CHAPTER 3

RESULTS AND DISCUSSION

3.1 Ions analysis by ion chromatograph

3.1.1 Measurement of ion concentrations

In this study, two groups of ion species in the samples were measured. Anions including acetate (CH_3COO^-), formate ($HCOO^-$) , chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) and cations including sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were analyzed by ion chromatograph (IC). Chromatograms of mixed anion and cation standards are shown in Figure 3.1 and Figure 3.2, respectively.

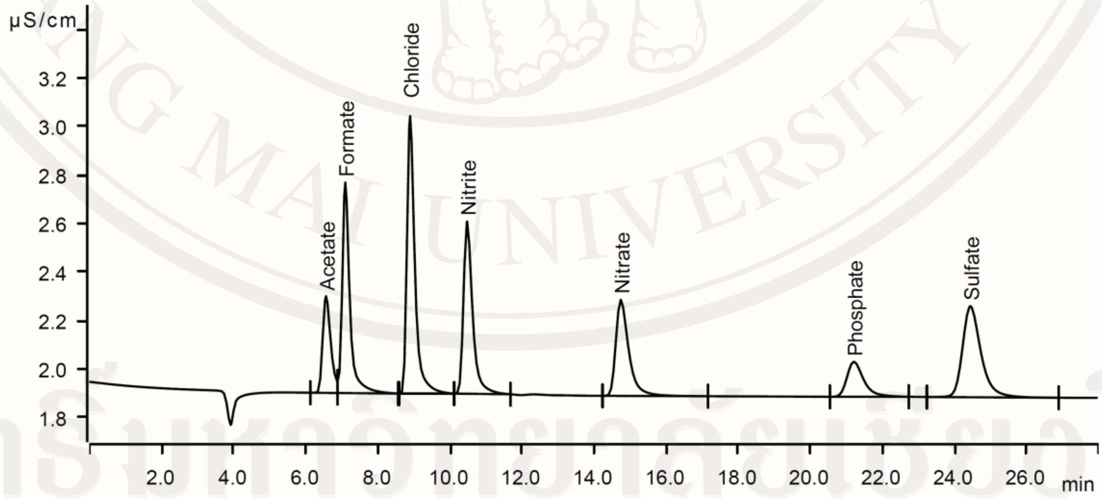


Figure 3.1 Chromatogram of 0.8 μg/mL mixed anion standards

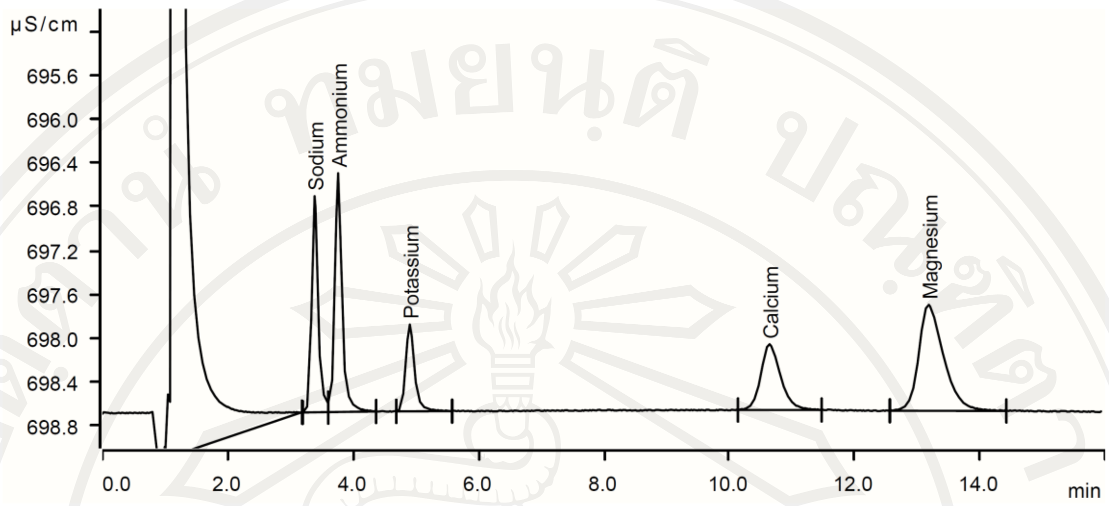


Figure 3.2 Chromatogram of 0.8 μg/mL mixed cation standards

3.1.2 Standard calibration curves of ions

In each analytical run, the mixed standard solutions of anions and cations ranged from 0.05 to 10.0 μg/mL were prepared and analyzed by IC. The calibration curve of each ion standard was constructed using ion concentrations versus peak areas. The calibration curves for the quantification of ion species were linear, with the coefficients of determination (R^2) being 0.995 or greater as illustrated in Table 3.1. The calibration curves for determination of anions and cations are shown in Figure 3.3 and Figure 3.4, respectively.

Table 3.1 Examples of calibration equations of ions and their coefficients of determination

Ion species	Linear equation	Coefficients of determination (R^2)
CH_3COO^-	y = 0.115x + 0.009	0.997
$HCOO^-$	y = 0.276x – 0.002	0.999
Cl^-	y = 0.399x – 0.016	0.999
NO_2^-	y = 0.288x – 0.014	0.999
NO_3^-	y = 0.223x – 0.008	0.999
PO_4^{3-}	y = 0.120x – 0.013	0.998
SO_4^{2-}	y = 0.294x – 0.007	1.000
Na^+	y = 0.275x + 0.012	0.999
NH_4^+	y = 0.381x – 0.011	0.999
K^+	y = 0.162x + 0.001	0.999
Ca^{2+}	y = 0.275x + 0.006	0.999
Mg^{2+}	y = 0.565x – 0.000	0.999

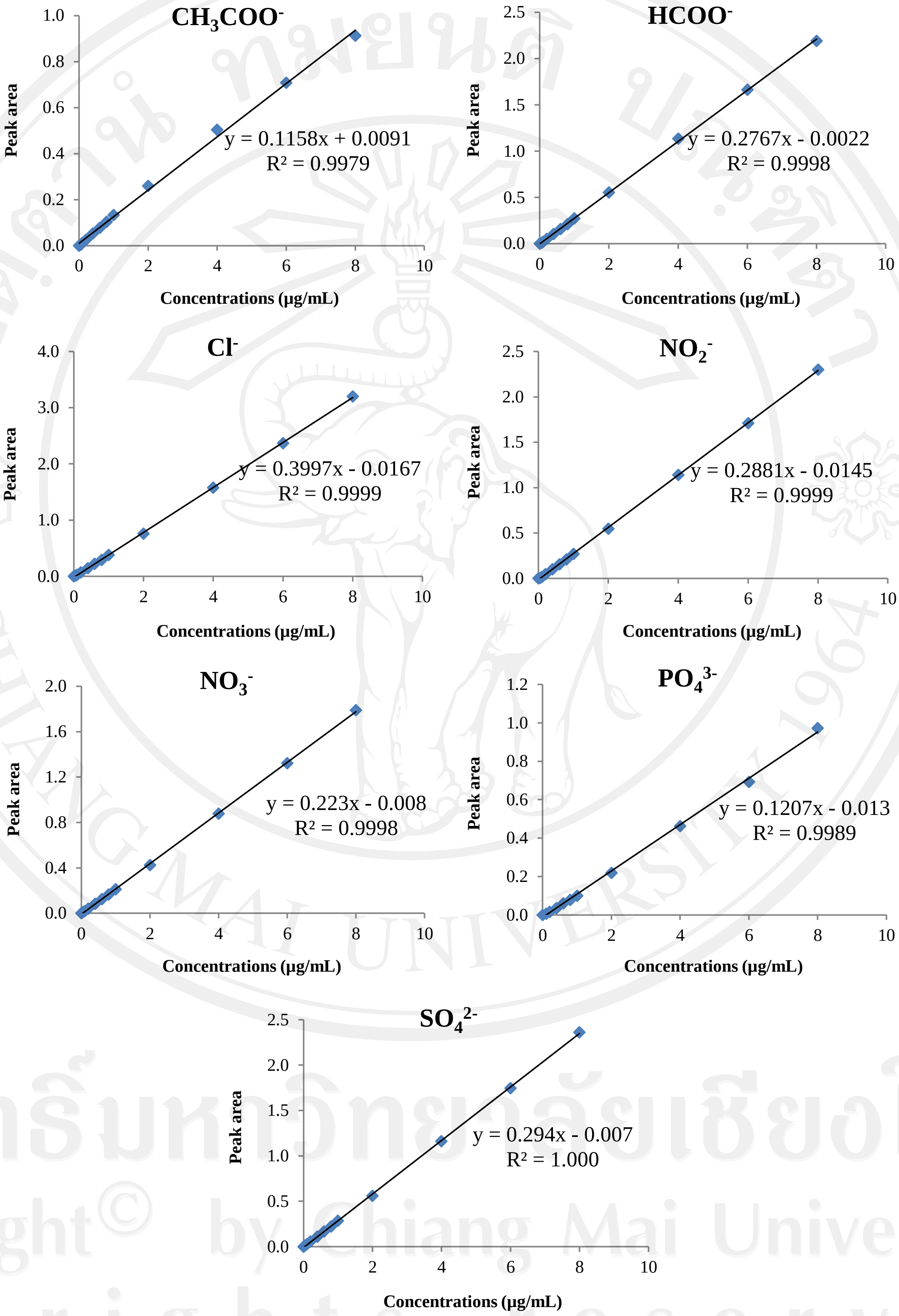


Figure 3.3 Examples of calibration curves for determination of anions

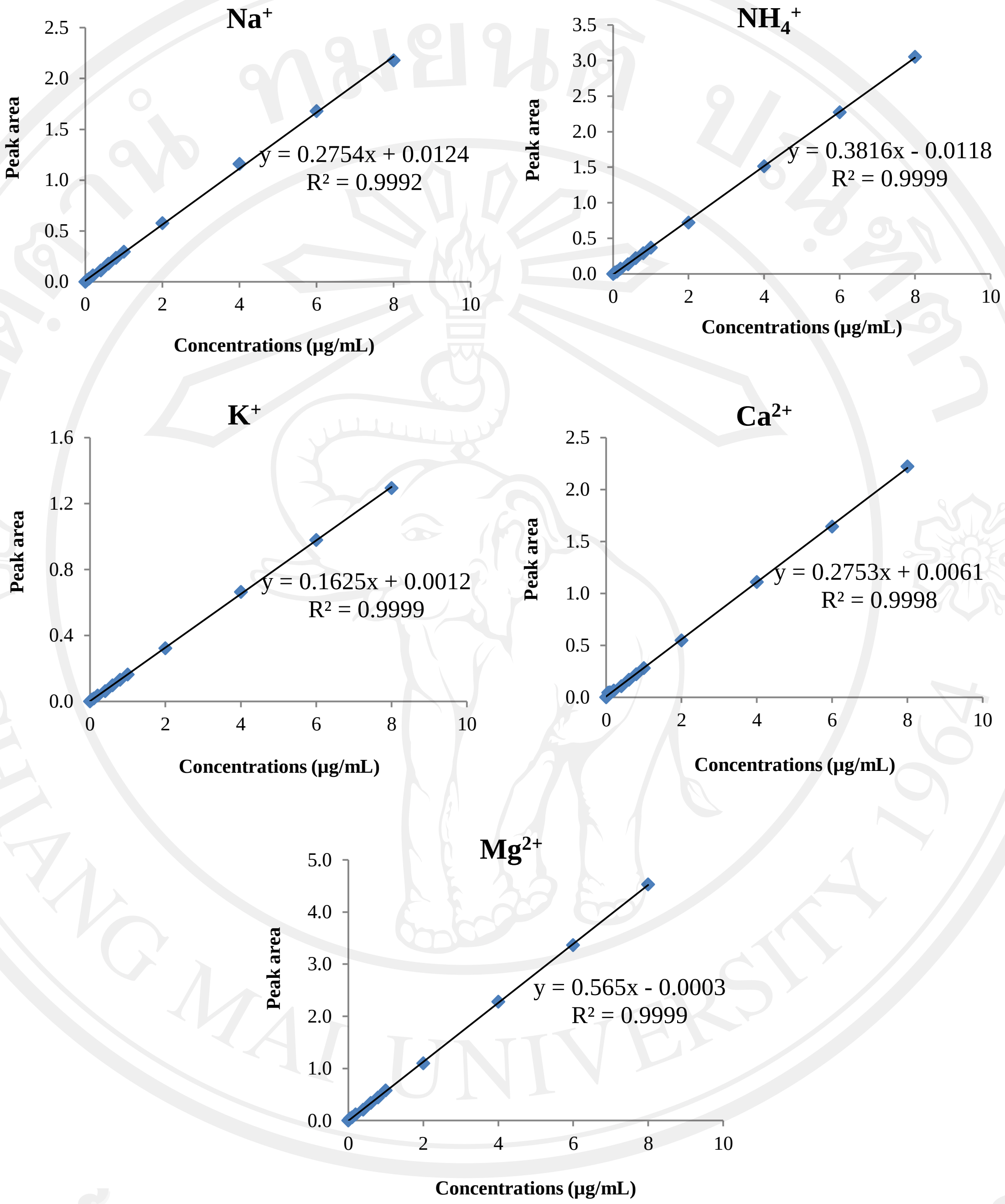


Figure 3.4 Examples of calibration curves for determination of cations

3.1.3 Analytical characteristics of ion chromatograph

1) Repeatability

The repeatability of anions and cations analyzed by ion chromatograph (IC) was determined with 5 injections of a 0.8 µg/mL mixed anion and cation standards. The precision was estimated by relative standard deviation (%RSD) as shown in Table 3.2. The %RSD of individual ion at 0.8 µg/mL ranged from 0.2-2.8%, which revealed very good repeatability of injections.

2) Reproducibility

The reproducibility was checked by injecting of a 0.8 µg/mL mixed anion and cation standard solutions once a week for 5 continuous weeks. The precision was estimated by %RSD as shown in Table 3.3. It was found to be very good precision of all ions ranged from 0.8-3.8% RSD.

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

Limit of detection (LOD = 3SD) and limit of quantification (LOQ = 10SD) of IC were determined by 5 injections of a 0.1 µg/mL mixed anion standard and a 0.05 µg/mL mixed cation standard. LOD of ions ranged from 0.004-0.028 µg/mL or 0.025-0.186 µg/m^3, while LOQ ranged from 0.012-0.094 µg/mL or 0.083-0.619 µg/m^3, as are shown in Table 3.4.

Table 3.2 Repeatability of ion chromatograph for ion analysis

No. of injection	Concentrations (µg/mL)										
	CH_3COO^-	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.833	0.800	0.788	0.791	0.730	0.783	0.809	0.789	0.788	0.815	0.799
2	0.834	0.799	0.784	0.783	0.762	0.786	0.818	0.793	0.796	0.806	0.798
3	0.824	0.798	0.781	0.781	0.767	0.784	0.798	0.793	0.792	0.814	0.810
4	0.829	0.787	0.788	0.795	0.790	0.781	0.818	0.790	0.797	0.808	0.796
5	0.845	0.793	0.786	0.780	0.765	0.785	0.804	0.791	0.797	0.815	0.802
Average	0.833	0.795	0.785	0.786	0.763	0.784	0.809	0.791	0.794	0.812	0.801
Standard Deviation (SD)	0.008	0.006	0.003	0.007	0.021	0.002	0.009	0.002	0.004	0.004	0.006
Relative Standard Deviation (%RSD)	**0.9**	**0.7**	**0.4**	**0.8**	**2.8**	**0.2**	**1.1**	**0.2**	**0.5**	**0.5**	**0.7**

Table 3.3 Reproducibility of ion chromatograph for ion analysis

No. of injection	Concentrations (µg/mL)										
	CH_3COO^-	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.807	0.799	0.790	0.795	0.788	0.794	0.794	0.760	0.793	0.795	0.800
2	0.815	0.789	0.787	0.778	0.752	0.799	0.806	0.803	0.806	0.778	0.808
3	0.777	0.803	0.786	0.791	0.806	0.792	0.804	0.785	0.815	0.813	0.800
4	0.770	0.801	0.787	0.790	0.796	0.792	0.791	0.728	0.810	0.800	0.789
5	0.802	0.813	0.807	0.811	0.803	0.782	0.792	0.790	0.804	0.785	0.794
Average	0.794	0.801	0.792	0.793	0.789	0.792	0.797	0.773	0.805	0.794	0.798
Standard Deviation (SD)	0.020	0.009	0.009	0.012	0.022	0.006	0.007	0.029	0.008	0.013	0.007
Relative Standard Deviation (%RSD)	**2.5**	**1.1**	**1.1**	**1.5**	**2.8**	**0.8**	**0.9**	**3.8**	**1.0**	**1.7**	**0.9**

Table 3.4 Limit of detection and limit of quantification of IC for ion analysis

Ion species	Limit of Detection (LOD)		Limit of Quantification (LOQ)	
	µg/mL	µg/m^3*	µg/mL	µg/m^3*
CH_3COO^-	0.017	0.113	0.057	0.375
$HCOO^-$	0.028	0.186	0.094	0.619
Cl^-	0.005	0.031	0.016	0.103
NO_3^-	0.006	0.038	0.019	0.128
PO_4^{3-}	0.009	0.060	0.030	0.199
SO_4^{2-}	0.004	0.025	0.012	0.083
Na^+	0.022	0.147	0.074	0.489
NH_4^+	0.006	0.043	0.021	0.142
K^+	0.013	0.084	0.042	0.281
Ca^{2+}	0.009	0.062	0.031	0.207
Mg^{2+}	0.005	0.031	0.016	0.103

*The LOD of ions in air (µg/m^3) = [(LOD in solution (µg/mL)) × (final volume of solution (45 mL))] / (average volume of air (6.8 m^3))

3.2 Percent recoveries of ions from PM10 extraction

To find out the optimum extraction conditions for anions and cations in PM10 samples by using ultrasonication, extraction conditions including temperature (35 ºC and 45 ºC), volume of deionized water (30, 45 and 60 mL) and duration (15, 30 and 45 minutes) were optimized.

The 0.3 mL of 100 µg/mL mixed anions standard solution was spiked onto a half of the quartz filter and extracted under the conditions as mentioned above. The final concentrations were 0.5, 0.7 and 1.0 µg/mL. Recoveries of anions extracted from each condition are shown in Table 3.5. The results revealed that good recoveries (85 to 115%) of anions from all extraction conditions (n = 18) were obtained, except for condition number 2, 8, 10, 11, 14 and 16. The condition number 5 (35 ºC, 45 mL deionized water, 30 minutes) was selected because it uses low temperature, medium volume of extractant and appropriate extraction duration. The condition was further tested by varying the final concentrations of ions. The final concentrations were performed at low concentrations (0.1, 0.3, 0.5, 0.8 and 1.0 µg/mL) and high concentrations (2, 4 and 8 µg/mL). Recoveries of anions and cations from each concentration are illustrated in Figure 3.5 and Figure 3.6, respectively. They were obtained from 3 replications of extraction. It was found that the recoveries of anions at low concentrations were 70-292%, while those at high concentrations were 91-105%. The recoveries of cations at low concentrations were 97-174%, while those at high concentrations were 89-97%. It can be seen that the recoveries of anions and cations at high concentrations were better than those at low concentrations. The variation of recoveries at low concentrations was high, which might possibly be caused from a variety of factors, such as the analytical characteristics of the individual analyte, sample matrices, contamination during extraction and analytical errors from the instrumentation.

Table 3.5 Percent recoveries of anions from different extraction conditions

Extraction conditions				% Recovery of ions						min	max	mean	SD	%RSD
Condition No.	Temperature (°C)	Volume (mL)	Duration (minutes)	CH_3COO^-	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}					
1	35	30	15	93	89	96	96	101	89	89	101	94	4	5
2			30	94	92	89	94	79	90	79	94	89	6	6
3			45	86	93	94	92	108	91	86	108	94	7	8
4		45	15	97	95	90	92	107	85	85	107	94	8	8
5			30	95	92	92	91	104	87	87	104	93	6	6
6			45	88	93	94	91	99	92	88	99	93	4	4
7		60	15	95	85	99	98	111	86	85	111	96	10	10
8			30	84	40	115	58	92	87	40	115	79	26	33
9			45	93	91	90	92	98	87	87	98	92	4	4
10	45	30	15	126	91	97	102	76	96	76	126	98	16	17
11			30	138	55	109	102	120	103	55	138	105	28	27
12			45	95	105	103	103	115	103	95	115	104	6	6
13		45	15	94	96	102	95	100	99	94	102	98	3	3
14			30	138	97	105	103	158	105	97	158	118	25	21
15			45	93	99	104	100	109	100	93	109	101	5	5
16		60	15	91	124	104	95	118	99	91	124	106	13	12
17			30	92	95	103	101	104	100	92	104	99	5	5
18			45	98	104	105	101	107	101	98	107	103	3	3

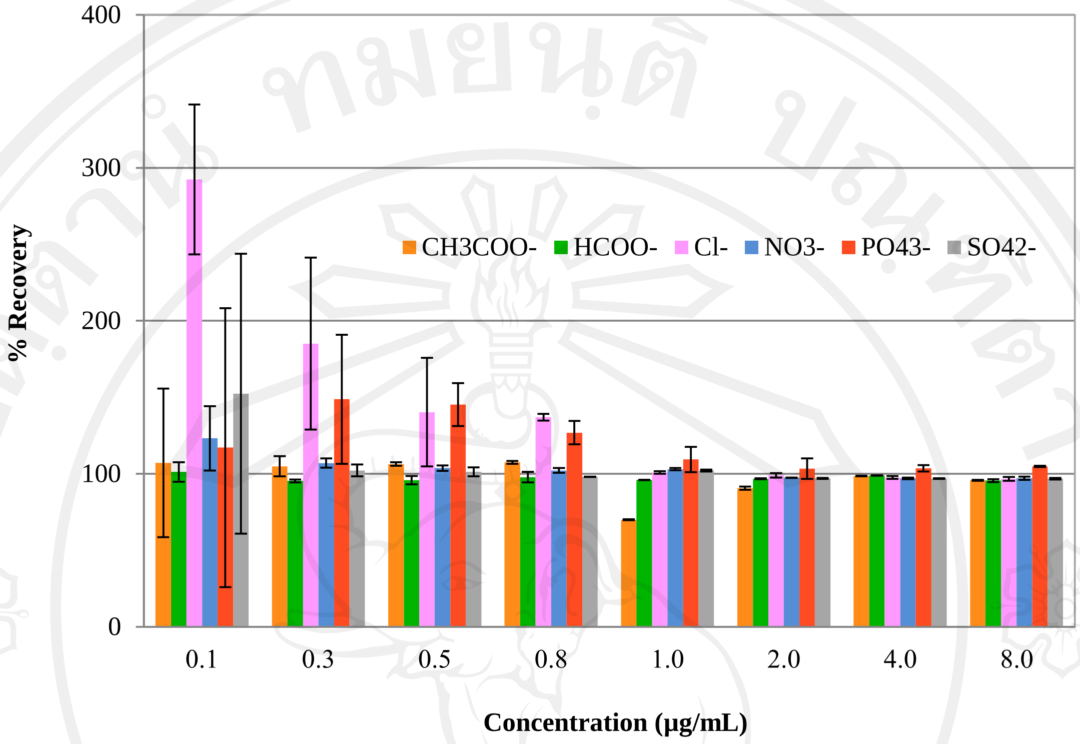


Figure 3.5 Percent recoveries (n = 3) of anions from the optimum extraction

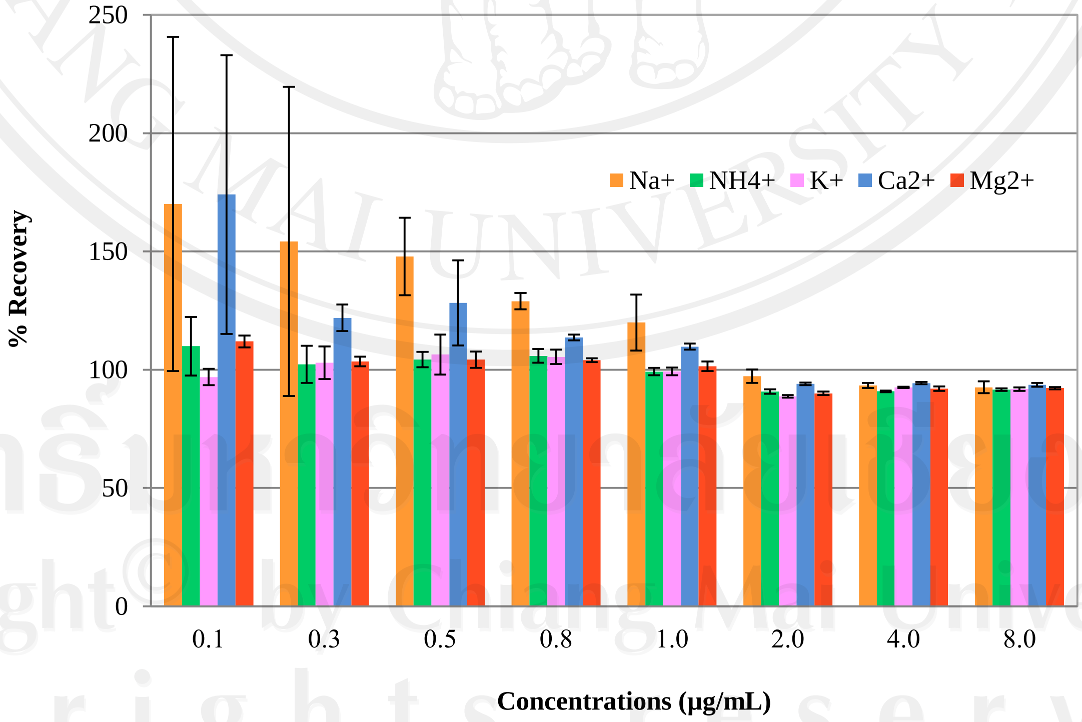


Figure 3.6 Percent recoveries (n = 3) of cations from the optimum extraction

3.3 PM10 in Chiang Mai ambient air

PM10 samples in ambient air were collected at the roof top of the nine-storey Science Complex Building1, Chiang Mai University (SCB1-CMU) using a mini volume air sampler. Each sample was collected within a period of 24 hrs 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 in dry season (n = 51) and twice a week in wet season (n = 7).

3.3.1 Comparison of PM10 concentrations obtained from SCB1-CMU and Air Quality Monitoring (AQM) stations in Chiang Mai Province

The location of SCB1-CMU station and the Air Quality Monitoring (AQM) stations of Pollution Control Department (PCD) in Chiang Mai Province at City Hall (CH) and Yupparaj Wittayalai School (YP) are depicted in Figure 3.7. The location of SCB1-CMU station (373 m above sea level) was approximately 60 m higher than the AQM stations (~ 310 m above sea level).

Figure 3.8 illustrates comparison of PM10 concentrations in ambient air obtained from SCB1-CMU, CH and YP stations (Appendix B-1). The trend of daily PM10 concentrations from SCB1-CMU station and AQM stations was almost the same. Concentrations of PM10 collected in the dry season were significantly higher than those in the wet season. The mean (min-max) of PM10 concentrations obtained in dry season (March - April 2010) from SCB1-CMU, CH and YP stations were 114 $\mu g/m^3$ (74-249 $\mu g/m^3$), 114 $\mu g/m^3$ (58-268 $\mu g/m^3$) and 123 $\mu g/m^3$ (66-280 $\mu g/m^3$), respectively, while those in wet season (July - August 2010) were 21 $\mu g/m^3$ (12-32 $\mu g/m^3$), 19 $\mu g/m^3$ (16-22 $\mu g/m^3$) and 25 $\mu g/m^3$ (18-31 $\mu g/m^3$), respectively. It can be seen that their concentrations in dry season were approximately 5-6 times higher than those in wet season. Among those, 17 samples (29%) from SCB1-CMU station, 18 samples (31%) from CH station and 21 samples (36%) from YP station were exceeded the National Ambient Air Quality Standards in Thailand for 24 hrs of 120 µg/m^3. The highest PM10 concentrations from SCB1-CMU, CH and YP stations were 249, 268 and 280 µg/m^3, respectively, which were found in March. This trend was almost the same as previous studies (Vinitketkumnuen et al., 2002; Chantara et al., 2009), which reported that the PM10 concentrations in Chiang Mai increased at the beginning of dry season (December) and reached its peak in March before decreasing by the end of April.

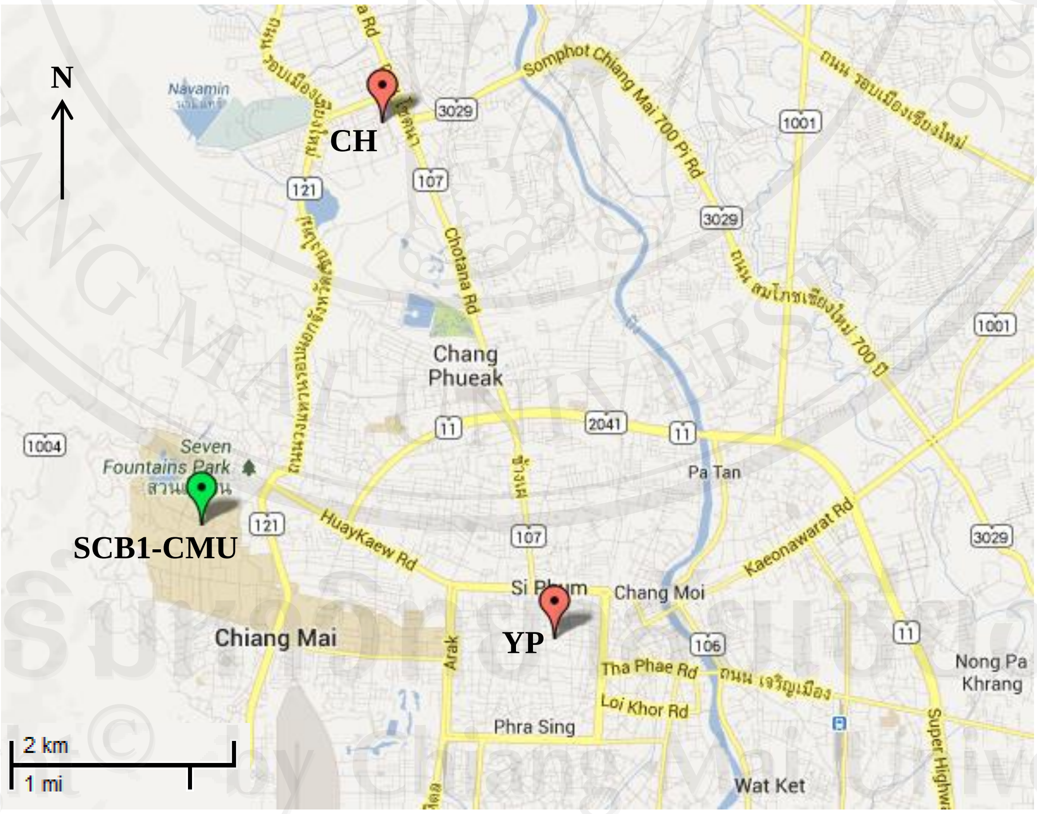


Figure 3.7 Location of SCB1-CMU station and AQM stations (CH and YP) (https://maps.google.com)

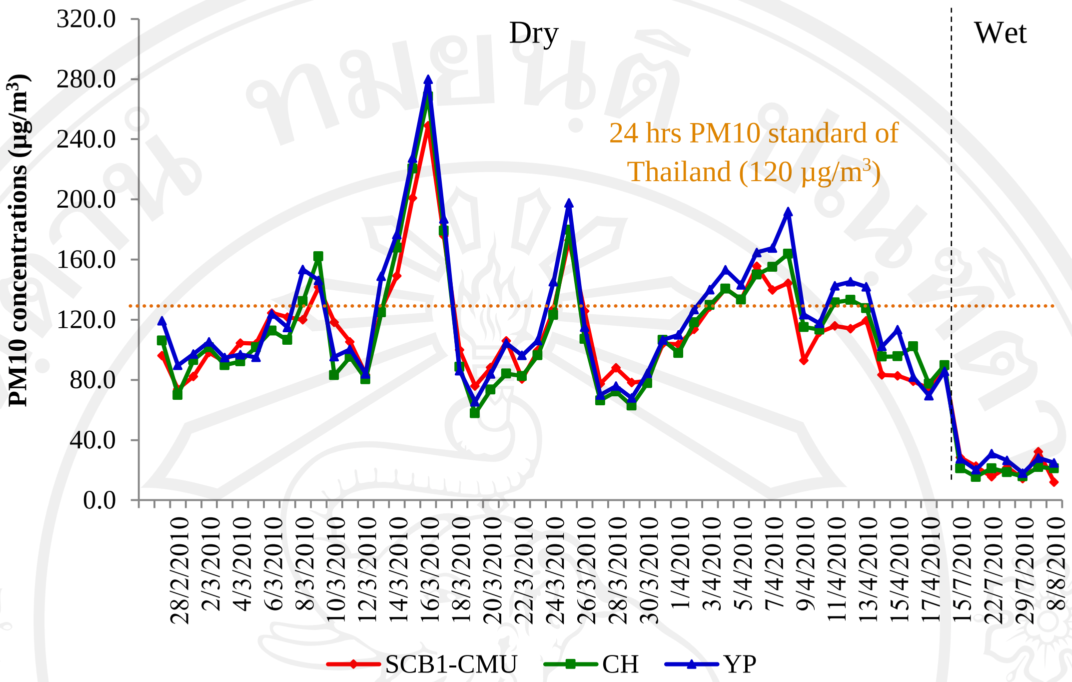


Figure 3.8 Comparison of PM10 concentrations in ambient air obtained from mini volume air sampler (SCB1-CMU) and AQM stations (CH and YP)

In dry season, Chiang Mai air quality is mainly influenced by biomass open burning. During dry period, fires are set for the most part in northern Thailand to clear land for subsequent cultivation by burning of agricultural waste. This method is an inexpensive means to advance crop rotation and control insects, disease and the emergence of invasive weed species (Estrellan and Iino, 2010). Therefore, Chiang Mai Province as well as other provinces in upper northern Thailand has been annually facing air pollution in almost every dry season.

3.3.2 Correlations between PM10 concentrations obtained from mini volume air sampler (SCB1-CMU) and AQM stations (CH and YP)

PM10 concentrations collected by mini volume air sampler at SCB1-CMU were compared with the values obtained from a tapered element oscillating microbalance (TEOM) at the AQM stations of the PCD, which are located at CH and YP stations. The Spearman correlation was used to examine their correlations. The correlation coefficient (r) and scatter plot are shown in Table 3.6 and Figure 3.9.

Table 3.6 Correlations of PM10 concentrations obtained from mini volume air sampler (SCB1-CMU) and TEOM (AQM stations)

Season			CH	YP
Dry (n = 51)	SCB1-CMU	r	0.891^{**}	0.899^{**}
		Sig.(2-tailed)	0.000	0.000
Wet (n = 7)	SCB1-CMU	r	0.356	0.414
		Sig.(2-tailed)	0.434	0.355

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

It was found that concentrations of PM10 obtained from mini volume air sampler (SCB1-CMU) and TEOM (CH and YP) in dry season were significantly correlated ($p < 0.01$), while those in wet season were not significantly correlated. It might be due to lower concentration of PM10 during wet season. Therefore, in wet season might have more affect from the meteorological conditions such as rain precipitation, wind speed and wind direction than that in dry season. The strong correlations were found in dry season. The correlation of PM10 concentrations monitored between SCB1-CMU and CH (r = 0.891) was similar with SCB1-CMU and YP (r = 0.899).

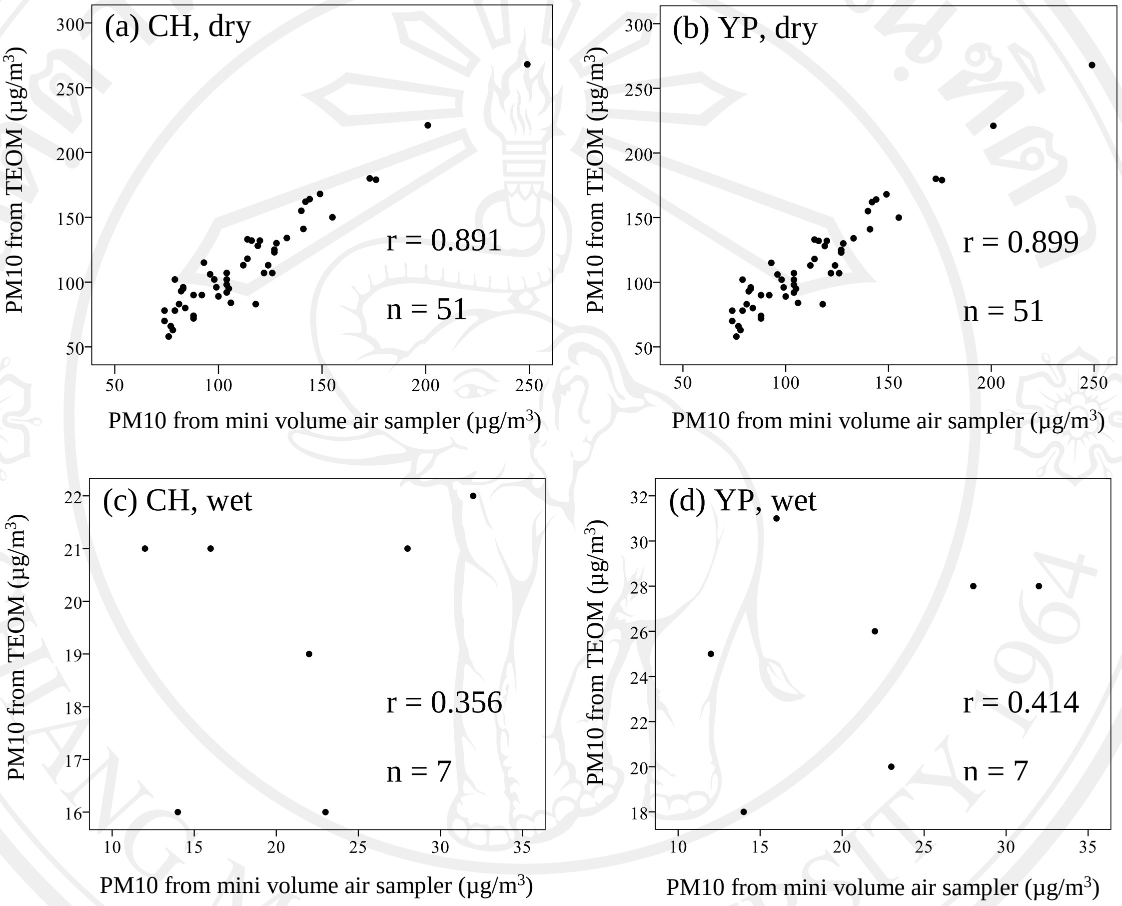


Figure 3.9 Scatter plots of PM10 concentrations obtained from mini volume air sampler (SCB1-CMU) and TEOM (AQM stations)

3.3.3 Values of electro-conductivity and pH of PM10 in ambient air

1) Electro-conductivity (EC) of PM10 in ambient air

EC value indicates level of ion contamination in water. High EC value indicates high ion contamination. EC value of deionized water is normally less than 0.15 mS/m. The EC values of PM10 samples collected during dry season were 0.34-

1.08 mS/m, while the mean ± SD was 0.63 ± 0.14 mS/m. The EC values collected during wet season ranged from 0.28-0.34 mS/m, while the mean ± SD was 0.30 ± 0.02 mS/m. Figure 3.10 shows the concentrations of PM10 affected to the EC values of the samples (Appendix B-2). It can be seen that high PM10 concentrations resulted in high ion concentrations and EC values, while low concentrations of those resulted in opposite direction.

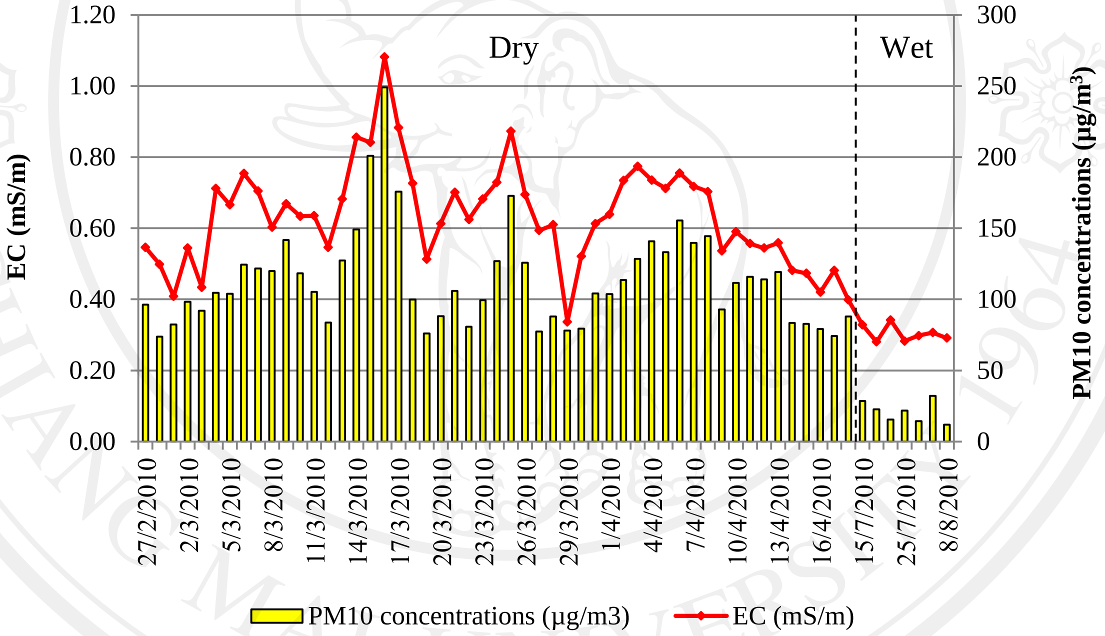


Figure 3.10 Variation of EC values and PM10 concentrations

2) pH of PM10 in ambient air

The variation of pH values in extracted solutions of PM10 are illustrated in Figure 3.11 (Appendix B-2). The mean pH values of PM10 samples collected during dry season (6.5 ± 0.2) and wet season (6.9 ± 0.2) were similar. The pH values collected in dry season ranged from 6.1-7.3, while in wet season ranged from 6.7-7.3.

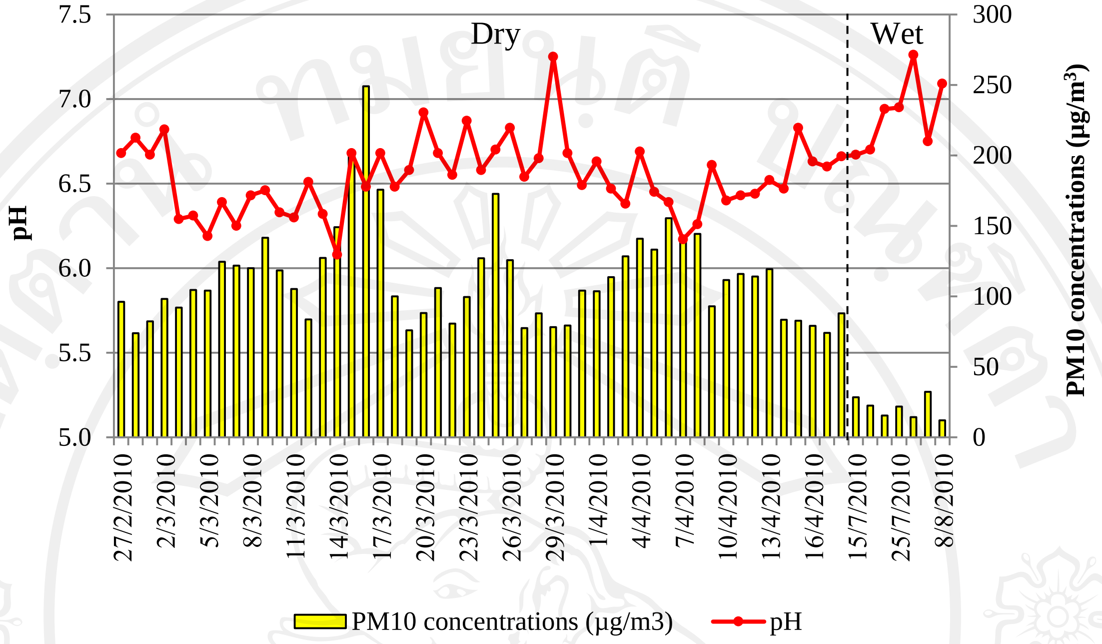


Figure 3.11 Variation of pH values and PM10 concentrations

3.3.4 PM10-bound ions

Ion concentrations extracted from PM10 samples are shown in Figure 3.12, Table 3.7, Appendix B-3 and B-4. The concentrations of total ions were found to have the same trend as PM10 concentrations. The mean concentrations of total ions in dry and wet seasons were 9.95 ± 2.89 µg/m^3 and 1.70 ± 0.33 µg/m^3, respectively. It can be seen that total ion concentrations obtained in the dry season was approximately 6 times higher than those in the wet season. Mean concentrations of ions collected during the dry season in a descending order were 3.94 µg/m^3 (SO_4^{2-}) > 2.55 µg/m^3 (NO_3^-) > 1.40 µg/m^3 (NH_4^+) > 0.95 µg/m^3 (K^+) > 0.44 µg/m^3 (Cl^-) > 0.29 µg/m^3 (Ca^{2+}) > 0.17 µg/m^3 (CH_3COO^-) > 0.05 µg/m^3 (Mg^{2+}). Concentrations of ions collected during wet season in a descending order were 1.06 µg/m^3 (SO_4^{2-}) > 0.39 µg/m^3 (NO_3^-) > 0.23 µg/m^3 (K^+), while the other ions were not detected. The dominant anion and cation in dry season were SO_4^{2-} and NH_4^+, respectively, while those in wet season were SO_4^{2-} and K^+, respectively.

The result was similar to the study of Chantara et al. (2009), which collected PM10 samples for 1 year during June 2005 to June 2006 to cover 3 seasonal periods including wet season (Jun-Sep), dry season (Dec-Mar) and transitioned periods (Oct-Nov and Apr-May) in Chiang Mai City. The results revealed that SO_4^{2-} was the highest anion concentrations in dry (0.004 µg/m^3) and wet season (0.001 µg/m^3), while for cation concentrations were NH_4^+ (0.001 µg/m^3) and Ca^{2+} (0.0008 µg/m^3), respectively. However, the ion concentrations in the study of Chantara et al. (2009) were much lower than those of this study. Furthermore, the result in the present study agreed with the study of Tsai et al. (2012). They collected PM10 samples by Ecotech MicroVol 1100 during February to April 2010 at Chiang Mai University. In their paper, PM10 < 120 µg/m^3 was designated as non-episodic pollution and PM10 ≥ 120 µg/m^3 as PM10 episodic pollution. It was found that SO_4^{2-} and NH_4^+ were the highest anion and cation during both episodes, respectively. Mean concentrations of SO_4^{2-} and NH_4^+ during non-episodic pollution were 1.99 µg/m^3 and 1.23 µg/m^3, respectively, while during episodic pollution they were 3.86 µg/m^3 and 2.71 µg/m^3, respectively. These concentration values were similar to the present study of SO_4^{2-} (3.94 µg/m^3) and NH_4^+ (1.40 µg/m^3) during dry season of 2010.

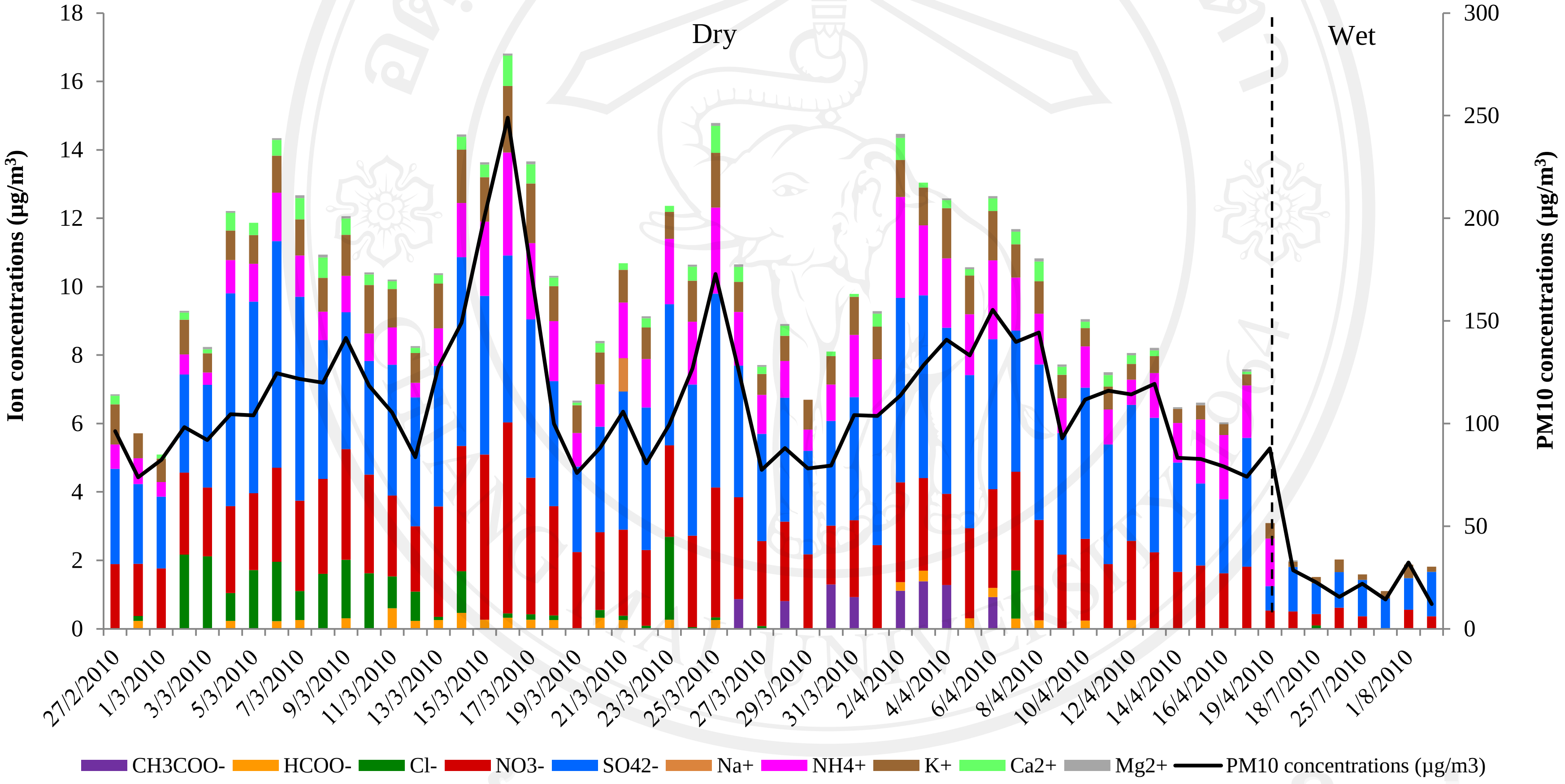


Figure 3.12 Concentrations of PM10 and ion species from ambient air samples

Table 3.7 Ion concentrations (µg/m^3) in dry and wet seasons 2010

Ion species	Dry 2010 (n = 51)				Wet 2010 (n = 7)			
	min	max	mean	SD	min	max	mean	SD
CH_3COO^-	ND	1.39	0.17	0.40	ND	ND	ND	ND
$HCOO^-$	ND	0.60	ND	0.16	ND	ND	ND	ND
Cl^-	ND	2.42	0.44	0.72	ND	0.10	ND	0.04
NO_3^-	0.53	5.58	2.55	0.82	ND	0.61	0.39	0.20
PO_4^{3-}	ND	ND	ND	ND	ND	ND	ND	ND
SO_4^{2-}	0.71	6.63	3.94	1.14	0.88	1.30	1.06	0.18
Na^+	ND	0.97	ND	0.14	ND	ND	ND	ND
NH_4^+	0.36	3.01	1.40	0.61	ND	ND	ND	ND
K^+	0.32	1.95	0.95	0.36	0.15	0.39	0.23	0.10
Ca^{2+}	ND	0.88	0.29	0.21	ND	ND	ND	ND
Mg^{2+}	ND	0.12	0.05	0.03	ND	0.04	ND	0.02
Total ions	**3.09**	**16.82**	**9.95**	**2.89**	**1.10**	**2.03**	**1.70**	**0.33**

ND = not detected (referred to detection limit in Table 3.4 (p. 91))

3.3.5 Correlations between PM10 and ion concentrations

Correlations between PM10 and ion concentrations in dry and wet seasons were examined using the Spearman correlation. It was found that concentrations of PM10 and individual ions in wet season were not significantly correlated. Therefore only the correlations in dry season are illustrated in Table 3.8. The correlations having a greater value than 0.70 are marked bold in the Table. PM10 concentrations were strongly correlated with concentrations of NO_3^- (r = 0.835), SO_4^{2-} (r = 0.749), K^+ (r =

0.737) and Ca^{2+} (r = 0.716). NO_3^- and Ca^{2+} indicate significant inputs from traffic, soil and roadside dust, while SO_4^{2-}indicates significant photochemical formation from anthropogenic activity and photochemical reactions (Tsai et al., 2012), while K^+ is a reasonable biomass burning marker (Engling et al., 2011). It can be concluded that pollutants from those mentioned sources impact on air quality of Chiang Mai during dry season. In addition, PM10 was fairly correlated with $HCOO^-$ (r = 0.586), NH_4^+ (r = 0.497) and Mg^{2+} (r = 0.459). The correlations between K^+ and NO_3^- (r = 0.771), Ca^{2+} and NO_3^- (r = 0.761) and Ca^{2+} and SO_4^{2-} (r = 0.711) were also strong.

Table 3.8 Correlation coefficients of PM10 and PM10-bound ions in dry season 2010

	PM10	CH_3COO^-	$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM10	1.000										
CH_3COO^-	0.124	1.000									
$HCOO^-$	0.586^{**}	-0.066	1.000								
Cl^-	0.143	-0.391^{**}	0.315^{*}	1.000							
NO_3^-	$\mathbf{0.835}^{**}$	0.100	0.616^{**}	0.313^{*}	1.000						
SO_4^{2-}	$\mathbf{0.749}^{**}$	0.125	0.534^{**}	0.232	$\mathbf{0.714}^{**}$	1.000					
Na^+	0.010	-0.061	0.093	0.072	0.019	0.029	1.000				
NH_4^+	0.497^{**}	0.313^{*}	0.393^{**}	-0.204	0.502^{**}	0.508^{**}	0.096	1.000			
K^+	$\mathbf{0.737}^{**}$	0.188	0.525^{**}	0.281^{*}	$\mathbf{0.771}^{**}$	0.557^{**}	0.014	0.394^{**}	1.000		
Ca^{2+}	$\mathbf{0.716}^{**}$	0.005	0.386^{**}	0.316^{*}	$\mathbf{0.761}^{**}$	$\mathbf{0.711}^{**}$	-0.072	0.269	0.607^{**}	1.000	
Mg^{2+}	0.459^{**}	-0.121	0.198	-0.099	0.382^{**}	0.328^{*}	-0.198	0.285^{*}	0.150	0.554^{**}	1.000

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

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

3.4 Composition of biomass samples

Three types of biomass, including rice straw, maize residue and leaf litter 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 (MR), Doi Saket (DK) and Chiang Dao (CD) districts, while maize residue was collected from MR, Mae Chaem (MC) and CD districts. Each biomass type was collected from three locations in each district. Biomass was randomly sampled by using a 1 m^2 grid. 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 district (nine grids) were homogenized and collected into a plastic bag for measurement of moisture content and carbon (C), hydrogen (H) and nitrogen (N) content. The number of samples for each biomass type from the three districts was three and the total sample number was 9 (three biomass types).

3.4.1 Moisture content

Moisture contents of three biomass types were ranged from 6 to 11% (Table 3.9). The mean moisture content of maize residue (11.24%) was higher than that of rice straw (9.24%) and leaf litter (6.51%).

Table 3.9 Moisture content of biomass samples

Biomass type	Sample code	Moisture content (%)
		Mean ± SD
Rice straw	R-MR	9.82 ± 0.72
(n = 3)	R-DK	8.48 ± 0.69
	R-CD	10.30 ± 0.32
	Average	**9.24 ± 0.98**
Maize residue	M-MR	13.25 ± 3.49
(n = 3)	M-MC	10.67 ± 3.06
	M-CD	10.87 ± 4.43
	Average	**11.24 ± 3.53**
Leaf litter	L-MR	6.38 ± 0.70
(n = 3)	L-DK	5.51 ± 0.69
	L-CD	7.63 ± 0.84
	Average	**6.51 ± 1.16**

3.4.2 C, H and N contents

C, H and N contents were not much different among different biomass types (Table 3.10) (Appendix C). The mean percent of C, H and N were ranged from 36.2-46.4%, 5.2-5.8% and 0.5-1.4%, respectively. Leaf litter contained higher C and H than the maize residue and rice straw, respectively. However, maize residue contained higher N than the other biomass. This might be related to fertilizer used during crop planting.

Table 3.10 C, H, N content of biomass samples

Biomass type	Sample code	Mean ± SD (%)		
		C	H	N
Rice straw	R-MR	36.60 ± 0.26	5.18 ± 0.17	0.27 ± 0.02
(n = 3)	R-DK	37.15 ± 0.29	5.04 ± 0.12	0.32 ± 0.08
	R-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 residue	M-MR	39.20 ± 0.35	5.03 ± 0.08	1.98 ± 0.15
(n = 3)	M-MC	39.54 ± 0.13	6.01 ± 0.19	1.25 ± 0.09
	M-CD	42.79 ± 0.17	5.97 ± 0.08	1.00 ± 0.18
	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
(n = 3)	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
	Average	**46.43 ± 1.75**	**5.84 ± 0.19**	**0.47 ± 0.22**

3.5 Emission of pollutants from biomass burning in the combustion chamber

PM10 and water-soluble samples were collected from burning experiment. Gas concentrations including CO, NO, NO_2 and SO_2 were measured by gas analyzer during the burning. The extracted solution of PM10 samples and water-soluble samples were measured for electro-conductivity (EC) and pH before ion analysis.

3.5.1 Emission of gases from biomass burning

The measured CO, NO, NO_2 and SO_2 concentrations from rice straw, maize residue and leaf litter burning in the chamber are presented in Table 3.11 (Appendix D-1). The EFs of gases based on the unit of g/kg from rice straw burning in a descending order were CO (52.8 ± 12.2) >> NO_2 (1.5 ± 0.5) > NO (0.8 ± 0.2) > SO_2 (0.4 ± 0.6). For maize residue burning emitted CO (40.8 ± 9.5) >> NO_2 (2.3 ± 0.6) > NO (1.8 ± 0.7), while EF of SO_2 was not detected. The burning of leaf litter emitted CO (54.0 ± 15.7) >> NO_2 (2.7 ± 0.6) > NO (1.7 ± 0.3) > SO_2 (0.2 ± 0.3). The EFs of CO, NO_2, NO and SO_2 emitted from biomass burning were 41-54, 1.5-2.7, 0.8-1.8 and ND-0.4 g/kg, respectively. It can be seen that the EFs of gases emitted from three types of biomass burning were found to be the same trend and the EF of CO (18-270 times) was much higher than the other gases. The EFs of CO from rice straw and leaf litter burning were similar (53-54 g/kg), which were higher than that from maize residue burning (41 g/kg). Comparison with other studies shows that the EF of CO emitted from rice straw burning in this study (52.8 ± 12.2 g/kg) was very close to that reported for Huizhou, China (Zhang et al., 2012) (53.2 ± 17.9 g/kg), while it was higher than those reported for California, USA (Kadam et al., 2000) (34.7 g/kg). However, it was lower than those reported for Xi’an, China (Cao et al., 2008) (68.0 ± 25.6 g/kg) and Beijing, China (Wei et al., 2012) (70.3 ± 2.3 g/kg). The EF of CO emitted from maize residue burning in this study (40.8 ± 9.5 g/kg) was slightly higher than the study of Wei et al. (2012) (36.5 ± 3.8 g/kg), but lower than the study of Cao et al. (2008) (67.6 ± 13.0 g/kg). In addition, the trend of gases emitted from rice straw and maize residue burning in this study were similar to the study of Cao et al. (2008), which reported that the EFs of gases from rice straw burning were CO (68.0 ± 25.6

Table 3.11 Concentrations of gas species emitted from biomass burning

Biomass type	Sample code	Concentrations (Mean ± SD)							
		ppm				EFs (g/kg)			
		CO	NO	NO_2	SO_2	CO	NO	NO_2	SO_2
Rice straw	R-MR	764 ± 69.6	8.2 ± 2.4	9.6 ± 1.9	0.64 ± 1.1	52.5 ± 5.0	0.6 ± 0.2	1.1 ± 0.2	0.1 ± 0.2
(n = 3)	R-DK	987 ± 94.2	10 ± 0.37	14 ± 1.7	5.6 ± 5.0	67.9 ± 5.9	0.7 ± 0.0	1.6 ± 0.2	0.9 ± 0.8
	R-CD	627 ± 145	13 ± 4.1	17 ± 4.7	0.63 ± 1.1	43.2 ± 10.5	1.0 ± 0.3	1.9 ± 0.6	0.1 ± 0.2
	Average	**768 ± 176**	**10 ± 3.2**	**14 ± 4.3**	**2.3 ± 3.6**	**52.8 ± 12.2**	**0.8 ± 0.2**	**1.5 ± 0.5**	**0.4 ± 0.6**
Maize residue	M-MR	283 ± 41.9	10 ± 2.3	9.1 ± 3.1	ND	39.0 ± 6.0	1.5 ± 0.3	2.0 ± 0.7	ND
(n = 3)	M-MC	240 ± 58.9	17 ± 3.7	12 ± 2.5	ND	32.8 ± 7.5	2.4 ± 0.6	2.7 ± 0.5	ND
	M-CD	371 ± 32.1	11 ± 4.6	10 ± 2.7	ND	50.6 ± 5.0	1.6 ± 0.7	2.1 ± 0.6	ND
	Average	**298 ± 70.1**	**12 ± 4.5**	**10 ± 2.8**	**ND**	**40.8 ± 9.5**	**1.8 ± 0.7**	**2.3 ± 0.6**	**ND**
Leaf litter	L-MR	372 ± 91.3	11 ± 2.1	13 ± 1.3	0.84 ± 1.5	49.6 ± 12.2	1.6 ± 0.3	3.0 ± 0.3	0.3 ± 0.4
(n = 3)	L-DK	517 ± 75.2	12 ± 2.2	10 ± 4.3	ND	71.2 ± 10.1	1.7 ± 0.3	2.3 ± 1.0	ND
	L-CD	304 ± 33.0	13 ± 2.8	12 ± 1.8	0.98 ± 1.4	41.2 ± 4.2	1.9 ± 0.4	2.7 ± 0.4	0.3 ± 0.4
	Average	**398 ± 113**	**12 ± 2.2**	**12 ± 2.8**	**0.60 ± 1.1**	**54.0 ± 15.7**	**1.7 ± 0.3**	**2.7 ± 0.6**	**0.2 ± 0.3**

ND = not detected

g/kg) >> NO (3.1 ± 0.9 g/kg) > NO_2 (0.3 ± 0.2 g/kg) > SO_2 (0.2 ± 0.3 g/kg), while from maize residue burning were CO (67.6 ± 13.0 g/kg) >> NO (3.3 ± 0.7 g/kg) > NO_2 (0.3 ± 0.1 g/kg) > SO_2 (0.04 ± 0.04 g/kg).

3.5.2 Emission of PM10 from biomass burning

The samples of PM10 were collected from burning of various types of biomass in the combustion chamber as illustrated in Figure 3.13.

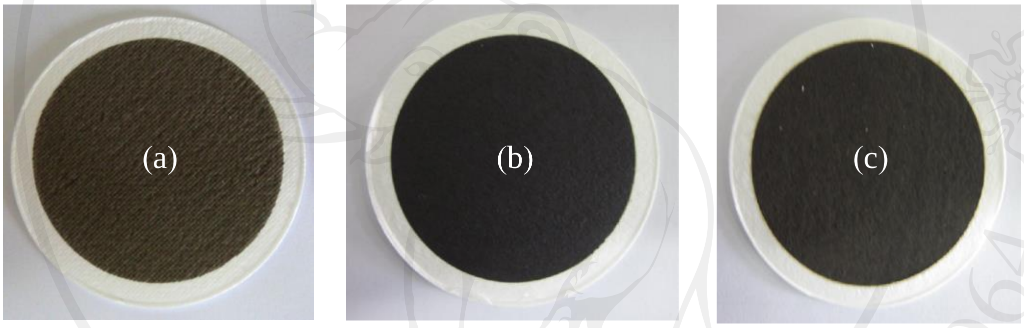


Figure 3.13 PM10 samples on quartz fiber filter from burning of (a) rice straw, (b) maize residue and (c) leaf litter in the combustion chamber

1) Values of EC and pH of PM10 samples

The average EC and pH values of the extracted solution of PM10 samples are shown in Table 3.12 (Appendix D-2). The average EC values from rice straw, maize residue and leaf litter burning were 7.06 ± 1.97, 5.60 ± 2.53 and 2.66 ± 0.73 mS/m, respectively. The highest EC value was found from rice straw burning, while the lowest value was found from leaf litter burning. The average pH values from all types of biomass were almost the same (5.0-5.4).

Table 3.12 EC and pH values of PM10 extracted solution

Biomass Type	Code	EC (mS/m) (n=3)	pH (n=3)
Rice straw	R-MR	7.69 ± 2.13	5.0 ± 0.0
	R-DK	5.89 ± 2.27	4.9 ± 0.2
	R-CD	7.62 ± 1.64	5.0 ± 0.1
	Average	**7.06 ± 1.97**	**5.0 ± 0.1**
Maize residue	M-MR	3.53 ± 0.67	5.4 ± 0.3
	M-MC	4.91 ± 1.31	5.5 ± 0.1
	M-CD	8.35 ± 2.23	5.4 ± 0.2
	Average	**5.60 ± 2.53**	**5.4 ± 0.2**
Leaf litter	L-MR	2.74 ± 0.22	5.0 ± 0.3
	L-DK	3.21 ± 0.74	4.9 ± 0.1
	L-CD	2.03 ± 0.68	5.0 ± 0.2
	Average	**2.66 ± 0.73**	**5.0 ± 0.2**

2) Emission factors (EFs) of PM10 and ions species from biomass burning

The PM10 samples collected from rice straw, maize residue and leaf litter burning in the chamber were analyzed for anions and cations. The minimum (min), maximum (max), mean and standard deviation (SD) of emissions of PM10 and ions are presented in Table 3.13 (Appendix D-3).

The EFs of PM10 from the burning in a descending order were leaf litter (1.52 ± 0.65 g/kg) > maize residue (0.90 ± 0.31 g/kg) > rice straw (0.69 ± 0.23 g/kg). The EF of PM10 emitted from leaf litter burning was about 2 times higher than those from rice straw and maize residue burning. The EF of PM10 from rice straw burning in this study (0.69 g/kg) was lower than the study of Zhang et al. (2012) (14.0 g/kg), which was designed different chamber. Furthermore, EFs of PM10 from open burning of rice straw in the other studies were 3.5 g/kg (Jenkins et al., 1996), 3.7 g/kg (Kadam et al., 2000), 9.4 g/kg (Kim Oanh et al., 2011) and 6.5 g/kg (Garivait et al., 2009). Similarly, EFs of PM10 from maize residue burning in this study (0.90 g/kg) were also lower than the studies of Jenkins et al. (1996) (6.2 g/kg) and Garivait et al. (2009) (13.0 g/kg).

The EFs of total ions from the biomass burning in this study were 133 ± 38 mg/kg (rice straw), 228 ± 116 mg/kg (maize residue) and 82 ± 26 mg/kg (leaf litter). EFs of total ions emitted from maize residue burning were approximately 2-3 times higher than those from rice straw and leaf litter burning. Furthermore, EFs of K^+, Cl^-, SO_4^{2-}, NH_4^+ and NO_3^- were found to be the dominant ions from all types of biomass burning. It was agreed with the study of Niemi et al. (2004), which revealed that K^+, SO_4^{2-}, NH_4^+ and NO_3^- were the major ions found during the Helsinki haze event caused by agricultural burning. In addition, concentrations of K^+, Cl^- and NO_3^- were high from the biomass burning period in the rural area of Korea (Ryu et al., 2007). Park et al. (2004) also reported that concentrations of K^+ and Cl^- were greatly high in the agricultural waste burning event in Korea.

EFs of ions emitted from rice straw burning in descending order were K^+ (46.9 ± 16.5 mg/kg) > Cl^- (45.8 ± 15.5 mg/kg) >> SO_4^{2-} (18.2 ± 5.4 mg/kg) > NH_4^+ (10.6 ± 4.4 mg/kg) > NO_3^- (8.7 ± 2.3 mg/kg), while those from maize residue burning were K^+ (85.6 ± 53.1 mg/kg) > Cl^- (79.2 ± 48.9 mg/kg) >> SO_4^{2-} (31.4 ± 14.9 mg/kg) > NH_4^+ (17.6 ± 9.7 mg/kg) > NO_3^- (12.5 ± 3.8 mg/kg). It can be seen that the emission patterns of ions from rice straw and maize residue burning were the same. EFs of each ion from maize residue burning were about 2 times higher than those from rice straw burning. Moreover, K^+ and Cl^- were the major cation and anion emitted from agricultural waste burning, respectively. However, EFs of ions from leaf litter burning in a descending order were SO_4^{2-} (20.4 ± 6.2 mg/kg) > K^+ (18.4 ± 10.9 mg/kg) > NO_3^- (15.0 ± 4.2 mg/kg) > Cl^- (14.4 ± 11.2 mg/kg) > NH_4^+ (12.4 ± 6.4 mg/kg). Concentrations of all ions emitted from leaf litter burning were almost the same.

K^+ and Cl^- are from biomass burning particles, and aerosol K^+ has been regarded as a common useful tracer of biofuel combustion and biomass burning emissions (Dibb et al., 1995; Liu et al., 2000; Dabell et al., 2004; Duan et al., 2004; Hsu et al., 2009). Combustion of plant matter, K^+ is a major cytoplasmic electrolyte, releases large amounts of K^+ -rich particles in the submicron size fraction (Andreae, 1983). In this study, K^+ and Cl^- were the major ions emitted from rice straw and maize residue burning, which might be related to the fertilizers and herbicides used on agricultural land.

EF of K^+ from rice straw burning in this study (47 mg/kg) was approximately 10-15 times lower than those reported by Turn et al. (1997) (480 mg/kg), Zhang et al. (2012) (640 mg/kg) and Cao et al. (2008) (715 mg/kg). For maize residue burning, EF of K^+ in this study (86 mg/kg) was about 2-8 times lower than Cao et al. (2008) (180 mg/kg) and Turn et al. (1997) (730 mg/kg). It revealed that emissions of ions in this study were much lower than those of the other studies. There are various possible factors, which could have affected the emission factors, such as the type of combustion chamber used, the specific burning conditions and the relevant biomass properties (moisture content, elemental composition, planting location, agricultural chemicals used, etc.). Obernberger and Thek (2004) revealed that the density of biomass influences the combustion behavior, as a higher density shows a longer burnout time. The moisture content of biomass has an influence on the net calorific value, the combustion efficiency and the temperature of the actual combustion. On the other hand, it was very difficult to indicate how each factor can directly affect the EFs.

The percentage of ions species from the burning of each biomass type is performed (Figure 3.14). It was found that the pattern of ion species emitted from rice straw and maize residue burning were almost the same. The percentage of major ions emitted from rice straw burning in a descending order were K^+ = Cl^- (35%) > SO_4^{2-} (14%) > NH_4^+ (8%) > NO_3^- (7%), while those from maize residue burning were K^+ (38%) > Cl^- (35%) > SO_4^{2-} (14%) > NH_4^+ (8%) > NO_3^- (6%). The K^+ and Cl^- were dominant ions from the burning of rice straw and maize residue, which were approximately 35-38%. Potassium was probably originated from fertilizers (Tsai et al., 2012), while Cl^- was likely came from herbicides used in the field. According to the information from intensive interviews with the farmers in the study sites, paraquat dichloride ($C_{12}H_{14}N_2Cl_2$) is widely used as a herbicide in maize plantation. Panuwet et al. (2012) studied about agricultural pesticide management in Thailand and reported that paraquat dichloride is one of the most imported herbicides used in Thailand besides glyphosate, 2,4-D, ametryn and atrazine. In case of leaf litter burning, the percentage of major ions in a descending order were SO_4^{2-} (25%) > K^+ (23%) > NO_3^- (18%) = Cl^- (18%) > NH_4^+ (15%). Apart from SO_4^{2-} and K^+, which were the dominant ions, the emission of other ions was almost the same amount.

Table 3.13 Emission factors of PM10 and ions from biomass burning

Biomass type		PM10	EFs of ions (mg/kg)											
		(g/kg)	CH_3COO^-	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Total
Rice straw	min	0.20	ND	0.14	22.33	3.99	0.08	9.62	0.08	5.19	24.92	0.00	0.00	67
(n = 9)	max	0.88	ND	0.36	75.56	10.88	3.55	27.49	2.41	19.40	81.71	0.21	0.05	196
	mean	**0.69**	**ND**	**0.26**	**45.83**	**8.73**	**1.20**	**18.18**	**0.78**	**10.61**	**46.87**	**0.07**	**0.01**	**133**
	SD	**0.23**	**ND**	**0.08**	**15.46**	**2.26**	**1.33**	**5.38**	**0.82**	**4.36**	**16.47**	**0.08**	**0.02**	**38**
Maize	min	0.42	ND	0.22	36.37	7.24	0.00	13.87	0.00	7.10	34.45	0.00	0.00	126
residue	max	1.43	ND	3.01	191.93	20.37	1.59	47.84	0.89	31.35	194.12	0.49	0.05	485
(n = 9)	**mean**	**0.90**	**ND**	**0.61**	**79.22**	**12.53**	**0.21**	**31.39**	**0.39**	**17.57**	**85.56**	**0.05**	**0.01**	**228**
	SD	**0.31**	**ND**	**0.91**	**48.92**	**3.79**	**0.52**	**14.90**	**0.36**	**9.73**	**53.09**	**0.16**	**0.02**	**116**
Leaf litter	min	0.66	ND	0.31	3.14	8.84	0.00	10.83	0.00	6.33	5.58	0.00	0.00	45
(n = 9)	max	2.97	ND	0.75	37.62	22.01	0.00	30.40	1.30	28.24	37.95	0.13	0.10	118
	mean	**1.52**	**ND**	**0.51**	**14.43**	**15.02**	**0.00**	**20.42**	**0.50**	**12.44**	**18.41**	**0.02**	**0.04**	**82**
	SD	**0.65**	**ND**	**0.14**	**11.17**	**4.18**	**0.00**	**6.16**	**0.51**	**6.44**	**10.90**	**0.04**	**0.03**	**26**

ND = not detected

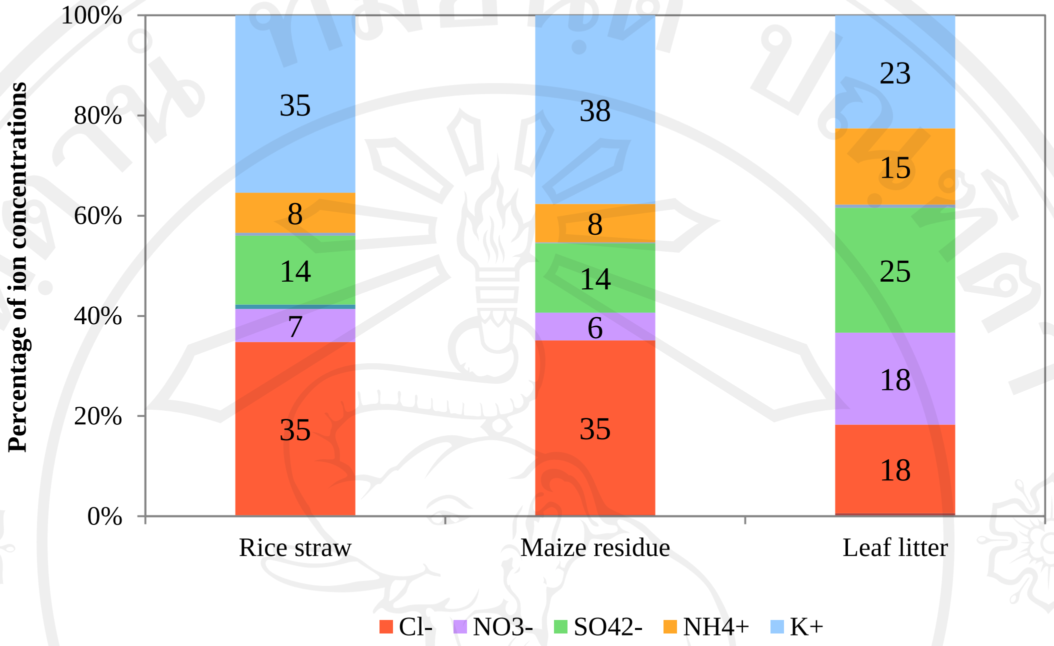


Figure 3.14 Percentage of ion species emitted from biomass burning for collecting PM10 samples

3) Correlations of PM10 and PM10-bound ions

Correlations between PM10 and individual ions were examined using the Spearman correlations as illustrated in Tables 3.14-3.16. The strong correlations were marked with bold values.

Rice straw burning

The significantly strong correlation ($p < 0.01$) was found between concentrations of PM10 and $HCOO^-$ (r = 0.826) and K^+ and Cl^- (r = 0.921). The relatively strong correlations ($p < 0.05$) were found between Na^+ and $HCOO^-$ (r = 0.703), Na^+ and PO_4^{3-} (r = 0.705), NH_4^+ and SO_4^{2-} (r = 0.797) and K^+ and NO_3^- (r = 0.733).

Maize residue burning

Strong correlation ($p < 0.01$) between K^+ and Cl^- (r = 0.929) was observed. The correlations between PM10 and NH_4^+ (r = 0.681), NH_4^+ and PO_4^{3-} (r = 0.745) and NH_4^+ and SO_4^{2-} (r = 0.767) were relatively strong ($p < 0.05$).

Interestingly, the concentrations between K^+ and Cl^- were strong correlated in rice straw and maize residue burnings. Lee et al. (2011) reported that K^+ and Cl^- have a high correlation near fires and derived that K^+ should exist in the form of KCl. These results were similar to the study of Panyakapo et al. (2008), which presented that K^+ had a strong correlation with Cl^- (r = 0.96), this findings show that part of the Cl^- came from a specific source. Furthermore, Khare et al. (2004) mentioned that K^+ is associated with the airborne particles, which are generated from biomass burning. In this study, high correlations between K^+ and Cl^- were found only in agricultural waste burning. It can be concluded that they were generated from the same source (agricultural waste enriched with fertilizer and herbicides) and should exist in the form of KCl.

Leaf litter burning

The concentrations between PM10 and NH_4^+ (r = 0.729) and PM10 and Mg^{2+} (r = 0.762) were relatively strong correlated ($p < 0.05$). Tn he relatively strong correlation among individual ions was found between NH_4^+ and Cl^- (r = 0.681) ($p < 0.05$).

Table 3.14 Correlation coefficients of PM10 and PM10-bound ions obtained from rice straw burning

	PM10	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM10	1.000										
$HCOO^-$	**0.826****	1.000									
Cl^-	0.173	0.248	1.000								
NO_3^-	-0.127	-0.159	**0.778***	1.000							
PO_4^{3-}	0.390	**0.705***	0.544	0.215	1.000						
SO_4^{2-}	-0.035	0.336	0.559	0.471	0.519	1.000					
Na^+	0.344	**0.703***	0.434	0.290	**0.705***	0.554	1.000				
NH_4^+	-0.017	0.303	0.367	0.122	0.477	**0.797***	0.196	1.000			
K^+	0.277	0.249	**0.921****	**0.733***	0.387	0.392	0.436	0.151	1.000		
Ca^{2+}	0.054	0.331	-0.131	-0.064	0.433	0.204	0.600	-0.165	-0.109	1.000	
Mg^{2+}	-0.123	0.245	-0.238	-0.353	0.442	-0.060	0.470	-0.099	-0.219	**0.714***	1.000

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

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

Table 3.15 Correlation coefficients of PM10 and PM10-bound ions obtained from maize residue burning

	PM10	$HCOO^-$	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM10	1.000										
$HCOO^-$	0.493	1.000									
Cl^-	0.077	0.468	1.000								
NO_3^-	0.168	0.664	0.140	1.000							
PO_4^{3-}	0.305	0.617	0.262	0.510	1.000						
SO_4^{2-}	0.562	**0.690***	0.653	0.532	**0.745***	1.000					
Na^+	-0.526	0.280	0.237	0.504	0.170	0.000	1.000				
NH_4^+	**0.681***	0.431	0.234	0.143	**0.745***	**0.767***	-0.329	1.000			
K^+	-0.060	0.449	**0.929****	0.236	0.075	0.483	0.481	0.000	1.000		
Ca^{2+}	-0.560	-0.425	-0.275	-0.555	-0.306	-0.548	-0.069	-0.274	-0.274	1.000	
Mg^{2+}	0.140	-0.425	-0.138	-0.347	0.306	0.137	-0.485	0.411	-0.411	-0.125	1.000

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

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

Table 3.16 Correlation coefficients of PM10 and PM10-bound ions obtained from leaf litter burning

	PM10	$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM10	1.000									
$HCOO^-$	0.159	1.000								
Cl^-	0.282	0.100	1.000							
NO_3^-	-0.203	0.217	-0.303	1.000						
SO_4^{2-}	0.424	0.390	0.353	0.367	1.000					
Na^+	0.156	-0.190	-0.124	0.443	0.128	1.000				
NH_4^+	**0.729**[*]	0.312	**0.681**[*]	-0.100	0.567	0.221	1.000			
K^+	-0.221	0.553	0.371	0.594	0.619	0.150	0.234	1.000		
Ca^{2+}	-0.023	-0.024	-0.506	0.365	0.091	**0.699**[*]	-0.137	0.000	1.000	
Mg^{2+}	**0.762**[*]	0.195	0.330	-0.306	0.111	-0.035	0.417	-0.231	-0.047	1.000

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

3.5.3 Water-soluble samples

The pollutants emitted from burning of each biomass sample in the combustion chamber were continuously collected for 2 hours in the smoke collector, which contains 10 L of deionized water. A pump was used for sucking air from the storage chamber into the smoke collector. The flow rate was 31 L/min. The water-soluble sample was measured for EC and pH. Another 100 mL of samples was evaporated by vacuum rotary until it was ~25 mL for further ion analysis by IC.

1) Emission factors (EFs) of gases from biomass burning

The concentrations of CO, NO, NO_2 and SO_2 were continuously measured by gas analyzer during biomass burning in the combustion chamber as shown in Table 3.17 (Appendix E-1). The results found that SO_2 was not detected from all types of biomass burning. The EFs of gases (g/kg) emitted from rice straw burning in a descending order were CO (53.3 ± 19.0) >> NO_2 (1.6 ± 0.5) > NO (0.9 ± 0.3). The burning of maize residue emitted CO (52.4 ± 8.8) >> NO_2 (3.6 ± 0.4) > NO (1.2 ± 0.5). Leaf litter burning emitted CO (49.7 ± 11.5) >> NO_2 (3.5 ± 0.7) > NO (1.3 ± 0.5). The trend of gases emitted from all types of biomass was the same. Carbon monoxide was the dominant gas. The EFs (g/kg) of CO, NO_2 and NO emitted from biomass burning were 50-54, 1.6-3.6 and 0.9-1.3, respectively.

The EFs of gases from the burnings of individual biomass type in the chamber during the PM10 sampling were compared with those during the sampling of water-soluble samples. They showed the same trend, which were CO >> NO_2 > NO > SO_2. The EFs of CO, NO_2, NO and SO_2 of PM10 samples ranged from 41-54, 1.5-2.7, 0.8-1.8 and ND-0.4 g/kg, respectively. Moreover, their emission values were almost

Table 3.17 Concentrations of gas species emitted from biomass burning for collecting water-soluble samples

Biomass type	Sample code	Concentrations (Mean ± SD)							
		ppm				EFs (g/kg)			
		CO	NO	NO_2	SO_2	CO	NO	NO_2	SO_2
Rice straw	R-MR	798 ± 279	10 ± 3.8	10 ± 4.7	ND	55.7 ± 19.5	0.7 ± 0.3	1.2 ± 0.5	ND
(n = 3)	R-DK	873 ± 336	12 ± 2.5	14 ± 3.4	ND	60.8 ± 23.4	0.9 ± 0.2	1.6 ± 0.4	ND
	R-CD	629 ± 235	14 ± 5.3	18 ± 3.0	ND	43.4 ± 16.5	1.0 ± 0.4	2.0 ± 0.4	ND
	Average	**767 ± 271**	**12 ± 4.0**	**14 ± 4.6**	**ND**	**53.3 ± 19.0**	**0.9 ± 0.3**	**1.6 ± 0.5**	**ND**
Maize residue	M-MR	443 ± 49.1	7.8 ± 1.9	15 ± 1.2	ND	60.2 ± 5.8	1.1 ± 0.3	3.3 ± 0.2	ND
(n = 3)	M-MC	357 ± 58.1	10 ± 4.7	17 ± 1.9	ND	48.5 ± 7.9	1.4 ± 0.7	3.7 ± 0.4	ND
	M-CD	337 ± 56.1	6.6 ± 2.3	17 ± 0.20	ND	46.5 ± 7.3	1.0 ± 0.3	3.8 ± 0.0	ND
	Average	**384 ± 67.5**	**8.2 ± 3.1**	**16 ± 1.6**	**ND**	**52.4 ± 8.8**	**1.2 ± 0.5**	**3.6 ± 0.4**	**ND**
Leaf litter	L-MR	318 ± 48.9	11 ± 2.9	14 ± 3.6	ND	43.9 ± 7.1	1.7 ± 0.4	3.1 ± 0.8	ND
(n = 3)	L-DK	440 ± 38.7	9.2 ± 2.6	15 ± 1.8	ND	60.5 ± 6.3	1.4 ± 0.4	3.4 ± 0.4	ND
	L-CD	322 ± 94.5	6.7 ± 3.7	17 ± 3.6	ND	44.7 ± 13.4	1.0 ± 0.6	3.9 ± 0.8	ND
	Average	**360 ± 82.5**	**9.1 ± 3.4**	**15 ± 3.1**	**ND**	**49.7 ± 11.5**	**1.3 ± 0.5**	**3.5 ± 0.7**	**ND**

ND = not detected

the same, when the same type and same amount of biomass samples were burned. This shows efficiency of the combustion chamber in terms of reproducibility.

2) Values of EC and pH of water-soluble samples

The average EC and pH values of water-soluble samples are performed (Table 3.18) (Appendix E-2). The average EC values from all types of biomass were similar, which ranged from 1.10-1.32 mS/m. The samples of rice straw burning showed the highest EC value. The average pH values from all types of biomass were almost the same (4.7-4.8).

Table 3.18 EC and pH values of water-soluble samples

Biomass Type	Code	EC (mS/m) (n=3)	pH (n=3)
Rice straw	R-MR	1.09 ± 0.31	4.9 ± 0.2
	R-DK	1.45 ± 0.16	4.8 ± 0.1
	R-CD	1.41 ± 0.03	4.7 ± 0.0
	Average	**1.32 ± 0.24**	**4.8 ± 0.2**
Maize residue	M-MR	0.96 ± 0.22	4.9 ± 0.2
	M-MC	1.30 ± 0.14	4.7 ± 0.0
	M-CD	1.04 ± 0.03	4.8 ± 0.1
	Average	**1.10 ± 0.20**	**4.8 ± 0.1**
Leaf litter	L-MR	1.03 ± 0.06	4.8 ± 0.0
	L-DK	1.16 ± 0.05	4.7 ± 0.0
	L-CD	1.16 ± 0.07	4.7 ± 0.0
	Average	**1.12 ± 0.08**	**4.7 ± 0.1**

3) Emission factors (EFs) of water-soluble ions from biomass burning

The EFs of water-soluble ions from three types of biomass burning are presented in Table 3.19 (Appendix E-3). EFs of total ions from rice straw, maize residue and leaf litter burning were 529 ± 141 mg/kg, 777 ± 215 mg/kg and 839 ± 157 mg/kg, respectively. Leaf litter burning emitted the highest EF of total ions, whereas the lowest EF of total ions was found from rice straw burning. Major ions emitted from all types of biomass burning were CH_3COO^-, NO_2^-, $HCOO^-$ and K^+. EFs of ions (mg/kg) from rice straw burning in a descending order were CH_3COO^- (235) > NO_2^- (83.9) > $HCOO^-$ (56.7) > K^+ (39.3), while those from leaf litter burning were CH_3COO^- (302) > NO_2^- (208) > $HCOO^-$ (97.4) > K^+ (74.9). For maize residue burning emitted CH_3COO^- (204) > NO_2^- (193) > K^+ (114) > $HCOO^-$ (79.9). It was shown that CH_3COO^- and NO_2^- were found to be the dominant ions from all types of biomass burning. EF of CH_3COO^- emitted from leaf litter burning (302 mg/kg) was approximately 1.3-1.5 times higher than those from burning of rice straw and maize residue (204-235 mg/kg). CH_3COO^- might be from biomass burning (Tsai et al., 2012) and primary emissions from vegetation and soil (Wang et al., 2007b). However, EFs of NO_2^- emitted from maize residue (193 mg/kg) and leaf litter burning (208 mg/kg) was similar, which were about 2.3-2.5 times higher than those from rice straw burning (83.9 mg/kg). Remarkably, NO_2^- was the dominant water-soluble ion. In case of PM10 samples, there was no NO_2^-, while NO_3^- was observed in these samples. As a result, the two reactions that have been primarily considered are the following (Finlayson-Pitts and Pitts, 2000):

$$2NO_{2(g)} + H_2O_{(l)} \longleftrightarrow 2H^+(aq) + NO_3^-{}_{(aq)} + NO_2^-{}_{(aq)}$$

$$NO_{(g)} + NO_{2(g)} + H_2O_{(l)} \longleftrightarrow 2H^+_{(aq)} + 2NO_2^-{}_{(aq)}$$

In this study, NO_2 and NO were emitted from biomass burning in the chamber. From these equations, water-soluble NO_2^- was emitted higher than water-soluble NO_3^-. Therefore, high concentrations of water-soluble NO_2^- were found. Due to the fact that NO_2^- is relatively short-lived in water because it can quickly convert to nitrate, while NO_3^- is highly soluble (dissolves easily) in water and is stable over a wide range of environmental conditions (Sinha et al., 2010). However, the experiment for collecting water-soluble samples in this study was not natural condition.

The percentage of major ion species emitted from biomass burning is shown in Figure 3.15. The ions emitted from rice straw burning in a descending order were CH_3COO^- (44%) > NO_2^- (16%) > $HCOO^-$ (11%) > K^+ (7%), while those from leaf litter burning were CH_3COO^- (36%) > NO_2^- (25%) > $HCOO^-$ (12%) > K^+ (9%). The emission patterns of major ions from the burning of rice straw and leaf litter were the same. However, maize residue burning emitted CH_3COO^- (26%) > NO_2^- (25%) > K^+ (15%) > $HCOO^-$ (10%). It can be revealed that CH_3COO^- and K^+ were the dominant anion and cation from all types of biomass burning, respectively. Acetate may be mostly from biomass burning (Tsai et al., 2012) and primary emissions from vegetation and soil (Wang et al., 2007b), while potassium might be related to the fertilizer used during the planting (Tsai et al., 2012).

Table 3.19 Emission factors of water-soluble ions from biomass burning

Biomass type		EFs of ions (mg/kg)												
		CH_3COO^-	$HCOO^-$	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Total
Rice straw	min	96.9	25.2	9.7	9.3	6.6	ND	7.0	0.0	15.5	8.7	0.0	0.0	327
(n = 9)	max	326.2	81.3	67.1	138.5	25.2	ND	19.3	47.3	33.4	79.5	68.3	3.6	774
	mean	**235.0**	**56.7**	**27.2**	**83.9**	**16.3**	**ND**	**11.6**	**12.4**	**22.9**	**39.3**	**23.1**	**0.9**	**529**
	SD	**72.0**	**17.2**	**20.3**	**44.1**	**5.2**	**ND**	**4.5**	**15.9**	**7.0**	**25.5**	**22.1**	**1.3**	**141**
Maize	min	80.9	28.7	20.9	115.6	12.7	ND	13.7	0.0	10.4	18.2	0.0	0.0	447
residue	max	549.5	129.3	95.4	260.8	47.9	ND	83.5	26.7	87.4	148.6	56.4	4.8	1,257
(n = 9)	**mean**	**204.0**	**79.9**	**50.6**	**192.8**	**31.0**	**ND**	**37.8**	**9.4**	**36.0**	**113.8**	**18.4**	**0.9**	**777**
	SD	**140.0**	**30.4**	**23.2**	**51.5**	**10.6**	**ND**	**25.1**	**10.0**	**21.4**	**41.2**	**20.7**	**1.7**	**215**
Leaf litter	min	117.6	62.9	0.0	96.6	9.3	ND	7.9	0.0	12.0	36.5	0.0	0.0	703
(n = 9)	max	540.3	117.1	98.8	331.0	56.1	ND	45.1	54.2	36.4	121.6	98.4	6.1	1,175
	mean	**301.9**	**97.4**	**29.2**	**208.5**	**32.0**	**ND**	**20.2**	**17.1**	**23.2**	**74.9**	**26.6**	**1.1**	**839**
	SD	**115.1**	**16.0**	**35.5**	**70.3**	**16.4**	**ND**	**10.8**	**18.1**	**8.2**	**29.1**	**34.6**	**2.1**	**157**

ND = not detected

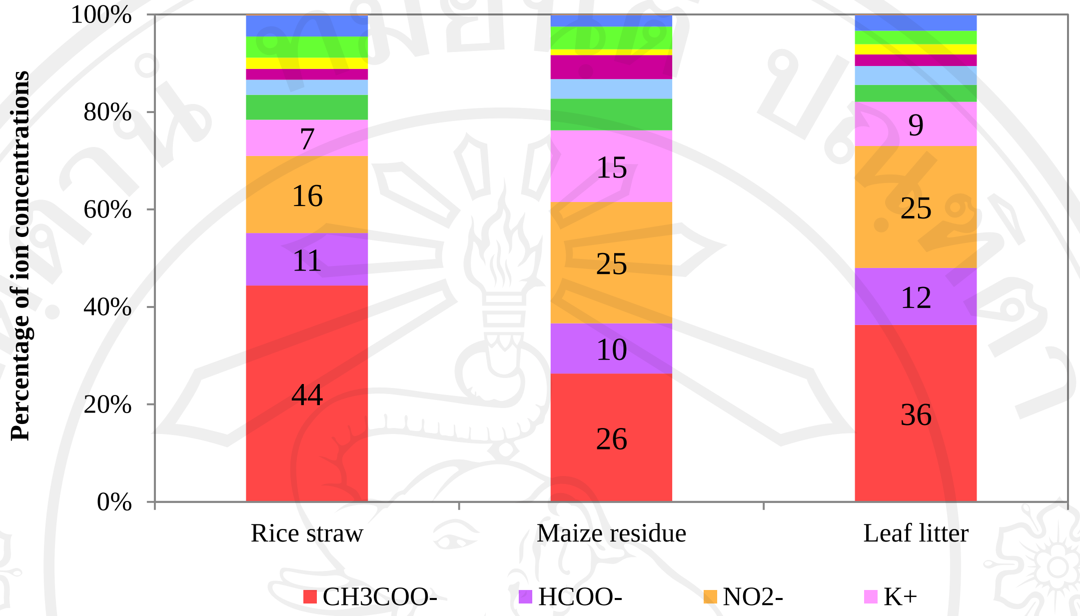


Figure 3.15 Percentage of ion species in water-soluble samples emitted from biomass burning in the chamber

4) Correlations of PM10-bound ions

Correlation coefficients of PM10-bound ions are shown in Tables 3.20-3.22. The Spearman correlation was used to examine their correlations. The strong correlations were marked bold in the Tables.

Rice straw burning

The correlation between Na^+ and NO_2^- concentrations was strong (r = 0.831) ($p < 0.01$), while that between Mg^{2+} and Cl^- was relatively strong (r = 0.749) ($p < 0.05$).

Maize residue burning

The correlations between Na^+ and NO_2^- (r = 0.678), NH_4^+ and SO_4^{2-} (r = 0.783) and K^+ and SO_4^{2-} (r = 0.783) were relatively strong ($p < 0.05$).

Leaf litter burning

The correlation between Na^+ and NO_2^- concentrations was strong (r = 0.848) ($p < 0.01$). The relatively strong correlation (r = 0.683) ($p < 0.05$) was found between NH_4^+ and SO_4^{2-}. The concentration of Ca^{2+} was strong correlated ($p < 0.01$) with CH_3COO^-, Cl^- and NO_3^-, which were -0.881, 0.919 and 0.915, respectively. The concentration of Mg^{2+} was strong correlated with NO_3^- (r = 0.842) ($p < 0.01$), while Mg^{2+} was relatively strong correlated ($p < 0.05$) with CH_3COO^- (r = -0.782), Cl^- (r = 0.756) and NO_2^- (r = 0.673). It can be seen that the concentrations between Ca^{2+} and CH_3COO^- and Mg^{2+} and CH_3COO^- were significantly negative correlations.

Notably, the correlation between Na^+ and NO_2^- was found from all types of biomass burning.

Table 3.20 Correlation coefficients of PM10-bound ions obtained from rice straw burning

	CH_3COO^-	$HCOO^-$	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
CH_3COO^-	1.000										
$HCOO^-$	**0.733***	1.000									
Cl^-	-0.467	**-0.833****	1.000								
NO_2^-	0.450	0.083	-0.017	1.000							
NO_3^-	-0.067	0.109	-0.059	-0.126	1.000						
SO_4^{2-}	-0.467	-0.467	0.117	-0.100	-0.075	1.000					
Na^+	0.305	-0.153	0.288	**0.831****	0.153	0.153	1.000				
NH_4^+	0.000	-0.067	-0.167	-0.150	0.544	0.367	0.085	1.000			
K^+	-0.067	-0.367	0.367	0.650	-0.243	0.517	**0.780***	-0.083	1.000		
Ca^{2+}	0.467	-0.117	0.317	0.533	0.142	-0.183	**0.729***	0.250	0.333	1.000	
Mg^{2+}	-0.037	-0.639	**0.749***	0.274	-0.238	0.073	0.409	0.091	0.402	0.493	1.000

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

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

Table 3.21 Correlation coefficients of PM10-bound ions obtained from maize residue burning

	CH_3COO^-	$HCOO^-$	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
CH_3COO^-	1.000										
$HCOO^-$	**0.800****	1.000									
Cl^-	0.300	0.167	1.000								
NO_2^-	-0.183	**-0.667***	0.200	1.000							
NO_3^-	-0.067	0.433	-0.617	**-0.767***	1.000						
SO_4^{2-}	-0.050	0.400	0.033	-0.417	0.617	1.000					
Na^+	-0.170	-0.458	0.051	**0.678***	-0.390	-0.136	1.000				
NH_4^+	-0.050	0.383	0.100	-0.533	0.517	**0.783***	-0.492	1.000			
K^+	0.100	0.267	0.267	-0.017	0.233	**0.783***	-0.119	0.567	1.000		
Ca^{2+}	0.407	0.119	0.373	0.288	-0.373	-0.051	**0.707***	-0.339	-0.051	1.000	
Mg^{2+}	0.274	0.292	-0.201	-0.018	0.365	0.602	0.316	0.256	0.566	0.464	1.000

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

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

Table 3.22 Correlation coefficients of PM10-bound ions obtained from leaf litter burning

	CH$_3$COO$^-$	HCOO$^-$	Cl$^-$	NO$_2^-$	NO$_3^-$	SO$_4^{2-}$	Na$^+$	NH$_4^+$	K$^+$	Ca^{2+}	Mg^{2+}
CH$_3$COO$^-$	1.000										
HCOO$^-$	0.600	1.000									
Cl$^-$	**-0.720***	-0.276	1.000								
NO$_2^-$	-0.617	-0.483	0.628	1.000							
NO$_3^-$	**-0.767***	-0.533	**0.937****	**0.717***	1.000						
SO$_4^{2-}$	0.217	-0.133	-0.285	-0.183	-0.133	1.000					
Na$^+$	-0.475	-0.068	0.494	**0.848****	0.458	-0.441	1.000				
NH$_4^+$	0.217	-0.067	0.151	0.150	0.283	**0.683***	-0.102	1.000			
K$^+$	-0.300	-0.050	0.326	0.650	0.200	-0.500	**0.797***	-0.350	1.000		
Ca^{2+}	**-0.881****	-0.458	**0.919****	0.610	**0.915****	-0.170	0.397	0.017	0.220	1.000	
Mg^{2+}	**-0.782***	-0.406	**0.756***	**0.673***	**0.842****	-0.109	0.463	0.158	0.059	**0.856****	1.000

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

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

3.6 Pattern of the ion composition from emission of biomass burning and Chiang Mai ambient air

Principal component analysis (PCA) was used to determine the possible sources of chemical composition in the study area. Only factor loadings higher than 0.5 were deemed to be statistically significant (Ayers and Yeung, 1996). The loadings having a greater value than 0.50 are marked bold in the table.

3.6.1 PCA of ion composition from biomass burning emission

1) PM10 sample

The varimax rotated principal component patterns of PM10 samples from biomass burning are presented in Table 3.23. There were four components contributing about 82% of the variance. The first component contributes 32% of the total variance with high loading of $HCOO^-$, Cl^-, SO_4^{2-}, NH_4^+ and K^+. The key markers in the second component were PO_4^{3-}, Na^+ and Ca^{2+}, with the percent variance of 21%. The third component contributes 17% of the variance with high loading of Mg^{2+}. The last component with high loading for NO_3^-, which contributes 13% of variance.

2) Water-soluble sample

The factor analysis for water-soluble ions from biomass burning was performed with four components, contributing about 84% of the variance (Table 3.24). The percentages of variance of component 1, 2, 3 and 4 were 26%, 21%, 21% and 16%, respectively. Component 1 provided high loading of NO_3^-, NH_4^+ and Ca^{2+}. The variables of component 2 were Cl^-, NO_2^-, Na^+ and K^+. The third component with high loading of SO_4^{2-} and Mg^{2+}. CH_3COO^- and $HCOO^-$ were found to be the key markers of the last component.

K^+ and Cl^- were found to be major ions in both PM10 and water-soluble samples emitted from biomass burning. They had high loading in component 1 (Table 3.23) and component 2 (Table 3.24) in case of PM10 and water-soluble samples, respectively. These results revealed that K^+ and Cl^- are key factors of biomass burning source.

Table 3.23 Principal component analysis of PM10 sample from biomass burning

Ions	Component			
	1	2	3	4
$HCOO^-$	**0.684**	0.207	0.184	0.300
Cl^-	**0.769**	0.161	0.576	-0.097
NO_3^-	0.113	-0.096	-0.056	**0.957**
PO_4^{3-}	0.193	**0.870**	-0.025	-0.224
SO_4^{2-}	**0.870**	-0.140	0.041	0.209
Na^+	-0.034	**0.909**	-0.064	0.244
NH_4^+	**0.911**	-0.163	-0.213	-0.086
K^+	**0.624**	0.181	0.706	0.051
Ca^{2+}	-0.258	**0.535**	0.025	-0.320
Mg^{2+}	0.100	0.176	**-0.891**	0.055
% of Variance	31.63	20.58	17.13	12.84
Cumulative %	31.63	52.21	69.34	82.18

Table 3.24 Principal component analysis of water-soluble samples from biomass burning

Ions	Component			
	1	2	3	4
CH_3COO^-	-0.040	-0.136	0.052	**0.924**
$HCOO^-$	0.086	0.096	0.265	**0.855**
Cl^-	0.268	**0.578**	0.291	-0.298
NO_2^-	0.144	**0.876**	0.092	0.096
NO_3^-	**0.983**	0.032	0.070	-0.014
SO_4^{2-}	0.161	0.006	**0.917**	0.069
Na^+	-0.024	**0.816**	-0.234	-0.042
NH_4^+	**0.840**	-0.058	0.483	0.155
K^+	-0.271	**0.674**	0.618	0.005
Ca^{2+}	**0.976**	0.173	0.007	-0.032
Mg^{2+}	0.201	0.020	**0.764**	0.310
% of Variance	26.05	20.76	20.61	16.46
Cumulative %	26.05	46.81	67.42	83.88

3.6.2 PCA of PM10-bound ion composition from Chiang Mai ambient air

In order to find possible association sources of ions in ambient air, factor analysis was carried out to determine the factors underlying the inter-correlations between the measured species. The results of PCA from Chiang Mai ambient air during dry (27 February - 19 April 2010) and wet season in 2010 (15 July - 8 August 2010) are given in Tables 3.25 and 3.26, respectively.

There were three components contributed during dry season in 2010. The first component with high loading of $HCOO^-$, NO_3^-, SO_4^{2-}, NH_4^+, K^+ and Ca^{2+}. $HCOO^-$ was originated from photochemical reaction (Tsai et al., 2012), while NO_3^- and SO_4^{2-} was derived from fuel combustion (Huang et al., 2009). NH_4^+ was come from agricultural activities (Migliavacca et al., 2005; Zhang et al., 2007). K^+ was originated from biomass burning (Hu et al., 2003; Zhang et al., 2007; Al-Khashman, 2009), while Ca^{2+} may come from soil resuspension (Zhang et al., 2007; Al-Khashman, 2009). The second component showed high loading of CH_3COO^- and Cl^-. CH_3COO^- believed to be due to biomass burning (Tsai et al., 2012) and primary emissions from vegetation and soil (Wang et al., 2007b). Cl^- might originate from sea salt (Hu et al., 2003; Al-Khashman, 2009). The last component derived from sea salt (Na^+) (Hu et al., 2003; Al-Khashman, 2009) and soil (Mg^{2+}) (Zhang et al., 2007; Al-Khashman, 2009).

In the wet season of 2010, two components contributed to Chiang Mai ambient air were found. Component 1 had high loading of SO_4^{2-} and Mg^{2+}, indicating from combustion fuel and soil, respectively. The component 2 contained high loading of Cl^-, NO_3^- and K^+, hereafter referred to sea salt (Cl^-), combustion fuel (NO_3^-) and biomass burning (K^+).

It can be seen that the key markers in component 1 of Chiang Mai ambient air during dry season were $HCOO^-$, NO_3^-, SO_4^{2-}, NH_4^+, K^+ and Ca^{2+}. This pattern was similar to the variables in component 1 of PM10 samples from biomass burning, which were $HCOO^-$, Cl^-, SO_4^{2-}, NH_4^+ and K^+. Therefore, it can be concluded that composition of ambient air during dry season 2010 might be affected from biomass burning.

Table 3.25 Principal component analysis of PM10-bound ions from Chiang Mai ambient air during dry season 2010

Ions	Component		
	1	2	3
CH_3COO^-	0.061	**0.749**	-0.127
$HCOO^-$	**0.688**	-0.169	-0.189
Cl^-	0.191	**-0.773**	-0.090
NO_3^-	**0.885**	0.048	0.142
SO_4^{2-}	**0.794**	-0.021	0.072
Na^+	0.121	0.011	**-0.760**
NH_4^+	**0.610**	0.599	0.064
K^+	**0.828**	0.116	-0.019
Ca^{2+}	**0.823**	-0.048	0.348
Mg^{2+}	0.354	-0.016	**0.766**
% of Variance	38.02	15.65	13.75
Cumulative %	38.02	53.67	67.42
Possible source	Photochemical reaction, fuel combustion, agricultural activities, biomass burning and soil	Biomass burning, vegetation, soil and sea salt	Sea salt and soil

Table 3.26 Principal component analysis of PM10-bound ions from Chiang Mai ambient air during wet season 2010

Ions	Component	
	1	2
Cl^-	-0.326	**-0.525**
NO_3^-	0.153	**0.847**
SO_4^{2-}	**0.912**	0.220
K^+	-0.654	**0.726**
Mg^{2+}	**0.813**	0.127
% of Variance	41.00	31.70
Cumulative %	41.00	72.70
Possible source	Combustion fuel and soil	Sea salt, combustion fuel and biomass burning

3.7 Emission rates (ERs) of pollutants from biomass burning in the combustion chamber

The ERs were calculated using Equation 2.3. The burned areas of rice field, crop field and forest in Chiang Mai Province during the dry season of 2010 (December 2009-April 2010) and 2011 (December 2010-April 2011) were estimated by MODIS (Moderate Resolution Imaging Spectroradiometer) Landsat 5 TM (Dontree et al., 2011) (Table 3.27). The percentages of burned area were calculated by dividing burned area by total area in each area type.

Table 3.27 Total area, burned area and percentages of burned area of rice field, crop field and forest in Chiang Mai in 2010 and 2011

Year	Area type	Total area* (km^2)	Burned area* (km^2)	Burned area (%)
2010	Rice field	1,013	111	11
	Crop field	651	326	50
	Forest	11,109	3,073	28
2011	Rice field	1,013	78	8
	Crop field	651	173	27
	Forest	11,109	615	6

* Source: Dontree et al. (2011).

The number of total area of rice field, crop field and forest in 2010 and 2011 was the same. Forest area occupies the largest area in Chiang Mai (11,109 km^2), which was approximately 11-17 times larger than the area of rice field (1,013 km^2) and crop field (651 km^2). About 3,073 km^2 of forest, 326 km^2 of crop field and 111 km^2 of rice field were burned in 2010, while about 615, 173 and 78 km^2 of those were burned in 2011, respectively. The percentages of burned area in 2010 in a descending order were crop field (50%) > forest (28%) > rice field (11%), while those in 2011 were crop field (27%) > rice field (8%) > forest (6%). The highest percent of burned area in 2010 and 2011 was found in crop field.

Remarkably, the total burned area in 2010 (3,510 km^2) was about 4 times higher than that in 2011 (866 km^2) due to the effects from rain amount in each year. The annual rainy day and rain amount in 2010 (112 days and 1156.0 mm) were slightly lower than in 2011 (144 days and 1307.6 mm). Particularly in dry season, there were only 9 rainy days (37.4 mm) 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). It can be concluded that the rain pattern in the dry season of year 2011 was unusual and extremely high. In this year, Thailand had big flood event. It therefore resulted in low open burning.

This result related with the concentrations of PM10 in Chiang Mai during that period. The PM10 concentrations at City Hall, air quality monitoring station of PCD in Chiang Mai in 2010 and 2011 (http://www.pcd.go.th) are illustrated in Table 3.28. It was found that 24 hrs of PM10 concentrations during dry season 2010 (November 2009-April 2010) ranged from 21.3-268.4 µg/m^3, while that in 2011 ranged from only 8.3-92.0 µg/m^3. Moreover, the numbers of days those PM10 concentrations exceeded the National Ambient Air Quality Standards in Thailand for 24 hrs of 120 µg/m^3 was 18 days in March (9 days) and April (9 days), while those in 2011 were not found.

The ERs of gases, PM10 and ion compositions of PM10 samples and water-soluble samples emitted from biomass burning were calculated from burning area in Chiang Mai Province (Equation 2.3) in 2010 and 2011.

Table 3.28 PM10 concentrations at City Hall stations in Chiang Mai in 2010 and 2011

Year	Season	Month	PM10 concentrations (µg/m^3) min	max	mean	Number of days PM10 > 120 µg/m^3
2010	Dry	Nov-09	24.5	56.6	38.4	-
		Dec-09	34.3	66.8	49.5	-
		Jan-10	21.3	62.3	41.2	-
		Feb-10	37.8	118.0	66.7	-
		Mar-10	57.8	268.4	111.2	9
		Apr-10	45.4	163.8	102.6	9
	Wet	May-10	10.0	63.9	36.0	-
		Jun-10	12.3	68.3	24.5	-
		Jul-10	14.8	25.1	18.7	-
		Aug-10	9.7	25.0	18.2	-
		Sep-10	14.1	26.3	18.2	-
		Oct-10	11.9	34.8	20.2	-
2011	Dry	Nov-10	30.2	59.9	40.9	-
		Dec-10	8.3	59.5	33.0	-
		Jan-11	26.6	70.7	48.7	-
		Feb-11	33.6	91.3	54.0	-
		Mar-11	18.5	92.0	52.2	-
		Apr-11	14.6	86.3	44.8	-
	Wet	May-11	13.8	45.5	24.6	-
		Jun-11	9.2	39.0	20.2	-
		Jul-11	9.4	35.9	19.3	-
		Aug-11	9.4	27.0	18.6	-
		Sep-11	11.5	61.8	20.1	-
		Oct-11	16.8	46.3	28.0	-

3.7.1 PM10 samples

1) ERs of gases

The ERs of gases including CO, NO, NO_2 and SO_2 from rice field, crop field and forest burning in 2010 and 2011 are given in Table 3.29.

Table 3.29 Gas emission rates of PM10 samples from biomass burning in 2010 and 2011

Year	Area type	ERs of gases (ton/year)				
		CO	NO	NO_2	SO_2	Total gases
2010	Rice field	4,000	58	120	30	4,208
	Crop field	9,200	410	520	ND	10,130
	Forest	99,000	3,200	4,900	300	107,400
2011	Rice field	2,800	40	81	20	2,941
	Crop field	4,900	220	280	ND	5,400
	Forest	20,000	640	980	70	21,690

ND = not detected

The ERs of gases emitted from burning of three area types in 2010 and 2011 were found to be the same trend, which were CO > NO_2 > NO > SO_2. The highest ERs of CO in 2010 (99,000 ton) and 2011 (20,000 ton) were from forest burning. ERs of gases in 2010 were approximately 1-5 times higher than those in 2011. Moreover, the ERs of total gases in 2010 in descending order were from forest burning (107,400 ton) > crop field burning (10,130 ton) > rice field burning (4,208 ton), while those in 2011 were from the burning of forest (21,690 ton) > crop field (5,400 ton) > rice field

(2,941 ton). This result can be seen that the trend of total gas emissions recorded from biomass burning in 2010 and 2011 were the same. ERs of total gases emitted from forest burning in 2010 and 2011 were approximately 88% and 72%, respectively.

2) ERs of PM10 and ion compositions

The ERs of PM10 and ion compositions from rice field, crop field and forest burning in 2010 and 2011 are shown in Table 3.30.

Table 3.30 PM10 and ion emission rates of PM10 samples from biomass burning in 2010 and 2011

ERs (ton)	2010			2011		
	Rice field	Crop field	Forest	Rice field	Crop field	Forest
PM10	52	205	2,794	36	109	560
CH_3COO^-	ND	ND	ND	ND	ND	ND
$HCOO^-$	0.02	0.14	0.94	0.01	0.07	0.19
Cl^-	3.44	17.94	26.57	2.41	9.54	5.32
NO_3^-	0.66	2.84	27.66	0.46	1.51	5.54
PO_4^{3-}	0.09	0.05	ND	0.06	0.03	ND
SO_4^{2-}	1.36	7.11	37.60	0.96	3.78	7.53
Na^+	0.06	0.09	0.92	0.04	0.05	0.18
NH_4^+	0.80	3.98	22.90	0.56	2.12	4.59
K^+	3.52	19.38	33.90	2.47	10.30	6.79
Ca^{2+}	<0.01	0.01	0.04	<0.01	<0.01	<0.01
Mg^{2+}	<0.01	<0.01	0.07	<0.01	<0.01	0.01
Total ions	10	52	151	7	27	30

ND = not detected

The ERs of PM10 emitted from burning of forest, crop field and rice field in 2010 were 2,794, 205 and 52 ton, respectively, while those in 2011 were 560, 109 and 36 ton, respectively. Approximately 92% and 79% of PM10 were emitted from forest burning in 2010 and 2011, respectively. The results of another relevant study in Chiang Mai revealed that 80% of burning area in the Northern Thailand was in the forest area and only 20% was in the agriculture area (Kim Oanh and Leelasakultum, 2011). Furthermore, ERs of total ions from open burning in 2010 in descending order were from burning of forest (151 ton; 71%) > crop field (52 ton; 24%) > rice field (10 ton; 5%), while those in 2011 were from burning of forest (30 ton; 47%) > crop field (27 ton; 42%) > rice field (7 ton; 11%). The ERs of open burning in Chiang Mai Province for PM10 and total ions in both years were the same pattern. The ERs of PM10 and total ions in 2010 were about 1-5 times higher than those in 2011.

In 2010, the top three ions emitted from burning of rice field and crop field were K^+ (3.5 and 19.4 ton) > Cl^- (3.4 and 17.9 ton) > SO_4^{2-} (1.4 and 7.1 ton), while those from forest burning were SO_4^{2-} (37.6 ton) > K^+ (33.9 ton) > NO_3^- (27.7 ton). In 2011, the same trend was observed with ~ 1-5 times lower than those found in 2010. The highest ER emitted from all types of biomass burning in 2010 was SO_4^{2-} (37.6 ton) from forest burning. Nevertheless, the highest ER in 2011 was K^+ (10.3 ton) from crop field burning.

3.7.2 Water-soluble samples

1) ERs of gases

The trend of ERs of gases emitted from burning of three land use types in 2010 and 2011 were the same, which was CO > NO_2 > NO > SO_2. The highest emission was CO from forest burning, which was 91,000 ton in 2010 and 18,000 ton in 2011 (Table 3.31). The ERs of gases in 2010 were approximately 1-5 times greater than those in 2011.

Table 3.31 Gas emission rates of water-soluble samples from biomass burning in 2010 and 2011

Year	Area type	ERs of gases (ton/year)				
		CO	NO	NO_2	SO_2	Total gases
2010	Rice field	4,000	66	120	ND	4,186
	Crop field	12,000	270	810	ND	13,080
	Forest	91,000	2,500	6,400	ND	99,900
2011	Rice field	2,800	46	84	ND	2,930
	Crop field	6,300	150	430	ND	6,880
	Forest	18,000	500	1,300	ND	19,800

ND = not detected

Furthermore, the ERs of total gases emitted from burnings of forest, crop field and rice field in 2010 were 99,900 ton, 13,080 ton and 4,186 ton, respectively, while those in 2011 were 19,800 ton, 6,880 ton and 2,930 ton, respectively. Total gas emissions from burning of three area types in 2010 and 2011 were the same trend.

Approximately 85% and 67% of the ERs of total gases were emitted from forest fire in 2010 and 2011, respectively. It can be seen that, most of the ERs of gases from three area types burning of water-soluble samples and PM10 samples were not much different. Moreover, the trend of their emissions was the same.

2) ERs of water-soluble ions

The ERs of total ions from biomass burning in 2010 in descending order were from forest burning (1,532 ton; 88%) > crop field burning (175 ton; 10%) > rice field burning (40 ton; 2%), while those in 2011 were from burning of forest (307 ton; 72%) > crop field (93 ton; 22%) > rice field (28 ton; 7%) (Table 3.32). ERs of total ions from biomass burning in 2010 and 2011 were the same trend. ERs of total ions in 2010 were approximately 1-5 times higher than those in 2011.

The top three ERs of ions emitted from rice field burning and forest burning in 2010 were CH_3COO^- (17.6 and 556.0 ton) > NO_2^- (6.3 and 384.0 ton) > $HCOO^-$ (4.3 and 179.3 ton), while those from crop field burning were CH_3COO^- (46.2 ton) > NO_2^- (43.6 ton) > K^+ (25.8 ton). The same trend was observed in 2011, which was approximately 1-5 times lower than that found in 2010. It can be seen that, the first two ERs of ions from three area types burning in 2010 and 2011 were the same, which were CH_3COO^- and NO_2^-, respectively. The ER of CH_3COO^- was highest in 2010 (556.0 ton) and 2011 (111.4 ton), which was emitted from forest burning.

Table 3.32 Ion emission rates of water-soluble samples from biomass burning in 2010 and 2011

ERs (ton)	2010			2011		
	Rice field	Crop field	Forest	Rice field	Crop field	Forest
CH_3COO^-	17.64	46.18	556.04	12.37	24.55	111.37
$HCOO^-$	4.26	18.09	179.30	2.99	9.62	35.91
Cl^-	2.04	11.46	53.78	1.43	6.09	10.77
NO_2^-	6.30	43.65	383.98	4.42	23.21	76.91
NO_3^-	1.23	7.02	58.88	0.86	3.73	11.79
PO_4^{3-}	ND	ND	ND	ND	ND	ND
SO_4^{2-}	0.87	8.57	37.20	0.61	4.56	7.45
Na^+	0.93	2.14	31.57	0.65	1.14	6.32
NH_4^+	1.72	8.15	42.65	1.20	4.33	8.54
K^+	2.95	25.76	137.95	2.07	13.69	27.63
Ca^{2+}	1.73	4.17	49.07	1.22	2.22	9.83
Mg^{2+}	0.07	0.21	2.04	0.05	0.11	0.41
Total ions	40	175	1,532	28	93	307

ND = not detected

3.8 Atmospheric acid deposition from Chiang Mai Monitoring Station

3.8.1 Dry deposition monitoring (EANET, 2003)

The dry deposition samples were collected by four-stage filter pack for determination of acidic gases and particles in atmosphere. The sampling was carried out for every 10 days continuously. Therefore, 3 samples per month were collected. All filters were extracted and analyzed for anions and cations by IC. Each filter was used to collect and analyze for the different parameters. The first stage filter (PTFE; F0) was analyzed for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}. The second stage filter (Polyamide; F1) was analyzed for Cl^-, NO_3^-, SO_4^{2-} and NH_4^+. The alkali impregnated cellulose filter (F2) in the third stage was analyzed for Cl^- and SO_4^{2-}. The acid impregnate cellulose filter (F3) was analyzed for only NH_4^+.

3.8.1.1 Quality assurance and quality control for dry deposition monitoring

Reference materials (blind samples) in the form of filter pack were obtained once a year from the Inter-laboratory Comparison Project under the Acid Deposition Monitoring Network in East Asia (EANET) to test efficiency of extraction and analysis methods. Accuracy of the methods was considered from the results in comparison with prepared values of the reference material, which are low and high concentrations. Sample numbers represented year and concentration range. They were extracted according to the EANET method as described in the topic 2.8.2 (subtopic 7). Percent differences between prepared values and measured values of less than or equal to 15% were considered good and those between 15% and 30% were classed as acceptable. The analyzed ion concentrations of the filter samples in 2010 and 2011 are illustrated in Table 3.33.

It was found that analysis of Cl^-, SO_4^{2-} and NH_4^+ for high concentrations were highly accurate (<15%). For low concentrations, analysis of SO_4^{2-} was also highly accurate (<15%). However, analysis of Cl^- (15-16% difference) and NH_4^+ (2-16% difference) were good and acceptable for low concentrations.

Table 3.33 Quality control of extraction and analysis methods from filter samples in 2010 and 2011

Concentrations		2010				2011			
		No.	Cl^-	SO_4^{2-}	NH_4^+	No.	Cl^-	SO_4^{2-}	NH_4^+
Low	Prepared value (µg)	101	6.0	30.0	5.8	111	3.0	73.0	8.0
	Measured value (µg)		5.1	27.6	6.7		2.5	69.6	7.9
	%Difference		-15	-8	16		-16	-5	-2
High	Prepared value (µg)	102	27.0	90.0	45.0	112	32.0	110.0	26.0
	Measured value (µg)		24.8	85.7	45.9		30.3	105.0	24.0
	%Difference		-8	-5	2		-5	-5	-8

3.8.1.2 Acidic gas concentrations

The analysis results were used to determine the concentrations of air pollutants namely sulfur dioxide (SO_2), nitric acid (HNO_3), hydrogen chloride (HCl) and ammonia (NH_3). The total number of samples in 2010 was 36. The monthly mean concentrations of pollutant gases in 2010 are shown in Table 3.34 and Figure 3.16. The trend of gases based on the unit of nmol/m^3 during dry season in descending order were NH_3 (341) >> HNO_3 (61) > SO_2 (18) > HCl (15), while that during wet season were NH_3 (294) >> HNO_3 (66) > HCl (13) > SO_2 (4). Gas with the highest concentration was NH_3. Mean concentrations of NH_3 in dry season were higher than that in wet season. The main input of NH_3 to atmosphere was the fertilizer application and nitrification process. The high level of NH_3 was due to fertilizer used to improve the quality of soil for next agriculture period in wet season. Concentrations of SO_2, HNO_3, HCl and NH_3 in 2010 ranged from 1-48, 3-333, 6-30 and 95-835 nmol/m^3, respectively. The highest concentration of SO_2 and HCl were detected in March and

April, respectively, which were in dry period. However, the highest concentration of HNO_3 and NH_3 were found in May, which was the beginning of wet season.

The number of samples collected in 2011 was 36. The concentrations of gases during dry and wet seasons in 2011 are illustrated in Table 3.35 and Figure 3.17. Monthly mean concentrations of SO_2, HNO_3, HCl and NH_3 in 2011 ranged from 2-43, ND-14, 4-14 and 115-710 nmol/m^3, respectively. The mean concentrations of gases (nmol/m^3) in the dry season were NH_3 (168) >> SO_2 (15) > HNO_3 ~ HCl (11), while that in the wet season were NH_3 (202) >> SO_2 (9) > HCl (7) > HNO_3 (3). Gas with the highest concentration was always NH_3, as well as in 2010. Mean concentration of NH_3 in the wet season of 2011 was higher than that in dry season. This is because its concentration was very high in May, which was defined as rainy season. NH_3 concentration during the date of 11-20 May 2011 (1,448 nmol/m^3) was about 4-5 times higher than that 1-10 May (380 nmol/m^3) and 21-31 May 2011 (304 nmol/m^3). Moreover, the number of rainy day (total rain precipitation) during the date of 1-10, 11-20 and 21-31 May 2011 were 10 days (163.5 mm), 5 days (121.4 mm) an 5 days (40.4 mm), respectively. Therefore, during the period of 11-20 May 2011 might have high accumulated pollutants in air around sampling site. NH_3 concentration during wet season in 2010 (294 nmol/m^3) and 2011 (264 nmol/m^3) was similar. In addition, the concentration of NH_3 in the dry season of 2011 (168 nmol/m^3) was approximately 2 times lower than that of 2010 (341 nmol/m^3). The monthly mean concentrations of SO_2, HNO_3 and HCl in 2011 were highest in dry season (February-April).

Table 3.34 Monthly mean concentrations of acidic gases during dry and wet seasons 2010

Season	Month	Air Volume Correction (m^3)	Gas concentrations (nmol/m^3)			
			SO_2	HNO_3	HCl	NH_3
Dry	Nov-09	12.22	4.98	19.28	7.81	112.31
	Dec-09	10.96	5.25	24.78	6.78	172.82
	Jan-10	15.41	12.95	25.89	11.17	229.20
	Feb-10	13.20	22.80	59.00	15.97	338.91
	Mar-10	13.60	47.74	99.37	20.43	595.70
	Apr-10	9.40	16.36	138.24	29.61	596.48
	Average	12.46	18.35	61.09	15.30	340.90
	%		4.21	14.02	3.51	78.25
Wet	May-10	12.63	4.83	333.39	24.12	834.84
	Jun-10	12.45	3.26	29.67	5.79	306.62
	Jul-10	12.17	0.97	23.56	9.71	207.45
	Aug-10	13.58	1.87	3.06	6.99	95.41
	Sep-10	7.43	3.97	4.99	24.49	173.28
	Oct-10	13.10	6.00	4.09	6.92	146.90
	Average	11.89	3.48	66.46	13.00	294.08
	%		0.92	17.63	3.45	78.00
Year 2010	Average	12.18	10.91	63.78	14.15	317.49
	%		2.69	15.70	3.48	78.14

Table 3.35 Monthly mean concentrations of acidic gases during dry and wet seasons 2011

Season	Month	Air Volume Correction (m^3)	Concentrations (nmol/m^3)			
			SO_2	HNO_3	HCl	NH_3
Dry	Nov-10	13.47	5.82	11.76	7.11	141.48
	Dec-10	14.14	14.28	12.65	8.07	148.73
	Jan-11	14.09	7.95	10.61	8.70	172.54
	Feb-11	13.19	7.29	12.23	14.14	189.44
	Mar-11	13.32	9.91	14.36	14.13	164.61
	Apr-11	13.59	42.76	6.73	11.74	191.54
	Average	13.63	14.67	11.39	10.65	168.06
	%		7.16	5.56	5.20	82.07
Wet	May-11	13.22	36.17	9.12	8.84	341.92
	Jun-11	12.70	2.44	2.44	6.61	161.23
	Jul-11	13.74	2.53	2.56	6.37	114.87
	Aug-11	13.40	4.57	4.16	10.79	154.76
	Sep-11	12.96	1.86	0.41	5.00	258.08
	Oct-11	13.31	5.26	0.00	4.10	182.55
	Average	13.22	8.80	3.11	6.95	202.23
	%		3.98	1.41	3.14	91.47
Year 2011	Average	13.43	11.74	7.25	8.80	185.15
	%		5.51	3.41	4.13	86.95

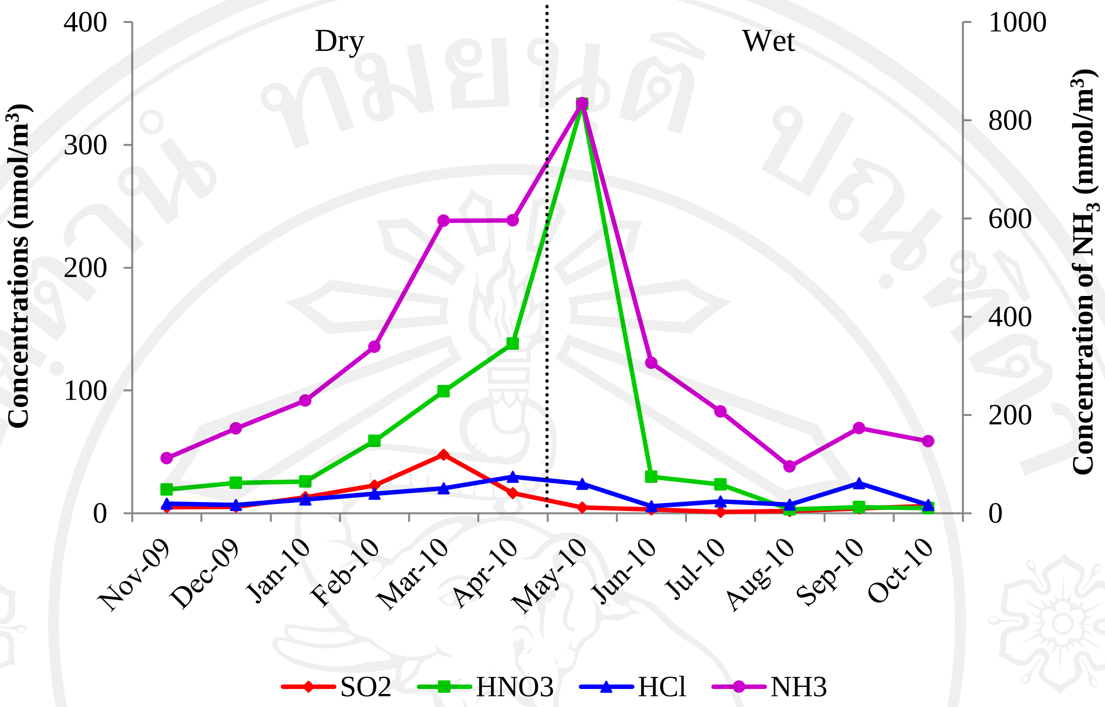


Figure 3.16 Monthly mean concentrations of acidic gas in 2010

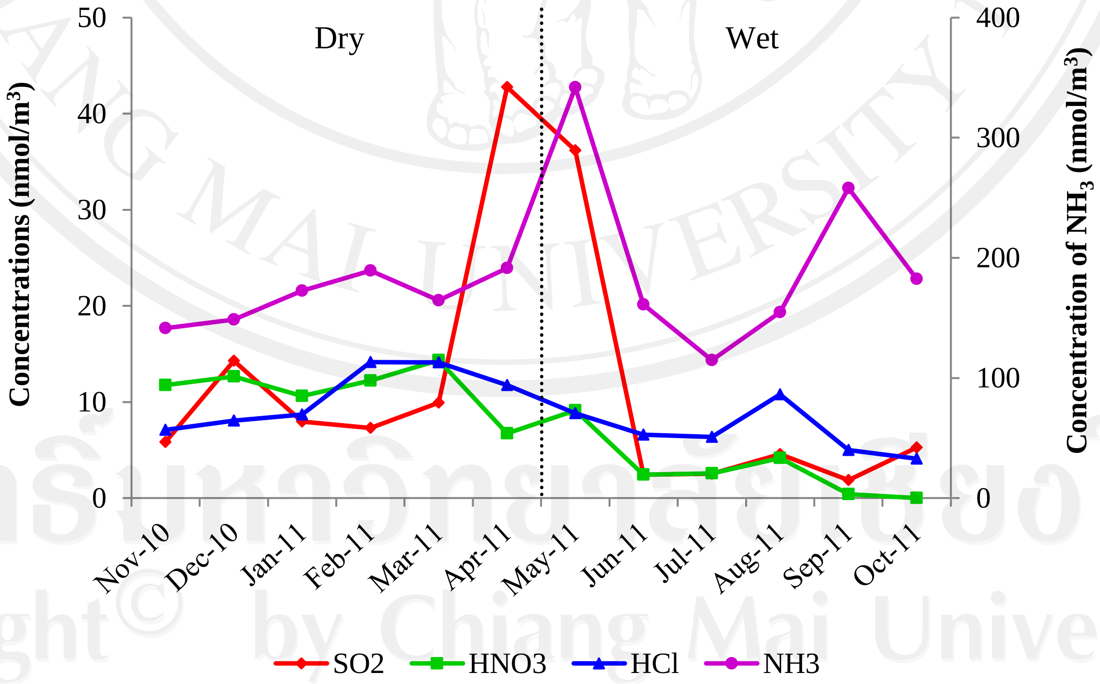
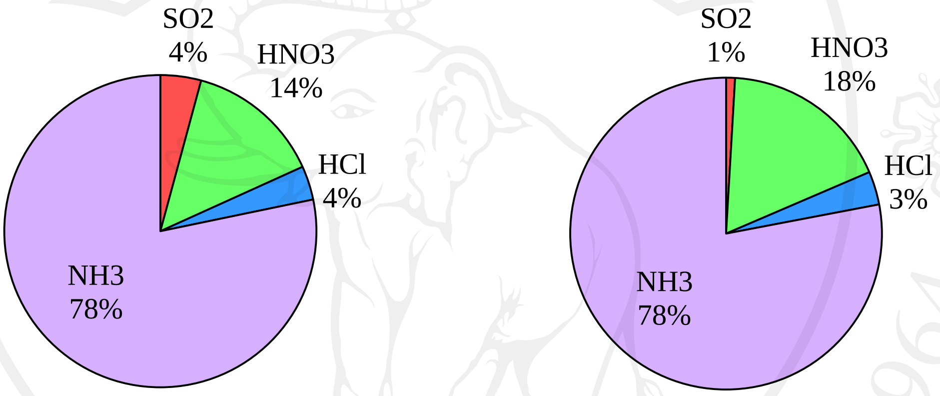


Figure 3.17 Monthly mean concentrations of acidic gas in 2011

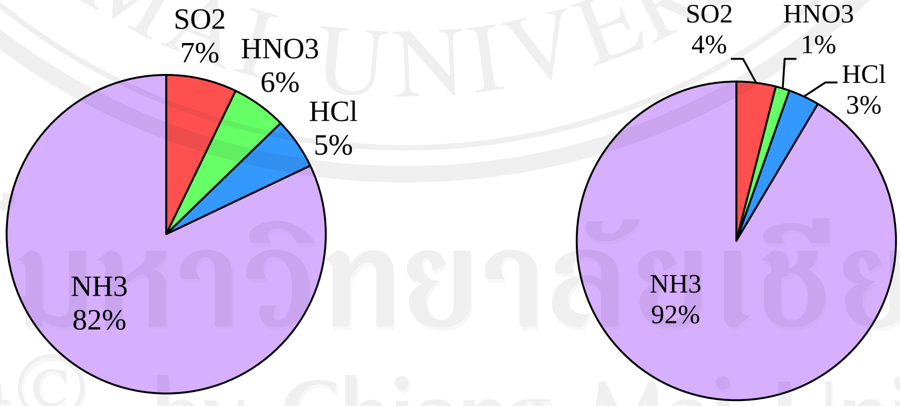
The relative percentages of total acidic gases in 2010 based on unit of nmol/m^3 in the dry season were NH_3 (78%) >> HNO_3 (14%) > SO_2 ~ HCl (4%), while that in the wet season were NH_3 (78%) >> HNO_3 (18%) > HCl (3%) > SO_2 (1%) (Figure 3.18). Similarly with the results in the dry season 2011 were NH_3 (82%) >> SO_2 (7%) > HNO_3 (6%) > HCl (5%), while that in the wet season were NH_3 (92%) >> SO_2 (4%) > HCl (3%) > HNO_3 (1%) (Figure 3.19).



(a) Dry, 2010

(b) Wet, 2010

Figure 3.18 Relative percentage of acidic gas concentrations during (a) dry, 2010 and (b) wet, 2010



(a) Dry, 2011

(b) Wet, 2011

Figure 3.19 Relative percentage of acidic gas concentrations during (a) dry, 2011 and (b) wet, 2011

3.8.1.3 Particle ion concentrations

The particle ions in the atmosphere were also collected by the four-stage filter pack at the same time with gas collection. Concentrations of acid particles were obtained by analysis of extracted samples using ion chromatography. The variation of monthly mean concentration of ions in particles during dry and wet seasons in 2010 is illustrated in Table 3.36 and Figure 3.20.

In 2010, mean ion concentrations (nmol/m^3) are as follows; SO_4^{2-} (14.7), NO_3^- (125.5), Cl^- (3.8), NH_4^+ (161.8), Na^+ (6.7), K^+ (9.8), Mg^{2+} (1.4) and Ca^{2+} (11.6). The highest concentration of cation and anion in the dry and wet seasons of 2010 were NH_4^+ (104 and 219 nmol/m^3) and NO_3^- (62 and 189 nmol/m^3), respectively. It can be seen that the concentrations of NH_4^+ and NO_3^- in the wet season were approximately 2-3 times higher than that in the dry season. However, most of monthly mean concentrations of NH_4^+ and NO_3^- during dry season were higher than that in wet season and they were highest in May (wet season). The main source of NH_4^+ is fertilizer applying in agriculture fields, while NO_3^- is emitted from combustion fuel.

Most of monthly mean concentration of particles was highest at the end of dry period (April) and the beginning of wet period (May). However, the concentration of SO_4^{2-} was highest in November (dry season), while that of Na^+ and Cl^- was found in September (wet season).

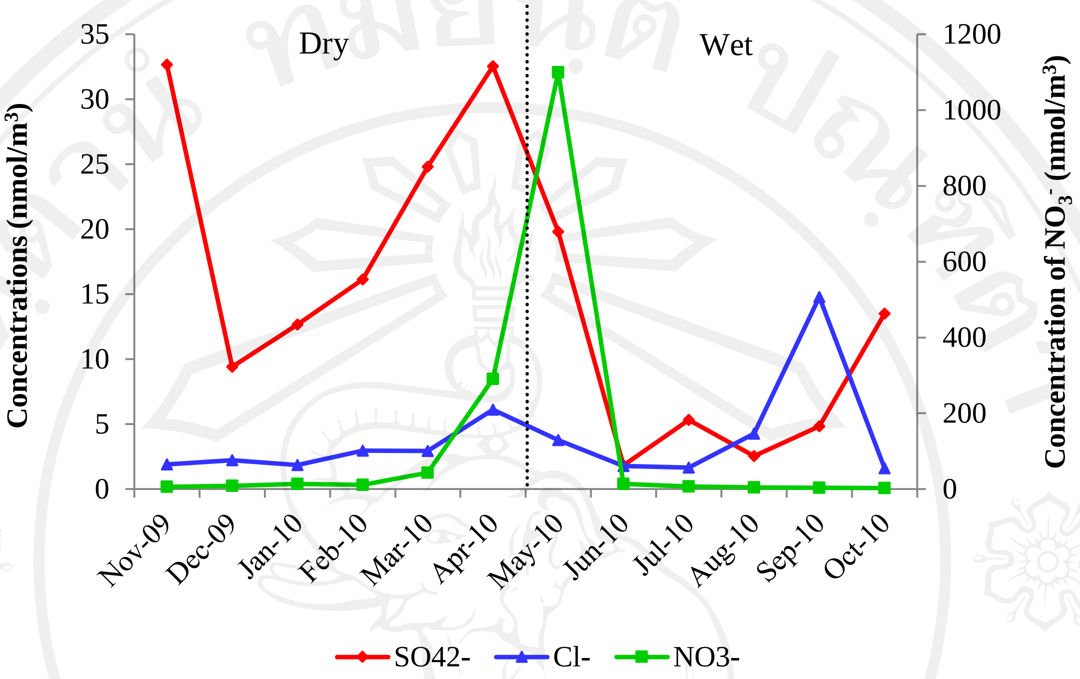
Table 3.36 Monthly mean concentrations of particle ions during dry and wet seasons in 2010

Season	Month	Air Volume Correction (m^3)	Concentrations ($nmol/m^3$)							
			SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Dry	Nov-09	12.22	32.67	6.44	1.90	58.08	4.57	9.97	1.45	10.76
	Dec-09	10.96	9.41	8.86	2.22	18.89	8.18	9.64	0.62	7.32
	Jan-10	15.41	12.66	13.62	1.85	32.23	2.34	9.28	1.07	6.54
	Feb-10	13.20	16.14	11.26	2.97	33.98	4.32	13.43	0.78	15.69
	Mar-10	13.60	24.81	43.11	2.94	84.53	6.32	22.35	2.63	18.13
	Apr-10	9.40	32.55	290.69	6.11	398.81	13.60	33.08	4.66	31.25
	Average	12.46	21.37	62.33	3.00	104.42	6.56	16.29	1.87	14.95
	%		9.26	27.01	1.30	45.25	2.84	7.06	0.81	6.48
Wet	May-10	12.63	19.82	1099.99	3.77	1259.46	12.26	9.48	1.92	32.90
	Jun-10	12.45	1.84	13.40	1.78	16.47	4.00	0.34	0.00	5.24
	Jul-10	12.17	5.33	7.27	1.65	13.07	4.33	1.95	0.67	2.58
	Aug-10	13.58	2.55	4.66	4.26	5.59	2.22	0.00	0.31	1.64
	Sep-10	7.43	4.82	3.81	14.80	1.89	16.26	6.99	2.75	4.27
	Oct-10	13.10	13.51	2.48	1.61	18.05	2.15	1.55	0.00	2.33
	Average	11.89	7.98	188.60	4.65	219.09	6.87	3.39	0.94	8.16
	%		1.81	42.90	1.06	49.83	1.56	0.77	0.21	1.86
Year	Average	12.18	14.68	125.47	3.82	161.75	6.71	9.84	1.40	11.55
2010	%		4.38	37.43	1.14	48.25	2.00	2.93	0.42	3.45

Table 3.37 Monthly mean concentrations of particle ions during dry and wet seasons in 2011

Season	Month	Air Volume Correction (m^3)	Concentrations ($nmol/m^3$)							
			SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Dry	Nov-10	13.47	51.79	2.49	2.67	70.24	23.02	16.45	0.00	6.30
	Dec-10	14.14	9.24	3.17	2.58	10.48	7.45	6.67	0.33	4.85
	Jan-11	14.09	22.54	3.64	2.43	28.75	5.94	12.29	0.86	6.92
	Feb-11	13.19	18.11	5.67	2.96	26.85	3.76	15.23	0.69	9.29
	Mar-11	13.32	15.22	6.29	2.44	23.47	4.80	9.52	0.00	6.59
	Apr-11	13.59	14.95	2.43	3.59	17.98	5.99	8.13	1.04	8.22
	Average	13.63	21.98	3.95	2.78	29.63	8.49	11.38	0.49	7.03
	%		25.64	4.61	3.24	34.57	9.91	13.28	0.57	8.20
Wet	May-11	13.22	6.67	7.97	3.41	7.53	6.21	7.51	0.93	1.42
	Jun-11	12.70	8.21	5.74	9.01	8.77	6.97	6.58	0.73	6.10
	Jul-11	13.74	2.62	3.61	1.06	6.45	2.52	3.55	0.70	2.94
	Aug-11	13.40	3.08	4.23	2.36	2.26	2.35	1.78	0.00	1.36
	Sep-11	12.96	3.58	2.67	3.10	1.04	5.77	1.60	0.10	2.96
	Oct-11	13.31	11.07	1.29	2.89	10.09	0.00	3.79	0.40	3.24
	Average	13.22	5.87	4.25	3.64	6.02	3.97	4.13	0.48	3.00
	%		18.72	13.56	11.59	19.20	12.65	13.18	1.52	9.58
Year 2011	Average	13.43	13.92	4.10	3.21	17.83	6.23	7.76	0.48	5.02
	%		23.78	7.01	5.48	30.45	10.64	13.25	0.82	8.57

(a) Anion



(b) Cation

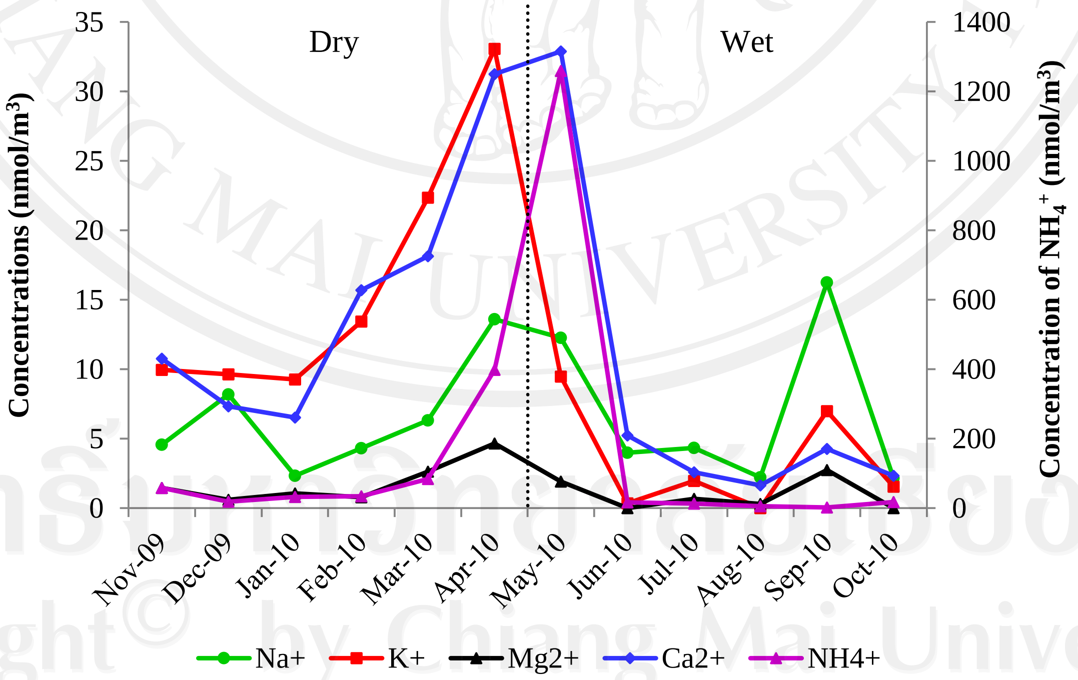
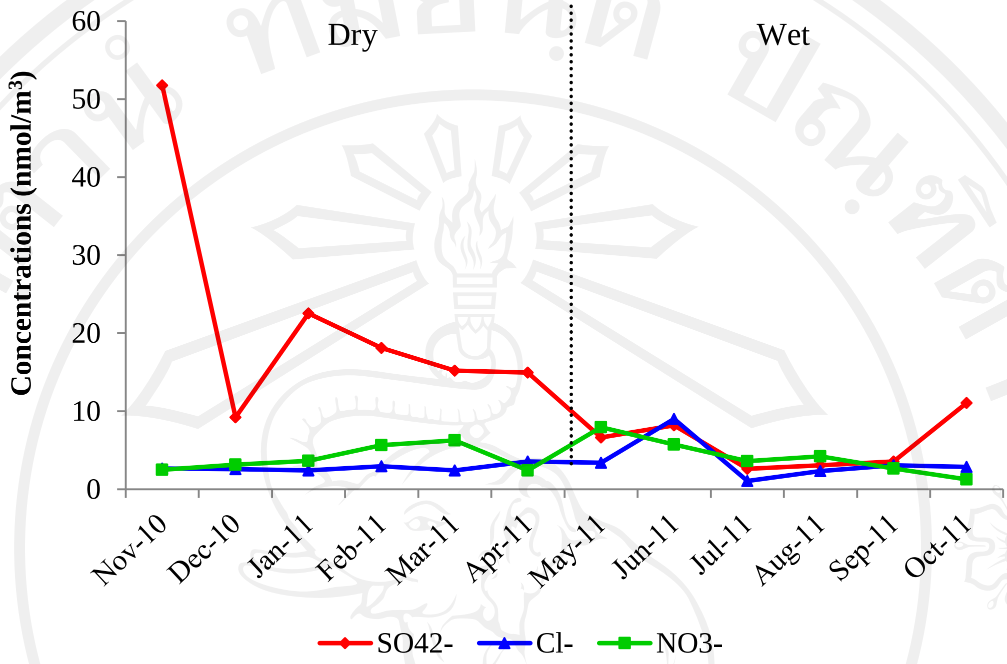


Figure 3.20 Monthly mean variability of particle ions in 2010, (a) anion concentrations and (b) cation concentrations

(a) Anion



(b) Cation

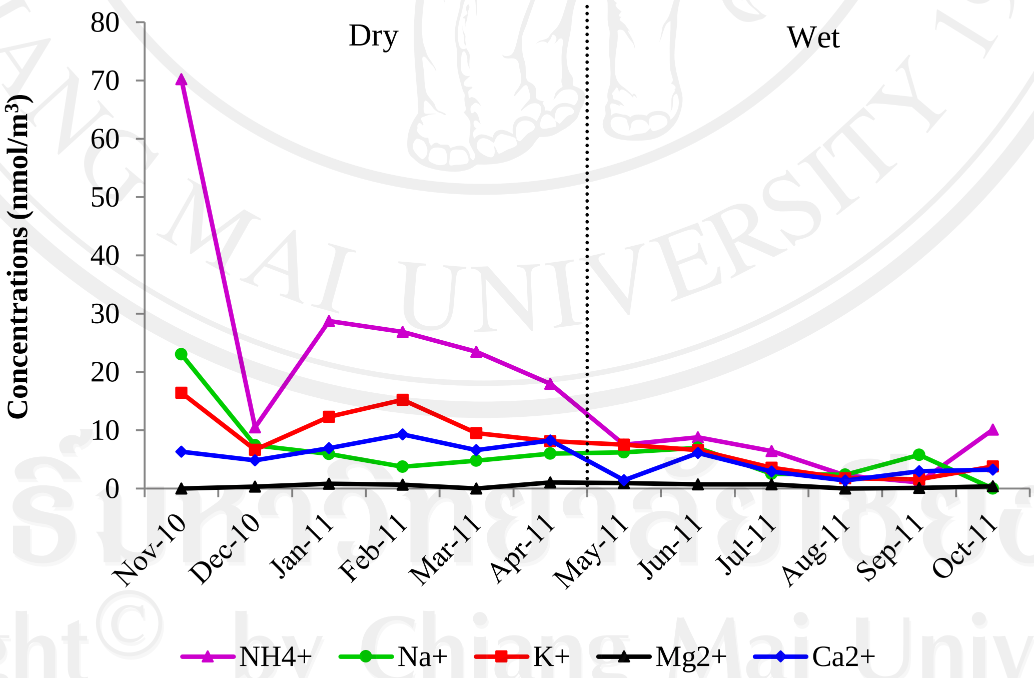
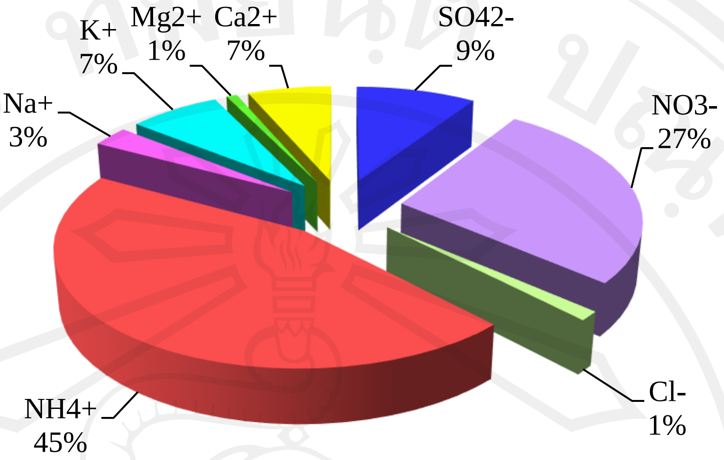


Figure 3.21 Monthly mean variability of particle ions in 2011, (a) anion concentrations and (b) cation concentrations

The monthly mean concentration of ions in particles during dry and wet seasons in 2011 is illustrated in Table 3.37. The concentrations (min-max) of ions in particles (nmol/m^3) were as follows: SO_4^{2-} (3-52), NO_3^- (1-8), Cl^- (1-9), NH_4^+ (1-70), Na^+ (ND-23), K^+ (2-16), Mg^{2+} (ND-1) and Ca^{2+} (1-9). Mean concentrations (in dry and wet seasons) of NH_4^+ (29.6 and 6.0 nmol/m^3) and SO_4^{2-} (22.0 and 5.9 nmol/m^3) were found to be the dominant cation and anion, respectively. It can be seen that the concentrations of NH_4^+ and SO_4^{2-} in the dry season were approximately 4-5 times higher than that in the wet season. In 2010, the highest concentration of cation was NH_4^+, while that of anion was NO_3^-. The mean concentration of NH_4^+ during dry (104 nmol/m^3) and wet season (219 nmol/m^3) in 2010 were approximately 4-37 times higher than that in 2011 (29.6 and 6.0 nmol/m^3). Most of monthly mean concentration of particle in 2011 was highest in the dry season, especially in November as depicted in Figure 3.21.

The order of equivalent ion concentrations in the dry season of 2010 was NH_4^+ (45%) > NO_3^- (27%) > SO_4^{2-} (9%) > K^+ ~ Ca^{2+} (7%) > Na^+ (3%) > Cl^- ~ Mg^{2+} (1%), while those in the wet season of 2010 was NH_4^+ (50%) > NO_3^- (43%) > Ca^{2+} ~ SO_4^{2-} (2%) > Na^+ ~ Cl^- ~ K^+ (1%) > Mg^{2+} (0%) as depicted in Figure 3.22. The descending order of particle ions (%) during dry season 2011 were NH_4^+ (35%) > SO_4^{2-} (26%) > K^+ (13%) > Na^+ (10%) > Ca^{2+} (8%) > NO_3^- (5%) > Cl^- (3%) > Mg^{2+} (1%), while those during wet season were NH_4^+ ~ SO_4^{2-} (19%) > NO_3^- (14%) > K^+ ~ Na^+ (13%) > Cl^- (12%) > Ca^{2+} (10%) > Mg^{2+} (2%) (Figure 3.23).

(a) Dry, 2010



(b) Wet, 2010

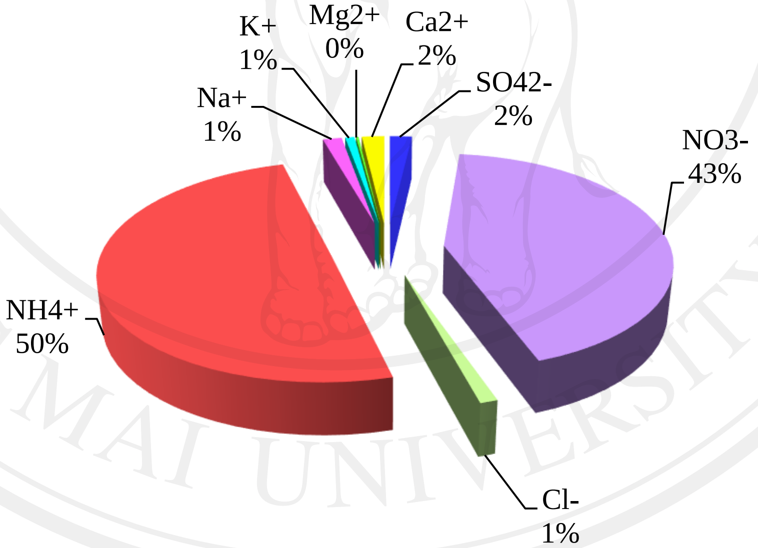
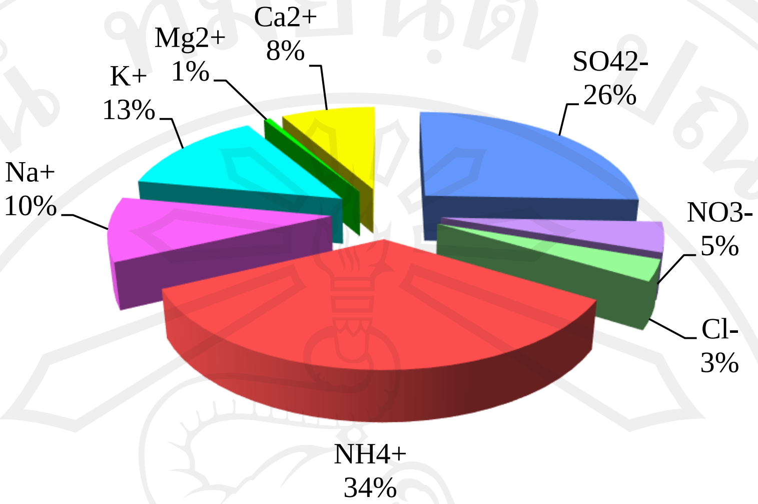


Figure 3.22 Relative percentage of particle ions during (a) dry, 2010 and (b) wet, 2010

(a) Dry, 2011



(b) Wet, 2011

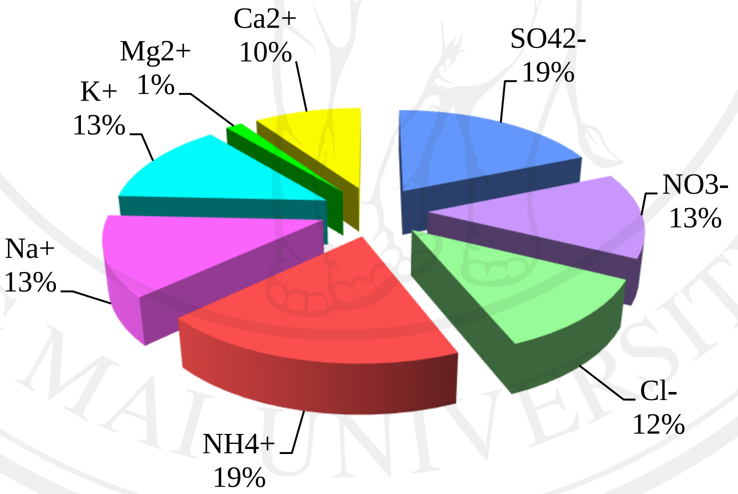


Figure 3.23 Relative percentage of particle ions during (a) dry, 2011 and (b) wet, 2011

3.8.1.4 Dry deposition amount

The concentrations of pollutants in atmosphere collected by 4-stage filter pack were reported in concentration unit per volume of air sample (nmol/m^3). Its deposition amount can be calculated by multiply with the deposition velocity factor (V_d). Puxbaum and Gregori (1998) calculated the deposition velocity (V_d) of gases in north-eastern Austria, while Rao et al. (1992) calculated the V_d of aerosols in Pune city, India (Table 3.38). Therefore, this V_d values were used for calculation of the deposition amount of dry samples in this study.

Table 3.38 The mean deposition velocities of gases and particles for deposition amount calculation

Gas	Dry deposition velocity (cm/s)	Particle	Dry deposition velocity (cm/s)
SO_2	0.31	SO_4^{2-}	0.53
HNO_3	2.40	NO_3^-	1.50
HCl	2.40	Cl^-	1.10
NH_3	0.81	NH_4^+	0.18
		Na^+	0.91
		K^+	0.89
		Mg^{2+}	1.00
		Ca^{2+}	2.97

The monthly dry deposition amount in 2010 and 2011 are presented in Tables 3.39 and 3.40, respectively. The highest dry deposition in gas form in 2010 was HNO_3 (3,000 mg/m^2; 62% of total dry deposition in gas form), while that in 2011 was NH_3 (794 mg/m^2; 55%). HNO_3 is the secondary pollutant, which is produced in the atmosphere from natural and anthropogenic emissions of primary gas-phase pollutant such as nitrogen oxides (NO_x) (Biswas et al., 2008). Anthropogenic emissions of NO_x are primarily from power generation, motorized transportation and other industrial and domestic combustion processes (Finlayson-Pitts and Pitts, 2000). Nitrogen oxides react with hydroxyl radical and produce HNO_3 via complex photochemical reactions. NH_3 contained in air samples was assumed to be from animal waste and fertilized soils (Migliavacca et al., 2005; Zhang et al., 2007). NH_3 and the changing of nitrogen compound occur in nature by nitrification process. The highest dry deposition amount in particle form in 2010 was NO_3^- with a value of 3,630 mg/m^2 (78% of total dry deposition in particle form). However, SO_4^{2-} was the highest dry deposition in 2011 with a value of 220 mg/m^2 (31%). NO_3^- and SO_4^{2-} particles might be emitted from fuel combustion around the sampling site (Huang et al., 2009).

Table 3.39 Monthly dry deposition amount in 2010

Month	Deposition amount (mg/m^2)											
	Gas				Particle							
	SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Nov-09	2.6	75.6	17.7	40.2	43.1	15.5	1.9	4.9	2.5	9.0	0.9	33.2
Dec-09	2.7	97.1	15.4	61.8	12.4	21.4	2.2	1.6	4.4	8.7	0.4	22.6
Jan-10	6.7	101.5	25.3	82.0	16.7	32.8	1.9	2.7	1.3	8.4	0.7	20.2
Feb-10	11.7	231.3	36.2	121.2	21.3	27.1	3.0	2.9	2.3	12.1	0.5	48.4
Mar-10	24.6	389.5	46.3	213.0	32.7	103.9	3.0	7.1	3.4	20.2	1.7	55.9
Apr-10	8.4	541.9	67.2	213.3	43.0	700.8	6.2	33.6	7.4	29.8	2.9	96.4
May-10	2.5	1306.8	54.7	298.5	26.2	2652.0	3.8	106.0	6.6	8.5	1.2	101.5
Jun-10	1.7	116.3	13.1	109.6	2.4	32.3	1.8	1.4	2.2	0.3	0.0	16.2
Jul-10	0.5	92.4	22.0	74.2	7.0	17.5	1.7	1.1	2.3	1.8	0.4	8.0
Aug-10	1.0	12.0	15.9	34.1	3.4	11.2	4.3	0.5	1.2	0.0	0.2	5.1
Sep-10	2.0	19.5	55.5	62.0	6.4	9.2	15.0	0.2	8.8	6.3	1.7	13.2
Oct-10	3.1	16.0	15.7	52.5	17.8	6.0	1.6	1.5	1.2	1.4	0.0	7.2
Total deposition	**67.4**	**2999.9**	**385.1**	**1362.2**	**232.4**	**3629.9**	**46.3**	**163.4**	**43.7**	**106.5**	**10.6**	**427.8**
Percent of deposition (%)	**1.4**	**62.3**	**8.0**	**28.3**	**5.0**	**77.9**	**1.0**	**3.5**	**0.9**	**2.3**	**0.2**	**9.2**

Table 3.40 Monthly dry deposition amount in 2011

Month	Deposition amount (mg/m^2)											
	Gas				Particle							
	SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Nov-10	3.0	46.1	16.1	50.6	68.3	6.0	2.7	5.9	12.5	14.8	0.0	19.4
Dec-10	7.4	49.6	18.3	53.2	12.2	7.6	2.6	0.9	4.0	6.0	0.2	15.0
Jan-11	4.1	41.6	19.7	61.7	29.7	8.8	2.5	2.4	3.2	11.1	0.5	21.4
Feb-11	3.8	47.9	32.1	67.7	23.9	13.7	3.0	2.3	2.0	13.7	0.4	28.7
Mar-11	5.1	56.3	32.0	58.9	20.1	15.2	2.5	2.0	2.6	8.6	0.0	20.3
Apr-11	22.0	26.4	26.6	68.5	19.7	5.9	3.6	1.5	3.2	7.3	0.7	25.4
May-11	18.6	35.8	20.1	122.3	8.8	19.2	3.4	0.6	3.4	6.8	0.6	4.4
Jun-11	1.3	9.6	15.0	57.6	10.8	13.8	9.1	0.7	3.8	5.9	0.5	18.8
Jul-11	1.3	10.0	14.4	41.1	3.5	8.7	1.1	0.5	1.4	3.2	0.4	9.1
Aug-11	2.4	16.3	24.5	55.3	4.1	10.2	2.4	0.2	1.3	1.6	0.0	4.2
Sep-11	1.0	1.6	11.3	92.3	4.7	6.4	3.1	0.1	3.1	1.4	0.1	9.1
Oct-11	2.7	0.0	9.3	65.3	14.6	3.1	2.9	0.8	0.0	3.4	0.3	10.0
Total deposition	**72.5**	**341.1**	**239.5**	**794.4**	**220.5**	**118.7**	**38.9**	**18.0**	**40.5**	**84.0**	**3.6**	**185.7**
Percent of deposition (%)	**5.0**	**23.6**	**16.5**	**54.9**	**31.1**	**16.7**	**5.5**	**2.5**	**5.7**	**11.8**	**0.5**	**26.2**

3.8.1.5 Comprehensive analysis for dry deposition data

1) Ion pair correlation

Correlations between ion compositions for particles in the dry and wet seasons of 2010 were examined using the Spearman correlation (Table 3.41 and 3.42). The correlations between a neutralized ion (NH_4^+) and the major anions (NO_3^- and SO_4^{2-}) were considered. During dry season, the correlations of NH_4^+ and NO_3^- ($r = 0.851$) and NH_4^+ and SO_4^{2-} ($r = 0.666$) were relatively strong. Considering the degree of correlations, the formation of NH_4NO_3 was higher than $(NH_4)_2SO_4$, meaning that NH_4NO_3 was influent in this area during dry season 2010. Inversely, the relatively strong correlation of NH_4^+ and SO_4^{2-} ($r = 0.648$) and NH_4^+ and NO_3^- ($r = 0.571$) were observed in the wet season of 2010. It can be revealed that $(NH_4)_2SO_4$ had a higher influence in this area than NH_4NO_3 in the wet season.

Table 3.41 Correlation of chemical species for particles in the dry season of 2010

Ions	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	1.000							
NO_3^-	0.401	1.000						
Cl^-	0.201	0.368	1.000					
NH_4^+	**0.666****	**0.851****	0.408	1.000				
Na^+	0.818**	0.573*	0.418	0.740**	1.000			
K^+	0.866**	0.643**	0.201	0.777**	0.816**	1.000		
Mg^{2+}	0.764**	0.654**	0.241	0.826**	0.740**	0.857**	1.000	
Ca^{2+}	0.878**	0.579*	0.480*	0.717**	0.829**	0.891**	0.826**	1.000

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

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

Table 3.42 Correlation of chemical species for particles in the wet season of 2010

Ions	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	1.000							
NO_3^-	0.558*	1.000						
Cl^-	0.007	0.250	1.000					
NH_4^+	**0.648****	**0.571***	-0.271	1.000				
Na^+	0.440	0.348	0.616**	0.220	1.000			
K^+	0.553*	0.218	0.027	0.320	0.595**	1.000		
Mg^{2+}	0.498*	0.631**	0.382	0.353	0.463	-0.004	1.000	
Ca^{2+}	0.738**	0.759**	0.373	0.501*	0.722**	0.624**	0.542*	1.000

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

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

The Spearman correlation between a neutralized ion (NH_4^+) and the major anions (SO_4^{2-}) for particles in the dry and wet seasons of 2011 was analyzed (Table 3.43 and 3.44). The strong correlation of NH_4^+ and SO_4^{2-} (r = 0.977) was found during dry season. In the wet season, the correlation between NH_4^+ and SO_4^{2-} was relatively strong (r = 0.785). This result means that $(NH_4)_2SO_4$ had a higher influence in this area during dry season than that in the wet season. In 2010, the correlation between NH_4^+ and SO_4^{2-} during dry (r = 0.666) and wet season (r = 0.648) were relatively strong. It can be revealed that the influence of $(NH_4)_2SO_4$ was higher in 2011 than in 2010.

Table 3.43 Correlation of chemical species for particles in the dry season of 2011

Ions	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	1.000							
NO_3^-	0.352	1.000						
Cl^-	-0.191	-0.226	1.000					
NH_4^+	**0.977****	0.350	-0.219	1.000				
Na^+	0.399	0.102	0.293	0.358	1.000			
K^+	0.825**	0.484*	0.045	0.796**	0.554*	1.000		
Mg^{2+}	0.313	0.316	-0.223	0.262	0.335	0.339	1.000	
Ca^{2+}	0.748**	0.585*	0.106	0.680**	0.531*	0.905**	0.501*	1.000

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

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

Table 3.44 Correlation of chemical species for particles in the wet season of 2011

Ions	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	1.000							
NO_3^-	0.463	1.000						
Cl^-	0.655**	0.432	1.000					
NH_4^+	**0.785****	0.418	0.291	1.000				
Na^+	0.195	0.744**	0.431	0.130	1.000			
K^+	0.487*	0.280	0.262	0.268	-0.067	1.000		
Mg^{2+}	0.477*	0.257	0.338	0.509*	0.091	0.660**	1.000	
Ca^{2+}	0.728**	0.413	0.427	0.513*	0.181	0.406	0.221	1.000

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

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

2) Source analysis of major ion composition

In order to find out the possible association sources of ions in particles, factor analysis was carried out in order to determine the factors underlying the inter-correlations between the measured species. The varimax rotated principal component patterns for atmospheric ion concentrations during dry and wet seasons in 2010 are presented in Table 3.45. Only factor loadings higher than 0.5 were deemed to be statistically significant (Ayers and Yeung, 1996). The loadings having a greater value than 0.50 are marked bold in the table. There were three components contributed to the dry deposition during dry and wet seasons in 2010.

In the dry season of 2010, the first component had the high loadings of SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+}. SO_4^{2-} was derived from the combustion process (Huang et al., 2009), while K^+ was originated from biomass burning (Hu et al., 2003; Zhang et al., 2007; Al-Khashman, 2009). Mg^{2+} and Ca^{2+} may come from soil resuspension (Zhang et al., 2007; Al-Khashman, 2009). The second component showed high loadings of NO_3^- and NH_4^+. NO_3^- was probably come from the combustion process (Huang et al., 2009), while NH_4^+ was believed to be due to agricultural activities (Migliavacca et al., 2005; Zhang et al., 2007). The last component showed high loadings for Na^+ and Cl^-, hereafter referred to sea salt (Hu et al., 2003; Al-Khashman, 2009).

In the wet season of 2010, the first component indicated the combustion process, agricultural activities and the soil characteristics, with the marker variations of SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+}. The second component represented the contribution of the sea salt (Na^+ and Cl^-) and biomass burning (K^+). The last component with high loadings of Mg^{2+} probably came from soil resuspension.

The varimax rotated principal component patterns for dry deposition during dry and wet seasons in 2011 are shown in Table 3.46. In the dry season 2011, there were three factors contributed to the dry deposition. The first component with high loadings of SO_4^{2-}, NH_4^+, Na^+ and K^+ indicated combustion fuel, agricultural activities, marine source and biomass burning, respectively. The key marker variables of the second factor were NO_3^-, Mg^{2+} and Ca^{2+}, hereafter referred to combustion fuel (NO_3^-) and soil (Mg^{2+} and Ca^{2+}). The last component with high loading of Cl^- came from marine source. During wet season in 2011, there were three components contributed to the dry deposition. The first component represented the contribution of the combustion fuel (SO_4^{2-}), agricultural activities (NH_4^+) and soil resuspension (Ca^{2+}). The second component indicated the marine source, biomass burning and soil with the marker variations of Cl^-, K^+ and Mg^{2+}, respectively. The last component showed high loading for NO_3^- and Na^+, which originated from combustion fuel and marine source.

From the results of PCA, it can be revealed that biomass burning might influent on dry deposition for both years 2010 and 2011. In dry season of 2010 and 2011, component 1 has high loading of K^+ indicating biomass burning source. The variances of component 1 in 2010 and 2011 were 44% and 34%, respectively.

Table 3.45 Factor analysis of chemical composition in dry deposition during dry and wet seasons in 2010

Ions	Dry (n = 18)			Wet (n = 18)		
	1	2	3	1	2	3
SO_4^{2-}	**0.958**	0.022	-0.056	**0.798**	0.063	0.016
NO_3^-	0.052	**0.973**	0.222	**0.888**	0.143	0.141
Cl^-	-0.042	0.184	**0.958**	-0.169	**0.873**	0.420
NH_4^+	0.312	**0.942**	0.091	**0.921**	0.141	0.116
Na^+	0.572	0.135	**0.678**	0.270	**0.942**	0.050
K^+	**0.909**	0.178	0.206	0.528	**0.801**	-0.214
Mg^{2+}	**0.910**	0.330	0.139	0.185	0.110	**0.966**
Ca^{2+}	**0.736**	0.165	0.619	**0.907**	0.175	0.038
% of Variance	44.29	25.68	23.53	43.88	29.73	14.92
Cumulative %	44.29	69.97	93.50	43.88	73.61	88.53
Possible source	Combustion process, biomass burning and soil resuspension	Combustion process and agricultural activities	Sea salt	Combustion process, agricultural activities and soil resuspension	Sea salt and biomass burning	Soil resuspension

Table 3.46 Factor analysis of chemical composition in dry deposition during dry and wet seasons in 2011

Ions	Dry (n = 18)			Wet (n = 18)		
	1	2	3	1	2	3
SO_4^{2-}	**0.928**	0.206	-0.189	**0.932**	0.153	0.046
NO_3^-	0.007	**0.816**	-0.045	0.444	0.072	**0.797**
Cl^-	-0.075	-0.001	**0.933**	0.196	**0.818**	0.19
NH_4^+	**0.861**	0.232	-0.298	**0.903**	0.109	0.168
Na^+	**0.777**	-0.181	0.343	0.070	0.040	**0.965**
K^+	**0.658**	0.639	0.304	-0.032	**0.936**	-0.137
Mg^{2+}	0.029	**0.801**	-0.163	0.223	**0.847**	0.102
Ca^{2+}	0.284	**0.917**	0.149	**0.724**	0.13	0.314
% of Variance	34.07	33.58	15.70	31.23	29.02	22.00
Cumulative %	34.07	67.65	83.35	31.23	60.25	82.25
Possible source	Combustion fuel, agricultural activities, marine source and biomass burning	Combustion fuel and soil	Marine source	Combustion fuel, agricultural activities and soil	Marine source, biomass burning and soil	Combustion fuel and marine source

3.8.2 Wet deposition monitoring

Wet precipitation samples were collected on a daily basis by automatic precipitation collector (wet-only collector). EC and pH were measured by conductivity meter and pH meter, respectively. Ion substances that dissolved in rain precipitations play an important role in changing of acidic value of rain samples. In this study, anions including CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} and cations including Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} in the rain samples were analyzed by ion chromatograph. Sampling was carried out at the same place and same period with dry deposition.

3.8.2.1 Quality assurance and quality control for wet deposition monitoring

The accuracy of chemical analysis was done by analysis of the artificial rain samples provided from the Inter-laboratory Comparison Project 2010 and 2011 under the Acid Deposition Monitoring Network in East Asia (EANET). Accuracy of the analysis was considered from the results by comparison with prepared values (low and high concentrations). The artificial rain sample was diluted 100 times by deionized water. They were measured for EC, pH and analyzed for ion concentrations by IC. The differences between prepared values and measured values of less than or equal to 15% were considered good and those between 15% and 30% were classified as acceptable. In order to check the accuracy of data, ion balance (R_1) and EC balance (R_2) were calculated and compared with required criteria for R_1 and R_2 (see more detail in subsection 3 of the section 2.8.3). The results in 2010 and 2011 are presented in Table 3.47.

Table 3.47 Quality control of extraction and analysis methods from artificial rain samples in 2010 and 2011

Year	Concentrations		pH	EC	Ion species (µmol/L)								R_1	R_2
				(mS/m)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	(%)	(%)
2010	Low	Prepared value	5.1	1.3	24.7	14.4	16.6	20.7	17.0	2.8	8.1	3.3		
	(No. 102)	Measured value	5.0	1.3	23.1	12.2	15.7	19.9	16.0	2.5	7.5	3.1	2.1	-0.9
		%Difference	-1	0	-6	-15	-5	-4	-6	-11	-7	-6		
	High	Prepared value	4.5	4.0	77.0	47.0	52.0	60.0	52.1	8.9	26.0	13.0		
	(No. 101)	Measured value	4.5	3.8	73.8	43.0	49.5	55.8	48.0	7.5	24.2	12.0	0.1	0.9
		%Difference	-1	-3	-4	-9	-5	-7	-8	-16	-7	-8		
2011	Low	Prepared value	4.6	2.2	35.4	20.8	23.7	20.4	29.2	2.3	9.1	4.3		
	(No. 112)	Measured value	4.4	2.1	33.7	20.1	22.7	19.5	27.6	2.5	10.0	4.3	7.5	9.9
		%Difference	-4	-3	-5	-3	-4	-4	-5	9	10	0		
	High	Prepared value	5.5	3.5	56.7	37.8	76.4	53.7	57.5	10.4	47.6	13.7		
	(No. 111)	Measured value	5.2	3.4	55.4	37.9	75.1	51.4	55.2	12.1	48.5	13.6	1.2	2.7
		%Difference	-6	-3	-2	0	-2	-4	-4	16	2	-1		

It was found that analysis of pH and EC were greatly accurate for both low and high concentrations (0-6% difference). Most of analyzed ions including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} were good (<15%) for both low and high concentrations. Analysis of K^+ in low concentration sample was also accurate (9-11% difference), while that in high concentration was acceptable (16%). The values of R_1 and R_2 are in acceptable ranges.

3.8.2.2 Precipitation data

The number of rain samples collected at the sampling site by wet-only collector during November 2009 to October 2010 was 99 samples with 1166 mm precipitation (Table 3.48). There was no rain in February 2010. In the dry season (November 2009 - April 2010), only 10 rain samples with rain precipitation of 68 mm were collected. Eighty-nine rainy days (1098 mm) were detected in the wet season (May - October 2010). The highest number of rain samples (25 days) and rain precipitation (418 mm) were found in August.

The data of precipitation in 2011 (November 2010 - October 2011) is presented in Table 3.49. There were no rains 3 months in November, January and February during the study period. The total number of rainy days collected in 2011 was 120 days with rain precipitation of 1615 mm. In the dry season of 2011 (November 2010 - April 2011), 21 rain samples (158 mm) were collected, while in wet season (May - October 2011), 99 samples (1457 mm) were collected. The number of rainy days and amount of precipitation in dry season 2011 (21 days, 158 mm) was about 2 times higher than that in 2010 (10 days, 68 mm), while those in the wet seasons of 2011 (99 days, 1457 mm) and 2010 (89 days, 1098 mm) were not much different in terms of rainy days, but precipitation amount was quite difference (~350 mm).

The highest frequency of rain and precipitation during dry season in 2011 were detected in April, which was 13 days with 81 mm precipitation. During wet season in 2011, the number of rain samples were highest in August (21 samples), while the highest rain precipitation was collected in September (347 mm).

Table 3.48 Precipitation data during dry and wet seasons in 2010

Season	Month	Number of rain precipitation (day)	Total rain precipitation (mm)
Dry	Nov-09	1	0.8
	Dec-09	1	8.2
	Jan-10	3	40.5
	Feb-10	0	0.0
	Mar-10	3	11.4
	Apr-10	2	6.6
	Total	10	67.5
Wet	May-10	7	98.0
	Jun-10	11	115.4
	Jul-10	19	166.7
	Aug-10	25	417.5
	Sep-10	14	197.1
	Oct-10	13	103.6
	Total	89	1098.3
Total (12 months)		99	1165.8

Table 3.49 Precipitation data during dry and wet seasons in 2011

Season	Month	Number of rain precipitation (day)	Rain precipitation (mm)
Dry	Nov-10	0	0.0
	Dec-10	1	8.3
	Jan-11	0	0.0
	Feb-11	0	0.0
	Mar-11	7	68.7
	Apr-11	13	81.0
	Total	21	158.0
Wet	May-11	20	325.3
	Jun-11	12	228.3
	Jul-11	16	110.4
	Aug-11	21	338.4
	Sep-11	20	347.0
	Oct-11	10	107.3
	Total	99	1456.7
Year 2011	Total	120	1614.7

3.8.2.3 Measurement of acidity and alkalinity (pH) and electro-conductivity (EC)

The simply way to determine acid precipitation can be done by measuring pH value of the precipitation, which refers to pH < 5.6. The distribution of pH values in 2010 are depicted in Figure 3.24. Most of the pH values in 2010 presented in this study (77%) were in a range of 6.01-6.50. About 11% of the samples had pH values lower than 5.6. The samples with pH values above 6 may suggest a quantity of inputs of alkaline species into precipitation in the sampling site.

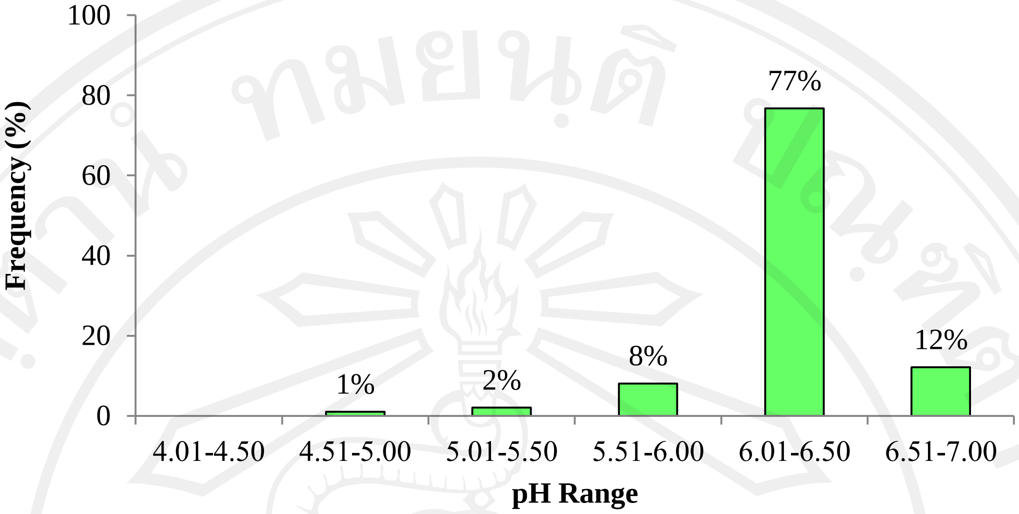


Figure 3.24 Frequency distribution of precipitation pH values in 2010 (n = 99)

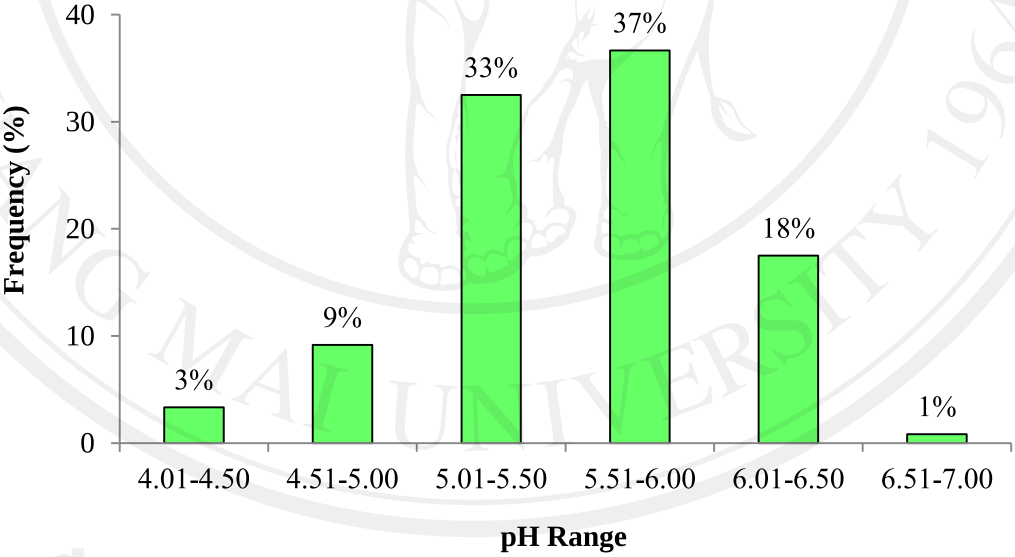


Figure 3.25 Frequency distribution of precipitation pH values in 2011 (n = 120)

Total number of collected samples in 2011 was 120 and precipitation volume was 1614.7 mm. The percent frequency distribution of pH for the rain samples is plotted in Figure 3.25. Most of the pH values in 2011 (37%) were range from 5.51-

6.00. Comparison with the result in 2010 found that most of pH values in 2010 were also in range of 5.51-6.00 but they have higher frequency distribution of pH (77% from 99 rain samples) than that in 2011. In 2011, 33% of pH values were range from 5.01-5.50, which was the second most frequency distribution.

Monthly mean pH values, EC values together with rain precipitation in 2010 are illustrated in Figure 3.26. The mean pH values in 2010 ranged from 5.13 to 6.69. Monthly mean pH was lowest in March 2010 (pH < 5.6), which also had low amount of precipitation. Low pH value might be from the large amount of pollutants in the atmosphere such as biomass burning in the area around the sampling site. Moreover, there were no rains in February. Therefore, when the rain started in March, these pollutants were eluted from the atmosphere. However, the mean value of pH during the study period was 6.19.

EC values indicate level of ion contamination in precipitation. High EC value indicates high ion contamination. EC value of deionized water is normally less than 0.15 mS/m. The mean EC values in 2010 were 0.52 mS/m. The minimum detected monthly mean EC value (0.25 mS/m) was in August 2010 whereas its maximum value (5.28 mS/m) was in March 2010. High value of EC in March could be influenced by accumulated in the air due to no rain scavenging in the previous month (February). When rain started in March, these pollutants were washed out from the atmosphere. Consequently, in the rain contains high concentrations of the pollutants. During wet season in 2010, the monthly mean EC values were decreased due to high amount of precipitation.

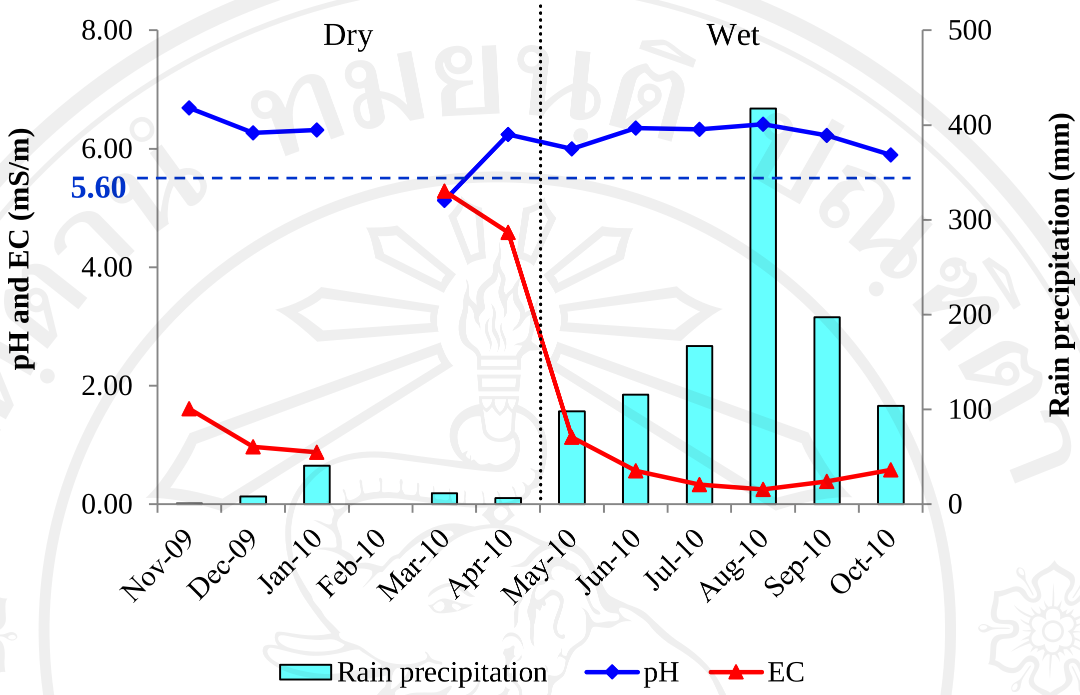


Figure 3.26 Variation of monthly amount of mean pH values, EC values and rain precipitation in 2010

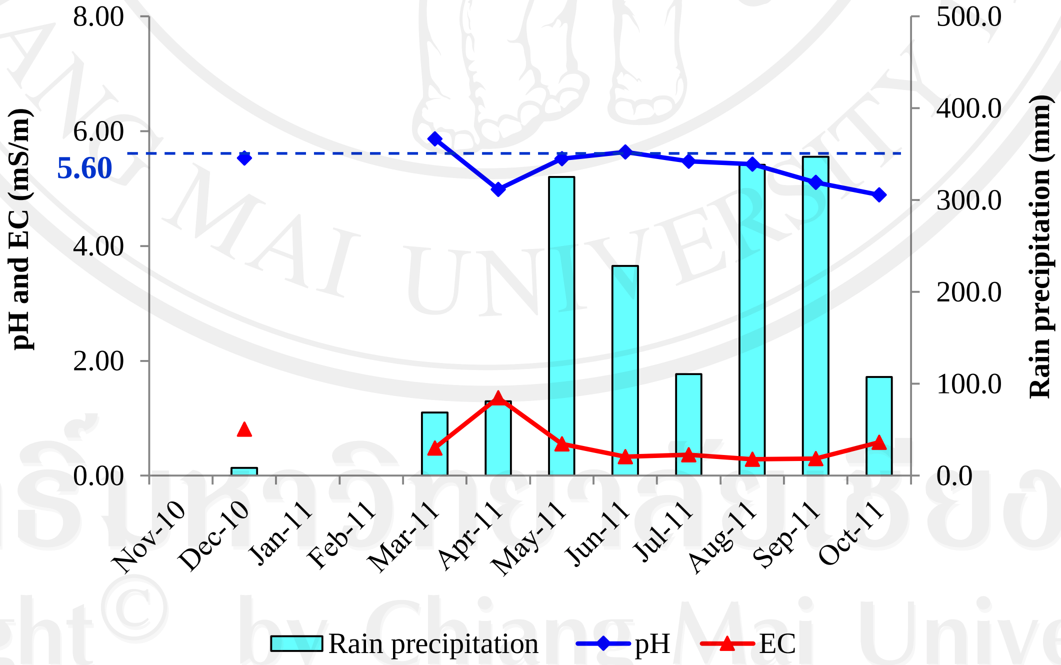


Figure 3.27 Variation of monthly amount of mean pH values, EC values and rain precipitation in 2011

Monthly mean pH values, EC values and the rain precipitation in 2011 are presented in Figure 3.27. The mean pH values were in a range of 4.89-5.87. It can be seen that most of the monthly mean pH in 2011 was lower than 5.6. The lowest of monthly mean pH value was found in October although there was 107.3 mm of the rain precipitation in this month. This result might be from the large amount of pollutants in the atmosphere around the sampling site especially in the wet season.

The minimum monthly mean EC value (0.29 mS/m) in 2011 was found in August, while its maximum value was in April (1.35 mS/m). In 2010, the lowest monthly mean EC value (0.25 mS/m) was also in August, while the highest was found in March (5.28 mS/m). The lowest EC values in 2010 and 2011 were similar, while the highest EC value in 2010 was about 4 times higher than that in 2011.

There was no rain in three months of November, January and February during dry season of 2011. The first rain started in December with a low precipitation (8.3 mm) and a slightly high of EC value (0.81 mS/m). The rain occurred again in March with rain precipitation of 68.7 mm and low EC value (0.48 mS/m). The EC values in March and April were different, while their rain precipitation was similar. However, the mean EC values of rain samples in the dry season of 2011 (0.88 mS/m) were about 3 times lower than that in 2010 (2.67 mS/m). It can be revealed that the amount of pollutants in the atmosphere around the sampling site in the dry season of 2011 might be lower than that in 2010.

3.8.2.4 Ion composition in rain samples

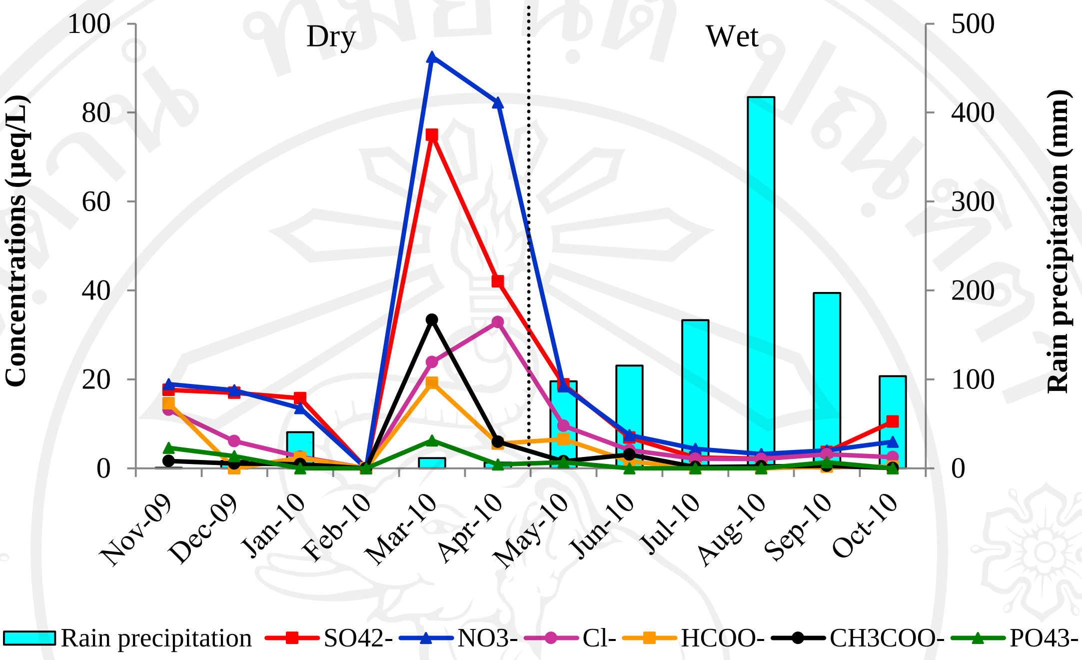
Monthly volume weighted means concentrations of the major chemical components in 2010 based on the unit of μeq/L are illustrated in Table 3.50. Monthly mean anion and cation concentrations together with precipitation amount in 2010 are depicted in Figure 3.28. It was found that all of ion concentrations were highest in the dry season of 2010 (March and April) due to low amount of rain precipitation and period of non-precipitation for 1 month. The highest monthly mean concentrations of cation and anion during dry and wet seasons in 2010 were NH_4^+ (87.0 and 15.5 μeq/L) and Ca^{2+} (38.9 and 6.9 μeq/L), respectively. The concentrations of NH_4^+ and Ca^{2+} in the dry season were approximately 6 times higher than that in wet season.

Monthly volume weighted means concentrations of the chemical components in 2011 are shown in Table 3.51. Monthly mean anion and cation concentrations together with rain precipitation in 2011 are presented in Figure 3.29. The results found that most of ion concentrations were highest in April 2011 (dry season) although there was the first rain in March after period of non-precipitation for 2 months. During dry season in 2011, the highest monthly mean ion concentration was found in NH_4^+ (41.7 μeq/L), followed by SO_4^{2-} (24.5 μeq/L). For wet season of 2011, the first two dominant ions were NH_4^+ and NO_3^-, which were 21.7 and 16.1 μeq/L, respectively. The concentrations of NH_4^+ in the dry season of 2011 (29.7 μeq/L) were about 3 times higher than that in wet season (11.8 μeq/L). Comparison with the result in 2010 found that NH_4^+ was also the dominant ion in the rain samples in 2010. However, NH_4^+ concentration during dry season in 2010 (87.0 μeq/L) was much higher than that during wet season (15.5 μeq/L) approximately 6 times.

Table 3.50 Monthly volume weighted mean in µeq/L of the major chemical composition in rain sample during dry and wet seasons in 2010

Season	Month	Precipitation (mm)	Volume weighted mean concentrations (µeq/L)												pH	EC
			SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+		
Dry	Nov-09	0.8	17.6	18.9	13.2	14.6	1.7	4.6	93.8	6.1	5.7	29.7	9.0	0.2	6.69	1.61
	Dec-09	8.2	16.9	17.5	6.1	0.0	1.0	2.7	54.1	2.2	5.1	20.9	3.2	0.5	6.27	0.97
	Jan-10	40.5	15.8	13.5	2.6	2.4	0.9	0.0	34.9	1.6	3.9	6.5	3.0	0.5	6.32	0.87
	Feb-10	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mar-10	11.4	75.0	92.5	23.9	19.2	33.4	6.3	230.7	8.8	21.9	86.6	17.6	7.5	5.13	5.28
	Apr-10	6.6	42.0	82.2	32.9	5.5	5.9	0.9	199.0	24.2	22.0	178.8	21.7	0.6	6.24	4.59
	Total	67.5	167.3	224.7	78.6	41.7	43.0	14.4	612.5	42.8	58.7	322.5	54.5	9.3		
	Average	11.3	28.5	34.1	9.7	5.4	6.9	1.5	87.0	5.2	8.9	38.9	7.4	1.7		
	%		12.1	14.5	4.1	2.3	2.9	0.6	37.0	2.2	3.8	16.5	3.2	0.7		
Wet	May-10	98.0	18.9	18.4	9.6	6.5	1.6	1.4	45.8	6.7	4.9	40.9	3.7	1.0	6.00	1.13
	Jun-10	115.4	6.9	7.5	4.1	1.5	3.1	0.0	14.7	3.6	0.4	11.7	1.1	0.4	6.35	0.56
	Jul-10	166.7	2.4	4.4	2.2	0.0	0.3	0.0	12.3	1.6	0.1	3.6	0.0	0.5	6.33	0.33
	Aug-10	417.5	2.1	3.2	2.1	0.0	0.4	0.0	8.9	1.7	0.0	2.8	0.0	0.4	6.41	0.25
	Sep-10	197.1	3.7	4.0	3.1	0.3	0.5	1.3	17.0	2.6	1.3	1.8	0.4	0.6	6.22	0.38
	Oct-10	103.6	10.5	6.0	2.5	0.3	0.1	0.0	16.6	2.4	0.1	0.8	0.0	1.3	5.89	0.58
	Total	1098.3	44.5	43.5	23.5	8.8	5.9	2.7	115.2	18.4	6.9	61.6	5.2	4.2		
	Average	183.1	5.2	5.6	3.2	0.8	0.8	0.4	15.5	2.5	0.8	6.9	0.5	0.6		
	%		12.2	13.1	7.5	2.0	1.8	0.9	36.2	5.9	1.8	16.1	1.2	1.4		
Year 2010	Total	1165.8	211.8	268.2	102.2	50.4	48.9	17.2	727.8	61.3	65.5	384.1	59.7	13.5		
	Average	97.2	6.6	7.3	3.6	1.1	1.1	0.4	19.6	2.7	1.2	8.7	0.9	0.6		
	%		12.2	13.5	6.6	2.1	2.1	0.8	36.4	5.0	2.3	16.2	1.7	1.2		

(a) Anion



(b) Cation

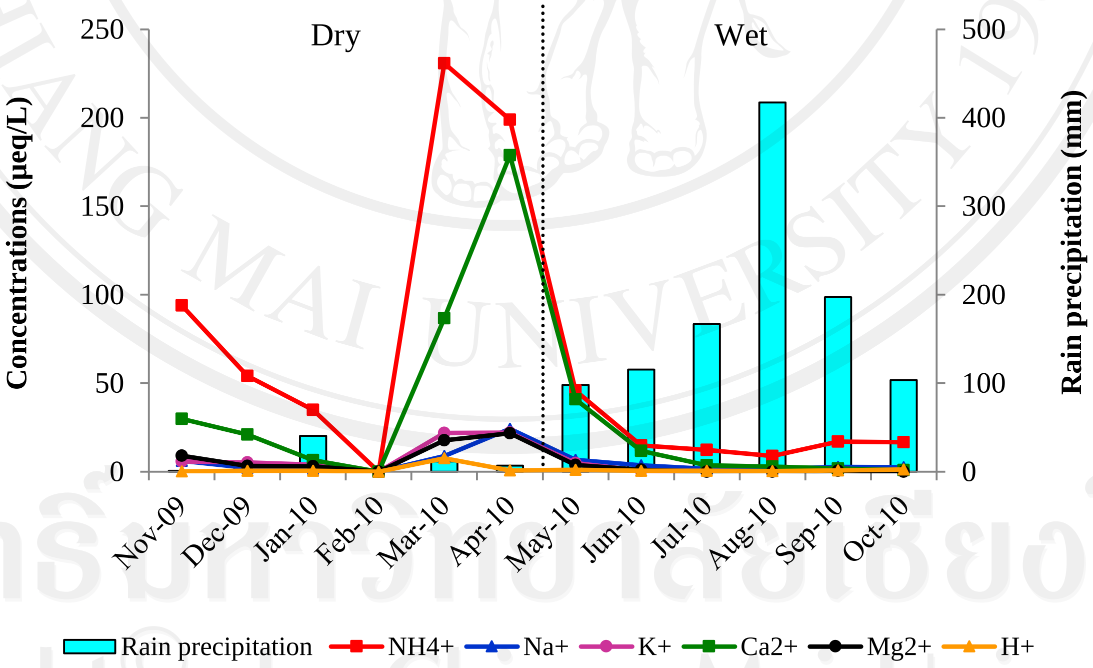
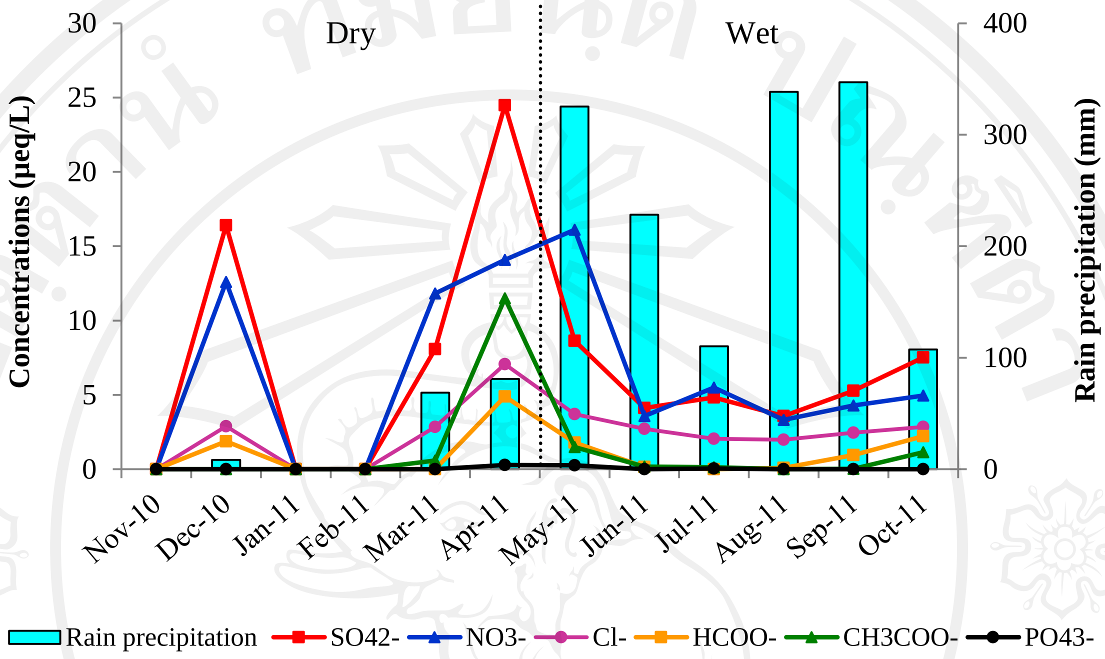


Figure 3.28 Monthly mean variability of ion composition in rain sample of 2010, (a) anion concentrations and (b) cation concentrations

Table 3.51 Monthly volume weighted mean in µeq/L of the major chemical composition in rain sample during dry and wet seasons in 2011

Season	Month	Precipitation (mm)	Volume weighted mean concentrations (µeq/L)												pH	EC
			SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+		
Dry	Nov-10	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Dec-10	8.3	16.4	12.6	2.9	1.9	0.0	0.0	36.5	3.5	2.4	7.8	0.0	3.0	5.53	0.81
	Jan-11	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Feb-11	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mar-11	68.7	8.1	11.8	2.9	0.0	0.6	0.0	14.7	2.3	1.6	7.1	1.1	1.4	5.87	0.48
	Apr-11	81.0	24.5	14.1	7.1	4.9	11.5	0.3	41.7	4.7	4.9	12.7	2.5	10.4	4.98	1.35
	Total	158.0	49.0	38.5	12.8	6.8	12.1	0.3	92.8	10.6	8.9	27.5	3.5	14.7		
	Average	26.3	16.9	13.0	5.0	2.6	6.1	0.1	29.7	3.6	3.3	10.0	1.7	6.1		
	%		17.2	13.3	5.1	2.7	6.3	0.1	30.2	3.7	3.4	10.2	1.8	6.2		
Wet	May-11	325.3	8.6	16.1	3.7	1.8	1.5	0.3	21.7	4.4	2.1	4.2	0.5	3.0	5.52	0.56
	Jun-11	228.3	4.1	3.6	2.7	0.2	0.2	0.0	11.1	3.4	0.1	3.1	0.2	2.3	5.64	0.33
	Jul-11	110.4	4.8	5.5	2.0	0.0	0.1	0.1	10.2	2.2	3.5	7.5	0.6	3.3	5.48	0.37
	Aug-11	338.4	3.6	3.3	2.0	0.1	0.0	0.0	8.5	2.4	1.4	2.2	0.1	3.7	5.43	0.29
	Sep-11	347.0	5.3	4.3	2.5	1.0	0.0	0.0	6.2	3.0	0.2	5.3	0.1	7.8	5.11	0.29
	Oct-11	107.3	7.5	5.0	2.8	2.2	1.2	0.0	13.2	2.6	1.2	10.8	0.8	12.8	4.89	0.58
	Total	1456.7	34.0	37.8	15.8	5.2	3.0	0.3	70.8	18.0	8.5	33.3	2.3	33.1		
	Average	242.8	5.6	6.7	2.7	0.4	0.3	0.1	11.8	3.1	0.5	4.6	0.3	5.0		
	%		13.6	16.4	6.5	1.0	0.8	0.1	28.7	7.7	1.1	11.2	0.7	12.1		
Year 2011	Total	1614.7	82.9	76.3	28.6	12.0	15.1	0.6	163.7	28.6	17.5	60.8	5.8	47.7		
	Average	134.6	6.7	7.4	2.9	0.6	0.9	0.1	13.5	3.2	0.7	5.1	0.4	5.1		
	%		14.4	15.8	6.2	1.3	1.9	0.2	29.0	6.9	1.6	11.0	1.0	10.9		

(a) Anion



(b) Cation

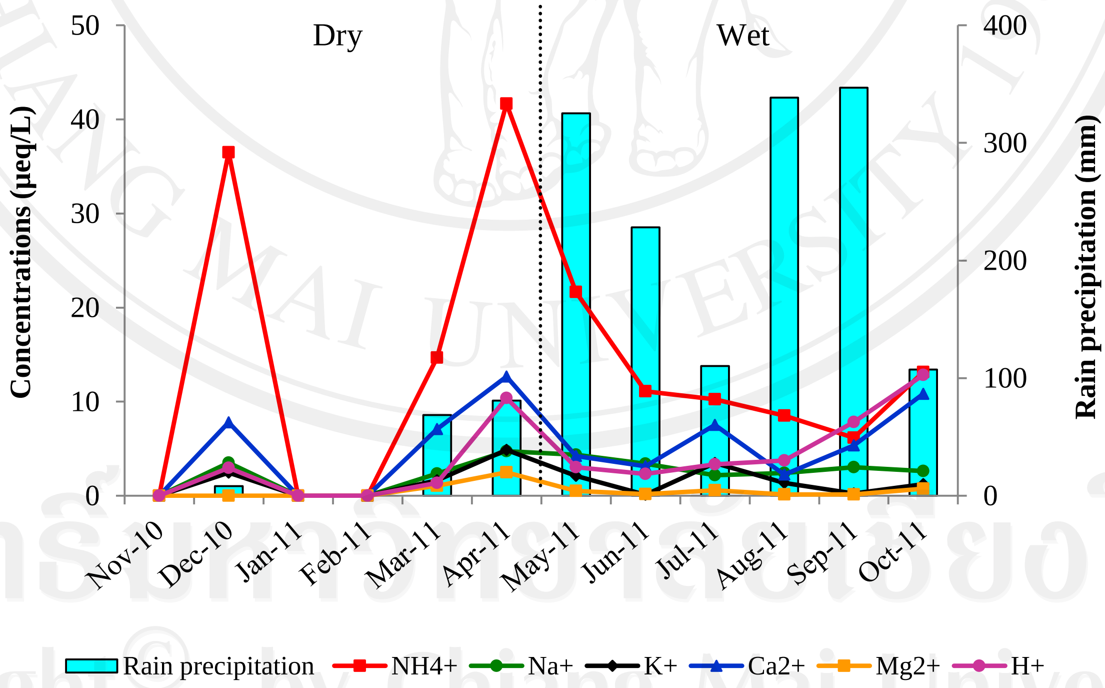
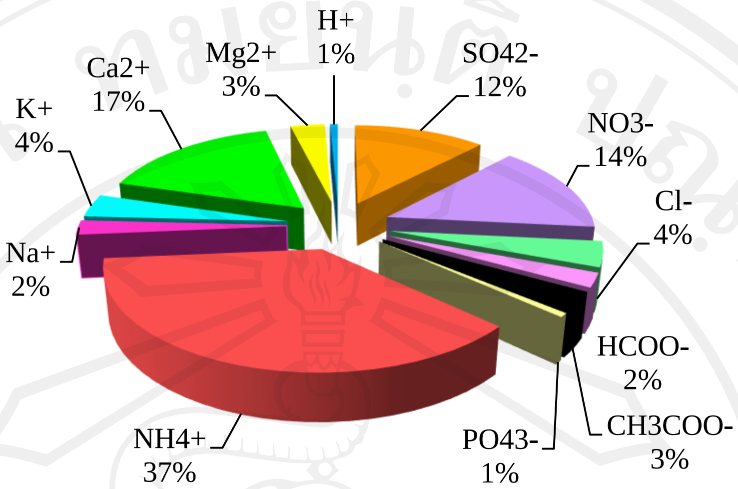


Figure 3.29 Monthly mean variability of ion composition in rain sample of 2011, (a) anion concentrations and (b) cation concentrations

The relative percentages of caions and anions during dry season 2010 were NH_4^+ (37%) > Ca^{2+} (17%) > NO_3^- (14%) > SO_4^{2-} (12%) > Cl^- ~ K^+ (4%) > Mg^{2+} ~ CH_3COO^- (3%) > $HCOO^-$ ~ Na^+ (2%) > H^+ ~ PO_4^{3-} (1%), while those during wet season 2010 were NH_4^+ (36%) > Ca^{2+} (16%) > NO_3^- (13%) > SO_4^{2-} (12%) > Cl^- (8%) > Na^+ (6%) > CH_3COO^- ~ $HCOO^-$ ~ K^+ (2%) > H^+ ~ Mg^{2+} ~ PO_4^{3-} (1%) as shown in Figure 3.30. The descending order of caions and anions (%) during dry season 2011 were NH_4^+ (30%) > SO_4^{2-} (17%) > NO_3^- (13%) > Ca^{2+} (10%) > CH_3COO^- (6%) ~ H^+ (6%) > Cl^- (5%) > Na^+ (4%) ~ K^+ (4%) > $HCOO^-$ (3%) > Mg^{2+} (2%) > PO_4^{3-} (0%), while those during wet season 2011 were NH_4^+ (29%) > NO_3^- (16%) > SO_4^{2-} (14%) > H^+ (12%) > Ca^{2+} (11%) > Na^+ (8%) > Cl^- (6%) > K^+ (1%) ~ $HCOO^-$ (1%) ~ CH_3COO^- (1%) ~ Mg^{2+} (1%) > PO_4^{3-} (0%) (Figure 3.31).

(a) Dry, 2010



(b) Wet, 2010

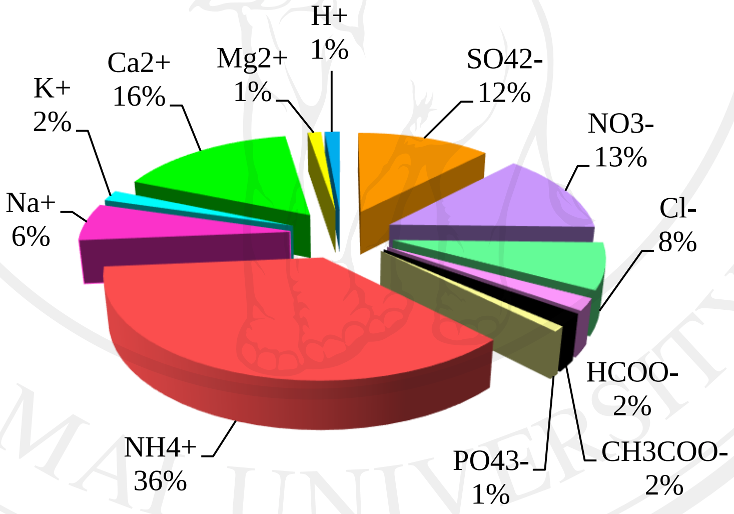
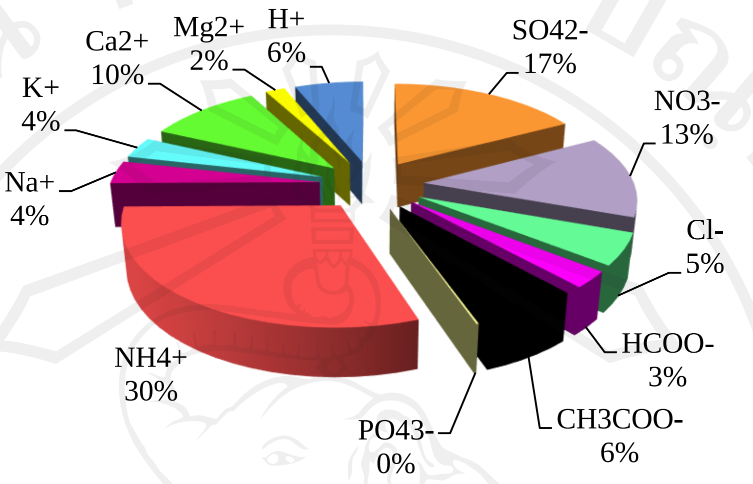


Figure 3.30 Relative percentage of total anions and cations based on unit of µeq/L during (a) dry, 2010 and (b) wet, 2010

(a) Dry, 2011



(b) Wet, 2011

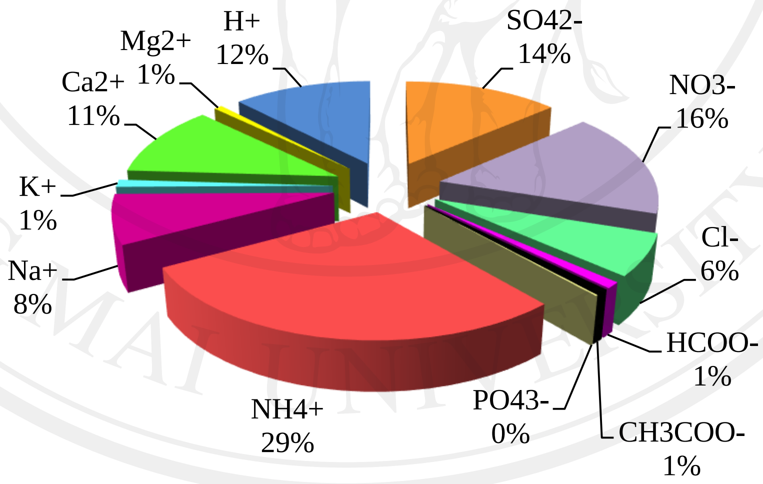
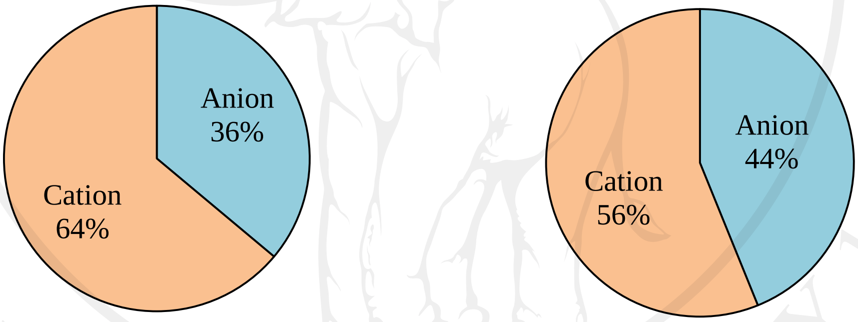


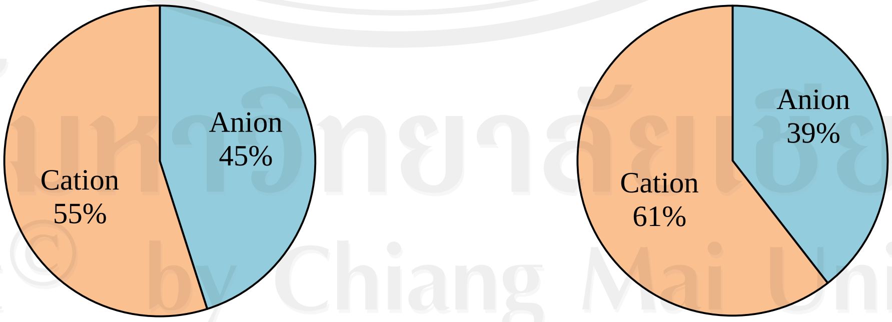
Figure 3.31 Relative percentage of total anions and cations based on unit of µeq/L during (a) dry, 2011 and (b) wet, 2011

The ratio between total cations and total anions during dry and wet seasons 2010 was 64:36 and 56:44, respectively as shown in Figure 3.32. The ratio between total cations and total anions in dry season 2011 was 55:45, while that in wet season 2011 was 61:39 (Figure 3.33). It can be revealed that total cations were higher than total anions in both years. It may be because other anion species including glutarate, succinate, malate, malonate, tartarate, maleate, fumarate, oxalate, phthalate and citrate (Tsai et al., 2012) are not analyzed in this study. Moreover, bicarbonate (HCO_3^-) concentrations were calculated based on pH values of rain samples only when they were higher than 6 (pH > 6).



(a) Dry, 2010 (b) Wet, 2010

Figure 3.32 Percentage of ions (µeq/L) during (a) dry, 2010 and (b) wet, 2010



(a) Dry, 2011 (b) Wet, 2011

Figure 3.33 Percentage of ions (µeq/L) during (a) dry, 2011 and (b) wet, 2011

3.8.2.5 Wet deposition amount

The wet deposition amount is the value of ion concentrations deposited per area unit. In this study, the deposition amount per square meter (m^2) was calculated. The deposition amounts of wet samples in 2010 and 2011 are shown in Tables 3.52 and 3.53. NH_4^+ was the major cation of wet deposition in 2010 (413 mg/m^2) and 2011 (400 mg/m^2). Percentage of NH_4^+ in 2010 and 2011 were 21% and 16% of total wet deposition, respectively (Figure 3.34). However, the major anion of wet deposition in 2010 and 2011 was NO_3^-, its values (%) were 525 mg/m^2 (27%) and 737 mg/m^2 (30%), respectively. Therefore, it could be assumed that the major sources of pollutants were from anthropogenic activities, which probably came from agricultural activities and combustion fuel.

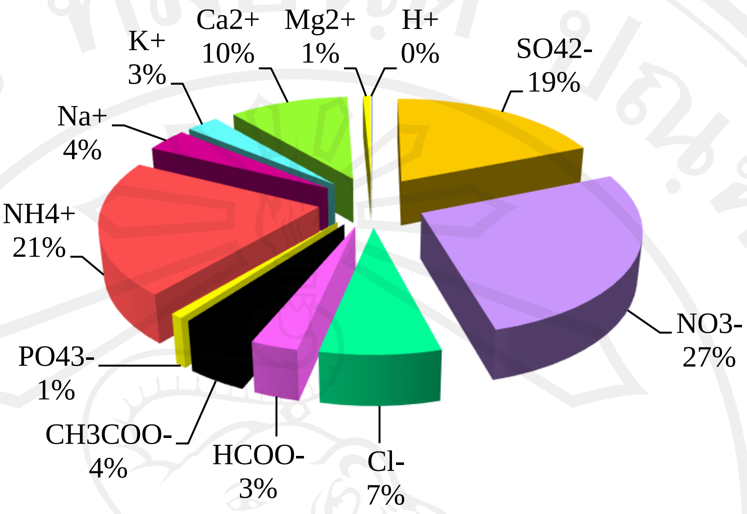
Table 3.52 Monthly wet deposition amount in 2010

Month	Deposition amount (mg/m^2)											
	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
Nov-09	0.7	0.9	0.4	0.5	0.1	0.1	1.4	0.1	0.2	0.5	0.1	0.0
Dec-09	6.7	8.9	1.8	0.0	0.5	0.7	8.0	0.4	1.6	3.4	0.3	0.0
Jan-10	30.7	33.9	3.7	4.4	2.2	0.0	25.5	1.5	6.2	5.3	1.5	0.0
Feb-10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mar-10	41.1	65.4	9.7	9.8	22.5	2.3	47.4	2.3	9.8	19.8	2.4	0.1
Apr-10	13.3	33.7	7.7	1.6	2.3	0.2	23.7	3.7	5.7	23.6	1.7	0.0
May-10	88.7	111.7	33.2	28.7	9.3	4.3	80.9	15.1	18.8	80.3	4.4	0.1
Jun-10	38.4	53.4	16.7	8.0	21.0	0.0	30.6	9.5	1.8	27.2	1.5	0.1
Jul-10	19.4	45.5	12.8	0.0	2.6	0.0	37.0	6.0	0.6	12.2	0.0	0.1
Aug-10	42.4	84.1	30.4	0.4	9.6	0.0	66.8	15.9	0.5	23.3	0.1	0.2
Sep-10	34.8	49.4	22.0	3.1	6.3	8.4	60.5	11.6	10.2	7.0	1.1	0.1
Oct-10	52.1	38.3	9.2	1.6	0.4	0.0	31.0	5.7	0.4	1.6	0.0	0.1
Total deposition	**368.3**	**525.2**	**147.6**	**58.1**	**76.8**	**15.9**	**412.8**	**71.8**	**55.8**	**204.1**	**13.1**	**0.8**
Percent of deposition (%)	**18.9**	**26.9**	**7.6**	**3.0**	**3.9**	**0.8**	**21.2**	**3.7**	**2.9**	**10.5**	**0.7**	**0.0**

Table 3.53 Monthly wet deposition amount in 2011

Month	Deposition amount (mg/m^2)											
	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
Nov-10	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0
Dec-10	6.5	6.5	0.9	0.7	0.0	0.0	5.5	0.7	0.8	1.3	0.0	0.0
Jan-11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Feb-11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mar-11	26.6	50.4	6.9	0.0	2.4	0.0	18.2	3.7	4.4	9.7	0.9	0.1
Apr-11	95.2	70.7	20.3	17.8	55.1	0.7	60.9	8.8	15.4	20.6	2.4	0.8
May-11	134.8	324.9	42.9	26.3	28.7	2.7	127.1	32.6	26.7	27.5	2.0	1.0
Jun-11	45.2	50.8	22.0	1.7	2.5	0.0	45.7	17.9	1.0	14.4	0.5	0.5
Jul-11	25.6	37.6	8.0	0.0	0.9	0.2	20.4	5.6	15.0	16.6	0.8	0.4
Aug-11	58.4	69.9	23.8	1.3	0.1	0.0	52.0	18.8	18.2	15.2	0.5	1.3
Sep-11	87.9	92.6	30.3	15.0	0.4	0.0	38.5	24.2	3.1	37.1	0.6	2.7
Oct-11	38.8	33.0	10.8	10.7	7.3	0.0	25.5	6.4	5.2	23.2	1.0	1.4
Total deposition	**519.1**	**737.3**	**167.9**	**76.6**	**101.5**	**8.6**	**399.7**	**125.6**	**97.7**	**174.7**	**18.7**	**19.3**
Percent of deposition (%)	**21.2**	**30.1**	**6.9**	**3.1**	**4.1**	**0.4**	**16.3**	**5.1**	**4.0**	**7.1**	**0.8**	**0.8**

(a) 2010



(b) 2011

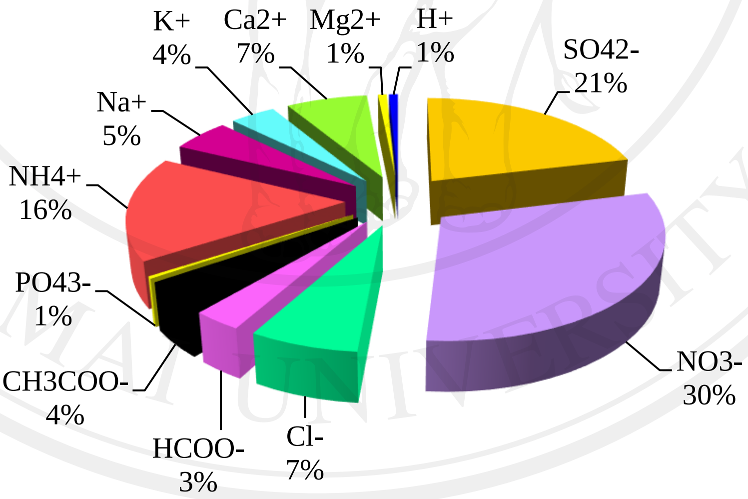


Figure 3.34 Relative percentage of wet deposition amount base on unit of mg/m^2 in (a) 2010 and (b) 2011

3.8.2.6 Comprehensive analysis for wet deposition data

1) Data screening

Comprehensive analysis such as neutralization factor (NF), correlation and principle component analysis (PCA) were calculated. In order to get high precision and correct data, it is necessary to do quality control. Data quality of rain samples was checked by ion balance (R_1) and conductivity balance (R_2). R_1 and R_2 values illustrate the accuracy of ion analysis and EC measurement, respectively. The calculated values were then compared with the criteria set up by the Acid Deposition Monitoring Network in East Asia (EANET).

Ion balance (R_1) and conductivity agreement check (R_2) of the rain samples in 2010 are shown in Table 3.54. Among 99 rain samples of this study, about 52% of R_1 and 90% of R_2 were accepted, while 47% of both R_1 and R_2 were accepted. Ion and conductivity balances are illustrated in Figure 3.35, which R_1 distribution values were higher than that in R_2.

Table 3.54 Ion balance (R_1) and conductivity agreement check (R_2) in 2010

Sample (N)	R_1 (N)	R_1 (AA)	%	R_2 (N)	R_2 (AA)	%	R_1&R_2 (N)	R_1&R_2 (AA)	%
99	99	51	52	99	89	90	99	47	47

Sample (N): Number of samples

R_1 (N) : Number of samples measured and calculated ion balance (R_1)

R_1 (AA) : Number of samples within allowable ranges for R_1

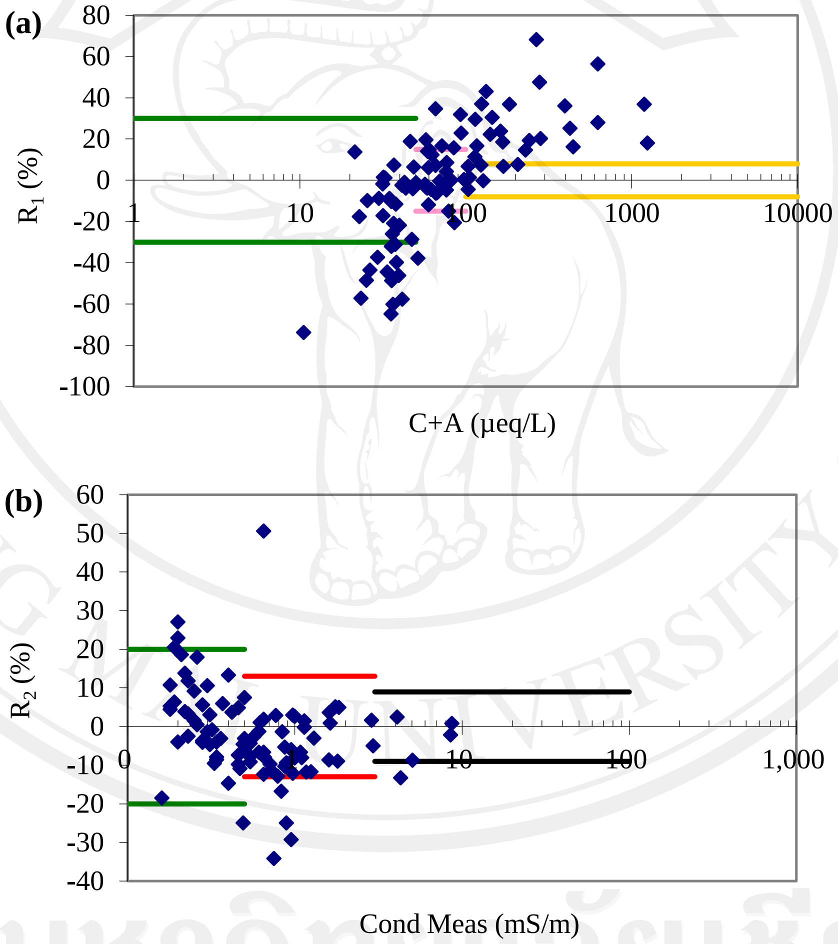
R_2 (N) : Number of samples measured and calculated conductivity agreement (R_2)

R_2 (AA) : Number of samples within allowable ranges for R_2

R_1&R_2 (N) : Number of samples measured and calculated both R_1 and R_2

R_1&R_2 (AA) : Number of samples within allowable ranges for both R_1 and R_2

R_1 and R_2 calculated including concentration of additional measured constituents (formate, acetate and phosphate)



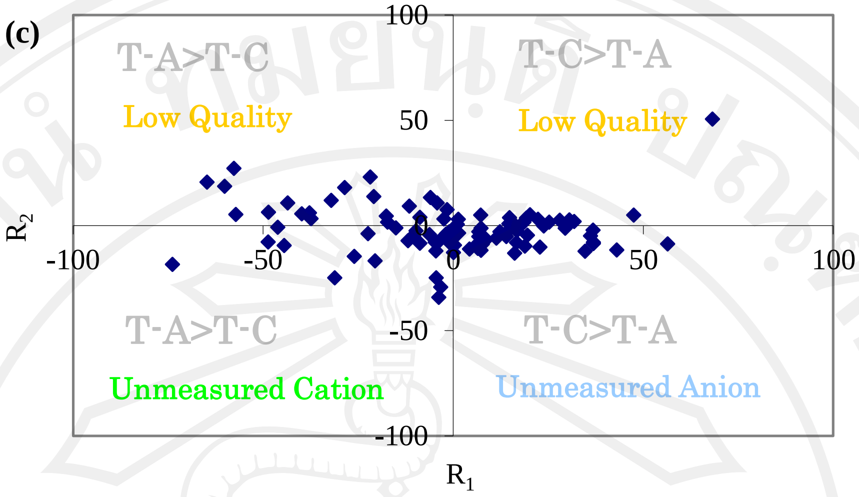


Figure 3.35 Values of R_1 and R_2 of wet-only samples in 2010 (a) Distribution of R_1 (ion balance), (b) R_2 (conductivity balance) and (c) R_1 and R_2 relation

Table 3.55 showed ion balance (R_1) and conductivity agreement check (R_2) of the rain samples in 2011. In wet-only samples (n = 120), about 43% of R_1 and 74% of R_2 were accepted, while 36% of both R_1 and R_2 were accepted. Ion and conductivity balances are illustrated in Figure 3.36, which R_1 distribution values were higher than that in R_2. Comparison with the result in 2010 found that among 99 rain samples in 2010, about 52% of R_1 and 90% of R_2 were accepted, while 47% of both R_1 and R_2 were accepted. It can be revealed that percentage of samples within allowable ranges for R_1, R_2 and both R_1 and R_2 in 2010 were higher than that in 2011.

Table 3.55 Ion balance (R_1) and conductivity agreement check (R_2) in 2011

Sample (N)	R_1 (N)	R_1 (AA)	%	R_2 (N)	R_2 (AA)	%	R_1&R_2 (N)	R_1&R_2 (AA)	%
120	120	51	43	120	89	74	120	43	36

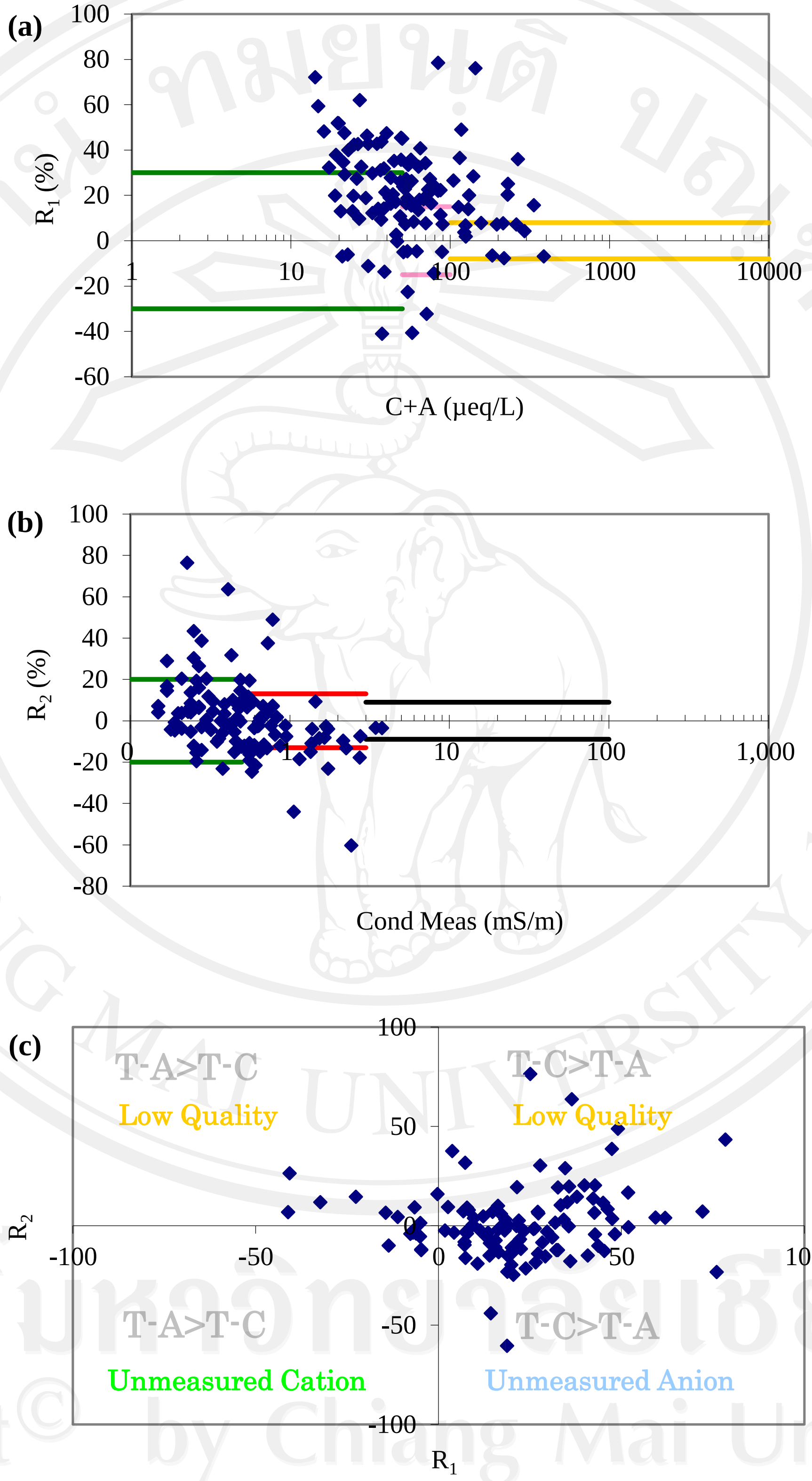


Figure 3.36 Values of R$_1$ and R$_2$ of wet-only samples in 2011 (a) Distribution of R$_1$ (ion balance), (b) R$_2$ (conductivity balance) and (c) R$_1$ and R$_2$ relation

2) Acid neutralization

In case that all the nss-SO_4^{2-} and NO_3^- existed in the form of free acid forms, the summation of those should equal to H^+ (Hu et al., 2003). Concentrations of nss-SO_4^{2-} and NO_3^- were 6.26 and 7.26 µeq/L, respectively. Therefore, the summation was 13.53 µeq/L. From these values, the pH should be 4.87, but from the measurement it was 6.19 which is lower by 1.32 pH. It indicated that the rain precipitation had some neutralization. From previous studies (Saxena et al., 1996; Das et al., 2005), NH_4^+, Ca^{2+}, K^+ and Mg^{2+} have been used to validate by calculating neutralization factor. In this study, neutralization factors for NH_4^+, Ca^{2+}, Na^+, K^+ and Mg^{2+} are shown in Table 3.56.

Table 3.56 Neutralization factors of the major ions in the rain samples in 2010

Ions	NH_4^+	Ca^{2+}	Na^+	K^+	Mg^{2+}
NF	1.42	0.63	0.19	0.09	0.07

Neutralization factors (NF) of ions in rain samples in descending order were $NH_4^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$. This feature suggests that in rain samples, the acidity is mainly neutralized by NH_4^+ based on the fact that NH_4^+ concentration was the highest cation concentrations, which probably resulted from agricultural activities surrounded the sampling area. However, the NF values of Ca^{2+} were higher than Na^+, K^+ and Mg^{2+}, which indicating the influence of soil resuspension. The contribution of Na^+, K^+ and Mg^{2+} to the overall neutralization process is very low.

From the difference of the summation of nss-SO_4^{2-} and NO_3^- from H^+, it was indicated that acid neutralization was occurred (Hu et al., 2003). Normally, neutralization is frequently reported and attributed to NH_4^+ and Ca^{2+} (Vong, 1990). Therefore, it was expected that the summation of concentrations of H^+, NH_4^+ and Ca^{2+} correlated with summation of concentrations of nss-SO_4^{2-} and NO_3^- in the event that the acidity of the rain precipitation is mainly neutralized by NH_4^+ and Ca^{2+}. This hypothesis was confirmed by the scatter plots between those two summation values as presented in Figure 3.37. The correlation coefficient being 0.854.

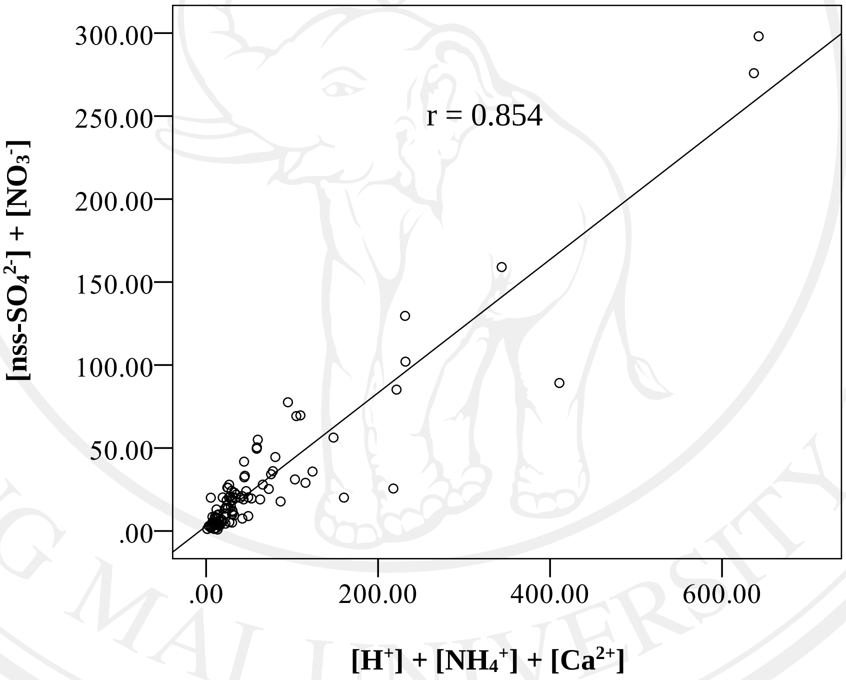


Figure 3.37 Correlation of ([nss-SO_4^{2-}] + [NO_3^-]) and ([H^+] + [NH_4^+] + [Ca^{2+}]) (n = 99)

The neutralization factors (NF) of major cations in rain samples of 2011 are given in Table 3.57. It was found that NF of ions were $NH_4^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$. This trend was similar with the result in 2010. As is seen NH_4^+ is the ion with the highest neutralization effect and the next order is Ca^{2+}.

Table 3.57 Neutralization factors of the major ions in the rain samples in 2011

Ions	NH_4^+	Ca^{2+}	Na^+	K^+	Mg^{2+}
NF	0.96	0.36	0.23	0.05	0.03

Hu et al. (2003) reported that the summation of all nss-SO_4^{2-} and NO_3^- existed in the form of free acid forms should equal to H^+. Concentrations of nss-SO_4^{2-} and NO_3^- were 6.28 and 7.35 µeq/L, respectively. Therefore, the summation was 13.63 µeq/L. From these values, the pH should be 4.87, but from the measurement it was 5.29 which is lower by 0.42 pH. It means that the rain samples had some neutralization.

From the difference of the sum of nss-SO_4^{2-} and NO_3^- from H^+, it was estimated that nss-SO_4^{2-} and NO_3^- to be in a neutralized form. Such neutralization is frequently reported and attributed to NH_4^+ and/or $CaCO_3$ (Vong, 1990). It is expected that the sum ($[H^+] + [NH_4^+] + [Ca^{2+}]$) to correlate with ($[\text{nss-}SO_4^{2-}] + [NO_3^-]$) if the acidity of the precipitation is mainly neutralized by typical bases in the atmosphere, i.e. NH_3 and soil dust. Indeed, the data confirmed the hypothesis as shown in Figure 3.38. The correlation coefficient was 0.775.

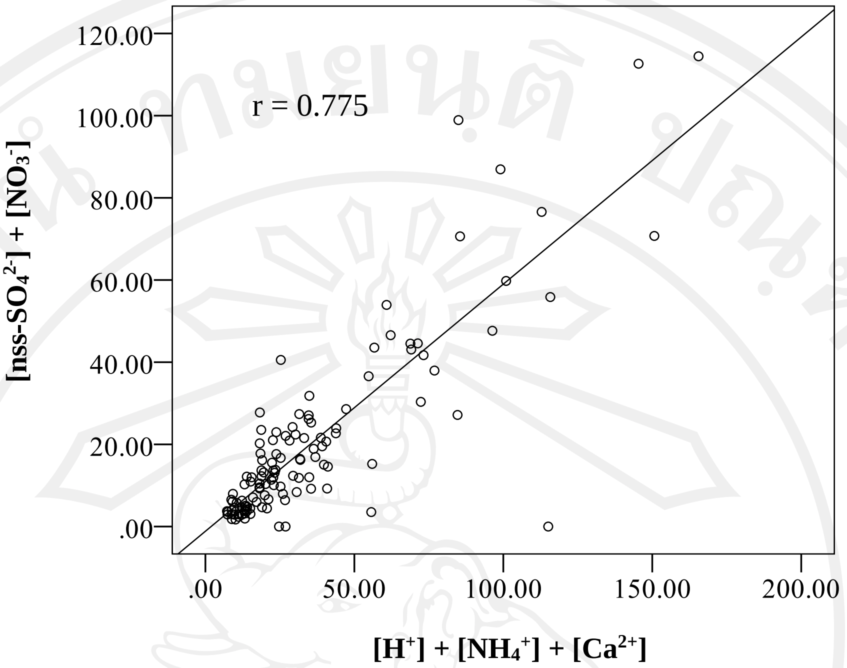


Figure 3.38 Correlation of ([nss-SO_4^{2-}] + [NO_3^-]) and ([H^+] + [NH_4^+] + [Ca^{2+}]) (n = 120)

3) Ion pair correlation

The Spearman correlations between various ion species in the rain samples during dry and wet seasons in 2010 were calculated in order to identify their relationship as shown in Tables 3.58 and 3.59, respectively. In the dry season of 2010, the correlations of NH_4^+ and NO_3^- (r = 0.976), Na^+ and NO_3^- (r = 0.891), K^+ and NO_3^- (r = 0.988), Ca^{2+} and NO_3^- (r = 0.939) and Mg^{2+} and NO_3^- (r = 0.948) were strong correlated. It can be revealed that these base cations greatly neutralized the acid nitrate compound during this period. In the wet season of 2010, the relatively strong correlation between NH_4^+ and SO_4^{2-} (r = 0.761) and NH_4^+ and NO_3^- (r = 0.769) were presented. Moreover, the fairly correlated was found between H^+ and SO_4^{2-} (r = 0.489) and H^+ and NO_3^- (r = 0.358). It suggested that the main acidity of rain precipitation was neutralized by NH_4^+. This result contributed with ammonium/sulfate/nitrate system, whereby NH_3 first reacts with H_2SO_4 to form $(NH_4)_2SO_4$ and NH_4HSO_4, and then the remaining NH_3 will be taken up by HNO_3 to form NH_4NO_3 (Hu et al., 2003).

Noticeably, the correlation between K^+ and Cl^- during dry season in 2010 was found to be strong (r = 0.964), while that during wet season was relatively strong (r = 0.689).

Correlations among ions in precipitation during dry and wet seasons in 2011 are calculated and depicted in Table 3.60 and 3.61, respectively. A correlation was seen between SO_4^{2-} and NO_3^- in the dry (r = 0.563) and wet season of 2011 (r = 0.743), indicating their origin from similar sources. This was due to similarity in their behavior in precipitation and result of the emissions of their precursors SO_2 and NO_x. Similarly, a correlation was seen between Ca^{2+} and Mg^{2+} in the dry (r = 0.919) and wet season of 2011 (r = 0.714), suggesting the common source of these ions from natural source (crustal origin). During dry season, other good correlations (r = 0.671-0.902) were observed between major cations including NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} and major anion of SO_4^{2-} and NO_3^-. Similarly, other relatively good correlations (r = 0.260-0.609) were observed during wet season between major cations including NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} and major anion of SO_4^{2-} and NO_3^-.

Most of the well-correlated pairs were found during dry season, which have common occurrence in precipitation as a result of atmospheric chemical reactions probably from the reaction of the acid in the atmosphere such as HNO_3 and H_2SO_4 with alkaline compounds rich in carbonate materials, carried into the atmosphere by wind-blown dust. This shows that the wind carried dust and soil plays an important factor in the chemistry of rain sample. The strong correlated were found between

NH_4^+ and SO_4^{2-} (r = 0.877), K^+ and SO_4^{2-} (r = 0.892), Ca^{2+} and NO_3^- (r = 0.902) and Mg^{2+} and NO_3^- (r = 0.880). The ammonium compounds applied to soil can escape into atmosphere by means of gaseous NH_3 or as NH_4NO_3 and $(NH_4)_2SO_4$ particles. When NH_4NO_3 and $(NH_4)_2SO_4$ particles were incorporated in rain, they change NO_3^- and SO_4^{2-} concentrations, but do not affect the pH. However, when ammonium was incorporated in rain, it can neutralize the acidity of rain sample (Al-Momani et al., 1995).

Noticeably, the correlation between K^+ and Cl^- during dry season in 2011 was strong correlated (r = 0.910), while that during wet season was fairy correlated (r = 0.226). Comparison with the results of 2010 found that in the dry season of 2010 was found the strong correlation between K^+ and Cl^- (r = 0.964), while that correlation in wet season was relatively strong (r = 0.689). It can be seen that the strong correlation between K^+ and Cl^- was found in the dry season of 2010 and 2011.

Table 3.58 Correlation of chemical species for rain sample in the dry season of 2010

Ions	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
SO_4^{2-}	1.000											
NO_3^-	0.612	1.000										
Cl^-	0.564	0.952^{**}	1.000									
$HCOO^-$	0.563	0.456	0.500	1.000								
CH_3COO^-	0.794^{**}	0.648^{*}	0.576	0.738^{*}	1.000							
PO_4^{3-}	0.657^{*}	0.557	0.682^{*}	0.797^{**}	0.682^{*}	1.000						
NH_4^+	0.576	**0.976****	0.964^{**}	0.563	0.648^{*}	0.650^{*}	1.000					
Na^+	0.345	**0.891****	0.867^{**}	0.388	0.406	0.356	0.879^{**}	1.000				
K^+	0.624	**0.988****	**0.964****	0.419	0.612	0.569	0.964^{**}	0.867^{**}	1.000			
Ca^{2+}	0.527	**0.939****	0.988^{**}	0.532	0.600	0.682^{*}	0.952^{**}	0.842^{**}	0.952^{**}	1.000		
Mg^{2+}	0.547	**0.948****	0.973^{**}	0.530	0.565	0.652^{*}	0.948^{**}	0.894^{**}	0.960^{**}	0.973^{**}	1.000	
H^+	0.309	0.552	0.382	0.050	0.467	0.150	0.539	0.309	0.491	0.358	0.298	1.000

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

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

Table 3.59 Correlation of chemical species for rain sample in the wet season of 2010

Ions	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
SO_4^{2-}	1.000											
NO_3^-	0.753^{**}	1.000										
Cl^-	0.713^{**}	0.728^{**}	1.000									
$HCOO^-$	0.442^{**}	0.204	0.163	1.000								
CH_3COO^-	0.186	0.160	0.261^{*}	0.236^{*}	1.000							
PO_4^{3-}	0.225^{*}	0.209^{*}	0.283^{**}	0.104	0.008	1.000						
NH_4^+	**0.761^{**}**	**0.769^{**}**	0.803^{**}	0.213^{*}	0.158	0.267^{*}	1.000					
Na^+	0.626^{**}	0.622^{**}	0.885^{**}	0.230^{*}	0.207	0.235^{*}	0.740^{**}	1.000				
K^+	0.503^{**}	0.647^{**}	**0.689^{**}**	0.080	0.132	0.368^{**}	0.735^{**}	0.611^{**}	1.000			
Ca^{2+}	0.514^{**}	0.617^{**}	0.570^{**}	0.207	0.230^{*}	0.214^{*}	0.556^{**}	0.480^{**}	0.596^{**}	1.000		
Mg^{2+}	0.474^{**}	0.484^{**}	0.572^{**}	0.149	0.132	0.457^{**}	0.491^{**}	0.539^{**}	0.652^{**}	0.542^{**}	1.000	
H^+	**0.489^{**}**	**0.358^{**}**	0.203	0.435^{**}	0.033	0.152	0.311^{**}	0.199	0.045	0.065	0.131	1.000

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

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

Table 3.60 Correlation of chemical species for rain sample in the dry season of 2011

Ions	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
SO_4^{2-}	1.000											
NO_3^-	**0.563****	1.000										
Cl^-	0.795**	0.806**	1.000									
$HCOO^-$	0.425	0.290	0.460*	1.000								
CH_3COO^-	0.606**	0.192	0.546*	0.510*	1.000							
PO_4^{3-}	0.189	0.298	0.507*	0.539*	0.387	1.000						
NH_4^+	**0.877****	**0.752****	0.896**	0.282	0.404	0.212	1.000					
Na^+	**0.762****	**0.671****	0.928**	0.564**	0.517*	0.507*	0.813**	1.000				
K^+	**0.892****	**0.707****	**0.910****	0.460*	0.643**	0.459*	0.879**	0.797**	1.000			
Ca^{2+}	**0.688****	**0.902****	0.875**	0.255	0.235	0.341	0.862**	0.772**	0.782**	1.000		
Mg^{2+}	**0.709****	**0.880****	0.891**	0.234	0.331	0.424	0.830**	0.732**	0.850**	**0.919****	1.000	
H^+	0.545*	0.122	0.431	0.426	0.813**	0.153	0.390	0.462*	0.502*	0.125	0.124	1.000

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

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

Table 3.61 Correlation of chemical species for rain sample in the wet season of 2011

Ions	SO_4^{2-}	NO_3^-	Cl^-	$HCOO^-$	CH_3COO^-	PO_4^{3-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+
SO_4^{2-}	1.000											
NO_3^-	**0.743****	1.000										
Cl^-	0.471**	0.499**	1.000									
$HCOO^-$	0.066	0.008	0.079	1.000								
CH_3COO^-	0.184	0.250*	0.190	0.366**	1.000							
PO_4^{3-}	0.124	0.178	0.203*	0.157	0.272**	1.000						
NH_4^+	**0.511****	**0.592****	0.414**	-0.009	0.136	0.109	1.000					
Na^+	**0.351****	**0.437****	0.755**	0.086	0.149	0.092	0.410**	1.000				
K^+	**0.260****	**0.363****	**0.226***	-0.022	0.350**	0.181	0.442**	0.165	1.000			
Ca^{2+}	**0.522****	**0.410****	0.379**	-0.035	0.152	-0.002	0.269**	0.218*	0.199*	1.000		
Mg^{2+}	**0.609****	**0.468****	0.414**	-0.031	0.312**	0.052	0.415**	0.278**	0.492**	**0.714****	1.000	
H^+	0.172	0.037	-0.072	0.156	0.046	0.079	-0.241*	-0.260**	-0.051	0.260**	0.142	1.000

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

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

4) Source analysis of major ion composition

In order to find possible association sources of ions in rain precipitations, factor analysis was carried out to determine the factors underlying the inter-correlations between the measured species. The results are shown in Table 3.62.

The factor analysis identified that there was three components contributed to wet deposition during dry season in 2010, while that during wet season was four components. In dry season, component 1 provided high loading on SO_4^{2-}, NO_3^-, NH_4^+, K^+, Ca^{2+} and Mg^{2+}. It associated reasonably with fuel combustion process (SO_4^{2-} and NO_3^-), agricultural activities (NH_4^+), biomass burning (K^+) and soil (Ca^{2+} and Mg^{2+}). The variables of the component 2 were $HCOO^-$ and CH_3COO^-. $HCOO^-$ might be from photochemical reaction (Tsai et al., 2012). CH_3COO^- may come from biomass burning (Tsai et al., 2012) and primary emissions from vegetation and soil (Wang et al., 2007b). The last component was high loading of Na^+ and Cl^-, which originated from sea salt.

In the wet season of 2010, the component 1 represented the fuel combustion (SO_4^{2-} and NO_3^-), sea salt (Na^+ and Cl^-) and soil (Ca^{2+} and Mg^{2+}). Component 2 with high loading of NH_4^+ and K^+ came from agricultural area and biomass burning, respectively. The key marker variables of component 3 were $HCOO^-$ and CH_3COO^-, which originated from photochemical reaction, biomass burning, vegetation and soil.

Table 3.62 Factor analysis of chemical composition in wet deposition during dry and wet seasons in 2010

Ions	Dry (n = 10)			Wet (n = 89)			
	1	2	3	1	2	3	4
SO_4^{2-}	**0.770**	0.501	0.190	**0.773**	0.044	0.371	0.301
NO_3^-	**0.588**	0.545	0.575	**0.817**	0.122	0.120	0.132
Cl^-	0.611	0.294	**0.729**	**0.902**	0.299	0.090	0.047
$HCOO^-$	0.243	**0.925**	0.183	0.295	0.129	**0.842**	0.072
CH_3COO^-	0.168	**0.956**	0.219	0.065	0.002	**0.886**	-0.001
NH_4^+	**0.616**	0.530	0.571	0.530	**0.587**	0.117	0.118
Na^+	0.149	0.232	**0.956**	**0.859**	0.191	-0.043	0.064
K^+	**0.883**	0.110	0.433	0.515	**0.779**	-0.046	-0.045
Ca^{2+}	**0.662**	0.174	0.720	**0.856**	-0.026	0.269	-0.121
Mg^{2+}	**0.931**	-0.018	0.352	**0.778**	0.353	0.232	-0.137
% of Variance	39.84	31.66	25.66	39.95	17.45	15.06	9.27
Cumulative %	39.84	71.50	97.16	39.95	57.40	72.46	81.73
Possible source	Fuel combustion, agricultural activities, biomass burning and soil	Photochemical reaction, biomass burning, vegetation and soil	Sea salt	Fuel combustion, sea salt and soil	Agricultural activities and biomass burning	Photochemical reaction, biomass burning, vegetation and soil	-

Table 3.63 shows the varimax rotated principal component patterns for individual precipitation during dry and wet seasons in 2011. There were three components contributed to wet deposition during dry season. The first component with high loading of SO_4^{2-}, NO_3^-, NH_4^+, K^+, Ca^{2+} and Mg^{2+} indicated that they originated from combustion fuel (SO_4^{2-} and NO_3^-), agricultural activities (NH_4^+), biomass burning (K^+) and soil (Ca^{2+} and Mg^{2+}). The key marker variables of the second component were $HCOO^-$ and CH_3COO^-, which come from photochemical reaction ($HCOO^-$), biomass burning and emission from vegetation and soil (CH_3COO^-). The last component originated from sea salt (Na^+ and Cl^-).

In the wet season of 2011, four components contributed to wet deposition were found. The first component represented the contribution of the combustion fuel (SO_4^{2-} and NO_3^-), sea salt (Na^+ and Cl^-), agricultural activities (NH_4^+) and soil resuspension (Ca^{2+} and Mg^{2+}). The second component originated from photochemical reaction ($HCOO^-$), biomass burning and emission from vegetation and soil (CH_3COO^-). The third component showed high loading for K^+, which come from biomass burning.

From PCA results, it can be reported that wet deposition in 2010 and 2011 may be affected from biomass burning. During dry season of 2010 and 2011, component 1 has high loading of K^+, which originated from biomass burning. The percent variance of component 1 in 2010 and 2011 was approximately 40%.

Table 3.63 Factor analysis of chemical composition in wet deposition during dry and wet seasons in 2011

Ions	Dry (n = 21)			Wet (n = 99)			
	1	2	3	1	2	3	4
SO_4^{2-}	**0.821**	0.493	-0.063	**0.857**	0.011	0.093	0.216
NO_3^-	**0.768**	0.174	0.107	**0.833**	0.035	0.079	0.114
Cl^-	0.560	0.402	**0.711**	**0.834**	0.045	0.174	-0.242
$HCOO^-$	0.191	**0.860**	0.245	0.011	**0.929**	0.013	0.006
CH_3COO^-	0.197	**0.906**	0.157	0.042	**0.914**	0.167	0.012
NH_4^+	**0.933**	0.195	0.024	**0.865**	0.105	0.134	-0.119
Na^+	0.422	0.474	**0.757**	**0.640**	0.145	0.040	-0.494
K^+	**0.763**	0.379	0.473	0.465	-0.132	**0.721**	-0.128
Ca^{2+}	**0.911**	-0.049	0.364	**0.850**	-0.063	0.005	0.022
Mg^{2+}	**0.823**	0.030	0.530	**0.891**	-0.052	0.185	0.025
% of Variance	40.00	27.04	23.28	41.86	15.46	11.58	10.12
Cumulative %	40.00	67.04	90.32	41.86	57.32	68.90	79.02
Possible source	Combustion fuel, agricultural activities, biomass burning and soil	Photochemical reaction, biomass burning, vegetation and soil	Sea salt	Combustion fuel, sea salt, agricultural activities, and soil	Photochemical reaction, biomass burning, vegetation and soil	Biomass burning	-