CHAPTER 2

EXPERIMENTAL

2.1 Apparatus, chemicals and instruments

2.1.1 Apparatus

1) 100 to 1000 µl and 1 to 10 mL micropipette, Brand, Germany
2) 5, 10 mL graduate pipette, Witeg, Germany
3) 10, 20 mL transfer pipette, Witeg, Germany
4) 2000 mL volumetric flask, Technico, England
5) 5, 10, 1000 mL volumetric flask, Duran, Germany
6) 25, 50, 100 mL polypropylene volumetric flask, Kartell, Italy
7) 50, 100, 250, 400, 600 mL beaker, Duran, Germany
8) 1000, 2000 mL bottle, Duran, Germany
9) 1000 mL funnel, Alltech, Belgium
10) In-line filter cap, Alltech, Belgium
11) Stainless steel mesh filter support ring, Alltech, Belgium
12) 0.45 µm, 47 mm nylon membrane filter, Vertical, Thailand
13) 0.45 µm, 13 mm cellulose acetate syringe filter, Vertical, Thailand
14) Polypropylene tube, NIPRO (Thailand) Corp., Ltd., Thailand
15) Polypropylene test tube with cap 50 mL
16) Four-Stage filter holder, Nilu, Norway
17) Filter membrane (F0), 1.0 µm, 47 mm polytetrafluoro-ethylene (PTFE), Whatman 41, UK

18) Filter membrane (F1), 1.0 µm, 47 mm polyamide, Pall, USA
19) Filter membrane (F2, F3), No. 41, 47 mm cellulose, Whatman, UK
20) Filter paper chromatography, No.590, 400 x 400 mm cellulose, ADVANTEC, Japan
21) Thermometer, Brannan, England
22) Plastic bucket
23) Plastic tweezers
24) Petri dish plastic
25) Desiccators
26) Stainless steel roller blade cutter

2.1.2 Chemicals

1) Acetate (CH_3COO^-) standard solution 1000 µg/mL, AccuSPEC, Canada
2) Formate ($HCOO^-$) standard solution 1000 µg/mL, AccuSPEC, Canada
3) Chloride (Cl^-) standard solution 1000 µg/mL, Merck, Germany
4) Nitrate (NO_3^-) standard solution 1000 µg/mL, Merck, Germany
5) Phosphate (PO_4^{3-}) standard solution 1000 µg/mL, Merck, Germany
6) Sulfate (SO_4^{2-}) standard solution 1000 µg/mL, Merck, Germany
7) Sodium (Na^+) standard solution 1000 µg/mL, Merck, Germany
8) Ammonium (NH_4^+) standard solution 1000 µg/mL, Merck, Germany
9) Potassium (K^+) standard solution 1000 µg/mL, Merck, Germany
10) Calcium (Ca^{2+}) standard solution 1000 µg/mL, Merck, Germany
11) Magnesium (Mg^{2+}) standard solution 1000 µg/mL, Merck, Germany
12) Sodium carbonate anhydrous (Na_2CO_3), 99.9%, Scharlau, Spain

13) Sodium hydrogen carbonate ($NaHCO_3$), 99.7%, Scharlau, Spain

14) Sulfuric acid (H_2SO_4), 95-97%, Merck, Germany

15) Nitric acid (HNO_3), 65%, Merck, Germany

16) 2,6-Pyridinedicarboxylic acid, 99%, Sigma-Aldrich, India

17) Potassium carbonate (K_2CO_3), 99%, QRëC, New Zealand

18) Ortho-Phosphoric acid (H_3PO_4), 85%, Labscan, Thailand

19) Hydrogen Peroxide (H_2O_2), 40% m/v in water, Carlo Erba, Italy

20) Thymol (2-isopropyl-5-methyl phenol), 99.5%, Labchem , Australia

21) Powdered Precision Cleaner, Alconox, USA

22) Deionized water (conductivity < 0.15 mS/m), Chemistry Department, Chiang Mai University

23) Milli Q water , Chemistry Department, Chiang Mai University

2.1.3 Instruments

1) Analytical balance, AB304-S, Mettler Toledo, Switzerland

2) Analytical balance, Pioneer PA4102, Ohaus, USA

3) Microbalance, MX5, Mettler Toledo, Switzerland

4) Ultrasonicator, P 300 H, Elma, Germany

5) Ultrasonicator, T 490DH, Elma, Germany

6) Ultrasonicator, 690D, Crest, Malaysia

7) Oven, UE 400, Memmert, Germany

8) Vacuum pump, Rocker 300, Keika Ventures, USA

9) Vacuum pump, CP 6 P M 7488 1, Millipore, USA

10) Moisture analyzer, MA50, Sartorius, Germany

11) CHNS/O analyzer, PE2400 Series II, Perkin Elmer, USA

12) Conductivity meter, CyberScan CON 1500, Eutech, Singapore

13) Conductivity meter, D-82362, Inolab, Germany

14) pH meter, 744, Metrohm, Switzerland

15) Wet-only collector, Model 301, Acrochem Metrics Inc., USA

16) Combustion chamber, consisting of

    a) Gas analyzer, 350-XL, Testo, Germany

    b) Temperature sensor, 6 Channel Temperature Indicator, Thailand

    c) Rotating-Vane Vacuum Pump, FY-1.5B, Mizu, Thailand

17) MiniVol^{TM} Tactical Air Sampler, AIRmetrics, USA, consisting of

    a) MiniVol^{TM} TAS Pump Module

    b) Programmable Timer

    c) Battery Packs and a Battery Charger

    d) Filter Holder Assemblies with customer selected size selective inlets

    e) Cassette and Cassette separator

    f) 47 mm Quartz fiber filter, CAT No. 1851-047, Whatman, UK

    g) All Weather Carrying Case

    h) Universal Mounting Bracket or Light Weight Tripod

    i) Grease

18) Rotavapor, R-215, Büchi Labortechnik AG, Switzerland, consisting of

    a) Vacuum Controller, V-850

    b) Rotavapor, R-215

    c) Heating Bath, B-491

    d) Vacuum Pump, V-700

e) Cooling, CTL 901

f) Glass assembly V

g) Woulff bottle

19) Ion Chromatograph, 882 Compact IC plus, Metrohm, Switzerland, consisting of

a) 838 Advanced Sample Processor

b) Anion guard column, Metrosep A Supp 4/5 Guard

c) Anion separation column, Metrosep A Supp5 250/4.0 mm

d) Anion self-generating suppressor

e) Cation guard column, Metrosep RP 2 Guard/3.5

f) Cation separation column, Metrosep C4-100/4.0 mm

g) Conductivity detector

h) Output, MagIC Net 2.6

2.2 Experimental framework

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

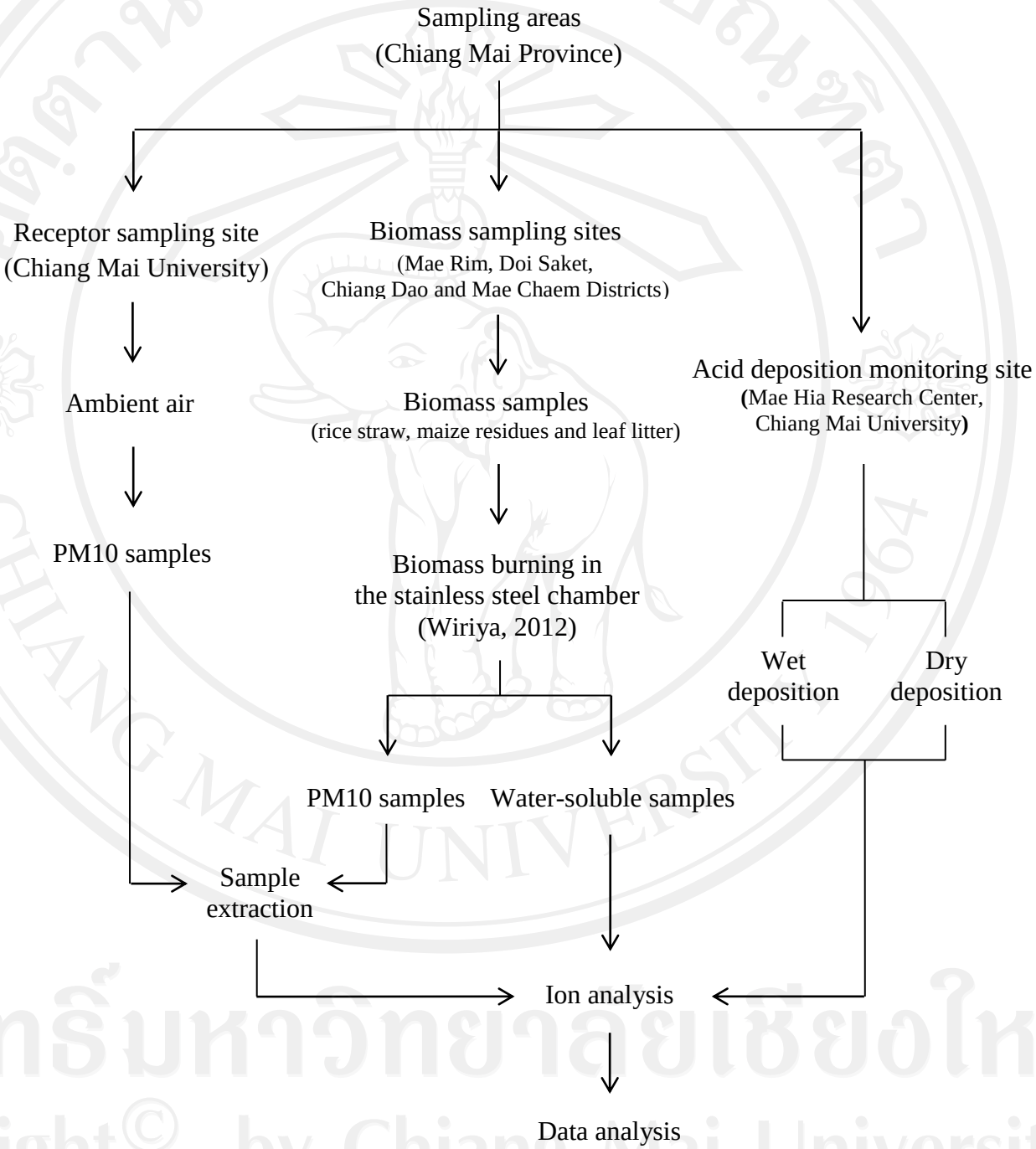

Figure 2.1 Diagram of experimental framework

2.3 Ion chromatography

2.3.1 Preparation of eluent

1) Preparation of eluent for anion analysis

A mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ solution was used as an eluent. The eluent stock solution was prepared by dissolved 3.4046 g Na_2CO_3 and 0.8426 g $NaHCO_3$ in deionized water and diluted with the resultant solution to 100 mL volumetric flask. This stock solution was then used to prepare a solution of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ by pipetting 20 mL of it into 2000 mL volumetric flask and adjusted volume by deionized water. Anions were identified using a Metrosep A Supp 4/5 guard column, a Metrosep A Supp5 250/4.0 mm analytical column and an anion self-regenerating suppressor. The system was regenerated by a solution of 100 mM H_2SO_4 pumped through a suppressor unit simultaneously with deionized water.

2) Preparation of eluent for cation analysis

The eluent solution for cation analysis was 1.7 mM HNO_3 and 0.7 mM 2,6-pyridinedicarboxylic acid. 237 µL of HNO_3 was pipetted using micropipette. 0.236 g of 2,6-pyridinedicarboxylic acid was weighed. They were mixed and dissolved in deionized water before adjusted the volume to 2000 mL in a volumetric flask. Cations were identified using a Metrosep RP 2/3.5 guard column and a Metrosep C4-100/4.0 mm analytical column.

Because the system inlet line was very small, therefore air or small particles in eluents could block in the system, causing baseline noise and shortening the life-time of the column. Both of eluents (for anion and cation analysis) were filtered by a

filter holder set with nylon membrane filter (pore size 0.45 µm, 47 mm diameter) and degassed by vacuum and ultrasoniccation prior to analysis.

2.3.2 Analysis of ions

An ion chromatograph (882 Compact IC plus, Metrohm, Switzerland) was used for the determination of major anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and major cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}). The analysis conditions of ion chromatograph are detailed in Table 2.1

Table 2.1 Conditions of ion chromatograph for anion and cation analysis

Analysis item	Anions	Cations
Eluent	3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$	1.7 mM HNO_3 and 0.7 mM 2,6-Pyridinedicarboxylic acid
Guard column	Metrosep A Supp 4/5	Metrosep RP 2/3.5
Analysis column	Metrosep A Supp5 250/4.0 mm (250×4.0 mm)	Metrosep C4-100/4.0 mm (100×4.0 mm)
Carrier material	Polyvinyl alcohol with quarternary ammonium groups	Silica gel with carboxyl groups
Suppressor	Anion self-regenerating suppressor with DI water/100mM H_2SO_4	-
Particle size	5 µm	5 µm
Max. pressure	15 MPa	20 MPa
Flow rate	0.70 mL/min	0.90 mL/min
Temperature	20-60 ºC	20-60 ºC
pH range	3-12	2-7
Injection loop	20.0 µL	20.0 µL
Detector	Conductivity	Conductivity

2.3.3 Analytical characteristics for ion analysis

1) Repeatability

The repeatability is the closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and after short intervals of time) (IUPAC Compendium of Chemical Terminology, 2012). The repeatability was checked by 5 times continuously injection of a 0.8 µg/mL mixed standard solution of anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into IC under the optimum conditions.

2) Reproducibility

The reproducibility is the closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or after different intervals of time) (IUPAC Compendium of Chemical Terminology, 2012). The reproducibility was checked by injecting a 0.8 µg/mL mixed standard solution anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into IC under the optimum conditions for 5 weeks (once a week).

The results of the repeatability and reproducibility were estimated by standard deviation and the relative standard deviation (RSD) as calculated by using Equation 2.1.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100 \qquad \text{Eq. 2.1}$$

Where % RSD is a percentage relative standard deviation

SD is a standard deviation

$\bar{x}$ is an average value

3) Limit of detection (LOD) and limit of quantification (LOQ)

The LOD is the lowest concentration of the analyte that can be detected with a given degree of confidence. LOQ is a parameter for quantitative assays for low levels of compounds in the sample matrices and used particularly for determination products or low levels of active constituent in a product.

The LOD and LOQ were checked by injecting 5 times of the lowest concentration (0.1 µg/mL) of mixed anions standard (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and the lowest concentration (0.05 µg/mL) of mixed cations standard (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into ion chromatographic system under the optimum conditions. The LOD was obtained from 3 times, while LOQ was obtained from 10 times, of standard deviation from measurement of standard solution (US EPA, 2010).

2.3.4 Preparation of calibration curve

For quantitative analysis, a calibration curve for individual ion species was constructed. The commercial individual ion standard solution (1000 µg/mL) from Merck and AccuSPEC Company was used as stock solution. Mixed standard solution of anions was prepared and diluted with deionized water to concentration of 10 µg/mL. The 10 µg/mL standard solution was used for preparation of working standard

solutions, which ranged from 0.05-8 µg/mL. The same process was done for cations standard solution.

Mixed standard solutions were injected into ion chromatograph (IC) columns under optimum conditions. In case that the concentration of ion in some samples is higher than the range of calibration, those samples are diluted to obtain a concentration within the range of calibration. The dilution factor is multiplied afterwards to gain the true sample concentrations. The working standard solutions were freshly prepared from the mixed stock standard solution every analysis day. The important point, mixed standard was prepared in a polypropylene volumetric flask to avoid ion exchange. Then calibration curve of each ion was plotted between peak areas (y axis) against ion concentrations (x axis).

2.4 Optimization of extraction conditions for PM10-bound ions

Extraction conditions of ions in PM10 samples using ultrasonication including temperature, extraction volume of deionized water and time were optimized. PM10 samples are collected on quartz filters, therefore clean fresh quartz filters are also extracted and used as a blank for optimization of PM10-bound ion extraction conditions.

Half of a quartz filter was put into a 250 mL beaker, and then 0.3 mL of 100 µg/mL mixed anions standard solution (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were spiked onto the filter and left for 15 minutes before extraction. Then deionized water (30, 45 and 60 mL) was added and covered with paraffin film to each beaker. The final concentrations were 0.5, 0.7 and 1.0 µg/mL. Time duration for ion extraction including 15, 30 and 45 minutes were performed. Temperature of water in

the water bath of the ultrasonicator was set at 35 and 45 ºC for each batch of extraction. All conditions (n = 18) were extracted for 3 replications. All samples (n = 54) were extracted using an ultrasonicator with the power effective of 380 Watt (P 300 H, Elma, Germany). Extracted solution was filtered with a cellulose acetate membrane packed inside a syringe. The solution was then analyzed for anions by IC. The percent recovery of each ion was calculated to illustrate the extraction efficiency by using Equation 2.2.

$$\% \text{ Recovery} = \frac{MV}{SV} \times 100 \qquad \text{Eq. 2.2}$$

Where MV is a measured value

SV is a spiked value

The best condition (35 ºC, 45 mL deionized water, 30 minutes) from optimization of anions extraction was selected for a further optimization of extraction conditions for cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions. Concentrations of the spiked solutions after extraction were adjusted to 0.1, 0.3, 0.5, 0.8 and 1.0 µg/mL (low concentration series) and 2, 4 and 8 µg/mL (high concentration series). The concentrations of 0.1, 0.3, 0.5, 0.8 and 1.0 µg/mL were prepared by spiking 0.3 mL of 15, 45, 75, 120 and 150 µg/mL of mixed cation and anion standard solutions, respectively on the quartz fiber filter. After that 45 mL of deionized water were added. Similarly, 2.4 mL of 37.5, 75 and 150 µg/mL of the mixed cation and anion standard solutions were spiked onto the filters following with 45 mL of deionized

water to obtain final concentrations of 2, 4 and 8 µg/mL, respectively. Three replications were performed for each concentration. The quartz filters containing mixed cations (n = 24) and anions standard solution (n = 24) were extracted in 45 mL deionized water using an ultrasonicator for 30 minutes under controlled temperature of 35 ºC. The extracted solution was filtered and analyzed by IC. Percent recovery of the individual ion at each concentration was calculated according to Equation 2.2.

2.5 PM10 sampling from ambient air

2.5.1 PM10 sampling site

The sampling site is at the roof top of the nine-storey Science Complex Building1 (SCB1), Chiang Mai University. It is located at latitude 18^{o} 48' 5" N and longitude 98^{o} 57' 12" E (Figure 2.2). The elevation is 373 m above mean sea level. This sampling site is selected for PM10 monitoring to avoid effects from traffic emission.

Figure 2.3 shows PM10 sampling from ambient air by mini volume air sampler at roof top of the SCB1.

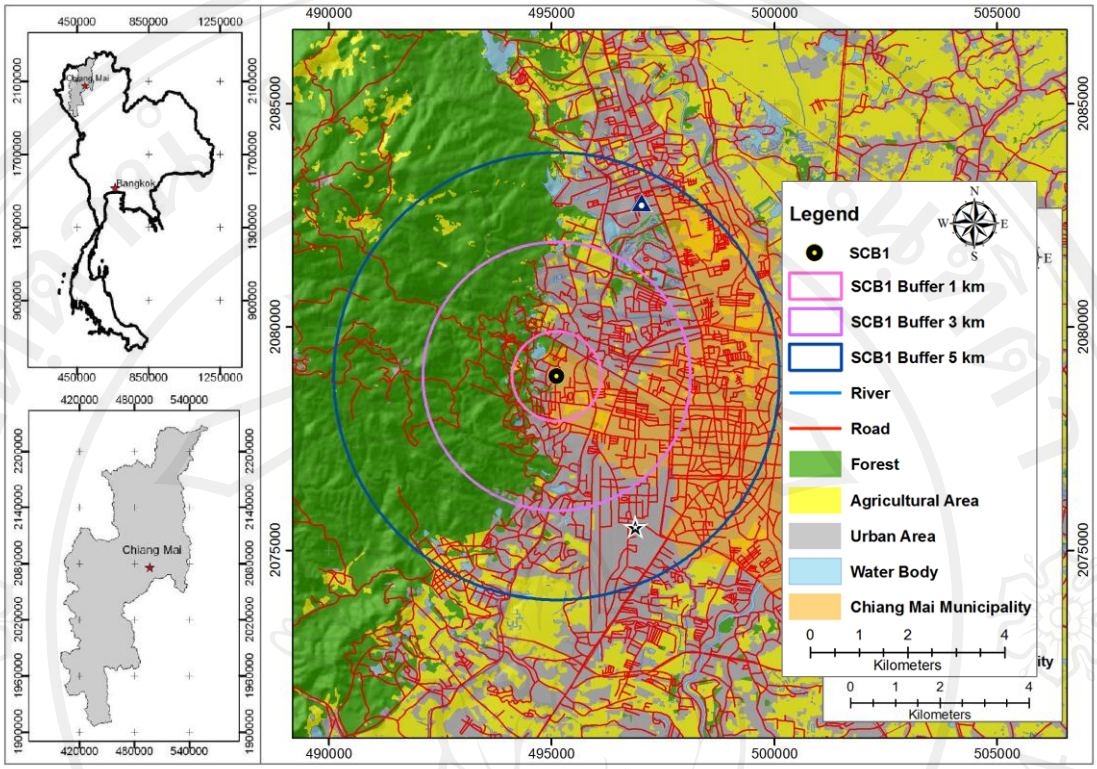

Figure 2.2 Land use profile of sampling site (SCB1)

Figure 2.3 PM10 sampling by mini volume air sampler at roof top of the SCB1

2.5.2 Sampling duration

PM_{10} samples from ambient air were collected in dry season (27 February to 19 April 2010) and wet season (15 July to 8 August 2010). Sampling frequency was on a daily basis for dry season (n = 51) and twice a week in wet season (n = 7). Samples were collected at the same time from the same site within a period of 24 hrs.

2.5.3 PM10 sampling

Steps of PM10 sample collection by a mini volume air sampler are described as follows.

1) The pre-exposed quartz filter (Ø 47 mm, Whatman, UK) was weighed by using six point microbalance weight scale (Mettler Toledo, Switzerland). Each filter was weighed at least three times before and after sampling. It was stored in desiccators before and after sampling for at least 24 hours.
2) Before the PM_{10} sampling started at each sampling site, the actual flow rate of the mini volume air sampler (Airmetrics, USA) was calibrated by measuring transfer standard pressure of manometer in inches of water at different rotameter indication in range of 4.0-6.5 L/min (Appendix A).
3) The mini volume air sampler was placed 1.5-2.0 m above ground at each sampling site. A weighed filter was inserted into a pre-separator. Two or three drops of grease solutions in hexane were dripped onto an impactor, in order to restrain unwanted PM sizes, whereas the selected size of sample was passed through the filter. Air was automatically pumped with a flow rate of 5 L/min through a particle size separator for 24 hours. Parameters

required include ambient temperature, barometric pressure, sampling date and time.

4) After 24 hours sampling, the filter was kept in a petri dish plastic, then transferred into desiccators before post-exposure weight. PM_{10} concentration was reported in terms of $\mu g/m^3$. The PM_{10} sample was kept under cool conditions in a freezer, waiting for extraction.

2.5.4 PM10 extraction

After the sampling and the sample preparation, a sampling filter was cut into two half by a stainless steel roller blade cutter. One half was for metal analysis (Chaichana, 2011), while another half was for ion analysis in this work. PM10 samples from ambient air were extracted under the optimum condition obtained from the topic 2.4.

2.5.5 Chemical analysis

The extraction solution was divided into two parts. The first part (25 mL) was for measurement of electro-conductivity (EC) and pH. The second part (20 mL) of the extraction solution was filtered by cellulose acetate syringe filter (pore size 0.45 μm, Ø 13 mm) and analyzed for anions and cations by IC.

1) Electro-conductivity

The Electro-conductivity (EC) is the simply method to determine the total dissolved inorganic substances in solution. EC of the samples were measured by

CyberScan CON 1500, Eutech, Singapore. The measurement was expressed in mS/m unit. During the measurement temperature of water bath was controlled at 25 °C.

2) pH

The pH of sample is determined electrometrically, using pH standard solutions with a glass electrode in combination with a reference electrode. In this study, Metrohm pH meter was used. Using instrument that has temperature compensation can control the temperature effect on electrometric pH measurement. A temperature of 25°C is recommended for pH measurement.

3) Ion analysis

The extraction solution was filtered by cellulose acetate syringe filter before analysis of anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) by IC.

2.6 Biomass burning experiment

2.6.1 Sampling sites for biomass residues

Three types of biomass, including rice straw from rice field, maize residue from crop planting area and leaf litter from the mixed deciduous forest were collected in the harvest season from December 2009 to February 2010. Each biomass type was collected from 3 districts of Chiang Mai Province. Rice straw and leaf litter were collected from Mae Rim, Doi Saket and Chiang Dao districts, while maize residue was collected from Mae Rim, Mae Chaem and Chiang Dao districts (Figure 2.4). Those biomass were identified as being widely burned as well as frequent open

burning in these districts of Chiang Mai Province**.** Sample details are provided in Table 2.2. The information of 4 districts is given in Table 2.3.

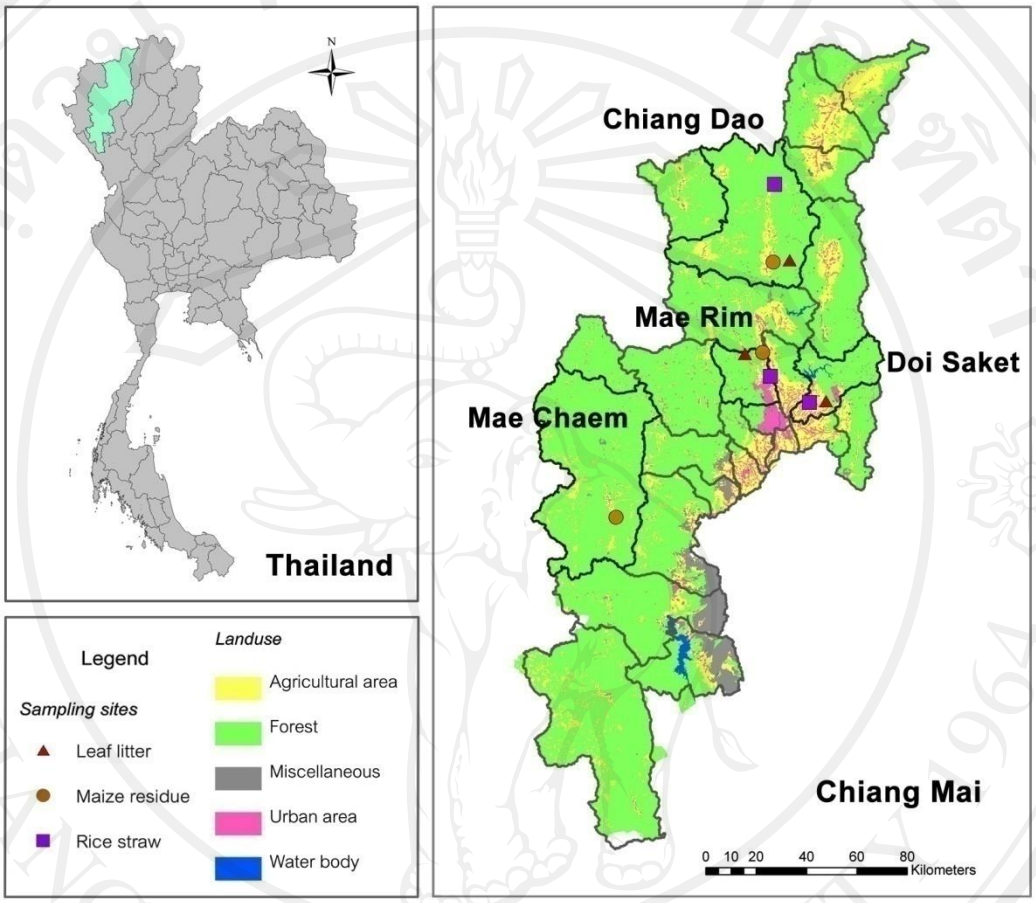

Figure 2.4 Biomass sampling sites in Chiang Mai Province

Table 2.2 Sampling sites, sample types and sample numbers

Location	Sample type	Sample code	North latitude East longitude	Elevation above sea level (m)	Number of samples
Mae Rim	Rice straw	R-MR	18° 56' 31" 98° 58' 20"	315.2	3
	Maize residue	M-MR	19° 1' 34" 98° 56' 34"	326.4	3
	Leaf litter	L-MR	18° 1' 20" 98° 55' 59"	396.8	3
Doi Saket	Rice straw	R-DK	18° 49' 22" 99° 40' 12"	315.0	3
	Leaf litter	L-DK	18° 51' 9" 99° 10' 57"	356.1	3
Chiang Dao	Rice straw	R-CD	19°37' 51" 98°59' 19"	604.0	3
	Maize residue	M-CD	19° 21' 5" 98° 58' 56"	433.8	3
	Leaf litter	L-CD	19° 21' 31" 99° 2' 44"	550.5	3
Mae Chaem	Maize residue	M-MC	18° 26' 2" 98° 23' 30"	487.0	3
	Total				**27**

Table 2.3 Information of sampling sites for biomass samples

Details	Sampling districts			
	Mae Rim (MR)	Doi Saket (DS)	Chiang Dao (CD)	Mae Chaem (MC)
Total area (km^2)	454 (100%)	652 (100%)	2,166 (100%)	3,347 (100%)
Forest area (km^2)	272 (60%)	472 (72%)	1,777 (82%)	2,938 (88%)
Rice field area (km^2)	37.2 (8%)	64.2 (10%)	36.0 (2%)	51.1 (2%)
Crop area (km^2)	25.5 (6%)	10.4 (2%)	89.8 (4%)	114 (3%)
Number of sub-districts	11	14	7	8
Number of villages	91	112	91	75
Population number	82,943	64,116	81,853	57,214
Population density (persons/km^2)	182.7	98.3	37.8	17.1
Over view	Tourist area and agricultural area (soybean and rice field)	Major area for rice cultivation	Rural farming area, mainly rice fields and crop in the valley	Mountainous area, majority corn and vegetable planting

Source: Chiang Mai Province Official Site, Thailand, 2012 (http://www.chiangmai.go.th/newweb/main/)

2.6.2 Biomass sampling

Each biomass type was collected from three locations in each district. Biomass was randomly sampled by using a 1 m^2 grid (Figure 2.5). In one location three grids were sampling. The residue inside the grid was collected and put in a labeled plastic bag and transported to the laboratory. Biomass samples from each location (three grids) were homogenized and collected into a plastic bag for the burning experiment. The number of samples for each biomass type from the three districts was nine and the total sample number was 27 (three biomass types). Each type of biomass was analyzed for moisture content and carbon (C), hydrogen (H) and nitrogen (N) content.

2.6.3 Measurement of moisture and C, H, N contents of biomass samples

1) Moisture content

The homogenized biomass samples were cut into small pieces by a stainless scissors. Approximately 2 g of samples were weighed for relative moisture content measurement using a moisture analyzer (MA50, Sartorius, Germany).

2) Basis element (C, H, N)

The homogenized 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, USA) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

(a)

(b)

(c)

Figure 2.5 Biomass sampling for (a) rice straw, (b) maize residue and (c) leaf litter

2.6.4 Preparation of biomass samples for burning experiment

The homogenized biomass samples were cut and weighed on a 2-digit balance before the burning experiment. Approximately 20 g of rice straw and 10 g of maize residue and leaf litter were weighed (Figure 2.6). Nine replications for each type of biomass were burned in the combustion chamber. Five blank samples were alternately collected during the burning experiments**.**

Figure 2.6 Biomass samples for burning experiment; rice straw (R), maize residue (M) and leaf litter (L)

2.6.5 Combustion chamber for biomass burning

A combustion chamber was designed by Environmental Chemistry Research Laboratory (ECRL), Faculty of Science, Chiang Mai University (Wiriya, 2012) for investigation of air pollutants emitted from biomass burning. Details of the chamber are shown in Figure 2.7 and Table 2.4.

2.6.6 Operation of the chamber

Firstly, 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. Burning process took about 1 minute. Concentrations of gases including CO, NO, NO_2 and SO_2 were continuously measured throughout the burning experiment using a gas analyzer (350-XL, Testo, Germany). The stabilization of pollutant gas concentrations emitted from the burning took approximately 5 minutes. Then, pollutants in the storage chamber were collected. The chamber was cleaned every time before the next burning experiment.

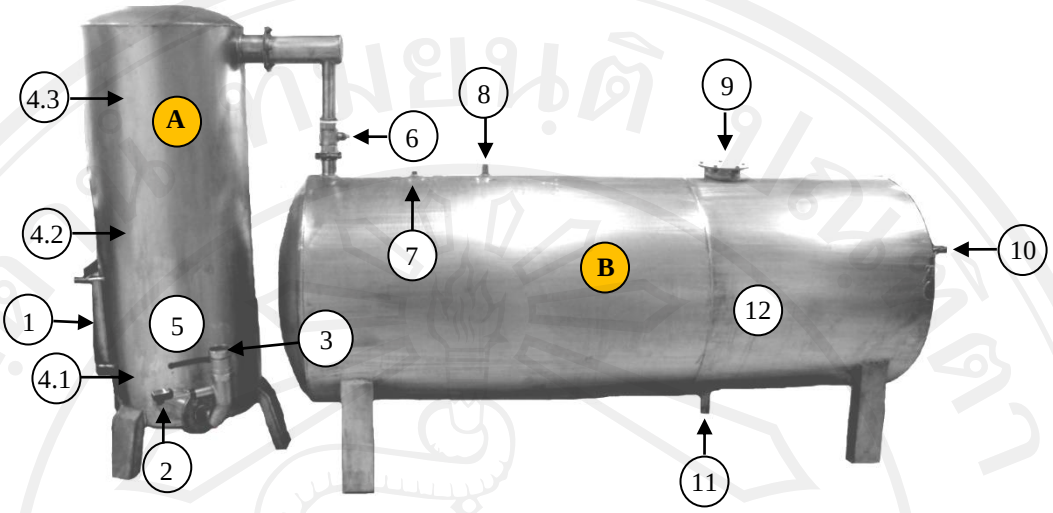

Figure 2.7 Combustion chamber; (A) combustion part and (B) air pollutant storage part
Source: Wiriya, 2012

Table 2.4 Composition and function of the combustion chamber

No.	Composition	Function
(A) Combustion part (∅: 0.50 m, 1.23 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 (∅: 0.76 m, 2.00 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

2.6.7 Collecting of PM10 and water-soluble samples from biomass burning in the chamber

PM10 and water-soluble samples were collected from the burning experiment. Water-soluble sample was collected both in forms of particulate and gas, which can be dissolved in water.

1) PM10 sample

The PM10 collecting was started by opening a valve between the storage chamber and the air sampler. PM10 emitted from biomass burning were continuously collected on a quartz fiber filter (Ø 47 mm, Whatman, UK) in a mini volume air sampler (Airmetrics, USA) at the flow rate of 5 L/min for 5 hours. The steps of PM10 sample collection are described in the topic 2.5.3. Collected filter samples were kept in petri dish plastic and stored in a freezer (-4 ºC) until they were extracted and analyzed (topic 2.4).

2) Water-soluble sample

The smoke collector was constructed for collecting of water-soluble pollutants emitted from biomass burning in the combustion chamber. The 20 L plastic bucket was used as a smoke collector (Figure 2.8). It contains 10 L of deionized water. A pump was used for sucking air from the storage chamber into the smoke collector. Its flow rate was 31 L/min. Each sample was continuously collected for 2 hours. After that 25 mL of water-soluble sample was collected in a polyethylene bottle and kept in refrigerator at 4 °C waiting for EC and pH measurement. Another 100 mL of samples was evaporated by vacuum rotary (R-215, Büchi Labortechnik

AG, Switzerland) at 72 mbar pressure and 60 °C of bath temperature. The solution was evaporated until it was ~25 mL and kept for further ion analysis by IC.

Figure 2.8 Smoke collector

2.6.8 Analysis of EC, pH and ions of PM10 and water-soluble samples

The extracted solution of PM10 samples and water-soluble samples were measured for EC and pH obtained from the topic 2.5.5. After that, both samples were filtered by cellulose acetate syringe filter (pore size 0.45 µm, Ø 13 mm) before analysis for anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) by IC obtained from section 2.3.1 and 2.3.2.

2.7 Emission factors and emission rates of pollutants from biomass burning

2.7.1 Emission factors

Emission factors (EFs) is a representative value that attempts to relate 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, 2012c). In this study, EFs were reported in terms of mass of pollutant emitted per unit mass of dry fuel consumed.

2.7.2 Emission rates

Emission rates (ERs) is emission of air pollutant in terms of mass of pollutant emitted per year. It used to quantify air pollutant emission from biomass burning. Traditionally, ERs for a specific species (i) are calculated as the product of burned area (A), fuel load (FL), combustion completeness (CC) and specific emission factors (EFs) as shown in Equation 2.3 (Langmann et al., 2009).

$$ER(i) = A \times FL \times CC \times EF(i) \qquad \text{Eq. 2.3}$$

Where, A is burned area (km^2); FL is fuel load (kg/km^2) calculated from the weight of biomass collected in 1 m^2 grid of sampling. Combustion completeness (CC) of rice straw, maize residue and leaf litter was 1.0. EF is an emission factor of dry biomass (weight of pollutant/weight of biomass; g/kg or mg/kg).

2.8 Atmospheric acid deposition

2.8.1 Sampling site

The sampling site was located at meteorological station in the area of Mae Hia Research Center, Chiang Mai University, Muang District, Chiang Mai Province (Figure 2.9). This station was located at 98º 55' 54.3" E and 18º 45' 40.3" N. Its elevation was 334 meter above sea level. The sampling site was classified by Acid Deposition Monitoring Network in East Asia (EANET) criteria as rural site since 2000. However, due to rapid development of the city of Chiang Mai in the past 10 years, this study site should therefore be classified as sub-urban area. The surrounding detail of sampling site in different scales is shown in Table 2.5 and Figure 2.10.

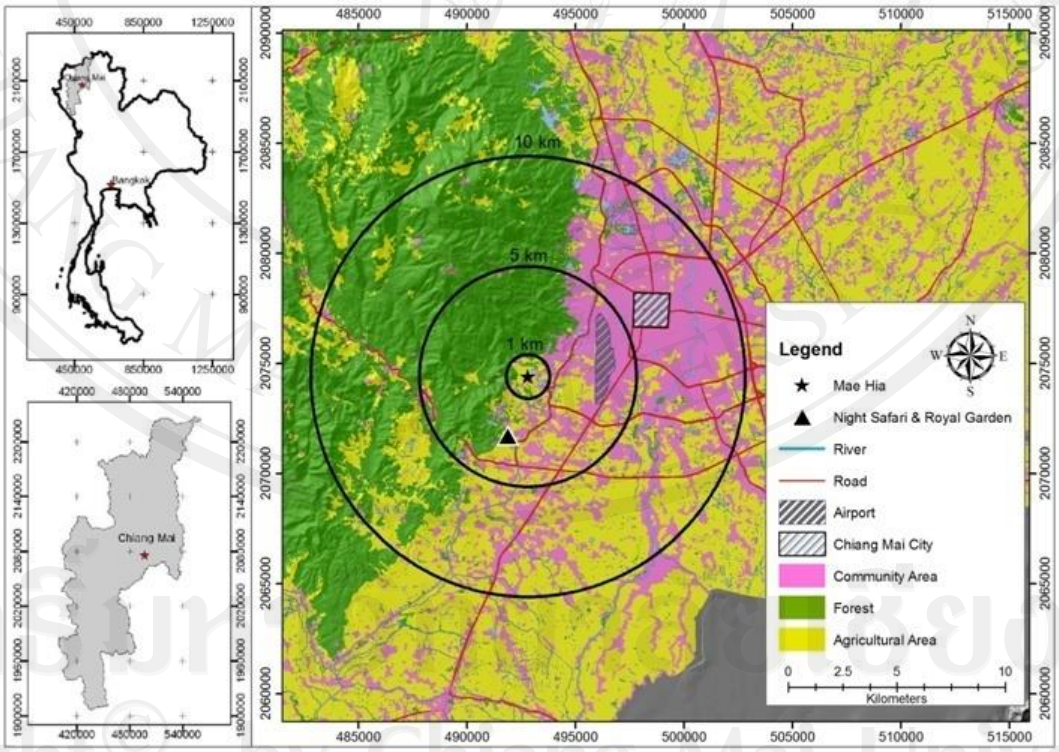

Figure 2.9 Land use profile of Mae Hia Research Center

Table 2.5 Surrounding of sampling site

Scale Type	Radian	Details
Onsite Scale	0 - 100 m	80% of Mae Hia Research Center are used for research purposes stock for students of Agriculture and Veterinary Faculties. The rest of the areas are used for the office building, parking lot, etc.
Local Scale	100 m - 10 km	Most of the area are forest, communities and agricultural areas. Other land use is airport, tourist attractions (night safari and Royal garden), Chiang Mai City, golf course, etc
Regional Scale	10 - 50 km	The radian of this scale covers forest, communities, agricultural areas, industrial estate, etc.

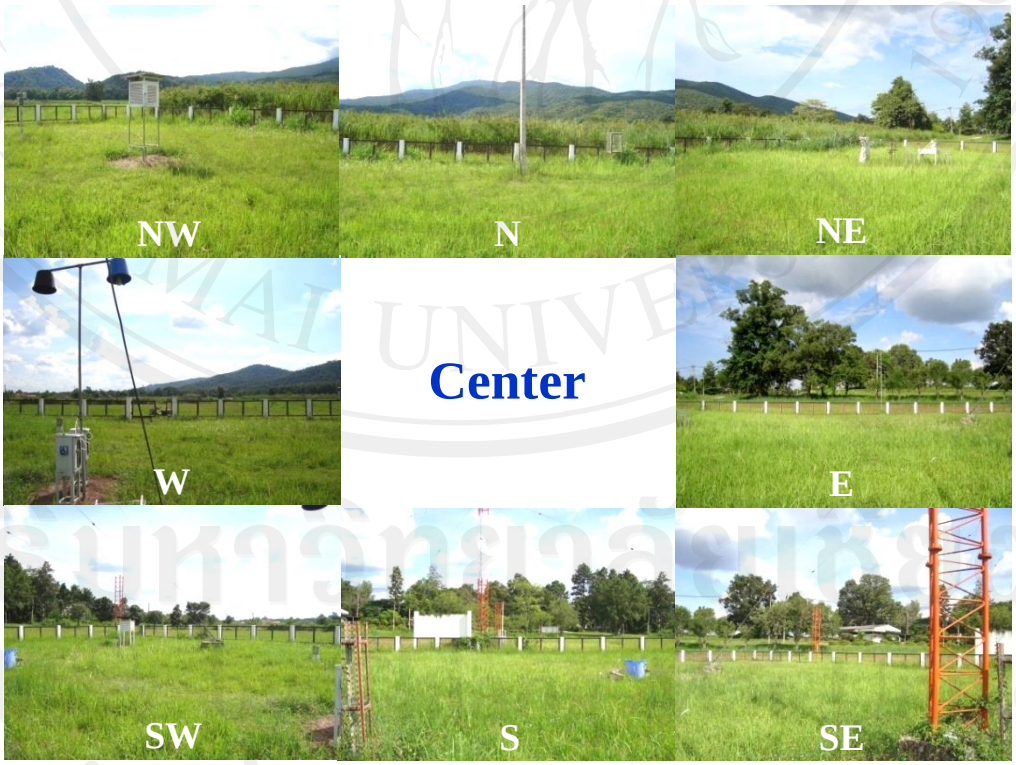

Figure 2.10 Surrounding of sampling site

2.8.2 Dry deposition (EANET, 2003)

1) Sampling of dry deposition samples

A dry deposition sample is proposed to measure the level of air pollution in atmosphere. The main pollutants such as SO_2, HNO_3, HCl, NH_3, and aerosols were collected by four-stage filter pack (Nilu, Norway). It was operated by connect with sampling set, which controlled an inlet height and flow rate.

The inlet of air sampling holder was set up at the height of about 3 meters above the ground. During sampling period, the diaphragm pump was set for stable flow rate (1 L/min). Gas volume meters with flow rate meters (of float type) were also acceptable. In this case, the flow rate meter and gas volume meter were set up consequently after the pump to measure flow rate and volume under the condition of atmospheric pressure. Air volumes counted by gas volume meters was used for calculation of ambient air concentration. The filter pack sampling system is illustrated in Figure 2.11.

The four-stage filter pack is composed of four filters in line with the air stream as shown in Figure 2.12. Aerosols were collected on the first filter (F0: made of polytetrafluoro-ethylene; PTFE), while the gaseous substances such as SO_2, HNO_3, HCl and NH_3 will pass though this filter. The second filter (F1: made of polyamide) collects all HNO_3 and partial SO_2, HCl and NH_3 from the sampling air. The remaining SO_2 and HCl react with alkali substance on the third filter (F2: made of cellulose). The remaining NH_3 reacts with acid substance on the fourth filter (F3: made of cellulose) after passing through the first, second and third filter. The specifications of filters and collected species are summarized in Table 2.6.

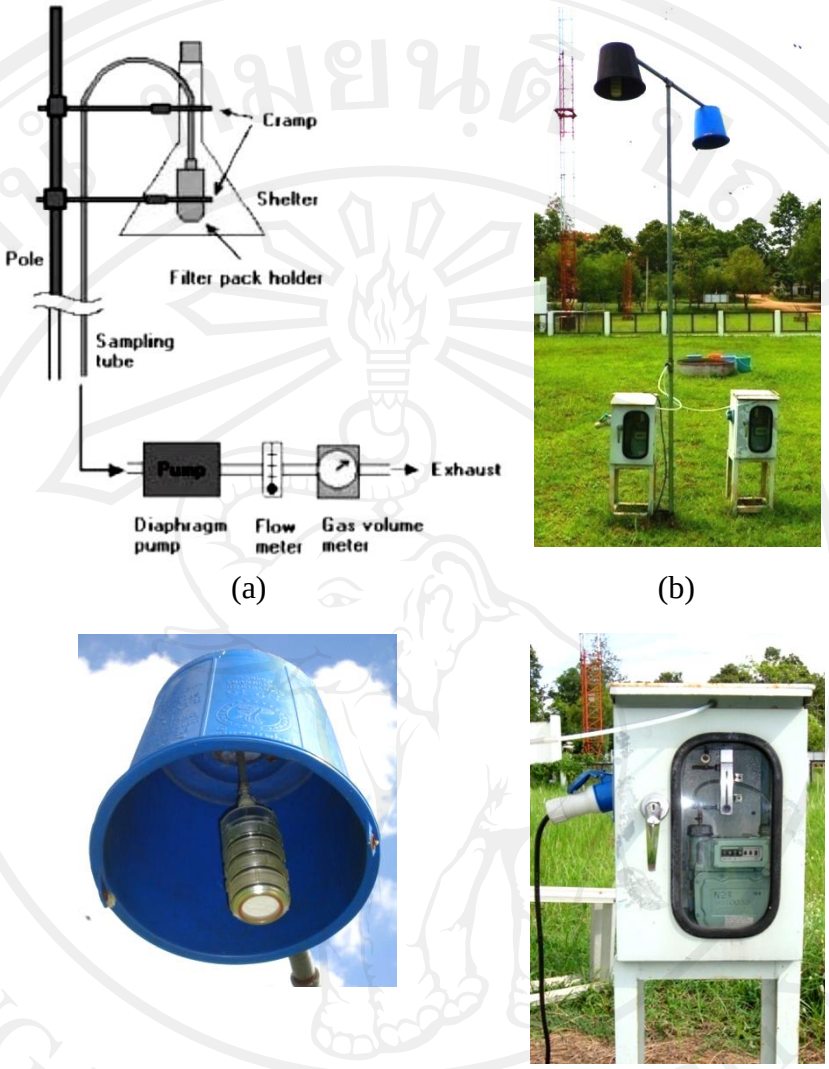

Figure 2.11 Filter pack sampling system and onsite condition

(a) Schematic diagram of filter pack sampling system

(b) On-site filter pack sampling set

(c) Connection of filter pack holder

(d) Pump

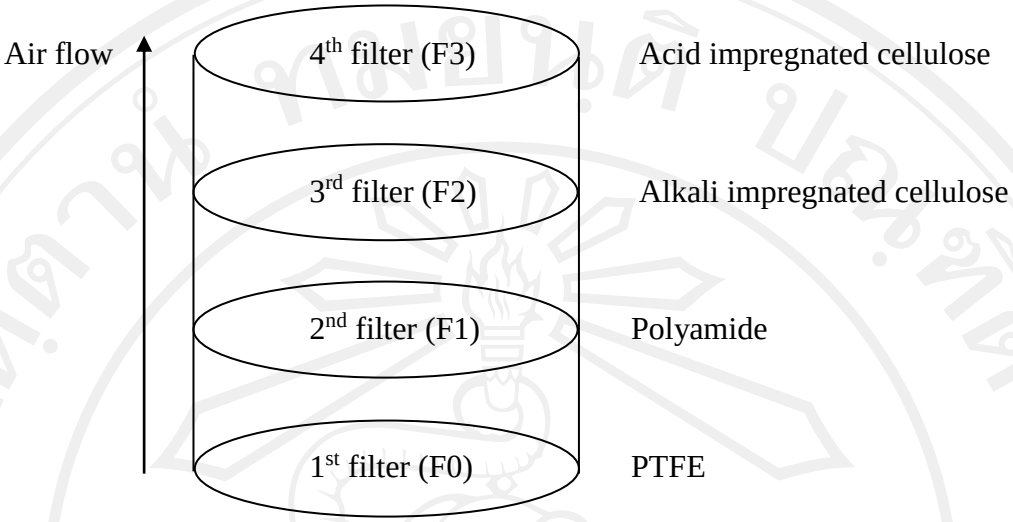

Figure 2.12 Schematic diagram of four-stage filter pack

Table 2.6 Specifications of filters and collected species

Stage	Filter type	Collected species
1st(F0)	Polytetrafluoro-ethylene (PTFE) or Teflon	Aerosol
2nd(F1)	Polyamide or Nylon	HNO_3, Partial SO_2, HCl, NH_3
3rd(F2)	Cellulose impregnated by K_2CO_3	SO_2, HCl
4th(F3)	Cellulose impregnated by H_3PO_4	NH_3

2) Preparation of four-stage filter pack

Filters and impregnate solution were handled in the laboratory only under the clean conditions. Moreover they should not be exposed to air longer than necessary due to a possible uptake of gases by filters or solutions. Disposable plastic gloves and tweezers should always be used when handling filters. Only a clean filter holder should be used to prevent excess contamination. The filters are mounted on the filter

holder using clean plastic tweezers, taking into account the necessity to prevent the leak in the filter holder. Filters, especially impregnated one, were always sealed up to avoid the contamination by unexpected ambient pollutants before and after the sampling time.

The first two layers (F0 and F1) of filter pack sampling set are not necessary to impregnate with any solution. By the way, the other two layer filters (F2 and F3) are used for trapping remaining gases.

2.1) Preparation of impregnate solution

Impregnate solutions were carefully prepared under the clean laboratory condition. Because the contamination is easily occurred and it will affect to the blank samples, therefore plastic gloves were used to handle in this step. All glassware were washed by deionized water and dried in an oven at 60°C. After dried, cleaned glass wears were prevented from contamination by kept in plastic zip bag.

2.1.1) Alkaline impregnate solution (F2), 6% K_2CO_3 + 2% glycerin

Alkaline impregnated solution for the third layer of a four-stage filter pack was the potassium carbonate solution. 15 g of K_2CO_3 and 5 mL of glycerin were dissolved in 250 mL deionized water to make the solution.

2.1.2) Acid impregnate solution (F3), 5% H_3PO_4 + 2% glycerin

14.7 mL of H_3PO_4 and 5 mL of glycerin were mixed in 250 mL deionized water. It was used as acid impregnated solution.

2.2) Impregnation of filters

Impregnate solution was divided into three parts in clean beakers. Then, cellulose filters were soaked in 1st, 2nd and 3rd beaker, respectively using clean plastic tweezers. The excess alkaline (F2) and acid (F3) solution on cellulose filters were

absorbed by a large cellulose sheet (No.590, ADVANTEC, Japan). After that, the impregnated filters were kept in a petri dish and packed in a plastic zip bag to prevent from contamination.

3) Filter pack installation

Prepared filters packs were connected with a sampling set at the monitoring site which was connected and operated by flow meter and pump. The flow rate of air input was 1 L/min. Details of sampling such as time, ambient temperature and air volume were recorded. Operation of sampling was for every 10 days continuously. Therefore, 3 samples per month were collected.

4) Sample collection

The flow rate of pump was checked before stop the sampling. Filter pack holder set was disconnected from the sampling set after switch off the operation of the pump. Then, the air volume was recorded. The filter pack holder set was closed with plastic cap or para-film and stored in clean plastic zip bag to avoid absorption after stop sampling. The collected filter pack was transferred to laboratory waiting for extraction and ion analysis.

5) Sample extraction

Extractions of filters sample were necessary in order to bring all analytes into liquid form. Each filter type required a specific extracted solution for a different proposes.

The filters of F0, F1 and F3 and their laboratory blanks were extracted by 20 mL of deionized water contained in polypropylene tubes with caps and sonicated in the ultrasonicator (T 490DH, Elma, Germany) for 30 minutes. After extraction process, insoluble matters were filtered out by cellulose acetate membrane (pore size

0.45 μm, Ø 13 mm). Filtrated samples were stored in polyethylene bottles and kept in refrigerator at 4°C. The extraction processes were also applied to use with the third stage filters (F2), which were extracted by 20 mL of 0.05% v/v H_2O_2. Analyzed species and extracted solution for each filter are shown in Table 2.7.

Table 2.7 Analyzed species and extracted solution for each filter

Stage	Filter type	Collected species	Extraction solution
1st(F0)	PTFE	Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}	20 mL DI water
2nd(F1)	Polyamide	Cl^-, NO_3^-, SO_4^{2-}, NH_4^+	20 mL DI water
3rd(F2)	Cellulose	Cl^-, SO_4^{2-}	20 mL 0.05% v/v H_2O_2
4th(F3)	Cellulose	NH_4^+	20 mL DI water

6) Ion analysis

The filtrated samples and their laboratory blanks were analyzed for anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) by IC obtained from the topic 2.3.1 and 2.3.2.

7) Quality assurance and quality control for dry deposition monitoring

Filter samples from the Inter-laboratory comparison project under the Acid Deposition Monitoring Network in East Asia (EANET) were analyzed by IC in terms of 3 parameters: Cl^-, SO_4^{2-} (from the filter samples impregnated by K_2CO_3) and NH_4^+

(from the filter samples impregnated by H_3PO_4) in the extracted solution. The details of samples are shown in Table 2.8.

In the case of alkali (K_2CO_3) impregnated filters, 20 mL H_2O_2 solution (0.05% v/v) were poured into a beaker and ultrasonicated for 30 minutes. Acid (H_3PO_4) impregnated filters were handled in the same way as alkali impregnated filters, only deionized water was used instead of H_2O_2. The insoluble matters were filtered out of the extracted solutions using a cellulose acetate membrane (pore size 0.45 μm, Ø 13 mm). Filtrated solutions were analyzed by IC under the same conditions with the real samples.

Table 2.8 Details of filter samples

Details	Container	Number of samples	Note
Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3 replicates (a, b, c)	Filter was impregnated by K_2CO_3. (Blank)
	Polyethylene centrifuge tube	3 replicates (a, b, c)	Known quantities of the solution which contains Cl^- and SO_4^{2-} were added.
Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3 replicates (a, b, c)	Filter was impregnated by H_3PO_4. (Blank)
	Polyethylene centrifuge tube	3 replicates (a, b, c)	Known quantity of the solution which contains NH_4^+ was added.

2.8.3 Wet deposition (EANET, 2010)

1) Sample collection

Rain samples were collected on a daily basis using an automatic wet-only collector. Sample recovery was made at 9.00 am local time. Wet-only collector consists of bucket, a lid and a sensor, which was set at height of 120 cm as shown in Figure 2.13. Before raining occurs, about 1-5 g of thymol was put into the bucket. It has effective in preventing microbial uptake and conversion of organic acids such as formic and acetic acid in regions where they are contained in rain sample. Rainfall sensors immediately response to activate the opening of the lid. After rain event, the rain sample was transfer into a cleaned bottle and washed the bucket with deionized water (EC < 0.15 mS/m) and put in place. Rain gauge was used for measurement of precipitation amount in millimeter unit to compare the efficiency of rain sample collection.

Collected rain samples were labeled and transferred to the laboratory, Faculty of Science, Chiang Mai University. They were weighted and analyzed for EC, pH and ion concentrations.

Figure 2.13 Wet-only collector

2) Chemical analysis

Rain samples were divided into two parts. The first part was measured for EC and pH obtained from section 2.5.5. The second part was filtered by cellulose acetate syringe filter (pore size 0.45 μm, Ø 13 mm) before analysis of anions (CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) by IC obtained from the topic 2.3.1 and 2.3.2.

3) Quality assurance and quality control for wet deposition monitoring

The low and high concentrations of artificial rain samples from the Inter-laboratory comparison project under the Acid Deposition Monitoring Network in East Asia (EANET) was analyzed by IC under the same conditions with the real samples. The sample was first 100 times diluted by deionized water and then divided into 3 parts (a, b and c). Each part was injected 3 times to IC under the optimum conditions. The analytical result was used to calculate ion and conductivity balance in order to check the accuracy of analysis.

3.1) Cation and anion balance (R_1)

The principle of electroneutrality in precipitation requires that total anion equivalents must be equal to total cation equivalents. According to this principle, ion balance in a precipitation sample can be calculated by the following equation:

$$R_1 = [(C - A) / (C + A)] \times 100\% \qquad \text{Eq. 2.4}$$

Where C and A represents cation and anion equivalents, respectively.

This is simplified from of the corresponding equation used by US EPA where the denominator is the average of the two sums.

$$A\ (\mu eq/L) = \Sigma C_{Ai} \times V_i \quad \text{Eq. 2.5}$$

Where C_{Ai} is the concentration of i-th anion in µmol/L, V_i is the valence of the given ion.

$$C\ (\mu eq/L) = 10^{(6\text{-}pH)} / 1.008 + \Sigma C_{ci} \times V_i \quad \text{Eq. 2.6}$$

Where C_{ci} is the concentration of i-th cation in µmol/L. If the unit µg/mL is used, it should be converted as follows:

$$(\mu mol/L) = (\mu g/mL) \times 1000/MW \quad \text{Eq. 2.7}$$

Where the molecular weight (MW) for anions and cations is given in Table 2.9.

When pH is greater than 6 and R_1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be included for the computation of R_1 and R_2. When formic acid, acetic acid, or both are measured, formate and acetate ions should be considered in the evaluation of R_1 and R_2. The concentrations (µeq/L) of these weak acids will be calculated from the discussion constant, K_a and pH as follows:

$$\left[HCO_3^-\right] = P_{CO_2} H_{CO_2} K_{a1} / \left[H^+\right] = \left(360\times10^{-6}\right)\left(3.4\times10^{-2}\right)10^{pH-6.35+6}$$

$$= 1.24\times10^{pH-5.35} \quad \text{Eq. 2.8}$$

$$[HCOO^-] = [HCOOH]\,Ka / [H^+] = [HCOOH] \times 10^{pH - pKa}$$

$$= [HCOOH] \times 10^{pH - 3.55} \quad \text{Eq. 2.9}$$

$$[CH_3COO^-] = [CH_3COOH]\,Ka / [H^+] = [CH_3COOH] \times 10^{pH - pKa}$$

$$= [CH_3COOH] \times 10^{pH - 4.56} \quad \text{Eq. 2.10}$$

Constants for HCO_3^-, $HCOO^-$ and CH_3COO^- are included in Table 2.9.

Air concentration of CO_2 in equilibrium with precipitation samples is assumed to be 360 ppm. Dissociation constants in terms of pK_a for carbonic, formic, and acetic acids are 6.35, 3.55, and 4.56, respectively.

Table 2.9 Basic constants of each ion (EANET, 2000)

Ion	Molecular weight (MW)	Molar conductivity (λ) S cm^2 / mol
HCO_3^-	61.02	44.5
CH_3COO^-	59.10	40.9
$HCOO^-$	45.00	54.6
Cl^-	35.45	76.3
NO_3^-	62.01	71.5
PO_4^{3-}	94.97	69.0 × 3
SO_4^{2-}	96.06	80.0 × 2
H^+	1.008	349.7
Na^+	22.99	50.1
NH_4^+	18.04	73.5
K^+	39.10	73.5
Ca^{2+}	40.08	59.8 × 2
Mg^{2+}	24.31	53.3 × 2

The required ion balances of precipitation analyses are given in Table 2.10.

Table 2.10 Required criteria for R_1 (EANET, 2000)

(C + A), μeq/L	R_1, %
<50	±30
50-100	±15
>100	±8

3.2) Electric conductivity balance (R_2)

For dilution solutions (e.g. below 10^{-3} M), the total conductivity can be calculated in mS/m from the molar concentrations and molar conductivity (at infinity dilution) of the individual ions. The calculation is as follows:

$$\Lambda_{calc} = \sum c_i \ \Lambda_i^{\ 0} \ \times 10^{-4} \qquad \text{Eq. 2.11}$$

Where Λ_{calc} denotes the calculated conductivity of the solution (in mS/m), Ci the ionic concentration of the i-th ion (in μmol/L), Λ_i^0 the molar conductivity (in S cm^2/mol) at infinite dilution and 25 °C.

Thus

$$\Lambda_{calc} = \{349.7 \times 10^{(6\text{-pH})} \times 80.0 \times 2c(SO_4^{2-}) + 71.5c(NO_3^-) + 76.3c(Cl^-) + 73.5c(NH_4^+) + 50.1c(Na^+) + 73.5c(K^+) + 59.8 \times 2c(Ca^{2+}) + 53.3 \times 2c(Mg^{2+})\} / 10000 \qquad \text{Eq. 2.12}$$

Where c(ion) denotes the ionic concentrations in μmol/L of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25 °C (Table 2.9).

The calculation conductivity values can then be compared to the observed value for precipitation samples as the relation below:

$$R_2 = ((\Lambda_{calc} - \Lambda_{meas}) / (\Lambda_{calc} + \Lambda_{meas})) \times 100\% \quad \text{Eq. 2.13}$$

This is similar to the equation for the calculation of cation and anion balance.

The required comparison criteria of measured and calculated ionic and conductivities are expressed in Tables 2.10 and 2.11, respectively. If the required ionic and conductivity comparison criteria have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the resulted did not meet the required criteria.

Table 2.11 Required criteria for R_2 (EANET, 2000)

Λ_{meas}, mS/m	R_2, %
<0.5	±20
0.5-3	±13
>3	±9

4) Neutralization of acidity

Neutralization is a chemical reaction in which a base reacts with an acid to create water and a salt. In chemical terms, neutralization results from the interaction of ions in the acid and base. This reaction can occur between organic and inorganic compounds, between two inorganic compounds, between two organic compounds and by adding a base to an acid or vice versa.

The acidity (pH) of precipitation is determined by the relative proportion of acids and bases in solution or rain sample. Major ions typically present in rain sample are hydrogen (H^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). Sequeira (1982) pointed out that sulfate and nitrate are not quantitative indicators of acid deposition unless the relative alkali deposition is negligible or corrected for neutralization. In principle, changes in pH can be brought about as well by changes in the concentrations of neutralizing substances as by changes in the concentrations of the strong acids. Substances which are recognized for their abilities to neutralize the atmospheric acidic load are fine wind-blow soil particles (Ca and Mg), K and NH_3 (Bubenick, 1984; Das et al., 2005). Neutralization of the acids by these base cations are validated by calculation of the neutralization factors (NF) by following equations (Possanzini et al., 1988).

$$NF_{Xi} = [X_i] / ([SO_4^{2-}] + [NO_3^-]) \qquad \text{Eq. 2.14}$$

where X_i is the chemical component of interest, with all the ions expressed in µeq/L

When the NF value of one specific component, it means that the component plays major roll in acid neutralization. Normally, NH_4^+ and Ca^{2+} are the dominant neutralization substances depend on the sampling site. On the other hand, neutralization by Mg^{2+} and K^+ is negligible (Kulshrestha et al., 1996; Hu et al., 2003; Thepanondh et al., 2005; Das et al., 2005).

2.9 Statistical data analysis

The data obtained from experiments were compiled and analyzed by statistical method. Data analysis to identify relationships between ion compositions was calculated by correlation. Principal component analysis (PCA) was used to determine the pattern of chemical composition in the study.