CHAPTER 3

RESULTS AND DISCUSSION

3.1 Analytical Characteristics of Ion Chromatograph and Spectrophotometer

3.1.1 Repeatability and Reproducibility

a) Precision of ion analysis by Ion Chromatograph

- **Repeatability**

The repeatability of ion analysis by IC is shown in Table 3.1. Relative standard deviation (RSD) of individual ion concentrations obtained from five injections ranged from 2.5 – 4.6%.

- **Reproducibility**

The reproducibility was checked by injecting a 0.40 µg/mL mixed standard solution (see section 2.3.1 a). The results of reproducibility were estimated by standard deviation (SD) and the %RSD as shown in Table 3.1. The RSD of ion concentrations was 0.5 – 2.6%

Table 3.1 Repeatability and reproducibility of ion chromatograph

No. of injection	Concentration (µg/mL)									
	Repeatability					Reproducibility				
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	0.41	0.39	0.42	0.40	0.39	0.42	0.40	0.41	0.42	0.42
2	0.41	0.40	0.41	0.39	0.40	0.41	0.40	0.42	0.42	0.42
3	0.42	0.41	0.41	0.39	0.41	0.39	0.40	0.41	0.42	0.42
4	0.41	0.44	0.40	0.43	0.39	0.42	0.40	0.42	0.42	0.42
5	0.40	0.42	0.42	0.42	0.39	0.42	0.40	0.41	0.42	0.42
Average	0.41	0.41	0.41	0.41	0.40	0.41	0.40	0.41	0.42	0.42
SD	0.01	0.02	0.01	0.02	0.01	0.01	0.00	0.00	0.00	0.00
%RSD	2.5	4.6	3.1	4.1	2.7	2.6	0.6	0.6	0.6	0.5

3.1.2 Limit of detection (LOD) and limit of quantification (LOQ) of Ion Chromatograph

In this study, LOD and LOQ were obtained by 7 injections of 0.1 µg/mL standard solution. Their concentrations were calculated from the calibration curve in ranges of 0.1 to 4.0 µg/mL for cation. Limit of detection and limit of quantification values of all analyzes are shown in Table 3.2.

Table 3.2 Limit of detection and limit of quantification of IC for each ion

No. of injection	**Concentration (μg/mL)**				
	Na^+	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
1	0.186	0.115	0.070	0.105	0.214
2	0.186	0.123	0.075	0.097	0.204
3	0.189	0.120	0.066	0.098	0.210
4	0.192	0.108	0.073	0.103	0.225
5	0.187	0.110	0.077	0.102	0.216
6	0.188	0.109	0.079	0.105	0.218
7	0.191	0.110	0.075	0.103	0.222
Average	0.188	0.113	0.074	0.102	0.216
SD	0.002	0.006	0.004	0.003	0.007
LOD	0.007	0.018	0.013	0.010	0.021
LOQ	0.071	0.059	0.044	0.032	0.071

3.2 Preparation of solutions

a) Calibration curve of ion analysis

In each analytical run, 7 concentrations (0.1, 0.2, 0.4, 0.8, 1.0, 2.0 and 4.0 μg/mL) of cation calibration standards were prepared and analyzed by IC. The calibration curve of each ion standard was constructed using concentrations of standard solution versus peak area. Concentration range must cover at least 95% of ion concentrations of samples. The calibration curves for the quantification of ionic species were significantly linear, with the coefficients of determination (r^2) being 0.995 or greater. The calibration curves for determination of cation are shown in Figures 3.1

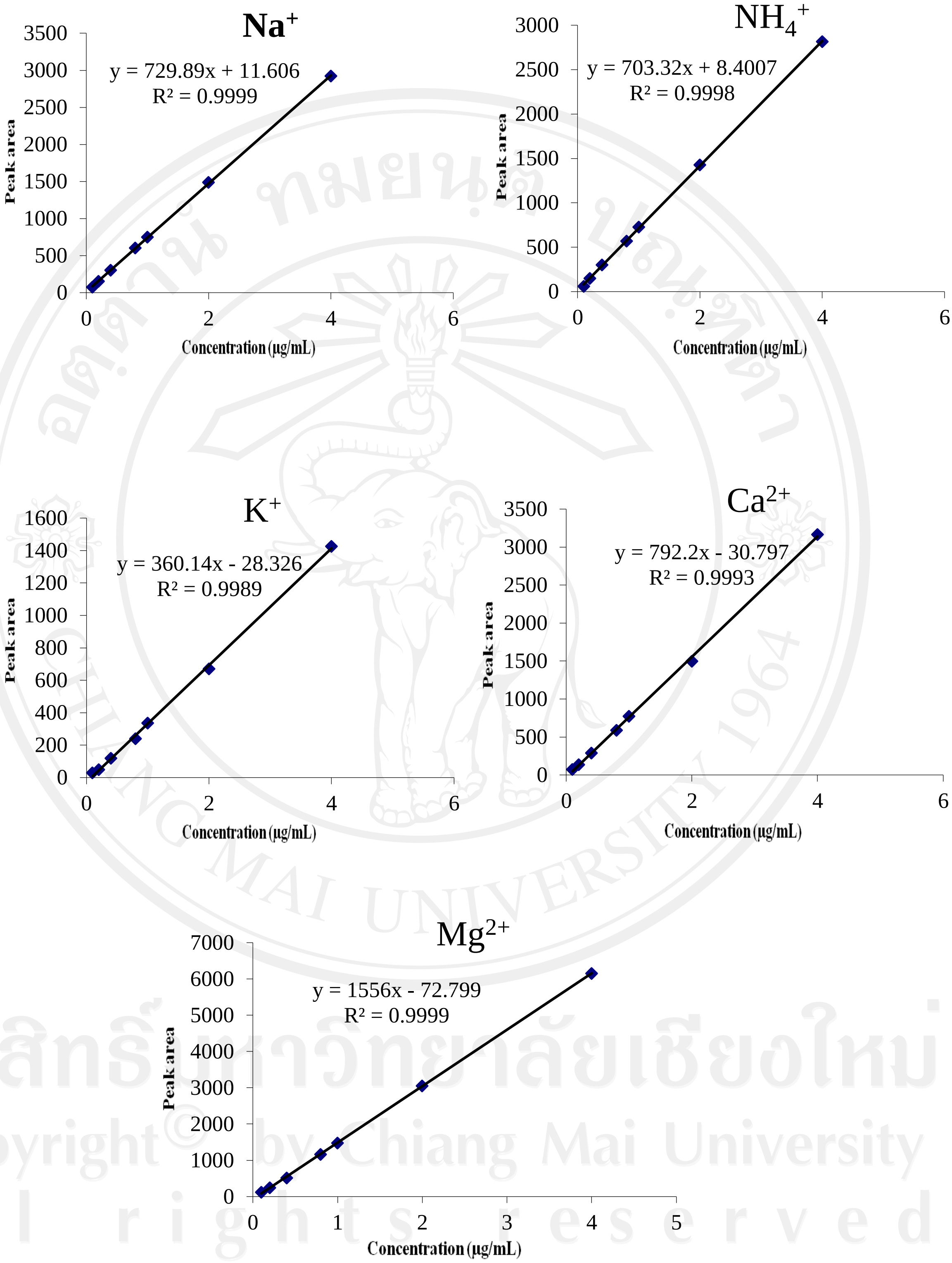


Figure 3.1 Calibration curve for determination of cations: Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}

3.3 Percent recovery of ions from sample preparation

To obtain the optimum extraction conditions of cations in PM_{10} samples by using ultrasonication, extraction conditions including duration, volume of Milli-Q water and temperature were tested. Due to Khamkaew (2010) demonstrated to find the optimum extraction conditions and found optimum conditions for anion extractions.

Therefore, the optimum extraction conditions of anions in PM_{10} sample from Khamkaew (2010) are applied to use with cations in this study. So the appropriate extraction conditions via extract the filter in 30 mL of Milli-Q water at room temperature (25 ºC) for 30 minutes. Then, these extraction conditions were applied to find out percent recoveries of cation extraction by 10 replications. Percent recoveries were obtained by spike of 0.3 µg/mL of each cation standard solution (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) onto quartz fiber filter (n=10). It found that percent recovery of cations were $Mg^{2+} > K^+ > NH_4^+ > Na^+ > Ca^{2+}$ and the result are shown in Table 3.3.

Table 3.3 Percent recoveries of standard solution cations

No.	**% Recovery of sample**				
	Na^+	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
1	85.8	88.7	88.8	84.5	92.1
2	89.6	88.8	89.8	87.4	90.6
3	85.1	86.9	87.6	84.6	90.7
4	89.5	88.6	89.3	84.5	91.1
5	87.2	89.9	91.3	85.8	92.2
6	89.5	89.5	90.4	86.7	93.0
7	91.5	88.9	91.2	87.1	92.3
8	89.7	89.8	92.3	86.4	92.8
9	87.3	90.0	90.9	83.7	91.6
10	90.8	90.0	92.6	86.4	92.2
Average	**88.6**	**89.1**	**90.4**	**85.7**	**91.9**
SD	**2.1**	**0.9**	**1.6**	**1.3**	**0.8**
%RSD	**2.4**	**1.0**	**1.7**	**1.5**	**0.9**

3.4 Fire maps and Backward Trajectory

3.4.1 Fire maps

Fire count maps, displaying the active burning hot spots, were derived from MODIS (Moderate Resolution Imaging Spectroradiometer) satellite images. The data were analysed using a standard MODIS MOD14 Fire and Thermal Anomalies Product algorithm.

Each of fire maps (Figure 3.2) accumulates the locations of the fires detected by MODIS on board the Terra and Aqua satellites over a 10-day period. Each colored dot indicates a location where MODIS detected at least one fire during the compositing period. Color ranges from red where the fire count is low to yellow where number of fires is large. The compositing periods are referenced by their start and end dates (julian day). The duration of each compositing period was set to 10 days. In addition, this study emphasizes on Northern part of Thailand and perimeter regions both in wet and dry season (Appendix A) as shown in Figure 3.3. It demonstrates clearly different fire incident between wet and dry season that in dry season was much more fire count than wet season.

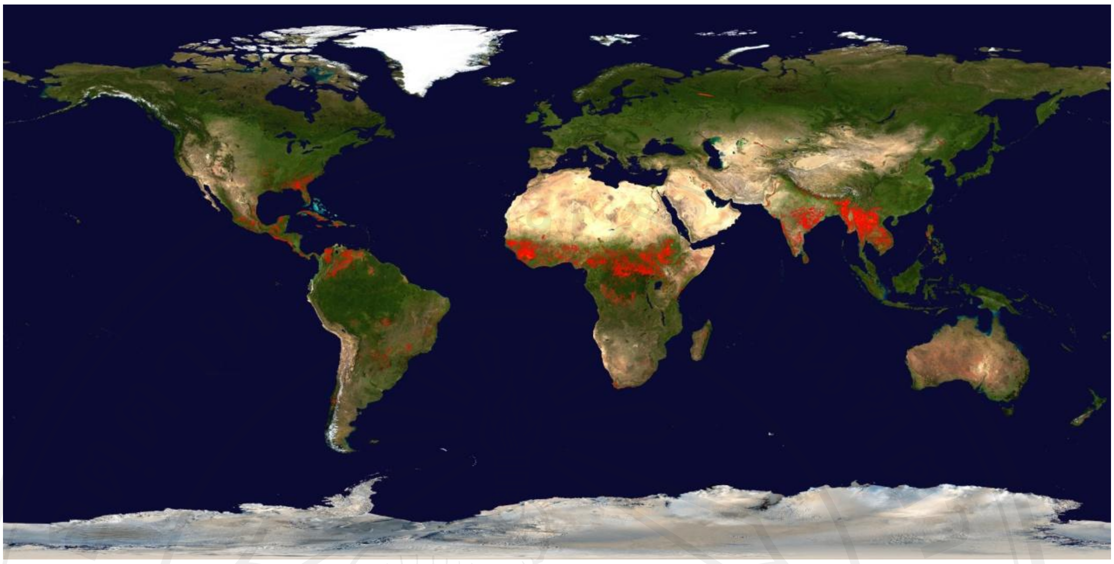
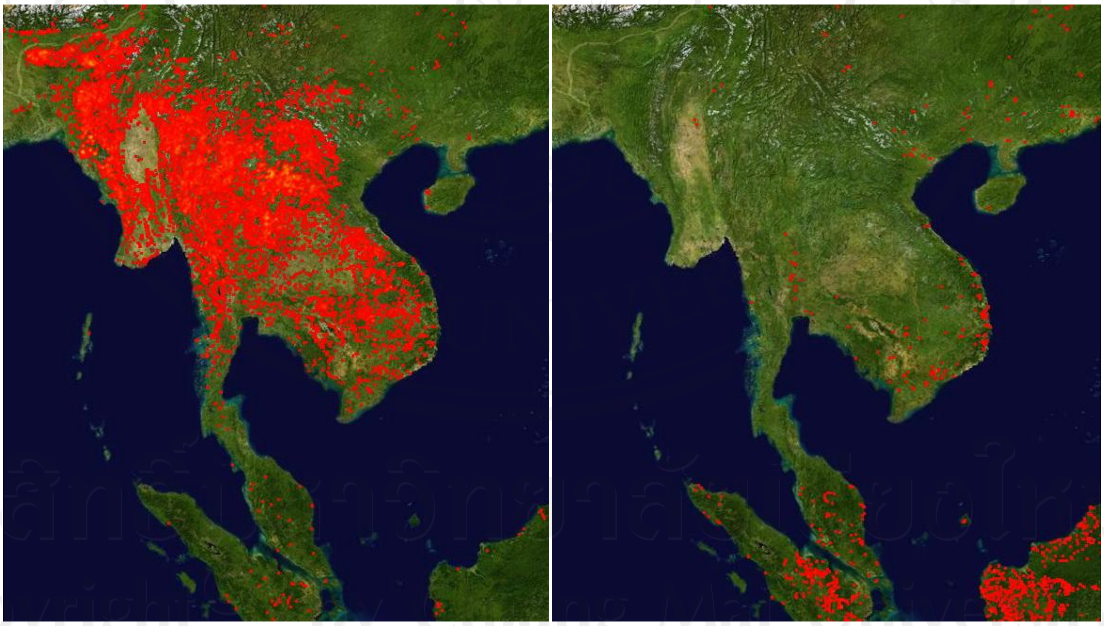


Figure 3.2 Fire count map detected by MODIS satellite image

(Source: http://modis.gsfc.nasa.gov/data/dataprod/dataproducts.php?MOD_ NUMBER=14)



(a) **(b)**

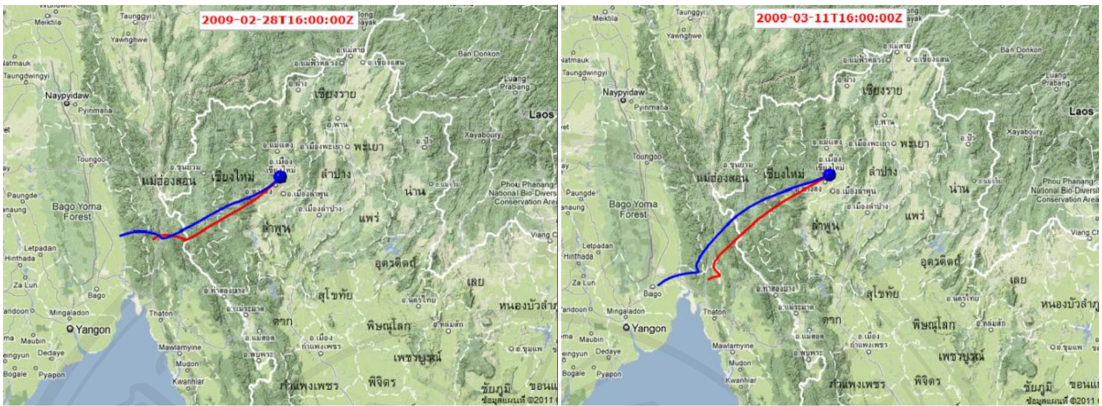
Figure 3.3 Fire count maps of Thailand and perimeter regions in dry (a) and wet (b) season

(Source:http://modis.gsfc.nasa.gov/data/dataprod/dataproducts.php?MOD_ NUMBER=14)

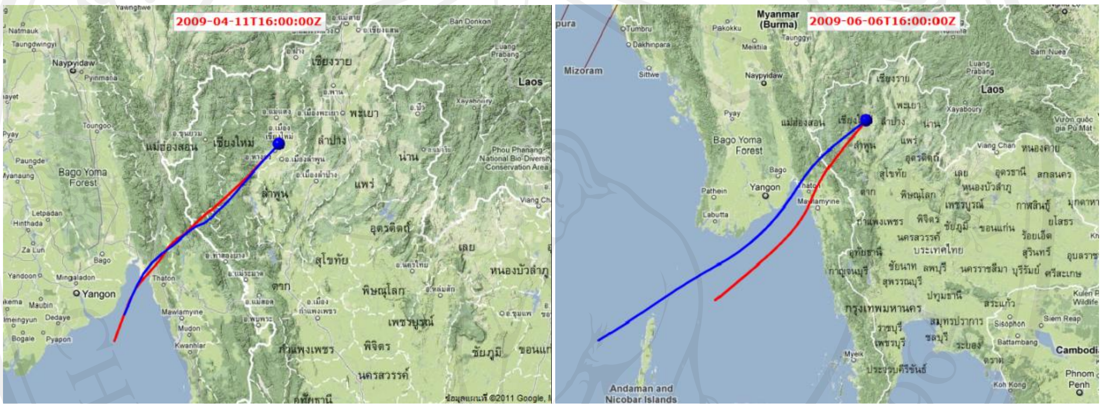
3.4.2 Backward Trajectory model

Trajectory analyses are commonly used in air quality studies to examine the source regions of air parcels moving into a given area, or the likely paths air parcels would take following a plume from a point source. The purpose of this study was to identify backward trajectories of air masses arriving in Chiang Mai to see air transport patterns. One-day backward trajectories at an altitude of 500 and 1000 m in Chiang Mai were calculated between February 2009 to August 2009 using HYSPLIT Model developed by the Air Resources Laboratory of the United States National Oceanic and Atmospheric Administration (NOAA). Each backward trajectory contained endpoints describing the hourly location of an air mass in latitude and longitude coordinates.

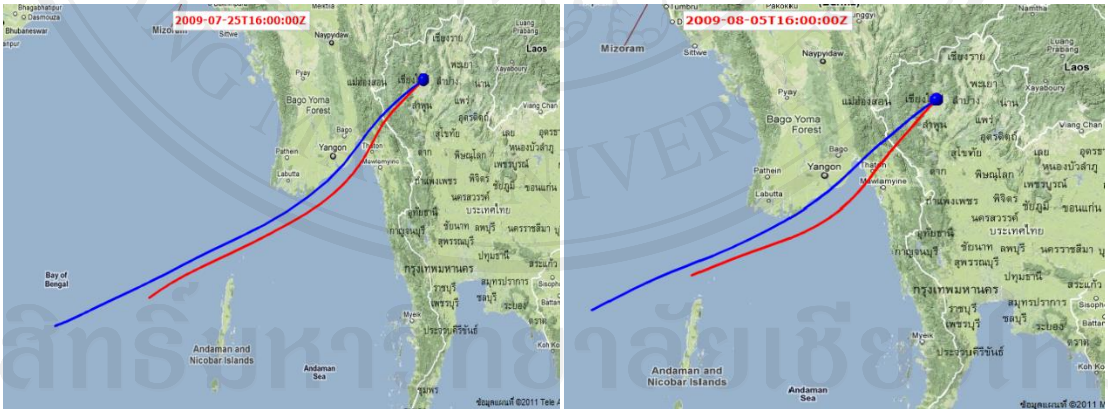
According to the results, southwest direction was the main transport patterns coming to Chiang Mai (see Appendix B). At the begining of hot-dry season especially in February and March, a short range transport pattern was observed. Therefore, sources of air pollutant in the dry season was from local activities including biomass burning and forest fire. Otherwise, in wet season most of wind transport pattern still from the southwest direction but with longer distance. Consequently, long transport range from Andaman Sea had also affect on pollutant concentrations. These samples contained higher sea-salt ions, but less crustal dust and forest fire. In order to understand air mass transport pattern in each month, the representative air transport patterns are shown in Figure 3.4.



(a) 28th February (b) 11st March



(c) 11st April (d) 6th June



(e) 25th July (f) 5th August

Figure 3.4 Air mass transport patterns to Chiang Mai during February to August 2009

3.5 PM_{10} concentrations

PM_{10} samples have been collected from two sites in Chiang Mai using the Airmetrics Minivol™ Portable Air samplers. The air sampler was placed on shelf above ground with 2 meter height level at each sampling site to avoid dust or ground particles contamination. Each sample was collected within a period of 24 hours intervals. Sampling was conducted twice a week, including a working day and a weekend day. Sampling was carried out for 6 months in the dry season (February - April 2009) and the rainy season (June - August 2009) at Yupparaj Wittayalai School (YP) and Mae Hia Research Center (MH) which assumed to be a background site.

3.5.1 Comparison of PM_{10} concentrations obtained from mini volume and Taper Element Oscillating Microbalance (TEOM)

In order to prove the efficiency of the equipments used for PM_{10} sampling. PM_{10} concentrations were collected by Airmetrics Minivol™ Portable Air samplers and compared with tapered element oscillating microbalance (TEOM) value from the air quality monitor station which is located at YP sampling site (see Appendix D) belong to the Pollution Control Department (PCD). The result is shown in Table 3.4 and Figure 3.5. It was found that mean concentrations of PM_{10} obtained from the mini volume air sampler and TEOM were 74.2±48.1 and 56.6±48.5, respectively. The error average was 17.6 $\mu g\ m^{-3}$. The SPSS test (t-test) showed no significant difference ($p > 0.05$) between TEOM and mini volume air samplers. Concentrations of PM_{10} collected from mini volume air sampler were well correlated with PM_{10} collected from TEOM (Figure 3.6). Their correlations were relatively higher in the dry season ($r = 0.981$) than in the wet season ($r = 0.862$). Therefore it can be explain that was demonstrate reliability of the techniques which used in this experiment in comparison with high efficiency equipments.

Table 3.4 Twenty-four hour PM_{10} concentrations (μg m^{-3}) obtained from Taper Element Oscillating Microbalance (PCD) and mini volume air sampler (this study)

Month	**Average±SD**		
	TEOM	**mini volume**	**Difference**
February	127.0±45.2	147.0±47.3	20.0
March	97.1±56.2	117.3±45.2	20.2
April	56.6±25.8	67.9±22.7	11.3
June	21.6±5.2	38.4±6.9	16.8
July	25.0±9.4	43.4±11.0	18.4
August	29.1±9.6	48.1±11.8	19.0
Average	**56.6±48.5**	**74.2±48.1**	**17.6**

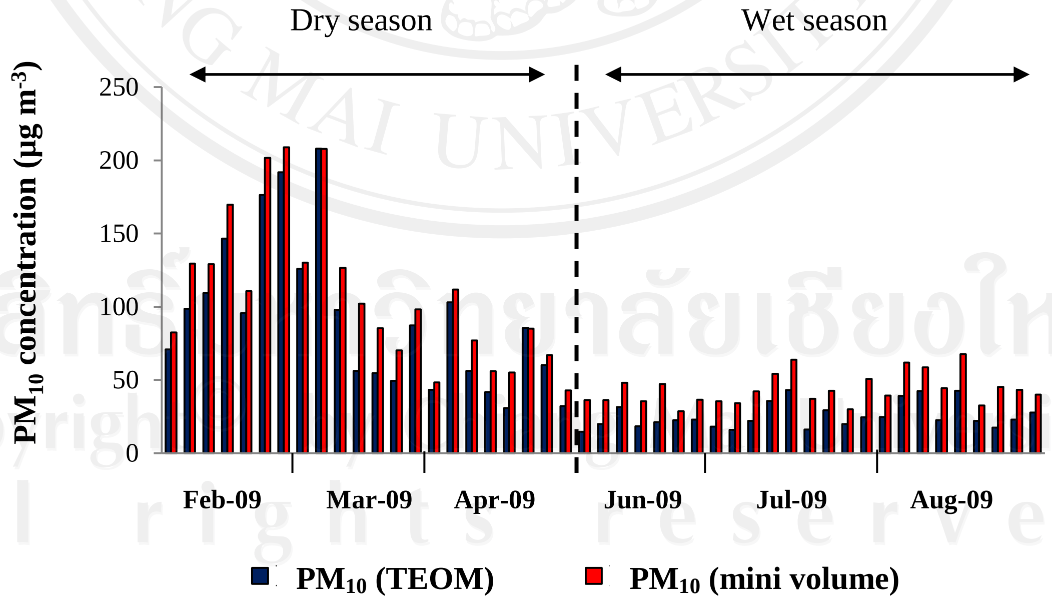


Figure 3.5 PM_{10} concentrations obtained from mini volume air sampler and Taper Element Oscillating Microbalance (TEOM)

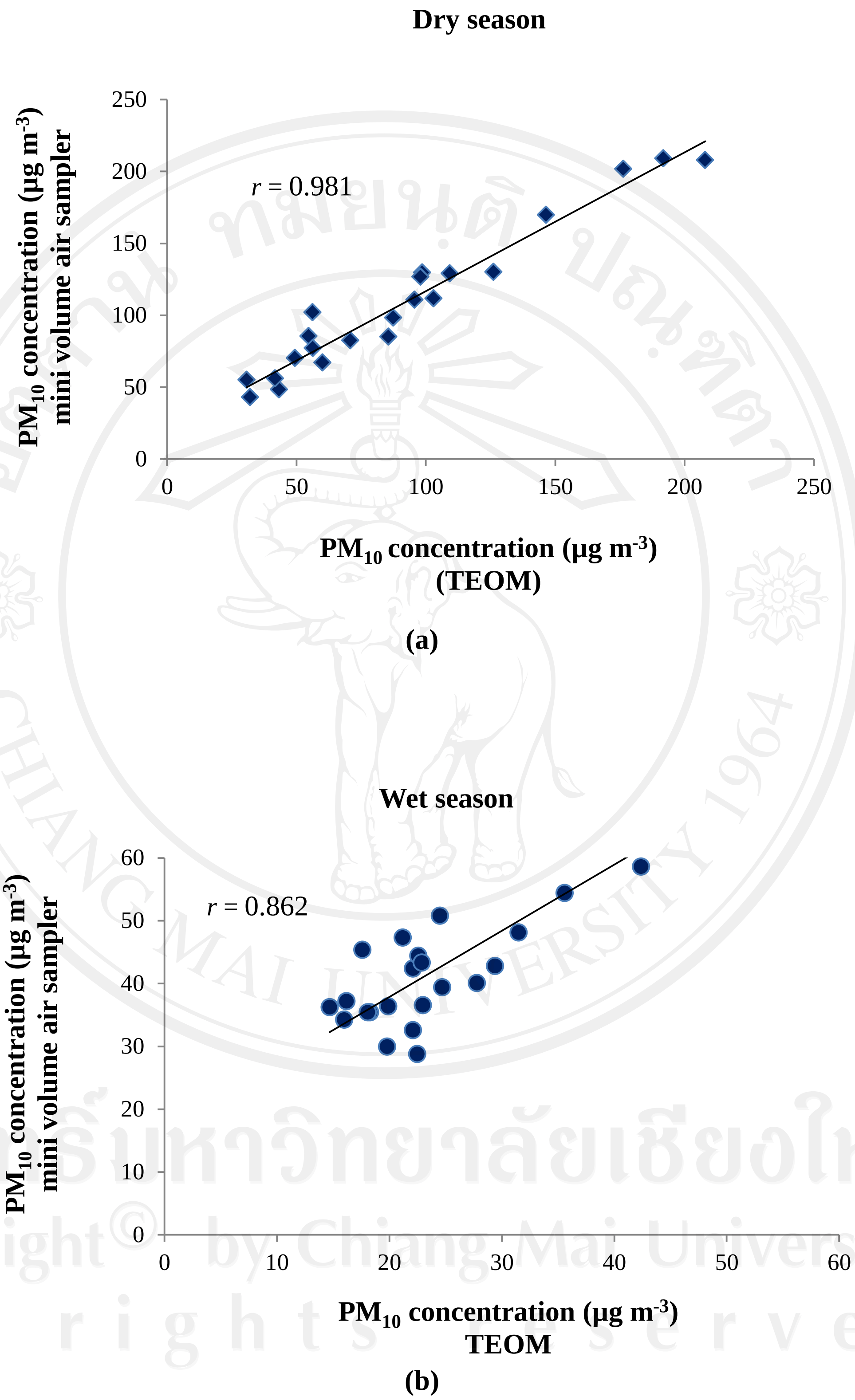


Figure 3.6 The correlation between PM_{10} collected by mini volume air sampler (a) and Taper Element Oscillating Microbalance (TEOM) (b)

3.5.2 PM_{10} concentrations and their monthly variation

During February to August 2009 for 6 months of the PM_{10} sampling, total of 59 samples of PM_{10} were collected from the two sampling sites. The number of PM_{10} samples at the YP site was 22 in the dry season and 25 in the wet season. At the MH site were collected only in the dry season (18 March - 30 April 2009), with the number of PM_{10} samples only 12. Monthly average PM_{10} of two sampling sites are shown in Table 3.5 and Figure 3.7. The PM_{10} concentrations of the YP station varied from 28.7 µg m^{-3} (June) to 209.0 µg m^{-3} (March), meanwhile the MH site varied from 14.9 µg m^{-3} to 91.5 µg m^{-3}. The average PM_{10} concentrations of YP site were highest in February (147.5±47.3 µg m^{-3}) and lowest in June (38.4±6.9 µg m^{-3}). Due to Thailand's standard for ambient air quality is 120 µg m^{-3} (PCD, 2009), the average PM_{10} concentrations of YP in February were highest and higher than the standard value. There was about 17% of the PM_{10} samples of YP site were higher than the limit standard value. The results exposed that the PM_{10} concentrations were high in the dry season (February and March) before decreasing in April. The lower concentration was found in the wet season due to high precipitation. The monthly values of rain precipitations were 16.7 mm (March), 97.9 mm (April), 140.2 mm (June), 124.0 mm (July) and 126.8 mm (August) (Northern Meteorological Center, 2009). The seasonal average of PM_{10} concentrations at YP sites were in the range from 43.7±10.7 µg m^{-3} in wet season to 108.9±50.6 µg m^{-3} in dry season and MH sites were 47.3±21.2 µg m^{-3} in the dry season. This result was similar to that reported by Chantara *et al.* (2009), which mention that the mean PM_{10} concentrations were in the range from 38.28±11.80 µg m^{-3} in the rainy season (June-July 2005) to 81.67±29.91 µg m^{-3} in the dry season (February-April 2006). Similar to

Vinitketkumnuen *et. al. (*2002) with the daily levels of PM_{10} in the ambient air were measured in Chiang Mai from March 1998 to October 1999 were range from 27.29 to 173.40 µg/m^3 and the annual average was 86.38 µg/m^3.

The PM_{10} concentrations were significantly different ($p < 0.05$) in each month (Table 3.5). Seasonal difference of PM_{10} concentrations was distinct between dry and wet seasons. Seasonal concentrations of PM_{10} concentrations were significantly different ($p < 0.05$), which agreed with previous study. PM_{10} concentrations in the dry season were approximately 2 times higher than those in the wet season (Chantara *et al*, 2009). The PM_{10} concentrations at the urban site (YP) were approximately 2 times higher than those at the sub-urban site (MH). This trend is agreed with the work of Janssen *et al*. (1997). They found that PM_{10} concentration were on average 1.3 times higher at urban street sites than at background sites in the Netherlands due to traffic emissions.

Table 3.5 PM_{10} concentrations (µg m^{-3}) collected from two sampling sites

Sampling Station	**Season**	**Month**	**N**	**PM_{10} (µg m^{-3})**		
				Average ±SD	**Min**	**Max**
YP	Dry	February	7	147.5 ± 47.3^{a}	82.5	209.0
		March	7	117.3 ± 45.2^{a}	70.3	207.9
		April	8	67.9 ± 22.7^{b}	42.9	111.7
		Average	**22**	**108.9 ± 50.6**		
	Wet	June	7	38.4 ± 6.9^{b}	28.7	48.1
		July	9	43.4 ± 11.0^{b}	29.9	63.8
		August	9	48.1 ± 11.8^{b}	32.5	67.7
		Average	**25**	**43.7 ± 10.7**		
		Dry+Wet	**47**	**74.2 ± 48.1**		
MH	Dry	March	4	46.5 ± 8.3	38.3	56.9
		April	8	47.7 ± 26.0	14.9	91.5
		Average	**12**	**47.3 ± 21.2**		

YP = Yupparaj Wittayalai School; MH = Mae Hia Research Center

[a, b] = Significant difference ($p < 0.05$)

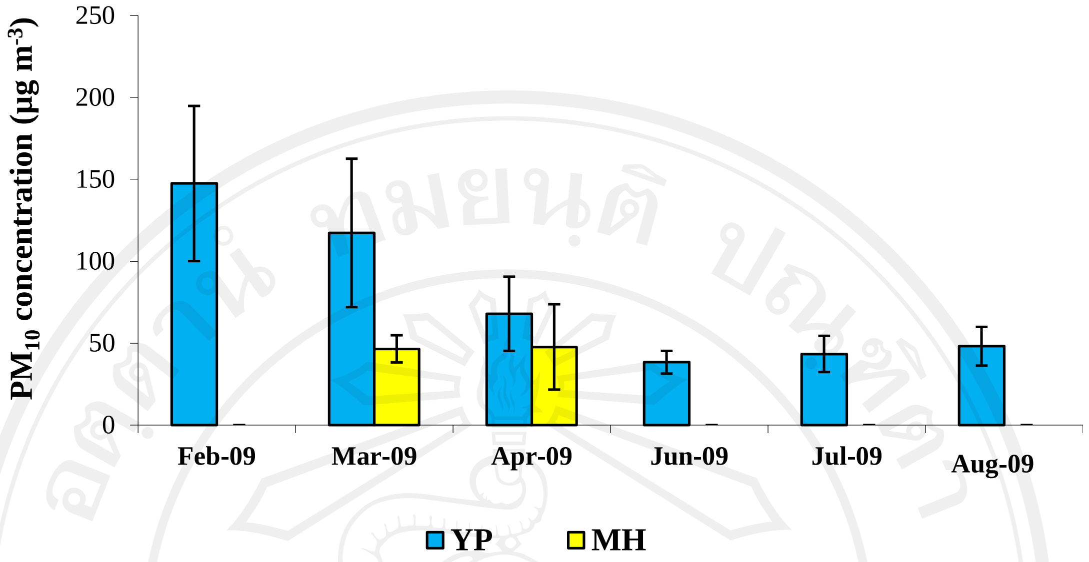


Figure 3.7 Monthly average PM$_{10}$ concentrations (µg m^{-3})

3.6 Values of pH and Electro Conductivity of PM$_{10}$ samples

3.6.1 pH of PM$_{10}$ samples

47 PM$_{10}$ samples and their pH values of YP site were 5.5-7.9 (see Appendix E). Temporal variation of pH values from extract solutions of PM$_{10}$ are shown in Figure 3.8. The highest monthly mean pH value of samples (7.6±0.2) was observed in June 2009, while the lowest values of those (5.6±0.1) were observed in February and March 2009. Chantara *et al.* (2009) reported that more than 45% of the PM$_{10}$ samples from YP station had pH value less than 5.6. Seasonal variation of the pH values illustrated that low pH values were inspected in the dry season especially in March and April. pH values of samples from the YP site were lower than those of MH site as shown in Table 3.6. This is because MH is located in sub-urban area with lower human activities than the YP site. In agree with Shen et al., (2009) indicated that Ion balance calculations indicate that PM from haze and straw combustion was acidic while the DSs samples were alkaline and the fireworks' PM was close to neutral.

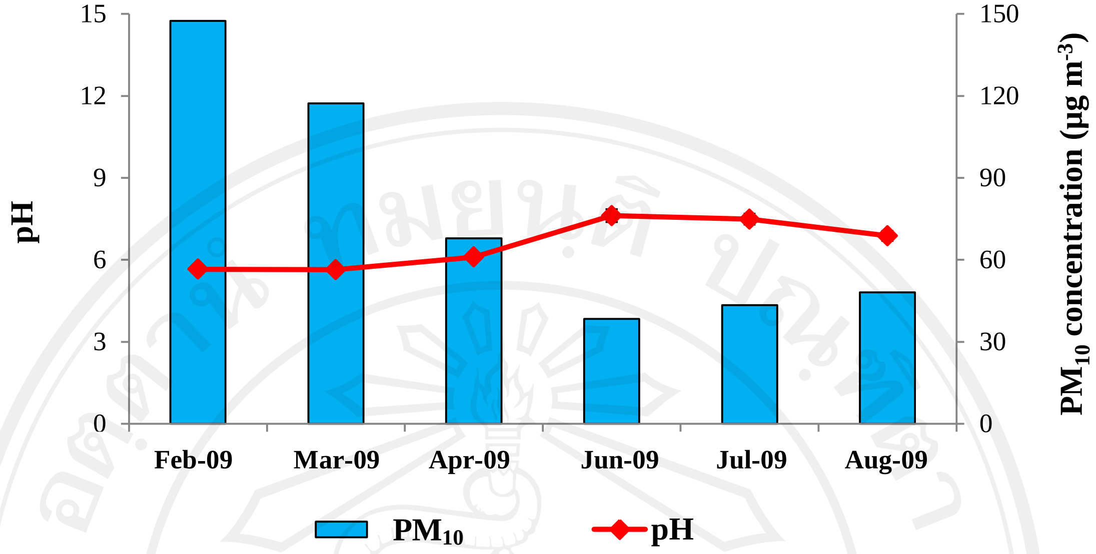


Figure 3.8 Variation of pH of PM_{10} extracted solutions from February to August 2009

Table 3.6 pH values of PM_{10} extracted solution from two sampling sites

Sampling station	Season	Month	Average ± SD
YP	Dry	February	5.6±0.14
		March	5.6±0.07
		April	6.1±0.10
		Average	**5.8±0.24**
	Wet	June	7.6±0.23
		July	7.5±0.20
		August	6.9±0.18
		Average	**7.3±0.35**
MH	Dry	March	6.5±0.03
		April	6.0±0.36
		Average	**6.2±0.38**

3.6.2 Electro conductivity (EC) of PM_{10} samples

The electro conductivity or EC of the PM_{10} extract solution directly shows the contamination concentration of the level of ionic contamination. Accordingly, through monitoring the electro conductivity of the PM_{10} extract solution. Therefore high EC value indicates high ionic contamination, EC value of deionized water is normally less than 1.5 µS/m. The mean EC values of 47 PM_{10} samples at YP site were 11.3±3.1 µS/m (see Appendix E). The maximum detected EC values were in February (15.0±2.5 µS/m) meanwhile the minimum were occurred in June and August (8.2±3.7 and 8.2±1.8 µS/m, respectively). The concentrations of PM_{10} and the EC values of the samples are shown in Figures 3.9. It can be demonstrated that PM_{10} and EC both are relate to each other with high PM_{10} concentrations resulted in high ion concentrations and EC values, while low concentrations can affected in opposite result. The results of YP with MH sites in the dry season, it reveals that EC values of YP site lower than MH site as shown in Table 3.7. Ali-Mohamed *et al.* (1996) reported that the conductivity of the water-soluble particulate matter were relatively high in moderate weather, during March-May 1991, in Daih (DH) were higher than in Karbabad (KB).

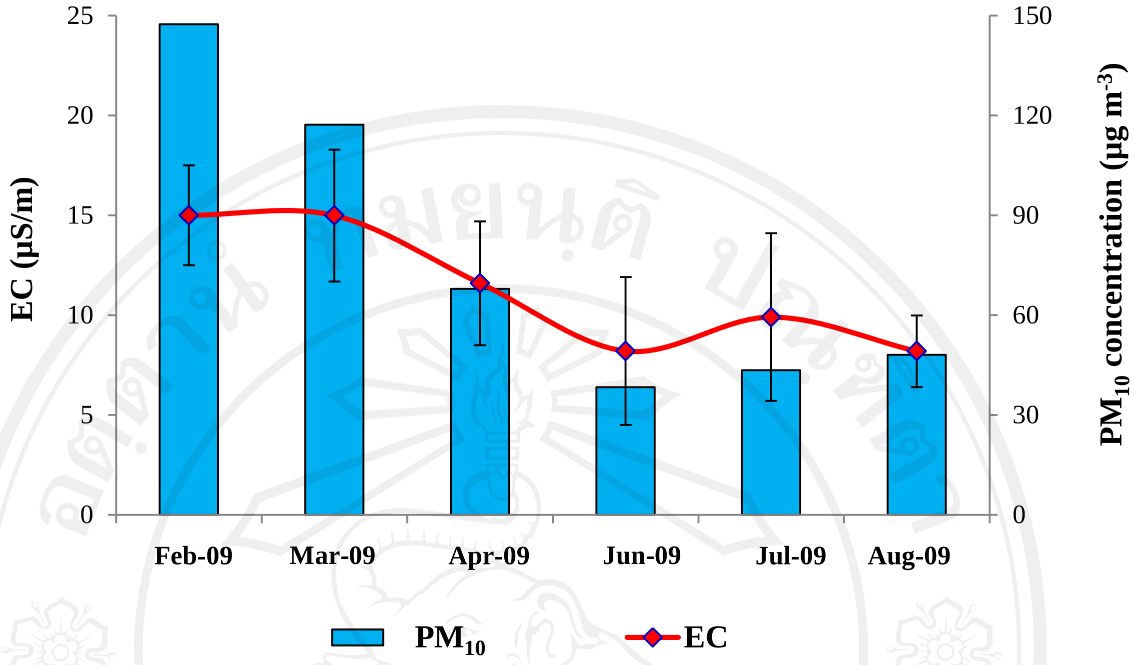


Figure 3.9 Monthly average EC vales from February to August 2009

Table 3.7 EC values (µS/cm) of PM$_{10}$ extracted solution from two sampling sites

Sampling station	Season	Month	Average EC ± SD
YP	Dry	February	15.0±2.5
		March	15.0±3.3
		April	11.6±3.1
		Average	**13.7±3.3**
	Wet	June	8.2±3.7
		July	9.9±4.2
		August	8.2±1.8
		Average	**9.6±2.7**
MH	Dry	March	9.0±3.4
		April	11.8±3.1
		Average	**10.9±3.4**

3.7 Cation concentrations in PM_{10} samples

The cation components (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) have been ultrasonically extracted from quartz filter samples with 30 mL of Milli-Q water for 30 minutes at room temperature and then determined by Ion Chromatograph (Metrohm, Switzerland). Chromatograms of mixed cation standards are shown in Figure 3.10. The major cation constituents of PM_{10} from YP and MH sites were ammonium (NH_4^+), sodium (Na^+) and calcium (Ca^{2+}) (see Appendix E). Calcium was the greatest contributor to the ionic elements of PM_{10} in both YP and MH sites, which agreed with previous study such as Smichowski *et al*. (2009), perform the elemental composition of water soluble and acid soluble size-fractionated airborne particulate matter ($PM_{2.5}$ and $PM_{2.5–10}$) was investigated and found that Ca and Mg were the elements that showed the higher concentrations. Moreover, in the fine fraction and the coarse fraction, the element that was found at higher mean seasonal concentrations was Ca with 3.5 and 4.8 $\mu g/m^3$ respectively. Shen *et al*. (2009) investigated during dust storms and several types of pollution events, including haze, biomass burning, and fireworks displays. Aerosol mass concentrations were up to 2 times higher during the particulate matter (PM) events than on normal days. During dust storms, the concentrations of secondary aerosol components were low, but Ca^{2+} was abundant, and Mg^{2+} and Ca^{2+} were more abundant in TSP than $PM_{2.5}$. While PM from straw combustion showed high K^+ and Cl^-.

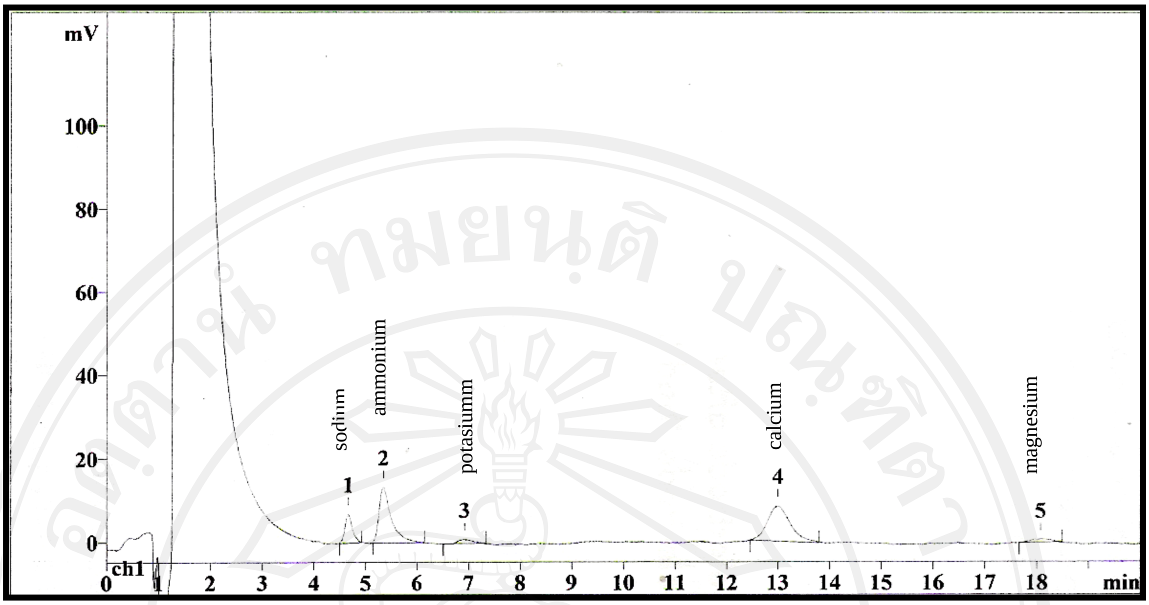


Figure 3.10 Chromatogram of 0.80 µg/mL mixed cations standard

The average concentrations of cation species analyzed from PM_{10} samples are presented in Table 3.8. It was found that trend of average concentrations of these five ions were harmonic and similar. The mean concentrations of cations in a descending order were $Ca^{2+} > Na^{+} > NH_4^{+} > K^{+} > Mg^{2+}$. Seasonal concentrations of Na^{+}, NH_4^{+}, K^{+}, Ca^{2+} and Mg^{2+} at YP site were significantly different ($p < 0.05$) between seasons. This result is well agreed with Chantara *et al.* (2009), which reported that seasonal variation of cations (Na^{+}, NH_4^{+}, K^{+}, Ca^{2+} and Mg^{2+}) were significantly higher in the dry season than in the rainy season. Variation of Na^{+}, NH_4^{+}, K^{+}, Ca^{2+} and Mg^{2+} concentrations is shown in Figure 3.11. It was found that the average cations concentration in the dry season collected at the YP was approximately 2 times higher than that the MH site. The dominant cation in the dry season and rainy season was Ca^{2+} similar to Eleftheriadis *et al.* (1998) found that ions sulphate and calcium make the largest portion of anions and cations, respectively. Due to the result of Ca^{2+} and

Na^+ are higher than other cations in all season both two sites causes by two main reasons, the first one is sea-salt from southwester wind direction from Andaman sea (according to article 3.4.2). The latter one reason is usage of $CaCl_2$ and NaCl in the Royal Rain Making Project. Especially, The mass concentration of the cations were higher in dry season than in wet season. The high concentration in dry season might be caused by the strong winds and less ground humid, which could carry lots of crustal and pollution matters from outside areas to Chiang Mai. The low concentrations in rainy season might be related to more precipitation that would wash out more aerosols. Crustal dust make Ca^{2+} be a highest level of cation concentration which agreed with Ali-Mohamed and Ali (2001). They investigated that the presence of Ca^{2+} and Mg^{2+} cations in the sandy soil in Muharraq island were expected mainly from the soil, whereas the Na^+ cation were expected to come mainly from the sea-salt particle evaporates. In addition to Ali-Mohamed and Matter (1996) illustrated that high values of Ca^{2+} is generally indicative of dust contamination.

Table 3.8 Monthly average concentrations (µg m^{-3}) of cations in PM$_{10}$ samples from two sampling sites

Sampling Station	Season	Month	N	Average ± SD					
				PM$_{10}$	**Na^{+}**	**NH$_4^{+}$**	**K^{+}**	**Ca^{2+}**	**Mg^{2+}**
YP	Dry	Feb	7	147.0	1.1 ± 0.2^{ab}	2.9 ± 1.0^{a}	2.4 ± 0.7^{a}	3.3 ± 0.8^{ab}	0.2 ± 0.1^{b}
		Mar	7	117.3	1.5 ± 0.8^{a}	2.6 ± 1.1^{ab}	1.8 ± 1.0^{a}	4.2 ± 0.7^{a}	0.3 ± 0.1^{a}
		Apr	8	67.9	1.7 ± 0.7^{a}	1.0 ± 0.7^{ab}	0.9 ± 0.4^{b}	3.0 ± 1.2^{ab}	0.5 ± 0.1^{ab}
		Average	**22**	**108.9**	**1.5±0.7**	**2.2±1.2**	**1.7±1.0**	**3.5±1.0**	**0.3±0.2**
	Wet	Jun	7	38.4	1.9 ± 0.8^{a}	0.4 ± 0.1^{b}	0.2 ± 0.1^{b}	2.0 ± 0.9^{b}	0.1 ± 0.1^{b}
		Jul	9	43.4	0.7 ± 0.2^{b}	0.4 ± 0.2^{ab}	0.5 ± 0.1^{b}	3.3 ± 1.1^{ab}	0.3 ± 0.1^{b}
		Aug	9	48.1	0.5 ± 0.5^{b}	0.5 ± 0.1^{b}	0.5 ± 0.1^{b}	2.5 ± 0.6^{b}	0.2 ± 0.1^{b}
		Average	**25**	**43.7**	**1.0±0.7**	**0.4±0.1**	**0.4±0.2**	**2.6±1.0**	**0.2±0.1**
		Dry+Wet	**47**	**74.2**	**1.2±0.8**	**1.2±1.2**	**1.0±1.0**	**3.0±1.3**	**0.3±0.1**
MH	Dry	Mar	4	46.5	1.6±0.4	1.3±0.6	0.9±0.1	0.9±0.2	0.3±0.1
		Apr	8	47.7	1.8±0.8	1.0±0.6	0.8±0.4	1.2±0.6	0.5±0.3
		Average	**12**	**47.3**	**1.7±0.7**	**1.1±0.6**	**0.8±0.3**	**1.1±0.5**	**0.5±0.3**

YP = Yupparaj Wittayalai School; MH = Mae Hia Rearch Center $^{a,\ b,\ ab,}$ = Significant difference ($p < 0.05$)

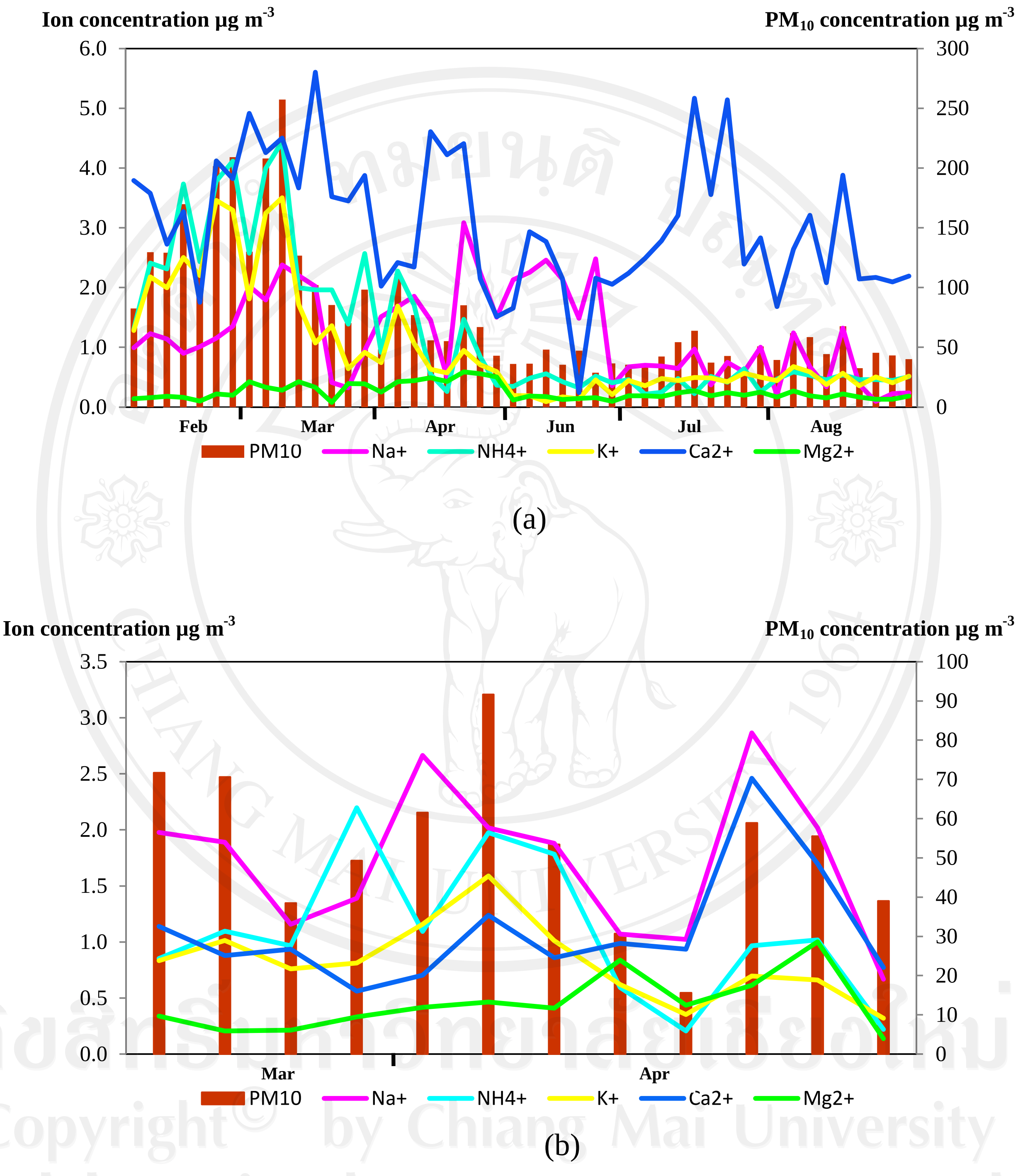


Figure 3.11 The variation of the PM_{10}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} concentrations; a) YP and b) MH stations.

3.8 The seasonal variation of PM_{10}, PM_{10}-bound concentrations and forest fire area

Forest fire is a substantial source of air pollution during winter. The forest fire information was optain from Thailand Forest Fire Control Division in the year 2009, In dry season of 2009 (January - April) forest fire in Chiang Mai was detected 1,388 times and 8,884.25 rais were damaged. On the PM_{10} sampling days (22 days), there were 380 fire frequency occured and 2,447 rais damage area (Table 3.9 and Figure 3.12).

Table 3.9 Chiang Mai forest fire frequency and damage area from Feb-Apr 2009

Date	Forest fire frequency	Damage area (rai)
4-Feb-09	13	62
11-Feb-09	9	41
14-Feb-09	20	101
18-Feb-09	20	111
21-Feb-09	19	110
25-Feb-09	40	264
28-Feb-09	45	353
4-Mar-09	54	341
7-Mar-09	34	321
11-Mar-09	33	290
14-Mar-09	22	115
18-Mar-09	0	0
21-Mar-09	4	26
25-Mar-09	3	7
28-Mar-09	7	28
1-Apr-09	15	84
4-Apr-09	12	67
8-Apr-09	11	58
11-Apr-09	3	10
15-Apr-09	1	3
22-Apr-09	12	36
25-Apr-09	3	19
29-Apr-09	0	0
Total	**380**	**2447**

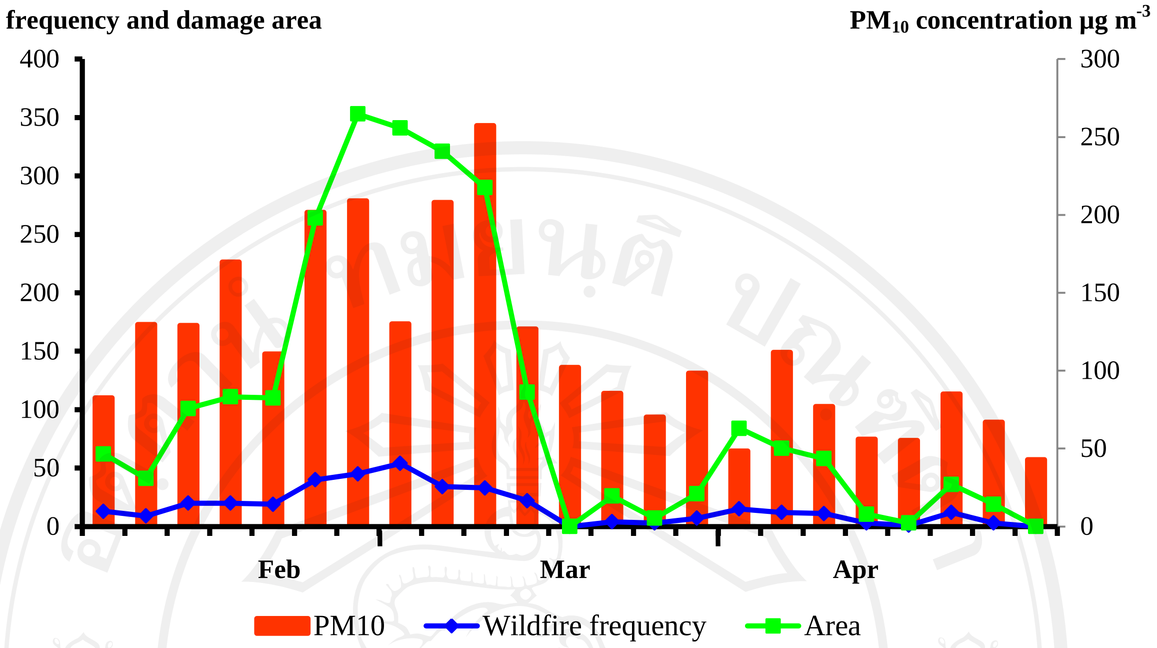


Figure 3.12 Variation of PM_{10} ($\mu g/m^3$) at YP site, forest fire frequency and damage area (rai)

The monthly average concentrations of damage area (DA), PM_{10} and PM_{10}-bound ions (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) obtained from YP station. It was found that trends of all pollutant concentrations were similar. Their concentrations were highest in February and still high in March and obviously decreased in April until August due to high precipitation. The highest concentrations are usually observed in the dry season, while the lowest concentrations tend to occur in the wet season. The average concentrations of pollutants PM_{10}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) in the dry season collected at the YP site were approximately 2 times higher those of the MH site. The pattern of seasonal variation is occurred under conditions of humidity and temperature (USEPA, 2004). Seasonal concentrations of the pollutants were significantly different ($p < 0.05$). In the previous study (Chantara *et al*., 2009) pollutant concentrations in the dry season were approximately 2-4 times higher than those in the wet season.

In the months of winter, concentrations are high and they fall in April and through the summer months. This trend follows the number of reported forest fires. Monthly averages of $PM_{2.5}$ from 4 stations varied from 15.39 to 138.31 µg/m^3 and 27.29 to 173.40 µg/m^3 for PM_{10} (Vinitketkumnuen *et al., (*2002). Furthermore, in all six cities (Bandung, Bangkok, Beijing, Chennai, Manila and Hanoi), the levels of PM_{10} and $PM_{2.5}$ were high, especially during the dry season. The average concentrations of $PM_{2.5}$ and PM_{10} in the cities ranged, 44-168 and 54-262 µg/m^3 in the dry season, and 18-104 and 33-180 µg/m^3 in the wet season respectively (Oanh *et al.,* 2006). Zhuang *et al*. (2005) studied the seasonal cycle and source of $PM_{2.5}$ and TSP aerosol in Shanghai found that Ca^{2+}, Na^+ and Mg^{2+} partly from the soil, were frequently observed of higher concentrations in winter. The concentration of K^+ in TSP sample was much higher in winter than those in spring, summer and autumn, indicating that K^+ was primarily related to the burning activities, which were enhanced in the cold season.

3.9 Correlation analysis

3.9.1 Yupparaj Wittayalai School station

All parameters including PM_{10}, Na^{+}, NH_4^{+}, K^{+}, Ca^{2+} Mg^{2+} and DA obtained from all measuring techniques were analyzed to find out correlation of each pair (Table 3.10-3.12). The data of forest fire damage area (DA) from Forest Fire Control Division in the year 2009 were well correlated with PM_{10} concentrations in the dry season (r = 0.829) as shown in Table 3.10. However, in dry season DA still highly correlated to some PM_{10}-bound cations, especially NH_4^{+} and K^{+} (r = 0.788 and r = 0.833 respectively). But there were no correlation DA and PM_{10} in wet season due to no forest fire occure.

Noticeably, strong correlation of PM_{10} to NH_4^{+} and K^{+} concentrations in the dry season (r = 0.958 and r = 0.964 respectively). It can be concluded that NH_4^{+} and K^{+} are the major chemical component of PM_{10}. Moreover, most of the relationship of five water-soluble are positive correlation. Especially the correlation between NH_4^{+} and K^{+} in dry season were very strong (r = 0.933). While other cations correlation were relatively low, the correlation between Na^{+} to Mg^{2+} was fair (r = 0.549). These results explained that NH_4^{+} and K^{+} are most PM_{10} related cations which agreed with previous studies, which they reported that the major ionic species were Cl^{-}, SO_4^{2-}, K^{+} and NH_4^{+} from Savanna fires (Andreae *et al.*, 1998) and K^{+}, Cl^{-}, and SO_4^{2-} from fires of the Amazon basin (Yamasoe *et al*., 2000). In addition, during the biomass burning period, fine K^{+} increased significantly by 326% compared to the normal period. Also NH_4^{+} and K^{+} were the dominant ionic species observed during the biomass burning period. K^{+} is a highly useful tracer for pyrogenic aerosols because the combustion of plant matter, which contains K^+ as a major electrolyte within its cytoplasm (Kim *et al.*, 2007).

In wet season NH_4^+ and K^+ were not the major chemical component of PM_{10} but were replaced by Ca^{2+} and Mg^{2+}. The correlation level of Ca^{2+} and Mg^{2+} to PM_{10} were relatively fair (r = 0.449 and r = 0.563 respectively). Other cations correlation were relatively low, the correlation between K^+ to Mg^{2+} was fair correlation (r = 0.586). The presence of Ca^{2+}, K^+ and Mg^{2+} in PM samples suggests that they are contributed by re-suspended road dust (in the form of carbonates, bicarbonates and silicates). The other source for Ca^{2+}, K^+ and Mg^{2+} is marine aerosol (Kim *et al.*, 2006). In addition, the K^+ can also emitted by plants through respiration mechanism controlled by hot and humid conditions (Chandra Mouli *et al.*, 2003).

Table 3.10 Pearson's correlation of PM_{10} and PM_{10}-bound cations at YP site and damage area in Chiang Mai Province in dry season

	PM_{10}	**DA**	**Na^+**	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
PM_{10}	1						
DA	.829**	1					
Na^+	.175	.224	1				
NH_4^+	.958**	.788**	.085	1			
K^+	.964**	.833**	.081	.933**	1		
Ca^{2+}	.350	.286	.171	.286	.207	1	
Mg^{2+}	-.388	-.245	.549**	-.469*	-.517*	.056	1

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

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

Table 3.11 Pearson's correlation of PM$_{10}$ and PM$_{10}$-bound cations at YP site and Chiang Mai Province in wet season

	PM$_{10}$	**Na^{+}**	**NH$_4^{+}$**	**K^{+}**	**Ca^{2+}**	**Mg^{2+}**
PM$_{10}$	1					
Na^{+}	-.032	1				
NH$_4^{+}$	-.026	.043	1			
K^{+}	.383	-.501*	.240	1		
Ca^{2+}	.449*	-.055	-.053*	.390	1	
Mg^{2+}	.563**	-.035	-.014	.586**	.668**	1

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

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

Table 3.12 Pearson's correlation of PM$_{10}$ and PM$_{10}$-bound cations at YP site and damage area in Chiang Mai Province in dry and wet season

	PM$_{10}$	**Na^{+}**	**NH$_4^{+}$**	**K^{+}**	**Ca^{2+}**	**Mg^{2+}**
PM$_{10}$	1					
Na^{+}	.293*	1				
NH$_4^{+}$	.964**	.262	1			
K^{+}	.970**	.215	.957**	1		
Ca^{2+}	.465**	.169	.403**	.390**	1	
Mg^{2+}	.163	.422**	.138	.097	.354*	1

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

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

3.9.2 Mae Hia Research Center site

The relatively between the various cation species in particles, PM_{10} and forest fire damage area in dry season at MH site. Pearson correlation (r) was carried out on cations, PM_{10} and forest fire damage area. The Pearson correlation coefficients were calculated using SPSS for Windows (version 14) software that is significant at the 0.01 and 0.05 level. The resultant r values for cations, PM_{10} and forest fire damage area are shown in Table 3.13. The correlations coefficient (r) at 0.05 level of K^+ with PM_{10} and DA were strong correlated (r = 0.832 and 0.792, respectively) but less than in YP site. Correlation of NH_4^+ and K^+ in MH still high (r = 0.737) but less than YP site too. The correlation at 0.01 level between NH_4^+ to PM_{10} (r = 0.587) and NH_4^+ to DA (r = 0.614) were fair. Moreover, Na^+ to PM_{10} and Na^+ to DA their correlation was relatively fair (r = 0.664 and 0.669). These can explain that in dry season the concentrations of NH_4^+ and K^+ were highly relate to each other, but K^+ has a strongly correlation to either PM_{10} and DA than in the case of NH_4^+ which only fair corrlelation. In addition the two pollutant indicators (PM_{10} and DA) have no correlation because of MH site located at sub-urban area. Meanwhile in YP site located at the same site of the PCD air quality monitor station.

Table 3.13 Pearson's correlation of PM_{10} and PM_{10}-bound cations at MH site and damage area in Chiang Mai Province in dry season

	PM_{10}	**DA**	**Na^+**	**NH_4^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
PM_{10}	1						
DA	.554	1					
Na^+	.664*	.669*	1				
NH_4^+	.587*	.614*	.370	1			
K^+	.832**	.792**	.566	.737**	1		
Ca^{2+}	.220	-.005	.558	-.099	-.049	1	
Mg^{2+}	-.067	.058	.265	-.041	-.068	.536	1

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

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