

Wet deposition and estimates of aerosol wet scavenging coefficient for the location in north suburb of Nanjing

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Outline

- Introduction
- Experimental Methods
- Results and Discussion
- Preliminary Conclusions
- Future work

Introduction

- Aerosol from different emission sources would be transported and dispersed into atmosphere and cloud. While during raining day, some of them would be brought back to land by wet deposition and wet scavenging below cloud.

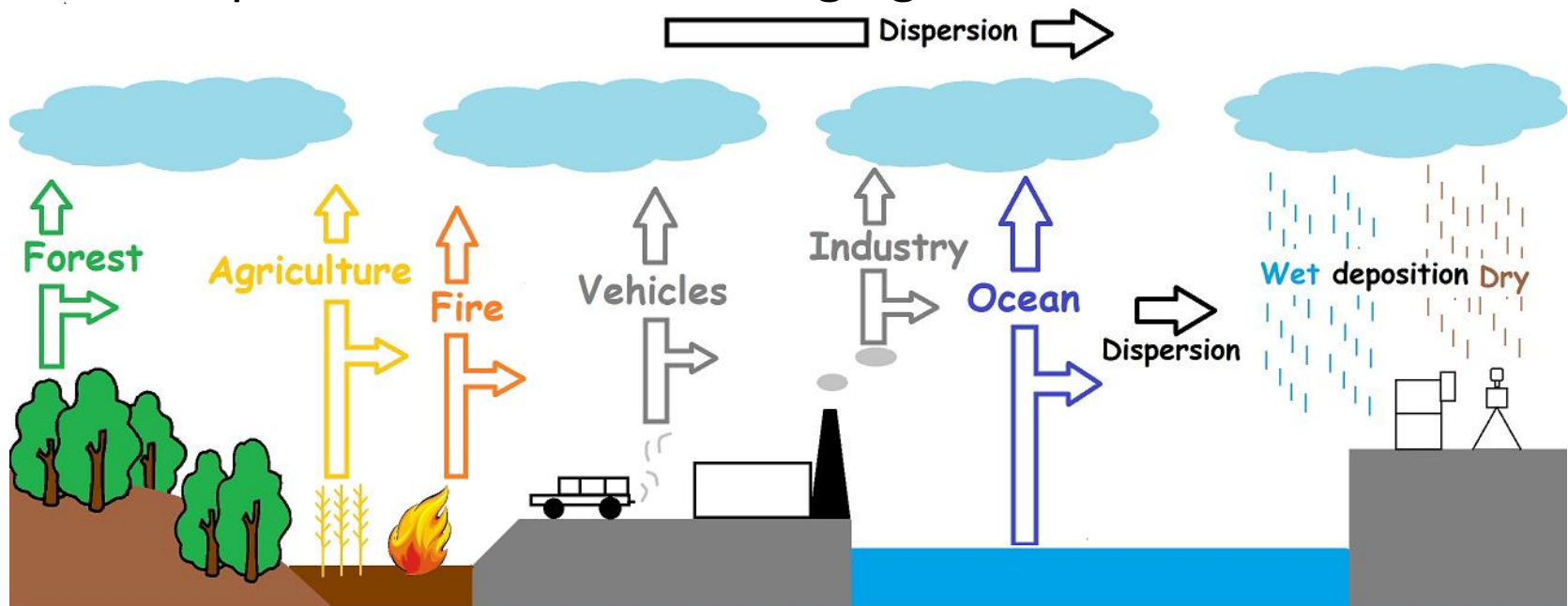


Fig.1 The sources, transport, transformation and removal of aerosols

Introduction

Background

- There have been some studies about wet deposition and wet scavenging which focused on physical characteristics of rain drops, ions concentration change, pollution gas in Shanghai, Nanchang, Nanjing and so on. But few observations and researches in suburb near heavy industry zone, roads with heavy traffic, farmland with biomass burning sometimes and construction sites which would make this research complicated but meaningful.

Introduction

Sampling site



Fig.2 The basic information of sampling site and distance between sampling site and observation site

Introduction

Main contents

1. Discussion the source and wet deposition of spring-summer and autumn-winter from 2015.4-2016.4 by measuring theirs pH, electric conductivity, ions, DOC, organic acid content to assess the source and chemical characteristics of different kinds of precipitation.
2. Discussion the estimates of aerosol wet scavenging coefficient.
 - 2.1 Measuring the change of 12-hours PM_{2.5} collection ions concentration to estimate the daily aerosol wet scavenging coefficient.
 - 2.2 Measuring the change of hourly PM_{2.5} observation ions concentration to estimate the hourly aerosol wet scavenging coefficient.

Experimental Methods

Rainwater samples

- The sampling site was on the roof of Wendelou Building, NUIST.
- The rainwater samples were collected by APS-3A every raining day and switched to next bottle position at 9 am next day. Each sample will be collected into a 500ml HDPE bottles. After collection, it would be ultrasonic vibrated for 15 mins to promote dissolution of particles in rainwater sample and heat the sample. Then a 60ml and a 250ml HDPE bottle would be used for subpackage.
- After then, we would measure sample's pH(Sartorius PB-10) and conductivity(OHAUS STARTER 3100C), then the sample would be frozen in -20°C for others detection and analysis.
- Samples would be filtered by $0.22\mu\text{m}$ filter before ion detection.

Experimental Methods

PM2.5 samples

- The research would refer to the 12 hours PM2.5 collection (by KC-6120) of each season. The collection would last for 30-40 days each season. This research would select more than 2 sample PM2.5 samples before raining days, also 2 sample after raining day. The numbers of samples during raining day depends on the time scale of raining.
- The research would refer to the hourly ion concentration of PM2.5 and pollution gases detected by MARGA ADR2080 monitoring instrument for aerosols and gases.

Results and Discussion

- Section 1

Discussion of the source and wet deposition

- Section 2

2.1 The estimates of daily aerosol wet scavenging coefficient.

2.2 The estimates of hourly aerosol wet scavenging coefficient.

Section1

The backward trajectory analysis

- The backward trajectory lines would explain the route of airflow before the raining day.
- We select the midpoint of raining time as the start time to do backward trajectory calculate.
- It outputs 4 lines eventually after clustering analysis as average trajectories.

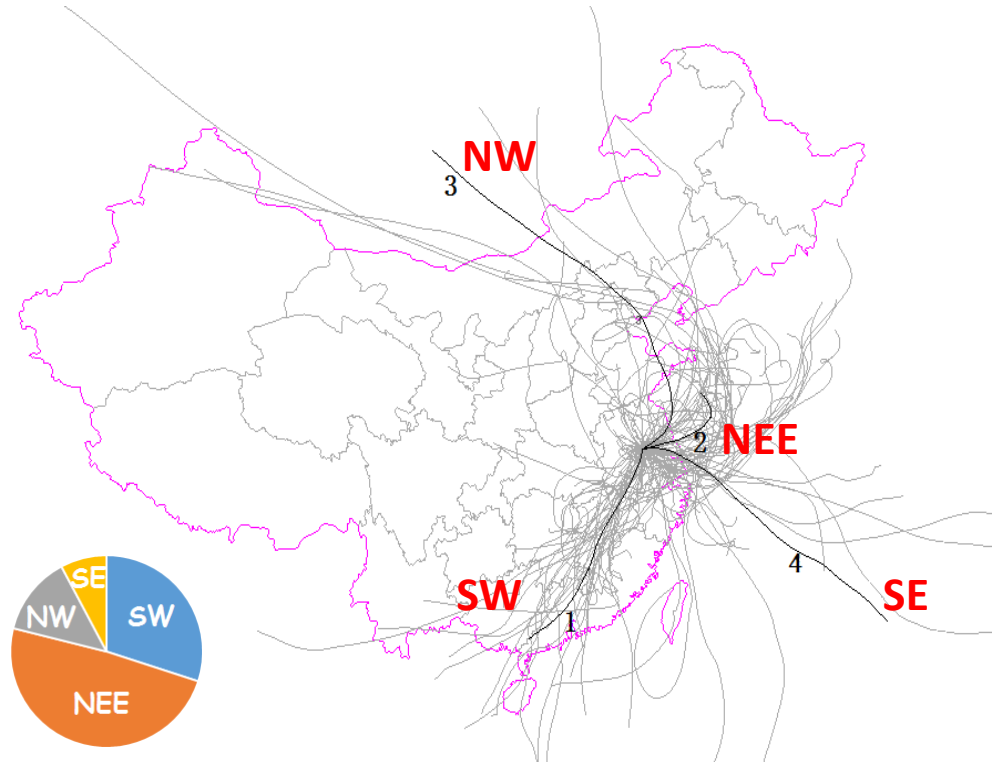


Fig.3 The 72-hours backtrack and clustering analysis of each raining day from April, 2015 to April, 2016 at 500m height(AGL)

The change of pH

- The pH shows obvious difference between spring, summer and autumn, winter.
- The pH shows obvious difference between NEE, NW and SW, SE which could point that the most acid aerosols and gases in 500m(AGL) were from direction of NEE and NW.

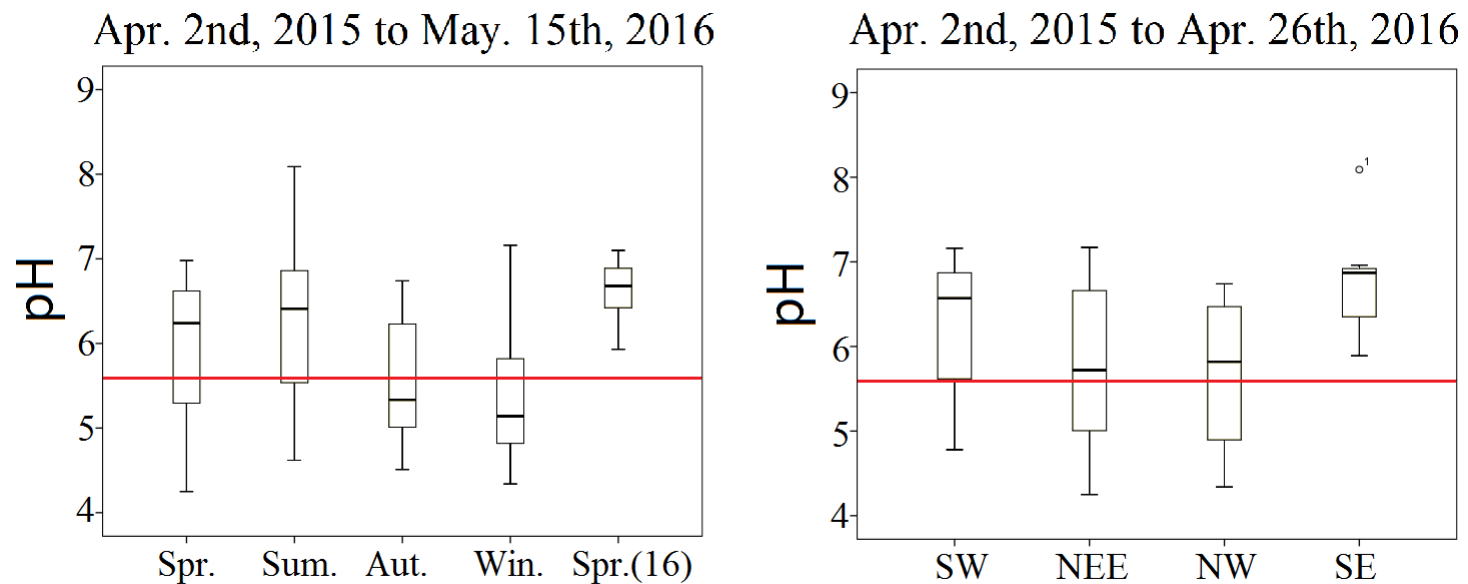


Fig.4 The seasonal change of pH and pH change with 4 clusters.

Principal component analysis of inorganic ions

Table 2 Rotated Component Matrix of inorganic ions

Rotated Component Matrix				
	Component			
	1	2	3	4
NH ₄ ⁺	0.843	0.1	0.274	0.172
SO ₄ ²⁻	0.832	0.417	0.194	0.136
NO ₃ ⁻	0.793	0.409	0.03	-0.05
Mg ²⁺	0.148	0.894	0.219	0.091
Ca ²⁺	0.481	0.768	0.016	0.043
Na ⁺	0.288	0.757	0.243	0.087
K ⁺	0.081	0.149	0.952	-0.062
Cl ⁻	0.261	0.206	0.9	0.058
F ⁻	0.12	0.113	-0.018	0.978
% of variance	51.08%	15.96%	10.36%	9.49%

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a Rotation converged in 6 iterations.

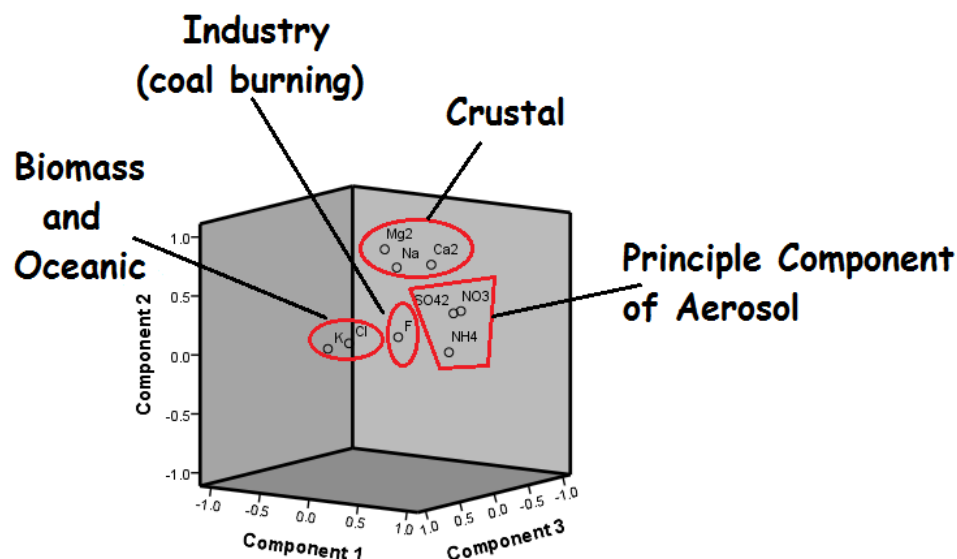
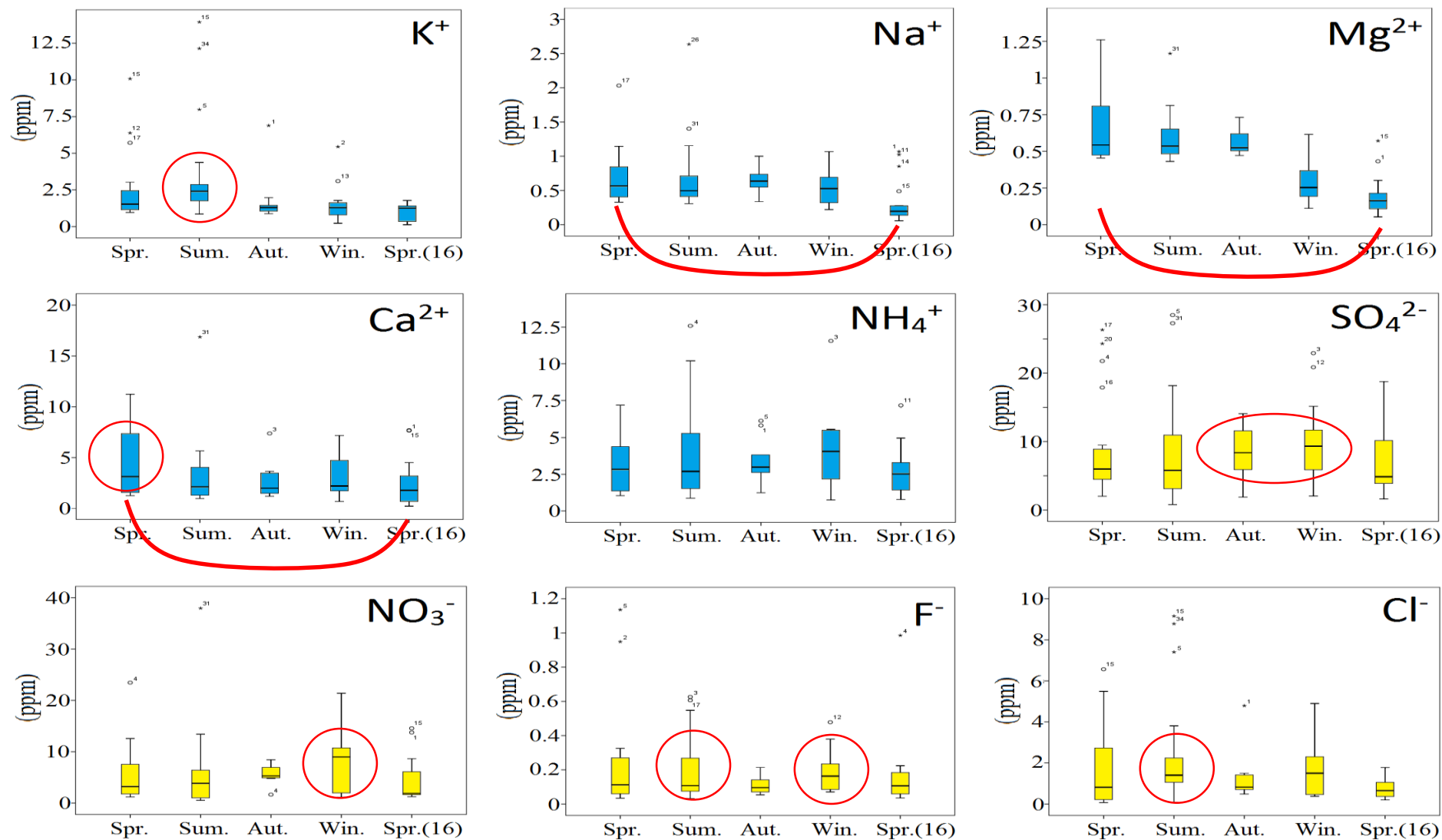


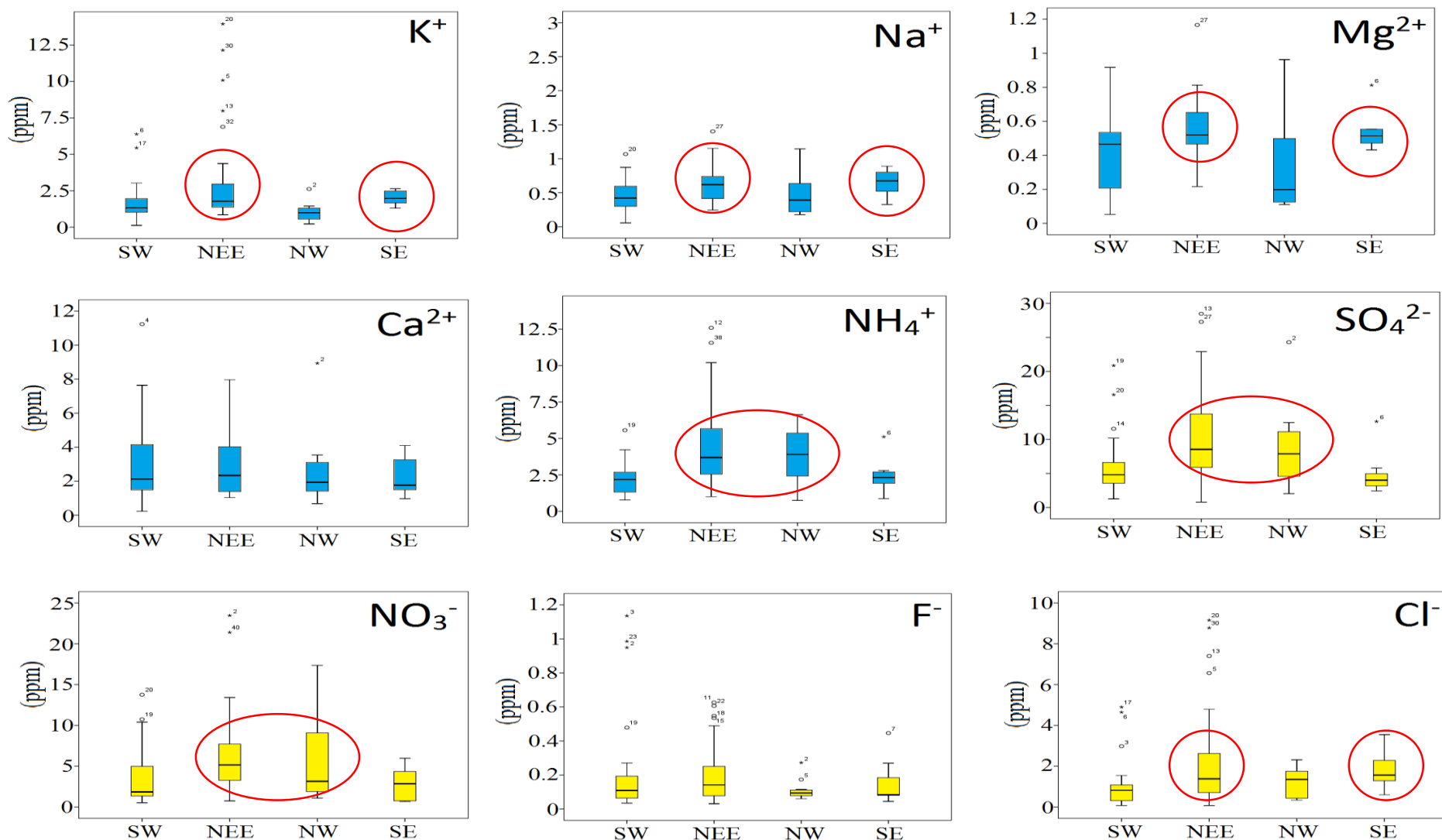
Fig.5 Component plot in rotated space of inorganic ions

The seasonal change of ions



Apr. 2nd, 2015 to May. 15th, 2016
Fig. 6 The seasonal change of inorganic ions

The change of ions with different trajectories



Apr. 2nd, 2015 to Apr. 26th, 2016

Fig. 7 The change of inorganic ions with different trajectories

Similar source or similar emission(table 3)

Correlations of all inorganic ions

		SO42-	NO3-	F-	Cl-	Na+	NH4+	K+	Mg2+	Ca2+
SO42-	Pearson Correlation	1	.767**	.294**	.458**	.625**	.828**	.272**	.555**	.717**
	Sig. (2-tailed)		.000	.004	.000	.000	.000	.008	.000	.000
NO3-	Pearson Correlation	.767**	1	.168	.360**	.467**	.579**	.189	.444**	.735**
	Sig. (2-tailed)	.000		.106	.000	.000	.000	.068	.000	.000
F-	Pearson Correlation	.294**	.168	1	.084	.176	.263*	-.048	.188	.241*
	Sig. (2-tailed)	.004	.106		.422	.089	.010	.644	.086	.019
Cl-	Pearson Correlation	.458**	.360**	.084	1	.431**	.353**	.889**	.370**	.282**
	Sig. (2-tailed)	.000	.000	.422		.000	.000	.000	.001	.006
Na+	Pearson Correlation	.625**	.467**	.176	.431**	1	.477**	.259*	.711**	.583**
	Sig. (2-tailed)	.000	.000	.089	.000		.000	.012	.000	.000
NH4+	Pearson Correlation	.828**	.579**	.263*	.353**	.477**	1	.246*	.373**	.419**
	Sig. (2-tailed)	.000	.000	.010	.000	.000		.017	.000	.000
K+	Pearson Correlation	.272**	.189	-.048	.889**	.259*	.246*	1	.366**	.176
	Sig. (2-tailed)	.008	.068	.644	.000	.012	.017		.001	.091
Mg2+	Pearson Correlation	.555**	.444**	.188	.370**	.711**	.373**	.366**	1	.715**
	Sig. (2-tailed)	.000	.000	.086	.001	.000	.000	.001		.000
Ca2+	Pearson Correlation	.717**	.735**	.241*	.282**	.583**	.419**	.176	.715**	1
	Sig. (2-tailed)	.000	.000	.019	.006	.000	.000	.091	.000	

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

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

Comparison to other sites

Table 4 Comparison of pH and ionic concentrations (µeq/L) in rainwater

Site	Na+	NH4+	K+	Mg2+	Ca2+	F−	Cl−	NO3−	SO42−	pH	SO4 ^{2−} /NO3 [−]	Type	Time Reference	
NUIST Pukou Nanjing China	24.84	197.19	57.06	39.14	155.35	9.83	47.64	89.58	170.83	5.81	1.91	Suburb	This study, 2015-2016	
Ya'an China	24.24	203.70	30.05	13.18	98.36	13.30	37.50	84.36	212.30	4.03	2.52	Semi-rural	2010–2011 Zhao et al. 2013	
Chengdu China	1.40	150.50	6.60	16.20	196.60	6.20	8.90	156.20	212.80	5.10	1.36	Megacity	2008 Wang and Han 2011	
Chongqing China	20.70	223.80	60.40	40.20	595.60	30.50	96.90	90.00	717.80	5.76	7.98	Megacity	2000–2009 Lu et al. 2013	
Beijing China	21.50	346.00	9.17	53.30	273.00	12.00	50.90	42.60	357.00	4.85	8.38	Megacity	2011–2012 Xu et al. 2015	
Beijing China	8.51	174.00	6.69	38.50	291.00	10.50	67.80	139.00	270.00	5.32	1.94	Megacity	2008 Xu et al. 2012	
Xi'an China	31.10	229.80	13.80	36.60	425.60	28.70	38.70	128.80	489.70	6.64	3.80	Megacity	2010 Lu et al. 2011	
Shenzhen China	10.50	24.1	1.00	2.26	21.40	0.53	19.80	12.30	38.40	4.90	3.12	Coastal	2005–2009 Huang et al. 2010	
Guangzhou China	18.00	66.00	9.00	9.00	131.00	12.00	21.00	52.00	202.00	4.49	3.88	Coastal	2005–2006 Huang et al. 2009	
Lei Gong Shan China	3.00	33.00	4.00	5.00	25.00		4.00	26.00	75.00	4.44	2.88	non-urban	2003 Aas et al. 2007	
Puding China	10.79	33.14	9.10	3.90	155.80	2.82	54.50	16.99	152.40	5.44	8.97	Rural	2008 Wu et al. 2012	
Lijiang China	0.98	20.80	2.01	10.90	50.10	0.60	2.04	7.00	23.70	6.07	3.39	Background	2012 Niu et al. 2014	
Jiuzhaigou China	38.00	13.40	21.20	41.10	149.80	21.00	37.20	12.70	70.50	5.95	5.55	Background	2010–2011 Qiao et al. 2015	
Seoul Korea	0.50	66.40	3.50	6.90	34.90		18.20	29.90	70.90	4.70	2.37	Various	1996–1998 Lee et al. 2000	
Tokyo Japan	7.00	40.40	2.90	11.50	24.90		55.20	30.50	50.20	4.52	1.65	Megacity	1990–2002 Okuda et al. 2005	
Singapore	2.79	19.13	7.20	6.54	16.06		34.21	22.30	83.47	4.20	3.74	Island	1999–2000 Hu et al. 2003	
Newark USA	0.90	24.40	1.30	3.30	6.00	1.10	10.70	14.40	38.10	4.60	2.65	Megacity	2006–2007 Song and Gao 2009	
Pune India	5.20	5.10	3.50	23.10	53.2	1	0.30	62.00	8.30	34.30	5.90	4.13	Megacity	2006–2009 Budhavant et al. 2011
Mexico	7.00	92.35	2.16	2.46	26.44		9.56	42.60	61.94	5.08	1.45	Megacity	2001–2002 Baez et al. 2007	

Higher

Lower

Organic acid(seasonal)

Apr. 2nd, 2015 to May. 15th, 2016

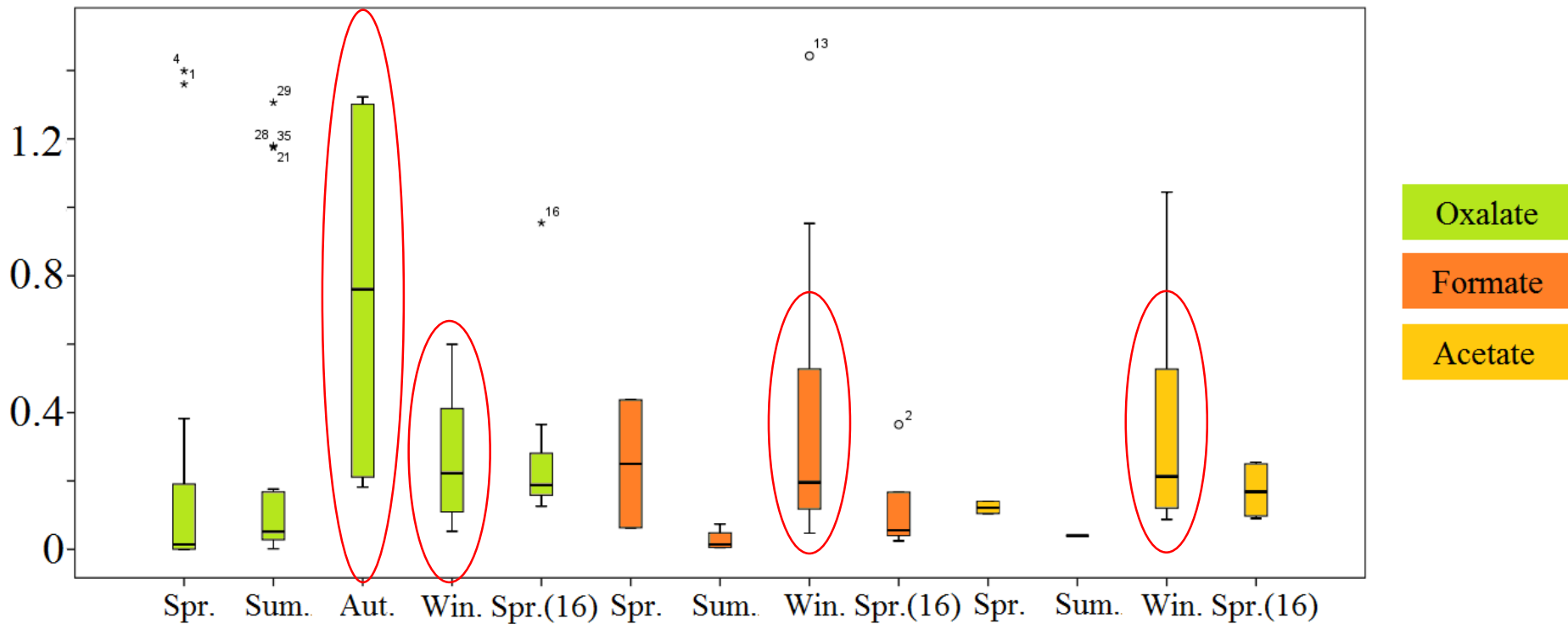


Fig. 8 The seasonal change of organic acids

Organic acid(trajjectory)

Apr. 2nd, 2015 to Apr. 26th, 2016

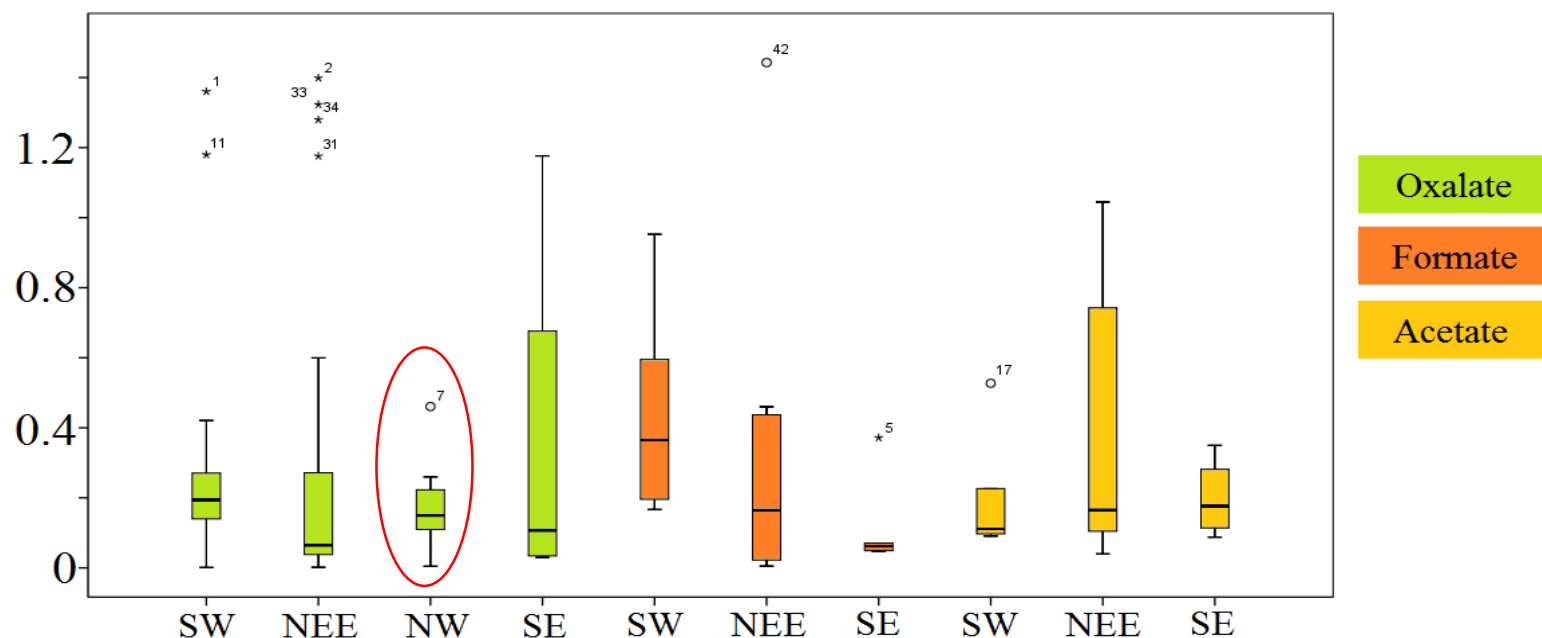


Fig. 9 The change of organic acids with different trajectory

- The formate and acetate cannot being detected in autumn which is a season prevailing NW wind, which proves that the formate and acetate are imported substance but not local.

Correlations and sources of organic acids

Table 5 Correlations of organic acids and some cations

Correlations of organic acids and some inorganic ions														
		Oxalate	Formate	Acetate	SO42-	NO3-	NO2-	F-	Cl-	Na+	NH4+	K+	Mg2+	Ca2+
Oxalate	Pearson Correlation	1	-.206	.057	.078	.528**	-.027	-.182	.004	.114	-.039	-.004	.008	.124
	Sig. (2-tailed)		.383	.829	.665	.002	.909	.311	.981	.526	.830	.981	.966	.491
Formate	Pearson Correlation	-.206	1	-.169	-.002	-.060	-.146	.186	.435*	.028	-.032	.433*	-.034	.058
	Sig. (2-tailed)	.383		.581	.994	.792	.635	.408	.043	.903	.888	.044	.882	.796
Acetate	Pearson Correlation	.057	-.169	1	.533*	.498*	.542	-.098	-.210	.334	.706**	-.214	-.024	.282
	Sig. (2-tailed)	.829	.581		.023	.035	.085	.698	.403	.176	.001	.393	.928	.256
*. Correlation is significant at the 0.05 level (2-tailed).														
**. Correlation is significant at the 0.01 level (2-tailed).														

- The correlation among organic acids is not significant, therefore, their emission sources are probably different.
- The emission sources of formate and potassium ion, acetate and ammonium ion are similar or there are different emission sources among them but the emission among the sources are similar.
- The emission sources of oxalate and nitrate ion, acetate and nitrate ion are similar or there are different emission sources among them but the emission among the sources are similar.

Dissolved organic carbon(DOC)

Table 6 Correlations of DOC and conductivity

The correlation of DOC and conductivity			
		Conductivity	DOC (ppm)
Conductivity	Pearson Correlation	1	.582**
	Sig. (2-tailed)		.000
DOC (ppm)	Pearson Correlation	.582**	1
	Sig. (2-tailed)	.000	
**. Correlation is significant at the 0.01 level (2-tailed).			

- DOC is a mainly dissolved component in rainwater which could determine the conductivity or TDS of water.
- The detection data of DOC(150402-151124) shows that the total organic acids(MSA, oxalate, formate, acetate) accounts for 11.2% of the DOC.

Preliminary Conclusions of Section 1

- The acid rain of sampling site is regarded as mixture acid referred to $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio and the seasonal change of SO_4^{2-} and NO_3^- caused seasonal pH distribution which shows:
Spring(16)>Summer>Spring>Autumn>Winter.
- The emission of industry, vehicles and agriculture mainly determined the chemical component of rainwater also affected the pH.
- The F⁻ in PCA shows that the emission of F⁻ in coal burning cannot be ignored.
- KCl was regarded as biomass burning some more than oceanic sources.
- The Na⁺, Mg²⁺, Ca²⁺ are regarded as crustal sources some more than oceanic sources.
- The oxalate is probably because of local emission while the formate and acetate should be long distance imported and with obvious seasonal distribution.
- DOC including organic acids is also an important factor which could affect the conductivity or TDS of rainwater that cannot be neglected

Future Work of Section 2(briefly)

The daily change of ion concentration in raining day

- The cations of most of 12-hours PM_{2.5} samples collected on Wendelou Building have already been detected.
- The anions of rest samples will be detected after we establish the method of detecting all kinds of organic acid.
- The estimates of daily aerosol wet scavenging coefficient will be analyzed with daily average temperature, wind and relative humidity.

The hourly change of ion concentration in raining days

- To calculate the wet scavenging rate by referring to hourly PM_{2.5} ion-observation in spring, 2016.
- To estimate the hourly aerosol wet scavenging coefficient of different ions.
- Combining with weather data including temperature, wind speed and relative humidity to find the change of different ions before, during and after raining.

Primary examples

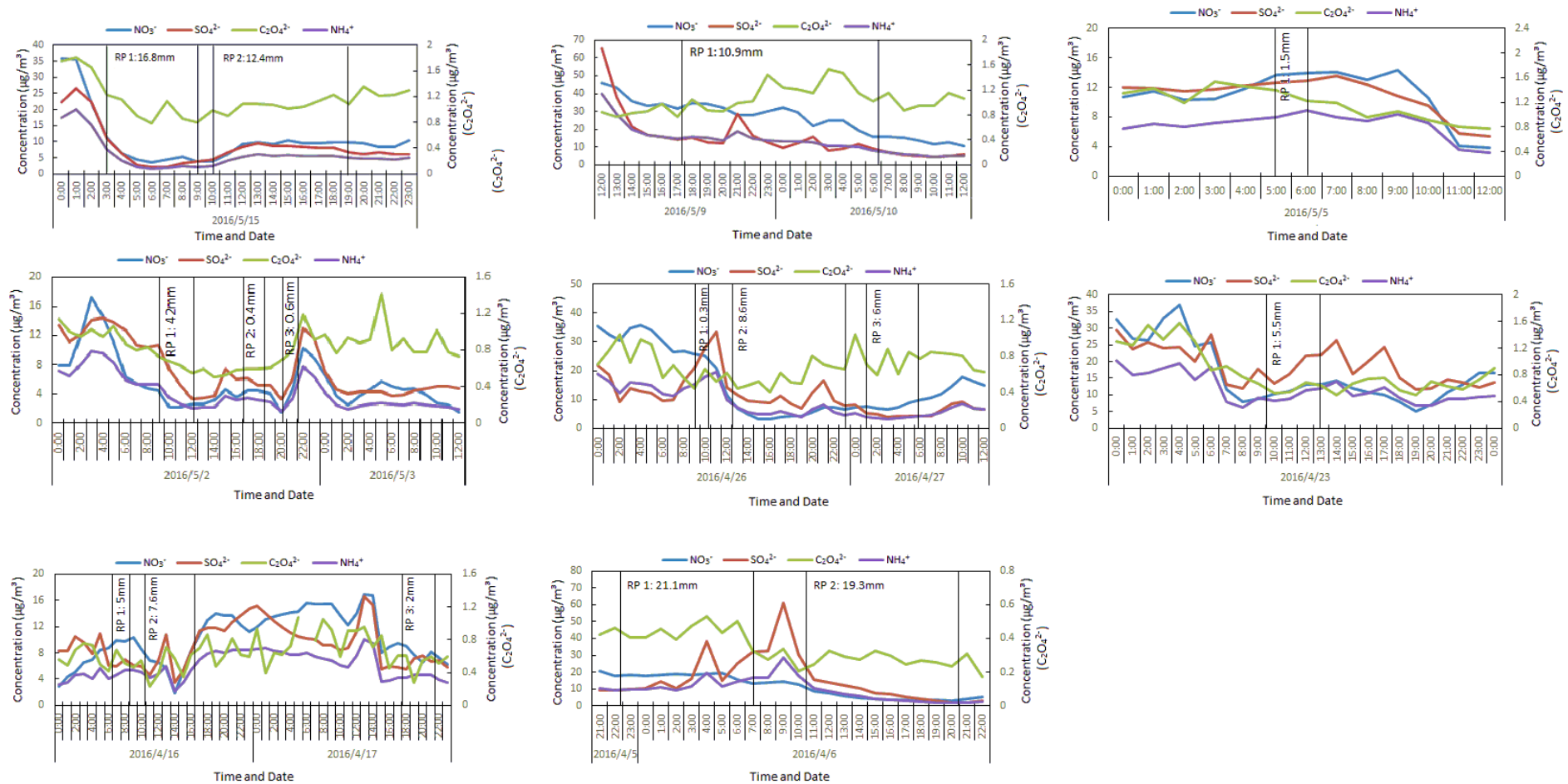


Fig.10 The hourly change of ions with gas precursor during raining day

Future work

Others

- Calculate backward trajectory of different height(eg. 1000m) to do further analysis of emission source.
- Combine with more meteorology factors to do further analysis of wet scavenging coefficient.
- Analyzing the changes or variance of continuous raining.
- A more particular analysis of local emission effect to raining.

THANKS