CHAPTER 3

RESULTS AND DISCUSSION

3.1 Method validation for PAHs analysis by GC-MS

The results of method validation analysis are given and discussed in the following sections.

3.1.1 Accuracy of PAHs analysis by GC-MS

Three replications of spiked PAHs standard and 3 replications of the dust NIST 1649b standard reference materials (SRM) urban were optimized for the extraction condition based on recovery studies.

a) Spiking method

0.5 ml solution of 0.2 µg/ml (final concentration 0.05 µg/ml) of mixed PAHs standard solution was spiked onto a quartz fiber filter (n=3) and extracted using the following conditions: A) 25 ml acetonitrile, 30 minutes for ultrasonication, B) 35 ml acetonitrile, 30 minutes for ultrasonication and C) 25 ml acetonitrile, 40 minutes ultrasonication. Recoveries of 16-PAHs from method A, B and C were 88-132 %, 82-134% and 73-135%, respectively (Figure 3.1).The results showed that methods A and B provided good recoveries. From one way ANOVA, there was no significant difference (p > 0.05) between methods A and B, and they provided significantly better recoveries than method C (p < 0.05). Therefore, method A was selected for extraction of the SRM and PM10 samples due to less solvent volume. The recoveries of 16 PAHs in the spiked unknown were 77 – 106 % (0.05)



 $\mu g/ml,$ low concentrations) and 83-104 % (0.5 $\mu g/ml,$ high concentrations) which

Figure 3.1 Percent recoveries of 16-PAHs from different extraction methods.

A: 25 ml acetonitrile, 30 min ultrasonication

B: 35 ml acetonitrile, 30 min ultrasonication

C: 25 ml acetonitrile, 40 min ultrasonication

b) Analysis of the Urban dust NIST 1649b SRM

The SRM is an atmospheric particulate material collected in an urban area. It was extracted based on condition A and analysed by GC-MS. The recoveries of 16 PAHs in the SRM were 37-141 % which were in ranges of the EPA quality control criteria (Table 3.1), except naphthalene (14%) and anthracene (150%).

were obtained from 3 replications of extraction.

	SRM 16	549b	Spiking	Method
Compounds	Certified value	% Recovery	% Recovery	% Recovery
	(µg/kg)	(n=3)	0.05 µg/ml (n=3)	0.5 µg/ml (n=3)
NAP	1,120	14	106	90
ACY	184	52	103	90
ACE	192	57	91	91
FLU	222	80	90	99
PHE	3,941	69	99	97
ANT	403	150	91	97
FLA	6,140	81	101	104
PYR	4,784	87	99	100
BaA	2,092	83	91	89
CHR	3,008	73	103	80
BbF	5,990	57	88	92
BkF	1,748	140	93	83
BaP	2,470	111	77	103
IND	2,960	111	95	92
DbA	290	38	95	85
BPER	3,937	89	90	91

Table 3.1 Percent recoveries of 16- PAHs from extraction of the SRM urban dust(NIST 1649b) and spiking method

3.1.2 Precision

a) Repeatability

The repeatability of 16-PAHs analyzed by GC-MS was determined with 7 injections of the 0.01 μ g/mL mixed PAHs standard. The precision was estimated by % RSD as shown in Table 3.2. It was found that %RSD of 16-PAHs ranged from 1.3 (BaP) to 14 % (BaA).

b) Reproducibility

The reproducibility of 16-PAHs analyzed by GC-MS was determined by injections of a 0.01 μ g/mL mixed PAHs standard solution for 7 continuous weeks. The precision was estimated by % RSD as shown in Table 3.3. It was found that %RSD of 16-PAHs ranged from 4.6 (NAP) to 32% (BbF).

 Table 3.2 Repeatability of standard preparation based on GC-MS analysis for PAHs

			G						-	a la contra
		6	Concen	itration (p	ig/mL)					
PAHs	1	2	3	4	5	6	7	Average	SD	%RSD
NAP	0.010	0.009	0.010	0.011	0.010	0.011	0.011	0.010	0.0005	4.7
ACY	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.0003	2.9
ACE	0.010	0.010	0.011	0.010	0.011	0.011	0.011	0.011	0.0004	3.4
FLU	0.011	0.011	0.010	0.010	0.010	0.010	0.011	0.011	0.0003	3.1
PHE	0.016	0.018	0.019	0.019	0.017	0.018	0.019	0.018	0.0014	7.9
ANT	0.011	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.0006	6.2
FLA	0.014	0.014	0.013	0.013	0.012	0.012	0.011	0.013	0.0011	9.0
PYR	0.015	0.015	0.014	0.013	0.012	0.012	0.012	0.013	0.0012	9.0
BaA	0.014	0.012	0.011	0.011	0.010	0.009	0.010	0.011	0.0016	14
CHR	0.022	0.021	0.020	0.020	0.019	0.019	0.019	0.020	0.0012	6.0
BbF	0.016	0.014	0.014	0.012	0.012	0.013	0.013	0.014	0.0015	10
BkF	0.012	0.013	0.013	0.010	0.013	0.011	0.010	0.012	0.0014	12
BaP	0.014	0.014	0.014	0.014	0.014	0.014	0.015	0.014	0.0002	1.3
IND	0.010	0.011	0.012	0.012	0.012	0.012	0.012	0.011	0.0008	7.2
DbA	0.011	0.011	0.012	0.013	0.013	0.012	0.013	0.012	0.0009	7.1
BPER	0.012	0.012	0.013	0.013	0.014	0.013	0.014	0.013	0.0009	6.6

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 Table 3.3 Reproducibility of standard preparation based on GC-MS analysis for

 PAHs

			Concen	tration (µ	ug/mL)			6)		
PAHs	1	2	3	4	5	6	7	Average	SD	%RSD
NAP	0.010	0.010	0.009	0.010	0.010	0.010	0.010	0.010	0.0005	4.6
ACY	0.013	0.010	0.012	0.013	0.009	0.007	0.013	0.011	0.0025	23
ACE	0.010	0.011	0.010	0.010	0.014	0.010	0.010	0.011	0.0015	13
FLU	0.010	0.010	0.010	0.010	0.010	0.006	0.010	0.009	0.0015	15
PHE	0.009	0.009	0.009	0.010	0.011	0.006	0.009	0.009	0.0015	17
ANT	0.010	0.009	0.009	0.010	0.013	0.005	0.008	0.009	0.0024	26
FLA	0.009	0.010	0.009	0.010	0.009	0.005	0.010	0.009	0.0017	19
PYR	0.009	0.012	0.009	0.010	0.009	0.006	0.011	0.009	0.0019	20
BaA	0.010	0.009	0.011	0.010	0.011	0.009	0.010	0.010	0.0007	7.2
CHR	0.009	0.009	0.009	0.010	0.012	0.007	0.010	0.009	0.0014	15
BbF	0.010	0.009	0.008	0.010	0.018	0.015	0.009	0.011	0.0036	32
BkF	0.009	0.008	0.011	0.010	0.011	0.012	0.010	0.010	0.0014	13
BaP	0.010	0.009	0.008	0.010	0.010	0.011	0.009	0.010	0.0012	12
IND	0.010	0.010	0.011	0.010	0.012	0.017	0.010	0.011	0.0026	22
DbA	0.011	0.009	0.014	0.010	0.015	0.017	0.011	0.012	0.0029	23
BPER	0.010	0.010	0.010	0.010	0.010	0.013	0.010	0.010	0.0012	11

3.1.3 Instrument detection limit

The instrument detection limits (IDL= 3SD) and limit of quantification (LOQ= 10SD) of GC-MS were calculated by using the smallest measure that can be detected with reasonable certainty for a given analytical procedure. The IDL of GC-MS was determined by 7 injections of a 0.001 μ g/mL mixed PAHs standard. The IDL of 16-PAHs ranged from 0.09 – 2.56 ng/ml or 0.03 – 0.72 ng/m³ while LOQ ranged from 0.30 – 8.53 ng/ml or 0.08 – 2.40 ng/m³, as are shown in Table 3.4.

0	Instrument detecti	on limit (IDL)	Limit of quant	ification (LOQ)
PAHs	ng/mL	ng/m ³ *	ng/mL	ng/m ³ *
NAP	0.15	0.04	0.49	0.14
ACY	0.09	0.03	0.30	0.08
ACE	0.94	0.26	3.12	0.88
FLU	0.09	0.03	0.30	0.09
PHE	0.18	0.05	0.60	0.17
ANT	0.79	0.22	2.62	0.74
FLA	0.3	0.08	0.99	0.28
PYR	0.3	0.08	0.99	0.28
BaA	0.29	0.08	0.98	0.27
CHR	0.34	0.09	1.12	0.32
BbF	1.5	0.42	5.02	1.41
BkF	1.25	0.35	4.17	1.17
BaP	0.55	0.15	1.83	0.52
IND	1.6	0.45	5.34	1.50
DbA	2.56	0.72	8.53	2.40
BPER	2.33	0.66	7.76	2.19

Table 3.4 Instrument detection limit of GC-MS

* The IDL of PAHs in air $(ng/m^3) =$ [(IDL in solution (ng/mL)) x (final volume of solution (2mL))] / (average volume of air (7.1 m^3))

3.1.4 Standard calibration curve

The individual calibration curve was constructed based on chromatographic peak areas obtained from 8 concentrations of 16-PAHs standard (0.001, 0.002, 0.004, 0.008, 0.01 0.02, 0.04 and 0.08 μ g/mL). Chromatograms of 0.08 μ g/mL of 16-PAHs and internal standards are shown in Figure 3.2. Internal calibration curve was constructed by using ratio of peak area between standard and internal standard (Std./IS) in the y axis and PAH concentrations in the x axis. Linear equations and values of variation coefficient (R²) were obtained (Table 3.5 and Figure 3.3). Values of R² ranged from 0.9986 to 0.9994.

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Figure 3.2 Chromatograms obtained from GC-MS (A) 0.08 µg/ml of 16-PAHs standards (B) PM10 sample from leaf litter burning in chamber and (C) PM10 sample from ambient air. The internal standards are marked with asterisk. Peaks: 1=NAP, 2=ACY, 3= D₁₀-ACE*, 4=ACE, 5=FLU, 6=PHE, 7=ANT, 8=FLA, 9=PYR, 10=BaA, 11=CHR, 12=BbF, 13=BkF, 14=BaP, 15= D12-PER*, 16=IND, 17=DBA and 18=BPER.

 PAHs	Linear equation	Variation coefficient (R ²)
NAP	Y= 2.4891X + 0.0012	0.9995
ACY	Y = 2.5714X + 0.0005	0.9997
ACE	Y = 3.3094X + 0.0021	0.9993
FLU	Y = 2.4349X + 0.0002	0.9993
PHE	Y=1.9210X - 0.0011	0.9996
ANT	Y=1.3633X - 0.0009	0.9993
FLA	Y=1.1250X - 0.0006	0.9998
PYR	Y=1.3491X - 0.0002	0.9998
BaA	Y= 3.2015X - 0.0007	0.9985
CHR	Y=4.3109X - 0.0027	0.9995
BbF	Y= 2.4777X + 0.0003	0.9989
BkF	Y=2.3634X - 0.0005	0.9982
BaP	Y = 2.0623X + 0.0002	0.9988
IND	Y = 1.0312X + 0.0002	0.9990
DbA	Y = 0.2245X + 0.0007	0.9962
BPER	Y = 1.3282X + 0.0002	0 9995

Table 3.5 Calibration equations and variation coefficient of PAHs

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Figure 3.3 Standard calibration curves of 16-PAHs



Figure 3.3 Standard calibration curves of 16-PAHs (continuted)

3.2 Composition of biomass samples

3.2.1 Moisture content

Moisture contents of the three biomass types are listed in Table 3.6. The average moisture content of maize residues (11.6%) was higher than that of rice straw (9.2%) and leaf litter (6.5%).

Biomass types	Code	Moistur	e conten	t (%)
Biolillass types	Code	Mean	±	SD
Rice straw		3		
	RS-MR	9.82	±	0.72
	RS-DK	8.48	±	0.69
	RS-CD	10.30	±	0.32
	Average	9.24	±	0.98
Maize residues		/ 1 /		
	M-MR	13.25	±	3.49
	M-CD	10.87	±	4.43
	M-MC	10.78	±	1.28
	Average	11.63	±	3.42
Leaf litter			Ċ	
	M-MR	6.38		0.39
	M-CD	5.51	±	0.65
	M-MC	7.63	±	0.75
	Average	6.51	±	1.09

Table 3.6 Moisture content of biomass residues

3.2.2 C, H and N composition

The composition of biomass in terms of C, H and N content was not much different among different biomass sources (Table 3.7). The C content of the leaf litter (44.4%) was significantly (p < 0.05) higher than that of rice straw (36.2%) and maize residue (40.5%). However, there was no significant difference (p > 0.05) between the C from rice straw and maize residue. H contents of those three types of biomass were almost the same (5.2 - 5.8 %). The N content of maize residues was significantly higher than that of rice straw and leaf litter. This is probably due to N fertilizer use in crop planting.

	بينين	Conc	centration (%) (r	n = 3)
Biomass Type	Code	C	Н	Ν
Rice straw	RS-MR	36.60 ± 0.26	5.18 ± 0.17	0.27 ± 0.02
	RS-DK	37.15 ± 0.29	5.04 ± 0.12	0.32 ± 0.08
	RS-CD	34.82 ± 0.10	5.29 ± 0.13	1.04 ± 0.07
	Average	36.19 ± 1.07	5.17 ± 0.16	0.55 ± 0.38
Maize residues	M-MR	39.20 ± 0.35	5.03 ± 0.08	1.98 ± 0.15
	M-CD	42.79 ± 0.17	5.97 ± 0.08	1.00 ± 0.18
	M-MC	34.82 ± 0.10	6.01 ± 0.18	1.25 ± 0.09
	Average	40.51 ± 1.73	5.67 ± 0.49	1.41 ± 0.46
Leaf litter	L-MR	46.00 ± 0.23	5.76 ± 0.17	0.55 ± 0.06
	L-DK	48.62 ± 0.16	6.05 ± 0.05	0.65 ± 0.16
	L-CD	44.68 ± 0.34	5.72 ± 0.13	0.21 ± 0.03
nŝiik	Average	46.43 ± 1.75	5.84 ± 0.19	0.47 0.22

Table 3.7 C, H, N content of biomass residues

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3.3 PM10 and PAHs emitted from biomass burning in the chamber

The PM10 samples were collected from burning of various types of biomass in the combustion chamber, as shown in Figure 3.4.



Figure 3.4 PM10 samples on quartz fiber filter from burning of (a) rice straw, (b) maize residues and (c) leaf litter in the combustion chamber

3.3.1 PM10 and PM10-bound PAHs from biomass burning

PM10 concentrations emitted from burning of various types of biomass are shown in Table 3.8. The PM10-bound PAHs are presented in Table 3.9 in the unit of μ g/g PM10.

The average amounts of PM10 samples emitted from biomass burning in the chamber in descending order were leaf litter (14.6 mg) > rice straw (11.8 mg) > maize residues (7.7 mg). Concentrations of 16-PAHs (μ g/gPM10) were 1.07 (rice straw) > 0.79 (maize residues) > 0.71 (leaf litter). Concentrations of BbF, CHR and FLA were relatively high in burning of all types of biomass. However, BbF was the PAH with the highest concentrations found in PM10 emitted from burning of rice straw (0.15 μ g/gPM10) and maize residue (0.09 μ g/gPM10). For burning of leaf litter, FLA was found to have the highest concentration (0.09 μ g/gPM10).

Biomass				ntration	n			
type			mg		n	ng/m ³		
		mean	±	SD	mean	±	SD	
Rice straw	RS-MR (n=6)	14.4	±	2.7	9.4	ŧ	1.8	
	RS-DK (n=6)	11.2	±	4.9	7.3	±	3.2	
	RS-CD (n=6)	10.0	±	4.5	6.5	±	2.9	
	Average	11.8	±	4.3	7.8	±	2.9	
Maized residues	M-MR (n=6)	6.3	±	1.8	4.2	±	1.2	
	M-CD (n=6)	10.0	±	3.4	6.6	±	2.3	
	M-MC(n=6)	6.9	±	1.7	4.5	±	1.1	
	Average	7.7	±	2.9	5.1	±	1.9	
Leaf litter	L-MR (n=6)	14.0	±	4.6	9.2	±	3.0	
	L-DK (n=6)	17.8	±	6.5	11.7	±	4.2	
	L-CD (n=6)	11.9	3	2.9	7.8	±	1.9	
	Average	14.6	±	5.2	9.6	±	3.4	

Table 3.8 PM10 emitted from biomass burning in the combustion chamber

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Table 3.9 PM10-bound PAHs from biomass burning in the combustion chamber

ND = not detected

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3.3.2 Correlation of PM10 and PAHs

a) Correlations of PM10 and PM10-bound PAHs

Correlations between PM10 and individual PAHs were examined using the Pearson correlations, as shown in Tables 3.10 to 3.12. The strong correlations were marked with bold values.

Rice straw

Strong correlation between PM10 and BaA (r=0.843) and CHR (r=0.893) (p<0.01) could be observed. Strong correlation was also found between ACY and 4 -ring PAHs. Strong correlations among individual PAHs in the same group of molecular structure such as 4-ring-PAHs (PHE and ANT (r=0.905), PHE and FLA (r=0.929), ANT and FLA (r=0.865), FLA and PYR (r=0.998), BaA and PYR (r=0.926)) as well as 5-ring PAHs were found.

Maize residues

The significantly strong correlation was found between concentrations of PM10 & ACY (r=0.834) and PM10 & CHR (r=0.851) (p<0.01). Strong correlation was also found between FLA and PYR (r=0.989). The correlations of 4-ring PAHs were strongly significantly correlated with 5-ring PAHs such as BaA and BbF (r=0.951), BaA and BkF (r=0.952), BaA and BaP (r=0.910), CHR and BbF (r=0.978), CHR and BkF (r=0.974) and CHR and BaP (r=0.956). BPER was also strongly significantly correlated with 5- ring PAHs that was same rice straw burning.

Leaf litter

There was no correlation between PM10 and PAHs. However, the significantly strong correlation was found between concentrations of ACY and PHE(r=0.934) (p<0.01). The 3-ring PAHs (PHE and ANT) were highly correlated (r>0.900) with 4- ring (FLA, PYR) (*p*<0.01). The highest correlation was found between FLA and PYR (r= 0.995). Both FLA and PYR were used for calculation of diagnostic ratio for identification of source of biomass burning (Jenkis et al., 1993; Yunker et al., 2002; Tobiszewski and Namiesnik 2012; Orecchio et al., 2009; Oros et al., 2006; Dvorská et al., 2011; Wong 2009). BPER was also strongly correlated with 5- ring PAHs, as found in rice straw and maize residues burning.

ลิ<mark>ปสิทธิ์มหาวิทยาลัยเชียงใหม่</mark> Copyright[©] by Chiang Mai University All rights reserved Table 3.10 Correlation coefficients of PM10 and PM10-bound PAHs obtained from rice straw burning

	NAP	ACY	ACE	FLU	рне	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IND	DbA	BPER	PM10
NAP	1.000	-		0/					\mathbf{S}								
ACY	-0.293	1.000															
ACE	-0.293	-0.143	1.000														
FLU	-0.557	0.350	0.163	1.000													
PHE	-0.268	0.993**	-0.109	0.363	1.000												
ANT	0.087	0.887**	-0.042	0.241	0.905**	1.000											
FLA	-0.397	0.920**	0.105	0.490	0.929**	0.865**	1.000										
PYR	-0.419	0.894**	0.134	0.522	0.902**	0.842**	0.998**	1.000									
BaA	-0.504	0.763*	-0.015	0.607	0.757*	0.661	0.908**	0.926**	1.000								
CHR	-0.495	0.519	0.041	0.680	0.515	0.455	0.749*	0.787*	0.943**	1.000							
BbF	-0.360	0.087	0.041	0.618	0.085	0.088	0.380	0.437	0.683	0.885**	1.000						
BkF	-0.309	0.085	0.007	0.621	0.079	0.103	0.364	0.421	0.662	0.867**	0.995**	1.000					
BaP	-0.311	0.172	0.078	0.530	0.169	0.209	0.474	0.528	0.746*	0.916**	0.979**	0.969**	1.000				
IND	-0.217	-0.154	0.064	0.502	-0.156	-0.094	0.151	0.214	0.478	0.739*	0.966**	0.969**	0.929**	1.000			
DbA	-0.465	0.136	0.136	0.200	0.086	0.011	0.296	0.337	0.410	0.505	0.572	0.586	0.565	0.552	1.000		
BPER	-0.250	-0.076	0.111	0.565	-0.072	-0.012	0.239	0.301	0.538	0.784*	0.978**	0.982**	0.945**	0.994**	0.567	1.000	
PM10	-0.550	0.509	0.370	0.711*	0.513	0.480	0.771*	0.812*	0.843**	0.893**	0.777*	0.769*	0.803*	0.647	0.647	0.720*	1.000

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

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

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Table 3.11 Correlation coefficients of PM10 and PM10-bound PAHs obtained from maize residues burning

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

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

.a Cannot be computed because at least one of the variables is constant.

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Table 3.12 Correlation coefficients of PM10 and PM10-bound PAHs obtained from leaf litter burning

	NAP	ACY	ACE	FLU	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IND	DbA	BPER	PM10
NAP	1.000			10													
ACY	0.683	1.000															
ACE	.a	.a	.a														
FLU	0.638	0.934**	.a	1.000													
PHE	0.613	0.666	.a 🗢	0.861*	- 1.000												
ANT	0.485	0.571	.a	0.784*	0.975**	1.000											
FLA	0.713	0.599	.a	0.779*	0.974**	0.948**	1.000										
PYR	0.665	0.535	.a	0.728	0.963**	0.957**	0.995**	1.000									
BaA	0.560	-0.009	.a	0.071	0.415	0.437	0.594	0.630	1.000								
CHR	0.575	0.036	.a	0.225	0.610	0.615	0.752	0.782*	0.923**	1.000							
BbF	0.222	-0.428	.a	-0.482	-0.205	-0.176	0.005	0.048	0.799*	0.577	1.000						
BkF	0.241	-0.382	.a	-0.455	-0.209	-0.181	-0.001	0.039	0.794*	0.553	0.997**	1.000					
BaP	0.502	-0.083	.a	-0.189	-0.028	-0.059	0.170	0.182	0.819*	0.580	0.924**	0.940**	1.000				
IND	0.279	-0.376	.a	-0.493	-0.308	-0.324	-0.099	-0.076	0.692	0.447	0.967**	0.969**	0.941**	1.000			
DbA	-0.395	-0.523	.a	-0.714	-0.739	-0.639	-0.648	-0.605	0.115	-0.201	0.580	0.611	0.437	0.573	1.000		
BPER	0.195	-0.472	.a	-0.582	-0.382	-0.405	-0.180	-0.158	0.600	0.374	0.930**	0.920**	0.875**	0.980**	0.528	1.000	
PM10	0.548	0.291	.a	0.155	0.231	0.290	0.376	0.399	0.638	0.434	0.530	0.562	0.607	0.480	0.301	0.361	1.000

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

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

.a Cannot be computed because at least one of the variables is constant.

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b) Correlations of PM10 and PAHs (tPAHs, ncPAHs, and cPAHs)

Correlations of PM10 and PAHs emitted from the burning of three types of biomass in the chamber were analyzed by Pearson correlation (Table 3.13).

Biomass types	11111	tPAHs	cPAHs	ncPAHs	PM10
Leaf litter					
	tPAHs	1.000			
	cPAHs	0.695**	1.000		
	ncPAHs	0.881**	0.272^{*}	1.000	
	PM10	0.598**	0.582^{**}	0.416*	1.000
Maize residue					
	tPAHs	1.000			
	cPAHs	0.966**	1.000		
	ncPAHs	0.846**	0.679**	1.000	
	PM10	0.601**	0.428^{*}	0.819**	1.000
Rice straw		1 20			
	tPAHs	1.000			
	cPAHs	0.903**	1.000		
	ncPAHs	0.921**	0.664**	1.000	
	PM10	0.935**	0.849**	0.857**	1.000

Table 3.13 Correlation between PAHs and PM10 from biomass burning

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

The concentrations of PM10 and PAHs (tPAHs, ncPAHs, and cPAHs) were moderately correlated (r = 0.598, r = 0.582 and r = 0.416, respectively) for leaf litter burning. Furthermore, tPAHs was strongly correlated (r = 0.881) with ncPAHs and also moderately correlated (r = 0.695) with cPAHs. Furthermore, ncPAHs was weakly correlated (r = 0.272) with cPAHs.

For maize residues, strong correlation was found between PM10 and ncPAHs (r=0.819) and fair correlations were found between PM10 and tPAHs (r = 0.601) and PM10 and cPAHs (r = 0.428). The very strong correlations were obtained between tPAHs and cPAHs (r = 0.966). Moreover, tPAHs and ncPAHs (r = 0.846) as well as cPAHs and ncPAHs (r = 0.679) were correlated with p < 0.01.

The correlation of PM10 and each group of PAHs (tPAHs, ncPAHs, and cPAHs) were strongly significantly correlated (r = 0.935, 0.849 and 0.857, respectively) for rice straw burning. Moreover, tPAHs was very highly correlated with cPAHs (r = 0.903) and ncPAHs (r = 0.921) while cPAHs was fairly correlated with ncPAHs (r = 0.664). The results revealed that burning of rice straw emitted PM10 containing higher amounts PAHs than those of leaf litter and maize residues.

3.3.3 Emission Factors of PM10 and PAHs from biomass burning

The samples of PM10 collected from the burning of biomass (leaf litter, maize residue and rice straw) in the chamber were analyzed for 16-PAHs. The maximum (max), minimum (min) average and standard deviation (SD) of emissions of PM10 and PAHs are shown in Table 3.14.

The maximum EF of PM10 from the burning in descending order were leaf litter (1.70 g/kg_{dry}) > rice straw (1.22 g/kg_{dry}) > maize residue (0.88 g/kg_{dry}). The EF of PM10 from burning leaf litter (1.22±0.29 g/kg_{dry}) was significantly (p < 0.05) higher than rice straw (0.89±0.25 g/kg_{dry}) and maize residue (0.59±0.13 g/kg_{dry}). However, there was no significant difference (p > 0.05) between the EF of PM10 from rice straw and maize residue. The EFs of PM10 from burning rice straw in this study was lower than other studies which were designed different chamber (Kadam *et al.*, 2000 (3.7 g/kg_{dry}); Kim Oanh *et al.*, 2011(9.4 g/kg_{dry})). Furthermore, The EFs from open burning of rice straw and maize were 6.5 and 13.0 g/kg_{dry} (Garivait, *et al.*, 2009).

Table 3.14 Emission factors of PM10 and PAHs from leaf litter, maize reside and rice

 straw burning in the chamber and TEQ of PAHs

Parameter		Leaf	litter				Ma	nize			Rice	straw	
	max	min	mean	SD		max	min	mean	SD	max	min	mean	SD
PM10			17		7								
(g/kg _{dry})	1.70	0.83	1.22	0.29		0.88	0.48	0.59	0.13	1.22	0.55	0.89	0.25
PAHs			-					2			_	-53	Öfe
(mg/kg _{dry})													
NAP	0.007	0.003	0.005	0.001		0.007	0.003	0.005	0.001	0.004	0.003	0.003	0.000
ACY	0.007	0.006	0.006	0.000		0.006	0.005	0.005	0.000	0.004	0.003	0.003	0.000
ACE	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.014	0.000	0.002	0.005
FLU	0.015	0.010	0.011	0.002		0.011	0.000	0.005	0.005	0.007	0.000	0.005	0.002
PHE	0.128	0.034	0.073	0.033		0.038	0.021	0.030	0.006	0.055	0.017	0.025	0.012
ANT	0.044	0.033	0.037	0.004		0.036	0.033	0.034	0.001	0.033	0.018	0.023	0.005
FLA	0.187	0.057	0.118	0.047		0.048	0.028	0.040	0.007	0.136	0.029	0.055	0.033
PYR	0.162	0.050	0.100	0.039		0.045	0.027	0.037	0.006	0.130	0.028	0.053	0.032
BaA	0.103	0.043	0.076	0.020		0.057	0.029	0.040	0.009	0.084	0.017	0.040	0.022
CHR	0.167	0.069	0.117	0.033		0.066	0.036	0.050	0.010	0.073	0.021	0.044	0.018
BbF	0.168	0.067	0.115	0.036		0.084	0.031	0.055	0.019	0.135	0.023	0.068	0.033
BkF	0.100	0.043	0.069	0.020		0.054	0.031	0.041	0.008	0.065	0.018	0.038	0.014
BaP	0.063	0.027	0.045	0.011		0.043	0.025	0.032	0.006	0.054	0.017	0.030	0.012
IND	0.074	0.035	0.055	0.014		0.050	0.031	0.041	0.007	0.055	0.022	0.034	0.010
DbA	0.037	0.031	0.034	0.002		0.037	0.000	0.022	0.016	0.022	0.000	0.017	0.007
BPER	0.062	0.028	0.047	0.013		0.039	0.024	0.032	0.006	0.041	0.015	0.026	0.008
tPAHs	1.154	0.550	0.910	0.277		0.603	0.341	0.469	0.106	0.746	0.256	0.465	0.213
ncPAHs	0.671	0.273	0.475	0.137		0.273	0.186	0.228	0.029	0.476	0.139	0.234	0.105
cPAHs	0.586	0.277	0.435	0.103		0.331	0.154	0.241	0.061	0.405	0.117	0.231	0.089
ТЕО	0.208	0.111	0.160	0.035		0.143	0.062	0.105	0.031	0.150	0.050	0.091	0.034

The EFs of total PAHs from the biomass burning were 0.910 ± 0.277 mg/kg_{dry} (leaf litter), 0.469 ± 0.106 mg/kg_{dry} (maize residue) and 0.465 ± 0.213 mg/kg_{dry} (rice straw). The PAHs with the highest EF was FLA (0.118 mg/kg_{dry}) from leaf litter burning and BbF (0.055 and 0.068 mg/kg_{dry}) from maize residue and rice straw burning,

respectively. The ratios of ncPAHs and cPAHs in tPAHs are shown in Figure 3.5. The average ncPAHs and cPAHs were 0.475 mg/kg_{dry} (52%) and 0.435 mg/kg_{dry} (48%), respectively from burning of leaf litter. They were 0.228 mg/kg_{dry} (49%) and 0.241 mg/kg_{dry} (51%), respectively from maize residue burning. The emissions of ncPAHs and cPAHs from burning rice straw were almost equal (0.234 and 0.231 mg/kg_{dry}, 50%:50%). The EF of tPAHs from burning of rice straw in this study (0.465 mg/kg_{dry}) was lower than other studies such as Keshtkar and Ashbaugh, (2007) (18.62 mg/kg_{dry}) and Kim Oanh *et al.*, (2011) (16.92 mg/kg_{dry}). There are a lot of possible factors, which could affect the results in each study. Therefore more detail such as types of burning chamber, temperature and moisture content, are needed, when compare data from various conditions of experiments

Estimation of carcinogenic health risks associated with the exposure of PM10bound PAHs can be calculated for toxicity equivalent concentrations (TEQs) (Nisbet and Lagoy, 1992; US EPA, 1993; Cecinato *et al.*, 1997). TEQs calculation is based on the toxic equivalent factors (TEFs) proposed by Nisbet and Lagoy(1992). The TEQ values of leaf litter (0.111-0.208 g/kg_{dry}) were higher than those of maize residues (0.062-0.143 g/kg_{dry}) and rice straw (0.050-0.150 g/kg_{dry}). The results showed that burning of leaf litter emitted higher pollutants (PM10 & PAHs) and could cause higher human health risk than burning of agricultural residues (maize residue and rice straw).

The emissions of tPAHs, ncPAHs, cPAHs and TEQs from the burning of each type of biomass had the same trend, which were leaf litter > maize residue ~ rice straw (Table 3.14 and Figure 3.5). The dominant PAHs emitted from three types of biomass burning were FLA, CHR and BbF. The MANOVA test revealed significant difference (p < 0.05) of the EFs of PM10 as well as individual PAHs from the burning of leaf litter

and the agricultural residues, while there was no significant difference between those of rice straw and maize residue.



Figure 3.5 Concentrations of tPAHs, ncPAHs and cPAHs and the relative percentages of ncPAHs and cPAHs from biomass burning.

3.3.4 PAHs profiles emitted from biomass burning

The profiles of PAHs and relative percentage emitted from biomass burning in the chamber are shown in Figures 3.6 - 3.8.

a) PAHs profile emitted from leaf litter burning

The concentrations of the high molecular weight PAHs (4 rings) emitted from leaf litter burning were generally higher than those of low molecular weight. FLA, CHR and BbF were the dominant PAHs. Each of them contributed to 13 % of 16-PAHs (~39%) (Figure 3.6). 5-6 rings of PAHs were moderately emitted from burning of leaf litter. Emissions of the low molecular weight PAHs were low.



Figure 3.6 Profile of PAHs emitted from the burning of leaf litter in the chamber

b) PAHs profile emitted from maize residue burning

The PAHs profile emitted from the burning of maize residue is shown in Figure 3.7. BbF (12%) and CHR (11%) were the major components among 16-PAHs. The high molecular weight PAHs (5-6 rings) and low molecular weight (3-4 rings) were moderately emitted. The low molecular weight PAHs (NAP, ACY and FLU) were of low emission. ACE was not detected from the emission.

c) PAHs profile emitted from rice straw burning

The PAHs profile from rice straw burning is illustrated in Figure 3.8. The dominant PAHs were BbF, PYR and CHR. They were accounted for 15%, 11% and 10 % of tPAHs, respectively. High molecular weight PAHs (5-6 rings) as well as low molecular weight (PHE, ANT, BaA, CHR) (4 rings) were moderately emitted. The emissions of low molecular weight PAHs (NAP, ACY, ACE and FLU) were low.



Figure 3.7 Profile of PAHs emitted from the burning of maize residues in the chamber



Figure 3.8 Profile of PAHs emitted from the burning of rice straw in the chamber

The 16-PAHs were clustered based on the number of aromatic rings in their structures (2-, 3-, 4-, 5- and 6-rings) and plotted as the percentage of compounds emitted from the burning of each biomass type (Figure 3.9). It was found that 4-ring PAHs were dominated in all three biomass types. The EFs of PAHs from burning leaf litter, maize residue and rice straw in descending order were 4-rings (36 - 45%) > 5 rings (29% - 33%) > 3 rings (12 - 16%) > 6 rings (11 - 15%) > 2 rings (1%).



Figure 3.9 Relative percentages of PAHs emitted from leaf litter, maize residues and rice straw burning

3.3.5 Diagnostic ratios of PAHs for biomass burning

PAHs diagnostic ratios have been used worldwide to determine their sources (Ravidra *et al.*, 2008a; Yunker *et al.*, 2002; Tobiszewski and Namiesnik 2012; Orecchio *et al.*, 2009; Galarneau, 2008). The diagnostic ratios have been used to discriminate petrogenic and pyrogenic (Pies *et al.*, 2008), petrol emissions and diesel

(Ravindra *et al.*, 2008b), different crude oil processing products and biomass burning (Yunker *et al.*, 2002). Therefore in this work their ratios were considered and proposed with a narrower range in order to specify as a marker for biomass burning. According to the strong correlations between FLA and PYR, BaA and CHR and IND and BPER (r~1.000), the new ratios of FLA/(FLA+PYR), BaA/(BaA+CHR) and IND/(IND+BPER) were proposed to distinguish biomass burning source in particular for leaf litter, maize residue and rice straw. The proposed values were compared with other studies (Table 3.14).

The FLA/(FLA+PYR) ratios with values of 0.53-0.55 for leaf litter burning, 0.51-0.53 for maize residue burning and 0.49-0.52 rice straw burning were proposed. The BaA/(BaA+CHR) ratio values of 0.37-0.44 (leaf litter), 0.43-0.46 (maize residue) and 0.43-0.55 (rice straw) as well as the values of IND/(IND+BPER) as 0.51-0.56 (leaf litter), 0.55-0.59 (maize residue), 0.56-0.59 (rice straw), respectively were also proposed. In order to be practical, all three values for three types of biomass were combined and proposed for burning of mixed biomass. The values of 0.49-0.55 were specified for FLA/(FLA+PYR), 0.37-0.55 for BaA/(BaA+CHR) and 0.51-0.59 for IND/(IND+BPER).

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Ratio		Source
FLA/(FLA+PYR)	0.53-0.55	leaf litter burning
	0.51-0.53	maize burning
	0.49-0.52	rice straw burning
	0.49-0.55	biomass burning
BaA/(BaA+CHR)	0.37-0.44	leaf litter burning
	0.43-0.46	maize burning
	0.43-0.55	rice straw burning
	0.37-0.55	biomass burning
IND/(IND+BPER)	0.51-0.56	leaf litter burning
	0.55-0.59	maize burning
	0.56-0.59	rice straw burning
	0.51-0.59	biomass burning

Table 3.15 Diagnostic ratios form biomass burning from this study

3.3.6 Principal Component Analysis (PCA) of PAHs for biomass burning

Principal component analysis (PCA) has been applied to identify the sources of PM10-bound PAHs. The factor analysis for 16-PAHs from burning biomass was performed with three factors respectively with an Eigen value >1, contributing ~80% of the variance. First factor contributes 50.86% of the total variance and high loading with PHE, PYR, BaA, CHR, BbF, BkF, BaP, IND, and BPER. Therefore, loading scatter plots for three factors were grouped PYR, BaA, CHR, BkF, BaP, IND, and BPER. These results can be used for identification of the biomass burning source.

DAHe		Component	9/
IAIIS	1	2	3
NAP	0.139	0.880	0.098
ACY	0.403	0.824	-0.136
ACE	0.308	0.130	0.778
FLU	-0.458	0.485	0.409
PHE	0.659	0.535	-0.172
ANT	-0.212	0.722	-0.564
FLA	0.244	0.217	-0.686
PYR	0.834	0.190	-0.053
BaA	0.975	0.136	-0.101
CHR	0.969	0.179	-0.069
BbF	0.812	-0.353	0.416
BkF	0.970	-0.068	0.042
BaP	0.950	-0.057	0.053
IND	0.933	-0.001	0.036
DBA	-0.483	0.526	-0.050
BPER	0.944	0.011	0.106
% of Variance	50.86	20.51	9.85
Cumulative %	50.86	71.37	81.22

Table 3.16 PCA for biomass burning from biomass burning



Figure 3.10 Loading scatter plot of PAHs from biomass burning

3.3.7 Emission rates (ERs) of PM10 and PAHs from open burning

The ERs were calculated using Equation 2.4. The burnt areas of rice straw, maize residue and leaf litter (forest fire) in Chiang Mai Province were estimated by MODIS Landsat 5 TM (Dontree *et al.*, 2011) (Table 3.17). The percentages of burnt area were calculated by divide with total area in each type.

Table 3.17 Total area, burnt area and percentages of burnt area of forest, rice field and crop in Chiang Mai during the dry season of 2010 and 2011

		~ (n)	5		
Year	Biomass type	Total Area	Burnt Area	Burnt Area	
	/	(km ²)	(km ²)	%	
2010	Forest	11,109	3,073	27.66	
	Rice field	1,013	111	10.98	
	Crop	651	326	50.01	
2011	Forest	11,109	615	5.54	
	Rice field	1,013	78	7.7	
	Crop	651	173	26.58	

The information of burning period between December 2009-April 2010 (dry season 2010) and December 2010-April 2011 (dry season 2011) was summarized. Approximately 3,073 km² of forest, 326 km² of crop planting and 111 km² rice field were burnt in 2010 while about 615, 173 and 78 km², respectively were burnt in 2011. The percentages of burnt areas in descending order were crop (50%) > forest (28%) > rice field (11%) in 2010, while in 2011 the orders were crop (27%) > rice field (8%) > forest (6%). The burnt area in 2010 was obviously higher than that in 2011 due to amount of rain precipitation. The annual rainy day and rain amount in 2010 (112 days

and 1156.0 mm) were lower than in 2011(144 days and 1307.6 mm). There were only 9 rainy days with 37.4 mm precipitation in the dry season of 2010 (December 2009 – April 2010), while higher frequency of rain (28 days) and higher amount of precipitation (162.5 mm) were detected in the dry season of 2011 (December 2010 – April 2011).

Emission rates (ERs) of PM10 and PAHs calculated from burning area in Chiang Mai Province (Eq2) in 2010 and 2011 are given in Table 3.18.

 Table 3.18 PM10 and PAH emission rates from leaf litter, maize and rice straw in 2010

 and 2011

Parameter		2010			2011	
	Leaf litter	Maize	Rice straw	Leaf litter	Maize	Rice straw
PM10			E.			0
(Mg/year)	2,250	133.2	66.90	450.7	70.81	46.92
PAHs						
(kg/year)						
NAP	9.35	1.08	0.25	1.87	0.57	0.17
ACY	11.2	1.22	0.24	2.25	0.65	0.17
ACE	0.00	0.00	0.13	0.00	0.00	0.09
FLU	21.1	1.06	0.38	4.22	0.56	0.26
PHE	135	6.76	1.85	27.0	3.60	1.29
ANT	68.4	7.70	1.69	13.7	4.09	1.19
FLA	217	9.14	4.10	43.5	4.86	2.88
PYR	185	8.47	4.01	37.0	4.50	2.81
BaA	140	9.00	2.99	28.1	4.78	2.10
CHR	216	11.2	3.32	43.2	5.96	2.33
BbF	212	12.6	5.13	42.4	6.67	3.60
BkF	127	9.24	2.85	25.5	4.91	2.00
BaP	83.8	7.32	2.22	16.8	3.89	1.56
IND	101	9.18	2.56	20.3	4.88	1.80
DbA	62.1	4.96	1.25	12.4	2.64	0.88
BPER	86.5	7.21	1.92	17.3	3.83	1.35
tPAHs	1675_	106	34.9	336	56.4	24.5
ncPAHs	874	51.6	17.6	175	27.5	12.3
cPAHs	801	54.5	17.3	161	29.0	12.2

The ERs of PM10 in 2010 were 2,250, 133 and 67 Mg while in 2011 they were 451, 71 and 47 Mg from the burning of leaf litter, maize residue and rice straw, respectively. Approximately 90% and 80 % of PM10 were emitted from forest fire in 2010 and 2011, respectively. The results of another relevant study in Chiang Mai reveal that 80% of burning area in the northern part of Thailand was in the forest area and only 20% was in the agriculture area (Kim Oanh et al., 2000). In addition, ERs of tPAHs from the open burning in 2010 were 1,675 kg from forest fire, 106 kg from crop and 35 kg from rice field while those in 2011, the ERs were 336 kg from forest fire, 56 kg from crop and 24 kg from rice field. The ERs of open burning in Chiang Mai Province for PM10 and PAHs in both years were almost of the same pattern. The ERs of PM10 and PAHs in 2010 were 2 - 5 times higher than those in 2011. The ERs of nPAHs from burning forest, crop and rice field were 874 kg, 52 kg, and 18 kg, respectively, in 2010 while those from burning forest, crop and rice field, were 175 kg, 28 kg, and 12 kg, respectively, in 2011. The ERs of cPAHs were 804 kg, 54 kg, and 17 kg in 2010 from burning forest, crop and rice field, respectively. In 2011 they were 161 kg, 29 kg, and 12 kg, respectively. The emissions of PM10, tPAHs, ncPAHs, and cPAHs from the open burning both in 2010 and 2011 in the descending order were forest > crop > rice field.

3.4 Ambient PM10 concentrations at CMU site

3.4.1 PM10 concentrations and their seasonal variation

PM10 samples in ambient air of Chiang Mai were collected and analyzed in 3 periods; the dry season of 2010, the wet season of 2010 and the dry season of 2011(Table 3.19). Figure 3.11 shows comparison of PM10 concentrations in ambient air obtained from 3 stations; Science Complex Building 1, Chiang Mai University (SCB1-CMU) and Air Quality Monitoring (AQM) stations of Pollution Control Department (PCD) at Chiang Mai City Hall (CH) and Yuppraraj Wittayalai School (YP).



Figure 3.11 Comparison of PM10 concentrations in ambient air obtained from minivolume air sampler (SCB1-CMU) and AQM stations (CH and YP)

The PM10 concentrations in the dry season of 2010 from the SCB1-CMU station were nearly the same concentrations with those from the AQM stations. In the wet season 2010 and the dry season of 2011, PM10 concentrations from the SCB1-CMU station were lower than those from the AQM stations due to the fact that the location of SCB1-CMU station (373 meters above mean sea level) was higher than the AQM station (~ 310 meters above mean sea level) which made it less susceptible to the

traffic.

Season	(Concentration ($\mu g/m^3$)								
00	max	min	mean	SD						
Dry 2010 (n=11)	157.3	59.5	104.9	32.7						
Wet 2010 (n=42)	57.2	0.7	13.3	11.3						
Dry 2011 (n=41)	82.9	2.4	36.2	19.2						

Table 3.19 PM10 concentrations in each season

PM10 concentrations were high in the dry season of 2010 (59.48 - 154.30 μ g/m³) and low in the wet season of 2011 (0.73 - 57.17 μ g/m³) and in the dry season of 2011 (2.38 - 82.92 μ g/m³). The mean concentrations were 104.91±32.70, 13.28±11.34 and 36.24±19.16 in the dry and wet season of 2010 and dry 2011, respectively. PM10 concentrations over 6 years (2006-2011), measured at the CH station, Chiang Mai are shown in Figure 3.12. The trends of PM10 concentrations in each year have been found to be quite similar. The concentrations are high in the dry season and always highest in March. The most important factors are the amount of rain precipitation and scale and frequency of open burning. The PM10 concentrations in the rainy season are quite low and constant for about 6 months (May- October). Then the concentrations increased again at the beginning of the dry season (November) due to lower precipitation and higher burning activities in agricultural areas including the rice and corn plantation. The harvest season is normally from November to December.



Figure 3.12 Pattern of PM10 concentrations in Chiang Mai atmosphere obtained from the City Hall station during 2006-2011.

In the dry season of 2011, relatively low concentrations of PM10 were observed due to effects from meteorological conditions, especially the amount and frequency of rain precipitation. Figure 3.13 shows monthly precipitation and number of rainy days between 2010 and 2011. The annual total precipitation and rainy days in 2011 (1449.5 mm, 144 days) were higher than in 2010 (1156 mm, 112 days). The monthly precipitation varied between 0 - 471 mm and 0.6 - 293 while the number of rainy days ranged from 0 - 26 days and 1 - 25 days in 2010 and 2011, respectively. The highest total precipitation levels were recorded in August 2010 and May 2011, which was abnormal for precipitation trend in 2011. Precipitation levels in March and April in 2011 (60.4, 92.6 mm, respectively) were higher than in 2010 (4.3, 3.9 mm, respectively) (Table 3.20). Moreover, rainy days in March in 2011 (7 days) were higher than 2010 (2 days) which could influence the PM10 concentrations in 2011.

Season	Month	Tem	perature	(°C)	Relat	Relative Huminity (%)			un
Season	Wionui	MAX	MIN	Mean	MAX	MIN	Mean	(mm)	Days
	Januay	31.33	18.39	24.15	90.0	42.2	68.6	21.7	3
Dry 2010	Febuary	34.15	15.96	24.51	83.3	24.5	54.5	0	0
	March	35.78	20.80	27.80	78.1	30.6	53.8	4.3	2
	April*	39.08	24.78	31.60	70.9	26.5	47.8	3.9	2
	August*	31.33	24.22	27.12	94.3	66.5	83.0	470.6	26
Wet 2010	september*	32.51	24.01	27.49	93.7	59.7	79.9	196.2	17
	October*	31.44	23.69	26.91	92.2	57.9	78.2	169.6	16
	Januay*	29.33	17.35	22.75	90.7	43.5	69.6	2.6	2
Dry 2011	Febuary*	33.08	17.29	24.52	84.9	29.6	58.6	0.8	1
	March*	31.10	20.76	25.41	85.3	44.9	66.2	60.4	7
	April	33.53	22.55	27.33	88.5	48.1	69.8	92.6	15

Table 3.20 Monthly temperature, relative humidity, precipitation in the study period.

*Sampling periods

Focusing on the sampling months of the dry 2010 (April) and the dry 2011 (January - March), the precipitation amount was obviously different and rainy days in April in 2010 (2 days) was lower than 2011(15 days). Furthermore, relative humidity was lowest (47.8%) and mean temperature was highest (31.6 °C) in April of dry 2010. In the other hand, relative humidity was high in March (66.2 %) and April (69.8%) of dry 2011and mean temperature was the nearly same in wet season 2010. While the pressure vales of all periods were quite the same values. Moreover, the potential pollutant source such as open burning also plays an important role in dry season. Number of hotspots were high in April 2010 (3,901 spots) and very low (13 spots) in wet season (August – October 2010). In the dry season of 2011 (January – March), the number of hotspots was also high (3,911 spots). However, number of hotspots per day

in the dry season of 2010 (130 spots) was obviously higher than that in 2011 (43 spots). It can be seen that the scale of open burning was much higher in dry 2010 than in dry 2011. The results from hot spots were overlay with land use by ArcGIS. it was found that forest fire (60%) was highest in burning season.



Figure 3.13 Monthly precipitation and number of rainy days in 2010 and 2011 in Chiang Mai

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3.4.2 Correlations between PM10 concentrations obtained from a minivolume air sampler (SCB1-CMU) and AQM of PCD (CH and YP)

The PM10 concentrations collected by a minivolume air sampler at SCB-CMU were compared with values obtained from the tapered element oscillating microbalance (TEOM) at the AQM stations of the PCD, located at CH and YP stations, Chiang Mai Province. Their scatter plot and correlation coefficient values are shown in Figure 3.14. High correlation were obtained in dry season 2010 (r=0.881- 0.889) due to source of PM10 was the same. Potential source of PM10 in dry season in this area is probably open burning especially forest fire (Kim Oanh *et al.*, 2011)

In the wet season of 2010 and the dry season of 2011, moderate correlations (r= 0.680-0.716) were obtained. During these periods PM10 concentrations monitored at SCB1-CMU were underestimated, because it had less effect from traffic source, while the other two stations (PCD sites) are road-side location.

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Figure 3.14 Correlation between PM10 concentrations obtained from mini volume air sampler (SCB1-CMU) and TEOM (AQM stations). A1 (CH, dry 2010); A2 (YP, dry 2010); B1 (YP, wet 2010); B2 (YP, wet 2010); C1 (CH, dry 2011); C2 (YP, dry 2011)

3.5 PM10-bound PAHs

PM10 samples were analysed for PAHs by using GC-MS. The results are shown in Table 3.21. Concentrations of total PAHs were $10.03 - 44.26 \text{ ng/m}^3$ (dry 2010), $0.25 - 8.28 \text{ ng/m}^3$ (wet 2010) and $1.36 - 11.61 \text{ ng/m}^3$ (dry 2011). The mean concentrations of total PM10- bound PAHs were 25.87±10.13 ng/m³ (dry 2010), $3.12\pm2.18 \text{ ng/m}^3$ (wet 2010) and $4.58\pm2.18 \text{ ng/m}^3$ (dry 2011). They were lower than those reported by a previous study (Chantara et al., 2009) (6.7 ng/m³). The noncarcinogenic PAHs (ncPAHs) and carcinogenic PAHs (cPAHs) were calculated based on the criteria of US. EPA (1993) as shown in Table 3.21 and Figure 3.15. The concentrations of ncPAHs and cPAHs were found to have the same trend as PM10 concentrations. The ncPAHs concentrations were 10.29±2.93 ng/m³, 1.63±0.85 ng/m³ and 3.07±1.68 ng/m³ in dry 2010, wet 2010 and dry 2011, respectively. Their concentrations in dry season 2010 were 6 and 3 times higher than those in wet 2010 and dry 2011, respectively. The cPAHs were 15.59 ± 7.82 ng/m³, 1.49 ± 1.59 ng/m³ and 1.51 ± 0.74 ng/m³ in dry 2010, wet 2010 and dry 2011, respectively. Their concentrations in dry season 2010 were 10 times higher than those in wet 2010 and dry 2011. The relative percentage of cPAHs was higher than ncPAHs in dry season 2010 (60:40) (Figure 3.16). On the other hand, concentrations of ncPAHs were higher than those of cPAHs in wet season 2010 (52:48) and dry season 2011 (67:33).

Figure 3.18 illustrates PM10 and PAHs concentrations in the ambient air and ratios of individual PAHs in each season (Figure 3.17). The total PAHs concentrations were quite high in the dry season of 2010, and getting lower in the wet season of 2010 and slightly increasing in dry season 2011. The In dry 2010, PAHs concentrations in descending order were IND (5.047 ng/m³, 20%) > BPER (3.847 ng/m^3 , 15%) > FLA (2.780 µg/m³, 11%) > BaA (2.411 ng/m³, 9%) > BkF (2.396 ng/m³, 9%) > CHR (2.100 ng/m³, 8%), > FLU (1.906 ng/m³, 7%) > NAP (1.204 ng/m³, 5%) > PYR $(0.549 \text{ ng/m}^3, 2\%) > \text{DBA} (0.148 \text{ ng/m}^3, 1\%) > \text{BbF} (0.146 \text{ ng/m}^3, 1\%)$, while the rest was not detected. The concentrations of 16-PAHs in wet 2010 in descending order were IND (0.436 ng/m³, 14%) > NAP (0.369 ng/m³, 12%) > BPER(0.359 μ g/m³, 12%) > BbF (0.301 ng/m³, 10%) > BkF (2.396 ng/m³, 8%) > CHR (0.228 ng/m³, 7%), > BaA $(0.224 \text{ ng/m}^3, 7\%) > \text{FLA} (0.205 \text{ ng/m}^3, 7\%) > \text{PHE} (0.191 \text{ ng/m}^3, 6\%) > \text{FLU} (0.172 \text{ ng/m}^3, 7\%) > \text{F$ ng/m^3 , 5%) > ANT (0.171 ng/m^3 , 5%) > PYR (0.152 ng/m^3 , 5%) > BaP (0.040 ng/m^3 , 1%). In dry season 2011, the concentrations of 16-PAHs in descending order were NAP $(0.930 \text{ ng/m}^3, 20\%) > \text{IND} (0.599 \text{ ng/m}^3, 13\%) > \text{PYR} (0.513 \text{ ng/m}^3, 11\%) > \text{FLA}$ $(0.468 \text{ ng/m}^3, 10\%) > \text{ANT} (0.0.425 \text{ ng/m}^3, 9\%) > \text{BPER} (0.332 \mu\text{g/m}^3, 7\%) > \text{PHE}$ $(0.327 \text{ ng/m}^3, 7\%) > \text{BbF} (0.288 \text{ ng/m}^3, 6\%) > \text{CHR} (0.240 \text{ ng/m}^3, 5\%) > \text{BaP} (0.147)$ ng/m^3 , 3%) > BkF (0.131 ng/m³, 3%) > BaA (0.105 ng/m³, 2%) > FLU (0.071 ng/m³, 2%), while ACE, ACY and DBA were lower than instrument detection limits. It can be revealed that the dominant PAHs in dry 2010 were IND and BPER, while in wet season 2010 and dry season 2011 were NAP and IND.

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Dry 2011 (n=41) PAHs Dry 2010 (n=11) Wet 2010 (n=42) (ng/m^3) SD SD SD max min mean min mean min mean max max NAP 0.49 0.93 0.56 2.18 0.52 1.20 1.34 ND 0.37 0.29 2.30 ND ACY 0.002 0.01 ND ND ND 0.00 0.05 ND 0.01 0.02 0.08 ND ACE ND 0.07 ND 0.004 0.02 ND ND ND ND ND 0.00 ND FLU 1.91 0.15 0.29 ND 0.17 0.08 0.07 0.06 2.12 1.70 0.18 ND PHE ND ND ND 0.00 0.48 ND 0.15 0.83 ND 0.33 0.22 0.19 ANT 0.42 ND ND ND 0.00 0.67 ND 0.17 0.20 1.16 ND 0.27 FLA 2.78 1.40 ND 0.47 0.54 5.20 ND 1.70 ND 0.20 0.30 3.16 PYR 2.74 0.55 0.99 0.25 3.73 ND 0.51 0.64 ND 0.89 ND 0.15 0.14 BaA 4.77 ND 2.41 1.95 0.91 ND 0.22 0.29 0.43 ND 0.10 CHR 2.10 0.23 0.61 0.13 5.45 ND 1.47 0.60 ND 0.24 ND 0.24 BbF 1.60 0.29 0.29 1.39 ND 0.15 0.48 ND 0.30 0.40 1.02 ND 0.24 BkF 7.23 ND 3.34 2.39 0.25 0.40 0.82 ND 0.13 1.46 ND BaP 0.13 0.22 4.29 ND 2.40 1.94 0.42 ND 0.04 0.61 ND 0.15 IND 1.27 0.60 0.16 6.33 4.33 5.05 0.61 ND 0.44 0.45 0.96 0.352 DbA ND 0.49 ND ND ND ND ND ND 1.63 0.15 ND ND BPER 5.74 2.88 1.15 ND 0.36 0.40 ND 0.33 0.38 3.85 0.85 1.40 tPAHs 44.26 10.03 25.87 10.13 8.28 0.25 3.12 2.18 11.61 1.36 4.58 2.03 16.72 1.63 0.85 0.22 1.68 ncPAHs 5.70 10.29 2.93 3.93 0.25 9.45 3.07 cPAHs 27.54 4.33 15.59 7.82 ND 1.49 1.59 3.42 0.35 0.74 5.68 1.51

Table 3.21 Concentrations (ng/m³) of PM10- bound PAHs in the dry season of 2010, wet season of 2010 and dry season of 2011.

ND = not detected

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3.6 Correlations between PM10 and PAHs concentrations; PM10 and hotspots

Correlations between PM10 and PAHs and hotspots were examined using the Pearson correlation (Ravindra *et al.*, 2008).

3.6.1 Correlations of PM10 and individual PAH in each season

The Pearson correlation was used to examine correlations between PM10 and individual PAHs in three seasons: dry and wet season 2010 and dry season 2011. The results are demonstrated in Tables 3.22 - 3.24.

In the dry season of 2010, the PM10 concentrations were strongly correlated with concentrations of BPER (r=0.901) and FLU (r=0.812), FLA (r=0.786), PYR (r=0.749), CHR (r=0.819), BKF (r=0.874), and BaP (r=0.834). Furthermore, BPER was strongly correlated with some of 4-ring PAHs (PYR, BaA and CHR) and all of 5-ring PAHs. BkF was strongly related with FLU, CHR, BaA, and PYR while BbF was strongly related CHR and PYR. Moreover, CHR was correlated with FLU and 4-ring PAHs (PYR and BaA).

In the wet season of 2010, there was no correlation between PM10 and individual PAHs. However, BPER was strongly correlated with IND and 5-ring PAHs (BbF and BkF). BkF was well correlated with CHR and BbF. In Addition, BbF and CHR and ANT and PHE were highly correlated. In dry season 2011, there was no correlation between PM10 and individual PAHs as well. The strongly correlation was found only between FLA and PYR (r=0.902).

Due to high concentrations of PM10 and PAHs in dry 2010, many strong correlations were found between PM10 and individual PAH and among PAHs themselves. On the other hand, low concentrations of PM10 and PAHs found in wet 2010 and dry 2011 revealed no strong correlation between PM10 and PAHs and even among PAHs themselves. It can be concluded that meteorological condition particularly rain amount obviously affected on pollutant concentrations in ambient air. Consequently its chemical composition was also low in content and significant correlation among pollutant concentrations can rarely be observed.



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Table 3.22 Correlation coefficients of PM10, PM10-bound PAHs in the dry season of 2010

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

	NAP	ACY	ACE	FLU	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IND	DbA	BPER	PM10
NAP	1.000																
ACY	.a	.a															
ACE	.a	.a	.a														
FLU	0.586	.a	.a	1.000													
PHE	.a	.a	.a	.a	.a												
ANT	.a	.a	.a	.a	.a	.a											
FLA	0.066	.a	.a	0.348	.a	.a	1.000										
PYR	0.073	.a	.a	0.564	.a	.a	0.491	1.000									
BaA	-0.103	.a	.a	0.522	.a	.a	0.241	0.632*	1.000								
CHR	0.057	.a	.a	0.791**	.a	.a	0.426	0.844**	0.749**	1.000							
BbF	-0.137	.a	.a	0.468	.a	.a	0.552	0.821**	0.401	0.754**	1.000						
BkF	0.243	.a	.a	0.843**	.a	.a	0.320	0.722*	0.840**	0.902**	0.540	1.000					
BaP	0.345	.a	.a	0.672*	.a	.a	0.207	0.609*	0.718*	0.702*	0.316	0.851**	1.000				
IND	0.570	.a	.a	0.385	.a	.a	-0.067	0.077	0.346	0.150	-0.436	0.361	0.540	1.000			
DbA	0.523	.a	.a	0.366	.a	.a	0.000	0.248	0.259	0.205	-0.100	0.221	0.293	0.698*	1.000		
BPER	0.289	.a	.a	0.788**	.a	.a	0.537	0.924**	0.711*	0.898**	0.742**	0.862**	0.748**	0.271	0.404	1.000	
PM10	0.429	.a	.a	0.812**	.a	.a	0.362	0.786**	0.749**	0.819**	0.422	0.874**	0.834**	0.617*	0.531	0.905**	1.000

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

.a Cannot be computed because at least one of the variables is constant.

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FLU ANT PYR CHR BPER ACY ACE PHE BbF BkF BaP IND DbA NAP FLA BaA PM10 NAP 1.000 ACY -0.020 1.000 ACE 0.023 0.688** 1.000 FLU 0.114 -0.015 -0.008 1.000 PHE 0.500** .359* -0.353 0.008 1.000 0.439** .375* ANT 0.227 -0.519 0.716** 1.000 FLA -0.033 -0.049 0.301 -0.042 0.177 0.054 1.000 PYR 0.433** -0.221 -0.137 0.207 -0.106 -0.183 0.675** 1.000 -0.037 0.431** 0.278 -0.116 0.349* 0.183 0.380* 0.155 BaA 1.000 -0.300 CHR -0.034 0.566** .364* 0.572** 0.577** 0.074 -0.189 0.606** 1.000 0.615** -0.315 0.585** 0.022 -0.275 BbF -0.155 .356* 0.646** 0.549** 0.797** 1.000 BkF -0.224 0.534** .331* -0.274 0.485** 0.440** 0.053 -0.193 0.694** 0.805** 0.881** 1.000 BaP -0.076 0.114 -0.086 -0.115 0.311* 0.297 0.169 -0.196 0.281 0.412** 0.397** 0.399** 1.000 IND -0.103 0.522** 0.266 -0.399 0.502** 0.463** 0.066 -0.197 0.492** 0.656** 0.689** 0.620** 0.172 1.000 DbA .a BPER -0.275 0.577** 0.306* -0.419 0.502** 0.497** -0.375 0.487** 0.681** 0.751** 0.711** 0.257 1.000 -0.058 0.887** .a **PM10** 0.354* 0.066 0.052 -0.190 0.107 0.382* 0.161 0.133 -0.129 -0.015 0.091 -0.091 -0.080 0.028 0.056 1.000 .a

Table 3.23 Correlation coefficients of PM10, PM10-bound PAHs in the wet season of 2010

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

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

.a Cannot be computed because at least one of the variables is constant.

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	NAP	ACY	ACE	FLU	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IND	DbA	BPER	PM10
NAP	1.000								N.								
ACY	0.040	1.000															
ACE	.a	.a	.a														
FLU	-0.507	0.274	.a	1.000													
PHE	0.427**	0.342*	.a	-0.083	1.000												
ANT	0.466**	0.158	.a	-0.179	0.447**	1.000											
FLA	0.189	0.186	.a	0.017	-0.052	0.264	1.000										
PYR	0.226	0.144	.a	-0.074	-0.170	0.244	0.902**	1.000									
BaA	0.689**	-0.047	.a	-0.635	0.407**	0.426**	0.214	0.123	1.000								
CHR	0.183	0.056	.a	-0.258	.378*	-0.018	0.142	0.089	0.503**	1.000							
BbF	0.416**	0.115	.a	-0.085	0.265	0.286	0.152	0.088	0.336*	0.408**	1.000						
BkF	-0.374	0.242	.a	0.382*	0.166	-0.087	-0.052	-0.070	-0.267	0.327*	0.170	1.000					
BaP	-0.420	0.289	.a	0.478**	0.145	-0.188	-0.059	-0.091	-0.338	0.358*	0.146	0.517**	1.000				
IND	0.084	0.108	.a	0.031	0.249	0.153	0.330*	0.215	0.182	0.431**	0.609**	0.234	0.440**	1.000			
DbA	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a	.a		
BPER	0.284	-0.138	.a	-0.490	0.212	0.257	0.101	0.088	0.479**	0.500**	0.304	0.271	0.159	0.454**	.a	1.000	
PM10	0.157	-0.234	.a	-0.064	0.227	-0.104	-0.243	-0.310	0.157	0.196	0.292	-0.108	0.021	0.317*	.a	0.089	1.000

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

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

.a Cannot be computed because at least one of the variables is constant.

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3.6.2 Seasonal correlations between PM10 and its PAHs content (tPAHs, ncPAHs and cPAHs)

The correlation of PM10, tPAHs, ncPAHs and cPAHs are shown in Table 3.25. In the dry of 2010, PM10 concentrations were significantly correlated (p<0.01) with concentration of tPAHs (r = 0.936), ncPAHs (r = 0.773), and cPAHs (r=0.927). The very strong correlation was also found between tPAHs and cPAHs (r=0.991) while tPAHs and ncPAHs was moderately correlated (r=0.764). In the wet season of 2010, PM10 concentrations were significantly correlated (p<0.01) with tPAHs (r= 0.796) and with ncPAHs (r= 0.947). The moderate correlation (p<0.01) was found between tPAHs and ncPAHs (r=0.322). In the dry season of 2011, PM10 concentrations were significantly correlated (p<0.01) and with ncPAHs (r=0.619). Furthermore, No correlation was found between PM10 and cPAHs neither in wet season 2010 nor in dry season 2011. The results illustrated that the main PAHs found in those seasons were ncPAHs. Therefore, it could be suggested that cPAHs found in PM10 in dry season 2010.

3.6.3 Correlations between PM10 and the number of hotspots

PM10 concentrations obtained from a mini volume air sampler (SCB1, CMU) and from the City Hall (CH) - Air Quality Monitoring (AQM) station were plotted against the number of hotspots in Northern Thailand in dry season of 2010 and 2011. Due to very low number of hotspots in wet season, therefore the data of wet 2010 was not included for analysis. The correlations (p<0.01) between PM10 concentrations and the number of hotspots in the dry season of 2010 were relatively strong for both the CMU site (r=0.790, n=90) and the CH site (r=0.522, n=90), while

there was no correlation in the dry season of 2011. The results can be revealed that high amount of open burning in the northern part of Thailand in the dry season of 2010 resulted in high PM10 concentrations in the ambient air of Chiang Mai.

Season	Ċ	PM10	tPAHs	ncPAHs	cPAHs
Dry season 2010 (n=11)	PM10	1			
	tPAHs	0.936**	1		
	ncPAHs	0.773**	0.764**	1	
	cPAHs	0.927**	0.991**	0.700^{**}	1
Wet season 2010 (n=42)	PM10	1			
	tPAHs	0.796 ^{**}	1		
	ncPAHs	0.947**	0.558**	1	
V.	cPAHs	0.113	0.322*	-0.016	1
Dry season 2011 (n=41)	PM10	1			
	tPAHs	0.937**	12		
	ncPAHs	0.619**	0.036	1	
	cPAHs	-0.016	-0.114	0.215	1

Table 3.25 Correlations of PM10 and PAHs concentrations in each sampling period.

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

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

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Figure 3.19 Scatter plots between PM10 concentrations and number of hotspots. A1

(CMU site; A2 (CH site); B1 (CMU site); B2 (CH site)

3.7 Assessment of possible health effects based on PAHs concentrations

3.7.1 Toxicity equivalent concentration (TEQ) of PAHs

The toxicity equivalent concentration (TEQ) is used for estimation of human health risk from PAHs. It can be calculated using (Eq 3.1) (Nisbet and Lagoy 1992; Yang *et al.*, 2007; Yu *et al.*, 2008; Jia *et al.*, 2011; Vu *et al.*, 2011; Sarkar and Khillare 2012):

$$TEQ = \sum_{i} [C_i \times TEF_i]$$
 (Eq 3.1)

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. Benzo(a)pyrene (BaP) was used as a reference compound. The carcinogenic PAHs, which have lower potency than BaP, will be assigned to different TEF values. TEQ was calculated based on TEF values from various references as shown in Table 3.26.

PAHs		TEF _i	
	Nisbet and Lagoy (1992)	US EPA (1993)	Ceninato et al. (1997)
NAP	0.001	0	0
ACY	0.001	0	0
ACE	0.001	0	0
FLU	0.001	0	0
PHE	0.001	0	0
ANT	0.01	0	0
FLA	0.001		
PYR	0.001	0	0
BaA	0.1	0.1	0.06
CHR	0.01	0.01	0
BbF	0.1	0.1	0.07
BkF	0.1	0.1	0.07
BaP	1	1	1
IND	0.1	0.1	0.08
DbA	b ''' '	1	0.6
BPER	0.1	0	0

Table 3.26 Toxicity equivalent factors (TEF_i)

The TEQ values of PAHs in ambient air of Chiang Mai were calculated based on TEF values provided from different sources. The values are listed in Table 3.27. **Table 3.27** TEQs values of PAHs in ambient air of Chiang Mai.

6		Dry 201	0		Wet 201)		Dry 2011				
	Nisbet ^a	US EPA ^b	Cecinato ^c	Nisbet ^a	US EPA ^b	Cecinato ^c	Nisbet ^a	US EPA ^b	Cecinato ^c			
MAX	7.35	7.29	6.18	0.91	0.90	0.76	0.91	0.84	0.77			
MIN	0.46	0.43	0.35	0.00	0.00	0.00	0.04	0.04	0.03			
Mean	3.70	3.66	3.28	0.17	0.16	0.13	0.30	0.26	0.23			
SD	2.56	2.55	2.32	0.22	0.22	0.18	0.26	0.24	0.24			
^a Nisbet a	nd Lagoy	1992						•				

^bUS EPA 1993

°Ceninato et al., 1997

The range of the total TEQ values in the dry season of 2010 were 0.46 – 7.35 (Nisbet and Lagoy, 1992), 0.35 - 6.16 (Cecinato *et al.*, 1997) and 0.43 - 7.29 (US EPA, 1993). In wet season of 2011, the total TEQ were 0.00 - 0.91, 0.03 - 0.77 and 0.04 - 0.84, respectively. In dry season 2011 the values were 0.04 - 0.91, 0.00 - 0.76 and 0.00 - 0.90, respectively. The average of TEQs in dry season 2010 (3.28-3.70) was 20 times higher than in the wet season of 2010 (0.13-0.17) and 10 times higher than the dry season of 2011 (0.23-0.30). The TEQ values in Chiang Mai in the wet season of 2010 and the dry season of 2011 were lower than previous studies in Chiang Mai according to Pengchai *et al.* (2008) (0.75-1.60) and Chantara and Sangchan (2009) (0.95-1.76). However, in the dry season of 2010, they were higher than those of the previous studies. This is probably due to the higher PM10 concentrations in dry season 2010 which was effected from open burning.

3.7.2 The inhalation lung cancer risk (ILCR) assessment

The inhalation lung cancer risk (ILCR) was used for estimation of cancer risk from PAHs exposure. The equation proposed by USEPA (2005) (Eq 3.2) was used for calculation.

$$ILCR = TEQ \times IUR_{BaP}$$
 (Eq 3.2)

Where IUR_{BaP} is the inhalation unit risk defined as the risk of cancer from lifetime (70 years) inhalation of unit mass of BaP that calculated in terms of TEQ values in this study. The California Environmental Protection Agency (CEPA, 2004) and the World Health Organization (WHO, 2000) recommended a unit risk of cancer value for BaP as: IUR_{BaP} = 1.1×10^{-6} and 8.7×10^{-5} (ng/m³)⁻¹, respectively. The mean TEQs values were obtained from the calculation based on of Nisbet and Lagoy (1992), US EPA (1993), and Cecinato (1997). The ILCR values and the societal ILCR are shown in Table 3.28.

Table 3.28 ILCR values in Chiang Mai

Pollutant	TEQ	ILCR	The social ILCR	The social ILCR
level		TINT	(cases)	(cases/year)
High pollutant period	3.55	3.09 x10 ⁻⁴	524.7	7.5
Low pollutant period	0.20	1.74 x 10 ⁻⁵	29.6	0.4

The ILCR value can be ranged between 10^{-6} (lower-bound zero risk) and 10^{-4} (high potential health risk) (Liao and Chiang 2006; Sarkar and Khillare 2012). In this study there were 2 periods of pollutant level in ambient air, which were high pollutant period (April 2010) and low pollutant period (August – October 2010 and January – March 2011). The calculated ILCR showed high risk in high pollutant period

 (3.09×10^{-4}) , while that in low pollutant period (1.34×10^{-5}) was moderate. The societal ILCR was calculated by multiplying of the ILCR value with population of Chiang Mai in high pollutant period (524 cases/population or 7.5 cases/year), while it was low in low pollutant period (30 cases/population or 0.4 cases/year). It was found that the number of cases proposed in high episode was higher than the previous study performed in the cities of Chiang Mai and Lamphun in 2005 - 2006 (2 cases per year) (Pengchai *et al.*, 2008), but it was much lower than the study of Bangkok (27 cases per year). The sampling sites in Bangkok are the roadsides located in inner part of the metropolitan (30,000 – 90,000 cars/day) (Norramit et al, 2008).

3.8 Sources apportionment of PM10- bound PAHs

3.8.1 Diagnostic Ratios (DRs)

The diagnostic ratios (DRs) between some of the PAHs were considered as the "fingerprint" of an emission source (Khalili *et al.*, 1995; Dickhut *et al.*, 2000), because they presented the characteristics of the specific source. Table 3.29 shows the diagnostic ratios of PAHs attributed to specific sources from various references.

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Source	References
diesel engine	Kavourous 2011
gasoline engine	
wood combustion	
vehicular emissions	Pio, 2001
Broad-leaf tree	Wang 2009
shrub	
grass	Oros 2006
cooking smoke	He 2004
gasoline-powered motor vehicles	Schauer 1999
almost source	Alice 2011
coal combustion	
biomass burning	
	Kavourous 1999
vehicular emissions	Rogge 1993
grass, wood, coal combustion	Yunker 2002
fossil fuel combustion	
rice straw burning	Jenkis 1996
antracite+low-rank coal	Alice 2011
bituminous coal	
traffic	
biomass burning	
medical waste +tire combustion	
	Kavourous 2011,
diesel	Sicre 1987
gasoline	Simcik 1999
vehicular emissions	Cabuk 2010
combustion	Yunker 2002
	Source diesel engine gasoline engine wood combustion vehicular emissions Broad-leaf tree shrub grass cooking smoke gasoline-powered motor vehicles almost source coal combustion biomass burning vehicular emissions grass, wood, coal combustion fossil fuel combustion fossil fuel combustion rice straw burning antracite+low-rank coal bituminous coal traffic biomass burning medical waste +tire combustion diesel gasoline vehicular emissions

Table 3.29 PAHs diagnostic ratios from others studies.

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Table 3.29 PAHs diagnostic ratios from others studies (control	continued).
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Ratio	Source	References			
IND/(IND+BPER)					
< 0.37	bituminous coal	Alice 2011			
0.2-0.5	Liquid fossil fuel combustion	Wan-Li 2010			
0.6-0.64	rice straw burning	Jenkis 1996			
≤0.2	unburned petroleum (petrogenic)	Yunker 2002			
0.2-0.5	petroleum combustion				
>0.5	>0.5 grass, wood, coal combustion				
	لاستبيليل				
ANT/(ANT+CHR)					
0-0.3	almost	Alice 2011			
>0.64	asphalt produce + municipal waste combustion				
PHE/(PHE+ANT)					
> 0.7	> 0.7 lubricant and fossil fuels				
BbF/BkF		6			
>0.5	diesel	Pandey 1999, Park 2002			
PYR/BaP	LE SAL	AI			
~10	diesel	Ravindra 2009			
~1	gasoline				

FLA/(FLA+PYR), BaA/(BaA+CHR) and IND/(IND+BPER) were the conventional DRs to characterize the sources of PAHs in this study. Values of FLA/(FLA+PYR) and IND/(IND+BPER) higher than 0.5 indicated biomass burning (Kavourous *et al.*, 2001; Oros *et al.*, 2006; Dvorská *et al.*, 2011; Yunker *et al.*, 2002; Jenkis *et al.*, 1996), while the values lower than 0.5 indicated combustion fuel (Schauer *et al.*, 1999; Yunker *et al.*, 2002; Ma *et al.*, 2010). BaA/(BaA+CHR) higher than 0.35 indicated biomass burning (Alice *et al.*, 2011). FLA/(FLA+PYR),

BaA/(BaA+CHR) and IND/ (IND+BPER) vales were used in tertiary ratio method for PAHs source identification.

The tertiary ratio method for PAHs source identification involves a comparison of the ratios of pairs of frequently found PAH emissions. Those ratios were used in this study to find potential PAH sources (fuel combustion and biomass burning) in the dry and wet season 2010 and dry season 2011 (Figure 3.20).



Figure 3.20 Diagnostic ratios of PM10 – bound PAHs in the dry season of 2010, wet season of 2010 and dry season of 201

In the dry season of 2010, average values of FLA/(FLA+PYR), BaA/(BaA+CHR) and IND/(IND+BPER) ratios were 0.57 ± 0.05 , 0.88 ± 0.16 and 0.59 ± 0.06 , respectively. The calculated values were categorized as coming from the biomass-burning source >0.5 for (FLA/(FLA+PYR) and IND/(IND+BPER) and >0.34 for BaA/(BaA+CHR))) due to most values of DRs were in range of biomass burning in 3 dimensions of scatter plot. In wet season 2010, those values were 0.79 ± 0.30 , 0.58 ± 0.19 and 0.57 ± 0.21 , respectively. In dry season 2011, they were 0.54 ± 0.48 , 0.40 ± 0.13 and 0.71 ± 0.70 , respectively. The values in wet 2010 and dry 2011 were distributed on the lines at the border between fuel combustion and biomass burning, which did not clearly reveal the source.

3.8.2 Backward trajectory of air mass transfer

In order to gain more information on PM10 sources, both in terms of type and position (local or long range), backward trajectories of the air masses arriving at Chiang Mai during three periods (dry 2010, wet 2010, dry 2011), were analyzed by cluster analysis.

a) Air masses trajectory in dry season 2010

Air mass trajectory can be classified into 3 clusters for the dry season of 2010 (Figure 3.21).

The data of the dry season of 2010 (30 days in April 2010) were classified into 3 clusters. Clusters 1, 2, and 3 contained 33%, 37%, and 30%, respectively. All of them were originated from the continent in the west direction of Chiang Mai.



Figure 3.21 24-hours backward trajectory of clusters in dry season 2010

b) Air masses trajectory in wet season 2010

The air mass trajectory in wet season of 2010 was classified into 4 clusters as shown in Figure 3.22.

The air mass in cluster 1 (4%) and cluster 2 (9%), were originated from the Northern part of Vietnam and traveled over Northern of Laos and the Eastern part of Thailand before arriving Chiang Mai. The cluster 3 (29%) originated from the northern part of Laos. The major cluster was cluster 4 (58%), which was locally originated.



Figure 3.22 24-hours backward trajectories of clusters in wet season 2010

c) Air masses trajectory in dry season 2011

Air mass trajectory in the dry season of 2011 (January to March) was clustered into 4 groups (Figure 3.23).

The pattern of air mass movement was similar to that found in the rainy season. The frequency of all backward trajectories (90 day; 100%) was highest in cluster1 (76%) which came from western direction. It was originated in Myanmar and then moving to Mae Hong Son Province before approaching Chiang Mai. Cluster 2 (19%) was originated from the southeast of Chiang Mai while cluster 3 and 4 (1 and 4%, respectively) came from northern part and central of Laos.



Figure 3.23 24-hours backward trajectories of clusters in dry season 2011

3.8.3 Principal Component Analysis (PCA) for ambient PM10bound PAHs

Principal component analysis (PCA) has been applied to identify the sources of PM10-bound PAHs (Table 3.30) in the dry and wet season of 2010 and the dry season of 2011. In this statistical method a set of multiple inter-correlated variables is replaced by small number of independent variables (factors) by orthogonal transformations (rotations). This is achieved by diagnosing the correlation matrix of the variable, i.e., by computing their Eigen values. "Factor loadings" obtained after the varimax rotation give the correlation between the variables and the factors. Data are included in the matrix only if the Eigen value for the factor is greater than 1. The varimax procedure was adopted for rotation of the factor matrix to transfer the initial matrix into one that was easier to interpret. In the present study, the Statistical Package for Social Scientist (SPSS version 18.0) computer software was used to perform factor analysis. Results obtained by varimax rotated factor analysis

are given in Table 3.30 with loadings >0.5 are considered to be statistically significant (Masih, *et al.*, 2012).

In the dry season of 2010, most of PAHs (FLU, PYR, BaA, CHR, BkF, BaP, and BPER) had high loading in the first factor (69% of variance). They indicated biomass emissions by using the PCA loading from burning biomass in chamber. The second factor contained high loading of FLA, PYR, and BPER (12.25% of variance), which indicated traffic emission and biomass burning (Harrison *et al.*, 1996; Nielsen *et al.*,1996; Bzdusek *et al.*, 2004). Third factor had high loading of NAP and IND (9.10% of variance), which their potential sources remain unknown.

Four factor loadings were revealed in the wet season of 2010. Factor 1 contained 47.45% of variance with high loading of high molecular weight PAHs (CHR, BbF, BkF, IND, and BPER) and medium loading of ACY, PHE, BaA, which is associated with vehicle emission (Guo *et al.*, 2003; Harrison *et al.*, 1996; Fang *et al.*, 2004; Wang *et al.*, 2011). Factor 2 accounted for 15.35% of variance with high loading of NAP, FLA, and PYR, which indicated diesel emission (Caricchia *et al.*, 1999; Fang *et al.*, 2004). It can be seen that both factors suggested the same direction on an influence from traffic emission. High loading of PHE and ANT was found in the factor 3. They are markers of wood combustion (Ravindra *et al.*, 2006; Wang *et al.*, 2008; Bourotte *et al.*, 2005; Khalili *et al.*, 1995). The last factor contained high loading of ACE, FLU, and BaP (5.86 % of variance), which was unidentified.

Five loading factors were obtained in the dry season of 2011. Factor 1 contained FLA and PYR accounting for 35.50% of the total variances and suggesting diesel emission (Fang *et al.*, 2004; Caricchia *et al.*, 1999; Khalili *et al.*, 1995; Duval and Friedlander, 1981). Factor 2 (19.19% of the variance), contained BbF and BaP,

representing gasoline emission (Guo *et al.*, 2003; Fang *et al.*, 2004; Zhang *et al.*, 2008, Park *et al.*, 2002). Factor 3 had high loading of FLU, BaA, CHR, and BPER, which were considered as fossil fuels emission as main component and portion of them was associated with combustion sources (Harrison *et al.*, 1996; Nielsen *et al.*, 1996; Bzdusek *et al.*, 2004; Kong *et al.*, 2010). Those three factors shared the common traffic emission as the major pollutant source. Factor 4 (6.99% of variance) had high loading of NAP, PHE, ANT suggesting wood combustion (Ravindra *et al.*, 2006; Wang, *et al.*, 2008; Bourotte, *et al.*, 2005; Khalili *et al.*, 1995). The last factor contained 6.68% of variance with high loading of BbF and IND indicated vehicle emissions (Guo *et al.*, 2003; Simcik *et al.*, 1999; Rogge *et al.*, 1993).

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PAHs	Dry 2010 (n=11)			Dry 2010 (n=11) Wet 2010 (n=42)		Dry 2011(n=41)						
-	1	2	3	1	2	3	4	1	2	3	4	5
NAP	-0.047	0.219	0.944	-0.020	0.727	0.082	0.302	0.196	-0.454	0.365	0.623	0.137
ACY				0.649	-0.007	0.419	0.472					
ACE				0.402	0.002	0.446	0.606					
FLU	0.661	0.435	0.450	-0.421	0.363	-0.046	0.457	-0.031	0.372	-0.817	-0.058	-0.022
PHE				0.618	0.046	0.507	-0.132	-0.139	0.245	0.172	0.798	0.199
ANT				0.702	-0.222	0.544	-0.110	0.308	-0.079	0.054	0.786	-0.013
FLA	0.101	0.878	-0.044	0.096	0.837	0.055	-0.296	0.955	-0.002	0.013	0.035	0.045
PYR	0.682	0.614	-0.046	-0.209	0.857	-0.190	0.031	0.967	-0.050	0.041	-0.025	-0.061
BaA	0.939	0.063	-0.040	0.716	0.448	-0.030	-0.061	0.144	-0.223	0.720	0.440	0.155
CHR	0.841	0.453	-0.022	0.876	0.004	0.097	-0.055	0.099	0.465	0.629	0.095	0.320
BbF				0.879	-0.097	0.224	-0.079	0.200	0.182	0.166	0.309	0.713
BkF	0.904	0.275	0.205	0.891	-0.013	0.069	-0.125	-0.032	0.876	-0.001	0.027	-0.052
BaP	0.824	0.117	0.380	0.340	0.064	0.219	-0.636	-0.031	0.828	-0.127	-0.092	0.189
IND	0.378	-0.235	0.751	0.881	-0.084	-0.114	0.072	0.316	0.350	0.188	0.016	0.720
BPER	0.755	0.603	0.174	0.875	-0.243	0.051	-0.018	0.154	0.320	0.738	0.132	0.160
% of Variance	68.92	12.25	9.10	47.45	15.35	8.47	5.86	35.5	19.19	13.65	6.99	6.68
Cumulative %	68.92	81.17	90.27	47.45	62.8	71.27	77.13	35.5	54.69	68.34	75.33	82.01
Possible source	biomass burning	traffic , biomass burning	unknown	vehicle emission	diesel emission	wood combustion	unknown	vehicle emission	diesel emission	traffic emission	wood combustion	vehicle emissions
	a	60	ns	IJŃ	19	ng	18	SU	BG	Ûl	ήIJ	

Table 3.30 PCA for PM10-bound PAHs in the dry and wet season of 2010 and the dry season of 2011

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