (soya bean and rice field)
Doi Saket (DS)	
	
Location	Eastern part of Chiang Mai (Coordinates: 18°52′13″N 99°8′12″E)
Total area	652.0 km^2
Forest area	472.2 km^2 (72%)
Crop area	10.4 km^2 (2%)
Rice field area	64.2 km^2 (10%)
Population No.	64,116 persons
Population density	98.3 persons/km^2
Number of sub districts	14 sub-districts
Number of villages	112 villages
Over view	Major area for rice cultivation

Table 2.1 General information for each site (continued)

Districts	Details
Mea Chaem (MC)	
	
Location	Western part of Chiang Mai (Coordinates: 18°29′56″N 98°21′43″E)
Total area	3,347.2 km^2
Forest area	2,937.7 km^2 (88%)
Crop area	114.0 km^2 (3%)
Rice field area	51.1 km^2 (1%)
Population No.	57,214 persons
Population density	17.1 persons/km^2
Number of sub districts	8 sub-districts
Number of villages	75 villages
Over view	Mountainous area, majority corn and vegetable planting

Data from Chiang Mai Official Site (http://www.chiangmai.go.th/newweb/main/)

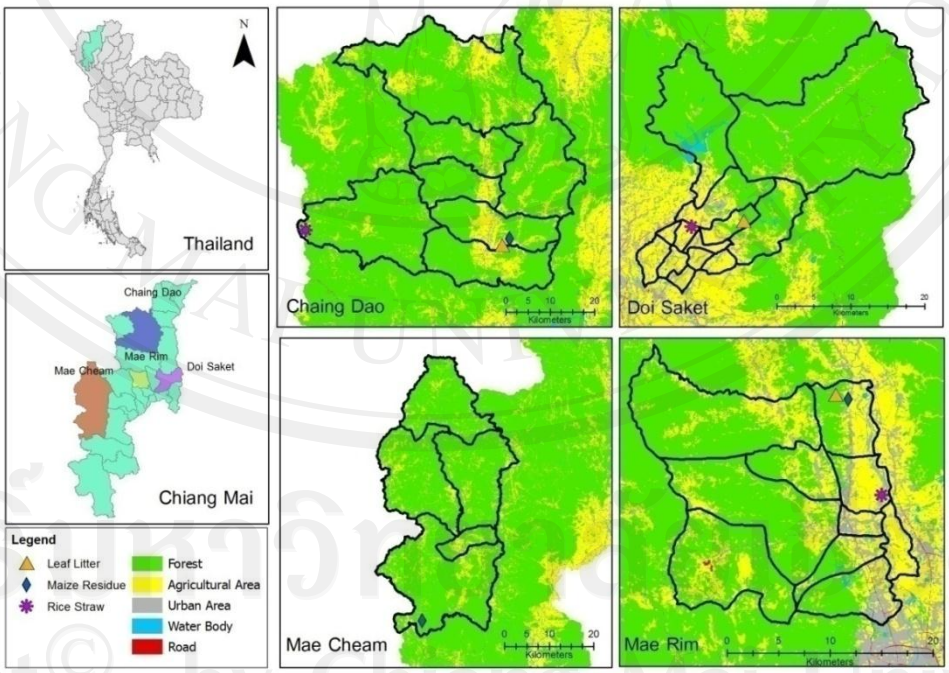


Figure 2.2 Map of biomass sampling sites in Chiang Mai Province

A map of biomass sampling site shown in Figure 2.2 and Table 2.2 list the sampling site, sample types and sample number. Biomass residues were collected in the harvest season from December 2009 to February 2010.

Table 2.2 Sampling sites, sample types and sample numbers

Sample media	Location	North latitude East longitude	Elevation above sea level (m)	Sample type	Sample code	Sample No.
Ambient air	CMU	18° 48' 5" 98° 57' 12"	373.0	PM10 from ambient air	-	**92**
Biomass	MR	18° 56' 31" 98° 58' 20"	315.2	Rice straw	RS	3
		19° 1' 34" 98° 56' 34"	326.4	Maize residue	M	3
		19° 1' 20" 98° 55' 59"	396.8	Leaf litter	L	3
	CD	19° 21' 31" 99° 2' 44"	550.5	Rice straw	RS	3
		19° 21' 5" 98° 58' 57"	433.2	Maize residue	M	3
		19° 21' 5" 98° 58' 56"	433.8	Leaf litter	L	3
	DK	18° 51' 9" 99° 10' 57"	356.1	Rice straw	RS	3
		19° 21' 5" 98° 58' 56"	433.8	Leaf litter	L	3
	MC	19° 21' 31" 99° 2' 44"	550.5	Maize residue	M	3
	Total					**27**

2.3.2 Collecting and preparation of biomass

The samples were randomly collected by using a 1-m^2 grid (Figure 2.3) for 3 replications at each location (Figure 2.4). Each sample was kept in a labeled plastic bag and transported to the laboratory. The moisture content as well as C, H, N content of each type of biomass was determined.

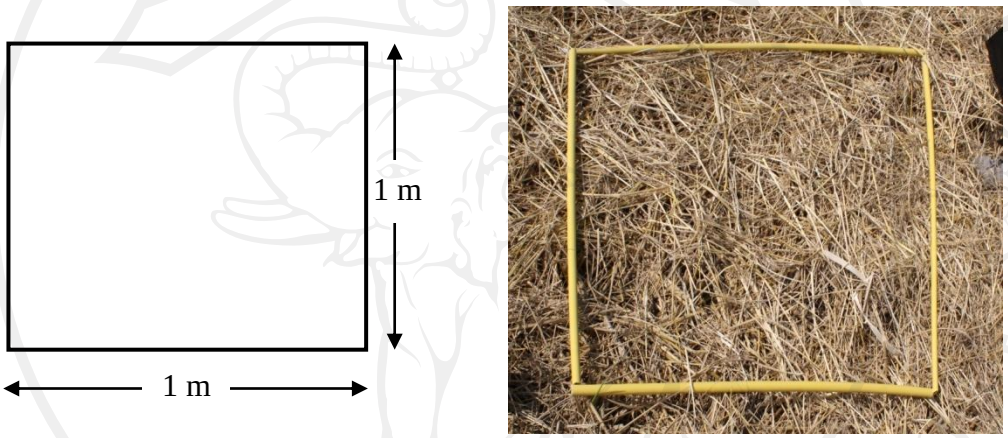


Figure 2.3 Grid of biomass sample collection

a) Moisture content

Biomass samples were cut into small pieces using stainless scissors, and then 2 g of samples were weighed for relative moisture content measurement using a moisture analyzer (MA50, Germany).

b) Basis elements (C, H and N)

Biomass samples were dried in an oven at a temperature of 80^{o}C for 24 hrs. The samples were cut into small pieces using stainless scissors and blended using a blender. Powder samples were sent for analysis for C, H and N content using a

CHNS/O analyzer (PE2400 Series II, Perkin Elmer, Germany) at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

(a)

(b)

(c)

Figure 2.4 Biomass sampling for (a) rice straw, (b) maize residues and (c) leaf litter

2.4 Biomass burning experiment

2.4.1 Design of a stainless steel chamber for biomass burning

A chamber was constructed with stainless steel. Its schematic sketch is shown in Figure 2.5. The chamber was designed as a close system and use ambient air in burning process (Kannan *et al.*, 2005). It has two main sections, namely a burning chamber and a storage chamber. The burning section was used for burning of biomass. The storage section was for PM10 sample collection from the burning. It was designed for protection of re-burning process of PM from a burning section. Details of the chamber are shown in Figure 2.6 and Table 2.3. The burning chamber had a diameter of 0.50 m and 1.20 m height, while the storage chamber had a diameter 0.75 m and 2.00 m height. The burning chamber contained an air inlet, an ignition point (liquefied petroleum gas), a biomass basket and three temperature sensors. The storage chamber was conducted with a gas analyzer (Testo 350 XL, UK), a minivol air sample and a vacuum pump.

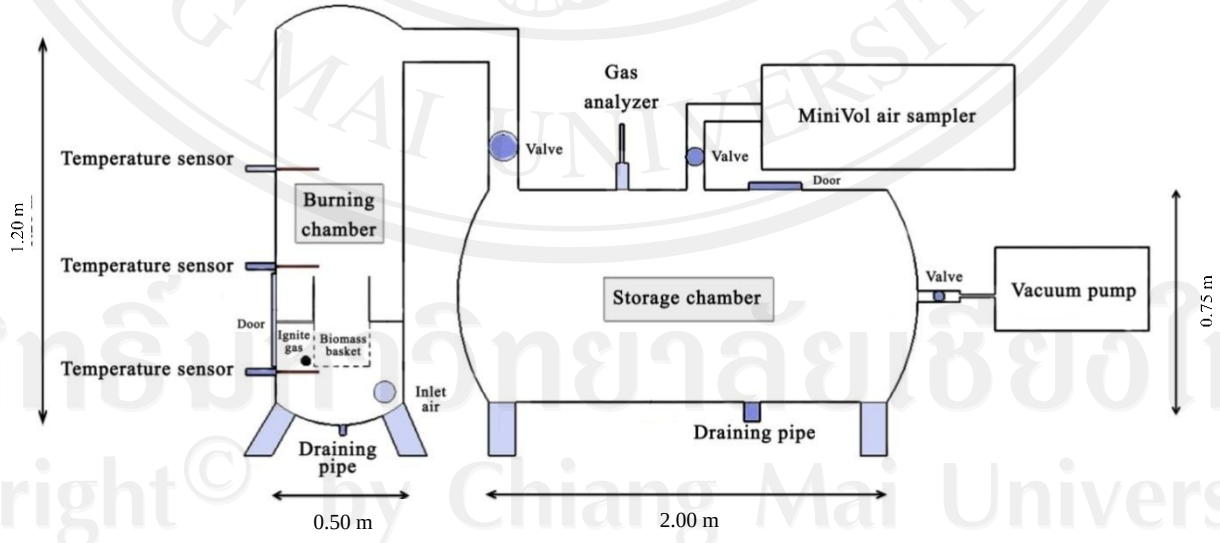


Figure 2.5 Schematic diagram of a chamber

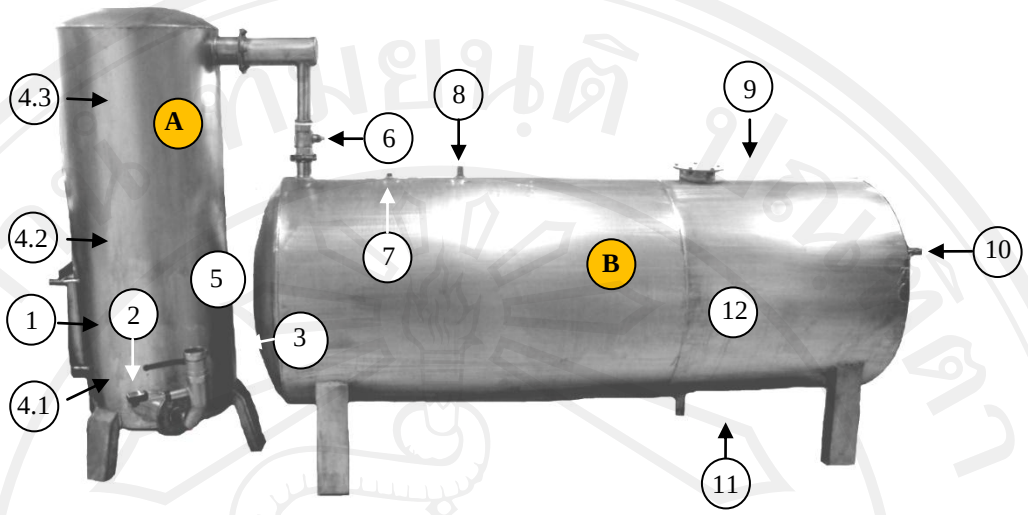


Figure 2.6 Combustion chamber; (A) combustion part and (B) air pollutant storage part

Table 2.3 Composition and function of the combustion chamber

No.	Composition	Function
A) Combustion part (∅:0.5 m, 1.50 m height)		
1	Door	To insert biomass
2	Air velocity	To measure air velocity
3	Air inlet	To provide fresh air during burning
4	Temperature sensor (3)	To measure temperature profile in different part of chamber
5	Biomass basket	To control area of burning
B)Air pollutant storage part (∅:0.85 m, 1.50 m height)		
6	Valve	To control air pollutant from biomass burning (from A into B part)
7	Gas analyzer connector	To measure air pollutants
8	Pressure gauge	To measure pressure
9	Door	To clean storage part
10	Vacuum pump air connector	To remove the air
11	Water drain	To release contaminated water
12	Air sampler connector	To connect with air sampler

2.4.2 Operation of the chamber

First of all, air inside the storage chamber was pumped out until it was nearly vacuum. Biomass sample was put into a basket inside the burning chamber. Liquefied petroleum gas was used for ignition providing temperatures between 500 - 800 ºC. The percent of oxygen (%O_2) was approximately 21.00 % before burning biomass. Burning process took about 1 minute, while stabilization of pollutant gas concentrations emitted from the burning took approximately 5 minutes. The %O_2 was about 19.00 % when burning process was finished. The PM10 collecting was started by opening a valve between the storage chamber and the air sampler. Each PM10 sample was collected for 5 hours with a flow rate of 5.0 L/min from the storage chamber using a minivolume air sampler (Airmetrics, USA). The samples were collected on quartz fiber filters (Ø 47 mm) from QM-A Whatman (Maidstone, UK). The filters were pre- and post-weighed by microbalance (MX5, Mettler Toledo, Switzerland). After PM10 collection, the filters were kept in a plate covered with aluminium foil, and then transferred into a desicator for 24 hours before being weighed and stored in a freezer until analysis. The chamber was cleaned every time before the next burning experiment. Blank samples were collected every after three samples. PM10 samples collected from biomass burning in the chamber were performed after background sampling (blank sample).

2.4.3 Preparation of biomass samples for burning experiment

Before the burning experiment, the biomass was homogenized, cut and weighed on a 2-digit balance. About 20 g of rice straw, 10 g of maize residue and 10 g leaf litter were used in each burning.

Table 2.4 General information of biomass burning in the combustion chamber

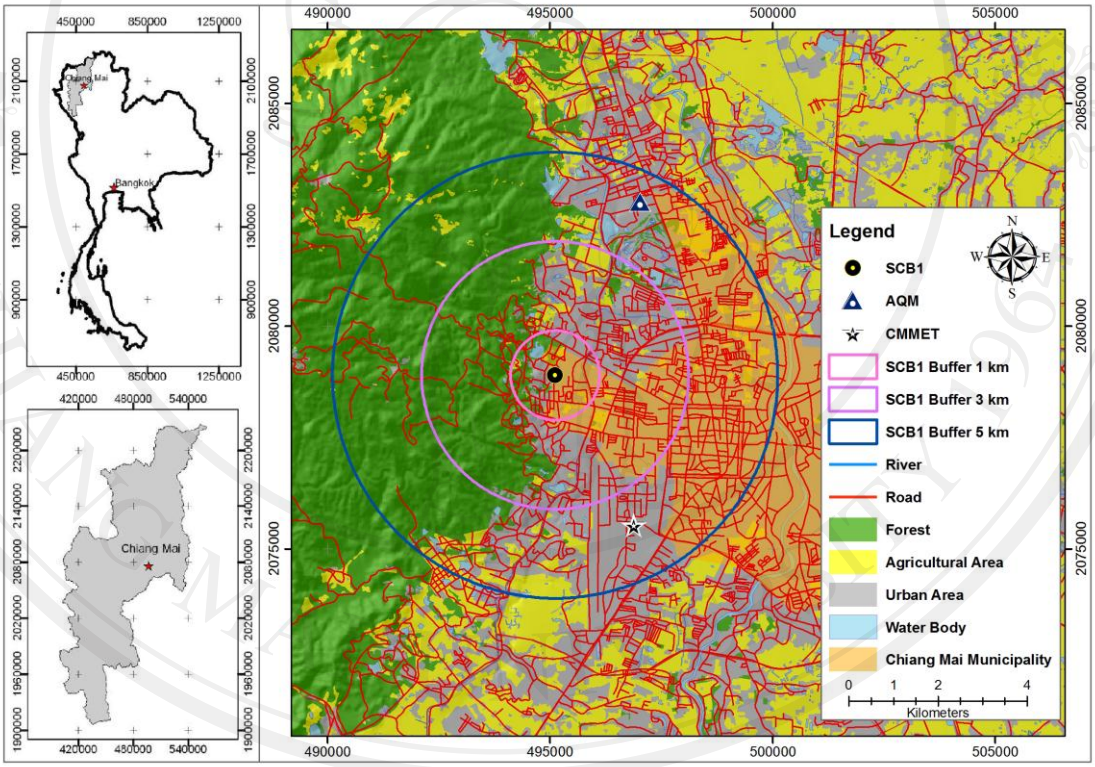
Biomass residue	Weight (g)	Number of samples	
		Blank sample	PM10 samples from biomass burning
Rice straw	20	3	9
Maize residue	10	3	9
Leaf litter	10	3	9

Figure 2.7 Biomass samples: rice straw (RS), maize residues (M) and leaf litter (L)

2.5 Sampling of PM10 in Ambient air

2.5.1 PM10 sampling site

The sampling site was located in Chiang Mai Province, Thailand. PM10 samples were collected at the roof top of the nine-storey building (SCBI), Chiang Mai University, at a height of 373 meters above the mean sea level (latitude 18^{o} 48' 5.13" N and longitude 98^{o} 57' 12.16" E) (Figure 2.2). This sampling site was selected for PM10 monitoring to avoid effects from traffic emission.



2.5.2 Sampling duration

PM10 samples were collected from ambient air using a Minivol air sampler (Airmetrics, USA) for 24 hours with a flow rate of 5 L/min (Figure 2.3). The sampling was carried out in the dry and wet seasons of 2010 and the dry season of 2011. The air sampler was placed about 1.5 m above ground at the site. The filters

were kept in a desiccator at least 24 hrs, and then pre-weighed and stored in plastic Petri dishes.

Eleven samples were collected in April 2010, representing the dry season, while 42 samples were collected during August-October 2010, representing wet season. The last 41 samples were collected from January-March 2011, representing another dry season. PM10 samples were collected on quartz fiber filters (Ø 47 mm) from QM-A Whatman (Maidstone, Kent, UK). The filters were pre-weighed using a microbalance. After PM10 collection, the filters were kept in an aluminium foil plate, and then transferred into a desicator for 24 hours before being re-weighed and stored in a freezer until analysis.

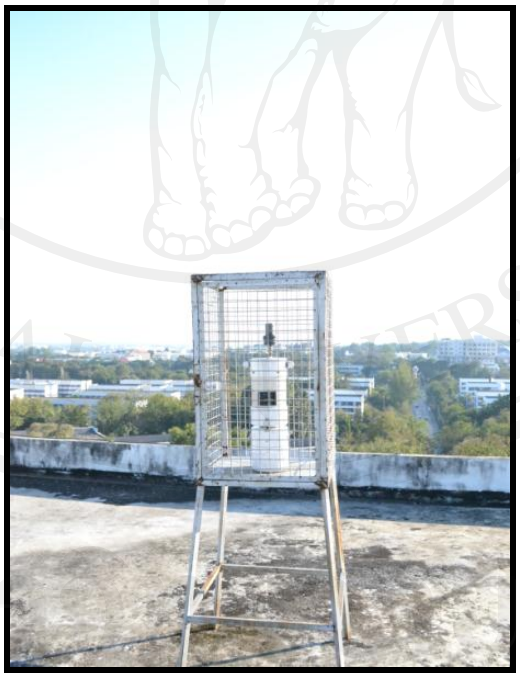


Figure 2.9 PM10 sampling by a Minivol air sampler at CMU

2.6 Preparation of PAH and internal standard solution

2.6.1 Preparation of mixed 16 PAHs standard solution

Sixteen polycyclic aromatic hydrocarbons (16-PAHs), including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BPER), were used as standards for analysis. A 1000 µg/ml mixed 16 PAHs stock solution was diluted with acetonitrile to a concentration of 10 µg/ml as an intermediate standard solution. Working solutions of 16 PAHs in a range of 0.001 – 1.0 µg/ml were prepared from intermediate and used for calibration curves.

2.6.2 Preparation of mixed internal standards

Five mg of each internal standard (D_{10}-acenaphthene and D_{12}-perylene) were weighed using a 4-decimal balance. They were added into a 100 mL volumetric flask, followed by acetonitrile to result in a concentration of 50 µg/ml. A 10 mL of 50 µg/mL internal standard solution was pipetted, and then adjusted with acetonitrile to 100 mL in volumetric flask to obtain a concentration of 5 µg/ml. The 5 µg/ml 0.2 ml of mixed solution was spiked into the mixed PAHs standard solutions and the extracted samples to achieve 0.5 µg/ml of the internal standard in 2 ml final volume.

2.7 Optimization of ultrasonic extraction

The quartz fiber filter spiked with mixed 0.5 ml of 0.2 µg/ml 16-PAHs standard was used for validation of extraction method. They were extracted with acetonitrile by using an ultrasonicator (Elma, Germany) under varied conditions; A) 25 ml acetonitrile, 30 minutes, B) 35 ml acetonitrile, 30 minutes and C) 25 ml acetonitrile, 40 minutes. All conditions were temperature controled (~10ºC) using ice. The extracted solutions were filtered through 45 µm nylon filter prior to evaporating be means of vacuum until it was nearly dried. The 0.2 ml of 5 µg/ml internal standards was spiked to the extracted solution and the volume was adjusted to 2 ml by acetonitrile. The aliquate was then analysed by GC-MS using the HP5 MS column (Agilent Technologies, U.S.A.). The best condition of the extraction was selected for PM10 sample extraction.

2.8 PM10 sample extraction and analysis

The quartz filters containing PM10 were extracted in 25 ml acetonitrile using an ultrasonicator (Elma, Germany) for 30 minutes under controlled temperature (~10ºC). The extracted solution was filtered through a 45 µm nylon filter prior to being evaporated by vacuum rotary until it was nearly dried. The mixture of internal standards was spiked into the extracted solution and the volume was adjusted to 2 ml with acetonitrile.

2.9 Optimization of GC-MS condition

The GC-MS condition for 16-PAHs analysis was optimized in terms of temperature program, injection mode and injection parameter. MS was used as the GC detector to achieve satisfactory separation and detection. A solution of 0.5 µg/ml of 16 PAHs solution mixed with 5 µg/ml of internal standard was injected into the GC-MS in the splitless mode. The optimum GC-MS condition is shown in Table 2.5.

Table 2.5 GC-MS conditions for 16-PAHs analysis

GC Parameter	Condition
GC	
Column	HP-5MS capillary column
Carrier Gas	Helium, Flow-rate 1 ml/min
Injection Mode	Splitless, 0.7 min
Injection Temperature	275 ºC
Temperature Program	
Initial Column Temperature	70 ºC
Initial Hold Time	2 min
Temperature Program	8 ºC/min to 280ºC and held 10 min
Post run Temperature	290ºC
Post run Hold Time	10 min
MS	
Detection Mode	SIM mode
Transfer Line Temperature	290ºC
Source Temperature	230ºC
Eletron Energy	70 eV
Ionization Mode	EI

Chromatographic parameters in terms of retention time and peak area of PAHs compounds were integrated using ChemStation software. Quantitaion was based on the ratio of the peak area of PAHs standard to deuterated internal standard. Moreover, the MS was operated in the SIM mode and was set at 5 minutes solvent delay. Characteristic ions of target PAHs were used for identification purpose (Table 2.6).

Table 2.6 Characteristic ions for PAHs

PAHs	Abbreviation	Molecular weight	Primary Ion	Secondary Ions	Retention Time (minutes)
Napthalene	NAP	128.17	128	129, 127	9.11
Acenaphthylene	ACY	152.19	152	151, 153	13.64
D_{10}-Acenaphthene*	D_{10}-ACE	154.21	164	162, 165	14.02
Acenaphthene	ACE	166.22	154	153, 152	14.18
Fluorene	FLU	178.23	166	165, 167	15.66
Phenanthrene	PHE	178.23	178	179, 176	18.44
Anthracene	ANT	202.25	178	179, 176	18.57
Fluoranthene	FLA	202.25	202	101, 203	21.97
Pyrene	PYR	228.29	202	101, 203	22.59
Benzo[a]anthracene	BaA	228.29	228	229, 226	26.19
Chrysene	CHR	252.31	228	229, 226	26.31
Benzo[b]fluoranthene	BbF	252.31	252	253, 126	29.67
Benzo[k]fluoranthene	BkF	252.31	252	253, 126	29.76
Benzo[a]pyrene	BaP	276.33	252	253, 126	30.95
D_{12}-Perylene*	D_{12}-PER	278.35	264	260, 213	31.21
Indeno[1,2,3-c,d]pyrene	IND	276.33	276	138, 227	37.35
Dibenzo[a,h]anthracene	DbA	128.17	278	139, 279	37.72
Benzo[g,h,i]perylene	BPER	152.19	276	138, 277	39.16

*Internal standards

The first IS (D_{10}-ACE) was used for NAP, ACY, ACE, FLU, PHE, ANT, FLA, and PYR, while the second IS (D_{12}-PER) was used for BaA, CHR, BbF, BkF, BaP, IND, DbA, and BPER. Two IS were used according to temperature programming.

2.10 Quality control of PAHs analysis

2.10.1 Use of standard reference materials (SRM)

Standard reference material (SRM; Urban Dust 1649b, U.S.A.) provided by the National Institute of Standards and Technology (NIST) was used for conditioning of quality control for PAHs analysis. The composition of PAHs in the SRM is shown in Table 2.7. Approximately 60 mg of the SRM was weighed and added onto a quartz fiber filter placed in a beaker. Three replications were performed in each batch. They were extracted and analyzed as described in Sections 2.7 and 2.8.

Table 2.7 Certified values of SRM urban dust NIST 1649b

PAHs	Measured Value (µg/kg)
Naphthalene	1.120 ± 0.420
Acenaphthylene	0.184 ± 0.026
Acenaphthene	0.192 ± 0.036
Fluorene	0.941 ± 0.047
Phenanthrene	0.403 ± 0.002
Anthracene	0.222 ± 0.016
Fluoranthene	6.140 ± 0.120
Pyrene	4.780 ± 0.029
Benzo(a)anthracene	2.092 ± 0.048
Chrysene	3.008 ± 0.044
Benzo(b)fluoranthene	5.990 ± 0.200
Benzo(k)fluoranthene	1.748± 0.084
Benzo(a)pyrene	2.470 ± 0.170
Indeno(1,2,3-cd)pyrene	2.960 ± 0.170
Dibenzo(a,h)anthracene	0.290 ± 0.004
Benzo(g,h,i)perylene	3.937 ± 0.052

2.10.2 Use of spiking method

A 600 µL of 2 µg/mL of the mixed PAHs standard solution was spiked onto a quartz fiber filter. It was left for ~ 30 minutes until it was nearly dried. Three replications were prepared. They were extracted and analyzed for PAHs using the same conditions as descibed in section 2.7. The recovery was calculated using Equation 2.1.

$$\% \text{ Recovery} = \frac{MV}{SV} \times 100 \qquad \text{Eq. 2.1}$$

Where MV is a measured value (mg/kg)

SV is a spiked value (mg/kg)

2.10.3 Precision of analysis method

a) Repeatability

Repeatability of GC-MS system was determined with 7 repeating measurements of a 0.5 µg/mL mixed standard solution by GC-MS under the optimum condition.

b) Reproducibility

Reproducibility of GC-MS system was determined by repeating measurements of a 0.5 µg/mL mixed standard solution by GC-MS under the optimum condition for 7 continuous weeks.

The results of the repeatability and reproducibility were estimated by relative standard deviation (RSD) as calculated by using Equation 2.2.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 2.2}$$

Where % RSD is a percentage relative standard deviation

SD is a standard deviation

$\bar{x}$ is an average value

2.11 Detection limit of GC-MS for 16-PAHs analysis

Detection limit is commonly understood to be the smallest concentration that can be measured with a particular technique. The detection limit was checked by injecting 7 times of the lowest concentration (0.001 µg/mL) of mixed 16-PAHs into the GC-MS system under the optimum condition. The detection limit was obtained the detector output at from the detector 3 times of the standard deviation (Taylor et al., 1987).

2.12 PM10 and PAHs source determination

2.12.1 Data analysis of ambient PM10 and PAHs

a) Pearson correlation

Pearson correlation (*r*) was implemented to identify the relationships between the total PAHs (tPAHs), carcinogenic PAHs (cPAHs), non-carcinogenic PAHs (ncPAHs) (see Table 1.1), and PM10. Moreover, the correlation between PM10 concentrations and the number of hotspots found in the northern part of Thailand, provided by the Fire Information for Resource Management System (FIRMS), was investigated.

b) Principal component analysis (PCA)

PCA was used to determine the possible sources of PAHs in each season. The PCA was performed with varimax rotation and the principal components (factor), having eigen values higher than 1 were used for identification of pollutant sources. The maximum percentages of total variance were used as the factors. Loading determined the most representative PAHs compound for each factor and generally a value of > 0.5 was selected (Ravindra et al., 2008).

c) Diagnostic ratios (DRs)

DRs of PAHs have recently come into common use as a tool for identifying and assessing pollutant emission sources. PAHs are always emitted as a mixture, and the relative molecular concentration ratios are considered (often only as an assumption) to be characteristic of a given emission source (Tobiszewski and Namiesnik 2012). Most DRs involve pairs of PAHs with the same molar mass and similar physicochemical properties (Mackay et al., 2006), so they ought to undergo similar environmental fate processes. Several DRs from previous studies have been used to estimate different sources. For examples, the ratio value of ANT/(ANT+PHE) less than 0.1 was recognized as petrogenic sources, while the value above 0.1 was classified as pyrogenic source (Pies et al., 2008). The ratio of BaP/(BeP+BaP) can be identified as fresh particles (~0.5) and photolysis of particles (<0.5) (Oliveira et al., 2011). The ratio of FLU/(FLU+PYR) has been used for petrol emissions (<0.5) and diesel emissions (>0.5) (Ravindra et al., 2008b). FLA/(FLA+PYR), B(a)A/(B(a)A+CHR) and IND/ (IND+BPER) were the conventional DRs to characterize the sources of PAHs in this study due to a number of references providing such ratios.

d) Backward trajectories

Backward trajectories arriving at the receptor (sampling site) were calculated using the hybrid single particle langrangian integrated trajectory (HYSPLIT) model. The 24-hours backward trajectories are available online at http://ready.arl.noaa.gov/HYSPLIT.php. Air mass trajectories for each individual day were clustered to determine the main trajectory direction arriving at the receptor using hierarchical clustering method.

e) The inhalation cancer risk (ICR) assessment

The inhalation cancer risk (ICR) was used for estimation of cancer risk from exposure to PAHs (Eq 2.3 and 2.4). The following equations were used (Wu et al., 2006; USEPA, 2005):

$$ICR = [\sum_i C_i \times TEF_i] \times IUR_{BaP} \quad \text{Eq 2.3}$$

$$ICR = TEQ \times IUR_{BaP} \quad \text{Eq 2.4}$$

Where C_i is the concentration of an individual PAH and TEF_i is the toxic equivalent factors. The development of the TEFs for PAHs can be used to characterize the carcinogenic properties of PAHs. IUR_{BaP} is the inhalation unit risk defined as the risk of cancer from a lifetime (70 years) in halation of unit mass of benzo[a]pyrene ($m^3/\mu g$). The toxicity equivalent concentration (TEQ) values were used from average values in terms of Nisbet and Lagoy (1992), US EPA (1993), and Cecinato (1997). The California Environmental Protection Agency (CEPA, 2004) and the World Health Organization (WHO, 2000) have recommended a unit risk of cancer value for benzo[a]pyrene as: $IUR_{BaP} = 1.1 \times 10^{-6}$ and 8.7×10^{-5} $(ng/m^3)^{-1}$, respectively

2.12.2 Data analysis of PM10 and PAHs from biomass burning in the chamber

a) Statistical analysis

In order to identify the relationships between the PAHs and PM10, Pearson correlation (*r*) was implemented. Diagnostic ratios (DRs) were used to determine the possible sources of PAHs in each biomass.

b) Emission factor and emission rate of pollutants from biomass burning

An emission factor (EF) is a representative value that relates the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (US EPA, 2011). EFs are calculated based on the measurements of flow rate and pollutant mass concentration using Equation 2.5 (Kim Oanh et al., 2010).

$$EF = \frac{(Conc.\ (ngm^{-3}) \times Flow\ rate\ (m^3h^{-1}) \times Sampling\ time\ (h))}{biomass\ burned\ (kg)} \quad \text{Eq 2.5}$$

EF of PM10 and PAHs were used for estimation of emission rate (ER) based on the area of burning, followed by Equation 2.6.

$$ER = EF \times Area\ of\ burning\ (km^2) \times biomass\ (kg/km^2) \quad \text{Eq 2.6}$$