CHAPTER 3

RESULTS AND DISSCUSSIONS

Acid deposition in the Northern part of Thailand has been monitored for a year (April, 2003 to March, 2004). 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, anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analysed. The meteorological data of the study site have been collected to evaluate the meteorological condition of the area. The sampling site was Meteorological Station belongs to Faculty of Agriculture, Chiang Mai University, located at Mae Hia Research Center.

3.1 Meteorological Data of Sampling Site

The meteorological data of sampling site was collected by staff of Mea Hea Research Center Office, Chiang Mai University. The summary of this meteorological data is shown in Table 3.1. Annual mean temperatures during study period was 25.7 °C. The highest temperature was 37.5 °C during day time in early and late of May, 2003. The lowest temperature was 5 °C in the night time in late of January, 2004. The annual mean of percentage humidity (%RH) was 69.3%, whereas 50.4 and 83.8% were minimum and maximum values, respectively (see all data in Appendix B).

The highest frequency of rainy days was found in September, 2003 with a number of 19 days. The total amount of rainfall during study period was 1362.5 mm. The maximum precipitation amount was 456.1 mm in September, 2003. In year 2003, the

total rain amount in Thailand was lower than normal, Especially in Northern part of Thailand which was 13 % lower than the previous year. Before the study period, the weather was relatively hot. Averages of annual temperatures were in high range. However, amount of rain in May, 2003 was higher than normal due to the low atmospheric pressure, which passed through Thailand in a short period of time until June, 2003. Since July, 2003 the rainfall in the others region in Thailand was increased excepted in Northern and North Eastern, because party the South West monsoon was moved to Thailand, especially in last of July, 2004. Thailand was affected by two storms (the tropical storm "Cony" and Typhoon "Imbudo"). The number of precipitation and amount of rainfall were increased in August and September, 2004 particularly in September, flood occurred in many provinces in the Northern included Chiang Mai. In late of rainy season the amount and spread of rain were mostly lower than normal. Also the high atmospheric pressure from China spreaded to the Northern region of Thailand. The temperature and rainfall were decreased in middle of October and significantly decreased at the end of October (www.tmd.go.th).

3.2 Wet Deposition Monitoring

The wet precipitation samples were collected by automatic precipitation collector (wet only collector). Chemical properties such as EC, pH and ion concentrations were measured.

3.2.1 Comparison of general precipitation data

The number of rainy day obtained from Mae Hia Research Center Office was 80 days. The other meteorological data were also provided from the same research center. However, the recorded of precipitation of this research was found the different data

between two types of collector (rain gauge and precipitation collector belongs to the Pollution Control Department). Table 3.2 shows the concluded data of precipitation days in study period. The precipitations collected by rain gauge were recorded as 94 days while the data from precipitation collector were 98 days. The difference was found in dry season (October, 2003 to February, 2004). The meteorological conditions in this season could accurate evaporation rate of rain water samples especially when precipitation is low. By the way, rain gauge 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. Another reason for this event is assumed by affect from wind velocity. In case of small precipitation with high wind velocity during precipitation, it might be affected to the direction of rain drops on the mouth of rain gauge.

Table 3.1 Meteorological data of sampling site

Meteorological condition		Months												Annual
		Apr' 03	May' 03	Jun' 03	Jul' 03	Aug' 03	Sep' 03	Oct' 03	Nov' 03	Dec' 03	Jan' 04	Feb' 04	Mar' 04	
Mean temperature (°C)	Max. daily	35.8	34.5	31.2	32.5	31.7	31.7	31.6	31.0	28.9	30.7	31.1	35.5	32.2
	Min daily	21.2	22.3	23.7	24.1	23.2	23.4	21.3	18.1	12.3	10.5	13.4	17.3	19.3
	Monthly	28.5	28.4	27.8	28.3	27.4	27.5	26.6	24.6	20.6	20.6	22.2	26.4	25.7
Mean Relative Humidity (%)	Max. daily	78.1	77.7	85.8	86.0	87.5	89.6	90.0	82.6	89.4	88.4	75.3	74.6	83.8
	Min daily	33.4	485	66.8	67.5	71.2	78.0	63.0	45.8	46.0	36.2	26.3	27.6	50.4
	Monthly	55.7	63.1	76.3	76.7	79.4	81.3	76.5	64.2	67.7	62.3	55.7	56.3	67.9
Total Precipitation amount (mm./month)		94.7	251.0	161.7	79.8	284.5	456.1	14.6	13.1	0	6.5	0.6	0	1362.5
Number of precipitation day (days)		1	9	16	14	15	19	3	1	0	1	1	0	80

Table 3.2 Comparison of precipitation data between rain gauge and precipitation collector

Months	Rain gauge		Precipitation collector	
	Number of rainy day* (Days)	Total precipitation (mm)	Number of rainy day** (days)	Total precipitation (g)
April'03	6	80.9	6	5,394.6
May'03	10	84.8	10	5,689.2
June'03	24	115.2	24	7,721.0
July'03	12	50.0	12	3,173.1
Aug'03	15	176.3	15	11,278.9
Sep'03	19	291.3	19	19,040.4
Oct'03	5	5.1	8	319.5
Nov'03	1	8.6	1	537.1
Dec'03	0	0.1	1	5.0
Jan'04	1	4.4	1	267.4
Feb'04	1	0.4	1	26.2
Mar'03	0	0.0	0	0.0
Total	94	817.0	98	52,452.4

Note ** Diameter of rain gauge = 150 mm*

*** Diameter of precipitation collector = 288 mm*

3.2.2 Measurement of Acidity and Alkalinity (pH)

The simply way to define the acid precipitation can be done by measure pH value of the solution. The acid precipitation refer to any precipitate form which is pH lower than 5.6. pH of the samples were measured by pH meter. The pH values of all wet sample are shows in Appendix A (Measurements results of wet precipitation). The distribution of pH values are shown in Figure 3.1.

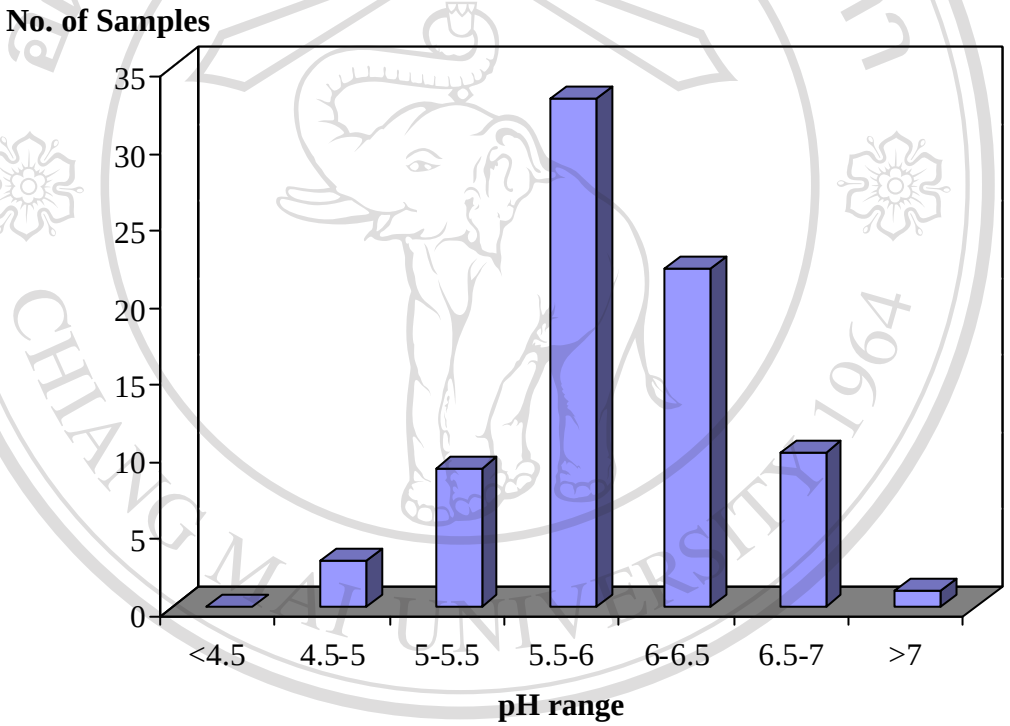

Figure 3.1 Distribution of pH of wet samples (78 samples)

The distribution of pH values of wet sample was made from 78 samples (precipitation amount > 4 g). Figure 3.1 shows the normal distribution which is the character of rain samples in clean area (Sarawut, 2005). Monthly mean values are shown in Figure 3.2. The precipitation was found to be slightly acids (pH<5.6) in 4 months (April, June, August and November, 2003). Three fourth of them were in dry

season excepted data of June which is in early of rainy season. The changing of meteorological condition was affected to sample concentrations. However, the annual mean pH in study period was 5.6. The lowest detected pH was 4.8. There was approximately 19% of rain samples which pH values were lower than 5.6.

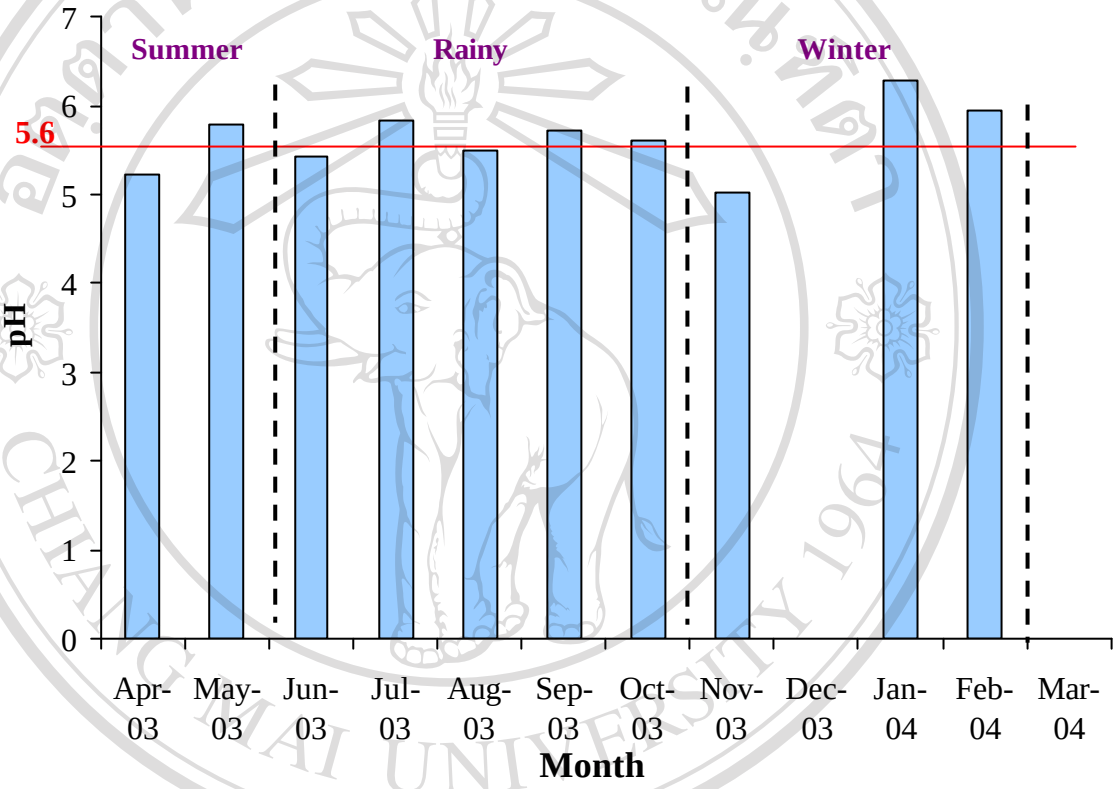

Figure 3.2 Monthly weight mean pH values from April, 2004 to March, 2003.

Note ** December, 2003; Low precipitation amount, pH could not be measured*

*** March, 2004; No precipitation.*

3.2.3 Measurement of Electro-Conductivity

The Electro-conductivity (EC) of samples was measured by the conductivity meter, Inolab Model 325. The monthly weight means EC were in range of 0.27-3.6 mS/m as shown in Figure 3.3. The annual mean EC in study year was 0.56 mS/m. The daily maximum EC was 6.12 mS/m in April, 2003 while the daily minimum was 0.16

mS/m in September, 2003. The frequency and amount of rainfall were affected to the EC levels of samples. The highest EC was found in dry season. Due to human activities in the area around the sampling site such as biomass burning and forest fire, Pollutants were released to the atmosphere. The increased of Total Dissolved Solid (TDS) in atmosphere affected to the EC of samples.

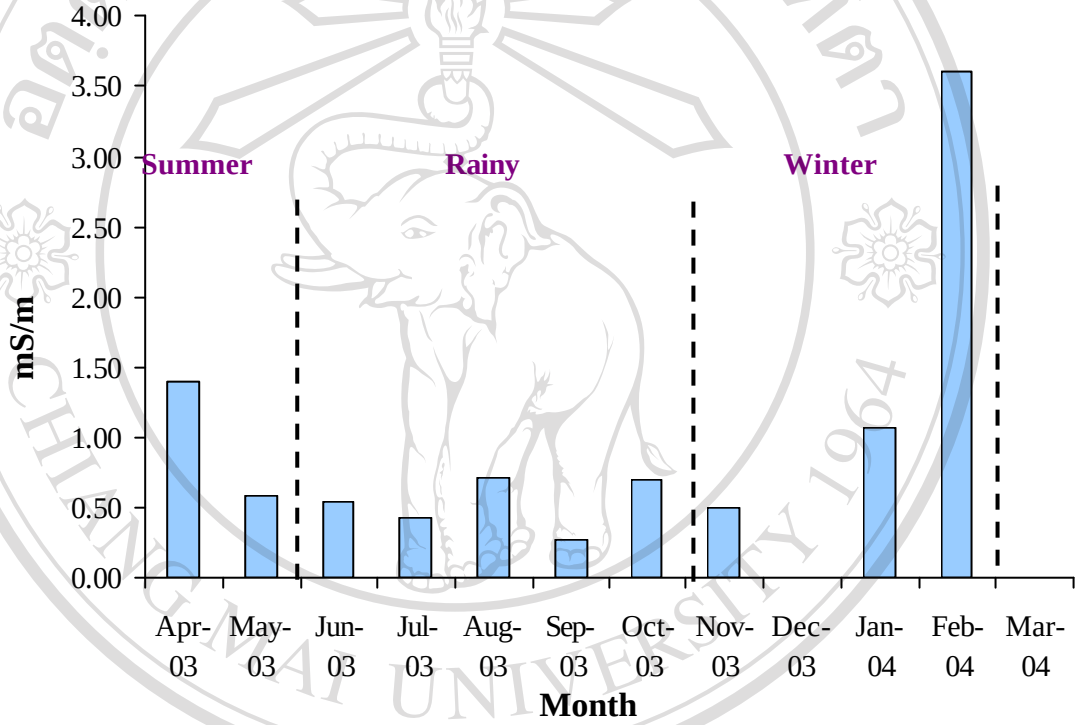

Figure 3.3 Monthly mean EC value from April, 2004 to March, 2003.

Note ** December, 2003 (1 sample, 5 g.); Low precipitation amount, EC could not be measured*

*** March, 2004; No precipitation.*

3.2.4 Measurement of ion concentration in rain samples

Ions contained in precipitate samples play an important role for changing of chemical properties of sample. Two types of ions contained in samples were measured in this study. Three species of anions namely SO_4^{2-}, NO_3^- and Cl^- and five cation

species namely NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed by ion chromatograph. Chromatograms of mixed standard are shown in Figures 3.4 and 3.5

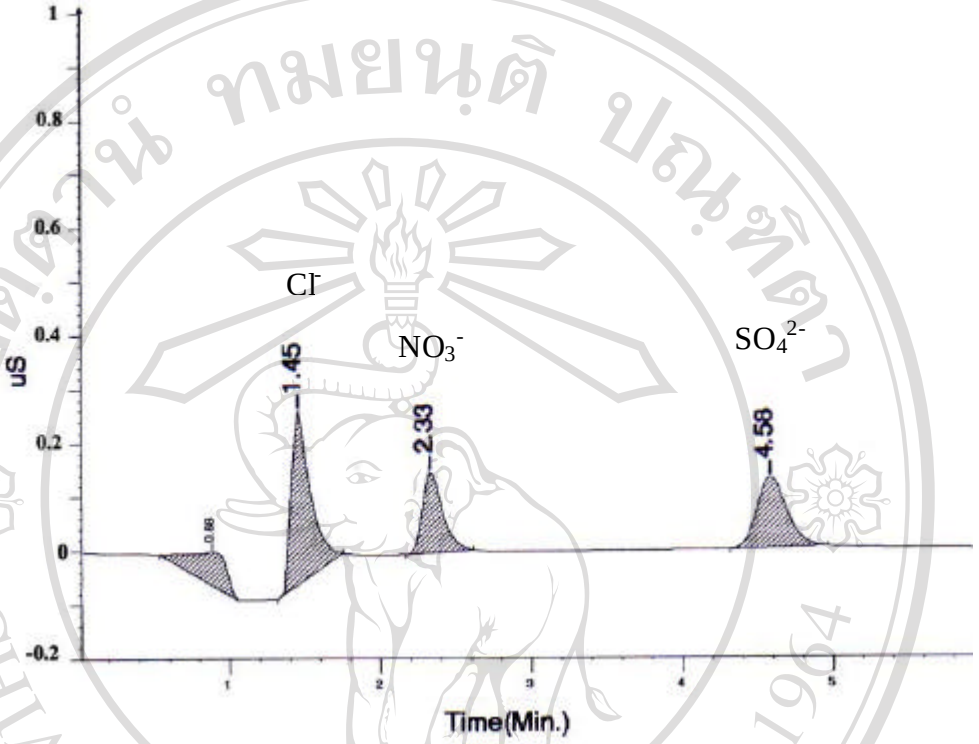

Figure 3.4 Chromatogram of 0.8 ppm mixed anions standard

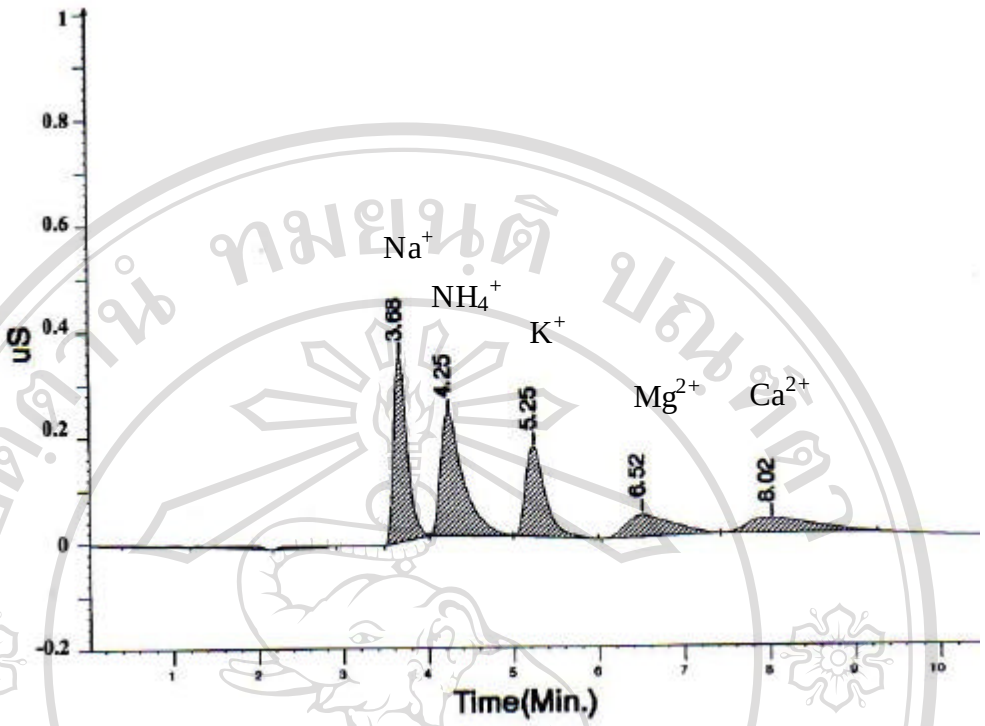

Figure 3.5 Chromatogram of 0.8 ppm mixed cations standard.

a) Calibration curve of ion analysis

In each analytical run, 6 concentrations of calibration standard were prepared and analyzed for it ions concentration. The calibration curve of each ion standard was drawn from concentrations of standard solution versus peak area. Concentration range was in acceptable concentration coefficient (r^2) was set at >0.995 to express the linearity of the curve 0.1-1.0 ppm. The calibration curve of each ion is shown in Figure 3.6.

b) Detection Limit

The detection limit in this study was obtained by 5 injection of 0.1 ppm standard solution. Their concentrations were calculated from the calibration curve in range 0.1-1.0 ppm. Detection limit was calculated as three time of standard deviation (Taylor, 1987). Results were shown in Table 3.3.

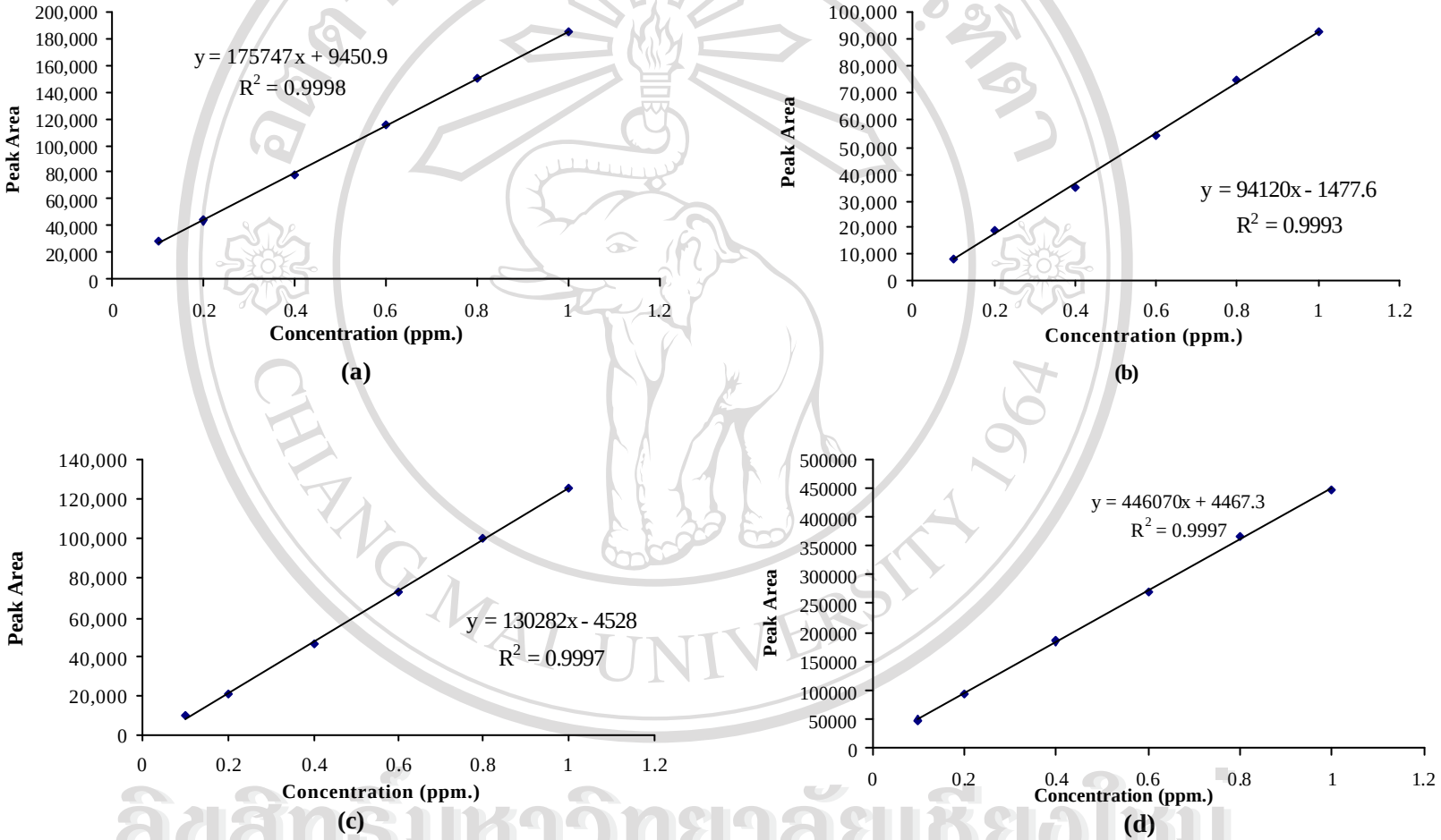

Figure 3.6 Calibration curves of ions and their equations, a) Chloride (Cl^-), b) Nitrate (NO_3^-), c) Sulfate (SO_4^{2-}), d) Sodium (Na^+).

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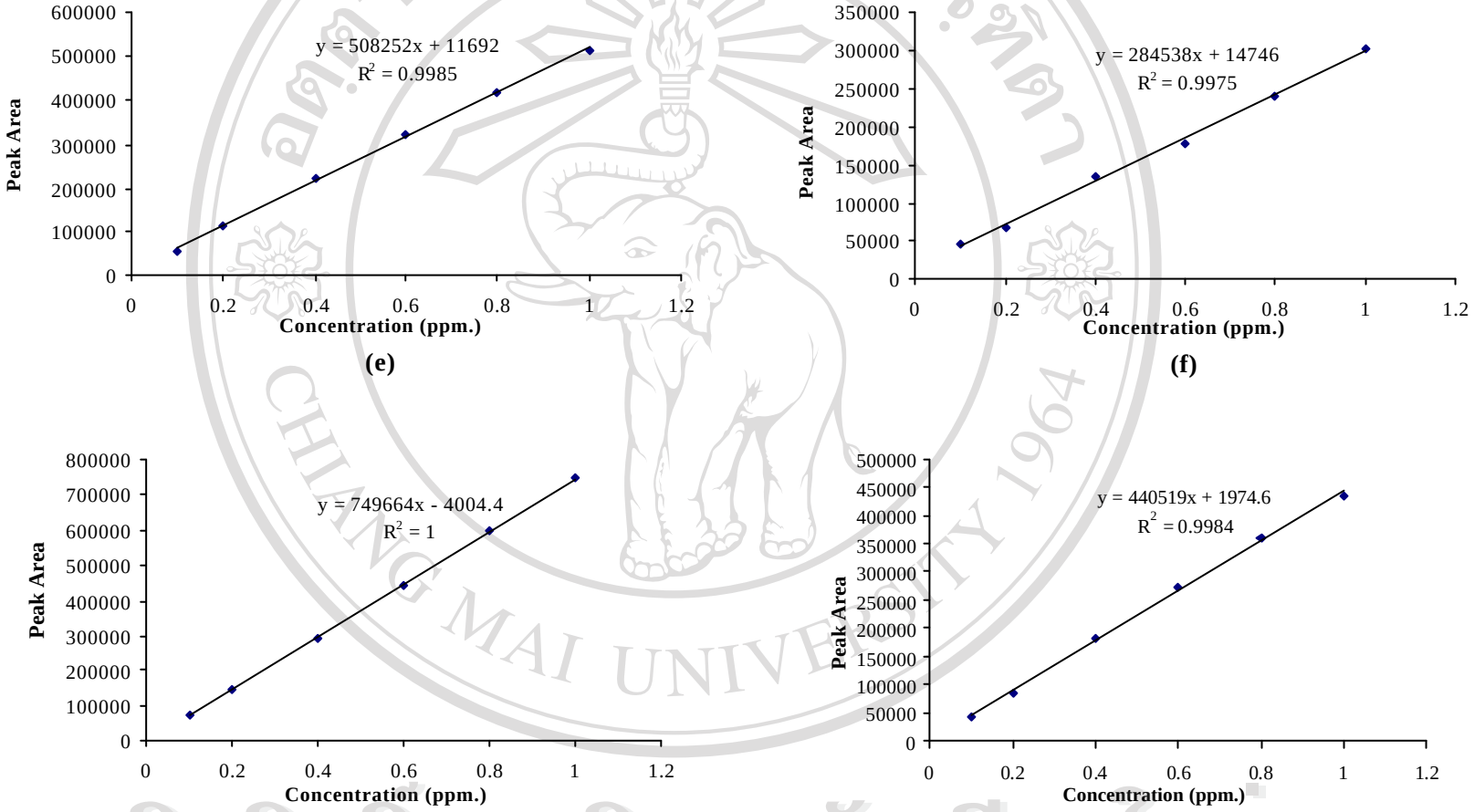

Figure 3.6 (Continued) Calibration curves of ions and their equations, e) Ammonium (NH_4^+), f) Potassium (K^+), g) Calcium (Ca^{2+}), h) Magnesium (Mg^{2+}).

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Table 3.3 Detection limit of IC for each ion

Analysis times	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)
1	0.113	0.113	0.145	0.094	0.119	0.115	0.112	0.067
2	0.110	0.093	0.152	0.092	0.119	0.118	0.114	0.067
3	0.113	0.109	0.141	0.090	0.123	0.117	0.114	0.068
4	0.114	0.105	0.149	0.093	0.125	0.119	0.113	0.070
5	0.106	0.105	0.155	0.093	0.129	0.123	0.118	0.069
Average	0.111	0.105	0.148	0.092	0.123	0.118	0.114	0.068
Standard Deviation (s)	0.003	0.007	0.005	0.001	0.004	0.003	0.002	0.001
Limit of Detection; LOD (3xs)	0.010	0.022	0.016	0.004	0.012	0.008	0.006	0.004
Limit of Quantification; LOQ (10xs)	0.034	0.074	0.054	0.014	0.041	0.027	0.021	0.013

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c) Ion contained in rain samples

Detected anion concentrations contained in wet precipitation samples were found in the different ranges. The results were concluded from 11 months because of un-precipitation in last sampling month (March, 2004). An example of analysis chromatogram of wet sample for anion and cation are shown in Figure 3.7 and 3.8

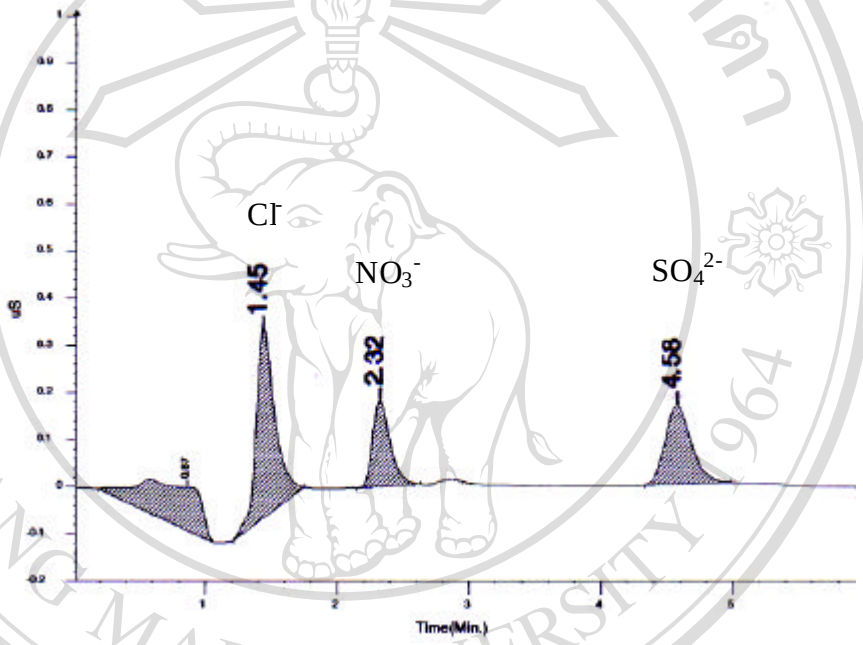

Figure 3.7 Chromatogram of anions detected from rain sample

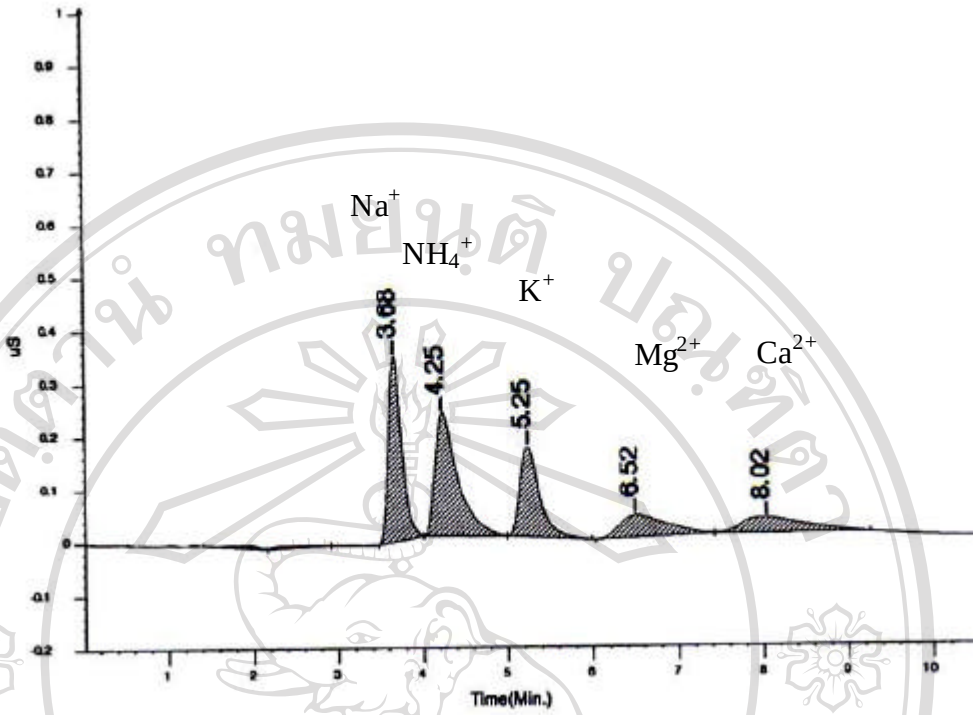

Figure 3.8 Chromatogram of cations detected from rain sample

I) Chloride ion

Chloride ion (Cl^-) contained in rain samples was highest in winter and lower in summer and rainy, respectively. The variation of Cl^- in ambient air is shown in Figure 3.9. The lowest weight mean concentration was found in September, 2003. The minimum detected concentration was 0.79 µeql/L in late of June, 2003. The low concentrations of ions in rain samples were due to high precipitation. The highest weight mean concentrations were found in February, 2004 followed by December and August, 2003, respectively. These peak concentrations showed high level of contaminations in the atmosphere. Others reasons would be effected from biomass burning in agricultural area from clearing of the land after harvest and forest fire. The amount of Cl^- accumulated in atmosphere also affected by the meteorological condition such as the relation between Cl^- concentration and amount of rainfall. The

concentrated samples were found in low amount of precipitation especially in dry season. However, the concentration in August, 2003 was not follow the reason above. The situation in this month was assume from the significantly increased of rain amount. Farmer normally start to prepare land to grow plant. Therefore, burning of biomass will be done with this purpose.

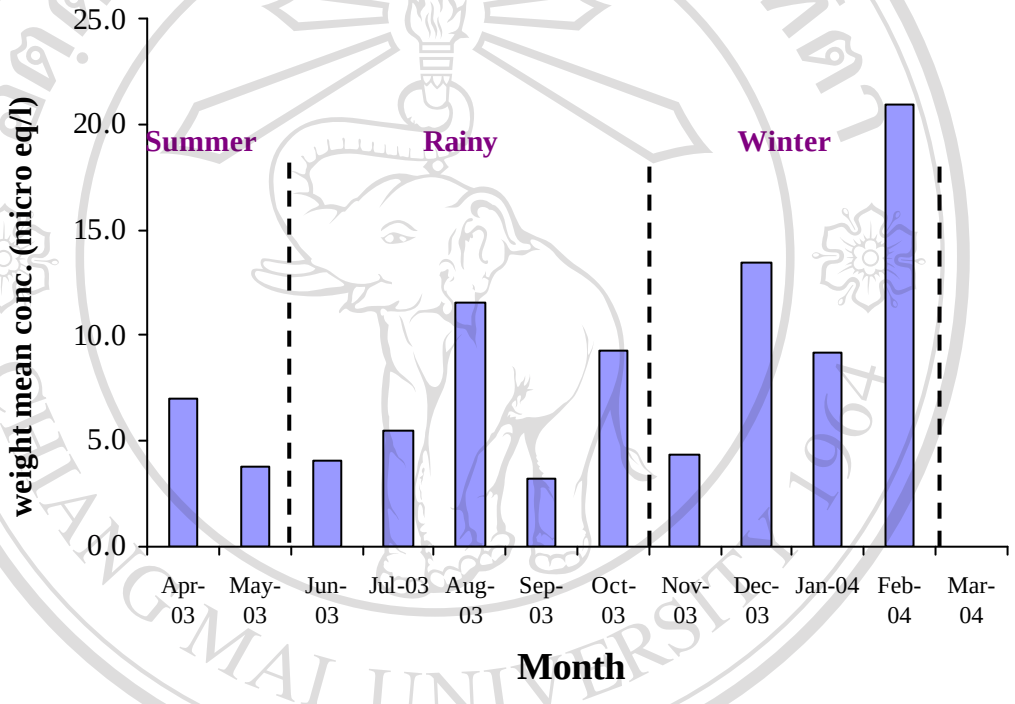

Figure 3.9 Monthly weight mean concentration of chloride ion.

Note *No precipitation in March, 2004*

II) Nitrate ion (NO_3^-)

Concentrations of nitrate ion (NO_3^-) contained in all samples were in range N.D.-137.10 µeq/L. Figure 3.10 shows monthly weight mean concentrations during study period. The minimum detected concentration was 0.48 µeq/L. The level of NO_3^- contamination in winter was significant different from other seasons. Winter season in Northern region was affected from the North East monsoon (www.tmd.go.th), which

passed through Chiang Mai City and some agriculture areas situation up-wind of the sampling site. Therefore, the main source of NO_3^- in winter was from those areas. Beside, the meteorological condition in winter season (low inversion) as well as geographical condition of Chiang Mai-Lumphun Basin, which is surrounded by mountains. Pollutants are possibly accumulated in this area.

Moreover, there was less precipitation in this period. Thus, the contaminated level was increased. However, the highest weight mean concentration was found in February, 2004 due to the same reason. Beside, the construction activity in the area close to sampling site could be also another reason.

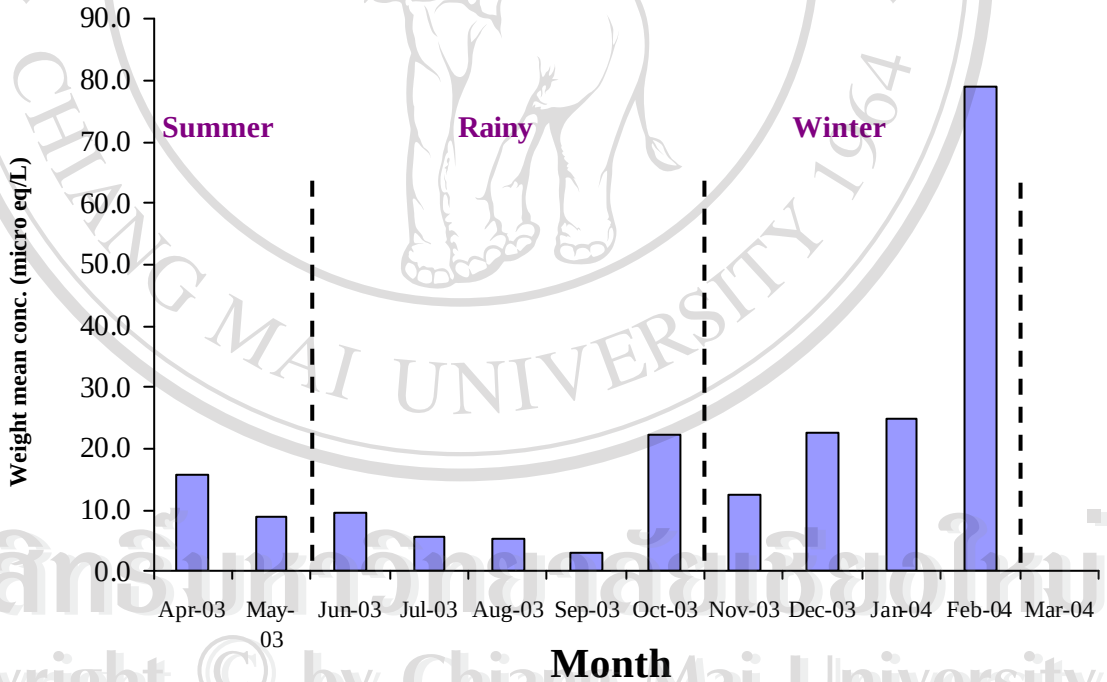

Figure 3.10 Monthly weight mean concentration of nitrate ion.

Note *No precipitation on March, 2004*

III) Sulfate ion

The detected concentration of sulfate (SO_4^{2-}) ion contained in rain samples was found in range 0.21-117.08 µeq/L. The weight mean concentration of SO_4^{2-} contained

in samples was 4.10 µeq/L. The maximum concentration was detected in February, 2004. Figure 3.11 shows the variation of sulfate concentrations in 12 months. The weight mean concentration in winter was also significant higher than summer and rainy season. It was similar to NO_3^- concentration, which high level in winter and highest in February, 2004. The main source of this pollutant was probably from Chiang Mai City. Other sources were biomass burning in agricultural area and forest fire.

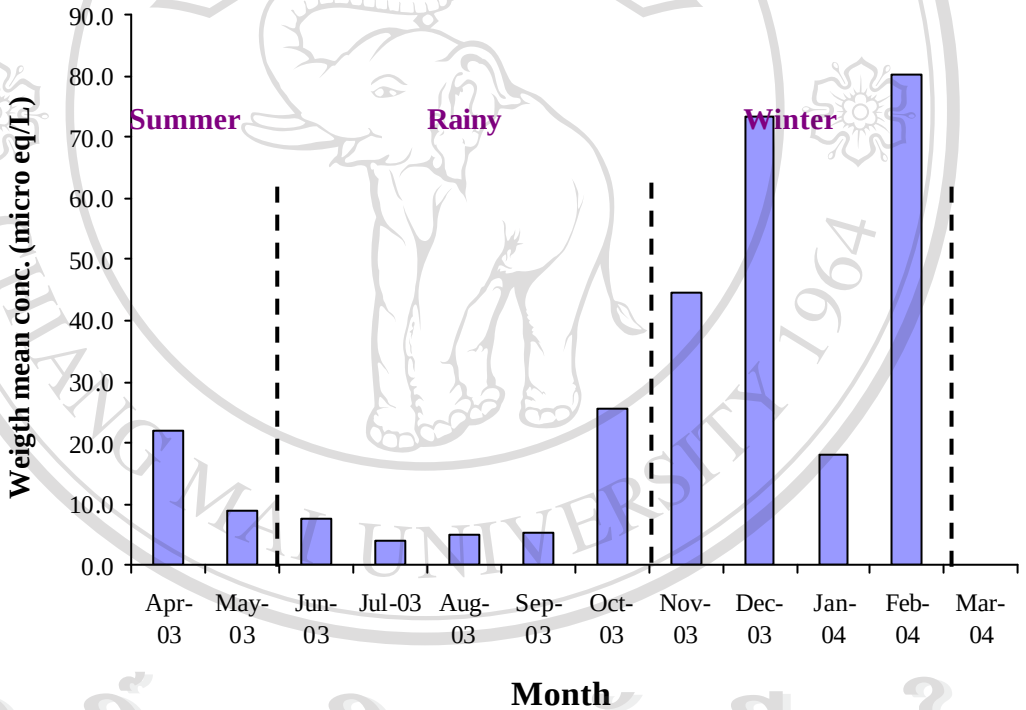

Figure 3.11 Monthly weight mean concentrations of sulfate ion

Note *No precipitation on March, 2004*

IV) Sodium ion

The concentration range of sodium ion (Na^+) was detected in range of N.D. to 83.12 µeq/L. The minimum detected value was 0.59 µeq/L. The trends of Na^+ concentrations were unstable in the study period. The highest weight mean

concentration was found in July, 2003 as shown in Figure 3.11. The significant higher value found in this month was assumed from the effect of South West monsoon which could transfer Na^+ in the cloud from the ocean to precipitate on the land.

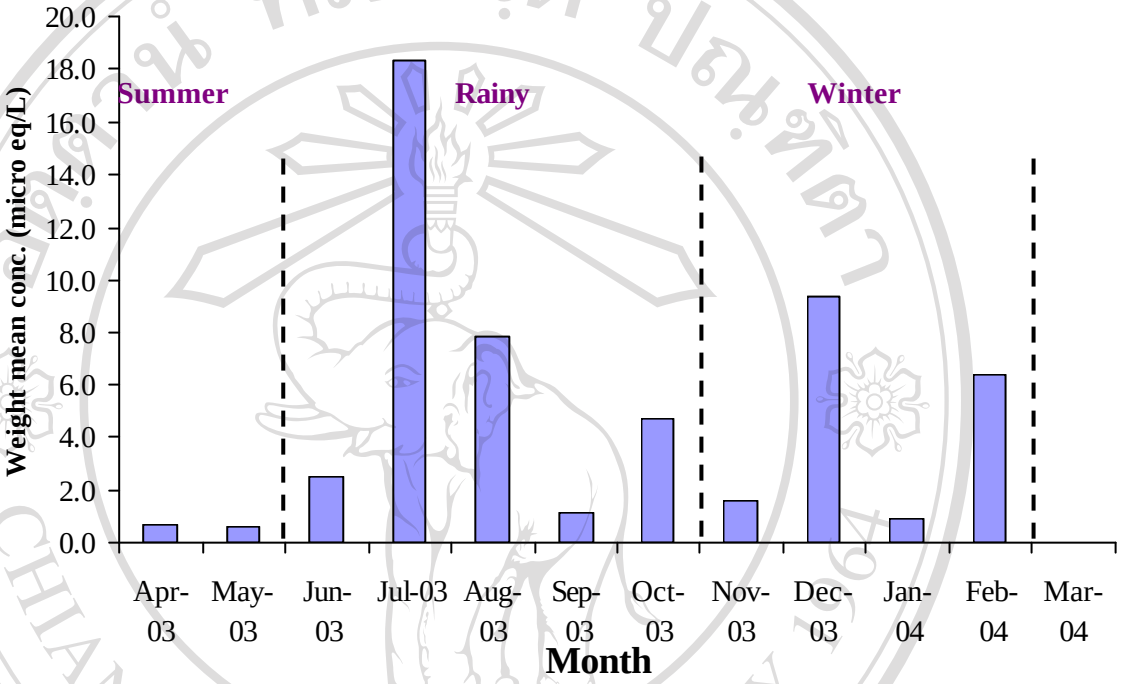

Figure 3.12 Monthly weight mean concentration of sodium ion (Na^+).

Note *No precipitation on March, 2004*

V) Ammonium ion

Ammonium ion (NH_4^+) contained in rain samples were found in range of N.D. to 229.16 µeq/L while the minimum detected concentration was 0.46 µeq/L. The highest weight mean concentration was found in winter. The values were decreased in summer and rainy season, respectively (Figure 3.13). Trend of NH_4^+ concentrations was the same as NO_3^- and SO_4^{2-} concentrations. As mentioned above, the direction of North East monsoon affected to NO_3^- and SO_4^{2-} concentrations. It also the reason of NH_4^+ level in atmosphere. The pollutants released from sources were transferred to sampling site by the prevailing wind. The major sources of NH_4^+ in atmosphere was

the high fertilizer used in agriculture activities and the combustion of human and animal waste.

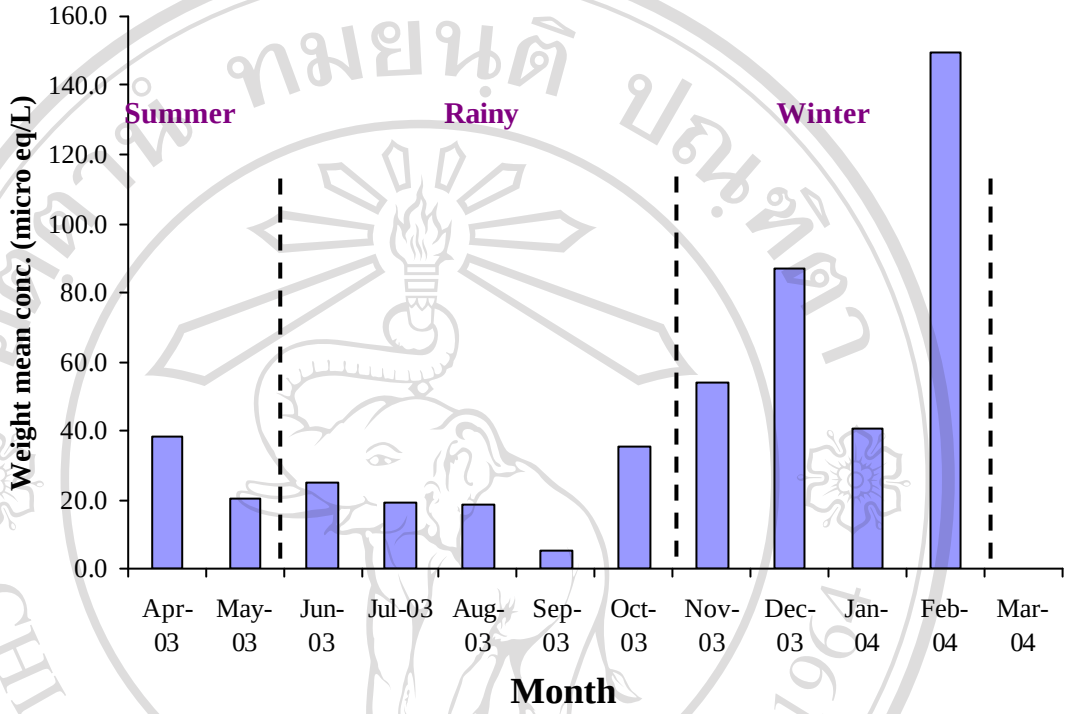

Figure 3.13 Monthly weight mean concentration of ammonium ion.

Note *No precipitation on March, 2004*

VI) Potassium ion (K^+)

The detected concentration range of potassium ion (K^+) contained in samples was N.D. to 200.76 µeq/L. The minimum detected concentration was 0.18 µeql/L. Most of monthly weights mean concentrations during study period were lower than 20 µmol/L excepted in December, 2003, which was 69.6 µmol/L (Figure 3.14). The reason of high concentration was the first rain after long time unprecipitation (45 days) as well as low rain amount (4.96 g). Therefore the first rain leached pollutants in atmosphere was occurred. The biomass burning in agricultural areas on the direction of monsoon

were increased potassium concentration in samples (Agriculture Office of Chiang Mai, 2004).

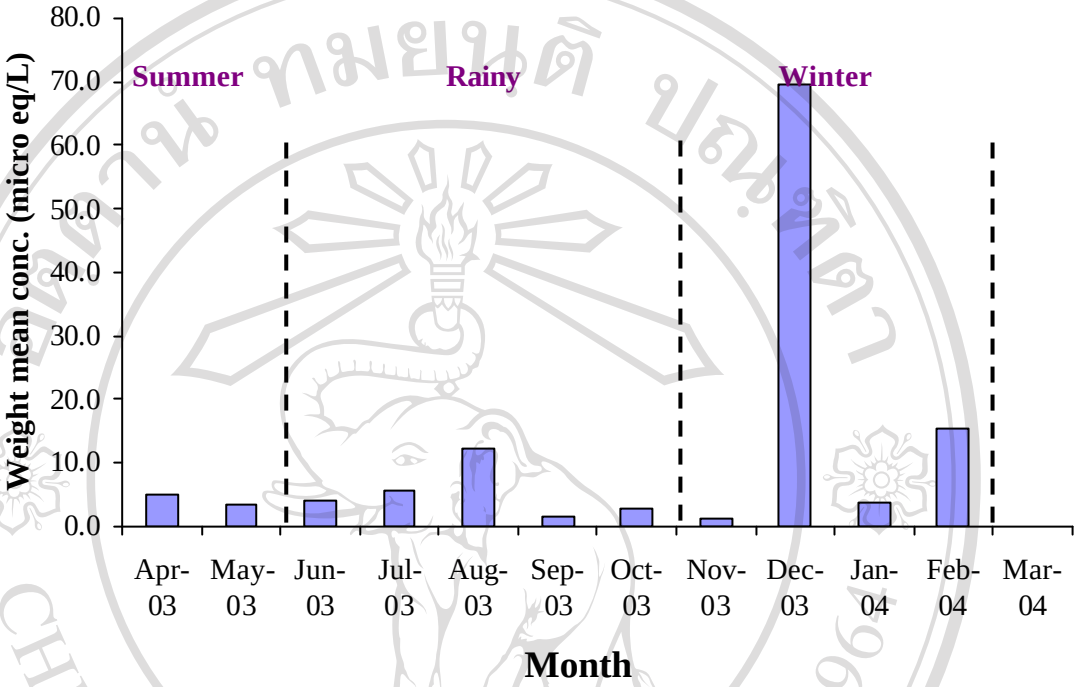

Figure 3.14 Monthly weight mean concentration of potassium ion.

Note *No precipitation on March, 2004*

VII) Magnesium ion

The detected concentration range of magnesium ion (Mg^{2+}) contained in samples was in range of N.D. to 175.57 µeq/L. The highest weight mean concentration was found in summer, following by rainy and winter, respectively (Figure 3.15). The sources of Mg^{2+} in samples were assumed from ash and dust caused from soil and agricultural activities. Small amount of rain samples in April to July was another factor of concentrated samples. The Mg^{2+} contained in dust was formed to bicarbonate (HCO_3^-) and Mg^{2+} by react with carbon dioxide (CO_2) and rain drops during precipitation, as equation (Howells, 1995);

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$$

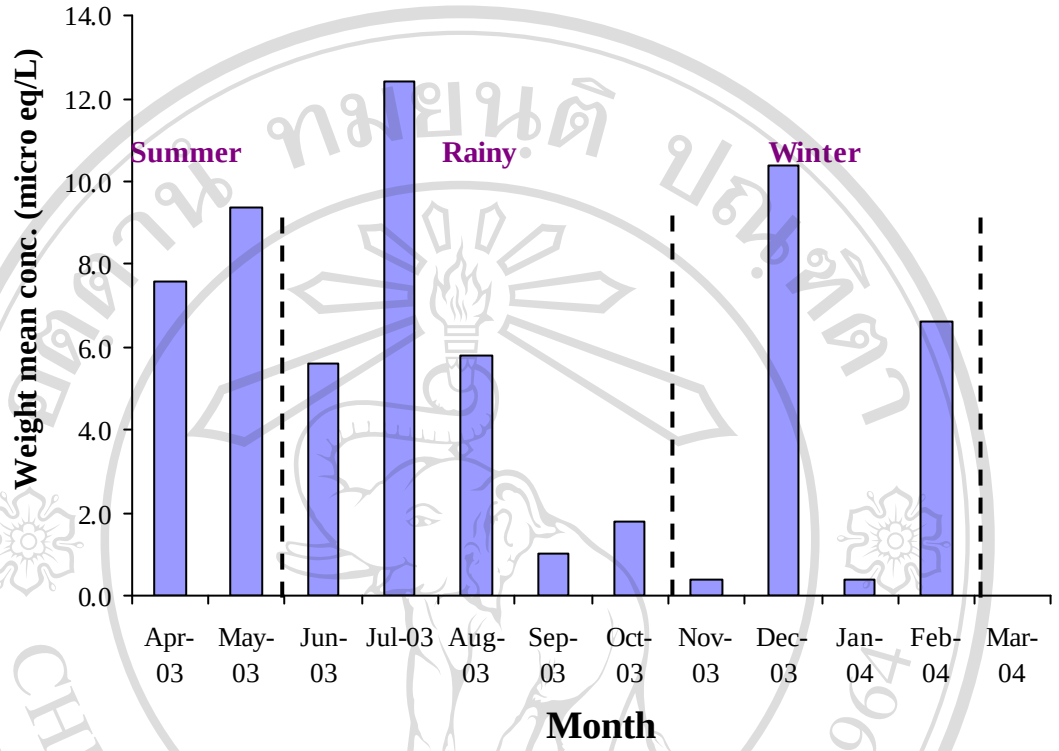

Figure 3.15 Monthly weight mean concentration of magnesium ion.

Note *No precipitation on March, 2004*

VIII) Calcium ion

The calcium ion (Ca^{2+}) concentration in rain samples were in range of N.D. to 275.24 µeq/L. The minimum detected concentration was 1.40 µeq/L. The Ca^{2+} contained in rain samples during study period was fluctuated. The weight mean concentration of Ca^{2+} in winter season was the highest followed by rainy and summer, respectively (Figure 3.16). The weight mean concentration of Ca^{2+} was compared to weight mean concentration of rain amount in the previous result. The significant relation of rain amount and concentration was found particularly during September, 2003 to February, 2004. The Ca^{2+} in atmosphere was emitted from biomass burning, soil dust and cement factory. Due to the construction of the new radio distribution

pole close to the sampling area in February, 2004. The cement used in construction project would be a reason of releasing calcium to atmosphere.

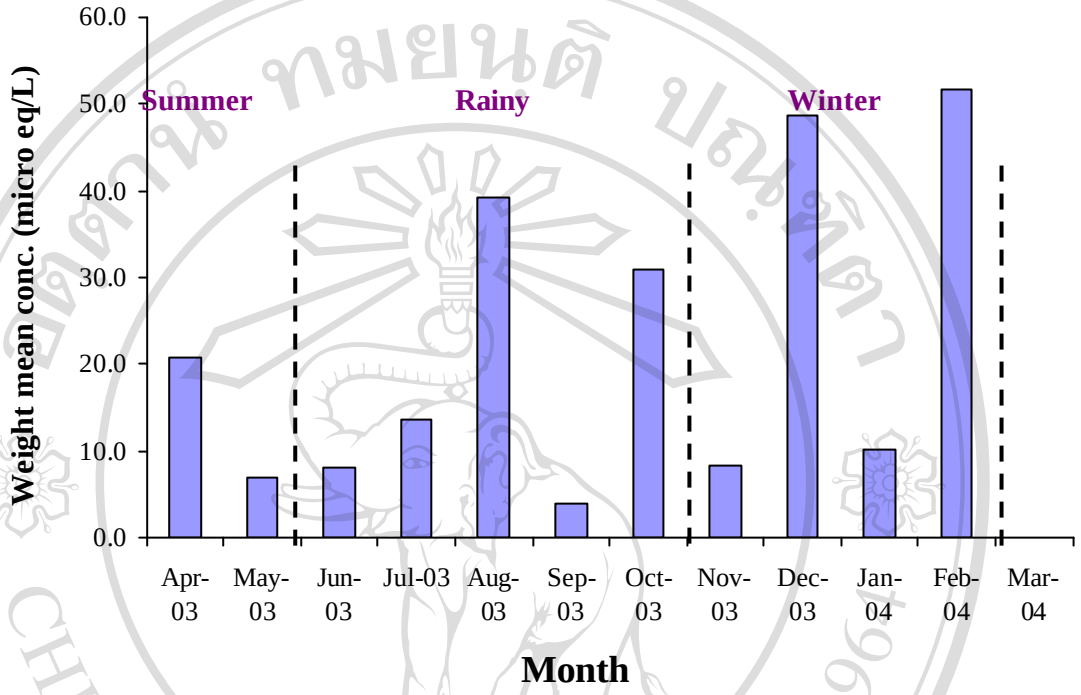

Figure 3.16 Monthly weight mean concentration of calcium ion

Note *No precipitation on March, 2004*

3.3 Quality Assurance and Quality Control

The results of chemical analysis of precipitation samples were calculated to R1 and R2 values. The analysis results were normally recorded in mg/L (ppm) unit then converted to µeq/L before used for calculation of ion balance (R1) and EC check (R2). Ion balance and EC check result of wet samples are shown in Figures 3.17 and 3.18

R1 and R2 values show the accuracy of ions analysis. Te calculated values were then compared with EANET criteria. Approximately 19% of R1 values were accepted, while 51% of R2 values.

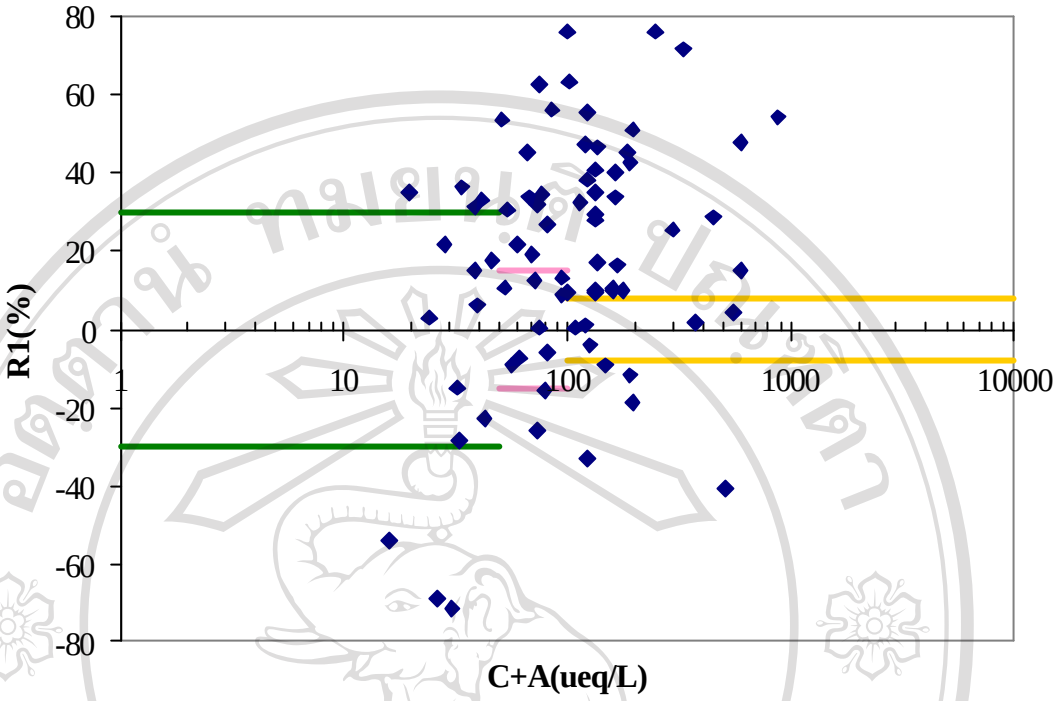

Figure 3.17 Distribution of R1 (Ion balance) of wet samples

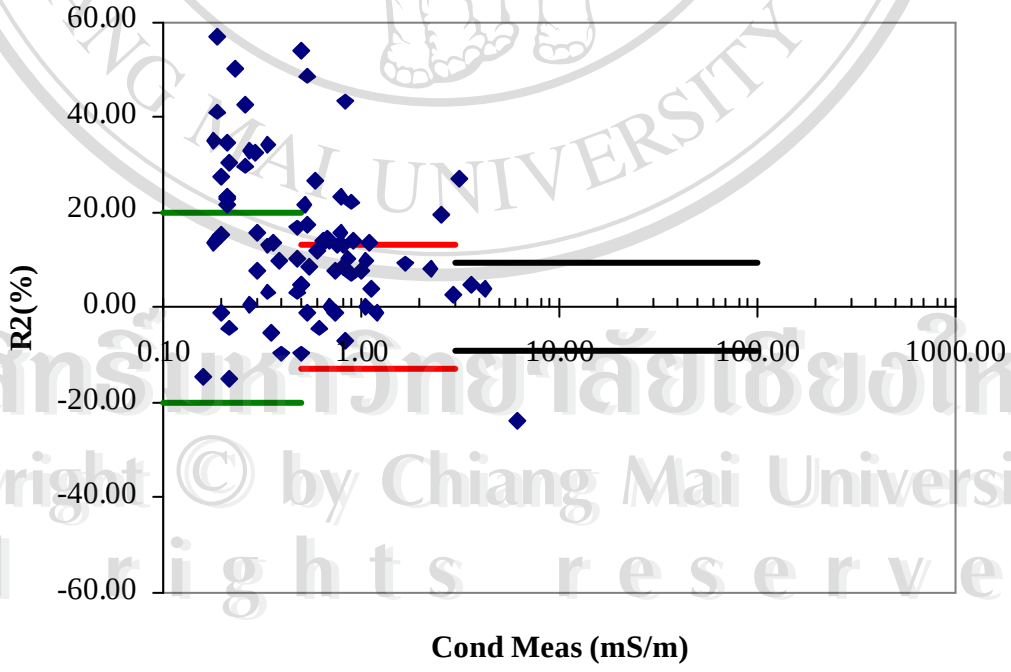

Figure 3.18 Distribution of R2 (EC check values) of wet samples

The accuracy of chemical analysis was done by analysis of the artificial rain provided by the Pollution Control Department (PCD). Artificial rains received from PCD were number 031 and 032 with serial number 088. The sample number 031 was high concentration whereas number 032 was low concentration. Both samples were 100 times diluted by milli Q water in three replications (a, b, c for no. 031 and d, e, f for no. 032) before EC, pH and ion concentration analysis, respectively. The results obtained are shown in table 3.4.

3.4 Dry Deposition Monitoring

Dry deposition samples were collected by 4 stages filter pack holder set to assess the 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^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. The second stage filter (Polyamide; F1) was analysed for Cl^-, NO_3^-, SO_4^{2-} and NH_4^+. The alkali impregnated filter (F2) in third stage was analysed for Cl^- and SO_4^{2-}. The acid impregnate filter (F3) in the last layer was analysed for only NH_4^+. The examples of analyzed chromatogram of each filter are shown in Figure 3.19-3.22.

Table 3.4 pH, EC and concentration of ion in Artificial Rain No. 031-032

Sample No.		pH	EC	Concentration (µmol/L)								R1	R2
		-	mS/m	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	(Ion balance)	(EC check)
Reference conc. (No.031)		4.52	3.44	44.70	30.90	66.00	46.10	6.90	20.50	7.00	48.30		
No.031	**a**	4.97	3.18	46.55	30.08	69.19	45.56	5.77	23.79	5.94	49.99	-5.75	-5.50
	b	4.70	3.21	46.17	30.10	68.85	45.33	5.78	22.90	5.97	50.57	-3.24	-0.86
	c	4.61	3.19	46.23	30.19	69.17	46.29	6.58	22.19	5.93	50.59	-2.03	2.03
Average		4.76	3.19	46.32	30.12	69.07	45.73	6.04	22.96	5.95	50.38	-3.67	-1.45
Standard deviation		0.19	0.02	0.20	0.06	0.19	0.50	0.46	0.80	0.02	0.34		
Reference conc. (No.032)		4.80	1.48	12.00	21.30	29.60	25.60	2.50	4.40	3.40	15.10		
No.032	**d**	4.95	1.32	12.02	20.73	29.24	25.5	2.31	5.6	3.12	14.14	-2.37	-0.58
	e	5.07	1.26	11.92	20.63	29.19	26.51	3.5	5.45	3.1	13.37	-3.30	-1.89
	f	4.81	1.43	11.99	20.75	29.6	24.79	2.33	4.91	3.13	14.48	-0.81	0.60
Average		4.94	1.34	11.98	20.70	29.34	25.60	2.71	5.32	3.12	14.00	-2.16	-0.62
Standard deviation		0.13	0.09	0.05	0.06	0.22	0.86	0.68	0.36	0.02	0.57		
De-ionized Water		7.61	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		

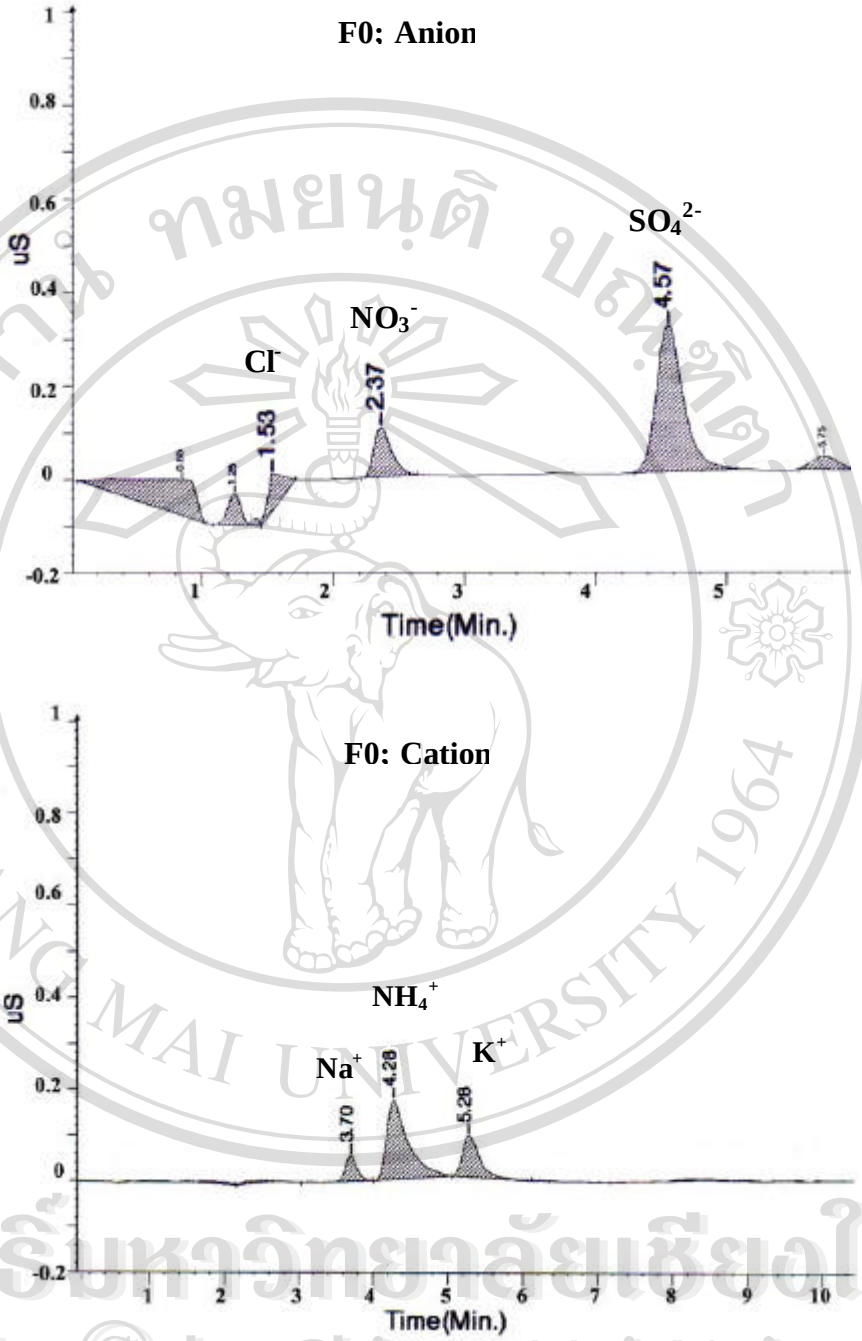

Figure 3.19 Chromatograms of anions and cations obtained from F0 filter

Note *Mg^{2+} and Ca^{2+} are not detected in this sample.*

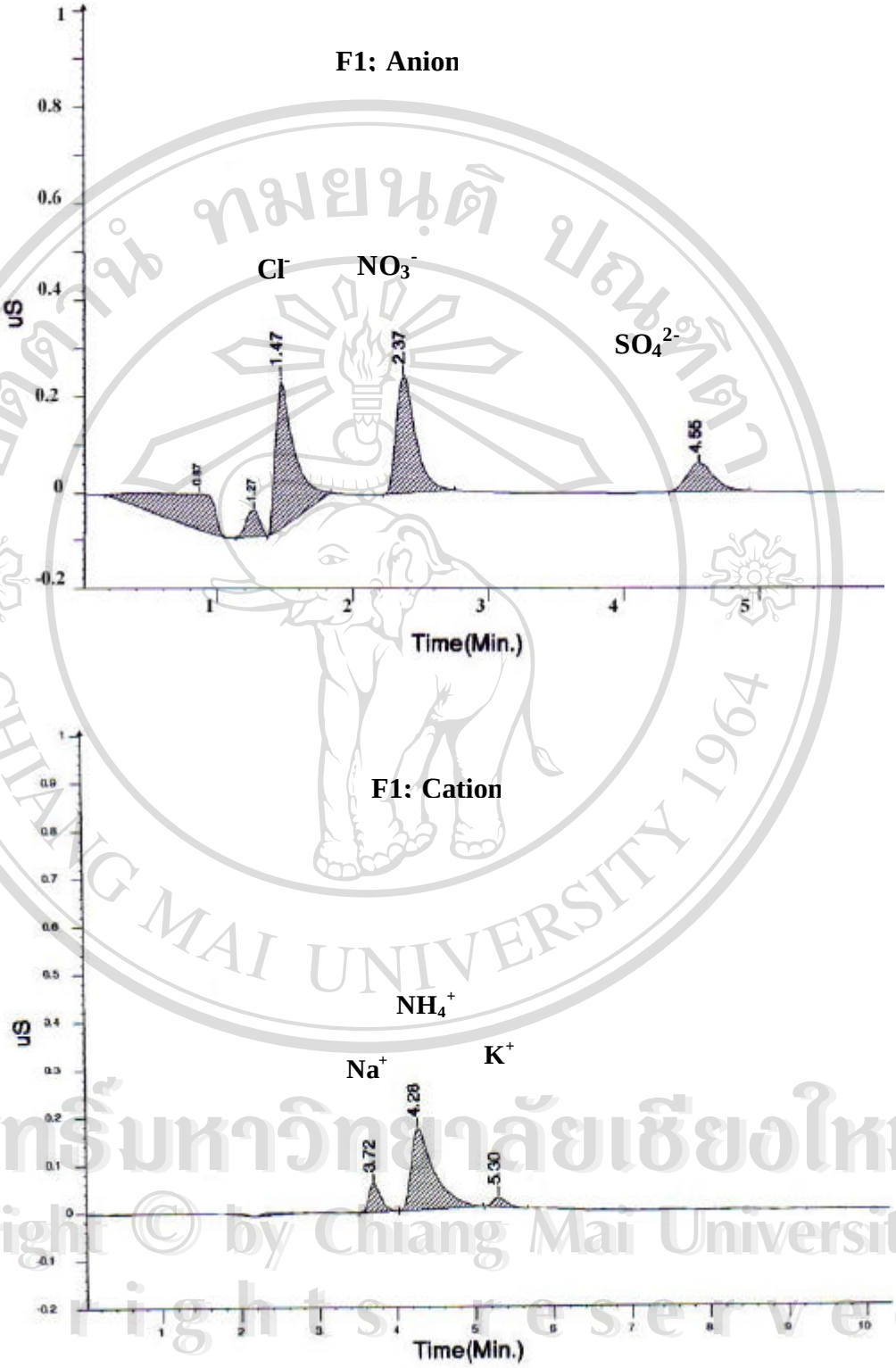

Figure 3.20 Chromatograms of anions and cations obtained from F1 filter

Note *Mg^{2+} and Ca^{2+} are not detected in this sample.*

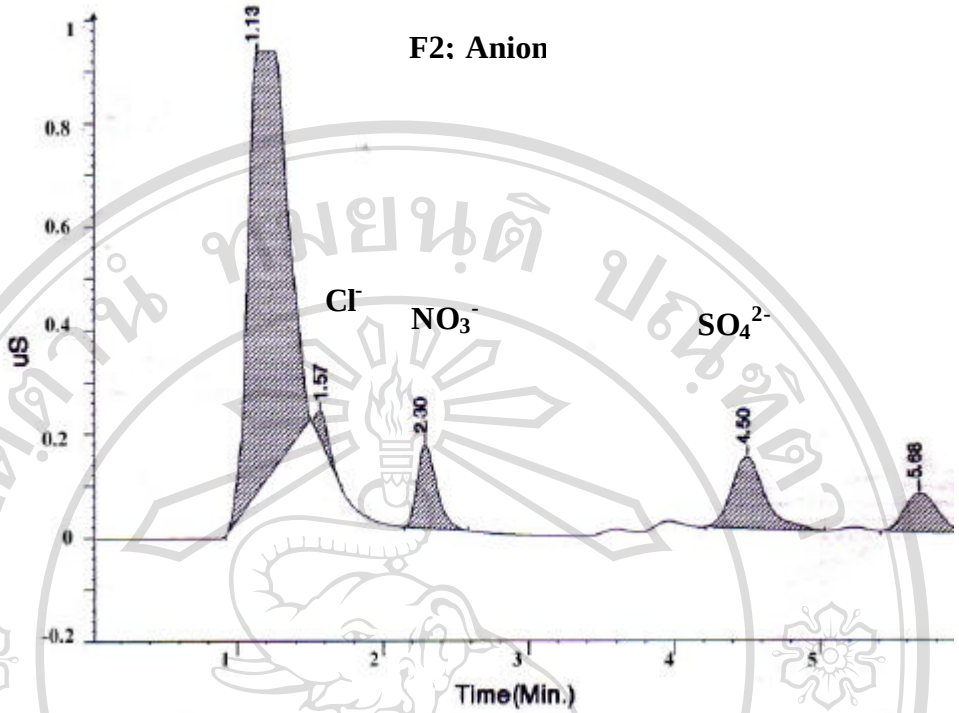

Figure 3.21 Chromatograms of anions obtained from F2 filter

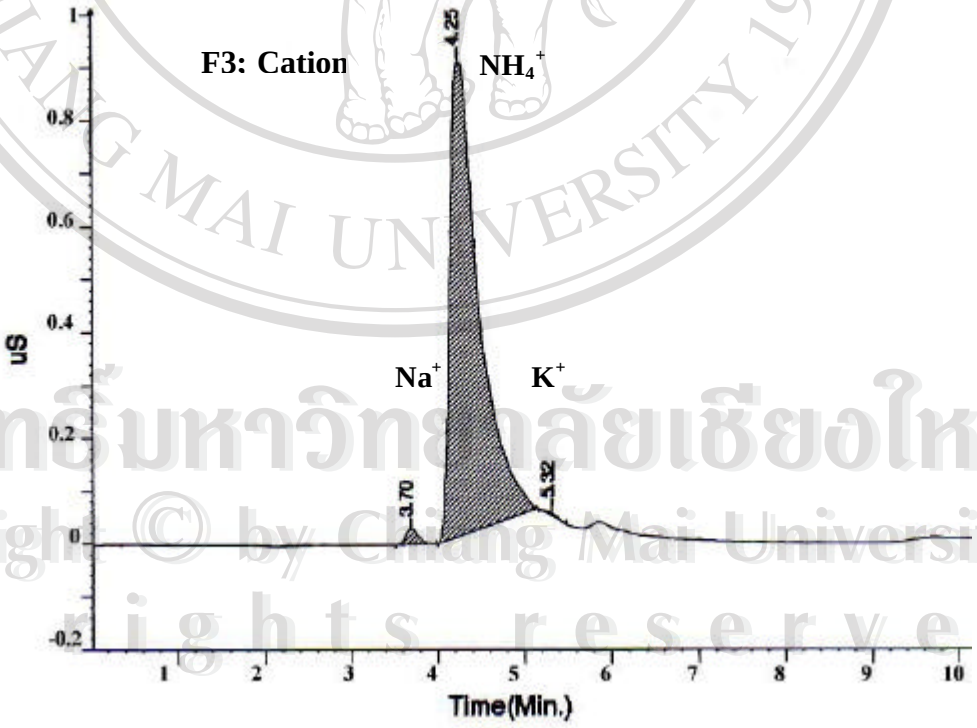

Figure 3.22 Chromatograms of cations obtained from F3 filter

Note *Mg^{2+} and Ca^{2+} are not detected in this sample.*

3.4.1 Acidic Gas Concentrations

The analysis results were used to determine the concentration of air pollutants namely sulfur dioxide (SO_2), nitric acid (HNO_3), nitrogen dioxide (NO_2) and ammonia (NH_3). The concentrations of pollutant gases are shown in Table 3.5

Table 3.5 Monthly concentration of pollutants during study period.

Months	Sample Concentration (nmol/m^3)			
	SO_2	HNO_3	HCl	NH_3
Apr-03	0.00	2.29	0.00	795.63
May-03	0.00	0.00	32.20	1037.22
Jun-03	5.62	4.97	24.72	462.50
Jul-03	5.22	5.37	5.05	107.69
Aug-03	1.79	4.29	4.51	0.00
Sep-03	2.94	2.41	0.00	79.36
Oct-03	23.27	10.72	1.43	87.50
Nov-03	62.34	2.56	6.97	167.17
Dec-03	20.93	25.45	14.28	153.59
Jan-04	41.33	28.10	9.99	286.30
Feb-04	17.56	37.51	12.74	284.74
Mar-04	31.22	47.73	29.65	509.53
Average	17.7	14.3	11..8	330.9

a) Sulfur dioxide; SO_2(g)

The concentrations of SO_2(g) were found in range of N.D. to 62.34 nmol/m^3 as shown in Figure 3.23. The concentrations of the first two months of study period were

non detected. The highest weight mean concentration was in November, 2003, which collected on 25 Nov to 2 Dec, 2003 (20 days after the last precipitation was detected). The highest concentration was detected in November, 2003 which was in the early of winter season. The main source of SO_2(g) was emitted directly from fossil fuel burning. Apart from that the north east monsoon in winter season, transported SO_2(g) from Chiang Mai City to sampling area. In addition, the change of meteorological condition from rainy to winter (Oct-Nov) was effected to the spread of pollutant plume in study area. Therefore, high accumulation of SO_2(g) might be occurred.

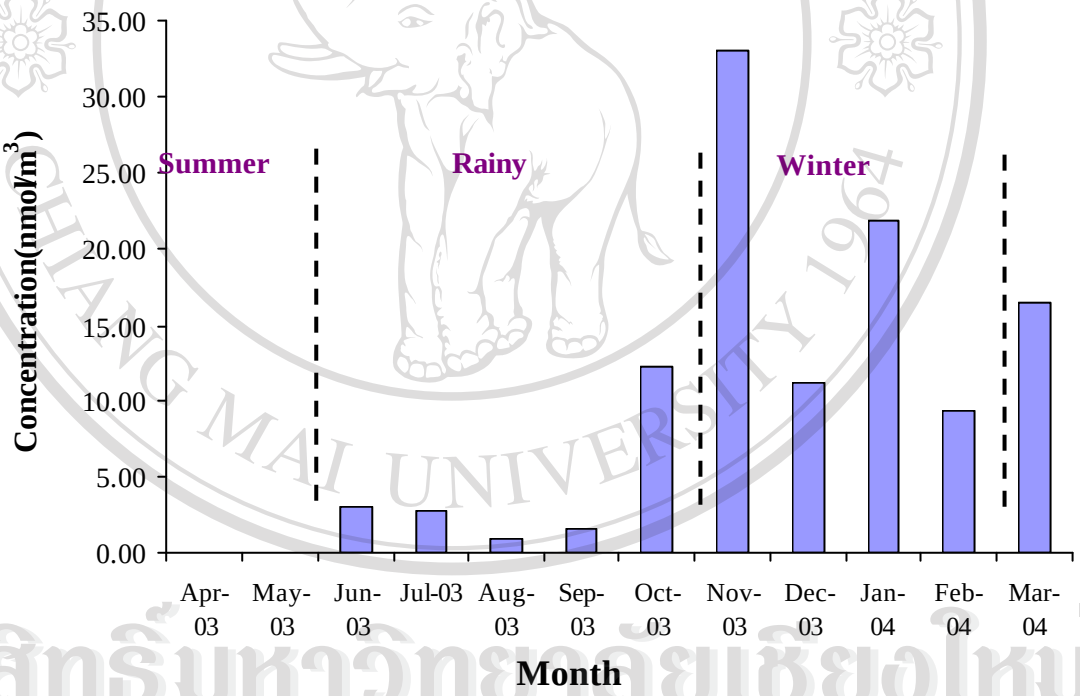

Figure 3.23 Monthly concentration of sulfur dioxide.

b) Nitric acid; HNO_3(g)

The concentrations of nitric acid (HNO_3(g)) in atmosphere ranged from N.D. to 47.7 nmol/m^3 as shown in Figure 3.24. The monthly levels of HNO_3(g) increased in winter until early of summer due to changing of the meteorological condition. In dry

condition (less of precipitation), samples became more concentrated particularly in March, 2004 (un-precipitation). Biomass burning in agriculture area and garbage burning in communities were assummed to be the main sources of nitric acid in winter. In addition, forest fire was another source of nitric acid in the summer time. The areas in Chiang Mai where often had forest fire were Jom Tong, Aom Koy and Mae Jam Districts. All together the fire occurred 544 times in one year which covered 6,351 rai damage areas (Forest fire Control Unit., 2004). The summer monsoon is prevailing through those areas, and then took the pollutants to the sampling site.

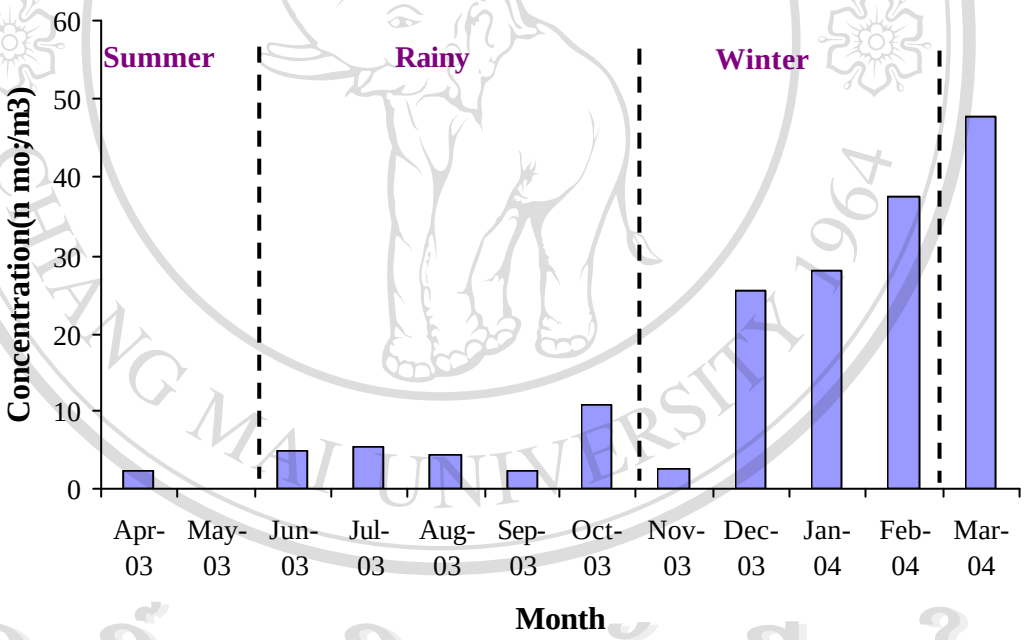

Figure 3.24 Monthly concentration of nitric acid.

c) Hydrochloric acid; HCl(g)

The range of hydrochloric acid (HCl(g)) concentrations found in dry deposition samples was N.D.-32.2 nmol/m^3. Most of high HCl concentrations was found in dry season (summer and winter). There was less of precipitation in dry season therefore the pollutant remained in the atmosphere. Non detected values were found in two

months (April and September, 2003) as shown in Figure 3.25. In September, there was high precipitation, so that the concentration of pollutant in air was decreased. However, the non detected value in April was not the same reason. The high concentration of blank sample probably from contaminated filters during preparation was assumed to be a main reason.

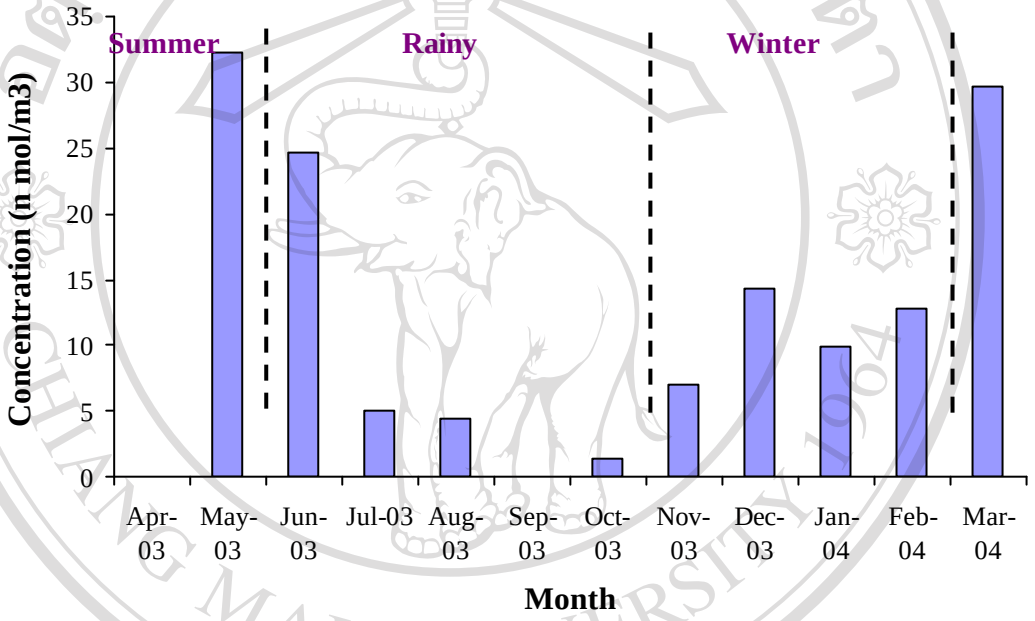

Figure 3.25 Monthly concentration of hydrochloric acid

d) Ammonia; NH_3(g)

The concentration of ammonia (NH_3(g)) in atmosphere was found in range of N.D.-1037.2 nmol/m^3. The highest concentration was in May, 2003 as shown in Figure 3.23. The main input of NH_3(g) to atmosphere were the fertilizer application and nitrification process. The high level of NH_3(g) in summer was due to fertilizer used to improve the quality of soil for next agriculture period in rainy season.

However the $NH_3(g)$ in other months were also found, but its concentration was lower than in summer because the wash out process caused by rain.

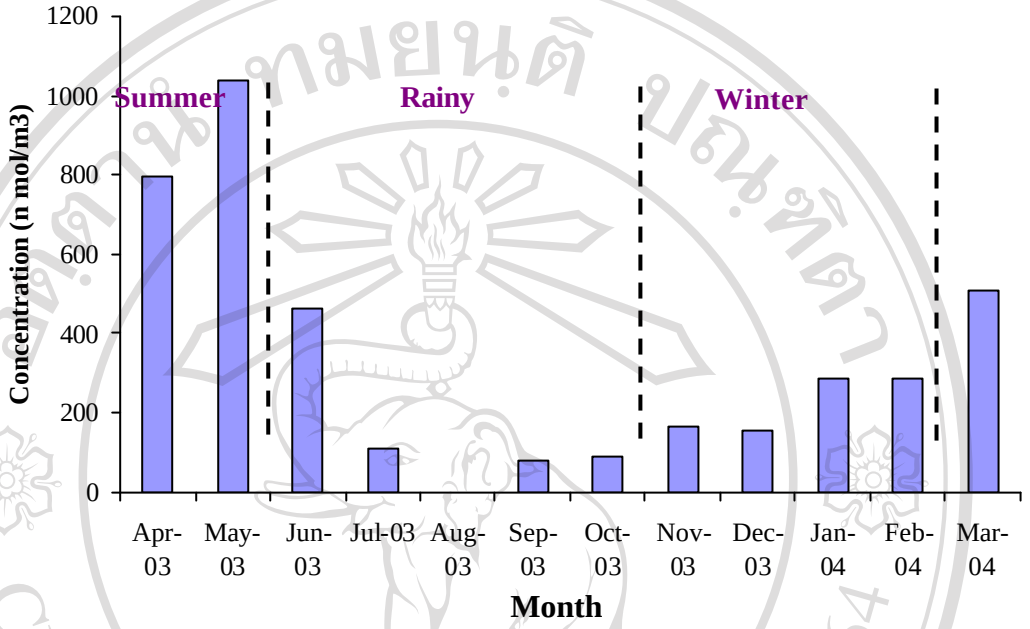

Figure 3.26 The monthly concentration of ammonia.

3.4.2 Acid particle concentration

The acid particles in the atmosphere were also collected by the 4-stage filter pack at the same time with gases collection. Concentration of acid particles was obtained by analysis of extracted samples using ion chromatography. The results of acid particle in atmosphere during study period are shown in Table 3.6.

Table 3.6 Monthly concentrations of acid particle collected by 4-stage filter pack

Month	Particle concentration (nmol/m^3)							
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Apr-03	N.D	4.76	0.93	6.59	220.94	26.24	5.08	40.50
May-03	N.D	1.42	30.34	32.21	123.34	17.47	27.94	167.62
Jun-03	N.D	4.84	1.86	N.D	8.44	N.D	7.05	N.D
Jul-03	2.25	4.82	6.89	9.94	16.46	10.96	1.26	13.19
Aug-03	N.D	9.75	0.54	N.D	6.74	6.41	2.30	18.86
Sep-03	0.31	1.51	7.06	N.D	9.31	2.08	74.92	4.62
Oct-03	4.76	0.75	59.20	N.D	107.64	N.D	1.28	6.69
Nov-03	0.51	0.21	3.01	N.D	3.95	0.82	0.02	0.10
Dec-03	N.D	12.03	88.27	N.D	118.67	21.37	0.11	10.80
Jan-04	15.47	2.32	N.D	N.D	7.84	2.72	N.D	8.52
Feb-04	2.80	30.85	23.38	2.49	54.19	29.72	1.87	17.65
Mar-04	1.75	38.02	55.44	10.69	100.21	52.76	4.38	34.32
Average	1.23	4.91	12.23	2.73	34.35	7.53	5.57	14.26

a) Chloride particles

Range of detected chloride concentration was N.D. to 15.47 nmol/m^3. Most of the chloride level contaminated in atmosphere was low. The detected chloride particle concentration was highest in winter season.

b) Nitrate particles

Concentration of detected nitrate particle was found in range of N.D. to 38.0 nmol/m^3. The highest detected concentration was found in March, 2004 which was the

early of summer (no precipitation). However the highest weight mean concentration was found in winter season, while the weight mean concentrations in summer and rainy season were similar. The pattern of NO3- concentrations found in dry deposition to the one detected were similar in wet precipitation. Therefore, the sources of NO_3^- could be the same.

c) Sulfate particles

The concentration of sulfate particle was found in range N.D. to 88.3 nmol/m^3. The highest concentration was detected in early of winter (December, 2003). However, the highest weight mean concentration was found in summer season followed by winter and rainy season, respectively. The level of sulfate particles in summer was affected by the meteorological in summer due to high temperature and long sunlight period. It related to the reaction of sulfur dioxide gas with ammonia in moist air.

d) Ammonium particles

The present of ammonium particle in atmosphere were detected in range of N.D. to 220.9 nmol/m^3. The highest concentration and seasonal weight mean concentration were found in summer (March, 2004). The main source of ammonium particles could probably derived from the use of fertilizer in agriculture activity.

e) Sodium particles

The seasonal weight mean concentration of Na^+ was found to be highest in summer. The main source of sodium was from the marine input especially in the area close to the sea. However, the sampling site in Chiang Mai might have less effect. Therefore the normal contamination level should be low or non detected. The

significant high concentration in May, 2003 might be affected from some kind of activity around sampling site such as biomass burning in agricultural area and forest fire.

f) Potassium particles

The detected concentration of potassium particles in all samples was found in range N.D. to 52.76 nmol/m^3. The seasonal weight mean concentration was also highest in summer. The high level of potassium particles was assumed from the effect of fertilizer usage.

g) Magnesium particles

The concentration of magnesium particles in atmosphere was found in range of N.D. to 74.92 nmol/m^3. The highest concentration was detected in rainy season. However, the highest seasonal weight mean concentration was also found in summer time like those in wet precipitation analysis. The main pollutant input was assumed from dust and biomass burning in agricultural activities.

h) Calcium particles

The monthly calcium particles concentration was found in range of N.D. to 167.6 nmol/m^3. The seasonal weight mean concentrations were highest in summer and reduced in winter and rainy season respectively. 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.

3.5 Seasonal variation of samples concentration

3.5.1 Seasonal concentration of wet samples

The concentrations of ions contained in samples had a seasonal variation. The variations of ion concentrations were affected by many factors particularly meteorological conditions. Table 3.7 shows the seasonal weight mean concentration of all detected ions in each season. In the early of this study was started from summer season (Apr to May, 03 and Mar, 04), rainy (June,03 to Oct,03) and winter (Nov,03 to Feb,04), respectively. Concentrated samples were found in dry season except Na^+ which was highest in rainy season. The highest Na^+ due to the effect of South West monsoon which transfered Na^+ in the cloud from the ocean to precipitate on the land. The highest mean concentration in wet sample was NH_4^+. The main source of NH_4^+ in atmosphere was the high fertilizer used in agriculture activities and the combustion of human and animal waste.

Table 3.7 The seasonal weight mean concentration of wet samples.

Month	Weight mean concentration (μeq/L)							
	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Summer	4.8	13.1	15.7	31.0	0.5	4.1	7.8	13.1
Rainy	4.4	4.5	5.6	11.3	3.5	3.7	3.2	10.1
Winter	6.5	18.7	37.2	52.9	1.6	2.8	0.6	10.4

3.5.2 Seasonal concentration of dry samples

The seasonal mean concentrations of acid gases and particles are shown in Table 3.8 Most of the high concentration samples were found in dry season especially

summer. Ammonia and ammonium ion were found as highest concentration in dry samples due to agricultural activities.

Table 3.8 The seasonal mean concentrations of acid pollutants collected by 4-stage filter pack

Seasons	Gases (nmol/m^3)				Particles (nmol/m^3)							
	SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Summer	10.4	16.7	20.6	780.8	28.9	14.7	0.6	148.2	16.5	32.2	12.5	80.8
Rainy	7.8	5.6	7.1	147.4	15.1	4.3	1.5	29.7	2.0	3.9	17.4	8.7
Winter	35.5	23.4	11.0	223.0	28.7	11.4	4.7	46.2	0.6	13.7	0.5	9.3

3.6 Deposition amount

3.6.1 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 3.9.

The total wet deposition was 1361.2 mg/m^2. The major ion of wet deposition was NO_3^- with 319.2 mg/m^2 as 23.4% of total wet deposition. However, SO_4^{2-} was the second major cause of wet deposition. It was 313.0 mg/m^2 as 23.0% of total wet deposition. Therefore, it could be assumed that the major sources of pollutant cause were from anthropogenic activities which probably from the vehicle internal combustion and fuel burning in industrial processes. The proportion of each ion parameter are concluded in Figure 3.27.

Table 3.9 Monthly wet deposition amount

Month	Deposition amount (mg/m^2)							
	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Apr-03	85.84	78.59	20.19	55.45	1.22	15.36	33.76	7.55
May-03	25.50	33.45	7.92	21.89	0.84	8.22	8.16	6.83
Jun-03	38.28	62.54	15.24	46.92	5.99	17.19	16.57	7.05
Jul-03	8.27	15.09	8.51	14.90	18.22	9.62	11.75	6.52
Aug-03	37.35	30.19	36.37	29.68	16.09	41.87	69.69	6.36
Sep-03	73.47	54.05	32.58	28.66	7.65	17.52	21.61	3.79
Oct-03	6.39	7.17	1.72	3.32	0.56	0.55	3.21	0.11
Nov-03	18.47	6.76	1.32	8.41	0.32	0.40	1.41	0.04
Dec-03	0.28	0.11	0.04	0.13	0.02	0.22	0.08	0.01
Jan-04	3.80	6.83	1.44	3.23	0.09	0.64	0.91	0.02
Feb-04	1.54	1.96	0.30	1.08	0.06	0.24	0.41	0.03
Mar-04	-	-	-	-	-	-	-	-
Total deposition	312.99	319.20	125.63	228.82	51.06	114.64	169.23	39.66
Percent of deposition (%)	23.0	23.4	9.2	16.8	3.8	8.4	12.4	2.9

Note *No precipitation on March, 2004*

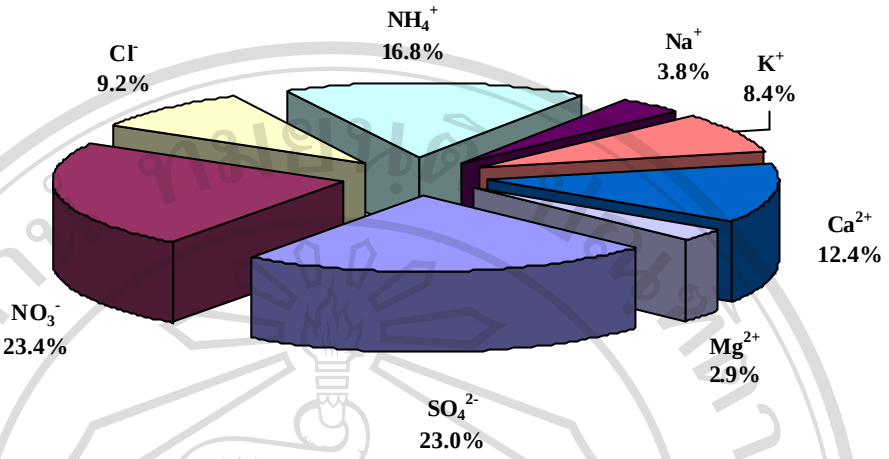

Figure 3.27 Percentage of ions in wet deposition

3.6.2 Dry deposition

The concentrations of pollutant in atmosphere collected by 4-stages filter pack were reported in concentration unit per volume of air samples (nmol/m^3). 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 out 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 3.10.

The highest dry deposition in gases form was ammonia with a number of 35.8 µg/m^2 (69.6% of total dry deposition in gas form). Ammonia contained in air samples was assumed from the fertilizer used and the changing of nitrogen compound in nature by nitrification process. However, dry deposition in particle form was sulfate with a value of 14.1 µg/m^2 (39.9% of total dry deposition in paricle form). Sulfate particle

was emitted from fuel burning in industrial processes. The comparison chart of acid pollutants in gas and particle form are shown in Figure 3.28 and 3.29

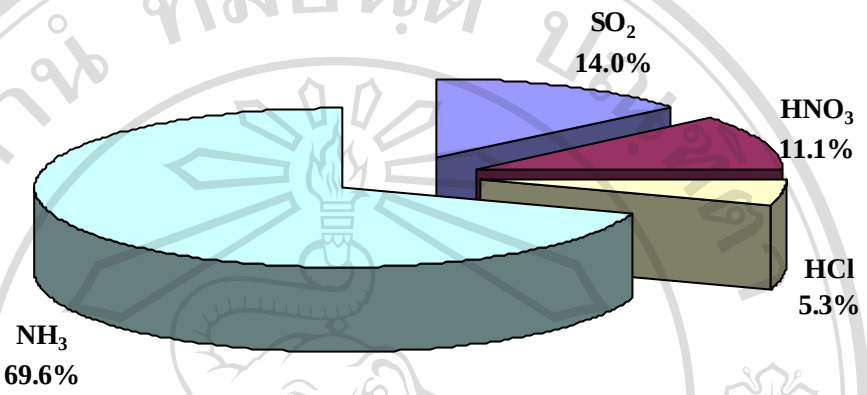

Figure 3.28 Percentage of gases deposition.

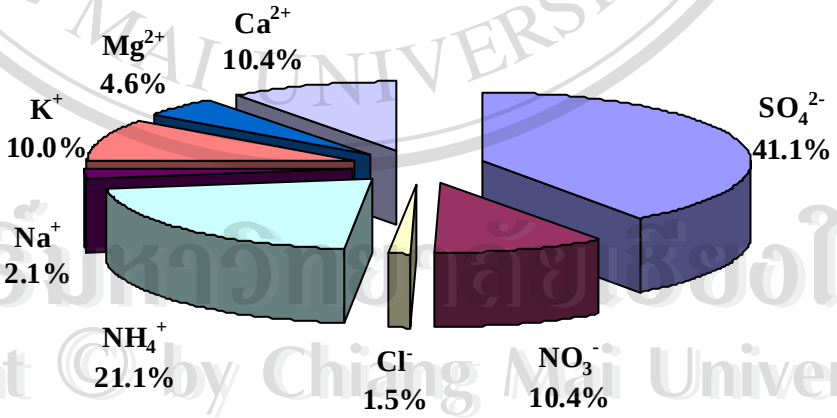

Figure 3.29 Percentage of particle deposition.

Table 3.10 Monthly dry deposition amount in study period

Month	Deposition amount ($\times 10^{-2}$ µg/m^{2}s)											
	Gases				Particles							
	SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Apr-03	0.0	0.1	0.0	7.2	0.05	0.2	0.0	2.1	0.1	0.5	0.1	0.5
May-03	0.0	0.0	0.6	9.4	1.5	0.05	0.0	1.2	0.4	0.4	0.4	1.9
Jun-03	0.2	0.2	0.5	4.2	0.1	0.2	0.0	0.1	0.0	0.0	0.1	0.0
Jul-03	0.2	0.2	0.1	1.0	0.4	0.2	0.04	0.2	0.1	0.2	0.02	0.1
Aug-03	0.1	0.1	0.1	0.0	0.03	0.3	0.0	0.1	0.0	0.1	0.03	0.2
Sep-03	0.1	0.1	0.0	0.7	0.4	0.05	0.01	0.1	0.0	0.04	1.0	0.1
Oct-03	0.8	0.4	0.03	0.8	3.0	0.02	0.1	1.0	0.0	0.0	0.02	0.1
Nov-03	2.1	0.1	0.1	1.5	0.2	0.01	0.01	0.04	0.0	0.02	0.0002	0.001
Dec-03	0.7	0.9	0.3	1.4	4.5	0.4	0.0	1.1	0.0	0.4	0.001	0.1
Jan-04	1.4	0.9	0.2	2.6	0.0	0.1	0.3	0.1	0.0	0.1	0.0	0.1
Feb-04	0.6	1.3	0.2	2.6	1.2	1.0	0.1	0.5	0.03	0.6	0.02	0.2
Mar-04	1.1	1.6	0.6	4.6	2.8	1.2	0.03	1.0	0.1	1.1	0.1	0.4
Total deposition	7.2	5.7	2.7	35.8	14.1	3.7	0.5	7.4	0.8	3.5	1.6	3.7
Percent of deposition (%)	14.0	11.1	5.3	69.6	39.9	10.4	1.5	21.1	2.1	10.0	4.6	10.4

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3.6.3 Total deposition amount

Total deposition amount was concluded from wet and dry deposition values. By the way, the deposition amount of SO_4^{2-}, SO_2, HNO_3, NH_3, NO_3^- and NH_4^+ were calculated to sulfur and nitrogen depositions. The conclusion of total deposition of each ion is shown in Table 3.11 and Figure 3.30

Table 3.11 Total deposition in study period

Type of deposition	**Deposition amount ($\mu g/m^2$)**							
	S	**N**	**Cl^-**	**N**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Wet ($x\ 10^4$)	10.4 (SO_4^{2-})	25.0 (NO_3^-)	12.6	17.8 (NH_4^+)	5.1	11.5	16.9	3.97
Dry	8.3 (SO_4^{2-}+ SO_2)	2.1 (HNO_3+ NO_3^-)	35.2	3.2 (NH_3+ NH_4^+)	0.8	3.5	3.7	1.6

Nitrogen was the major part of acid deposition in Chiang Mai. Due to the human activities such as fertilizer used in agriculture activity, vehicle internal combustion and the releasing from natural sources. The increasing of facilities demand due to growth of communities was rised up the pollution trend in this region.

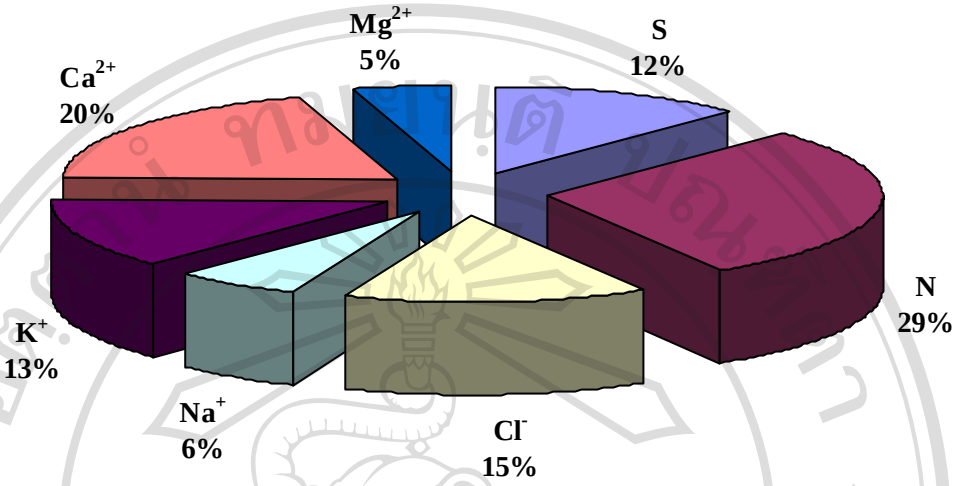

Figure 3.30 Percentage of total ion deposition during study period

Note *S = total deposition amount of sulfur compound (SO_4^{2-}, SO_2)*

N = total deposition of nitrogen compound (HNO_3, NH_3, NO_3^-, NH_4^+)

3.6.4 Comparison of deposition amount

Deposition amount calculated in this study was compared with other studies such as. Data from Research and Training in Re-Afforestation Station in Nakorn-Rachasrima Province, which was also qualified as rural site. The comparison data is shown in Table 3.13

Table 3.12 Comparison of total deposition.

Sampling site	Total Deposition amount ($\mu g/m^2$) x 10^4							
	S (SO_4^{2-}, SO_2)	**N** (HNO_3, NO_3^-)	**Cl^-**	**N** (NH_3, NH_4^+)	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Chiang Mai	10.4	25.0	12.6	17.8	5.11	11.5	16.9	4.0
Nakon-Rachasrima	36.9	24.6	18.8	27.2	30.8	7.1	20.0	7.5

Deposition amount of the Research and Training in Re-Afforestation Station was higher than the result of Chiang Mai particularly the major pollutants such as sulfur and nitrogen compounds. The main pollutant in Chiang Mai was nitrogen compound from vehicle combustion (HNO_3 and NO_3^-), while sulfur compound from fossil fuel burning was the major pollutant in the comparison site.