

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
ENGLISH ABSTRACT	iv
THAI ABSTRACT	vii
LIST OF TABLES	xv
LIST OF FIGURES	xviii
ABBREVIATIONS AND SYMBOLS	xxi
CHAPTER 1 INTRODUCTION	
1.1 Air pollution; situation in Asia	1
1.2 Particulate Matter	5
1.3 Polycyclic aromatic hydrocarbons (PAHs)	7
1.3.1 Definition and sources	7
1.3.2 Mechanisms and effects	12
1.4 Biomass	16
1.4.1 Biomass classification	16
1.4.2 Biomass composition	18
1.5 Sampling artifact	20
1.6 Gas Chromatography Mass Spectrometry (GC-MS) for PAHs analysis	23

1.6.1	Chromatographic retention	28
1.7	Geographical background, population and economic structure of Chiang Mai Province	30
1.8	Emission of atmospheric PAHs from various sources	31
1.9	Chamber for burning experiment	36
1.10	Research Objectives	38
CHAPTER 2 EXPERIMENTAL		39
2.1	Apparatus and chemicals	39
2.1.1	Instrument	39
2.1.2	Equipment and Apparatus	39
2.1.3	Chemicals	41
2.2	Experimental framework	42
2.3	Site description and collecting method for biomass samples	43
2.3.1	Sampling sites for biomass residues	43
2.3.2	Collecting and preparation of biomass	47
2.4	Biomass burning experiment	49
2.4.1	Design of a stainless steel chamber for biomass burning	49
2.4.2	Operation of the chamber	51
2.4.3	Preparation of biomass samples for burning experiment	51

2.5	Sampling of PM10 in Ambient air	53
2.5.1	PM10 sampling site	53
2.5.2	Sampling duration	53
2.6	Preparation of PAH and internal standard solution	55
2.6.1	Preparation of mixed 16 PAHs standard solution	55
2.6.2	Preparation of mixed internal standards	55
2.7	Optimization of ultrasonic extraction	56
2.8	PM10 sample extraction and analysis	56
2.9	Optimization GC-MS condition	57
2.10	Quality control of PAHs analysis	59
2.10.1	Use of standard reference materials (SRM)	59
2.10.2	Use of spiking method	60
2.10.3	Precision of analysis method	60
2.11	Detection limit of GC-MS for 16-PAHs analysis	61
2.12	PM10 and PAHs source determination	61
2.12.1	Data analysis of ambient PM10 and PAHs	61
2.12.2	Data analysis of PM10 and PAHs from biomass burning in the chamber	64
CHAPTER 3 RESULTS AND DISCUSSION		65
3.1	Method validation for PAHs analysis by GC-MS	65
3.1.1	Accuracy of PAHs analysis by GC-MS	65

3.1.2	Precision	67
3.1.3	Instrument detection limit	69
3.1.4	Standard calibration curve	71
3.2	Composition of biomass samples	76
3.2.1	Moisture content	76
3.2.2	C, H and N composition	76
3.3	PM ₁₀ and PAHs emitted from biomass burning in the chamber	78
3.3.1	PM ₁₀ and PM ₁₀ -bound PAHs from biomass burning	78
3.3.2	Correlation of PM ₁₀ and PAHs	81
3.3.3	Emission Factors of PM ₁₀ and PAHs from biomass burning	87
3.3.4	PAHs profiles emitted from biomass burning	90
3.3.5	Diagnostic ratios of PAHs for biomass burning	93
3.3.6	Principle Component Analysis (PCA) of PAHs for biomass burning	95
3.3.7	Emission rates (ERs) of PM ₁₀ and PAHs from open burning	97
3.4	Ambient PM ₁₀ concentrations at CMU site	99
3.4.1	PM ₁₀ concentrations and their seasonal variation	99
3.4.2	Correlations between PM ₁₀ concentrations	105

obtained from a minivolume air sampler (SCB1-CMU) and AQM of PCD (CH and YP).	
3.5 PM ₁₀ -bound PAHs	107
3.6 Correlations between PM ₁₀ and PAHs concentrations; PM ₁₀ and hotspots	113
3.6.1 Correlations of PM ₁₀ and individual PAH in each season	113
3.6.2 Seasonal correlations between PM ₁₀ and its PAHs content (tPAHs, ncPAHs and cPAHs)	118
3.6.3 Correlations between PM ₁₀ and the number of hotspots	118
3.7 Assessment of possible health effects based on PAHs concentrations	121
3.7.1 Toxicity equivalent concentration (TEQ) of PAHs	121
3.7.2 The inhalation lung cancer risk (ILCR) assessment	123
3.8 Sources apportionment of PM ₁₀ - bound PAHs	124
3.8.1 Diagnostics Ratios (DRs)	124
3.8.2 Backward trajectory of air mass transfer	128
3.8.3 Principal Component Analysis (PCA) for ambient PM ₁₀ -bound PAHs	131
CHAPTER 4 DISCUSSIONS	135
REFERENCES	138
APPENDICES	154

Appendix A	155
Appendix B	159
CURRICULUM VITAE	172

LIST OF TABLES

Table	Page
1.1 U.S. EPA priority 16-PAHs	11
2.1 General information of selected districts for biomass sampling	43
2.2 Sampling sites, sample types and sample numbers	46
2.3 Composition and function of the combustion chamber	50
2.4 General information of biomass burning in the combustion chamber	52
2.5 GC-MS conditions for 16-PAHs analysis	57
2.6 Characteristic ions for PAHs	58
2.7 Certified values of SRMs urban dust NIST 1649b	59
3.1 Percent recoveries of 16- PAHs from extraction of the SRM urban dust (NIST 1649b) and spiking method	67
3.2 Repeatability of standard preparation measured by GC-MS	68
3.3 Reproducibility of standard preparation measured by GC-MS	69
3.4 Instrument detection limit of GC-MS	70
3.5 Calibration equations and variation coefficient of PAHs	73
3.6 Moisture content of biomass residues	76
3.7 C, H, N content of biomass residues	77
3.8 PM10 emitted from biomass burning in the combustion chamber	79
3.9 PM10-bound PAHs from biomass burning in the combustion chamber	80
3.10 Correlation coefficients of PM10 and PM10-bound PAHs (rice straw)	83
3.11 Correlation coefficients of PM10 and PM10-bound PAHs (maize residues)	84

3.12	Correlation coefficients of PM10 and PM10-bound PAHs (leaf litter)	85
3.13	Correlation between PAHs and PM10 from biomass burning	86
3.14	Emission Factors of PM10 and PAHs from leaf litter, maize residue and rice straw burning in the chamber and TEQ of PAHs	88
3.15	Diagnostics ratio form biomass burning from this study	95
3.16	PCA for biomass burning from biomass burning	96
3.17	Total area, burnt area and percentages of burnt area of forest, rice field and crop in Chiang Mai during dry season of 2010 and 2011	97
3.18	PM10 and PAH emission rate from leaf litter, maize and rice straw in year of 2010 and 2011	98
3.19	PM10 concentrations in each season	101
3.20	Monthly pressure, temperature, relative humidity, precipitation in this study period.	103
3.21	Concentrations (ng/m ³) of PM10- bound PAHs in dry 2010, wet 2010 and dry 2011	109
3.22	Correlation coefficients of PM10, PM10-bound PAHs in dry season 2010	113
3.23	Correlation coefficients of PM10, PM10-bound PAHs in wet season 2010	116
3.24	Correlation coefficients of PM10, PM10-bound PAHs in dry season 2011	117
3.25	Correlations of PM10 and PAHs concentrations in each sampling period	119

3.26 Toxicity equivalent factors (TEF _i)	121
3.27 TEQs values of PAHs in ambient air of Chiang Mai	122
3.28 Yearly average of ILCR in Chiang Mai	123
3.29 PAHs diagnostic ratio from others studies	125
3.30 PCA for PM ₁₀ -bound PAHs in dry and wet 2010 and dry 2011	134

LIST OF FIGURES

Figure	Page
1.1 Mass and number distribution of particles	6
1.2 Structures of 16-PAHs compound	10
1.3 General formation schemes of PAHs, PCDDs, and PCDFs	14
1.4 Biomass structure	20
1.5 A schematic of GC-MS	24
1.6 A schematic of an ion source	25
1.7 A schematic of a quadrupole analyzer	26
1.8 Retention time	28
1.9 The calculation parameters of adjacent peak pair resolution	29
2.1 Diagram of experimental framework	42
2.2 Map of biomass sampling sites in Chiang Mai Province	45
2.3 Grid of biomass sample collection	47
2.4 Biomass sampling for (a) rice straw, (b) maize residues and (c) leaf litter	48
2.5 Schematic diagram of a chamber	49
2.6 Combustion chamber; (A) combustion part and (B) air pollutant storage part	50
2.7 Biomass samples: rice straw (RS), maize residues (M) and leaf litter (L)	52
2.8 Location of sampling site (SCB1)	53
2.9 PM10 sampling by a Minivol air sampler at CMU	54
3.1 Percent recoveries of 16-PAHs from different extraction methods.	66

3.2	Chromatogram obtained with A; 0.08 µg/ml of 16-PAHs B; sample from biomass burning in chamber C; sample from ambient air and 2 internal standards using GC-MS..	72
3.3	Standard calibration curves of 16-PAHs	74
3.4	PM ₁₀ samples on quartz fiber filter from burning of (a) rice straw, (b) maize residues and (c) leaf litter in the combustion chamber	78
3.5	Concentrations of tPAHs, ncPAHs and cPAHs and the relative percentage of ncPAHs and cPAHs from biomass burning.	90
3.6	Profiles of PAHs emitted from the burning of leaf litter in the chamber	91
3.7	Profiles of PAHs emitted from the burning of maize residues in the chamber	92
3.8	Profiles of PAHs emitted from the burning of rice straw in the chamber	92
3.9	Relative percentages of PAHs emitted from leaf litter, maize residues and rice straw burning	93
3.10	Loading scatter plot of PAHs from biomass burning	96
3.11	Comparison of PM ₁₀ concentrations in ambient air obtained from minivolume air sampler (SCB1-CMU) and AQM stations (CH and YP)	100
3.12	Pattern of PM ₁₀ concentrations in Chiang Mai atmosphere obtained from City Hall station during 2006-2011.	102
3.13	Monthly precipitation and number of rainy day in 2010 and 2011 in Chiang Mai	104
3.14	Correlation between PM ₁₀ concentrations obtained from mini volume air sampler (SCB1-CMU) and TEOM (AQM stations).	106

3.15	Concentrations of ambient PM ₁₀ , PM ₁₀ -bound PAHs and ratio of cPAHs and ncPAHs	110
3.16	The ratio cPAHs and ncPAHs	111
3.17	The relative percentage of PAHs	111
3.18	Concentrations of PM ₁₀ and PM ₁₀ -PAHs from ambient air samples	112
3.19	Scatter plots between PM ₁₀ concentrations and number of hotspots	120
3.20	Diagnostics ratio of PM ₁₀ – bound PAHs in dry season 2010, wet season 2010 and dry season 2011	127
3.21	24-hours backward trajectory of clusters in dry season 2010	129
3.22	24-hours backward trajectories of clusters in wet season 2010	130
3.23	24-hours backward trajectories of clusters in dry season 2011	131


ABBREVIATIONS AND SYMBOLS

$\mu\text{g}/\text{m}^3$	=	Microgram per cubic meter
$\mu\text{g}/\text{mL}$	=	Microgram per liter
$\mu\text{g}/\text{gPM}_{10}$	=	Microgram per gram of PM ₁₀
$\mu\text{g}/\text{kg}_{\text{dry}}$	=	Microgram per kilogram of biomass dry
μm	=	Micro-meter
μl	=	Micro-liter
ACE	=	Acenaphthylene
ACY	=	Acenaphthene
ANT	=	Anthracene
ASD	=	Asian dust storms
ATSDR	=	Agency for Toxic Substances and Disease Registry
AQM	=	Air Quality Monitoring
BaA	=	Benz[a]anthracene
BaP	=	Benzo[a]pyrene
BeP	=	Benzo[e]pyrene
BbF	=	Benzo[b]fluoranthene
BkF	=	Benzo[k]fluoranthene
BPER	=	Benzo[g,h,i]perylene
C	=	Carbon
CD	=	Chiang Dao district

CHR	=	Chrysene
CI	=	Chemical ionization
CMU	=	Chiang Mai University
CH	=	City Hall of Chiang Mai Province
CO	=	Carbon monoxide
COR	=	Coronene
cPAHs	=	Carcinogenic polycyclic aromatic hydrocarbons
CYC	=	Cyclopenta[c,d]pyrene
DBA	=	Dibenz[a,h]anthracene
D ₁₀ -ACE	=	D ₁₀ -Acenaphthene
D ₁₂ -PER	=	D ₁₂ -Perylene
DK	=	Doi Saket district
DRs	=	Diagnostic ratios
EF	=	Emission factor
EI	=	Electron ionization
ERs	=	Emission rates
EPA	=	Environment Protection Agency
FBC	=	Fluidized bed combustion
FLA	=	Fluoranthene
FLU	=	Fluorene
GC-MS	=	Gas chromatography mass spectrometry
Gg/y	=	Gigagram per year
H	=	Hydrogen

HP	=	High purity
HYSPLIT	=	Hybrid single particle langrangian integrated trajectory
ILCR	=	Inhalation lung cancer risk
IND	=	Indeno[1,2,3-cd]pyrene
IS	=	Internal standards
IARC	=	International Agency for Research on Cancer
km	=	kilometer
km ²	=	Square kilometer
kg	=	kilogram
L	=	Leaf litter
m	=	Meter
max	=	Maximum
min	=	Minimum
m/z	=	Mass per
ml	=	Milliliter
mg	=	Milligram
mm	=	Millimeter
mm Hg	=	Millimeter of Mercury
M	=	Maize residues
MC	=	Mea Chaem
MW	=	Molecular weight
Mg	=	Mega gram
MR	=	Mae Rim district
n	=	number of sample

ncPAHs	=	Non carcinogenic polycyclic aromatic hydrocarbons
ng	=	Nanogram
ng/m ³	=	Nanogram per cubic meter
N	=	Nitrogen
NAAQS	=	Nation Ambient Air Quality Standard
NAP	=	Naphthalene
ND	=	Non detected
NO _x	=	Nitrogen Oxide
O	=	Oxygen
PAC	=	Polycyclic aromatic compounds
PAHs	=	Polycyclic aromatic hydrocarbons
PCA	=	Principal Component Analysis
PCD	=	Pollution control department
PCDFs	=	Polychlorinated dibenzofurans
PCDDs	=	Polychlorinated dibenzopdioxin
PHE	=	Phenanthrene
PM	=	Particulate matter
PM1.0	=	Particulate matter (diameter less than 1.0 µm)
PM2.5	=	Particulate matter (diameter less than 2.5 µm)
PM10	=	Particulate matter (diameter less than 10 µm)
PR	=	Plain rice straw
PYR	=	Pyrene
RDF	=	Refuse-derived fuel
RS	=	Rice straw



Rs	=	Resolution
SD	=	Standard deviation
SIM	=	Selected Ion Monitoring
SRM	=	Standard reference material
SCB1	=	Science complex building 1
SPSS	=	Statistical package for the social sciences
SO ₂	=	Sulfur dioxide
TEF	=	The toxic equivalent factors
TEQ	=	The toxicity equivalent concentration
TSP	=	Total Suspended Particulate matter
tPAHs	=	Total polycyclic aromatic hydrocarbons
US	=	United States
VOCs	=	Volatile organic compounds
WHO	=	World Health Organization
YP	=	Yuppraraj Wittayalai School