CHAPTER 3

Results and Discussion

3.1 Validation of ion analysis by Ion chromatograph (IC)

3.1.1 Chromatograms and calibration curves of ions

Cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, NO_3^- and SO_4^{2-}) were analyzed by ion chromatograph (IC) under the optimum condition provided in topic 2.4. Chromatograms of anion and cation standards (0.8 µg/mL) are shown in Figures 3.1 and 3.2, respectively.

The solutions of mixed anion standard and cation standard ranged from 0.05 to 10.0 µg/mL were prepared. The calibration curve of each ion standard was constructed using ion concentrations with peak areas. Coefficients of determination (R^2) were found to be higher than 0.995. Linear equation, retention time and coefficients of determination (R^2) are shown in Table 3.1. Examples of the calibration curves for determination of anions and cations are shown in Figure 3.3 and 3.4, respectively.

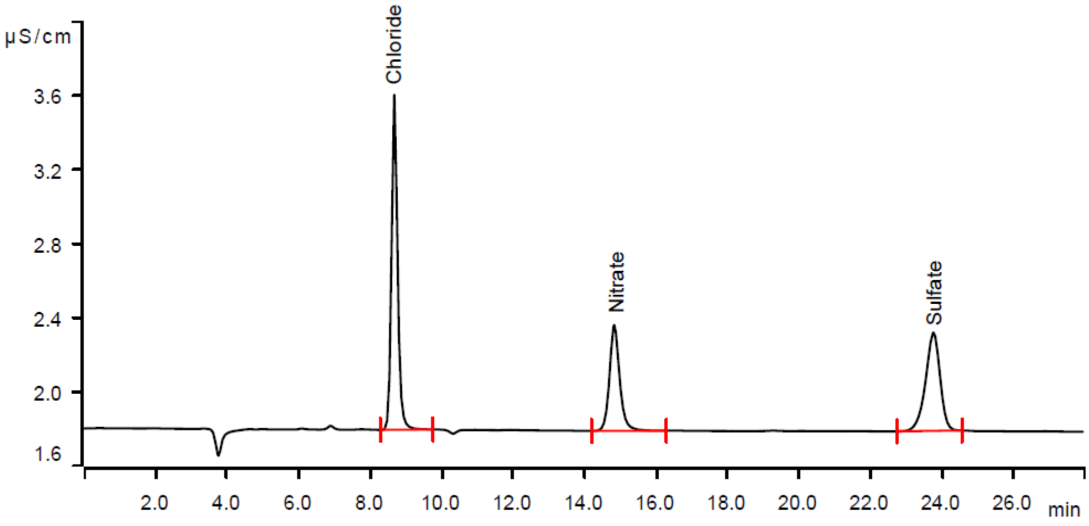


Figure 3.1 Chromatogram of mixed anion standard (0.8 µg/mL)

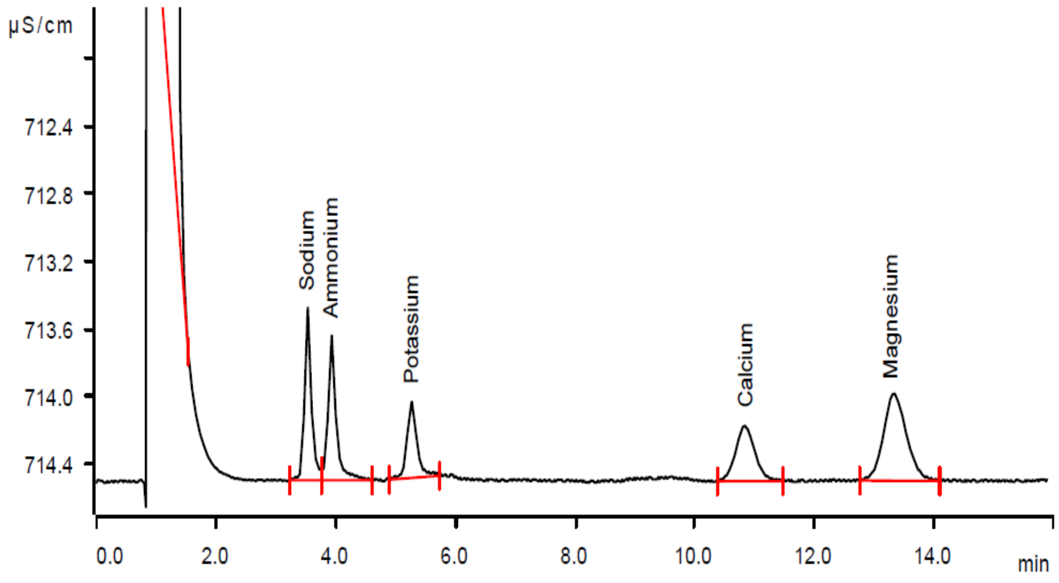


Figure 3.2 Chromatogram of mixed cation standard (0.8 μg/mL)

Table 3.1 The Retention times of ions from chromatograms of IC analysis, and examples of calibration curves for ion determination

Ion species		Retention times (min)	Ranges of standard concentrations (μg/mL)	Linear equations	Coefficients of Determination (R^2)
Anions	Cl^-	8.6	0.10-10.00	$y = 0.405x – 0.022$	1.000
	NO_3^-	14.8	0.10-10.00	$y = 0.222x – 0.009$	1.000
	SO_4^{2-}	23.7	0.10-10.00	$y = 0.294x – 0.004$	1.000
Cations	Na^+	3.5	0.10-10.00	$y = 0.294x + 0.015$	1.000
	NH_4^+	3.9	0.10-10.00	$y = 0.404x – 0.064$	0.999
	K^+	5.2	0.10-10.00	$y = 0.174x + 0.017$	0.999
	Ca^{2+}	10.8	0.10-10.00	$y = 0.268x + 0.030$	0.999
	Mg^{2+}	13.3	0.10-4.00	$y = 0.582x – 0.006$	1.000

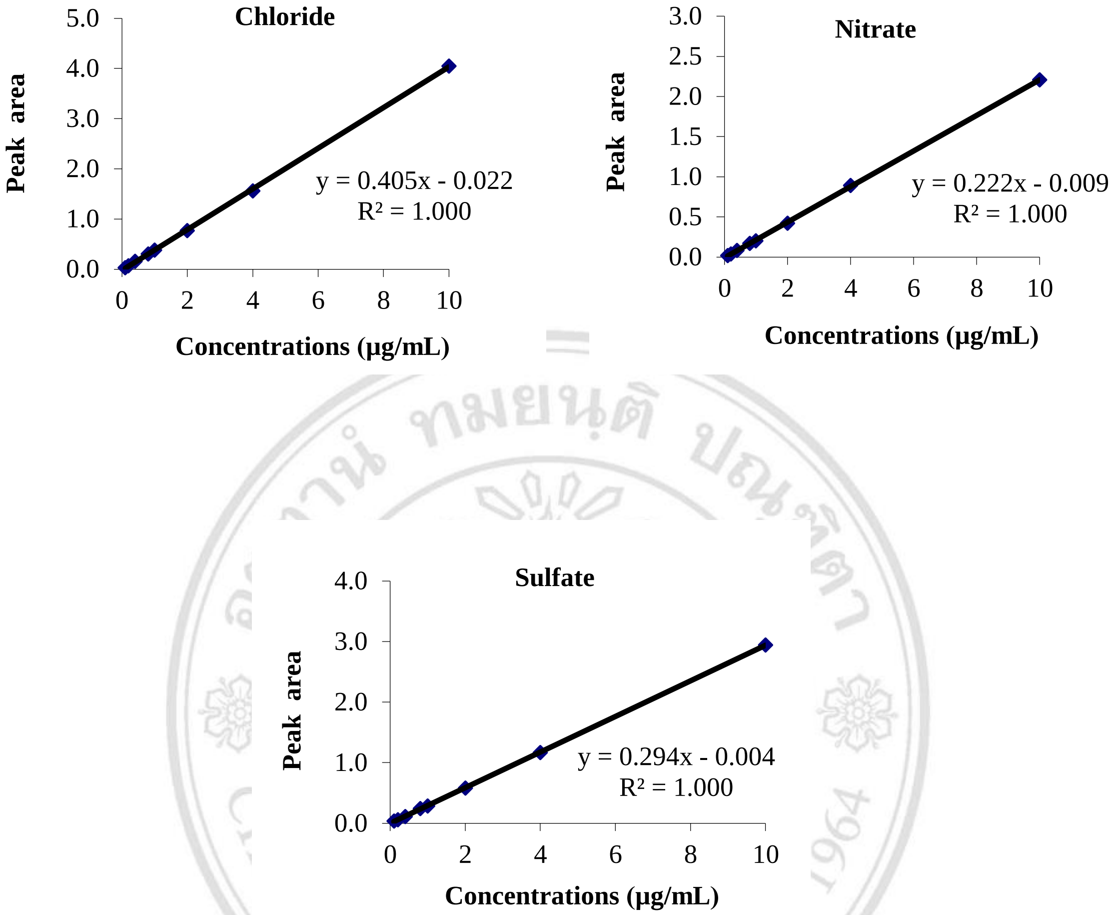


Figure 3.3 Calibration curves for determination of anions

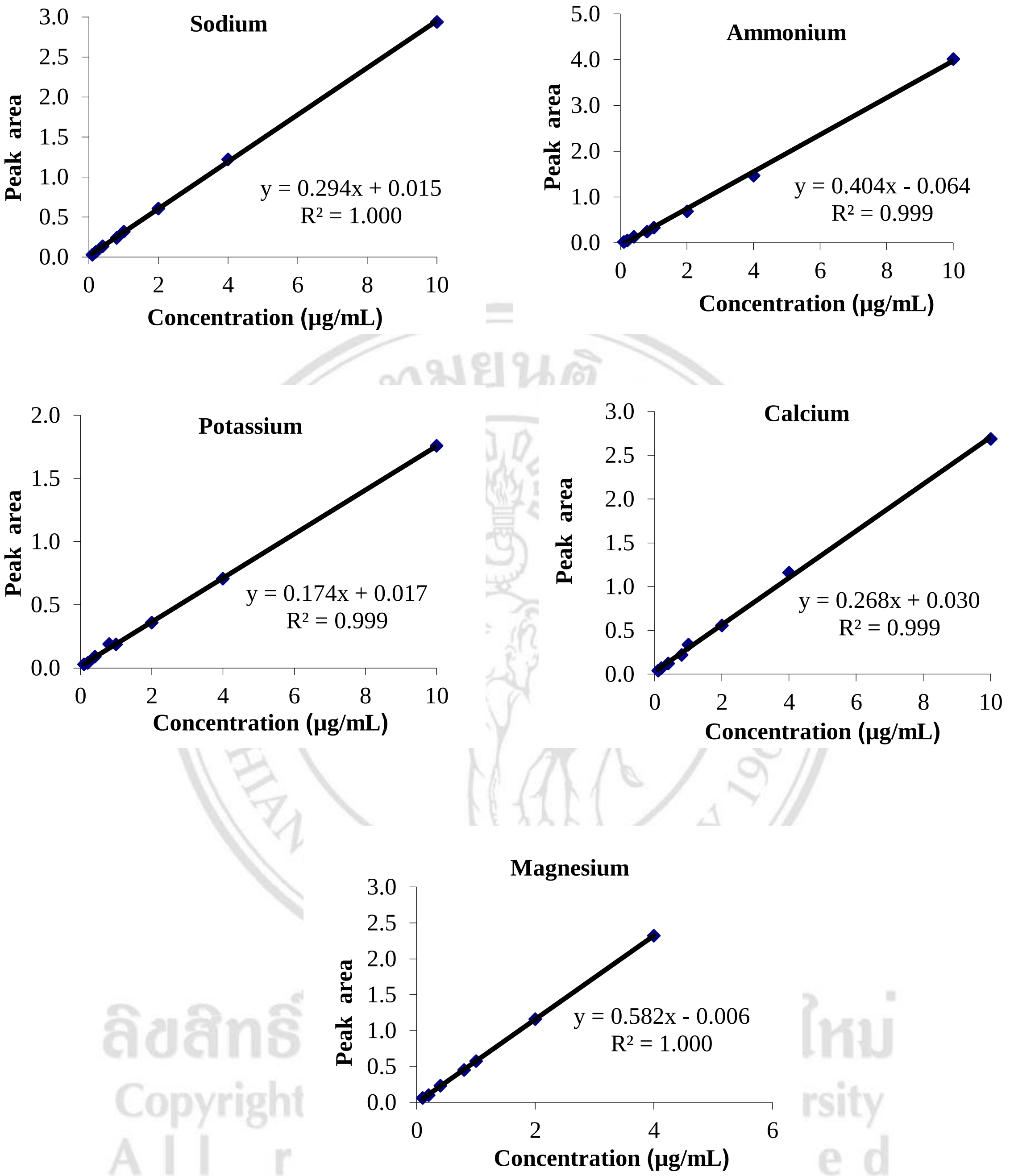


Figure 3.4 Calibration curves for determination of cations

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

Limit of detection (LOD) was calculated as three times of standard deviation (SD) (LOD = 3SD), while limit of quantification (LOQ) was calculated as ten times of standard deviation (LOQ = 10SD). Their values were determined by 5 injections of the lowest concentrations used for calibration curve construction (0.05 µg/mL) of mixed standard solutions. LOD values of ions ranged from 0.004-0.033 µg/mL, while LOQ values ranged from 0.012-0.109 µg/mL. LOD and LOQ (Table 3.2).

Table 3.2 Limit of detection and limit of quantification of ion chromatograph for ion analysis

No. of injection	Concentration (µg/mL)							
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
1	0.0490	0.0560	0.0521	0.0530	0.0654	0.0488	0.0511	0.0544
2	0.0519	0.0528	0.0504	0.0664	0.0595	0.0517	0.0557	0.0575
3	0.0497	0.0538	0.0589	0.0445	0.0529	0.0509	0.0525	0.0673
4	0.0548	0.0541	0.0521	0.0462	0.0614	0.0532	0.0626	0.0565
5	0.0494	0.0547	0.0551	0.0676	0.0552	0.0501	0.0589	0.0507
Average	0.0510	0.0543	0.0537	0.0555	0.0589	0.0509	0.0562	0.0573
SD	0.0024	0.0012	0.0033	0.0109	0.0050	0.0016	0.0047	0.0062
LOD	**0.0073**	**0.0035**	**0.0100**	**0.0328**	**0.0149**	**0.0049**	**0.0140**	**0.0186**
LOQ	**0.0245**	**0.0117**	**0.0334**	**0.1094**	**0.0497**	**0.0163**	**0.0467**	**0.0620**

3.1.3 Accuracy of ion analysis by Ion chromatography

1) Repeatability

The repeatability of anions and cations analyzed by ion chromatograph was determined with 5 injections of a 0.8 µg/mL mixed anion and 0.8 µg/mL mixed cation standards. The precision was estimated by relative standard deviation (%RSD) as shown in Table 3.3. The %RSD of individual ion at 0.8 µg/mL ranged from 0.58-2.47%, which revealed very good repeatability of injections.

Table 3.3 Repeatability of ion chromatograph for ion analysis

No. of injection	Concentration (µg/mL)							
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
1	0.7935	0.8231	0.8038	0.8150	0.8065	0.7071	0.7993	0.6792
2	0.8040	0.8318	0.8083	0.8176	0.8110	0.7061	0.7604	0.7065
3	0.8371	0.8495	0.8057	0.7985	0.8076	0.7202	0.7893	0.6848
4	0.7996	0.8386	0.8478	0.8231	0.7991	0.7046	0.7925	0.7013
5	0.8202	0.8356	0.8083	0.8132	0.8021	0.7152	0.8137	0.7162
Average	0.8109	0.8357	0.8148	0.8135	0.8052	0.7106	0.7910	0.6976
SD	0.0177	0.0096	0.0185	0.0091	0.0047	0.0068	0.0195	0.0154
%RSD	**2.18**	**1.15**	**2.28**	**1.12**	**0.58**	**0.95**	**2.47**	**2.20**

2) Reproducibility

The reproducibility was checked by injecting of a 0.8 µg/mL mixed anion and 0.8 µg/mL mixed cation standard solutions once a month for 5 continuous months. The precision was estimated by %RSD as shown in Table 3.4. It was found to be very good precision of all ions (0.66-3.73% RSD) was also found.

Table 3.4 Reproducibility of ion chromatograph for ion analysis

No. of injection	Concentration (µg/mL)							
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
1	0.8383	0.8391	0.7809	0.7747	0.8218	0.7440	0.7084	0.7712
2	0.8407	0.8505	0.8025	0.7722	0.8209	0.7550	0.7708	0.7525
3	0.8226	0.8421	0.7873	0.7766	0.8233	0.7644	0.7758	0.7732
4	0.8609	0.8435	0.7847	0.7476	0.8239	0.7582	0.7491	0.7760
5	0.8294	0.8356	0.7892	0.7473	0.7920	0.7758	0.7717	0.7605
Average	0.8384	0.8422	0.7889	0.7637	0.8164	0.7595	0.7552	0.7667
SD	0.0145	0.0056	0.0082	0.0149	0.0137	0.0117	0.0281	0.0099
%RSD	**1.73**	**0.66**	**1.04**	**1.95**	**1.67**	**1.55**	**3.73**	**1.29**

3.2 Analysis of atmospheric particulates deposition by four-stage filter pack

3.2.1 Atmospheric particulates deposition amount

Atmospheric particulates deposition amount was calculated by multiplication of monthly ion concentration in ambient air and its deposition velocity (V_d) (see detail of the calculation equation in Appendix A-1). Amount of particulate deposition in ambient air was reported in a unit of nmol/m^3 (see Table B, Appendix B). In this study, deposition amount was calculated by using the deposition velocities (V_d) from Rao et al., 1992, where the sampling site was located in urban area of Pune city, India. The study site was relatively similar to this study and therefore, the valuse of deposition velocities mentioned above were used in this study**.**

Particulate deposition samples were collected once a month in wet season for 4 months (July 2012 to October 2012) and every 10 days in dry season for 5 months (November 2012 to March 2013). Therefore, 12 samples were collected in wet season, while 15 samples were collected in dry season. In total, 27 samples were collected in this study.

The monthly mean particulate depositions in wet and dry seasons obtained from the four-stage filter pack are presented in Table 3.5**.** The values (mg/m^2) obtained from the four-stage filter pack method in wet season in descending order were Ca^{2+} (28.28) > NO_3^- (10.73) > SO_4^{2-} (5.13) > K^+ (4.20) > Na^+ (3.93) > Cl^- (2.06) > NH_4^+ (1.02) > Mg^{2+} (0.86), whereas those in dry season they were Ca^{2+} (65.59) > SO_4^{2-} (17.38) > NO_3^- (13.62) > K^+ (8.67) > Na^+ (4.33) > Cl^- (4.26) > NH_4^+ (1.19) > Mg^{2+} (1.03). It was found that the amount in wet season was significantly lower ($p < 0.05$) than that in dry season. Precipitation was found to be a main factor influencing on ion amount. High precipitation amount causes low atmospheric deposition. The total precipitation at the sampling site obtained from the acid deposition monitoring project, was high in wet season (652 mm, 58 days) and lower in dry season (120 mm, 19 days). The ion deposition amount in the dry season was approximately 2 - 3 times higher than that in the wet season.

Calcium ion was the major ion found in both wet and dry seasons. Its concentration was approximately 53% of all ions found. In order to check the quality of the data, blind samples (reference material) obtained from the Inter-laboratory Comparison Project was used to test efficiencies (accuracy and precision) of extraction and analysis methods. Accuracy of the methods was considered from the results in comparison with prepared values of the reference materials.

The blind samples contained high (121W) and low (122W) concentrations of ions. The result reveals that the analysis of Ca^{2+} was low accurate (> 30% difference) in both concentrations. The measured values were 24.5 and 10.0 µmol/L for high and low concentrations, respectively, while the prepared values were 18.6 and 5.6 µmol/L, respectively. It can be concluded that the values of Ca^{2+} found in this work was about 30-79% high than those existed in the atmosphere. This high value of Ca^{2} was probably due to some contamination in the deionized water used in the analysis. In addition, the cation column was also not in a good condition due to its long use period.

Table.3.5 Ion deposition collected by four-stage filter pack method and total precipitation

Season	Month	Ion deposition (mg/m^2)								Precipitation data			
		Anions			Cations					EANET*		MET CENTER**	
		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Total precipitation (mm)	No. of Rainy day	Total precipitation (mm)	No. of Rainy day
Wet	Jul-12 (n=3)	4.81	15.15	10.82	4.07	0.51	6.85	33.78	1.26	146	16	106	19
(n=12)	Aug-12 (n=3)	1.57	8.55	3.43	1.28	0.2	3.44	21.82	0.56	183	18	185	20
	Sep-12 (n=3)	1.63	8.65	2.12	5.58	0.2	0.97	14.94	0.82	248	15	180	17
	Oct-12 (n=3)	0.23	10.59	4.16	4.8	3.2	5.54	42.57	0.79	75	9	80	8
	Monthly mean±SD	**2.06±1.95**	**10.73±3.09**	**5.13±3.89**	**3.93±1.87**	**1.02±0.46**	**4.20±2.57**	**28.28±12.30**	**0.86±0.29**	**652*** **	**58**	**551*** **	**64**
Dry	Nov-12 (n=3)	2.93	10.9	11.38	3.17	0.91	6.1	70.82	0.76	50	9	39	7
(n=15)	Dec-12 (n=3)	3.75	2.79	8.72	2.55	0.31	2.56	36.82	0.31	5	2	1	2
	Jan-13 (n=3)	4.42	6.88	7.23	2.77	0.48	9.21	41.82	0.88	19	2	25	2
	Feb-13 (n=3)	5.31	21.28	33.44	10.3	2.16	16.83	90.78	1.46	39	4	32	5
	Mar-13 (n=3)	4.89	26.25	26.1	2.85	2.1	8.66	87.72	1.75	8	2	17	4
	Monthly mean±SD	**4.26±0.94**	**13.62±9.85**	**17.38±11.70**	**4.33±3.35**	**1.19±0.88**	**8.67±5.26**	**65.59±25.22**	**1.03±0.57**	**120*** **	**19**	**114*** **	**20**

* Data was obtained from the Acid Deposition Monitoring Network in East Asia

** Data was obtained from the Northern Meteorological Center

*** Total precipitation

3.3 Analysis of atmospheric particulates deposition by leaf-washing method

3.3.1 Leaf area of jambolan plum tree

In total 29 leaves, were randomly selected at 3 m height from around the canopy of jambolan plum tree, in which five leaves were used as blank. All leaves were measured for their surface leaf area by Image J 2X program. Leaf area were used for calculation of ion deposition. The leaf area for blanks and samples in each direction are shown in Table 3.6. The mean value of those 29 leaves were 5732 ± 1751 mm^2.

Leaf area of blank samples ranged from 3873-8900 mm^2, while their mean value was 7838 ± 2218 m m^2. For sample leaves, their leaf areas ranged from 3034-8945 mm^2, while the mean value (mm^2) of leaf area in each direction (N, NE, E, SE, S, SW, W and NW) were 5580 ± 397, 4911 ± 520, 3839 ± 697, 4001 ± 889, 5143 ± 658, 6316 ± 2307, 6329 ± 1181 and 6225 ± 556, respectively. Values of leaf area from all directions might be varied due to randomized selection of leaves and the photographic mistaken (see Table D, Appendix D).

Table 3.6 Leaf area of the sampling jambolan plum leaves

Sample type	Direction	Leaf No.	Leaf area (mm^2)		
				mean±SD	mean (m^2)
Blank	-	1	8852	7838±2218	0.0078
	-	2	3873		
	-	3	8900		
	-	4	8863		
	-	5	8702		
Samples	N	1	5314	5580±397	0.0056
		2	5389		
		3	6036		
	NE	1	5426	4911±520	0.0049
		2	4921		
		3	4386		
	E	1	4236	3839±697	0.0038
		2	4247		
		3	3034		
	SE	1	5008	4001±889	0.0040
		2	3326		
		3	3669		
	S	1	5898	5143±658	0.0051
		2	4839		
		3	4693		
	SW	1	5373	6316±2307	0.0063
		2	4629		
		3	8945		
	W	1	7656	6329±1181	0.0063
		2	5396		
		3	5934		
	NW	1	6297	6225±556	0.0062
		2	6742		
		3	5637		
	Mean (n=29)		**5732**		
	Standard Deviation (SD)		**1751**		

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

Monthly average pH and EC values for atmospheric particulates deposition are shown in Figure 3.5. Acid precipitation can be done by measuring pH value of the precipitation, which refers to pH < 5.6. The pH and EC values of deionized water were normally about 6.8 and 0.11 mS/m, respectively.

The average pH values of all samples ranged from 6.4 – 6.6. The samples with pH values above 6 may suggest a quantity of alkaline species in atmosphere. There was not much different of pH values in wet and dry season. However, the pH values in dry season was slightly lower than in the rainy season. Average pH values was highest in September 2012 (6.6 ± 0.03) and the lowest in March 2013 (6.4 ± 0.04).

The average EC value in wet season (0.15 ± 0.01 mS/m) was slightly lower than that in dry season (0.20 ± 0.02 mS/m). EC values indicate level of ion contamination in atmosphere. High EC value indicates high ion contamination. The minimum detected monthly average EC values was in August 2012 (0.14 ± 0.01 mS/m) whereas its maximum EC values was in March 2013 (0.22 ± 0.06 mS/m). High value of EC in March could be influenced by accumulated of particulates in the atmosphere or high concentrations of the pollutants with low precipitation in this month. Therefore, amount of precipitation was affected to EC values.

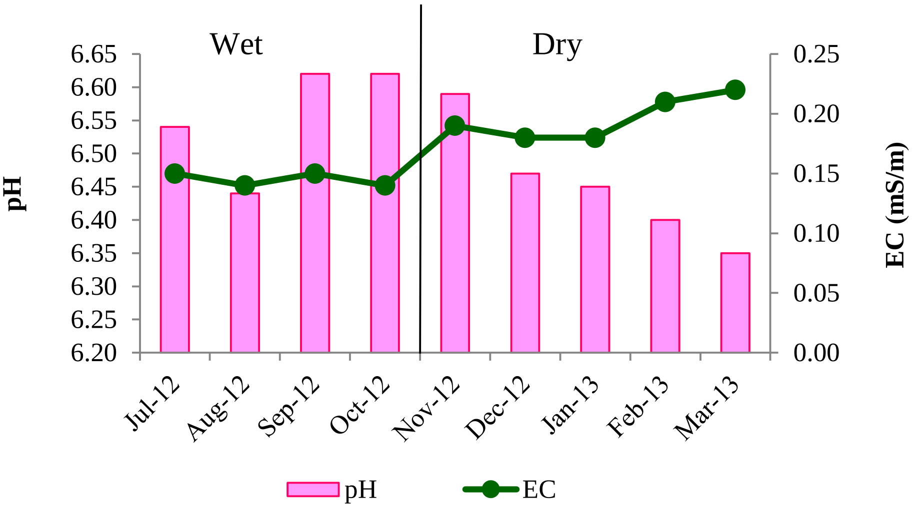


Figure 3.5 Variation of monthly pH and EC values

3.3.3 Particulate deposition amount

Samples were collected in wet season for 4 months (July 2012 – October 2012) and for 5 months in dry season (November 2012 – March 2013). Samples were collected once a month (n = 24) in wet season. In dry season, samples were collected every 10 days (n = 72). Particulate deposition amount was calculated into concentration in ambient air (µg/ml) multiply with weight of deionized water and divided by leaf area (m^2) (see detail of the calculation equation in Appendix A-2)

1) Effect of sampling direction

The average of ion deposition in each direction during wet and dry seasons are shown in Table 3.7 (see detail in Table C-1; Appendix C). Complete Randomized Design (CRD) was used for analysis of the difference of ion deposition among 8 directions. It was found that ion depositions collected from different directions were significantly ($p < 0.05$) different. It can be concluded that sampling direction affected to particulate deposition on leaf. Particulate deposition on leaf surface collected from northeast, east and southeast directions were higher than those from another directions. The main reason could be road dust, which was generated from traffic activity. In addition, it has also some biomass burning nearby in east and southeast directions. Moreover, it has been influenced by wind, which came from southeast, south and southwest directions.

Monthly ion depositions in each direction in wet and dry seasons are shown in Figure 3.6 and 3.7, respectively. Mean ion deposition in dry season was higher than that in wet season, especially for SO_4^{2-} and Ca^{2+} ions, which were anion and cation with the highest concentrations in every condition. Deposition of individual ion showed a similar trend, which was high value in northeast, east and southeast directions. Mean ion deposition in each direction for anions and cations in wet season are shown in Figure 3.8. Concentration of total cations was approximately 2-3 times higher than total anions. For anions, concentrations of NO_3^- and SO_4^{2-} were high, while among cations, Ca^{2+} was always the highest. In dry season, the order of ion concentrations was the same as in wet season. Cation deposition approximately 2-4 times higher than anions. Mean ion deposition in each direction in dry season is shown in Figure 3.9. In general mean of ion deposition in dry season was higher than that in wet season.

Table 3.7 Average of ion deposition (mg/m^2) in each direction during wet and dry season

Season	Ions	Directions							
		N	NE	E	SE	S	SW	W	NW
		Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD
Wet	Cl^-	0.55±0.46	0.88±0.58	1.07±0.70	0.76±0.35	0.87±0.62	0.77±0.50	0.81±0.22	0.52±0.47
	NO_3^-	0.59±0.25	0.90±0.42	1.11±0.51	0.91±0.22	0.65±0.20	0.57±0.39	0.54±0.17	0.84±0.26
	SO_4^{2-}	1.59±1.28	3.13±1.32	4.21±2.37	3.90±1.69	2.50±0.91	2.26±0.83	2.68±1.50	2.10±0.78
	Na^+	1.21±1.11	1.24±0.77	1.96±1.65	1.53±1.03	1.73±1.57	1.41±0.73	0.79±0.50	1.06±0.84
	NH_4^+	0.30±0.28	0.44±0.33	0.67±0.43	0.78±0.33	0.45±0.33	0.51±0.38	0.30±0.26	0.38±0.35
	K^+	0.66±0.23	0.81±0.18	1.02±0.27	1.12±0.19	0.86±0.45	0.62±0.16	0.61±0.09	0.69±0.05
	Ca^{2+}	7.05±3.09	8.11±2.74	10.68±3.88	9.48±4.47	7.26±3.32	6.41±2.95	6.09±2.63	5.94±2.78
	Mg^{2+}	0.20±0.04	0.16±0.07	0.23±0.05	0.23±0.08	0.18±0.03	0.17±0.05	0.14±0.07	0.13±0.05
Dry	Cl^-	3.19±0.55	3.35±0.86	3.61±0.98	4.04±0.78	3.13±0.57	3.00±0.88	2.54±0.82	3.10±1.13
	NO_3^-	6.76±3.99	7.86±5.82	9.91±6.90	10.70±7.62	6.53±3.24	6.44±4.32	5.18±2.36	4.92±2.21
	SO_4^{2-}	7.34±5.33	7.58±6.71	9.64±8.19	9.62±8.52	7.57±6.40	6.38±5.32	6.29±5.20	6.37±5.03
	Na^+	2.68±0.83	2.62±0.28	3.04±0.92	3.60±1.17	2.88±0.71	2.31±0.93	2.04±0.84	2.07±0.29
	NH_4^+	1.65±1.17	1.62±0.78	2.32±0.91	2.43±0.59	1.45±0.78	1.43±0.53	1.03±0.55	1.03±0.52
	K^+	4.28±2.97	3.49±2.26	6.85±4.87	5.59±3.04	3.70±2.28	2.84±1.62	3.41±1.89	2.51±1.83
	Ca^{2+}	37.93±19.21	42.37±21.79	55.42±26.14	54.88±26.90	41.19±18.90	37.12±16.25	35.54±15.81	37.42±14.91
	Mg^{2+}	1.20±0.60	1.48±1.09	2.01±1.03	2.18±1.21	1.07±0.63	1.26±0.43	1.29±0.58	1.06±0.59

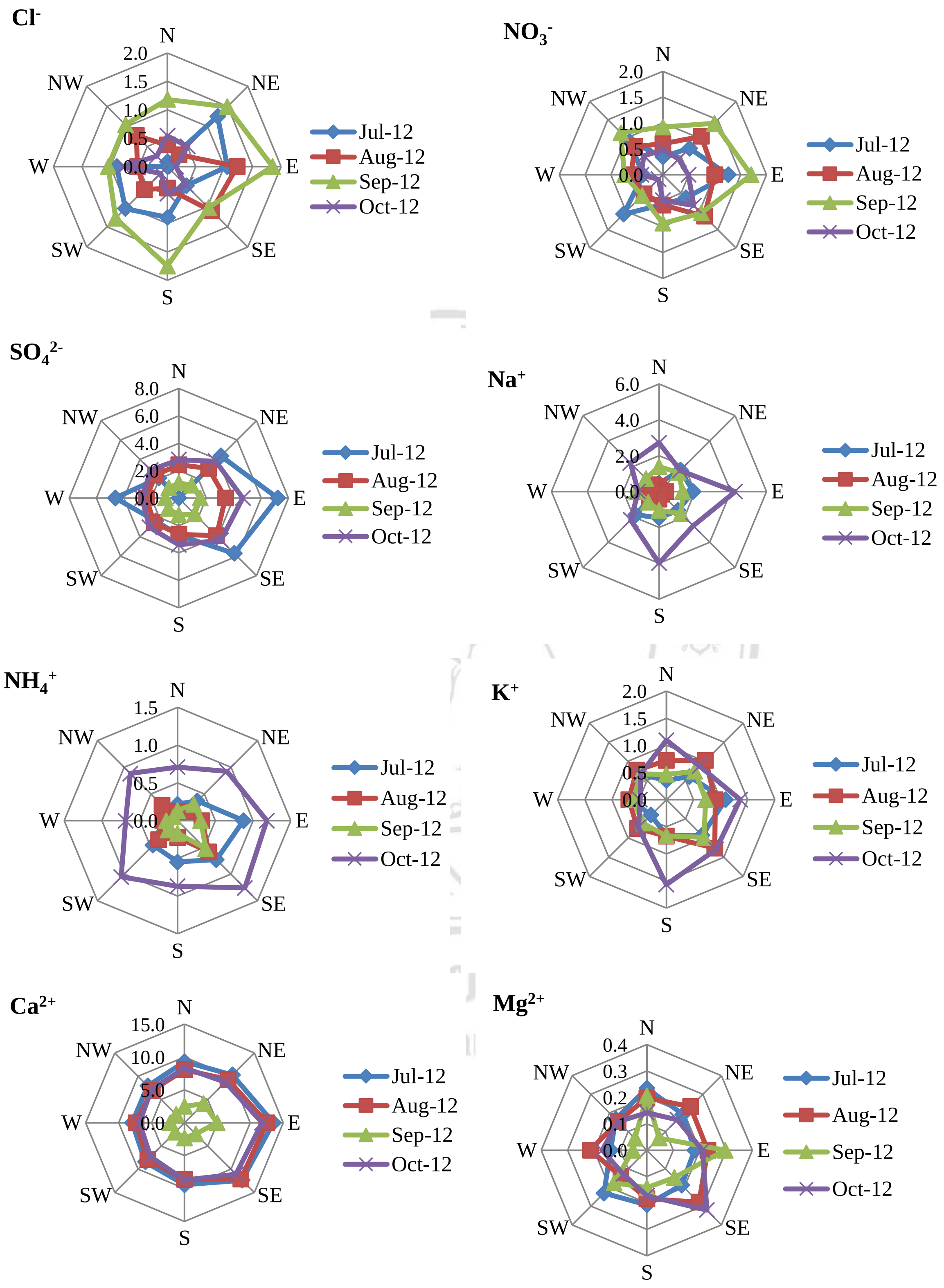


Figure 3.6 Monthly ion deposition (mg/m^2) in wet season collected by leaves in each direction

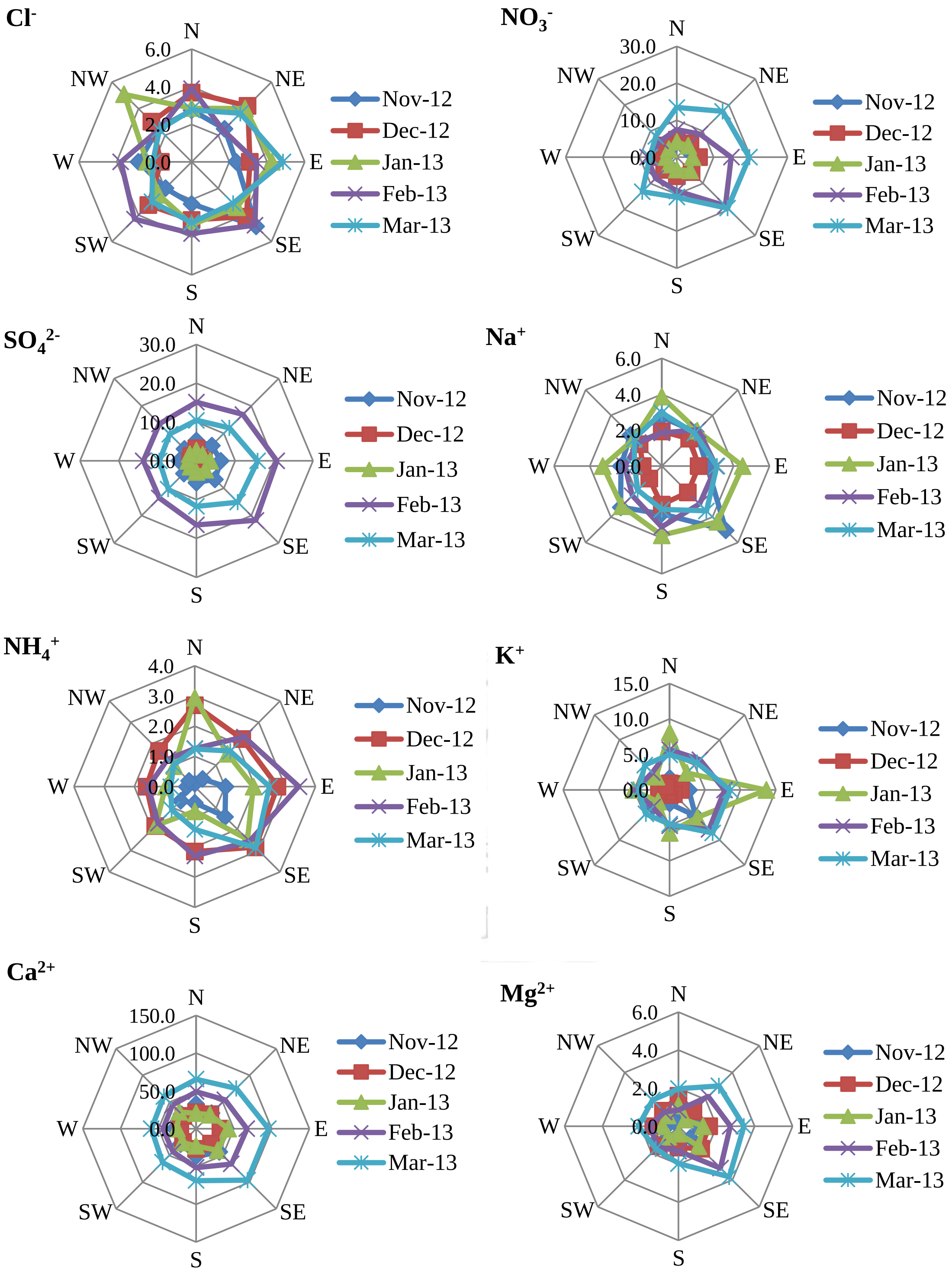


Figure 3.6 Monthly ion deposition (mg/m^2) in dry season collected by leaves in each direction

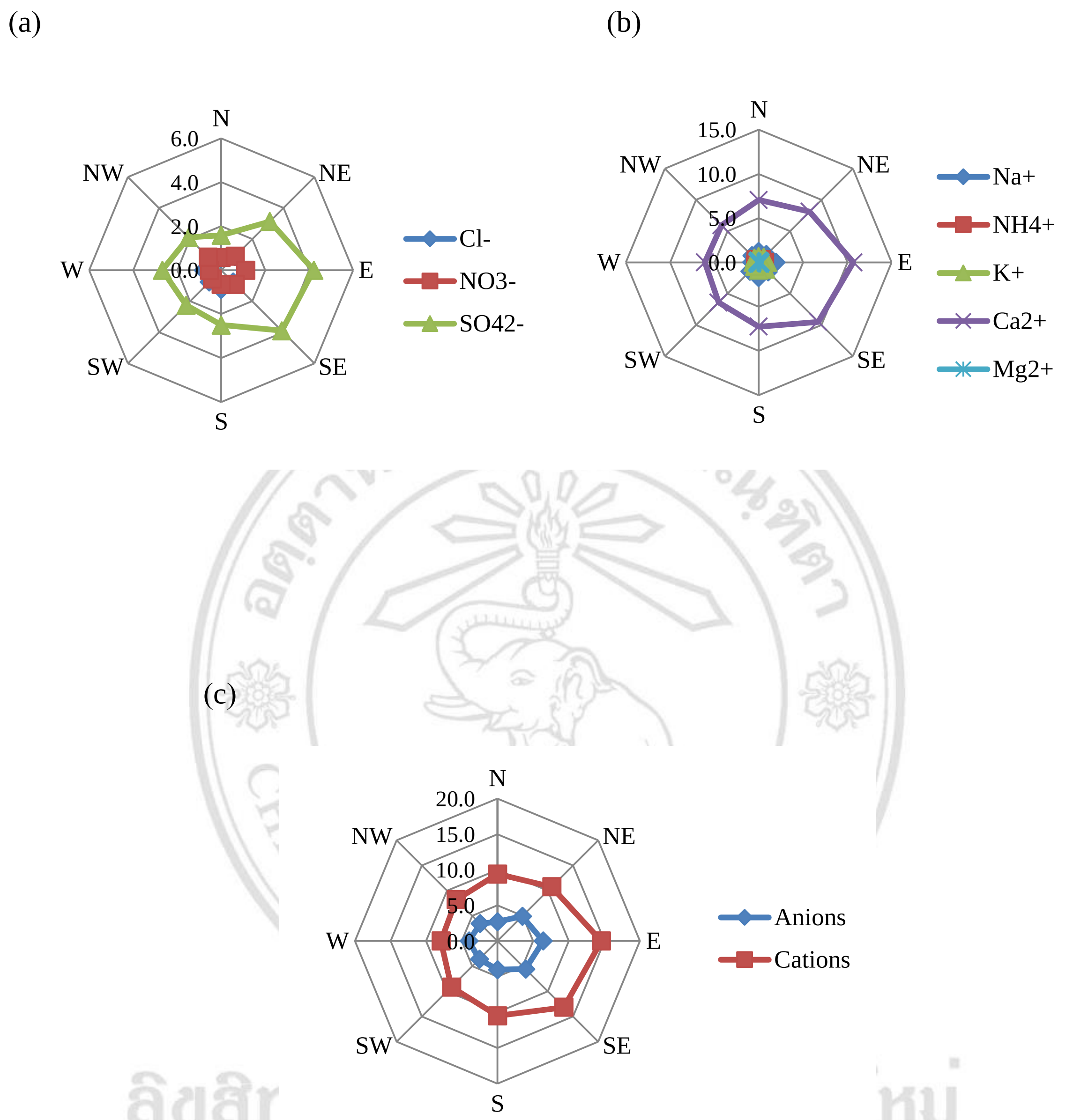


Figure 3.8 Mean ion deposition (mg/m^2) in each direction in wet season

(a) Mean deposition amount of anions.

(b) Mean deposition amount of cations.

(c) Mean of total anions and cations.

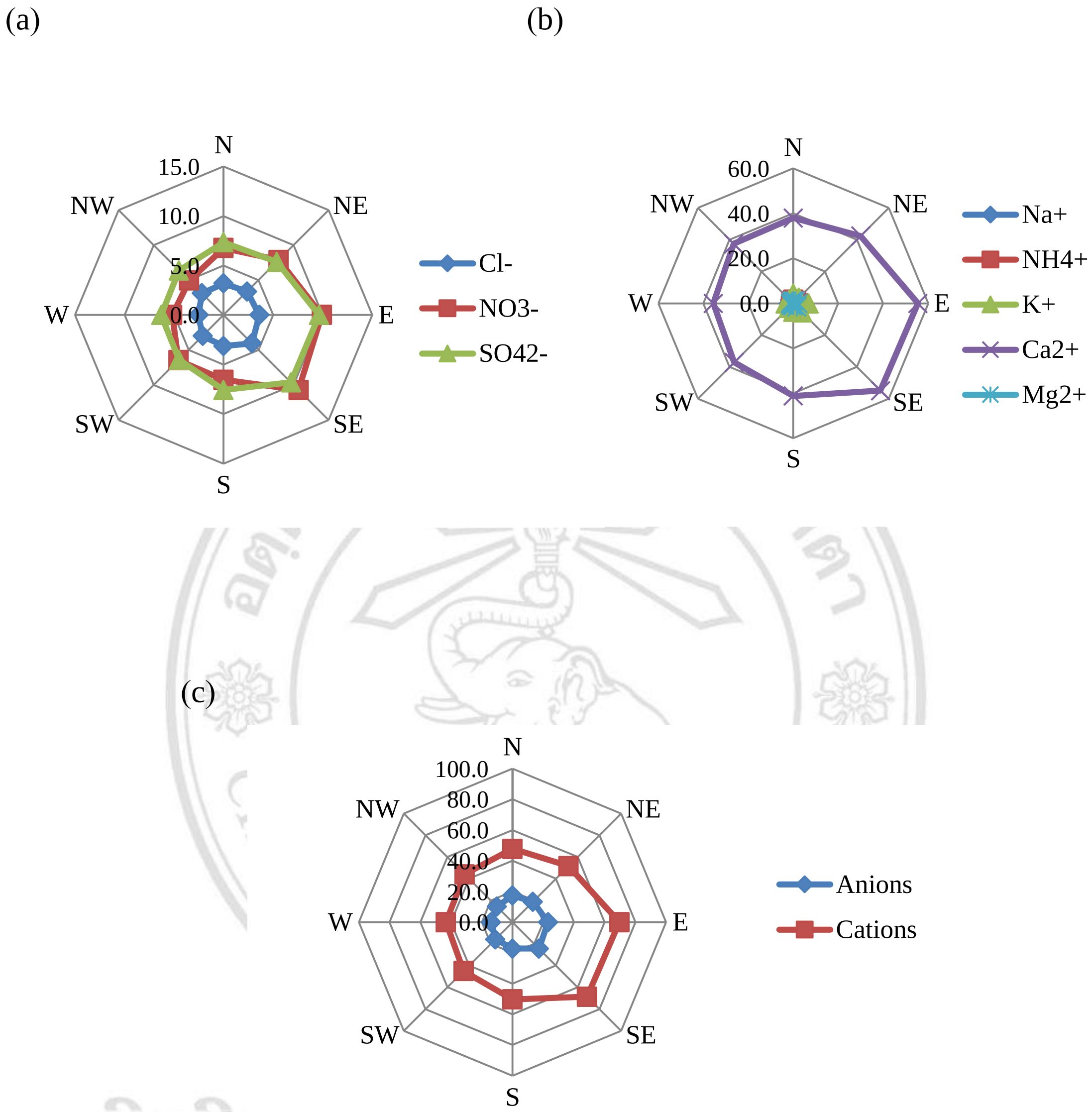


Figure 3.9 Mean ion deposition (mg/m^2) in each direction in dry season

(a) Mean deposition amount of anions.

(b) Mean deposition amount of cations.

(c) Mean of total anions and cations.

2) Effect of seasonal for sampling collection

Ion deposition amount and precipitation in wet and dry seasons are shown in Tables 3.8**.** It was found that amount of dry deposition in dry season was significantly higher ($p < 0.05$) than that in wet season. The main reason was amount of precipitation. Rain can wash out particulates depositied amount on leaf surface. Therefore, high precipitation in wet season (652 mm, 58 days) and lower amount in dry season (120 mm, 19 days) were related with the amount of ion deposition found in each season. The ion deposition amount in the dry season was approximately 2-6 times higher than that in wet season.

Ion depositions in a descending order in wet season were Ca^{2+} (7.63 mg/m^2) > SO_4^{2-} (2.79 mg/m^2) > Na^+ (1.37 mg/m^2) > Cl^- (0.79 mg/m^2)> NO_3^- (0.76 mg/m^2) > K^+ (0.80 mg/m^2) > NH_4^+ (0.41 mg/m^2) > Mg^{2+} (0.19 mg/m^2), while in dry season were Ca^{2+} (42.55 mg/m^2) > SO_4^{2-} (7.60 mg/m^2) > NO_3^- (6.78 mg/m^2) > K^+ (4.08 mg/m^2) > Cl^- (3.24 mg/m^2) > Na^+ (2.40 mg/m^2) > Mg^{2+} (1.44 mg/m^2) > NH_4^+ (1.30 mg/m^2).

Table.3.8 Ion deposition amount collected by leaf-washing method and total precipitation

Season	Month	Ion deposition (mg/m^2)								Precipitation data			
		Anions			Cations					EANET*		MET CENTER**	
		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Total precipitation (mm)	No. of Rainy day	Total precipitation (mm)	No. of Rainy day
Wet	Jul-12 (n=24)	0.75	0.73	3.63	1.18	0.45	0.67	9.89	0.19	146	16	106	19
(n=96)	Aug-12 (n=24)	0.65	0.78	2.84	0.4	0.29	0.85	9.1	0.2	183	18	185	20
	Sep-12 (n=24)	1.33	1.05	1.25	1.26	0.26	0.68	2.79	0.18	248	15	180	17
	Oct-12 (n=24)	0.42	0.48	3.45	2.62	0.64	1.01	8.73	0.18	75	9	80	8
	Monthly mean±SD	**0.79±0.39**	**0.76±0.24**	**2.79±1.08**	**1.37±0.92**	**0.41±0.17**	**0.80±0.16**	**7.63±3.26**	**0.19±0.01**	**652****	**58**	**551*****	**64**
Dry	Nov-12 (n=72)	2.77	3.77	5.35	2.95	0.58	2.26	33.24	0.66	50	9	39	7
(n=360)	Dec-12 (n=72)	3.26	2.58	1.73	1.47	0.88	0.97	24.72	1.38	5	2	1	2
	Jan-13 (n=72)	3.45	3.75	2.65	2.51	1.41	5.86	29.39	0.9	19	2	25	2
	Feb-13 (n=72)	3.6	10.14	16.45	2.54	2.05	5.52	52.38	1.79	39	4	32	5
	Mar-13 (n=72)	3.14	13.67	11.82	2.52	1.57	5.81	73.01	2.48	8	2	17	4
	Monthly mean±SD	**3.24±0.32**	**6.78±4.87**	**7.60±6.33**	**2.40±0.55**	**1.30±0.58**	**4.08±2.30**	**42.55±20.01**	**1.44±0.72**	**120****	**19**	**114*****	**20**

* Data was obtained from the Acid Deposition Monitoring Network in East Asia

** Data was obtained from the Northern Meteorological Center

*** Total precipitation

3.4 Comparison of atmospheric particulates deposition by four-stage filter pack and leaf-washing methods

3.4.1 Particulate deposition amount from both methods

Ion depositions in wet and dry seasons obtained from four-stage filter pack and leaf-washing method were significantly different ($p < 0.05$). The deposition amount obtained from leaf-washing method was affected by amount of precipitation, particularly in wet season. Moreover, this method depends mainly on free flow of particulate deposited on leaf surface. Therefore, particulate deposition amount from leaf-washing method was significantly lower than that of the four-stage filter pack. To be more specific, Ca^{2+} was the highest ion found from both methods. It has highest deposition amount in February and March 2013 and lowest in September 2012.

In addition, ion deposition amount by leaf-washing method (Figure 3.10) and four-stage filter pack method (Figure 3.11) during wet and dry seasons was similar. The first two ions from both methods were identical. Ca^{2+} and K^+ were highest for cations, while SO_4^{2-} and NO_3^- were highest for anions. Although, amount of ion deposition was different among the sampling methods but it has the same trend of deposition in both wet and dry seasons.

Overall, sulphate and nitrate were the dominant anions, while calcium was the major cations obtained from both methods. Therefore, leaf-washing method showed high potential to be used for sampling of atmospheric particulate deposition as an alternative in the wider area with lower operation cost.

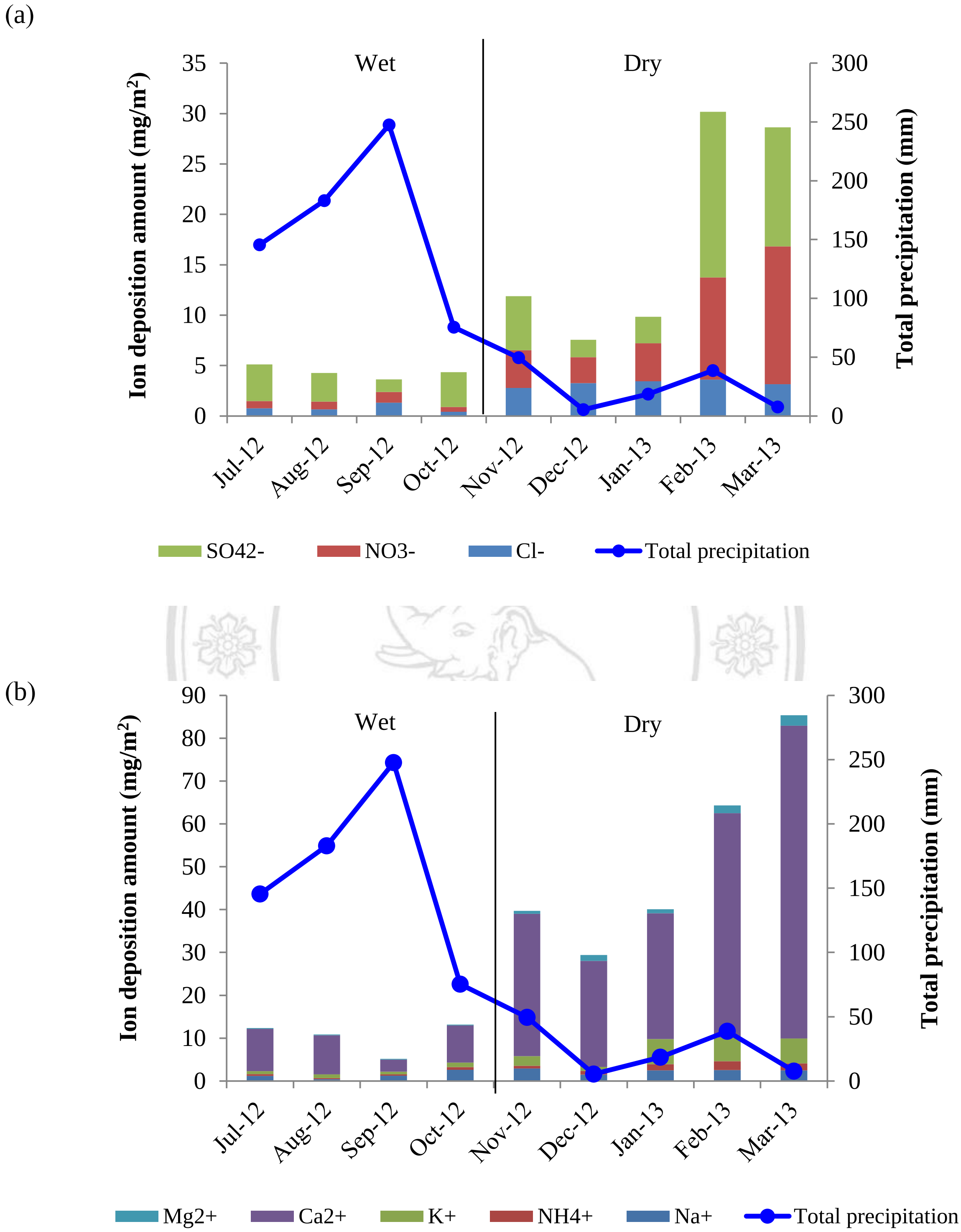
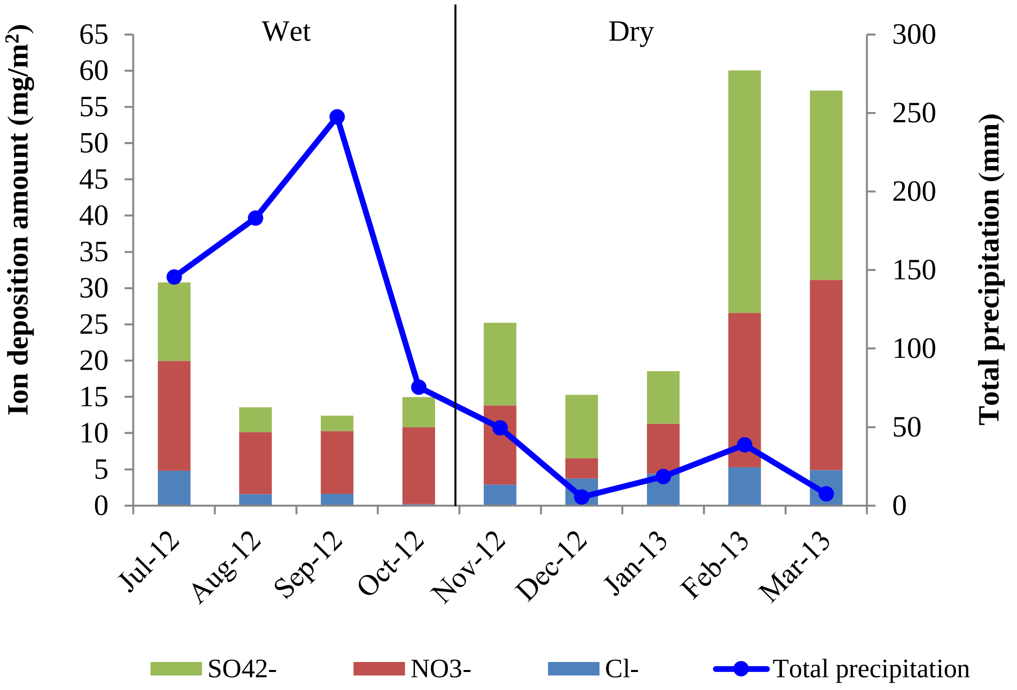


Figure 3.10 Ion deposition amount by leaf-washing method

(a) Ion deposition amount of anions

(b) Ion deposition amount of cations

(a)



(b)

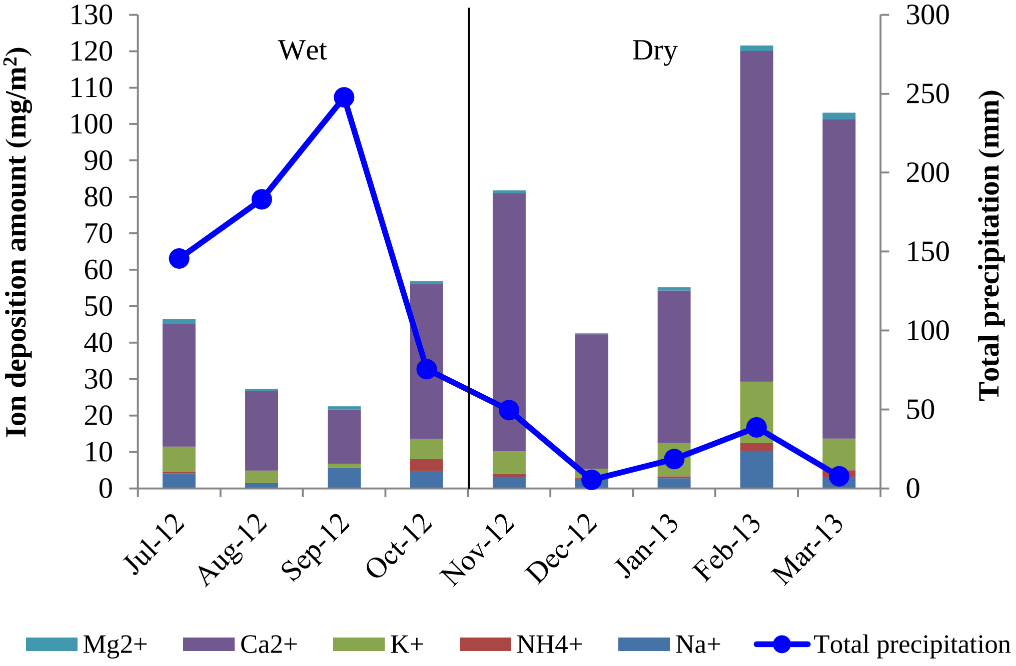


Figure 3.11 Ion deposition amount by four-stage filter pack method

(a) Ion deposition amount of anions

(b) Ion deposition amount of cations

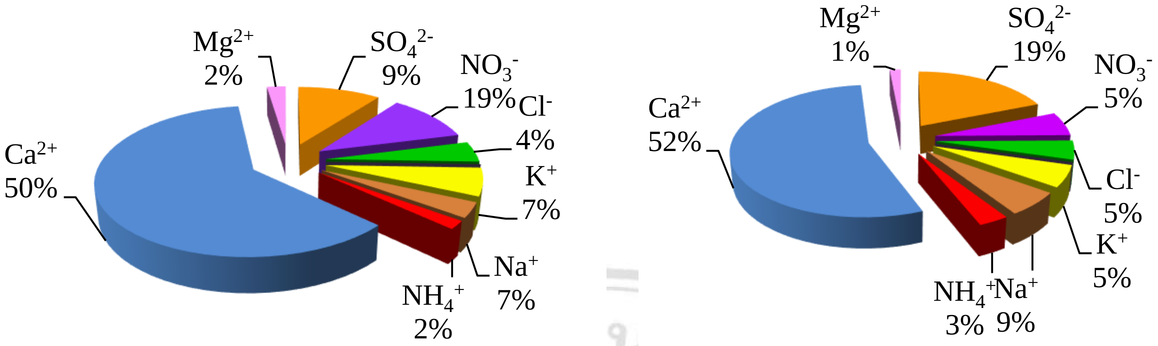
3.4.2 The relative percentage of ions

Ion deposition amount for both method during wet and dry season are presented into the relative percentage. It can be seen that the relative percentage of Ca^{2+}, SO_4^{2-} and NO_3^- were found to be the dominant cation and anion, respectively, which is the similarly of percentage for ion deposition amount in atmosphere at this area in wet and dry season from both method. From the result of relative percentage, for Ca^{2+} was the highest percentage. The percentage of Ca^{2+} was higher than 50% during both season, while is approximately 25-50 times higher than that in each ion during wet and dry season.

The relative percentage of ion deposition amount in atmosphere by Leaf-washing and four-stage filter pack method during wet and dry season are shown in Figure 3.12. Relative percentage of four-stage filter pack method were Ca^{2+} (50%) > NO_3^- (19%) > SO_4^{2-} (9%) > Na^+ (7%) ~ K^+ (7%) > Cl^- (4%) > NH_4^+ ~ Mg^{2+} (2%), while those in leaf-washing method were Ca^{2+} (52%) > SO_4^{2-} (19%) > Na^+ (9%) > NO_3^- ~ Cl^- ~ K^+ (5%) > NH_4^+ (3%) > Mg^{2+} (1%) in wet season. The relative percentage in descending order of four-stage filter pack method were Ca^{2+} (57%) > SO_4^{2-} (15%) > NO_3^- (12%) > K^+ (7%) > Cl^- ~ Na^+ (5%) > NH_4^+ ~ Mg^{2+} (1%), while that in the leaf-washing method were Ca^{2+} (62%) > SO_4^{2-} (11%) > NO_3^- (9%) > K^+ (6%) > Cl^- (5%) > Na^+ (4%) > NH_4^+ ~ Mg^{2+} (2%) in dry season.

Four-stage filter pack method *Leaf-washing method*

(a) Wet season (b) Wet season



(c) Dry season (d) Dry season

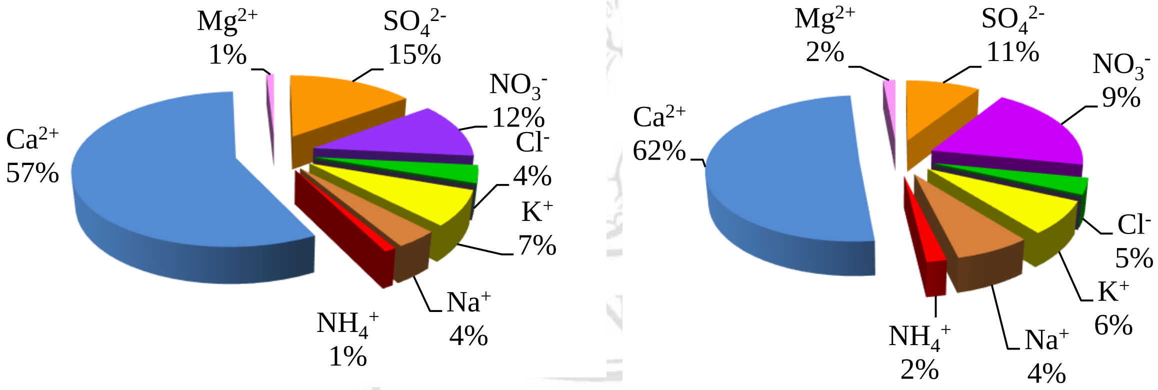


Figure 3.12 Relative percentage of total anions and cations by leaf-washing method and four-stage filter pack method during wet and dry season

3.4.3 Ion pair correlation

1) Correlation between leaf-washing and four-stage filter pack method

Ion deposition collected by leaf-washing and four-stage filter pack methods were used to examine their correlations between both methods. Relatively high correlations between pairs of the same ions: SO_4^{2-} & SO_4^{2-} (r = 0.893), Na^+ & Na^+ (r = 0.546) and Ca^{2+} & Ca^{2+} (r = 0.499), were observed in both seasons. In wet season they were fairly correlated, while in dry season, correlation between the two methods are potted and shown in Figure 3.13. The correlations between pairs of the same ions were ranged from r = 0.250 – 0.932. This means that the methods provided high correlations of same ions.

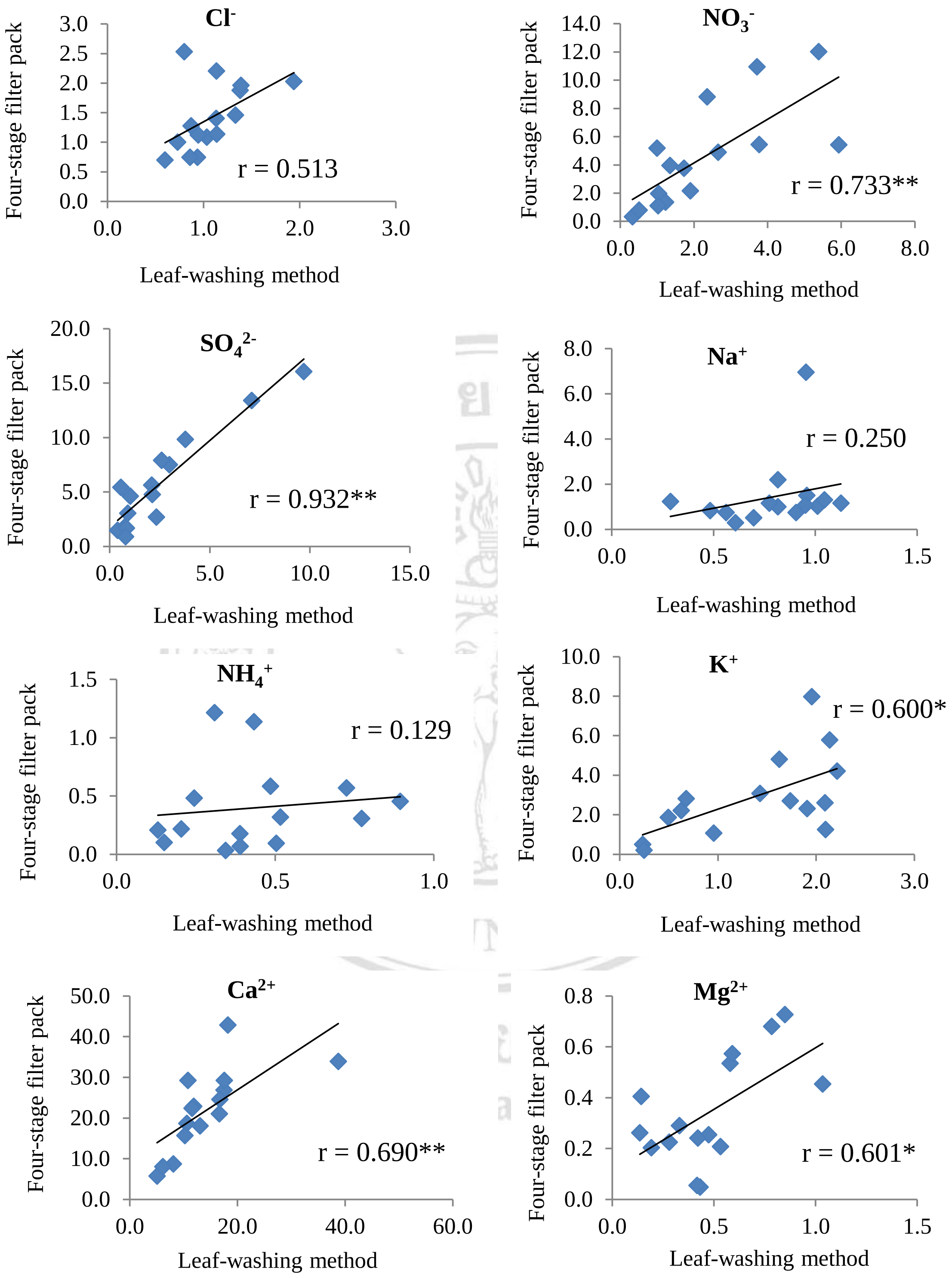


Figure 3.13 Correlation graph of leaf-washing method and four-stage filter pack method in dry season

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

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

2) Correlation between four-stage filter pack and leaf-washing method with meteorological conditions

The correlation between ion composition collected by four-stage filter pack (FP) and leaf-washing (LW) method with meteorological conditions in wet, dry and both seasons, which data was obtained from Northern Meteorological Center. Meteorological conditions (Pressure, P; Temperature, T; Relative humidity, RH; Precipitation, PT; Sunlight, S; Evaporation, E and Direction, D) were calculated in order to identify their relationship as shown in Table 3.9.

Four-stage filter pack method, the correlation of cations & precipitation (r = -0.984) was opposite correlated. In dry season, good correlation between anions & temperature (r = 0.606) and total ions & relative humidity (r = -0.582) were observed, while strong correlation were found between cations & temperature (r = 0.655), total ions & temperature (r = 0.652), anions & relative humidity (r = -0.664), anions & evaporation (r = 0.838), cations & evaporation (r = 0.697) and total ions & evaporation (r = 0.771). Similarly, strong correlation anions & temperature (r = 0.597), cations & temperature (r = 0.610), total ions & temperature (r = 0.634), anions & evaporation (r = 0.591), cations & evaporation (r = 0.543) and total ions & evaporation (r = 0.587) were observed during both seasons.

In case of leaf-washing method, in wet season was fairly correlated. The relatively good correlation were found between anions & temperature (r = 0.612) and total ions & temperature (r = 0.545). The correlation of anions & evaporation (r = 0.793), cations & evaporation (r = 0.890) and total ions & evaporation (r = 0.896) were relatively strong, while opposite correlation between anions & relative humidity (r = -0.758), cations & relative humidity (r = -0.812), total ions & relative humidity (r = -0.829) were observed in dry season.

The similarly in both season, relatively good correlation was found between anions & temperature (r = 0.489), while correlation of anions & evaporation (r = 0.741), cations & evaporation (r = 0.780) and total ions & evaporation (r = 0.803) were relatively strong. The opposite correlation between anions & relative humidity (r = -0.716), cations & relative humidity (r = -0.826), total ions & relative humidity (r = -0.828 were observed.

Table 3.9 Correlation between ion compositions by both methods and meteorological conditions in wet, dry and both seasons

Method	Seasons	Ions	P	T	RH	PT	S	E	D
FP	Wet	Anions	-0.568	0.010	-0.074	-0.496	-0.505	-0.693	0.668
		Cations	0.370	-0.871	-0.914	**-0.984***	0.483	0.134	0.058
		Total ion	0.050	-0.652	-0.719	-0.942	0.160	-0.179	0.313
	Dry	Anions	-0.244	**0.606***	**-0.664****	0.044	0.110	**0.838****	-0.113
		Cations	-0.258	**0.655****	-0.505	0.133	0.023	**0.697****	-0.062
		Total ion	-0.259	**0.652****	**-0.582***	0.100	0.059	**0.771****	-0.085
	Both seasons	Anions	-0.435	**0.597****	-0.313	0.212	-0.220	**0.591****	0.051
		Cations	-0.280	**0.610****	-0.192	0.164	-0.139	**0.543***	-0.041
		Total ion	-0.355	**0.634****	-0.249	0.191	-0.178	**0.587****	-0.006
LW	Wet	Anions	-0.542	-0.076	-0.221	-0.564	-0.454	-0.704	0.735
		Cations	-0.026	-0.558	-0.806	-0.736	0.119	-0.272	0.509
		Total ion	-0.091	-0.521	-0.766	-0.744	0.053	-0.336	0.557
	Dry	Anions	-0.393	**0.612***	**-0.758****	-0.124	0.316	**0.793****	0.002
		Cations	-0.269	0.479	**-0.812****	0.024	0.215	**0.890****	-0.140
		Total ion	-0.322	**0.545***	**-0.829****	-0.025	0.258	**0.896****	-0.099
	Both seasons	Anions	-0.127	**0.489***	**-0.716****	-0.183	0.305	**0.741****	0.028
		Cations	0.091	0.266	**-0.826****	-0.365	0.371	**0.780****	-0.051
		Total ion	0.025	0.350	**-0.828****	-0.323	0.367	**0.803****	-0.028

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

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

3.5 Factors affecting atmospheric particulate deposition

PM10 concentration indicated level of ion concentration in atmosphere. Concentrations of PM10 was obtained from the air quality monitoring station (AQM) belonged to the Pollution Control Department (PCD), while precipitation amount was obtained from the Acid Deposition Monitoring Network in East Asia (2000) as illustrated in Table 3.10.

The average PM10 concentrations was ranged about 21.5 – 97.7 µg/m^3 during wet and dry season. In dry season (54.5 ± 22.2 µg/m^3) were about 2 times higher than in the wet season (24.5 ± 4.98 µg/m^3). The highest of PM10 concentrations was found in March 2013 (97.7 ± 60.9 µg/m^3) and lowest in September 2012 (21.5 ± 9.85 µg/m^3). Amount of precipitation was ranged 5 – 248 mm. Highest of rain precipitation was in September 2012 and lowest in December 2012. Total precipitation amount in wet season was 652 mm, while 120 mm of precipitation amount was found that in dry season. Precipitation amount in wet season was approximately 5 times higher than in the dry season. Figure 3.14 shows the precipitation amount concentrations affected to PM10 concentrations. The trend of precipitation amount has decreased from wet season to dry season whereas PM10 concentrations have increased from wet season to dry season. It can be seen that precipitation amount resulted in low PM10 concentrations in wet season, while low precipitation amount of those resulted in high PM10 concentrations in dry season. Then, high PM10 concentrations indicates to high particulate deposition amount in dry season.

Table 3.10 Total precipitation (mm) and PM10 concentrations (μg/m^3)

Season	Month	Precipitation	PM10 concentration
Wet	Jul-12	146	22.5
	Aug-12	183	22.1
	Sep-12	248	21.5
	Oct-12	75	31.9
		652 (Total)	**24.5±4.98 (Mean±SD)**
Dry	Nov-12	50	27.0
	Dec-12	5	36.7
	Jan-13	19	53.0
	Feb-13	39	58.1
	Mar-13	8	97.7
		120 (Total)	**54.5±27.17 (Mean±SD)**

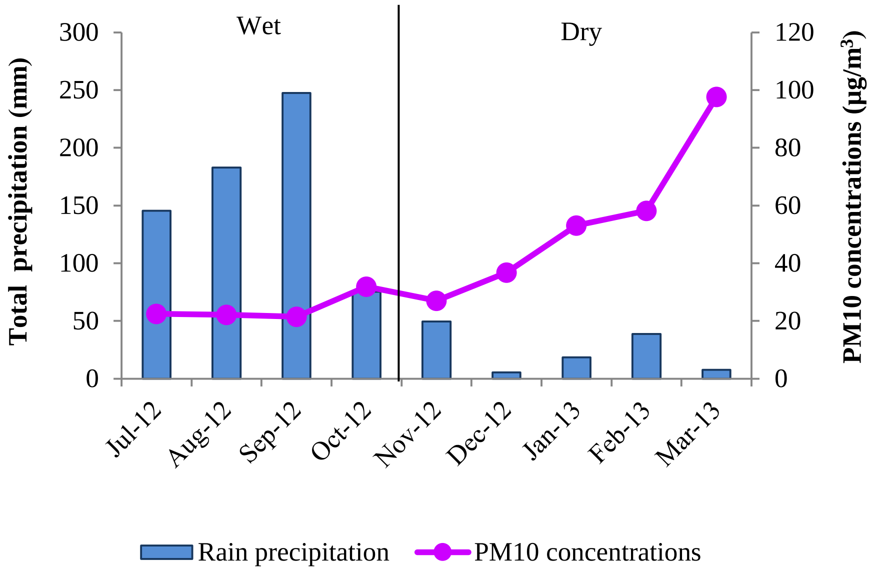


Figure 3.14 Variation of total precipitation and PM10 concentrations