CHAPTER 3

RESULTS AND DISSCUSSION

Acid depositions have been monitored for 16 months starting from September 2006 to December 2007 at Mea Hia Research Center, Chiang Mai University, Chiang Mai, Thailand. Wet and dry samples were collected by wet-only collector and four-stage filter pack, respectively. Chemical parameters of the collected samples including EC, pH, major anions (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) and major cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were analysed for wet deposition. Dry deposition samples were analysed for all ion species including NH₄⁺, Ca²⁺, K⁺, Mg²⁺, Na⁺, Cl⁻, NO₃⁻, and SO₄²⁻. The meteorological data of the study site have been collected to evaluate the meteorological condition of the area.

3.1 Meteorological Data of Sampling Site

The meteorological data of sampling site was collected by staff of Mae Hia Research Center Office, Chiang Mai University. The summary of this meteorological data is shown in Table 3.1. Mean temperature during study period was 21.9 °C. The highest temperature was 38.5 °C during day time in late of April, 2007. The lowest temperature was 8.0 °C in the night time in late of December, 2006. The annual mean of percentage humidity (%RH) was 76.2%, whereas 53.5 and 93.3% were minimum and maximum values, respectively. The highest frequency of rainy days within a month was found in September, 2007 with a number of 18 days. The total amount of rainfall during study period was 1217.6 mm. The maximum precipitation amount was 229.2 mm in May, 2007. Average annual rainfall in Chiang Mai was 1,200 mm. In 2006-2007, the total rainfall of Thailand was 4-7% higher than the average value. In Chiang Mai at the same period, the total rainfall was lower than the country average (www.cmmet.tmd.go.th). It was no rain precipitation for 5 months starting from November 2006-March 2007. Noticeably, amount of rain was high in May 2007, which was the beginning of rainy season. Its amount (229.8 mm) was generally above monthly average (121.9 mm). Total amount of precipitation in 2007 throughout Thailand is shown in Figure 3.1 and the meteorological data of the sampling site is illustrated in Table 3.1



Figure 3.1 Total amount of precipitation (mm) in 2007 (www.cmmet.tmd.go. th)

Table 3.1 Meteorological data of sampling site

								_										
						9	73			Months	197							
Meteorological	Condition	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Average
	Contantion	-06	-06	-06	-06	-07	-07	-07	-07	-07	-07	-07	-07	-07	-07	-07	-07	
Humidity	Max daily	98.0	98.4	98.1	95.3	94.1	85.9	74.8	79.0	95.8	95.4	95.2	96.9	97.0	97.0	97.0	95.1	93.3
(%)	Min daily	64.4	62.5	50.3	46.5	40.9	33.7	29.1	38.2	67.0	62.5	65.2	64.5	63.5	62.2	58.9	45.9	53.5
Monthly mean	-5	85.8	- 84.9	77.9	73.2	70.2	59.1	51.5	58.0	84.8	81.7	82.6	84.1	84.8	83.3	81.4	75.9	76.2
Temperature	Max daily	30.2	30.8	30.6	28.6	29.3	31.2	34.9	35.6	- 30.2	31.6	30.1	30.0	29.9	29.2	27.1	28.1	30.5
(°C)	Min daily	22.3	20.8	16.4	13.8	11.7	12.8	15.6	21.2	22.4	23.7	23.9	23.5	23.5	23.3	21.2	18.1	19.6
Monthly mean		25.2	24.0	20.4	17.5	14.9	15.9	19.3	25.6	25.1	26.3	25.6	25.2	24.8	23.3	20.2	16.9	21.9
Total Precipitati	on amount	186.5	95.0	0.0	0.0	0.0	0.0	0.0	11.6	220.8	156.8	76.2	135.7	158 5	C CT	63.7	0.0	1210.0*
Number of preci	nitation	160.5	93.0	0.0	0.0	0.0	0.0	0.0	44.0	229.0	130.8	70.2	133.1	138.5	12.2	03.7	0.0	1219.0
(days)	pration	17	9	0	0	0	0	0	J_5	18	12	11	17	19	9	8	0	125*
																		_
* Tot		n	S	51	Jł	14	15	51	18	J	a	31		38	Jð)	1	IJ

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3.2 Wet Deposition Monitoring

The wet precipitation samples were collected by automatic precipitation collector (wet only collector). EC, pH and ion concentrations were measured by conductivity meter, pH meter and ion chromatography, respectively.

3.2.1 Comparison of precipitation data

The number of rain samples collected at the sampling site by wet only collector during September 2006 to December 2008 was 125 samples, while data recorded by The Mae Hia Research Center Office and Chiang Mai Meteorological Center were 119 and 127 days, respectively. There were no rains for 5 months during the study period. Table 3.2 shows the average of percentage difference data of precipitation days, which was 105.0 % and 98.4 % from Mea Hea Research Center Office data and Chiang Mai Meteorological Center data, respectively. The Mea Hea Research Center Office data recorded precipitation data by rain gauge that was designed as non-cover container. The samples in the rain gauge also exposed directly to sunlight during the day time before next sample collection. So, an absence of sample might be occurred when small precipitation occurred. Which the number of precipitation was lower than the number of samples that collected by wet only collector. In July 2007, this month had precipitation occurred some area and small amount of rain precipitation, so percentage difference of this month was lowest. Accordingly, the number of precipitation of Chiang Mai Meteorological Center higher than the number of samples.

Month	Numbe	r of Rain Precip	itation	% Comp	oleteness
_	a	b	c	a&b	a&c
Sep-06	17 9	18	18	94.4	94.4
Oct-06	9	900	10	100.0	90.0
Nov-06	0		0	. 31	-
Dec-06	0	0	0	- 9	-
Jan-07	0		0	7 / •	-
Feb-07	0	0	0	-	24
Mar-07	0	0,57	0	- 2	85
Apr-07	5	0	4	-	125.0
May-07	18	17	20	105.9	90.0
Jun-07	12	12	11	100.0	109.1
Jul-07	11	10	17*	110.0	64.7
Aug-07	17	16	13 R	106.2	130.8
Sep-07	19	20	17	95.0	111.8
Oct-07	9	9	9	100.0	100.0
Nov-07	8	19818	188	100.0	100.0
Dec-07	C ⁰	v Chiai	ng ⁰ Ma	ai Univ	/ersitv
Total/			-0		
A I Average	125	n (195	1278	5 105.0 F	V 98.4 (

Table 3.2 Comparison of number of rain precipitation (September 2006-December 2007)

a = wet only collector (this work)

b = rain guage Mae Hia Meteorological Center

c = Chiang Mai Meteorological Center

* precipitation < 0.5mm = 5 days

3.2.2 Measurement of Acidity and Alkalinity (pH)

The simply way to determine acid precipitation can be done by measuring pH value of the precipitation, which refers to pH < 5.6. The pH values of all wet samples are shown in Appendix A (measurements results of wet precipitation). The distribution of pH values are shown in Figure 3.2.



Figure 3.2 Frequency distribution of precipitation pH values (n=120)

The sampling at the same study site has been done by Chirasathaworn (2005) in April 2003-March 2004 and Chantara and Chunsuk (2008) in August 2005-July 2006. Most of the pH values presented in this work (~90%) are in a range of 5.5-7.0, which are very well agree with Chirasathaworn's, while those found in the work of Chantara and Chunsuk was only 70% in those range. They also reported that about 29% of the samples had pH values lower than 5.6, which is relatively high ratio in comparison with this work (10%).

Monthly mean pH values together with precipitation amount are shown in Figure 3.3. The precipitation was found to be slightly acid (pH<5.6) in April 2007.

The changing of meteorological condition was affected to sample concentrations. The monthly VWM pH ranged from 4.80 to 6.95. However, the mean value of pH during the study period was 6.18. The lowest detected pH was 4.80.



Figure 3.3 Variation of monthly amount of precipitation and mean values of pH

In dry I period (November 2006 – April 2007), there was almost no precipitation except in April 2007. Figure 3.3 shows the amount of rain precipitation and pH of the samples. Monthly mean of pH values was lowest in April 2007, which also had lowest 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. When it started to rain again in April after long time of dry period, these pollutants were eluted from the atmosphere.

3.2.3 Measurement of Electro Conductivity (EC)

EC values indicate level of ionic contamination in precipitation. High EC value indicates high ionic contamination. EC value of deionized water is normally less than 0.15 mS/m. Number of rain water samples measured for EC were 120. The vwm EC values were 0.62 mS/m. The maximum detected EC value (2.16 mS/cm) was in April 2007 whereas its minimum values (0.43 mS/cm) was in August 2007. Figure 3.4 shows the amount of rain precipitation and the EC values of the samples.



Figure 3.4 Variation of monthly amount of precipitation and mean values of EC

The highest mean EC values was detected in the sample of dry I period (April 2007). It can be from the large amount of pollutants in the atmosphere around the sampling site. When rain started again, these pollutants were scavenged from the atmosphere. Consequently, in the rain itself contains high concentrations of the

pollutants. For wet II period (May - October 2007), the mean EC values were decreased due to high amount of precipitation.

3.3 Measurement of Ion Concentrations in Rainwater Samples

Ionic substances that dissolved in rainwater precipitations play an important role in changing of acidic value of rainwater samples. In this study, two groups of ionic species in the rainwater samples were measured. Anions including HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ and cations including Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ were analyzed by ion chromatograph. Chromatograms of mixed ion standard solution and rainwater sample are shown in Appendix C.

3.3.1 Calibration curve of ion analysis

In each analytical run, 7 concentrations $(0.1 - 4.0 \ \mu g/mL)$ of anions and cations calibration standards were prepared and analyzed by IC. The calibration curve of each ion standard was constructed using concentrations of standard solution versus peak area. Concentration ranges must cover at least 95% of ion concentrations of samples, whereas the regression value was controlled at $r^2 \ge 0.995$. The calibration curves for determination of anions and cations are shown in Figures 3.5-3.6.

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Figure 3.5 Example of calibration curves for determination of anions



Figure 3.6 Example of calibration curves for determination of cations

3.3.2 Accuracy of IC

a) Repeatability

The repeatability is the results of relative standard deviation (%RSD) of measurements repeated by the same analyst on the same instrument within a short time period. Detail of experiment is described in topic 2.9.1. The repeatability of ion chromatograph is shown in Table 3.3.

b) Reproducibility

The reproducibility was checked by injecting a 0.4 ppm mixed standard solution (see detail in topic 2.9.2). The results of reproducibility were estimated by relative standard deviation (%RSD) as shown in Table 3.4.

3.3.3 Limit of detection

The limit of detection (LOD) is the lowest amount of analyte which can be detected with an acceptable statistical significance. According to Taylor (1987), LOD was calculated as three times of standard deviation (SD) of the noise at zero concentration. In this study, LOD was obtained by 5 injections of 0.1 ppm standard solution. Their concentrations were calculated from the calibration curve in ranges of 0.1 to 1.0 ppm for anions and cations. Limit of detection values of all analytes are shown in Table 3.5.

3.3.4 Analytical performance

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The accuracy of chemical analysis was done by analysis of the artificial rainwater provided from the Inter-laboratory comparison project 2006 under the Acid Deposition Monitoring Network in East Asia (EANET) (2006 Round Robin Analysis Survey). Accuracy of the analysis was considered from the results in comparison with prepared values. The artificial rainwater was number 061 (high concentration) and 062 (low concentration), serial number 086. This rainwater was diluted 100 times by deionized water in three replications (a, b and c). They were measured for EC, pH and analysed for ion concentrations by ion chromatography. 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 topic 2.10). The result are shown in Tables 3.6 (high concentration) and Tables 3.7 (low concentration).

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No of injection		~	13	C C	oncentrat	ion (µg/r	nL) 🙎				
	HCOO ⁻	CH ₃ COO ⁻	Cl	NO ₃	PO4 ³⁻	SO_4^{2-}	Na ⁺	$\mathrm{NH_4}^+$	K^+	Ca ²⁺	Mg ²⁺
1	0.391	0.407	0.407	0.413	0.395	0.413	0.410	0.401	0.414	0.414	0.420
2	0.399	0.414	0.408	0.413	0.394	0.418	0.414	0.400	0.421	0.421	0.422
3	0.394	0.410	0.406	0.414	0.392	0.416	0.412	0.403	0.404	0.411	0.419
4	0.402	0.415	0.412	0.416	0.397	0.418	0.414	0.404	0.419	0.422	0.420
5	0.407	0.417	0.420	0.418	0.402	0.415	0.412	0.408	0.420	0.416	0.419
6	0.402	0.412	0.410	0.415	0.401	0.418	0.417	0.400	0.417	0.418	0.419
7	0.416	0.408	0.411	0.413	0.407	0.422	0.416	0.399	0.425	0.420	0.420
Average	0.402	0.412	0.410	0.415	0.398	0.417	0.413	0.402	0.417	0.418	0.420
StandardDeviation (SD)	0.008	0.004	0.005	0.002	0.005	0.003	0.002	0.003	0.007	0.004	0.001
Relative Standard Deviation (%RSD)	1.9	0.9	by .1	0.5	1.4	0.7	0.6	0.8	1.6	1.0	0.3 t
	r	ig	h	t s			es	s e	r	\mathbf{V}	e d

 Table 3.3 Repeatability of ion chromatograph

No of injection		0	V 3		Concentra	ation (µg/	mL)				
	HCOO ⁻	CH ₃ COO ⁻	Cl	NO ₃	PO ₄ ³⁻	SO4 ²⁻	Na ⁺	NH4 ⁺	K ⁺	Ca ²⁺	Mg^{2+}
1	0.402	0.415	0.412	0.416	0.397	0.418	0.414	0.404	0.419	0.422	0.420
2	0.401	0.414	0.414	0.418	0.400	0.416	0.412	0.407	0.420	0.424	0.426
3	3 0.402	0.414	0.416	0.418	0.398	0.417	0.415	0.405	0.417	0.425	0.424
Average	0.402	0.414	0.414	0.417	0.398	# 0.417	0.414	0.405	0.419	0.424	0.423
Standard Deviation (SD)	0.001	0.001	0.002	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.003
Relative Standard Deviation (%RSD)	0.1	0.2	0.5	0.3	0.4	0.2	0.4	0.4	0.4	0.3	0.7
			41	U	NT	VE	R				

Table 3.4 Reproducibility of ion chromatograph

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Table 3.5 Limit of detection	n of IC (Metro	ohm) for each io	n								
No of injection		~ ~	181		oncentrati	ons (µg/n	ıL)				
No. of injection	HCOO ⁻	CH ₃ COO ⁻	Cl	NO ₃	PO4 ³⁻	$\mathrm{SO_4}^{2-}$	Na ⁺	$\mathrm{NH_4}^+$	K ⁺	Ca ²⁺	Mg^{2+}
1	0.077	0.061	0.125	0.051	0.026	0.066	0.187	0.129	0.066	0.098	0.230
2	0.079	0.062	0.122	0.053	0.028	0.058	0.188	0.127	0.073	0.111	0.202
3	0.074	0.064	0.129	0.051	0.027	0.058	0.183	0.126	0.064	0.103	0.204
4	0.073	0.067	0.120	0.055	0.030	0.061	0.191	0.103	0.069	0.099	0.215
5	0.078	0.066	0.113	0.052	0.028	0.063	0.196	0.114	0.073	0.102	0.211
Average	0.076	0.064	0.122	0.053	0.028	0.060	0.189	0.118	0.070	0.104	0.212
Standard Deviation (SD)	0.002	0.003	0.006	0.002	0.002	0.003	0.005	0.011	0.004	0.005	0.011
Limit of Detection (3*SD)	0.007	0.008	0.018	0.006	0.005	0.010	0.015	0.033	0.013	0.016	0.033
Limit of Quantification (10*SD)	0.024	0.026	0.179	0.019	0.016	0.035	0.048	0.112	0.042	0.053	0.110
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Table 3.6 pH, EC and conc	entration	n of ions i	n artifici	al rainwat	er No. 06	1						
				9	19	91						
	pН	EC	0	110	Co	oncentratio	on (µmol/	(L)	82		R_1	R ₂
Sample No. 061	9	mS/m	SO4 ²⁻	NO ₃	Cl	NH4 ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺		
a	4.77	2.91	44.4	35.8	57.0	40.1	6.5	23.7	10.4	37.1	-3.6	0.0
b	4.74	2.92	44.6	35.9	57.1	40.3	6.4	23.8	10.6	37.7	-3.1	0.8
c	4.75	2.93	44.5	35.9	57.0	40.1	6.3	23.7	10.5	37.7	-3.3	0.3
Average conc.	4.76	2.92	44.5	35.9	57.0	40.2	6.4	23.7	10.5	37.5	-3.4	0.2
Prepared conc.	4.72	3.10	45.8	36.6	57.5	44.5	6.9	23.8	11.7	43.9		
% difference	0.8	-5.8	-2.8	-1.9	-0.9	-9.7	-7.2	-0.4	-10.3	-14.6	2	
ลขสา	n	5 L	JK	15	D	B	18	B	18	B	DIP	fIJ.
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		r i	g	h	t s		r	es	e	ľ	v e	C

Table 3.6 pH, EC and concentration of ions in artificial rainwater No. 061

	рН	EC	0		Co	oncentratio	on (µmol	/L)	62	20	R ₁	R ₂
Sample No. 062		mS/m	SO4 ²⁻	NO ₃ -	Cl	NH4 ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺		-
a	5.28	1.17	16.4	15.2	24.6	19.1	4.5	10.8	3.6	12.0	-2.1	-1.9
b	5.35	1.19	16.3	15.1	24.7	19.3	4.4	10.6	3.7	12.2	-2.4	-4.0
c	5.30	1.18	16.2	15.1	24.5	19.1	4.4	10.8	3.6	12.2	-1.8	-2.8
Average conc.	5.31	1.18	16.3	15.1	24.6	19.2	4.5	10.7	3.6	12.1	-2.1	-3.0
Prepared conc.	5.15	1.21	16.9	15.0	24.5	20.5	4.9	9.3	3.5	15.1		
% difference	3.1	-2.5	-3.6	0.7	0.4	-6.3	-8.2	15.0	2.7	-19.8	วให	1 1
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		r i	g	h	t s			es	e		ve	d

 Table 3.7 pH, EC and concentration of ions in artificial rainwater No. 062

From Tables 3.6 and 3.7, R_1 and R_2 values are in acceptable ranges and percentage of difference between analytical and prepared values of each parameter was not over ±15%. It can be deduced that the analytical method was qualified.

3.3.5 Ion Composition in Rainwater Samples

The concentrations of ions contained in rainwater samples were found in different range. The variations of ion concentrations were affected by many factors. The results were concluded from 16 months which was unprecipitated 6 months (November 2006 – March 2007 and October 2007). An example of analysis chromatogram of wet sample for anion and cation are shown in appendix C.

Monthly vwm concentrations of the major chemical components are illustrated in Table 3.9. Monthly average anion and cation concentrations together with precipitation amount are illustrated in Figures 3.7 and 3.8, respectively. It was found that most of ion concentrations were high in the dry I period due to low amount of rain precipitation and long period of non-precipitation for 5 months. Most of the lowest concentrations of anions and cations were found in June to July 2007 (Wet II period).

In order to compare seasonal variation of wet deposition of this study site, the data in this study was compared with previous studies (Chirarathaworn 2005; Chunsuk 2007). Due to different sampling period in each study, the data of this study was selected in the same sampling range of the pervious studies and re-calculated (Table 3.8). It was found that the vwm of all ion concentrations during 16 months of this study (September 2006 - December 2007) were higher than those of Chirarathaworn's (January 2004 - December 2004) and Chunsuk's (July 2005 -

August 2007). All ion concentrations of this study² were higher than Chunsuk's. The same trend was found when compare this study³ with Chiratathaworn's except for SO₄², which its concentrations were lower than in this study³ (Table 3.8). It suggested that contribution could also be from the tourist activities. The Royal Flora Ratchaphruek which was held in November 2006, to January 2007, at Mea Hia research center that drew 3.8 million visitors came to visit Chiang Mai. There was a lot of transportation and probably increasing of exhaust gas concentration. The highest concentrations were detected in March, 2007. Biomass burning in agriculture area and communities as well as forest fire were assumed to be the main sources of nitric acid in this period. In addition, frequency of forest fire was high between 1- 19 March, 2007. Chiang Mai-Lamphun basin is surrounded by mountains. In dry season, air pressure is high and inversion occurs. Under this condition, pollutants produced in the area are trapped in the ambient air and cause serious air pollution.

The relative of percentages of caions and anions were NH_4^+ (23%) > SO_4^{2-} (17%) > Ca^{2+} (16%) > NO_3^- (11%) > $Mg^{2+}(8\%)$ > CI^- (7%) > CH_3COO^- (5%) > $Na^+(5\%)$ > $HCOO^-$ (4%) > K^+ (3%) > H^+ (2%) > $PO_4^{-3-}(0.4\%)$ as shown in Figure 3.9. The highest percentage of total cations and anions are NH_4^+ and SO_4^{-2-} , respectively. Ca^{2+} was the second highest of cations and and its value is very closed to SO_4^{-2-} . The ratio between total cations and total anions is 51:49 (Figure 3.10).

hts

D.C	Sampling	Duration	Precipitations		Volu	me weig	ht mear	n concent	rations	(µeq/L))
References	0.0	(months)	9 (mm)	Cl	NO ₃	SO4 ²⁻	Na ⁺	$\mathrm{NH_4}^+$	\mathbf{K}^+	Ca ²⁺	Mg ²⁺
Chirasathaworn, 2005	Jan 04 - Dec04	12	1150.4	3.8	6.4	15.6	3.1	16.1	1.5	9.7	3.7
Chansuk, 2007	Aug 05 - Jul06	12	1743.6	3.5	6.8	9.2	1.6	17.1	1.3	8.9	2.3
This study ¹	Sep 06 - Dec 07	16, , , ,	1219.0	5.3	8.1	11.9	3.6	17.3	1.6	12.9	5.8
This study ²	Sep 06 - Aug 07	12	924.0	6.5	9.0	10.4	3.7	19.5	2.7	14.6	4.1
This study ³	Jan 07 - Dec07	12	937.5	6.2	7.9	10.9	3.0	18.7	2.9	16.8	2.7

Table 3.8 Comparison of ion composition of rainwater samples in different year study

¹ The same sampling period as presented in this study.

² Data selected from September 2006 – August 2007 (12 months) to be compared with Chansuk, 2007.

³ Data selected from January 2007 – December 2007 (12 months) to be compared with Chirasathaworn, 2007.

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Month	Precipitations					Volume we	eighted m	ean concer	ntrations ((µeq/L)					
	(mm)	SO_4^{2-}	NO ₃ -	Cl	HCOO ⁻	CH ₃ COO ⁻	PO ₄ ⁻³⁻	$\mathrm{NH_4}^+$	Na ⁺	K^+	Ca ²⁺	Mg^{2+}	$\mathrm{H}^{\!+}$	pН	EC
Sep-06	186.5	11.62	5.97	3.03	3.89	2.15	0.93	10.63	3.05	1.45	13.75	1.70	1.34	5.87	0.59
Oct-06	95.0	12.08	13.92	4.43	1.66	4.14	0.57	15.19	11.66	0.48	0.11	12.73	1.25	5.90	0.54
Nov-06	0.0	9	-	-	\sim				>	-	- 1				
Dec-06	0.0	-	-	-	-	-	-	-	-	-	-	-	~ /		
Jan-07	0.0	-	-	-		<u>, , , , , , , , , , , , , , , , , , , </u>	100	-	-	-	-	-	-		
Feb-07	0.0	5 -	-	-		- 6			-	-	-	-5			
Mar-07	0.0	5	-	-			3	<u> </u>	-	-	-	13	N.S		
Apr-07	44.6	18.10	25.57	6.98	23.00	39.78	0.34	84.07	2.66	4.85	20.30	6.25	9.25	5.03	2.16
May-07	229.8	12.90	8.91	7.04	2.50	4.57	0.57	15.66	2.95	1.97	14.64	4.01	0.85	6.07	0.59
Jun-07	156.8	7.44	5.92	6.68	1.84	1.68	0.00	14.78	1.27	3.39	13.32	1.23	0.98	6.01	0.47
Jul-07	76.15	9.04	4.05	6.11	2.39	0.71	0.07	13.29	3.61	7.76	19.29	4.04	0.42	6.38	0.44
Aug-07	135.7	6.78	6.44	6.69	0.71	0.80	0.02	16.92	2.67	1.19	21.78	1.05	0.38	6.42	0.43
Sep-07	158.5	13.84	6.50	4.16	0.05	0.67 -	0.00	12.91	5.03	2.25	17.05	1.88	0.46	6.33	0.57
Oct-07	72.2	16.80	6.79	2.98	0.00	0.77	0.00	14.09	2.75	2.83	12.16	0.56	0.55	6.26	0.63
Nov-07	63.7	20.04	10.46	4.01	0.00	6.44	0.00	25.64	1.74	2.77	11.14	2.08	1.47	5.83	0.86
Dec-07	0.0		5-			8	-	-					-1		
Total	1219.0	128.64	94.53	52.11	36.04	61.71	2.50	223.18	37.39	28.94	143.54	35.53	16.95	60.10	7.28
Average	76.2	11.9	- 8.1	5.3	2.6	3.7	0.3	17.3	3.6	1.6	12.9	5.8	1.2	5.93	0.62
%		16.0	10.9	7.1	3.5	5.0	0.4	23.3	4.8	2.2	17.4	7.8	1.6	3	ч <u>у</u>
A		r		g	h	ts	5	r	e	S	e	r	V	e	d

Table 3.9 Monthly volume weight means in μ eq/L of the major chemical composition in rainwater sample



Figure 3.8 Monthly average variability of cation concentrations on unit of µeq/L

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Mg2+

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3.4 Deposition amount

3.4.1 Wet deposition

The deposition amount is the value of ion concentration deposited per area unit. In this research, the deposition amount per square meter (m^2) was calculated. The deposition amounts of wet samples are shown in Table 3.10. The major cation of wet deposition was NH₄⁺ (161.91 ueq/m²), while SO₄²⁻ was the major anion (124.98 ueq/m²). Percentage of NH₄⁺ and SO₄²⁻ were 20.5 % and 15.8 % of total wet deposition, respectively as shown in Figure 3.11. 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 3.10 Monthly wet deposition amount in this study period

				919	1916	94	Ø	21				
Month					Depo	sition ar	nount (ueo	(m^2)	4	00		
	SO ₄ ²⁻	NO ₃	Cl	HCOO.	CH ₃ COO ⁻	PO ₄ ³⁻	$\mathbf{NH_4}^+$	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	\mathbf{H}^+
Sep-06	117.30	61.13	32.33	41.74	22.97	9.24	106.74	32.14	14.99	35.54	195.79	14.28
Oct-06	126.91	147.45	46.17	17.77	44.30	6.07	159.16	125.05	4.98	1.12	134.56	13.33
Nov-06	ST25	-	-			6-	-	-	-	-351	26-	-
Dec-06	305		-				-	-	-	22	5	-
Jan-07	-	-	-	-	-	Ξ.	->	-	-	-	-//	-
Feb-07	2		-	-		- 2	- /	-	_	3		-
Mar-07		× -	-	-	- 4	-7		<u> </u>	-	0	_	-
Apr-07	156.15	223.31	60.35	201.40	348.00	2.27	732.84	22.80	41.60	172.27	53.79	82.97
May-07	165.27	113.87	89.91	32.94	59.79	6.33	204.90	36.93	24.52	180.91	48.88	12.08
Jun-07	98.44	79.04	87.39	36.72	16.17	0.18	194.99	16.87	44.04	177.10	16.68	11.50
Jul-07	56.44	24.88	38.31	15.19	4.41	0.47	82.14	22.95	48.08	119.61	24.92	2.64
Aug-07	51.83	49.00	50.97	5.69	6.21	0.17	128.93	20.04	8.99	167.50	7.88	2.92
Sep-07	116.19	54.50	34.23	0.37	5.65	0.00	105.21	43.63	19.04	146.12	15.96	4.17
Oct-07	130.02	51.23	20.57	0.00	6.04	0.00	104.63	18.47	20.16	87.84	3.74	4.29
Nov-07	139.96	72.48	28.20	0.00	43.21	0.00	178.34	12.31	19.02	80.14	14.76	11.08
Dec-07	rig	nt ·	-	DY		ang	<u>5 IV</u>				ersi	IUY
Total			.2	h	t.s		r, e	S	e			
deposition	124.98	86.37	65.73	24.00	32.97	0.76	161.91	45.38	29.96	160.15	49.09	9.94
Percent of deposition(%)	15.8	10.9	8.3	3.0	4.2	0.1	20.5	5.7	3.8	20.2	6.2	1.3

3.5 Comprehensive analysis for wet deposition data

3.5.1 Data screening

Comprehensive analysis such as neutralization factor (NF), sea salt fraction (SSF) or marine contribution, principle component analysis and Pearson correlation were calculated. In order to get high precision and correct data, it is necessary to do quality control. Data quality of rainwater samples was checked by ionic balance (R_1) and conductivity balance (R_2). The data was rejected if it was not met the quality criteria (see more detail in topics 2.10 and 2.11). 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).

In wet-only samples, about 42% of R_1 and 73% of R_2 were accepted, while 36% of both R_1 and R_2 were accepted tube used for statistic analysis (Table 3.11). Ion and conductivity balances are shown in Figures 3.10, which are R_1 distribution values higher than R_2 .

Table 3.11 Ion balance (R_1) and conductivity agreement check (R_2)

	Sample (N)	R ₁ (N)	R_1 (AA)	%	R_2 (N)	R_2 (AA)	%	$R_1\&R_2$ (N)	$R_1\&R_2$ (AA)	%
a 2	120	120	50	42	120	88	73	120	43	36
Со	Sample (N	I): Num	ber of sa	mples	Chi	iang	Μ	lai L	Iniv	ersity

 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

- R₂ (N) : Number of samples measured and calculated conductivity agreement (R₂)
- 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)



(b)



Figure 3.12 Values of R_1 and R_2 of wet-only samples (a) Distribution of R_1 (ion balance), (b) R_2 (conductivity balance) and (c) R_1 and R_2 relation

Tables 3.11 illustrates ion balance and conductivity agreement check. In 120 wet-only samples, about 42% of R_1 and 73% of R_2 were accepted, while 36% of both R_1 and R_2 were accepted tube used for statistic analysis. Ion and conductivity balances are shown in Figure 3.12, which are R_1 distribution values higher than R_2 .

3.5.2 Acid neutralization

In case that all the nss-SO₄²⁻ and NO₃⁻ existed in the form of free acid forms, the summation of those should equal to H⁺ (Hu *et al.*, 2003). Concentrations of nss-SO₄²⁻ and NO₃⁻ were 11.90 and 8.10 μ eq/L, respectively. Therefore, the summation was 20.00 μ eq/L. From this figure, the pH should be 5.93, but from the measurement it was 6.18 which is lower by 0.25 pH. It indicated that the rainwater precipitation had some neutralization. From previous studies (Saxena *et al.*, 1996; Das *et al.*, 2005), NH₄⁺, Ca²⁺, K⁺ and Mg²⁺ have been used to validate by calculating neutralization factor (see details in topic 1.8.1). Neutralization factors for NH₄⁺, Ca²⁺ and Mg²⁺ are shown in Tables 3.12.

	$\mathrm{NH_4}^+$	Ca ²⁺	Mg^{2+}	K^+
NF	0.86	0.64	0.29	0.10

Table3.12 Neutralization factors of Ca²⁺, NH₄⁺, Mg²⁺ and K⁺

In the order of NF was $NH_4^+ > Ca^{2+} > Mg^{2+} > K^+$. This feature suggests that in rainwater 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 Mg^{2+} and K^+ that indicating the influence of soil resuspension.

From the summation of the nss-SO₄²⁻and NO₃⁻ from H⁺, it was indicated that acid neutralization was occurred (Hu *et al.*, 2003). Normally, neutralization is frequently reported and attributed to NH₄⁺ and Ca²⁺ (Vong, 1990). Consequently, it was expected that the summation of concentrations of H⁺, NH₄⁺ and Ca²⁺ correlated with summation of concentrations of nss-SO₄²⁻ and NO₃⁻ in the event that the acidity of the rainwater precipitation is mainly neutralized by NH₄⁺ and Ca²⁺. This hypothesis was confirmed by the scatter plots between those two summation values Figures 3.13.

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Figure 3.13 Correlation of $([H^+]+[NH_4^+]+[Ca^{2+}])$ and $(nss-[SO_4^{2-}]+[NO_3^-])$ (N=44)

3.5.3 Marine contribution

In order to estimate marine and non-marine contributions to the rainwater, different ratios, enrichment factors and sea salt fractions have been calculated using Na⁺ as reference element assuming that all Na⁺ are of marine origin (see more details in topic 1.8.2). The various ratios, enrichment factors, sea salt fractions and non-sea salt fractions for rainwater samples are concluded in Tables 3.13.

	Cl	SO4 ²⁻	Mg^{2+}	K^+	Ca ²⁺
Sea water ratio ^a	1.17	0.06	0.11	0.02	0.02
Rain water ratio ^a	1.46	3.29	1.59	0.53	3.55
EF ^a	9.25	54.58	13.97	24.46	162.12
SSF(%)	79.74	1.83	7.16	4.09	0.62
NSSF(%)	20.26	98.17	92.84	95.91	99.38

Table 3.13 Rainwater samples components with respect to sea (N=44)

^a With respect to Na; EF = enrichment factor; NSSF = non-sea salt fraction; SSF = sea salt fraction.

The recommended seawater ratio of Cl⁻/Na⁺ is 1.17, but in this study the ratio of Cl⁻/Na⁺ is 1.25 (Table 3.15). Consequently, enrichment factor values of Cl⁻ were slightly higher than 1, while enrichment factor from those of other ions were much greater than 1 for rainwater samples. This elevated ratio may be due to contribution of Cl⁻ from marine origin and partly from anthropogenic factor, whilst Ca²⁺, K⁺, Mg²⁺ and SO₄²⁻ are mainly from anthropogenic activities. Sea salt fraction values provides information of ion ratio from marine source. Table 3.12 reveals that most of ions fractions of Ca²⁺, K⁺, SO₄²⁻ and Mg²⁺ and a part of Cl⁻ appear to be from non-marine origin in rainwater samples.

3.5.4 Ion pair correlations

The daily rain precipitation amount and deposition of each ion were log-transformed to achieve a multivariate normal distribution. Pearson correlations between various ionic species in the samples were calculated in order to identify their relationship as shown in table 3.14. Pearson correlation coefficients were calculated using SPSS for Windows (version 15) software that is significant at the 0.01 level. The correlations of log-transfer dataset showed strong correlation between NH₄⁺ and NO₃⁻ (0.898), NH₄⁺ and SO₄²⁻ (r = 0.893), H⁺ and SO₄²⁻ (r = 0.860). It suggested that the main acidity of rainwater precipitation in this region was H_2SO_4 , which 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).

 Table 3.14 Correlations of log-transformed datasets chemical species for rainwater

 samples

Ions	SO4 ²⁻	NO ₃ -	Cl	HCOO.	CH ₃ COO ⁻	NH4 ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	H^{+}
SO4 ²⁻	1		11				7				
NO ₃ -	0.900	1	(3)		3						
SCI-2	0.671	0.713	1	6	(n)			5			
HCOO ⁻	0.844	0.631	0.637		Y						
CH ₃ COO ⁻	0.645	0.703	0.643	0.465	1))			4		
$\mathrm{NH_4}^+$	0.893	0.898	0.727	0.827	0.708	1			<u> </u>		
Na ⁺	0.725	0.728	0.659	0.620	0.547	0.669	1				
\mathbf{K}^{+}	0.734	0.693	0.740	0.833	0.596	0.731	0.752	1			
Ca ²⁺	0.620	0.655	0.734	0.469	0.467	0.620	0.737	0.670	1		
Mg^{2+}	0.846	0.847	0.700	0.508	-0.652	0.796	0.696	0.830	0.505	1	
H^{+}	0.860	0.789	0.546	0.758	0.779	0.832	0.586	0.665	0.480	0.718	1

3.5.5 Source analysis of major ion composition

In order to find possible association sources of ions in rainwater precipitations, factor analysis was carried out in order to determine the factors underlying the intercorrelations between the measured species. The method used was principle component analysis (PCA). A varimax rotation with Kaiser Normalization of Principle Components Analysis by SPSS program (SPSS for Windows version 15) was applied and the results are shown in Tables 3.15.

	Factor	loading
	1	2
$\log(\mathrm{SO_4^{2^-}})$	0.895	0.344
log(NO ₃ ⁻)	0.833	0.529
log(Cl ⁻)	0.518	0.795
log(HCOO ⁻)	0.762	0.489
log(CH ₃ COO ⁻)	0.257	0.735
log(NH ₄ ⁺)	0.825	0.410
log(Na ⁺)	0.558	0.734
$\log(K^{+})$	0.616	0.736
log(Ca ²⁺)	0.070	0.920
log(Mg ²⁺)	0.908	0.041
Eigenvalue	7.304	1.213
% of Variance	73.039	R 12.134
% of cumulative	73.039	85.173
Possible source	Fuel combustion and	Open burning and Soil
ลิขสิทธิมห	Agricultural activities	resuspension
$\frac{\text{Note}}{the others, but from cal-$	led in this data analysis due to culation of pH values.	its values were not from IC analysis as
All rig	hts ro	eserved

Table 3.15 Factor analysis of chemical composition in wet deposition (n=44)

The factor analysis identified that there was three factors contributed about 92 % of the variance to the log-transformed data set of wet percipitation. Given observation that only factor loadings higher than 0.5 are deem to be statistically

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significant (Ayer and Yeung, 1996 and Ungvari *et al.*, 2007). For factor 1, it provided high loading on the $SO_4^{2^-}$, NO_3^- , NH_4^+ , Mg^{2^+} and $HCOO^-$. It associated reasonably with fuel combustion process ($SO_4^{2^-}$ and NO_3^-) and neutralization components (NH_4^+ and Mg^{2^+}), which indicated that they come from agricultural area. The variables of the factor 2 were Cl⁻, Na^+ , Ca^{2^+} , K^+ and CH_3COO^- , hereafter referred to as the marine source (Cl⁻, Na^+ and K^+) (Hu *et al.*, 2003) and soil resuspend for Ca^{2^+} (Saxena *et al.*, 1996).

3.6 Dry Deposition Monitoring

Dry deposition samples were collected by 4-stages filter pack to determine level of acid gases and particles in atmosphere. Sampling was carried out at the same place and same period with wet deposition. All filters were extracted and analysed for determination of anions and cations by IC. Each filter was used to collect and analyse the different parameters. The first stage filter (PTFE; F0) was analysed for Cl⁻, NO₃⁻, $SO_4^{2^-}$, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺. The second stage filter (Polyamide; F1) was analysed for Cl⁻, NO₃⁻, $SO_4^{2^-}$ and NH₄⁺. The alkali impregnated filter (F2) in third stage was analysed for Cl⁻ and $SO_4^{2^-}$. The acid impregnate filter (F3) was analysed for only NH₄⁺. The examples of analyzed chromatogram of each filter are shown in Appendix C.

3.6.1 Analytical performance

The accuracy of chemical analysis was done by analysis of reference material (filter samples) provided from the Inter-laboratory comparison project 2006 under the Acid Deposition Monitoring Network in East Asia (EANET). Accuracy of the analysis was considered from the results in comparison with prepared values of the

reference material, which are high concentration (No.061d-1 and No.061d-2), and low concentration (No.061d-1 and No.061d-2). They were extracted by EANET method as described in Topic 2.12. The results are shown in Table 3.16.

	V	Low	concen	tration	High concentration			
	7	No.061d-1		No.061a-2	No.06	2d-1	No.062a-2	
5	_	SO4 ²⁻	Cl	NH4 ⁺	SO4 ²⁻	Cľ	NH4 ⁺	
M _{sol, Blank}	4	1.65	0.00	0.10	1.65	0.00	0.10	
324	а	37.17	5.22	7.74	131.65	39.39	62.40	
M _{sol} , Sample	b	36.39	4.99	7.40	132.23	39.17	64.12	
	c	37.05	5.44	7.40	130.23	38.60	62.24	
Average Conc.		36.87	5.22	7.51	131.37	39.05	62.92	
Prepare Conc.		40.00	3.50	6.50	140.00	40.00	50.00	
% Difference		-7.8	49.1	15.5	-6.1	-2.3	25.8	

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Table 3.16 Concentrations of ions in references filter samples based on unit μ mol/l

3.6.2 Acidic Gas Concentrations

The analysis results were used to determine the concentration of air pollutants namely sulfur dioxide (SO₂), nitric acid (HNO₃), hydrogen chloride (HCl) and ammonia(NH₃). The concentrations of pollutant gases are shown in Table 3.17. Concentrations of SO₂, HNO₃, HCl and NH₃ were in ranges of 2.95 - 26.37, 2.74 -53.04, 3.16-17.88, and 37.51 - 600.60 nmol/m³, respectively.

-			Sa	ample Concentra	ation (nmol/n	n ³)
	Month	Air Volume Correction(m ³)	SO ₂	HNO ₃	нсі	NH ₃
-	Sep-06	13.54	5.63	3.25	5.13	74.67
	Oct-06	13.17	18.25	2.74*	9.40	113.85
	Nov-06	13.25	2.72*	10.96	6.56	149.36
	Dec-06	13.78	18.28	24.01	9.07	142.60
	Jan-07	13.94	13.34	26.15	9.66	118.26
	Feb-07	13.72	17.59	47.84	16.33	254.41
	Mar-07	13.28	21.21	53.04**	17.03	600.60**
	Apr-07	13.91	26.37**	31.44	12.95	452.55
	May-07	13.61	2.95	8.74	8.73	133.76
	Jun-07	13.91	6.88	5.67	5.22	87.34
	Jul-07	14.60	7.38	6.54	5.98	66.57
	Aug-07	14.41	3.38	4.25	3.16*	56.65*
ลิข	Sep-07	S 14.03	13.88	7.63	7.52	115.53
	Oct-07	13.85	14.95	13.89	17.88**	102.24
CO	Nov-07	14.86	11.31	18 _{9.33}	5.97	e _{126.79}
A	Dec-07	13.30	t 7.19	26.33 S	11.78	202.57
-	Average	13.82	11.96	17.61	9.52	174.86

 Table 3.17 Monthly concentrations of pollutants during study period (*min**max)



Figure 3.15 Relative of percentage acidic gas concentration The most of highest vwm concentration of pollutants was in dry I period. Due to there was no rain during December 2006 to March 2007 no rain occurred therefore, high accumulation of acidic gases occured. The highest concentration of SO₂ (g) was detected in April 2007, which was in the dry I period. The main source of SO₂ was emitted directly from fossil fuel burning and internal combustion. The other contribution could also be from the tourist activities. Royal Flora Ratchaphruek which was held in November 2006, to January 2007, at Mea Hia research center that drew 3.8 million visitors came to visit Chiang Mai. There was a lot of transportation and probably increasing of exhaust gas concentration including SO₂. The highest concentrations of HNO₃, HCl, and NH₃ were detected in March, 2007. Biomass burning in agriculture area and communities as well as forest fire were assumed to be the main sources of nitric acid in this period. In addition, frequency of forest fire was high between 1- 19 March, 2007. Chiang Mai-Lamphun basin is surrounded by mountains. In dry season, air pressure is high and inversion occurs. Under this condition, pollutants produced in the area are trapped in the ambient air and cause serious air pollution. The main source of HCl was from sea salt which depend on distance of the land far from the sea. The main input of NH₃ to atmosphere was the fertilizer application and nitrification process. The high level of NH₃ was due to fertilizer used to improve the quality of soil for next agriculture period in rainy season. However, the NH₃ (g) in other months were also found, but its concentration was lower than in dry season because the wash out process caused by rain.

Data comparison of this study with the pervious one is shown in Table 3.18. It was found that most of gas concentrations of this year (2006-2007) were higher than the year before. This is probably due to the Royal Flora Ratchaphruek (November 2006 – January 2007) and smog episode (February – March 2007), which were the main contributors of gas concentrations found in the dry deposition.

The relative percentages of total acidic gases based on unit of nmol/m³ were NH₃ (81%) > HNO₃ (8%) > SO₂ (6%) > HCl (4%) that shown in Figure 3.15.

99

sampli	ng period				
	NHERD	Gas c	oncentrat	ion (nmo	l/m^3)
Periods	Source of data –	SO ₂	HNO3	HCl	NH ₃
Nov 05 – Apr 06	Acid Deposition Report, 2006	10.65	5.28	16.87	153.41
Nov 06 – Apr 07	This study	15.23	27.46	11.34	229.85

Table 3.18 Comparison of gas concentrations from the same study site in different

3.7 Particle ion concentrations

The particle ions in the atmosphere were also collected by the 4-stage filter pack at the same time with gas collection. Concentration of acid particles was obtained by analysis of extracted samples using ion chromatography. The results of particles in atmosphere during study period are shown in Table 3.19.

The variation of monthly mean concentration of ions in particles is depicted in Figure 3.16. The concentrations of ions in particles were found in range of SO_4^{2-} (3.04 - 67.69 nmol/m³), NO₃⁻ (1.90 - 38.16 nmol/m³), Cl⁻ (0.05 - 11.78 nmol/m³), NH₄⁺ (3.13 - 133.22 nmol/m³), Na⁺ (N.D. - 81.16 nmol/m³), K⁺(3.13 -133.22 nmol/m³), Mg²⁺ (N.D. - 16.83 nmol/m³) and Ca²⁺ (0.87 -25.78 nmol/m³), respectively. Most of high particle concentrations was found in dry I period, while the concentrations of both SO_4^{2-} and NH₄⁺ were the highest in wet II period (October 2007). The main source of SO_4^{2-} and NH₄⁺ can be come from the combustion fuel and using of fertilizer in agriculture activity. NO₃⁻ concentrations were high in dry season and low in wet season. Therefore, the sources of NO₃⁻ could be the same as wet deposition.

	Air				Particle(n	mol/m ³)			
Month	Volume Correction	SO42-	NO ₃ -	CI	NH4 ⁺	Na^+	K^+	Mg^{2+}	Ca ²⁺
Sep-06	13.54	15.86	3.98	0.45	28.20	3.78	5.58	0.06	11.15
Oct-06	13.17	18.69	0.49	0.44	47.38	18.01	4.50	4.28	4.55
Nov-06	13.25	46.24	6.47	9.16	67.84	0.24	10.27	15.66	0.87
Dec-06	13.78	58.92	7.77	0.05	96.87	2.87	14.33	16.83	1.94
Jan-07	13.94	42.85	12.46	1.79	36.60	9.55	18.67	1.97	14.09
Feb-07	13.72	40.15	14.47	1.01	80.73	7.48	37.19	2.71	21.04
Mar-07	13.28	43.16	38.16	2.55	62.97	11.78	55.29	3.94	17.20
Apr-07	13.91	12.03	7.78	1.20	21.34	10.41	5.72	2.49	17.66
May-07	13.61	21.23	7.74	4.17	28.10	8.98	7.78	3.78	25.78
Jun-07	13.91	6.06	5.40	11.78	4.50	29.13	8.08	10.42	9.46
Jul-07	14.41	4.49	5.86	0.73	3.13	4.81	2.01	0.99	11.11
Aug-07	13.78	58.92	7.77	0.05	96.87	2.87	14.33	16.83	1.94
Sep-07	14.03	3.04	1.90	1.93	5.24	6.18	1.42	0.00	5.10
Oct-07	13.85	67.69	2.30	0.53	133.22	7.19	7.66	1.42	7.61
Nov-07	14.86	32.10	7.19	-7.77	52.63	5.66	9.57	0.41	9.01
Dec-07	13.30	44.33	9.55	0.82	55.62	9.17	20.06	3.27	15.90
Average	13.77	32.24	8.71	2.78	51.33	8.63	13.91	5.32	10.90

Table 3.19 Monthly concentrations of particle ions collected by 4-stage filter pack

Most of the Cl⁻ level contaminated in atmosphere was low. The detected Cl⁻ concentration was the highest in June 2007. Variation of monthly concentration of Cl⁻ was same as Na⁺, which was come from marine sources. However, the sampling site in Chiang Mai might have less effect due to far distance from sea (~700 km). Others reasons would be affected from biomass burning in agricultural area from clearing of the land after harvest and forest fire (Andreae *et al.*, 1998), which effected K⁺

concentration. The concentration of Mg^{2+} was highest in December 2006 and August 2007. However, the highest seasonal weight mean concentration was also found in dry I period. The main pollutant input was assumed from dust and agricultural activities. The seasonal weight mean concentration of Ca^{2+} was the highest in dry I and early of wet II period and decrease in wet II and dry II period. The main source of Ca^{2+} was assumed from soil dust. Moreover, another important source might be from the same source as Mg^{2+} , which was added by the Ca^{2+} released from cement used in new By-Pass road construction project in Chiang Mai.

The order equivalent concentration of particle ions was NH_4^+ (33%) > SO_4^{2-} (22%) > K⁺ (14%) >Ca²⁺ (8%) and NO_3^- (8%) > Na⁺ (7%) > Mg²⁺ (4%) and Cl⁻ (4%). The highest percentages of cations and anions were NH_4^+ and SO_4^{2-} , respectively. They are dominant particle ions for cations and anions.





Figure 3.16 Monthly average variability of particles ion, (A) anion concentrations and (B) cation concentrations



Figure 3.17 Relative percentages of caions and anions based on unit of nmol/m³

3.8 Deposition amount

3.8.1 Dry deposition

The concentrations of pollutant in atmosphere collected by four-stage filter pack was reported in concentration unit per volume of air sample (nmol/m³). Its deposition amount can be calculated by multiply with the deposition velocity factor (V_d). Sarawut (2004) calculated the deposition velocity (V_d) of Mae Moh District, Lampang Province and found that the velocity was 0.53 cm/s. Therefore, this V_d factor was applied to calculate the deposition amount of dry samples in this study. The dry deposition amount in each month of study period is shown in Table 3.20. The highest dry deposition in gas form was NH₃ with a number of 27.33 x10⁻²µg/m² (54.81% of total dry deposition in gas form). NH₃ contained in air samples was assumed to be from animal waste and fertilized soils. NH₃ and the changing of nitrogen compound in nature by nitrification process. However, dry deposition in particle form was SO₄²⁻ with a value of 26.56 µg/m² (47.13% of total dry deposition in particle form). SO₄²⁻ particle was emitted from fuel burning in industrial processes. The comparison chart of acid pollutants in gas and particle form are shown in Figures

3.16 and 3.17. **adans university** Copyright[©] by Chiang Mai University All rights reserved

Table 3.20 Monthly dry deposition amount in study period

					318	219	66	7	0				
		Deposition Amount (x10 ⁻² µg/m ² s)											
			Gas	5			Particle						
	Month	SO ₂	HNO ₃	HCl	NH ₃	SO ₄ ²⁻	NO ₃	Cľ	$\mathbf{NH_4}^+$	Na^+	K ⁺	Mg ²⁺	Ca ²⁺
	Sep-06	0.29	0.11	0.10	0.71	0.81	0.13	0.01	0.27	0.05	0.12	0.00	0.24
	Oct-06	0.93	0.09	0.18	1.09	0.95	0.02	0.01	0.45	0.22	0.09	0.06	0.10
	Nov-06	0.14	0.36	0.12	1.43	2.35	0.21	0.17	0.65	0.00	0.21	0.20	0.02
	Dec-06	0.93	0.79	0.17	1.36	3.00	0.26	0.00	0.93	0.04	0.30	0.22	0.04
	Jan-07	0.68	0.86	0.18	1.13	2.18	0.41	0.03	0.35	0.12	0.39	0.03	0.30
	Feb-07	0.90	1.57	0.31	2.43	2.04	0.48	0.02	0.77	0.09	0.77	0.03	0.45
	Mar-07	1.08	1.74	0.32	5.74	2.20	1.25	0.05	0.60	0.14	1.14	0.05	0.37
	Apr-07	1.34	1.03	0.24	4.33	0.61	0.26	0.02	0.20	0.13	0.12	0.03	0.38
	May-07	0.15	0.29	0.16	1.28	1.08	0.25	0.08	0.27	0.11	0.16	0.05	0.55
	Jun-07	0.35	0.19	0.10	0.84	0.31	0.18	0.22	0.04	0.35	0.17	0.13	0.20
	Jul-07	0.29	0.19	0.11	0.86	0.23	0.19	0.01	0.03	0.06	0.04	0.01	0.24
	Aug-07	0.17	0.14	0.06	0.54	3.00	0.26	0.00	0.93	0.04	0.30	0.22	0.04
a c	Sep-07	0.71	0.25	0.14	1.10	0.15	0.06	0.04	0.05	0.08	0.03	0.00	0.11
	Oct-07	0.76	0.46	0.34	0.98	3.45	0.08	0.01	1.27	0.09	0.16	0.02	0.16
	Nov-07	0.58	0.31	0.11	1.21	1.63	0.24	0.15	0.50	0.07	0.20	0.01	0.19
Α	Dec-07	0.37	0.87	0.22	1.94	2.26	0.31	0.02	0.53	0.11	0.41	0.04	0.34
	Total		0								_		
	deposition	10.14	9.35	3.04	27.33	26.56	6.12	1.60	7.91	2.09	6.87	1.24	3.95
	Percent of												
	Deposition (%)	20.34	18.74	6.11	54.81	47.13	10.87	2.84	14.05	3.72	12.19	2.19	7.01

3.9 Comprehensive analysis for dry deposition data

3.9.1 Ion pair correlations

The relatively of log-transformed dataset between the various ionic species in particles. Pearson correlation (*r*) was carried out on dry deposition log transform data in term of deposition amount unit. Pearson correlation coefficients were calculated using SPSS for Windows (version 15) software that is significant at the 0.01 level. The resultant *r* values for dry deposition are shown in Table 3.21. The correlations coefficient (*r*) of dry deposition were strong correlated between NH₄⁺ and SO₄²⁻ (*r* = 0.756). It suggested that the main acidity of rainwater precipitation in this region was H₂SO₄, which was neutralized by NH₄⁺. This result contribution with ammonium/sulfate system, which NH₃ firstly reacted with H₂SO₄ to form (NH₄)₂SO₄ and NH₄HSO₄ (Hu *et al.*, 2003).

 SO_4^{2-} Cl \mathbf{K}^{\dagger} Mg^{2} Ca²⁻ Ions NO₃ $\mathrm{NH_4}^+$ Na SO_4^{2-} 1 0.191 1 NO₃⁻ ชียอโหบ Cl^{-} -0.222 0.221 $\mathrm{NH_4}^+$ -0.035 0.756 -0.1190.492 -0.028 0.368 0.138 Na K^+ 0.281 0.388 0.194 0.356 0.525 Mg^{2+} 0.301 0.078 0.126 0.284 0.265 0.090 1 Ca^{2+} 0.026 0.324 0.284 0.098 0.091 0.359 -0.305 1

Table 3.21 Correlations of log-transformed datasets chemical species for particles

3.9.2 Source analysis of major ion composition

In order to find 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 method used was principle component analysis (PCA). A varimax rotation with Kaiser Normalization of Principle Components Analysis by SPSS program (SPSS for Windows version 15) was applied and the results are shown in Table 3.22.

		Biomass burning and Sea-salt	and Agricultural activities	Soil resuspension
	Possible source	35.438	62.164	78.770
ΑΙ	% of cumulative	35.438	26.725 r_e s e	
Со	Eigenvalue	b ^{2.835} chia	ng ^{2.138} ai l	Jni ^{1.328} rsity
6	log(Mg ²⁺)	0.459	-0.087	0.756
	log(Ca ²⁺)	0.134	0.038	0.922
	$\log(K^{+})$	0.703	0.439	-0.111
	log(Na ⁺)	0.810	0.016	0.135
	log(NH ₄ ⁺)	0.008	0.971	0.057
	log(Cl ⁻)	0.762	-0.279	-0.049
	log(NO ₃ ⁻)	0.844	0.002	-0.263
	$\log(\mathrm{SO_4}^{2^-})$	-0.059	0.934	0.068
	705	These	2	33
	2024		Factor loadings	13224

Table 3.22 Factor analysis of chemical composition in dry deposition (n=48)

The factor analysis identified that there was three factors contributed about 79% of the variance to the log transformed dataset of dry data. Given observation that only factor loadings higher than 0.5 are deemed to be statistically significant (Ayer and Yeung, 1996 and Ungvari *et al.*, 2007). Three factor analysis were extracted from dry deposition .The first factor was high loadings for NO₃⁻, Cl⁻, Na⁺, and K⁺. It demonstrates biomass burning (NO₃⁻) and marine source (Cl⁻, Na⁺, and K⁺) (Hu *et al.*, 2003). The second factor was high loadings for SO₄²⁻ and NH₄⁺, which were associated with combustion fuel (SO₄²⁻) and animal waste and fertilized soils (NH₄⁺) (Andreas *et al.*, 2006).The last factor was high loading for Ca²⁺ and Mg²⁺, which can be indicated with soil resuspension (Ca²⁺ and Mg²⁺)(Xu *et al.*, 2007).

3.10 Suggestion for further study

Since 1998, acid deposition network was established. Chiang Mai was selected as one of the EANET sites to represent the northern part of Thailand. The study site (Mae Hia Research Center) was classified as rural site based on EANET criteria (EANET report, 2002). At present, Chiang Mai City is growing very fast resulting in increasing population density, expansion of community and transportation network. The study site is now surrounded by expanding roads and communities. Therefore, the study site should be re-classified as sub-urban site, which is proposed based on the results of wet and dry deposition of this study.