CHAPTER 3

RESULTS AND DISSCUSSION

Rainwater samples have been collected for one year starting from August 2005 to July 2006 by bulk and wet-only collectors at Mea Hia Research Center, Chiang Mai University, Chiang Mai, Thailand. Their precipitations as well as physical and chemical compositions including rainwater precipitations, electro-conductivity (EC), pH, major anions (Cl^-, NO_3^- and SO_4^{2-}) and major cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were measured and analyzed.

3.1 Comparison of rainwater precipitations

During August 2005 to July 2006, 122 rainwater samples were collected from each of two types of collectors. One is wet-only collector which consists of polyethylene (PE) bucket (Ø = 288 mm), a sensor and a lid and the other one is bulk collector which consists of a PE bottle and a PE funnel (Ø = 196 mm). A rain gauge was used as a standard collector to collect rain precipitation in this study. In order to check its efficiency of rain collector, water was pour into the rain gauge to reach levels of 1.0, 3.0 and 6.0 mm. Water at each level was weighed using analytical balance and the whole step was repeated for another 2 times. Their average values were calculated and converted into percent collection efficiency (%CE) as shown in Table 3.1. The result showed that %CE of the rain gauge was very high (94 – 109%).

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Table 3.1 The efficiency for collection rain precipitation of rain gauge

Weight of water (g)	Calculation amount of ppt.* M (mm)[a]	Amount of ppt.* R (mm)[a]	%CE (M/R)
8.38	1.1	1.0	109
7.23	0.9	1.0	94
7.72	1.0	1.0	100
22.62	2.9	3.0	98
22.84	3.0	3.0	99
22.79	3.0	3.0	99
45.96	6.0	6.0	100
46.44	6.0	6.0	101
46.05	6.0	6.0	100

[a] mm were calculated from weight of precipitation (g) as [100*(g)/¶r^2]*10

* ppt. is precipitation

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Table 3.2 Average of rainwater precipitation obtained from rain gauge, bulk and wet-only collectors

Months	Amount of precipitation (mm*)		
	Rain gauge[a]	Bulk collector	Wet collector
August 05	131.5	120.8	124.1
September 05	530.3	491.7	516.4
October 05	167.5	183.0	183.0
November 05	71.4	69.0	72.1
December 05	18.7	17.7	17.9
January 06	-	-	-
February 06	-	-	-
March 06	14.2	12.7	12.8
April 06	160.8	155.5	162.4
May 06	212.0	197.8	205.8
June 06	202.7	202.8	215.5
July 06	240.0	229.3	233.7
Total (mm)	**1749.1**	**1713.3**	**1743.6**

- No precipitation
[a] Diameter of rain gauge = 99 millimeters
* mm were calculated from weight of precipitation (g) as [100*(g)/¶r^2]*10

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Table 3.2 reveals average of rain precipitations in each month obtained from three types of collector (rain gauge, bulk and wet-only collectors) during the study period. Of those, the relative precipitations of rain in a descending order were rain gauge > wet collector > bulk collector. The total values of precipitations (annual rain) were 1749.1, 1743.6 and 1713.3 mm, respectively. The different data might occur form evaporation of rainwater and flow distortion depends on design of collector. The bulk collector was designed as non-cover container. So, the amount of rainwater was decreased because of evaporation during daytime.

Table 3.3 Evaporation of rain precipitation from bulk collector

Date	(pre-weight) (g)	(post-weight) (g)	weight loss (g)	mm loss*	Site $^{(a,b)}$
16/5/50	1389.78	1382.19	7.59	0.3	a
16/5/50	1350.31	1342.60	7.71	0.3	a
16/5/51	1364.85	1357.01	7.84	0.3	a
17/5/50	450.26	440.31	9.95	0.3	a
17/5/50	477.29	468.26	9.03	0.3	a
17/5/50	402.00	389.40	12.60	0.4	a
18/5/50	437.46	433.46	4.00	0.1	b
18/5/50	490.30	486.22	4.08	0.1	b
18/5/50	468.92	464.78	4.14	0.1	b

[*] mm were calculated from weight of precipitation (g) as [100*(g)/¶r^2]*10
[a] at the sampling site (outdoor)
[b] in the laboratory (indoor)

Table 3.3 illustrates evaporation of rain from bulk collector. Furthermore, it was found that the amount of rainwater in the bulk collector was less than that in the

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rain gauge. The amount of rainwater in the wet-only collector was quite stable. The reason might be from its design which its cover always close when no precipitation. So the problem with evaporation was hardly occurred as happen with a bulk collector, but might be occurred from water drop that was retained at the inner wall of the bucket.

Although the amount of rain precipitations which collected from those collectors were different, but they hove no significant difference ($p < 0.05$) among the amount of precipitation collected by those ones in statistic test (Table 3.4). The parametric test (RCB) was chosen for calculation the difference between three types of collectors due to variances of those dataset were not different.

Table 3.4 RCB test for equality of precipitation amount from three types of collectors

RCB test	F statistic	Significance, *p**
	0.008	0.992

* Statistically significant where *p* is less than or equal to 0.05

3.2 Measurement of Acidity and Electro Conductivity

3.2.1 pH of rainwater samples

The simply way to measure acidity of rainwater can be done by pH (potential hydrogen) measurement. The acid precipitation refers to any precipitate form which has pH lower than 5.6. Among 122 rainwater samples, 115 bulk samples and 117 wet-only samples were measured for pH, while the amount of precipitation of the rest were

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too low (< 0.5 mm in rain gauge). Temporal variability of monthly volume weighted mean pH values in bulk and wet precipitations are illustrated in Figure 3.1.

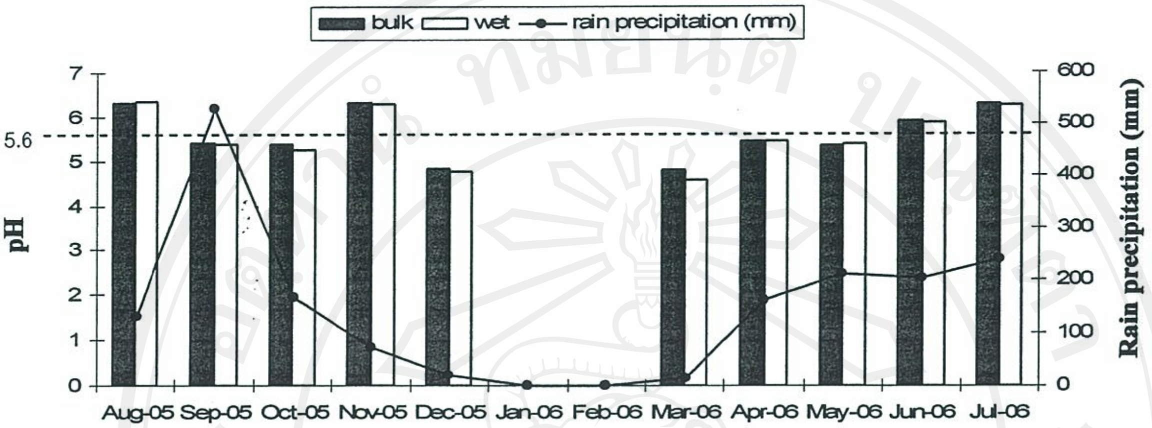

Figure 3.1 Temporal variation of pH in bulk and wet precipitation

The highest pH values of bulk and wet precipitations (6.33 and 6.34, respectively) were observed in August 2005, while the lowest values of those (4.66 and 4.58, respectively) were observed in March 2006. The rain precipitation was found to be slightly acids (pH < 5.6) in 6 months during study period. Figure 3.2 shows distribution of pH values obtained from both collectors. It was found that 26 % of bulk samples (n = 115) has pH lower than 5.6. The pH volume weight mean value of bulk samples was 5.5. In wet-only samples (n = 117), 73% of the samples had pH more than 5.6, while the rest were acidic (Figure 3.2). The volume weight mean value of wet-only samples was 5.48.

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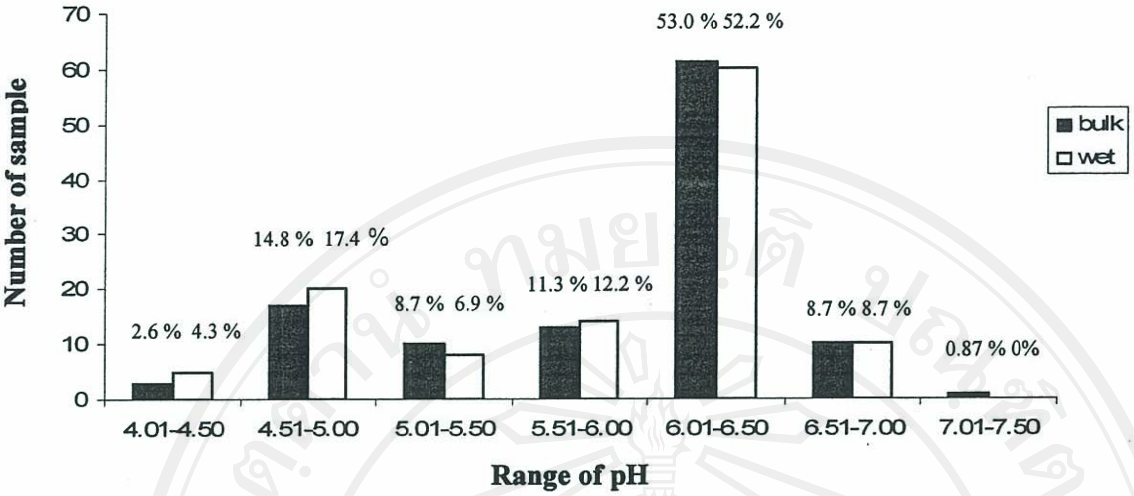

Figure 3.2 Distribution of pH values of bulk samples (n = 115) and wet-only samples (n = 117)

3.2.2 Electro-conductivity (EC)

Electro-conductivity or EC value indicates level of ionic contamination in water. High EC value indicates high ionic contamination, EC value of deionized water is normally less than 0.15 mS/m. Number of rain samples obtained from bulk and wet-only collectors, which could be measured for EC were 115 and 113, respectively. The mean EC values were 0.69 and 0.65 mS/m for bulk and wet-only samples, respectively (see more detail in appendix A). The maximum detected EC values for bulk and wet-only samples were in March 2006 (3.54 and 3.39 mS/m, respectively) whereas the minimum of those were in July 2006 (0.32 and 0.30 mS/m, respectively).

Figures 3.3 and 3.4 show the amount of rain precipitation and frequency of rain affected to the EC values of the samples. It can be seen that high frequency of rainfall and high amount of precipitation resulted in low EC values, while low amount of those resulted in opposite.

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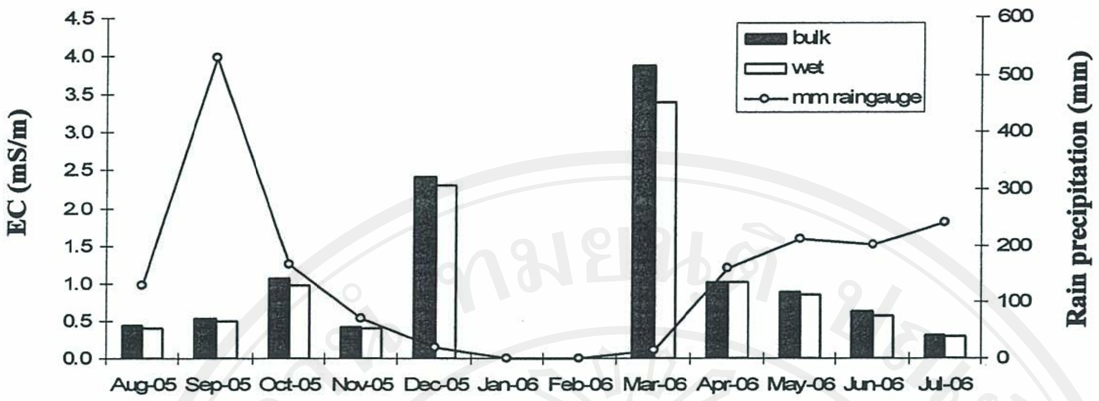

Figure 3.3 Monthly median EC vales from August 2005 to July 2006

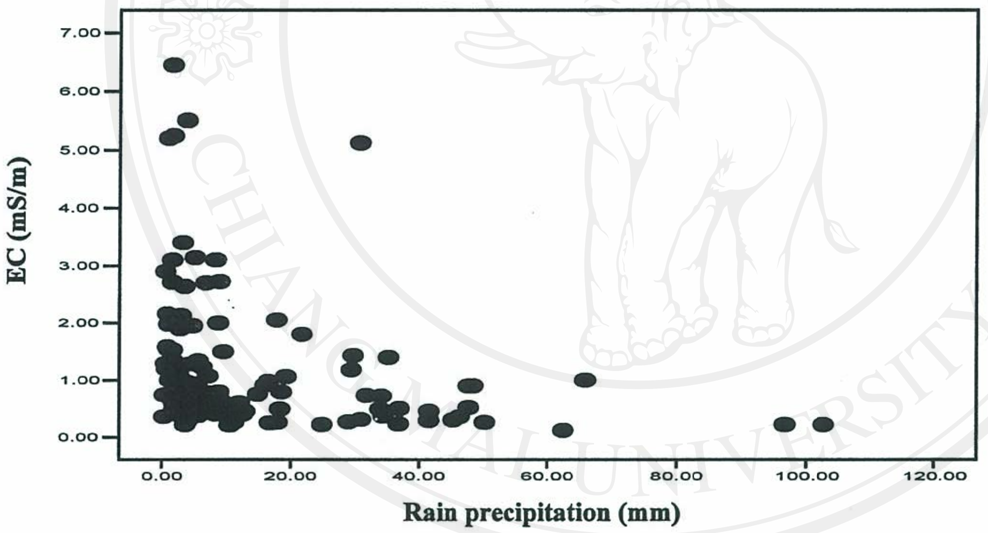

Figure 3.4 Relation between electro conductivity and amount of precipitation

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In dry season that had low frequency of precipitation such as in December 2006 and March 2006 (5 and 2 days, respectively), the mean EC values were lower than the others as shown in Figure 3.4. It 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, these pollutants were scavenged or eluted from the atmosphere.

Consequently, in the rain itself contains high concentrations of the pollutants. Figure 3.4 reveals that amount of precipitation is invert with EC values, which means that high precipitation, results in low EC value. On the other hand, low precipitation, causes high EC value due to dilution effect.

3.3 Measurement of Ion Concentration 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 Cl^-, NO_3^- and SO_4^{2-} and cations including Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} were analyzed by ion chromatograph. Chromatograms of mixed ion standards are shown in Figures 3.5 and 3.6.

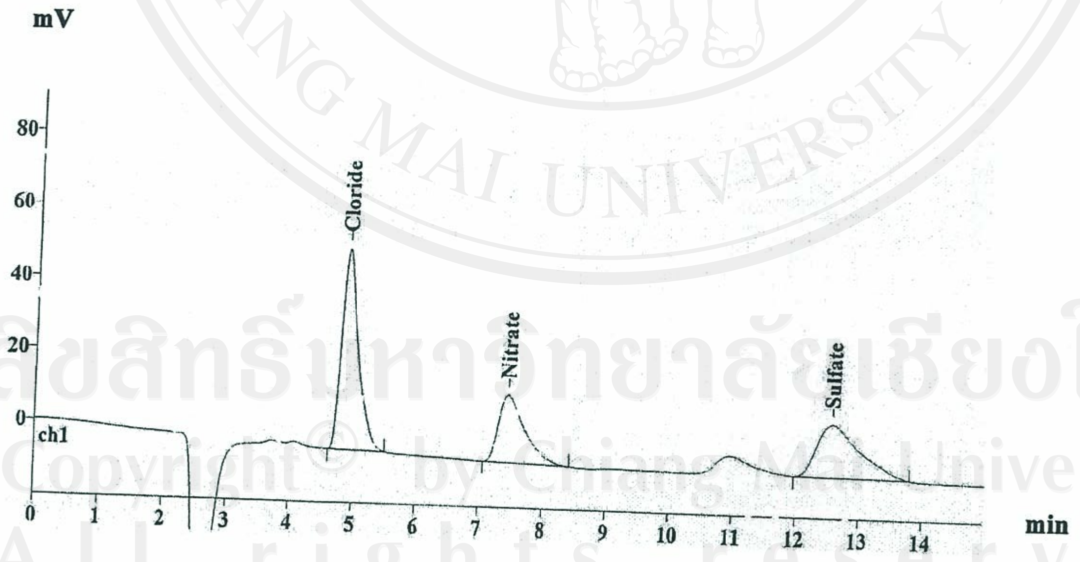

Figure 3.5 Chromatogram of 0.8 μg/mL mixed anions standard

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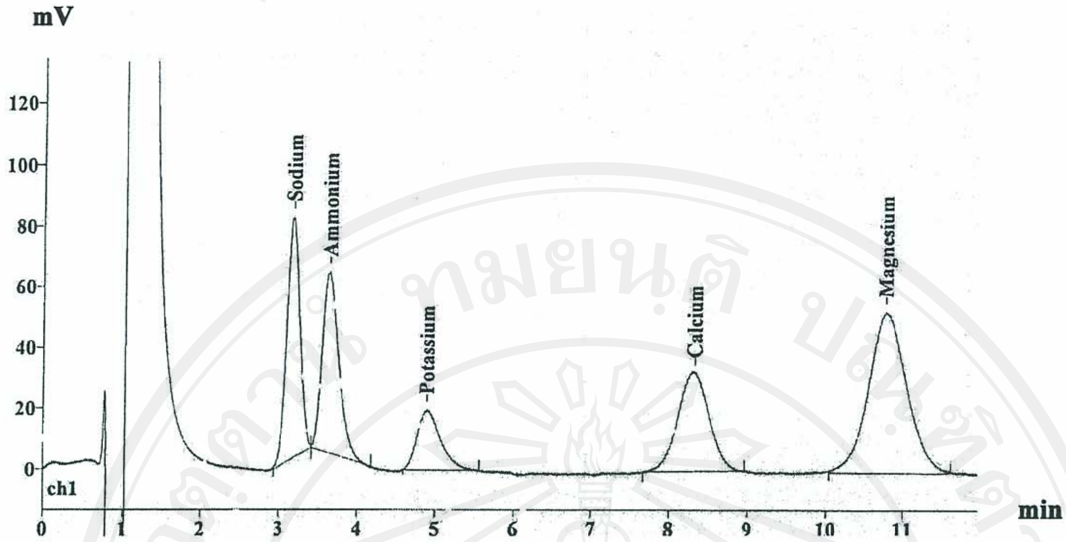

Figure 3.6 Chromatogram of 0.8 μg/mL mixed cations standard

3.3.1 Calibration curve of ion analysis

In each analytical run, 6 concentrations (0.2 – 1.0 μg/mL) for anions and 7 concentrations (0.1 – 1.0 μg/mL) for cations of calibration standard were prepared and analyzed by IC. The calibration curve of each ion standard was constructed by concentrations of standard solution versus peak area. Concentration ranges depend on concentration of ions by covered at least 95% of ion concentration of samples, whereas the regression value was controlled at $r^2 \geq 0.995$. The calibration curves of each ion are shown in Figure 3.7.

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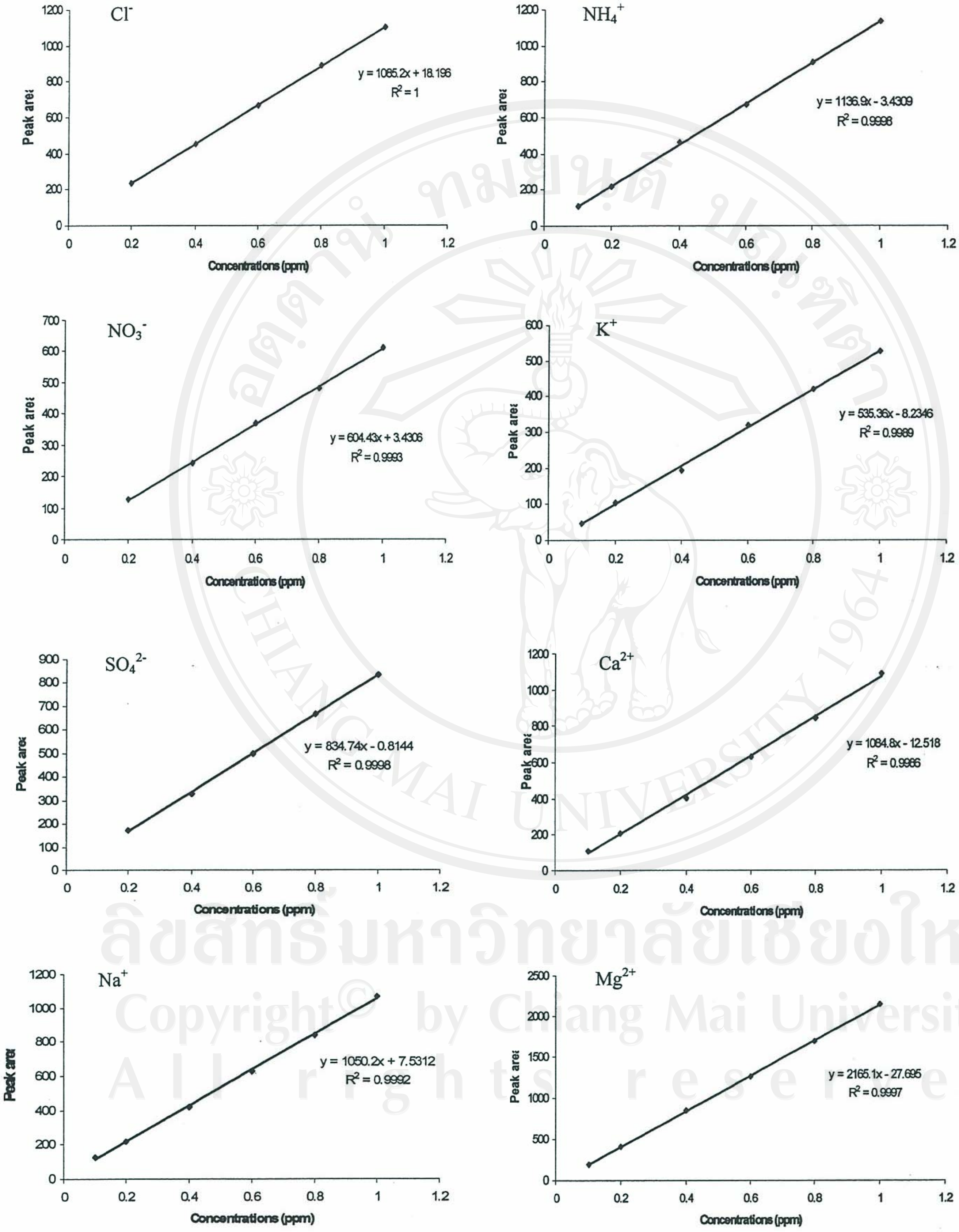

Figure 3.7 Calibration curves of each ion and their equation

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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 shot time period (see topic 2.8 a). The repeatability of ion chromatograph is shown in Table 3.5.

b) Reproducibility

The reproducibility was checked by injecting a 0.4 ppm mixed standard solution (see topic 2.8 b). The results of reproducibility were estimated by relative standard deviation (%RSD) and the related values as shown in Table 3.6

3.3.2 Limits 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 7 injections of 0.1 ppm standard solution. Their concentrations were calculated from the calibration curve in ranges of 0.2 to 1.0 ppm for anions and 0.1 to 1.0 ppm for cations. Limit of detection of all analytes of values are shown in Table 3.7.

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3.3.3 Analytical performance

The accuracy of chemical analysis was done by analysis of the artificial rainwater provided from the Inter-laboratory comparison project 2005 under the Acid Deposition Monitoring Network in East Asia (EANET) (2005 Round Robin Analysis

Survey). Accuracy of the analysis was considered from the results in comparison with prepared values. The selected artificial rainwater was number 052 (low concentration), serial number 79. 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 results are shown in Table 3.8.

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Table 3.5 Repeatability of ion chromatograph

No. of injection	Concentrations (μg/mL)							
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.412	0.410	0.420	0.409	0.394	0.394	0.436	0.421
2	0.412	0.407	0.418	0.410	0.399	0.427	0.414	0.424
3	0.409	0.408	0.417	0.416	0.414	0.413	0.423	0.414
4	0.409	0.405	0.417	0.418	0.424	0.434	0.409	0.418
5	0.410	0.405	0.416	0.425	0.410	0.403	0.414	0.426
6	0.418	0.408	0.415	0.419	0.402	0.401	0.421	0.423
7	0.405	0.403	0.414	0.414	0.399	0.416	0.420	0.415
Average	**0.411**	**0.407**	**0.417**	**0.416**	**0.406**	**0.413**	**0.420**	**0.420**
Standard Deviation (SD)	**0.004**	**0.002**	**0.002**	**0.005**	**0.010**	**0.014**	**0.009**	**0.005**
Relative Standard Deviation (%RSD)	**0.971**	**0.583**	**0.474**	**1.327**	**2.587**	**3.498**	**2.082**	**1.094**

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Table 3.6 Reproducibility of ion chromatograph

No. of injection	Concentrations (μg/mL)							
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.405	0.401	0.419	0.401	0.397	0.398	0.427	0.418
2	0.398	0.402	0.418	0.405	0.399	0.415	0.414	0.421
3	0.402	0.408	0.416	0.403	0.403	0.411	0.425	0.415
Average	**0.402**	**0.404**	**0.418**	**0.403**	**0.400**	**0.408**	**0.422**	**0.418**
Standard Deviation (SD)	**0.004**	**0.004**	**0.002**	**0.002**	**0.003**	**0.009**	**0.007**	**0.003**
Relative Standard Deviation (%RSD)	**0.874**	**0.938**	**0.366**	**0.496**	**0.764**	**2.178**	**1.659**	**0.718**

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Table 3.7 Limits of detection of IC (Metrohm) for each ion

Analysis times	Concentrations (µg/mL)							
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.092	0.098	0.103	0.093	0.103	0.106	0.102	0.112
2	0.089	0.099	0.100	0.095	0.096	0.087	0.122	0.110
3	0.085	0.100	0.100	0.097	0.101	0.088	0.089	0.100
4	0.084	0.106	0.096	0.100	0.107	0.088	0.102	0.104
5	0.088	0.099	0.103	0.099	0.108	0.109	0.102	0.109
6	0.092	0.102	0.102	0.098	0.097	0.097	0.108	0.105
7	0.093	0.098	0.100	0.100	0.098	0.070	0.109	0.103
Average	**0.089**	**0.100**	**0.100**	**0.097**	**0.101**	**0.092**	**0.105**	**0.106**
Standard Deviation (SD)	**0.003**	**0.002**	**0.003**	**0.003**	**0.005**	**0.013**	**0.010**	**0.004**
Limit of Detection (3*SD)	**0.011**	**0.009**	**0.007**	**0.008**	**0.014**	**0.040**	**0.030**	**0.013**
Limit of Quantification (10*SD)	**0.036**	**0.029**	**0.024**	**0.026**	**0.048**	**0.132**	**0.100**	**0.043**

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Table 3.8 pH, EC and concentration of ions in artificial rainwater No. 052

Sample No. 052	pH	EC	Concentration (μmol/L)								R_1	R_2
	-	mS/m	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}		
a	5.06	1.04	14.40	13.28	15.33	13.67	10.44	2.98	7.65	3.15	-0.1	0.2
b	5.05	1.05	14.30	13.28	15.23	13.49	10.29	3.15	7.65	3.02	-0.4	-1.3
c	5.04	1.04	14.37	13.33	15.33	13.49	10.44	2.98	7.65	3.15	-0.5	0.5
Average conc.	5.05	1.04	14.36	13.30	15.30	13.55	10.39	3.04	7.65	3.11	0.0	0.2
Prepared conc.	5.05	1.05	14.40	13.20	15.30	13.60	10.30	3.00	7.60	3.10		
% difference	0.0	1.0	0.3	-0.75	0.0	0.4	-0.9	-1.3	-0.7	-0.3		

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From table 3.8, 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.

3.3.4 Compositions of rainwater samples

Major anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) concentrations contained in rainwater samples were analysed by ion chromatograph. An example of analysis chromatogram of rainwater sample for anions and cations are shown in Figures 3.8 and 3.9, respectively.

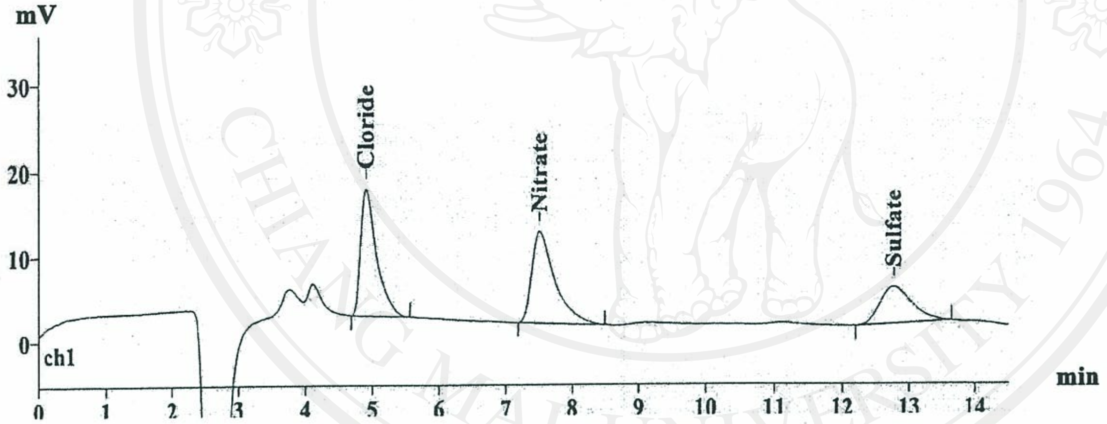

Figure 3.8 Chromatogram of anions detected in rainwater sample

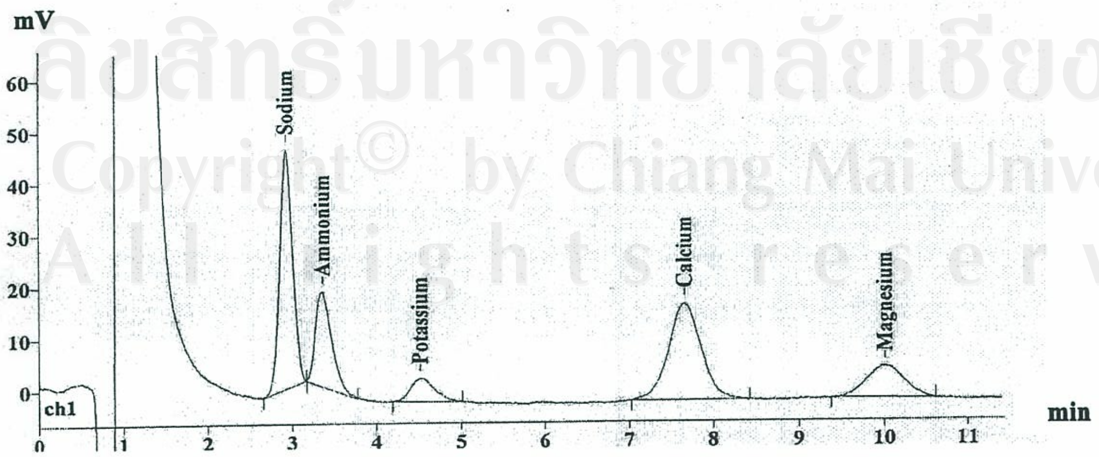

Figure 3.9 Chromatogram of cations detected in rainwater sample

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Monthly volume weighted mean concentrations of the major chemical components (N = 122) collected by bulk and wet-only collectors are summarized in Tables 3.9 and 3.10, respectively. Moreover, each ion concentration detected from both types of collectors is shown in Figures 3.10 and 3.11. It was found that most of ion concentrations in both bulk and wet-only precipitations were high in dry season (December 2005 to April 2006) due to low amount of rain precipitation, while low concentrations were found in rainy season. The highest concentrations of SO_4^{2-}, Na^+ and NH_4^+ were found in December 2005, whist those of Cl^-, NO_3^-, K^+, Ca^{2+} and Mg^{2+} were found in March 2006. On the other hand, the lowest concentrations of SO_4^{2-} (wet-only), Cl^-, Na^+, K^+ and Ca^{2+} were found in September 2005, whist SO_4^{2-} (bulk), NO_3^-, NH_4^+ and Mg^{2+} was found in July 2006 (see more detailed in Appendix A).

The total annually VWM cation concentrations were 39.7 and 34.5 μeq/L for bulk and wet-only precipitations, respectively, while those for anions were 22.2 and 19.5 μeq/L, respectively. The ratio between total cations and total anions in the unit of μeq/L from both bulk and wet precipitations during August 2005 to July 2006 is shown in Figure 3.12 and the proportion of each ion component is concluded in Figure 3.13.

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Table 3.9 Monthly volume weight means in μeq/L of the major chemical composition in rain samples from bulk collector

Month	Precipitations (mm)	Volume weighted mean concentrations (μeq/L)							
		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
August 2005 (n=16)	120.8	4.10	4.30	7.60	2.00	17.90	1.20	11.40	1.90
September 2005 (n=21)	491.7**	2.10*	4.40	5.90	0.30*	11.30	0.50*	6.10*	1.10
October 2005 (n=10)	183.0	3.50	10.30	28.70	2.20	33.50	1.10	13.10	2.50
November 2005 (n=6)	69.0	2.30	4.40	7.30	1.40	10.50	1.80	7.80	0.30
December 2005 (n=5)	17.7	14.20	40.00	68.50**	4.80**	84.50**	4.80	24.80	4.40
January 2006 (n=0)	0*	-	-	-	-	-	-	-	-
February 2006 (n=0)	0*	-	-	-	-	-	-	-	-
March 2006 (n=2)	12.7	14.60**	43.80**	54.20	4.40	66.70	12.20**	75.30**	19.10**
April 2006 (n=10)	155.5	5.30	14.50	12.90	2.60	30.70	3.60	16.50	3.60
May 2006 (n=16)	197.8	4.80	11.10	12.60	4.20	24.20	1.30	10.30	7.10
June 2006 (n=18)	202.8	4.20	6.50	8.50	4.70	17.50	3.80	14.70	1.20
July 2006 (n=18)	229.3	3.60	2.30*	5.10*	2.10	7.30*	1.10	11.90	0.70*
Total / Average (n=122)	**1713.3**	**3.70**	**7.40**	**11.10**	**2.20**	**18.80**	**1.60**	**11.60**	**2.40**

Note: - no precipitation
* min value
** max value

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Table 3.10 Monthly volume weight means in µeq/L of the major chemical composition in rain samples from wet-only collector

Month		Volume weighted mean concentrations (µeq/L)							
	Precipitations (mm)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
August 2005 (n=16)	124.1	4.10	3.80	6.70	0.90	16.70	0.50	7.70	3.10
September 2005 (n=21)	516.4 **	2.00*	4.20	2.50*	0.00*	10.30	0.10*	3.90*	1.20
October 2005 (n=10)	183.0	3.10	8.30	23.80	1.70	27.30	0.40	7.90	1.60
November 2005 (n=6)	72.1	2.00*	4.20	7.00	1.20	8.20	1.60	7.20	0.80
December 2005 (n=5)	17.9	13.50	37.80	64.10**	4.30	73.20**	4.40	21.00	3.20
January 2006 (n=0)	0*	-	-	-	-	-	-	-	-
February 2006 (n=0)	0*	-	-	-	-	-	-	-	-
March 2006 (n=2)	12.8	14.00*	41.50**	48.50	4.30	60.00	11.00**	53.80**	13.10**
April 2006 (n=10)	162.4	5.20	14.00	12.60	1.90	30.20	4.60	15.10	4.20
May 2006 (n=16)	205.8	4.70	10.40	12.40	4.40**	23.70	1.00	7.50	6.80
June 2006 (n=18)	215.5	3.60	6.30	7.30	3.40	16.40	3.40	15.90	0.80
July 2006 (n=18)	233.7	3.30	2.20*	5.50	1.30	6.90*	0.60	11.90	0.70*
Total / Average (n=122)	**1743.6**	**3.50**	**6.80**	**9.20**	**1.60**	**17.10**	**1.30**	**8.90**	**2.30**

Note: - no precipitation
* min value
** max value

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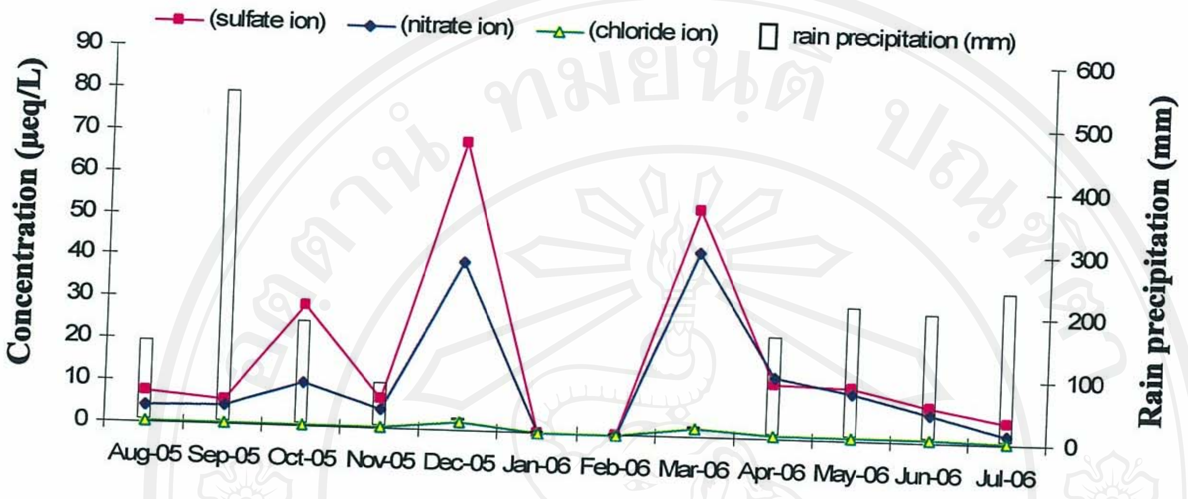

(a)

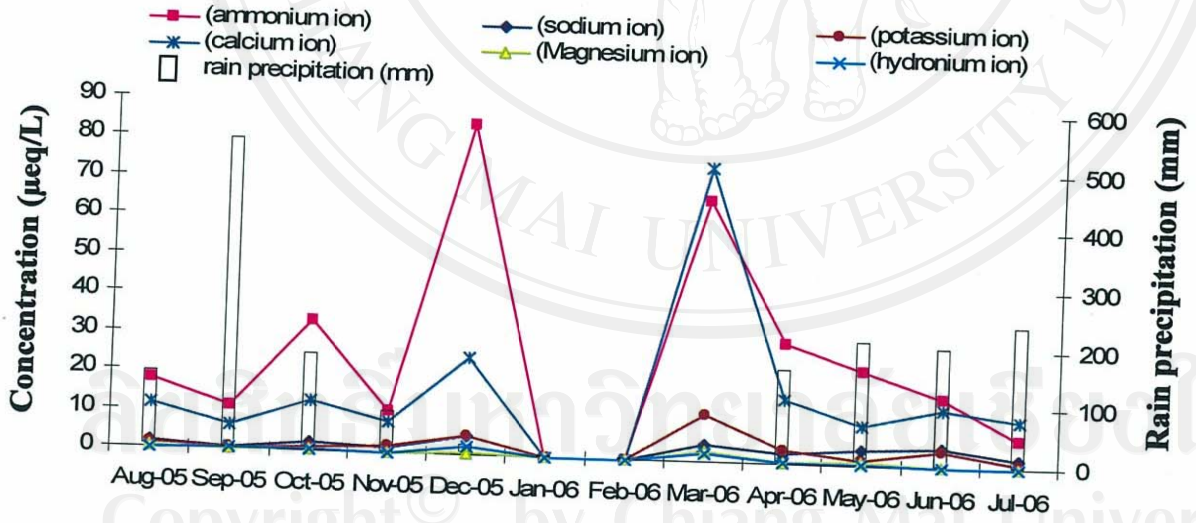

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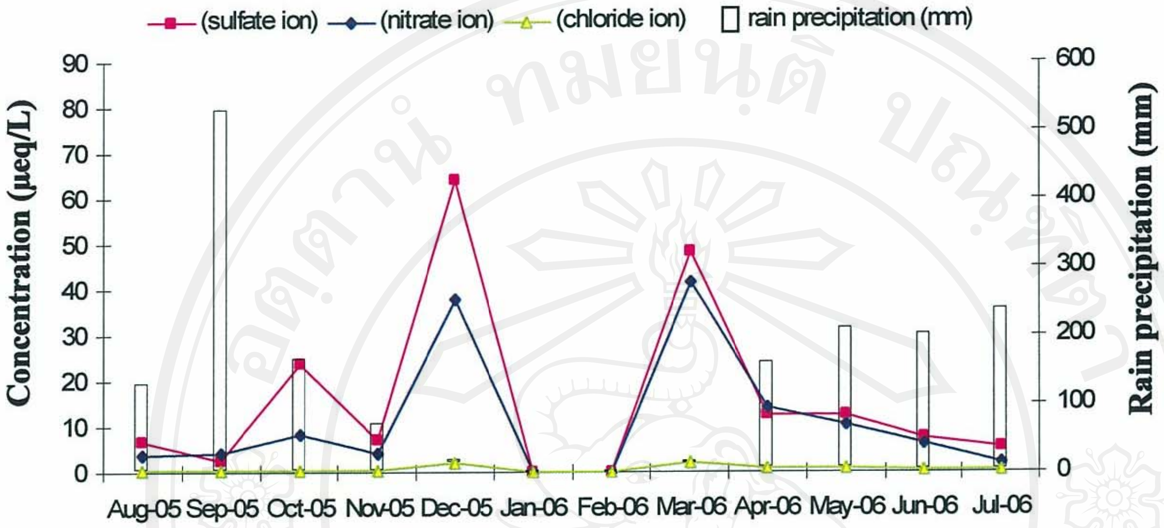
Figure 3.10 Monthly average variability of rain precipitation, (a) major anion concentrations and (b) cation concentrations in bulk precipitation



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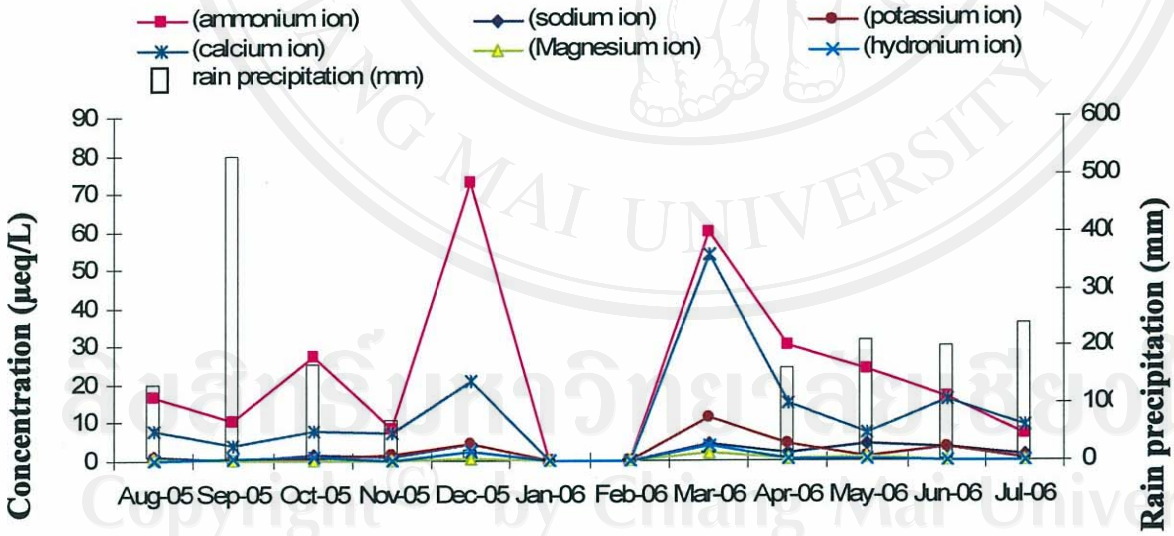

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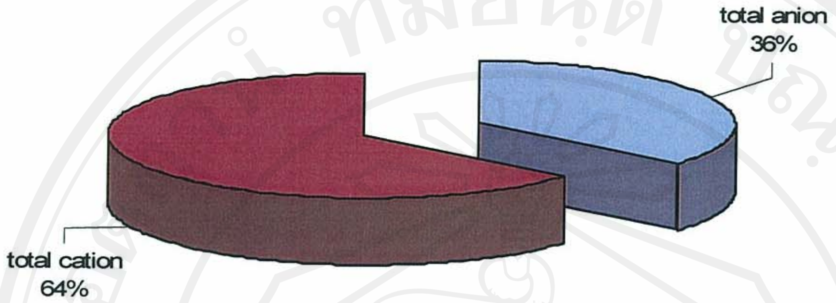
Figure 3.11 Monthly average variability of rain precipitation, (a) major anion concentrations and (b) cation concentrations in wet-only precipitation



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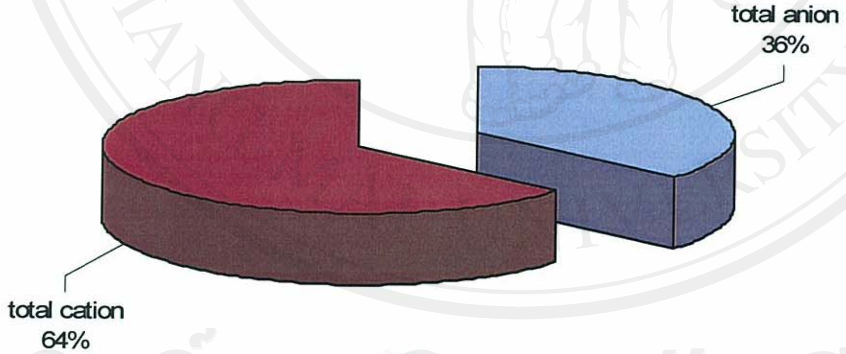

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Figure 3.12 Relative of percentage of total caions and anions base on unit of μeq/L from (a) bulk precipitation and (b) wet-only precipitation

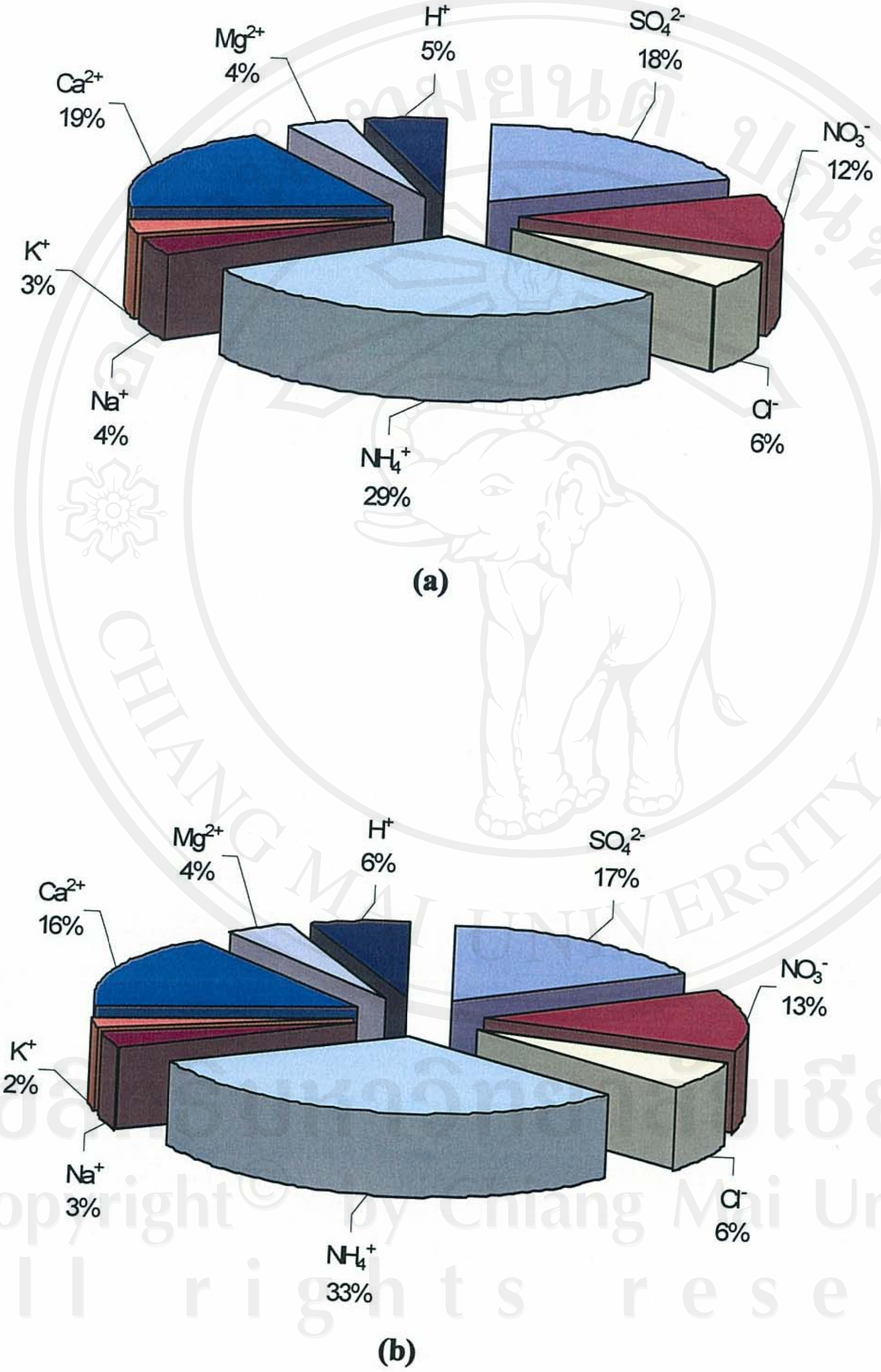

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Figure 3.13 Percentage of ions (μeq/L) in (a) bulk precipitation and (b) wet-only precipitation

3.4 Comparison of sampling collectors

Ion concentrations detected in rainwater samples collected from both bulk and wet-only collectors were compared. Mean ion concentrations in both types of samples were calculated as precipitation volume weighted means (VWM). Scatter plots of wet-only against bulk concentration measurements for each ion were constructed. After that, parametric test (Paired sample t-test) was performed to test differences of each pair of ion concentrations between the two collector types.

3.4.1 Mean ion concentrations

The ion concentrations of rainwater samples from Aug 2005 to July 2006 are shown in Figure 3.14.

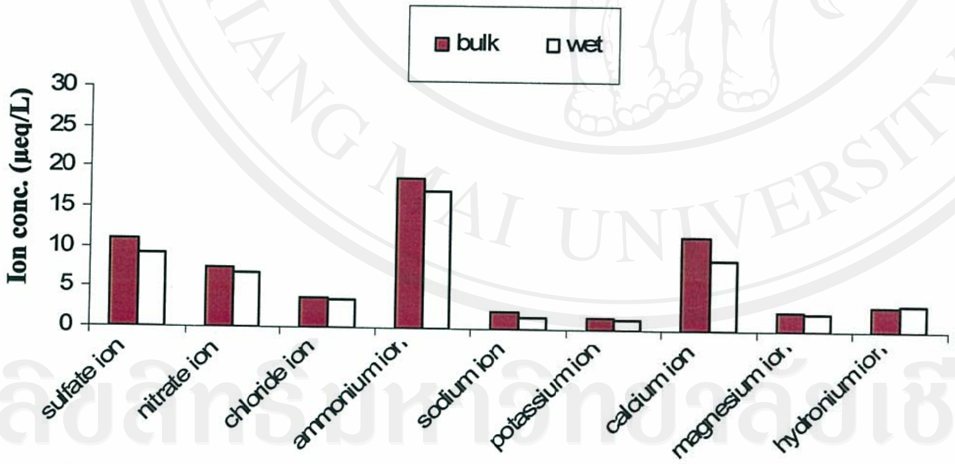

Figure 3.14 Concentrations of major ions in rainwater from August 2005 to July 2006

The order of relative ion concentrations of rainwater samples from bulk and wet-only collectors were similar. The relative VWM concentrations of anions and cations in a descending order were $SO_4^{2-} > NO_3^- > Cl^-$ and $NH_4^+ > Ca^{2+} > H^+ > Mg^{2+} > Na^+ > K^+$.

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The calculated VWM ion concentrations were higher in bulk precipitations than in wet-only for all ions except H^+ (Table 3.11). Ratios of ion concentrations (bulk over wet-only precipitations), in descending order was $Na^+ > Ca^{2+} > K^+ > SO_4^{2-} > NH_4^+ > NO_3^- > Cl^- > Mg^{2+} > H^+$. Relatively high difference was found in Na^+, Ca^{2+}, K^+ and SO_4^{2-} ratios, which their VWM concentrations were 1.37, 1.30, 1.23 and 1.21, respectively. The ratio of the VWM concentrations illustrated figures, which greater than 1. This may be resulted from turbulent deposition of gases and fine particles which could have been resuspended by the wind to a continuously-open sampler (bulk collector). On the other hand, the concentration of H^+ in bulk samples was lower than that in wet-only samples. It might be occurred from soil particles blown into the bulk collector by the wind and react with H^+ in the sample and release cations into the sample. This weathering reaction increases the concentration of cations and decreases the concentration of H^+ relative to samples collected with the wet-only collector (Ranalli *et al*., 1997).

Table 3.11 VWM concentrations of rainwater samples of bulk and wet-only collector and their ratios

Type of collectors	VWM concentrations (μeq/L)								
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	H^+
Bulk	3.70	7.40	11.10	2.20	18.80	1.60	11.60	2.40	3.10
Wet-only	3.50	6.80	9.20	1.60	17.10	1.30	8.90	2.30	3.30
Ratio (bulk/wet)	1.06	1.09	1.21	1.37	1.10	1.23	1.30	1.04	0.94

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3.4.2 Scatter plots of ion concentrations of bulk and wet-only precipitations

Scatter plot was used for comparison of ion concentrations obtained from bulk and wet-only precipitations. Each ion was separately plotted as shown in Figures 3.15 - 3.16. Every ion showed lower concentrations in bulk precipitations, which can be seen from the points under diagonal. The results agreed very well with the ratio of bulk/wet-only concentrations (Table 3.11).

3.4.3 Statistic test

Rainwater composition and properties such as pH, EC and major ion concentrations of both bulk and wet-only collectors were analyzed and compared. The Homogeneity's test was not rejects the null hypothesis of equality of error variances at the 0.01 confidential level. Consequently, differences between the average sample populations were tested using parametric test at (Paired sample t-test). The statistical differences between data form the bulk and the wet-only precipitation in μeq/L and μmol/m^2 collectors are shown in Table 3.12 and Table 3.13

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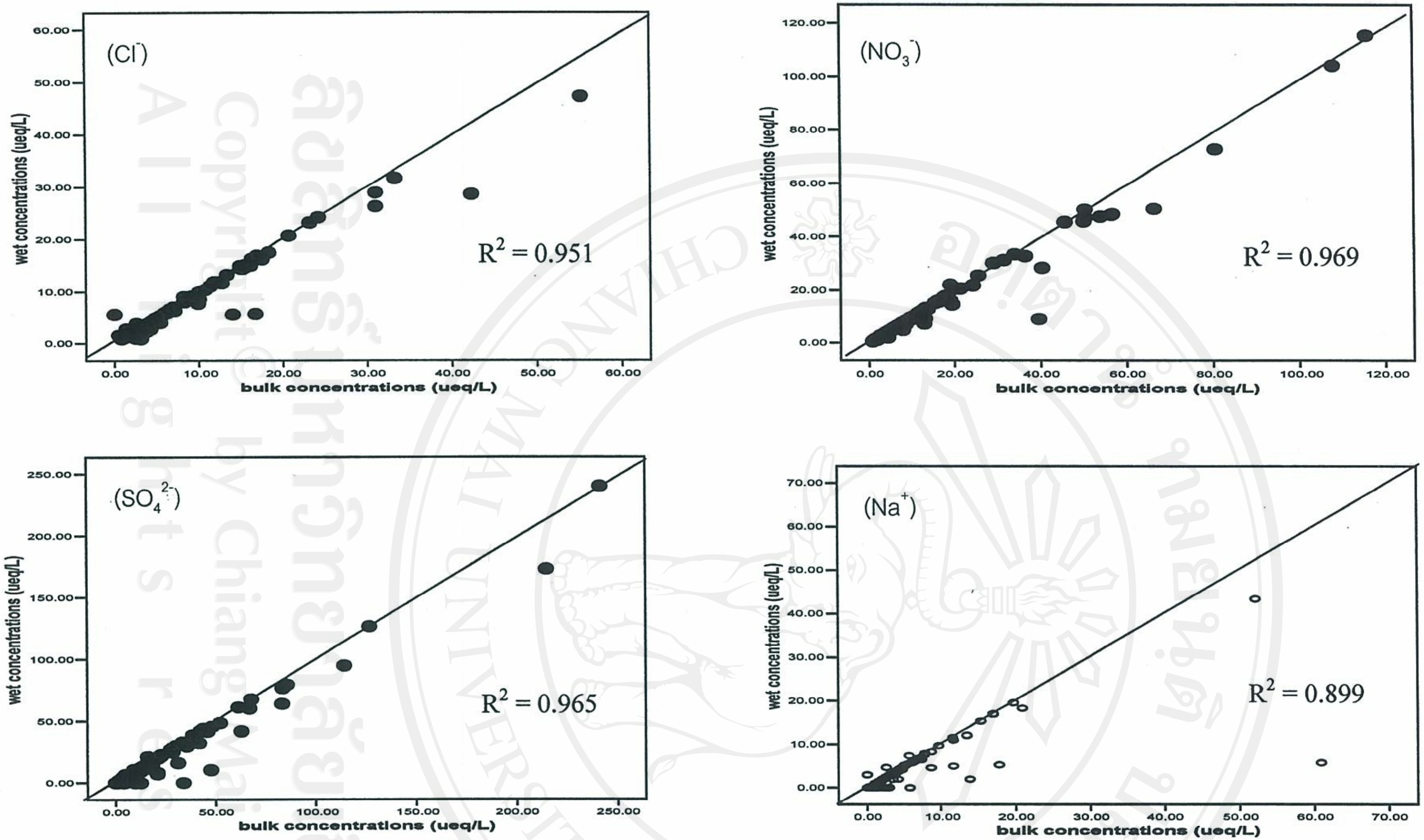

Figure 3.15 Scatter plots between bulk and wet-only concentrations of Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and Na$^+$

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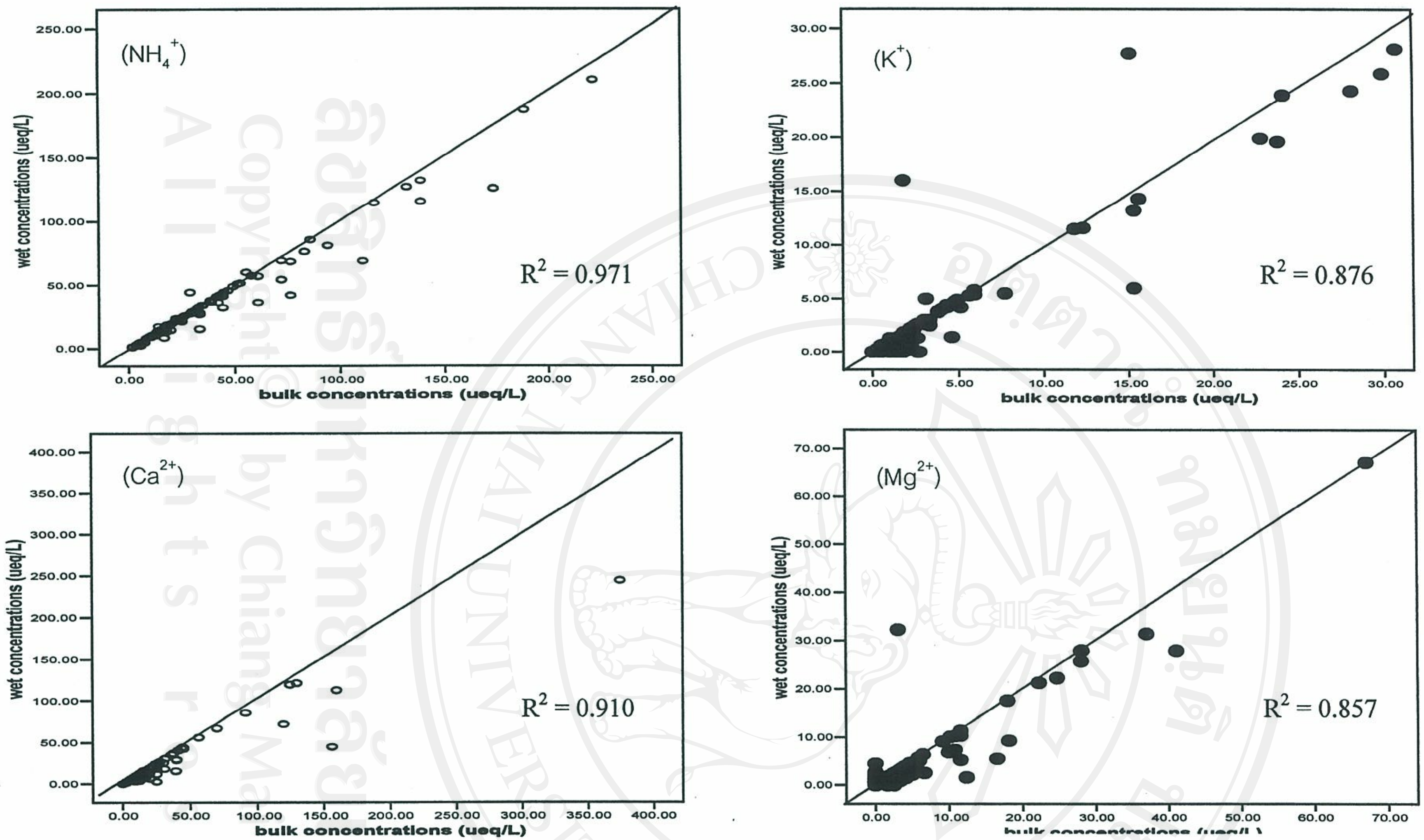

Figure 3.16 Scatter plots between bulk and wet-only concentrations of NH_4^+, K^+, Ca^{2+} and Mg^{2+}

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Table 3.12 VWM values of pH, EC and ion concentrations (μeq/L) of bulk and wet-only concentrations

Parameter	Wet-only	Bulk	Lavene's test[a]	*p*-value
pH[b]	5.48	5.52	**0.355**[c]	0.001
EC (mS/m)	0.65	0.69	**0.624**[c]	<0.001
Cl^-	3.50	3.70	**0.426**[c]	0.002
NO_3^-	6.80	7.40	**0.585**[c]	<0.001
SO_4^{2-}	9.20	11.00	**0.623**[c]	<0.001
Na^+	1.60	2.20	0.179	0.016
NH_4^+	17.10	18.60	**0.563**[c]	<0.001
K^+	1.30	1.60	0.994	0.095
Ca^{2+}	7.70	10.30	**0.299**[c]	0.001
Mg^{2+}	4.30	4.20	0.633	0.166

[a] Test the null hypothesis that the error variance of dependent variable is equal or not across groups
[b] pH-value were calculated as the negative logarithm of the corresponding VWM H^+
[c] Figure in bold indicate statistically significant where *p* is less than or equal to 0.01

Table 3.13 Ionic deposition of ion species (μmol/m^2) of bulk and wet-only concentrations

Parameter	Wet-only	Bulk	Lavene's test[a]	*p*-value
H^+	5749	5262	0.805	0.039
Cl^-	6076	6488	0.568	0.066
NO_3^-	11959	13013	**0.580**[b]	<0.001
SO_4^{2-}	8021	9705	**0.212**[b]	0.005
Na^+	2867	3790	**0.252**[b]	<0.001
NH_4^+	29877	32854	**0.480**[b]	<0.001
K^+	2320	2883	0.547	0.047
Ca^{2+}	7767	10119	**0.023**[b]	<0.001
Mg^{2+}	2017	2078	0.797	0.663

[a] Test the null hypothesis that the error variance of dependent variable is equal or not across groups
[b] Figure in bold indicate statistically significant where *p* is less than or equal to 0.01

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According to the pair tests, VWM concentrations of all components from bulk precipitation were significantly differences ($p<0.01$) from wet-only precipitation, except Na^+, K^+ and Mg^{2+}, while ionic deposition in μmol/m^2 unit of those ion were significantly different at 99% confidential level, except H^+, Cl^-, K^+ and Mg^{2+}.

Pair sampled t-test is a statistic which can be used to compare single ion between two collector types but it can not be used to conclude that whether or not bulk collector can be used instead of wet-only collector. In order to draw the conclusion, Multivariate Analysis of Variance (Manova) was chosen to answer this hypothesis. Manova is the technique that uses to analyze many variances of the quantitative factor (dependent variable) at the same time (multivariate test) which is in the General Linear Model. The limits of Manova are; (i) each pair of samples has to be correlated with each other (Bartlett's test of Sphericity was performed) and (ii) variance-covariance matrices of dependent variable in each group must not different (Box's test of Equality of Covariance Matrices was performed). The result from Manova is shown in Table 3.14.

Table 3.14 Multivariate test (*p*=0.01)

Statistic test	Significant (%)
Box's Test of Equality of Covariance Matrix[a] (Box's M)	0.752
Bartlett's Test of Spherical[b]	0.000
Multivariate Test (Pillai's Trace)[c]	0.763

[a] Tests the null hypothesis that the observed covariance matrices of the dependent variables are equal across group

[b] Test the null hypothesis that the residual covariance matrix is proportional to an identity matrix

[c] Used Pillai's Trace according to the result from Normality's test which each pair of ions are not normal distribution

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According to Box's M and Bartlett's test of Spherical, variance-covariance matrices of dependent variable in each group were not different and each pair of ion concentrations was correlated together (p=0.01). From the result of both statistic tests, Manova can be performed to compare the efficiency of bulk and wet-only collectors in this study. From Table 3.14, multivariate test revealed that the efficiency from both types of collector were not significantly different (p=0.01). So, it can be deduced that bulk collector can be used instead of wet-only collector at the study site mentioned in Chapter 2.

3.5 Comprehensive analysis

3.5.1 Data screening

Comprehensive analysis such as neutralization factor (NF), sea salt fraction (SSF) or marine contribution, Pearson correlation and source analysis 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 topic 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 bulk samples, about 44% of R_1 and 71% of R_2 values have met the criteria. While in wet-only samples, about 40% of R_1 and 67% of R_2 were accepted. Ion and conductivity balances of bulk and wet-only samples are shown in Figures 3.17 and 3.18, respectively.

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Among 122 rain samples of this study, about 6% of bulk samples and 4% wet-only samples had too small volume to perform the chemical analysis. Therefore, 115 and 115 samples of bulk samples and 113 and 117 of wet-only samples were measured for EC and pH, respectively as well as analysed for ion concentrations. After validation, 42 bulk and 31 wet-only samples were qualified for both R_1 and R_2 (see detailed in Appendix B). Figures 3.17 c and 3.18 c revealed that majority of bulk and wet-only samples were not met the criteria due to some anions such as $HCOO^-$, CH_3COO^-, F^-, PO_3^{2-} etc. were not analysed (total cations > total anions).

Table 3.15 shows annual volume weighted means (VWM) in μeq/L of the major chemical composition in rain precipitation. The total bulk concentration of anions and cations were 2065 and 2118 μeq/L, respectively. While those of the total wet-only concentrations were 1578 and 1547 μeq/L, respectively. Cation concentrations were higher than anion concentrations in both kinds of samples. From the table 3.15, the dominant ion with large concentration was NH_4^+. Its value in bulk samples was 17.7 μeq/L and in wet-only samples was 16.0 μeq/L. The relatively high concentration of NH_4^+ was contributed from agricultural activities around the sampling site. The ratios of NO_3^- and SO_4^{2-} concentrations in the rainwater from August 2005 to July 2006 were 0.64 and 0.57 for bulk and wet-only precipitations, respectively. They indicated that the contributions of H_2SO_4 and HNO_3 to the acidity of precipitation were about 40% and 60%, respectively.

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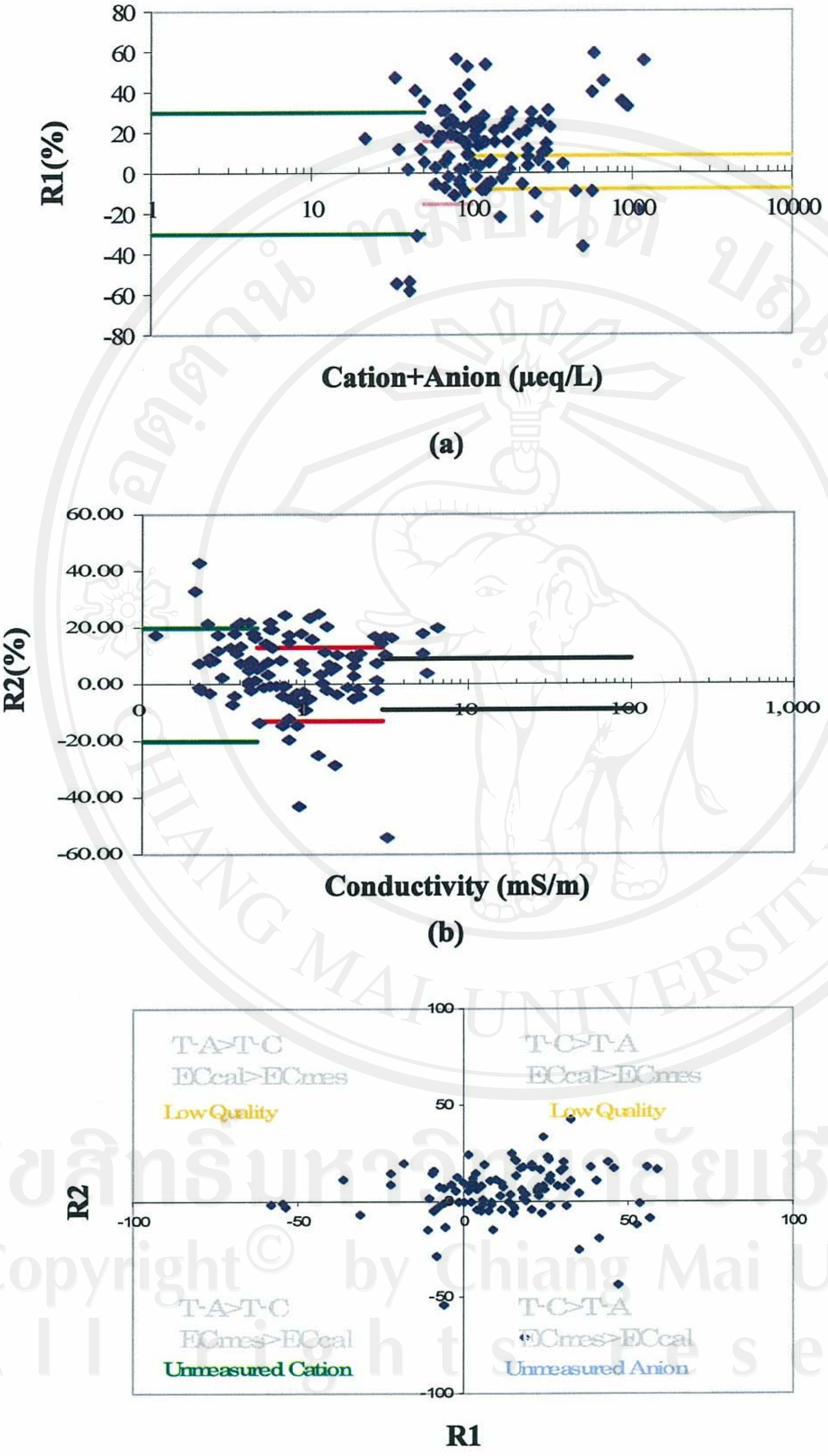

(a)

(b)

(c)

Figure 3.17 Values of R_1 and R_2 of bulk samples (a) Distribution of R_1 (ion balance), (b) R_2 (conductivity balance) and (c) R_1 and R_2 relation

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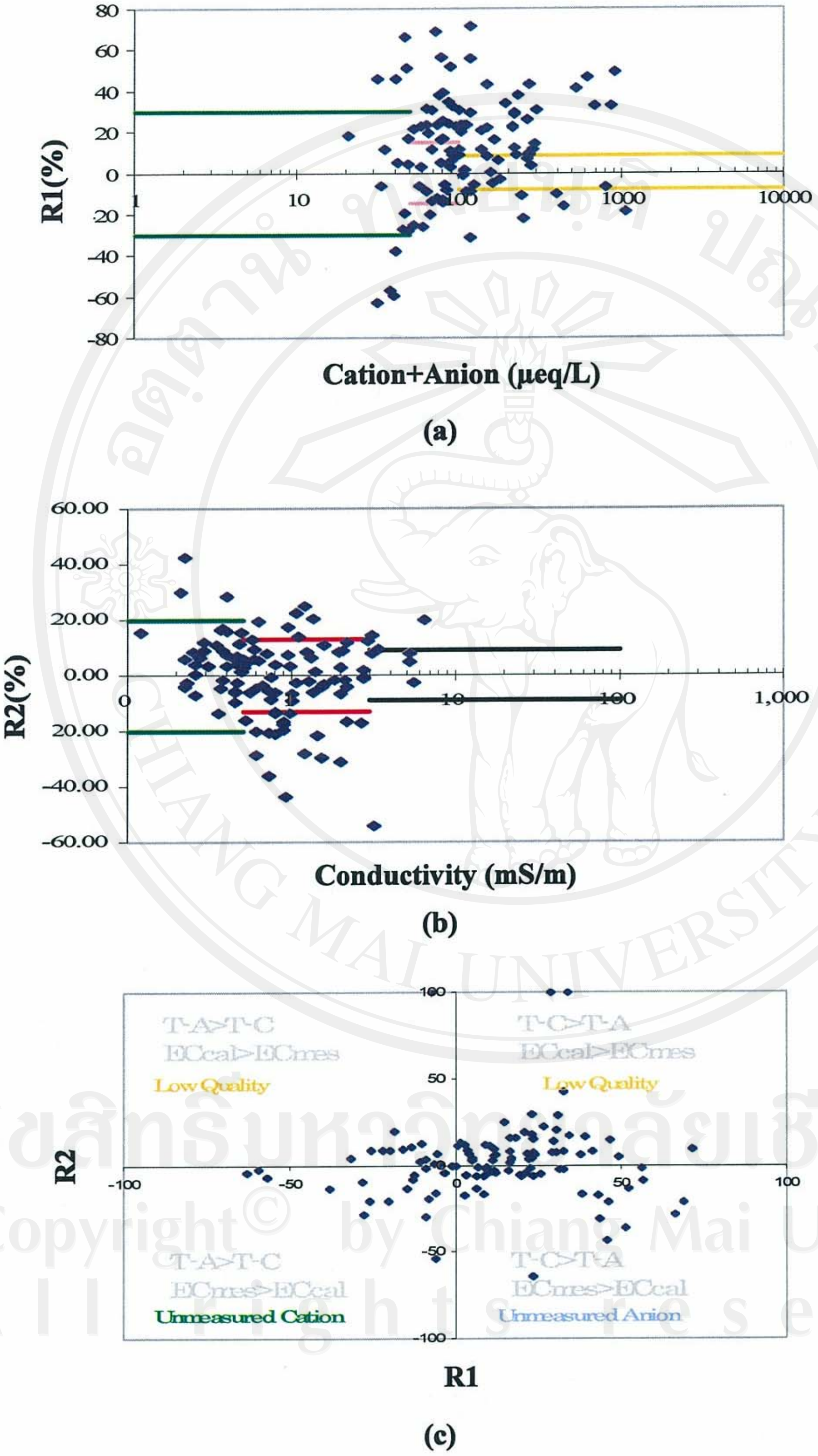

Figure 3.18 Values of R_1 and R_2 of wet-only samples (a) Distribution of R_1 (ion balance), (b) R_2 (conductivity balance) and (c) R_1 and R_2 relation

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Table 3.15 Annual volume weighted means (VWM) in μeq/L of the major chemical composition in rain precipitation

Chemical composition (μeq/L)	Bulk precipitation (n=42)	Wet-only precipitation (n=31)
Cl^-	3.50	3.80
NO_3^-	7.20	6.00
nss SO_4^{2-}*	11.20	10.60
Na^+	2.30	2.00
NH_4^+	17.70	16.00
K^+	1.30	0.80
Ca^{2+}	12.00	8.80
Mg^{2+}	1.80	1.30
pH**	5.71	5.62

* nss SO_4^{2-} is non-sea salt SO_4^{2-}

** pH value was calculated as the negative logarithm of the corresponding VWM H^+

3.5.2 Acid neutralization

In case all the nss-SO_4^{2-} and NO_3^- existed in the form of free acid forms, the summation of those should equal to H^+ (Hu *et al.*, 2003). In bulk precipitation, VWM concentrations of nss-SO_4^{2-} and NO_3^- were 11.20 and 7.20 μeq/L, respectively (see in Appendix C). Therefore, the summation was 18.40 μeq/L. From this figure, the pH should be 4.89, but from the measurement it was 5.71 which is lower by 0.82 pH. Base on the same calculation, pattern, pH value obtained from wet precipitation was 0.67 lower than in the real measurement. It indicated that the rainwater precipitation had some neutralization. From previous studies (Saxena *et al.*, 1996; Das *et al.*, 2005), NH_4^+, Ca^{2+}, K^+ and Mg^{2+} have been used to validate by calculating neutralization

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factor (see details in topic 1.11.1). Neutralization factors for NH_4^+, Ca^{2+} and Mg^{2+} are shown in table 3.16.

Table 3.16 Neutralization factors of NH_4^+, Ca^{2+}, K^+ and Mg^{2+}

	NH_4^+	Ca^{2+}	K^+	Mg^{2+}
Bulk (N=42)	0.94	0.64	0.07	0.10
Wet-only (N=31)	0.95	0.51	0.05	0.09

In both bulk and wet-only samples, the order of NF was $NH_4^+ > Ca^{2+} > Mg^{2+} > K^+$ (Table 3.16). This feature suggests that in both bulk and wet-only precipitations, 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, in bulk precipitations the NF values of Ca^{2+} and Mg^{2+} (crustal components) were higher than those of wet-only precipitations indicating the influence of dry deposition on bulk collector.

From the difference of the summation of the nss-SO_4^{2-} and NO_3^- from H^+, it was indicated that acid neutralization was occurred (Hu *et al.*, 2003). Normally, neutralization is frequently reported and attributed to NH_4^+ and Ca^{2+} (Vong, 1990). Consequently, it was expected that the summation of concentrations of H^+, NH_4^+ and Ca^{2+} correlated with summation of concentrations of nss-SO_4^{2-} and NO_3^- in the even that the acidity of the rainwater precipitation is mainly neutralized by NH_4^+ and Ca^{2+}. This hypothesis was confirmed by the scatter plots between those two summation values (Figures 3.19 and 3.20).

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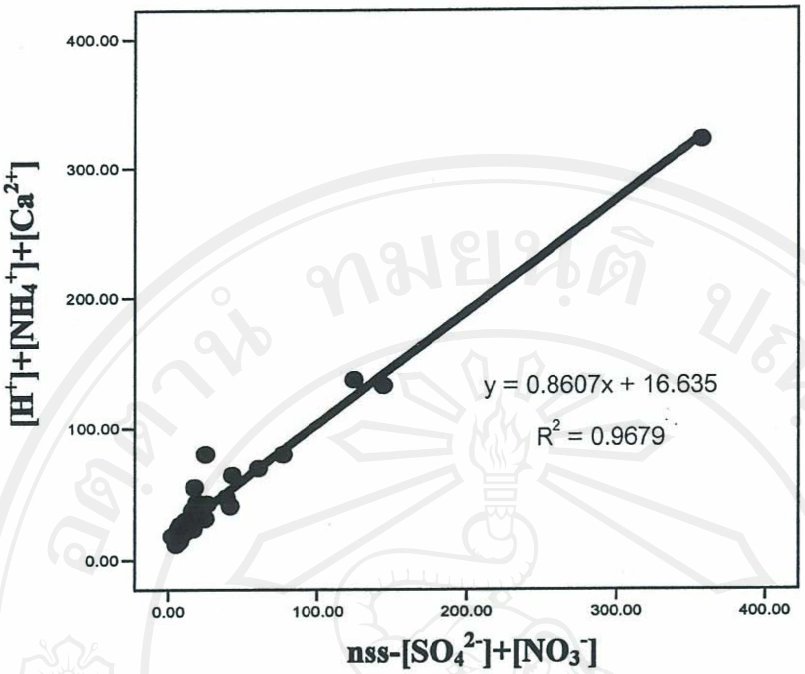

Figure 3.19 Correlation of ($[H^+]+[NH_4^+]+[Ca^{2+}]$) and (nss-$[SO_4^{2-}]+[NO_3^-]$) in bulk precipitations (N=42)

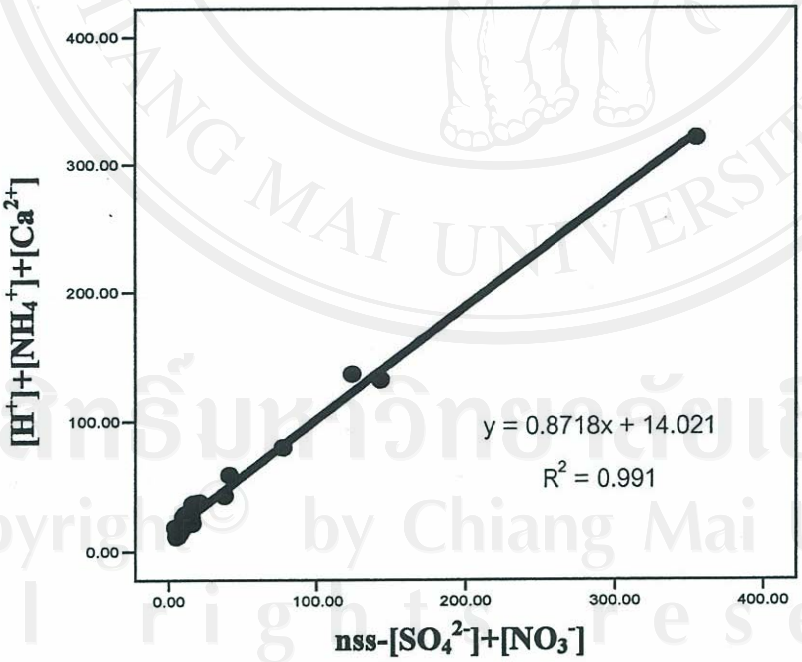

Figure 3.20 Correlation of ($[H^+]+[NH_4^+]+[Ca^{2+}]$) and (nss-$[SO_4^{2-}]+[NO_3^-]$) in wet-only precipitations (N=31)

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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 1.15 b). The various ratios, enrichment factors, sea salt fractions and non-sea salt fractions for bulk and wet-only precipitations are concluded in Tables 3.17 and 3.18, respectively.

Table 3.17 Bulk components with respect to sea (N=42)

	Cl^-	SO_4^{2-}	Mg^{2+}	K^+	Ca^{2+}
Sea water ratio[a]	1.166	0.0603	0.1137	0.0218	0.0219
Bulk ratio[a]	1.520	5.040	0.780	0.570	5.220
EF[a]	1.305	83.639	6.883	25.927	238.230
SSF (%)	76.62	1.20	14.53	3.86	0.42
NSSF(%)	23.38	98.80	85.47	96.14	99.58

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

Table 3.18 Wet-only components with respect to sea (N=31)

	Cl^-	SO_4^{2-}	Mg^{2+}	K^+	Ca^{2+}
Sea water ratio[a]	1.166	0.0603	0.1137	0.0218	0.0219
Wet-only ratio[a]	1.900	5.450	0.800	0.400	4.300
EF[a]	1.629	90.381	7.036	18.348	196.34
SSF (%)	61.37	1.11	14.21	5.45	0.51
NSSF (%)	38.63	98.89	85.79	94.55	99.49

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

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The recommended seawater ratio of Cl^-/Na^+ is 1.166 (see topic 1.15 b), but in this study the ratio of Cl^-/Na^+ is 1.305 and 1.629 for bulk and wet-only precipitations, respectively (Tables 3.17 and 3.18). Consequently, EF values of Cl^- were slightly higher than 1, while EF those of other ions were much greater than 1 for both precipitations. This elevated ratio may be due to contribution of Cl^- from marine origin and partly from anthropogenic or crustal sources, whilst K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} seemed to be diluted by marine source. Similarly, SSF value which is the value that can tell percentage of each ion in marine source. Tables 3.17 and 3.18 reveals that most of ions fractions of K^+, Ca^{2+} and SO_4^{2-} and Mg^{2+} and a part of Cl^- (23% in bulk and 39% in wet-only) appear to be from non-marine origin in both precipitations.

3.5.4 Ion pair correlations

In order to identify relationships between the various ionic species in rainwater precipitation, Pearson correlation (r) was carried out on both bulk and wet-only data. Pearson correlation coefficients were calculated using SPSS for Windows (version 12) software. The resultant r values for both bulk and wet-only are shown in appendix E. The study period covered two periods of rainy season, (August-October 05 and May-July 06) and one period of dry season (November 05-April 06). During the first period of rainy season (August-October 05) of the study, bulk data showed strong correlation between NH_4^+ and SO_4^{2-} ($r = 0.880$); followed by H^+ and SO_4^{2-} ($r = 0.848$); H^+ and NH_4^+ ($r = 0.773$) and NH_4^+ and NO_3^- (0.763) at $p = 0.01$. It suggested that the main acidity of rainwater precipitation in this region was H_2SO_4, which was neutralized by NH_4^+. The correlation of NH_4^+ and SO_4^{2-} was stronger than that of NH_4^+ and NO_3^-. This result agreed with ammonium/sulfate/nitrate system, whereby NH_3 first reacts with

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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). During the dry season (November 05 to April 06), both correlation coefficient (*r*) of bulk and wet-only participation were also strong, it suggested that all of ions were related with one another. The acidity values of this range seem to be occurred from NO_x and SO_2. During May to July 06, NH_4^+ and SO_4^{2-} also showed stronger correlation than NH_4^+ and NO_3^- due to the same reason as shown in the first rain period. Conversely, pH values depend on concentration of NO_x much more than concentration of SO_2 at $p = 0.01$.

3.5.5 Source analysis of major ion composition

In order to identify sources of ions in rainwater precipitations, 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 12) was applied and the results are shown in Tables 3.19 and 3.20.

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Table 3.19 Factor analysis of chemical composition in bulk precipitation (n=42)

Components	Factor 1	Factor 2	Factor 3
SO_4^{2-}	**.904**	.306	.251
NO_3^-	**.882**	.264	.353
Cl^-	**.639**	**.619**	.340
NH_4^+	**.902**	.293	.285
Na^+	.145	**.785**	.526
K^+	**.591**	.368	**.597**
Ca^{2+}	**.596**	.226	**.649**
Mg^{2+}	.339	**.907**	.059
H^+	**.920**	.247	.208
Eigenvalue	4.50	2.32	1.48
% of Variance	50.03	25.77	16.50
% of cumulative	50.03	75.80	92.30
Predicted source	Combustion and Agricultural	Sea-salt	Soil/Biomass

Table 3.20 Factor analysis of chemical composition in wet-only precipitation (n=31)

Components	Factor 1	Factor 2	Factor 3
SO_4^{2-}	**.918**	.306	.059
NO_3^-	**.929**	.264	.071
Cl^-	**.680**	**.683**	-.014
NH_4^+	**.921**	.361	.037
Na^+	.210	**.885**	.359
K^+	**.779**	.386	.425
Ca^{2+}	**.785**	.542	.093
Mg^{2+}	.446	**.863**	-.137
H^+	**.940**	.255	.061
Eigenvalue	5.36	2.88	0.35
% of Variance	59.61	31.97	3.90
% of cumulative	59.61	91.57	95.47
Predicted source	Combustion/Agricultural/ Soil and Biomass	Sea-salt	-

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The factor analysis identified that there was three factors contributed about 92 and 95% of the variance to the dataset of bulk and wet-only data, respectively. Given observation that only factor loadings higher than 0.5 are deem to be statistically significant (Ayer and Yeung, 1996 and Ungvari *et al.*, 2007). For factor 1, both bulk and wet-only datasets provided high loading on the SO_4^{2-}, NO_3^-, Cl^-, H^+, NH_4^+, K^+ and Ca^{2+}. It associated reasonably with combustion process (SO_4^{2-}, NO_3^-, Cl^- and H^+) and neutralization components (NH_4^+, K^+ and Ca^{2+}), which indicated that they come from agricultural area and soil. The key marker variables of the factor 2 were Cl^-, Na^+ and Mg^{2+}, hereafter referred to as the marine source (Hu *et al.*, 2003). Factor 3 shows high loading on Ca^{2+} and K^+ in bulk data set and suggests the contribution of soil re-suspension and combustion activities, respectively (Saxena *et al.*, 1996). The wet-only dataset showed difference of factor 3 from bulk dataset. This might be from the number of samples which was 42 and 31 of bulk and wet-only precipitation, respectively or might be occurred from soil resuspend and then fall into the bulk collector higher than wet-only collector.

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