Analysis on Chemical Characteristics of Wet Deposition in Four Seasons of Jiangbei New District, Nanjing

(Master’s Thesis)

YN-center

ESEI, NUIST

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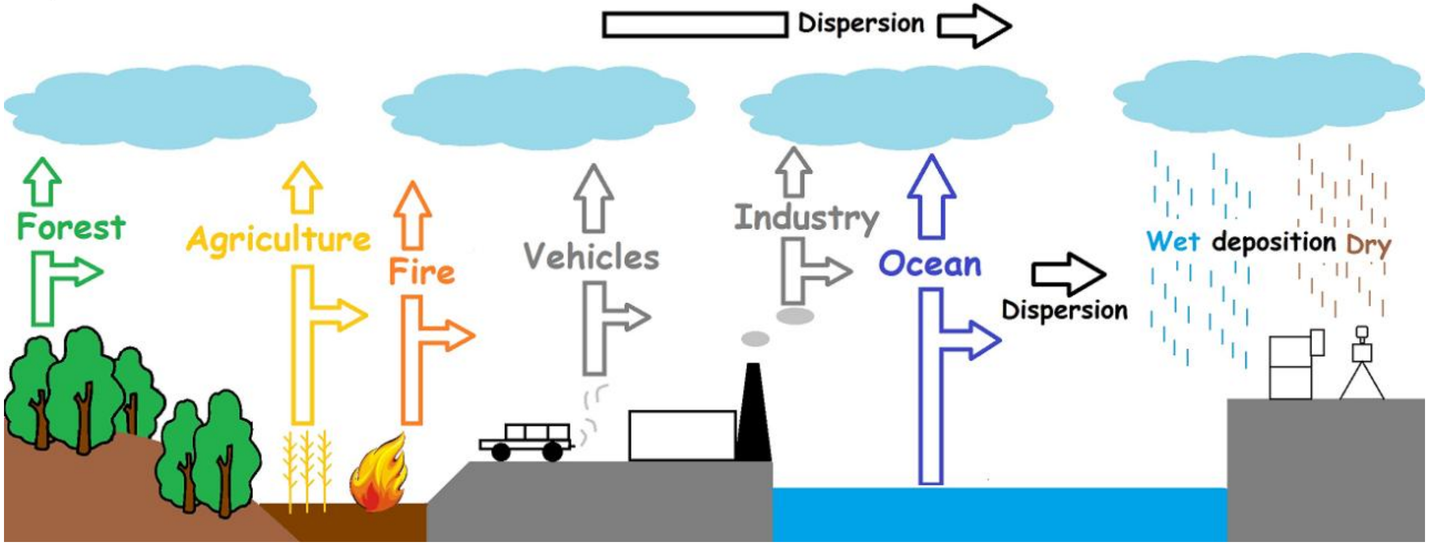
Background



Wet deposition is an important feedback atmospheric circulation and important process of the atmospheric environment and its spatial and temporal changes in physical and chemical properties. Great amount of pollution gas and particles from industry, agriculture, motors and biomass burning will be let out into atmosphere, also including emission from ocean, forest and some other nature source. They would stay below the cloud or dissolve in cloud and influence the chemical characteristics of rainwater.

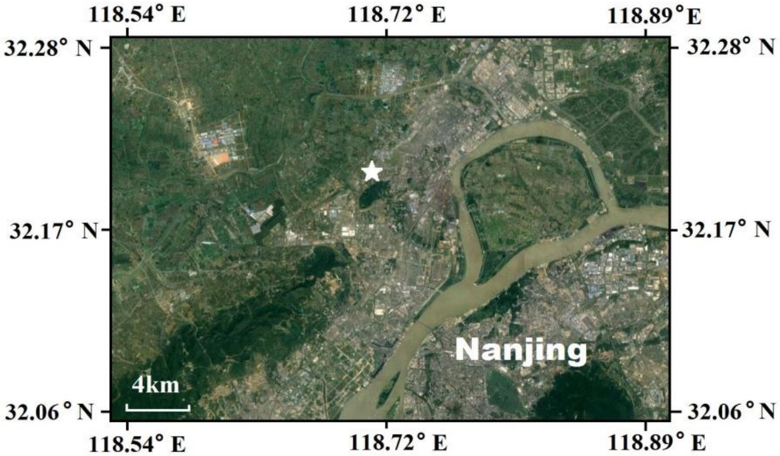
Research Progress

- Researchers have focused on the study of some regional organic components characteristics, including the temporal and spatial distribution of the chemical composition of precipitation, including the mechanism of transport and transfer. The environmental acidification and eutrophication caused by wet deposition is also gradually become a hot research.
- In recent years, with the intensification of air pollution and its impact is more significant, wet deposition and chemical properties have become the focus of research, and the study also began to upgrade from precipitation chemical composition analysis to organic matter. The relationship between the particles in the atmosphere are more complex and comprehensive research, but due to the lack of research and regional differences and the uncertainty of the object, there are some differences and discussion among countries and local research .
- **Therefore, further analysis of the various types of precipitation in the complex areas of water-soluble components of the study, as well as the change of chemical characteristics would be very important. It’s worthy to analyze the synchronized atmospheric particles sampling chemical components and atmospheric particulate matter water-soluble components on-line observation and atmospheric pollution of gas online Observations will also be particularly meaningful and valuable to do further analysis.**

Instruments and methods

- **Sampling Instruments：** APS－3A automatic rainwater sampler (Changsha Xiangnan Co.)， KC－6120 Atmospheric sampler(Qingdao Laoshan Co.)
- **Analytical Instrument：** ICS 5000+ Ion Chromatography (Thermo Fisher)， Tekmar Torch TOC Analyzer
- **Observation Instrument：** MARGA 1S Online water soluble ion and gas analyzer(Metrohm)
- **Method：** Back trajectory analysis, principal component analysis， correlation analysis, elemental enrichment factor, non-seasalt model。

Sampling sites



Innovation

- In this study, the main components of nitrogen (inorganic nitrogen) and the main soluble carbon (soluble organic carbon) components of wet deposition were analyzed. The combination analysis of soluble organic carbon and inorganic would be able to further explain the source of chemical characteristics of wet deposition.
- In this study, water-soluble ion analysis of half-day atmospheric PM2.5 samples before and after rain sampling was carried out, and the observation of hourly pollution gas and aerosol soluble chemical components before and after precipitation would help the analysis the effect of wet scavenging process on the components of atmospheric aerosols.

Chemistry characteristics of wet deposition

Seasonal change

Direction Change

Emission source

Components

Seasonal and trajectories' distribution

- **Seasonal：** Spring from 2015.Apr.1st~Jun.5th； Summer comes at Jun.6th， Autumn comes Oct.1st, winter comes at Nov.25th and the next spring comes at Mar.3rd , 2016。

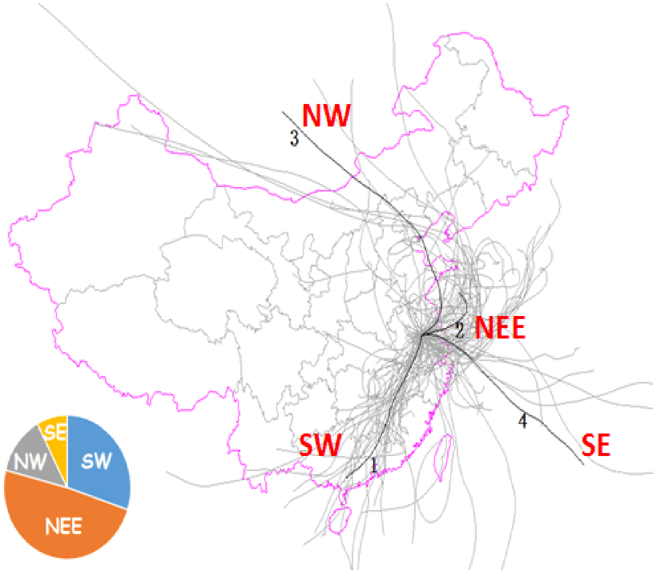


Fig.1 The 72-hours backtrack and clustering analysis of each raining day from April, 2015 to April, 2016 at 500m height(AGL)

Physical characteristics distribution of seasonal precipitation

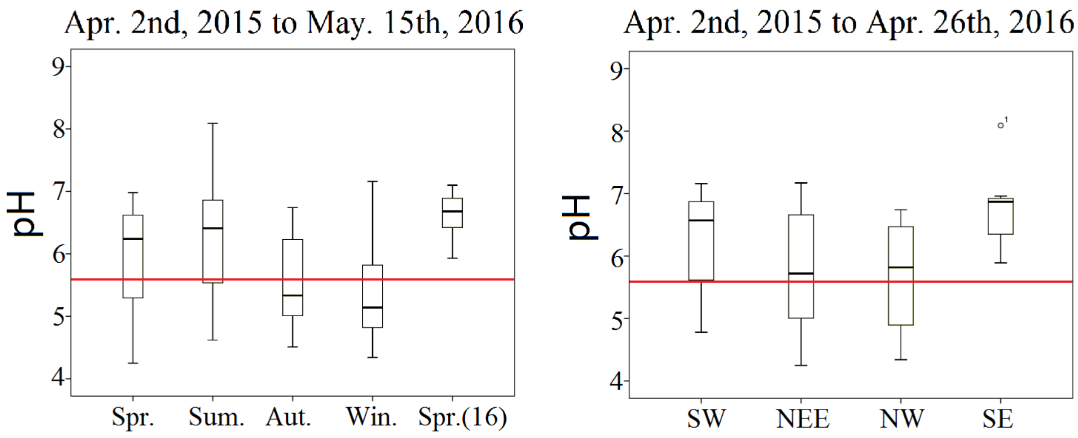


Fig.2 The seasonal change of pH and pH change with 4 clusters.
Red line is the pH of 5.6（Mark-value of acid rain）

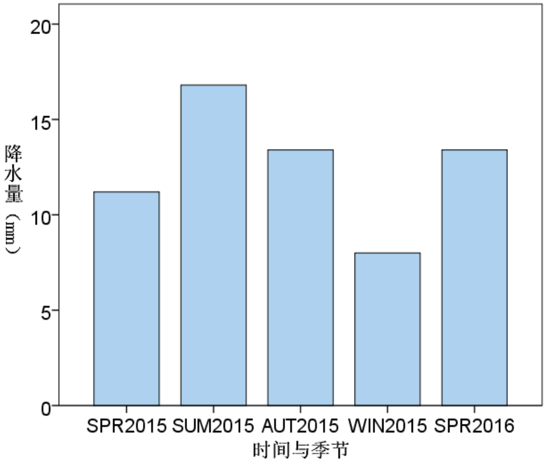


Fig.3 The seasonal precipitation distribution of NUIST

Preliminary characteristics of emission sources

Table 2 The PCA analysis with rotated component matrixa of inorganic ions

Components	1	2	3	4
NH_4^+	0.843	0.1	[redacted]	0.172
SO_4^{2-}	0.832	[redacted]	[redacted]	0.136
NO_3^-	0.793	[redacted]	[redacted]	-0.05
Mg^{2+}	[redacted]	[redacted]	[redacted]	0.091
Ca^{2+}	[redacted]	No public	[redacted]	[redacted]
Na^+	[redacted]	[redacted]	[redacted]	0.087
K^+	[redacted]	[redacted]	[redacted]	0.062
Cl^-	0.261	[redacted]	[redacted]	0.058
F^-	0.12	[redacted]	-0.018	0.978
Ratio（%）	51.08%	15.96%	10.36%	9.49%

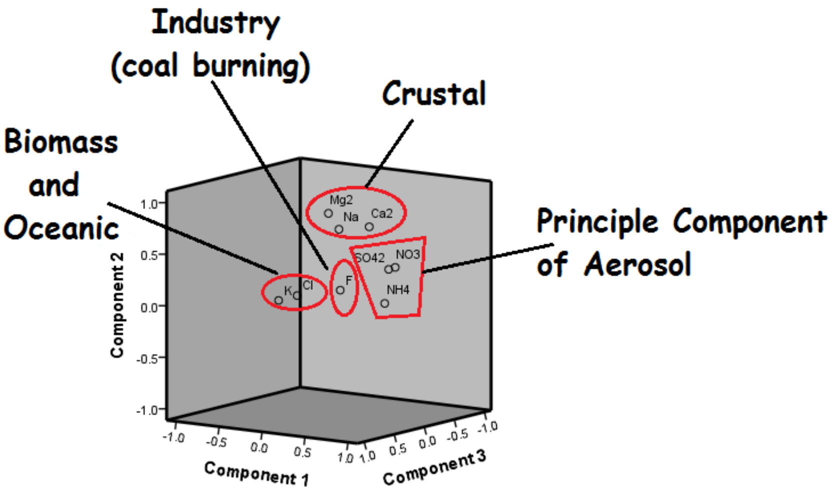
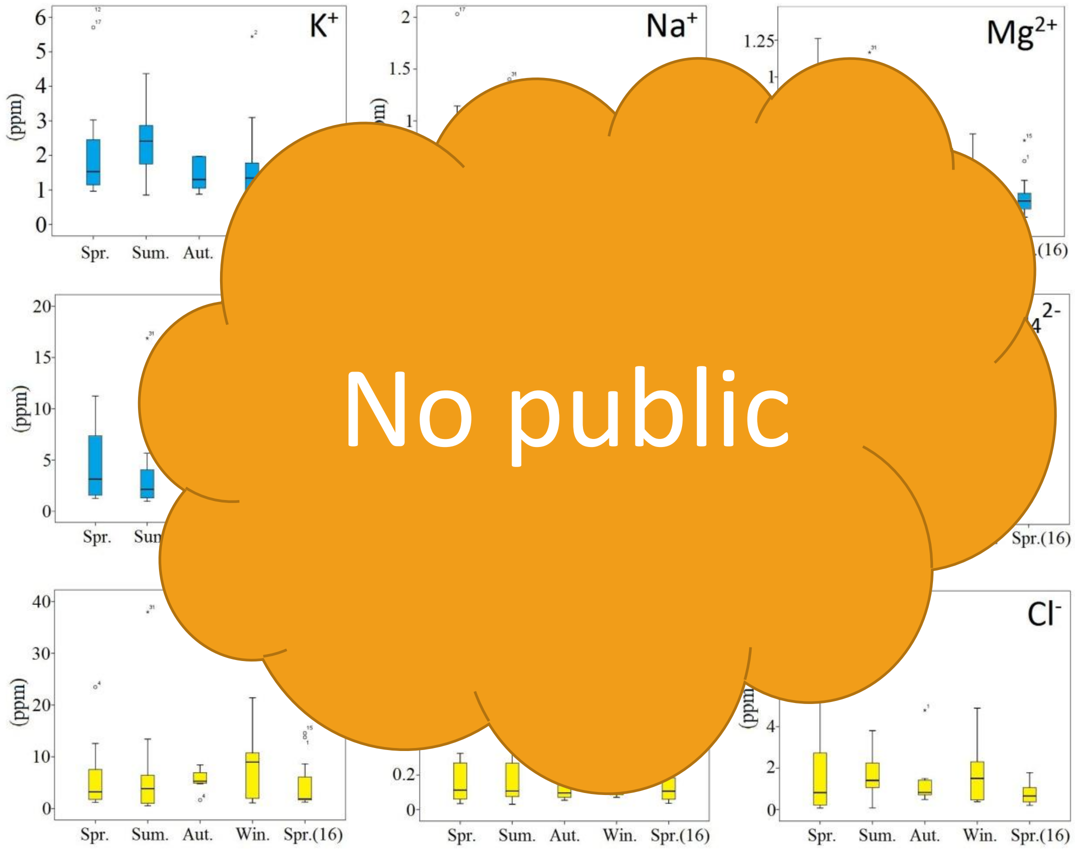


Fig.4 Component plot in rotated space of inorganic ions in rainwater

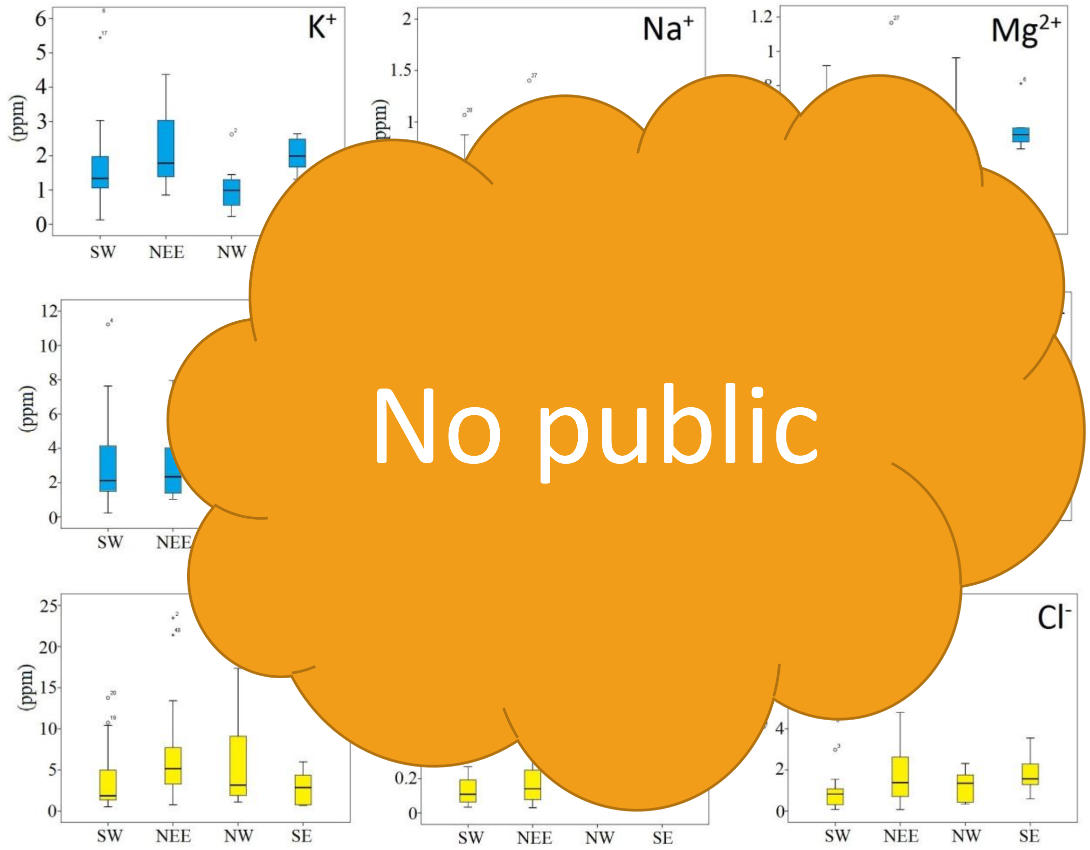
Seasonal distribution of inorganic ions



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

Fig.5The seasonal change of inorganic ions in rainwater

Distribution of trajectories in inorganic ions



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

Fig.6 The change of inorganic ions in rainwater with different trajectories

Further analysis of emissions source

Non-seasalt Model

Correlation Analysis

Enrichment Factor

Non-seasalt(NSS)

- NSS Analysis to K^+， $Mg^{2+}$and Ca^{2+}：

$$\rho_{[nss-Mg^{2+}]} = \rho_{Mg^{2+}} - 0.115\times\rho_{Na^+}$$
$$\rho_{[nss-Ca^{2+}]} = \rho_{Ca^{2+}} - 0.0373\times\rho_{Na^+}$$
$$\rho_{[nss-K^+]} = \rho_{K^+} - 0.0355\times\rho_{Na^+}$$

Table 3 Comparison of the concentration rates of nss-K^+, nss-Mg^{2+}, nss-Ca^{2+} in all seasons and periods

Period	K^+	Mg^{2+}	Ca^{2+}
NSS-ALL	[redacted]	[redacted]	[redacted]
NSS-Spr-15	[redacted]	[redacted]	[redacted]
NSS-Sum-15	[redacted]	[redacted]	[redacted]
NSS-Aut-15	[redacted]	[redacted]	[redacted]
NSS-Win-15	[redacted]	[redacted]	[redacted]
NSS-Spr-16	[redacted]	[redacted]	98.8%

No public

Correlation analysis

Table 4 The Pearson correlations of all inorganic ions

	SO_4^{2-}	NO_3^-	F^-	Cl^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	1								
NO_3^-	0.767**	1							
F^-	0.294**	[redacted]	[redacted]						
Cl^-	0.458*	[redacted]	[redacted]	[redacted]					
Na^+	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]				
NH_4^+	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]			
K^+	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	1		
Mg^{2+}	0.555**	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	0.366**	1	
Ca^{2+}	0.717**	0.735**	0.241*	[redacted]	0.583**	0.419**	0.176	0.715**	1

No public

*: $p<0.05$ showed significant correlation ; **: $p<0.01$ showed very significant correlation

EF analysis

- Soil and seawater sources：

$$EF_{soil} = \frac{[X/Ca^{2+}]_{rainwater}}{[X/Ca^{2+}]_{soil}}$$

$$EF_{seawater} = \frac{[X/Na^{+}]_{rainwater}}{[X/Na^{+}]_{seawater}}$$

Table 5 The EF analysis of rainwater comparing with seawater source and soil source

Site	Item	K^+/Ca^{2+}	Na^+/Ca^{2+}	Mg^{2+}/Ca^{2+}	Cl^-/Ca^{2+}	SO_4^{2-}/Ca^{2+}	NO_3^-/Ca^{2+}
NUIST	Ratio in soil	0.504	[redacted]	[redacted]	[redacted]	[redacted]	0.0021
	Ratio in rain	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	EF_{soil}	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	439.979

No public

Site	Item	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+	Cl^-/Na^+	SO_4^{2-}/Na^+	NO_3^-/Na^+
NUIST	Ratio in sea	0.022	[redacted]	[redacted]	[redacted]	[redacted]	—
	Ratio in rain	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	—
	$EF_{seawater}$	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	—

No public

Discussion about acid rain

Table 6 Comparison of pH and ionic concentrations (μeq/L) in

No public

Site	Na+	NH4+	K+	Mg2+	Ca2+	F−	Cl-	NO3−	SO42−	pH	SO4^{2-}/NO3^{-}	Type	Time Reference
NUIST Pukou Nanjing China	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]uburb	**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

Further analysis of other components

DOC

Inorganic Nitrogen

Relationship between DOC and each ion

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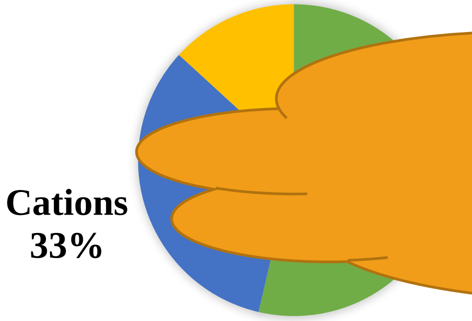


Fig.7 The proportion of DOC with other inorganic ions in rainwater

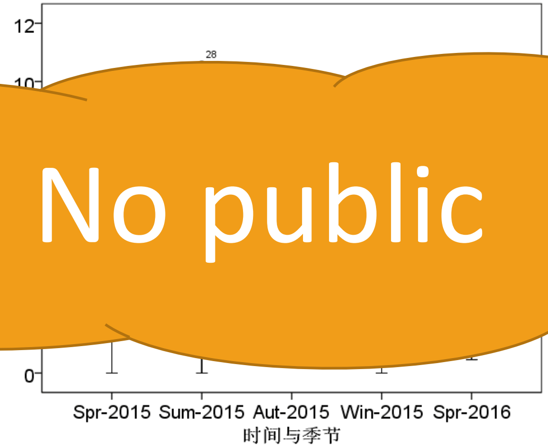


Fig.8 The seasonal change of DOC concentration

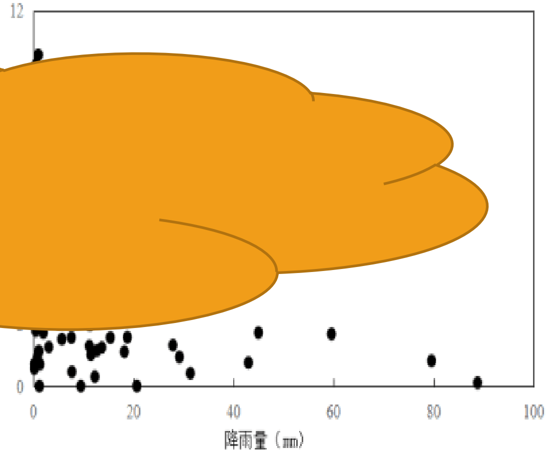


Fig.9 The correlation between the concentration of DOC and preciptation

Correlation and emission source

Table 7 The Pearson correlations of all inorganic ions and DOC

	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
DOC	-0.093	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	.520**

*： $p<0.05$ showed significant correlation； **： $p<0.01$ showed very significant correlation

Table 8 The PCA analysis with rotated component matrixa of inorganic ions

Components	1	2	3
F^-	-0.159	[redacted]	[redacted]
Cl^-	[redacted]	[redacted]	[redacted]
NO_3^-	[redacted]	[redacted]	[redacted]
SO_4^{2-}	[redacted]	[redacted]	[redacted]
Na^+	[redacted]	[redacted]	[redacted]
NH_4^+	[redacted]	[redacted]	[redacted]
K^+	[redacted]	[redacted]	[redacted]
Mg^{2+}	[redacted]	[redacted]	[redacted]
Ca^{2+}	[redacted]	[redacted]	0.042
DOC	[redacted]	[redacted]	0.031
Ratio（%）	22.2	20.4	17.5

Wet deposition characteristics of inorganic nitrogen

- Calculation of average amount of nitrogen deposition during sampling：

$$C = \sum_{i=1}^{n} C_i \times {P_i}/{\sum_{i=1}^{n} P_i}$$

Where C is the weighted average of months or years of inorganic nitrogen, Ci is the nitrogen concentration (ppm or mg / L) for each precipitation, and Pi is the

Table 9 The comparison with other cities and sites of TIN wet deposition

地点	浓度（mg/L）	选取背景类型	年降水量（mm）
江苏，南京，南信大	2.85	郊区	1334
吉林，公主岭	2.38	农村	596.9
山西，太原，阳曲	4.38	农村	538.9
北京，中国农大	5.01	城市	677.2
辽宁，大连	2.94	城市	689.6
山东，烟台，长岛	2.86	离岛	566.5
浙江，宁波，奉化	1.66	农村	1620
湖南，益阳，桃江	2.64	农村	1200.1
福建，福州	1.31	农村	1692.6
四川，成都，温江	3.98	郊区	786.3
广东，广州，白云	1.6	城市	1573.2

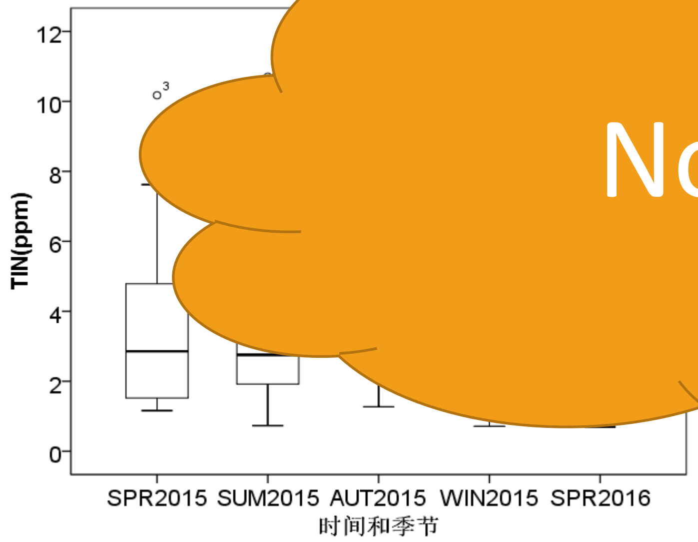
Seasonal variation of inorganic nitrogen and its correlation with DOC

Table 10 The correlation of DOC and inorganic N

	NO_3^--N	NH_4^+-N	TIN
DOC	0.65**	[redacted]	[redacted]

*: $p<0.05$ show [redacted]

No public



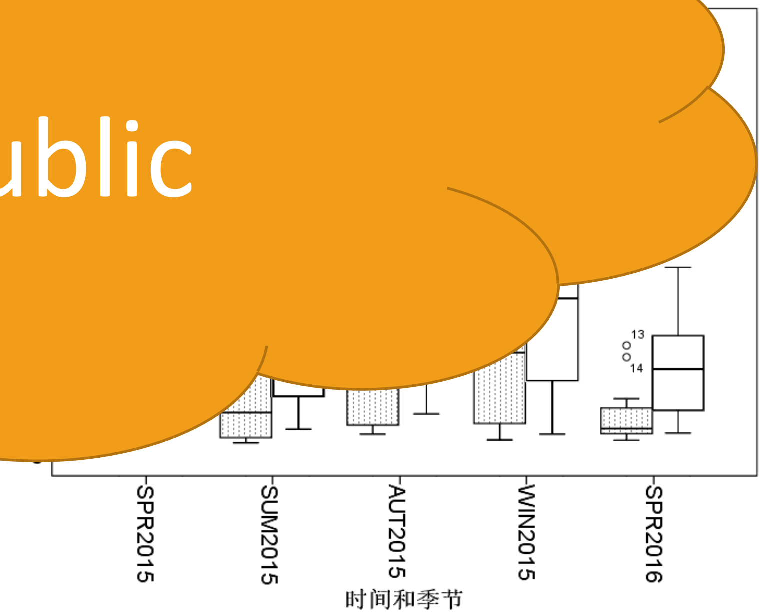


Fig. 10 The seasonal change of TIN

Fig. 11 The seasonal change ofNO_3^--N and NH_4^+-N

Wet scavenging of rainfall

- The scavenging effect of each component on the precipitation was evaluated by calculating the scavenging rate of each component. The specific formula is as follows：

$$S(\%) = \frac{C_{during} - C_{before}}{C_{before}}$$

Where S% represents the wet removal rate, C_{before} is the corresponding ion concentration of the atmospheric sample sampled before precipitation, and C_{during} is the corresponding ion concentration of the atmospheric sample sampled during precipitation

Table 12 The correlation between the wet scavenging ratios of PM2.5 and the wet deposition flux in rainwater

Ions	Correlation
$Na^+ \rightarrow Na^+$ (Rain Sample)	0.738^{**}
$NH_4^+ \rightarrow NH_4^+$ (Rain Sampl[redacted]	[redacted]
$K^+ \rightarrow K^+$ (Rain [redacted]	[redacted]
$Mg^{2+} \rightarrow Mg$[redacted]	[redacted]
$Ca^{2+} \rightarrow Ca$[redacted]	[redacted]
$F^- \rightarrow F^-$ ([redacted]	[redacted]
$Cl^- \rightarrow Cl^-$ (Rain Sa[redacted]	[redacted]
$NO_3^- \rightarrow NO_3^-$ (Rain Sample)	[redacted]
$SO_4^{2-} \rightarrow SO_4^{2-}$ (Rain Sample)	-0.621^{**}

No public

*：$p<0.05$ showed significant correlation； **：$p<0.01$ showed very significant correlation

The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in spring

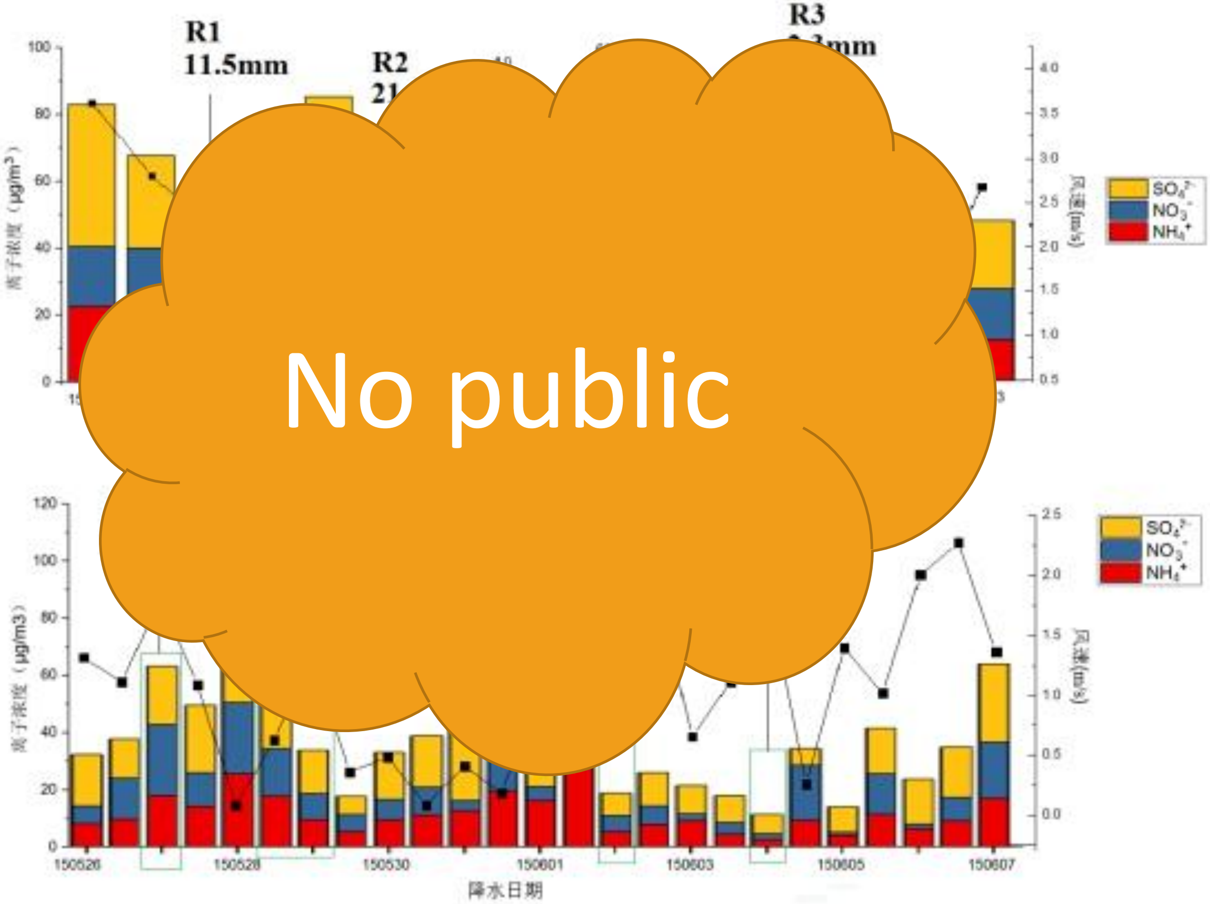


Fig.12 The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in spring at NUIST site, 2015(The green line area is the raining time)

The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in summer

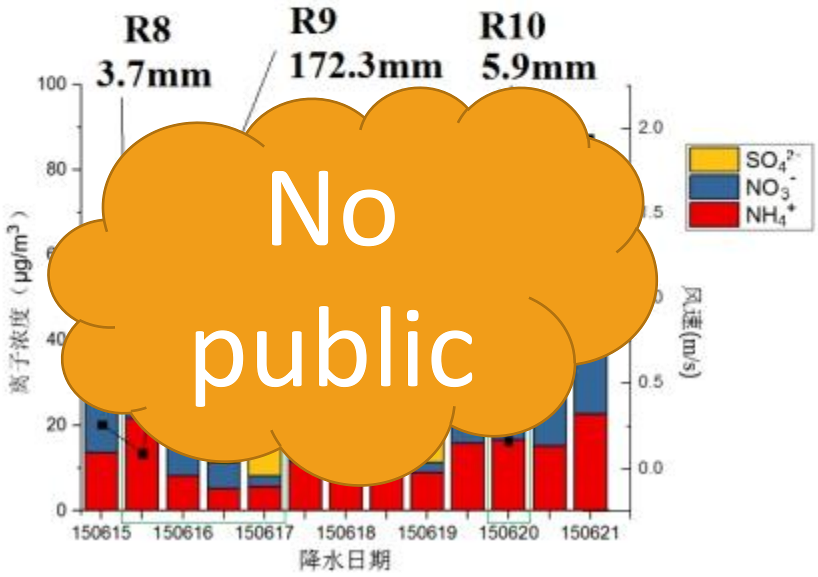


Fig.13 The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in summer at NUIST site, 2015(The green line area is the raining time)

The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in autumn

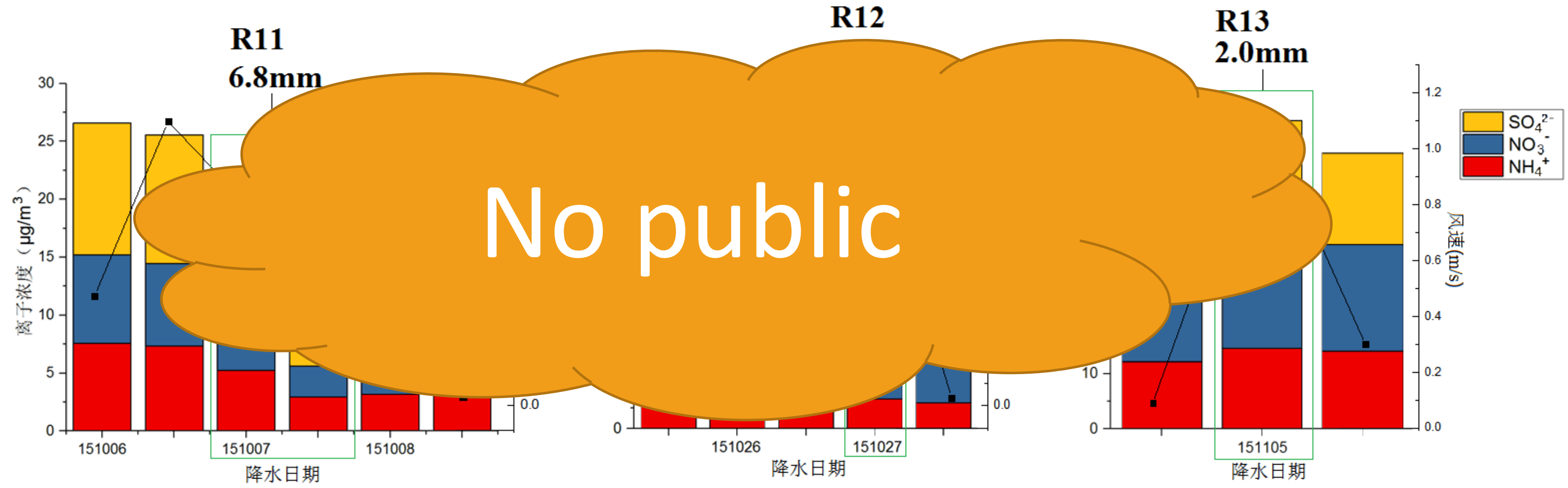


Fig.14 The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in autumn at NUIST site, 2015(The green line area is the raining time)

The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in winter

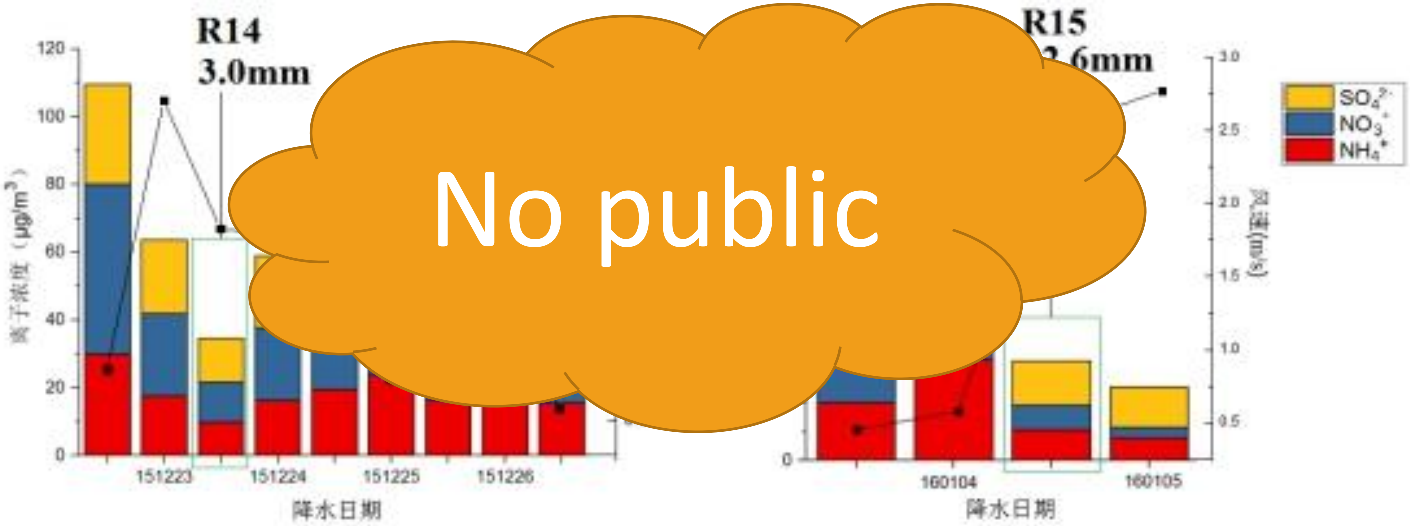


Fig.15 The change of NH_4^+, SO_4^{2-} and NO_3^- in PM2.5 during rainy day in winter at NUIST site, 2015(The green line area is the raining time)

The scavenging rate of other ions in the rainy days and the presence of the corresponding ions in the rain sample(Spring)

Table 13 The comparison between the wet scavenging ratios of PM2.5 and the wet deposition flux in rainwater samples(RS) in spring at NUIST site(μg/m²)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
R1	12.7%	-29.7%	-10.7%	36.8%	5.0%	[redacted]	[redacted]	[redacted]	-46.0%
R1-RS	1667.1	2973.3	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	15283.2
R2	-3.6%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R2-RS(μg/㎡)	2412.3	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R3	-27.1%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R3-RS(μg/㎡)	480.6	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R4	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R4-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R5-1	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R5-1-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R5-2	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R5-2-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	49213.2
R6	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	-78.9%
R6-RS(μg/㎡)	4572.7	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	34200.9
R7	-22.3%	-42.7%	[redacted]	[redacted]	[redacted]	[redacted]	-76.9%	-48.0%	-28.1%
R7-RS(μg/㎡)	75.4	421.8	171.1	61.5	[redacted]	[redacted]	154.1	735.5	1618.9
Average scavenging rate	-16.7%	-26.0%	-26.3%	4.6%	25.7%	133.0%	-33.0%	-24.2%	-28.5%

No public

The effect of precipitation on the scavenging of each ion in winter was：

$Cl^- > SO_4^{2-} > K^+ > NH_4^+ > NO_3^- > Na^+$

The scavenging rate of other ions in the rainy days and the presence of the corresponding ions in the rain sample(Summer)

Table 14 The comparison between the wet scavenging ratios of PM2.5 and the wet deposition flux in rainwater samples(RS) in summer at NUIST site(μg/m²)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
R8	-17.8%	58.6%	17.7%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	60.2%
R8-RS(μg/m²)	500.1	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	8754.1
R9-1	91.1%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
-		[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	
R9-2	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R9-1-RS(μg/m²)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R9-3	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R9-3-RS(μg/m²)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R10	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	-12.4%
R10-RS(μg/m²)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	23795.1
Average scavenging rate	-12.0%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	116.8%	-23.0%	2.8%

No public

The effect of precipitation on the scavenging of each ion in winter was：

$Ca^{2+}>NO_3^->Mg^{2+}>Na^+> NH_4^+>K^+> SO_4^{2-}$

The scavenging rate of other ions in the rainy days and the presence of the corresponding ions in the rain sample(Autumn)

Table 15 The comparison between the wet scavenging ratios of PM2.5 and the wet deposition flux in rainwater samples(RS) in autumn at NUIST site(μg/m^2)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
R11-1	-17.1%	-28.8%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	-37.5%
-			[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	
R11-2	-38.9%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R11-2-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R12	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R12-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R13	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	50.8%
R13-RS(μg/㎡)	369.1	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	5512.3
Average scavenging rate	-29.8%	-16.2%	[redacted]	[redacted]	[redacted]	[redacted]	44.4%	-21.0%	-7.4%

No public

The effect of precipitation on the scavenging of each ion in winter was：

$Na^+ > NO_3^- > Ca^{2+} > K^+ > NH_4^+ > SO_4^{2-} > Mg^{2+}$

The scavenging rate of other ions in the rainy days and the presence of the corresponding ions in the rain sample(Winter)

Table 16 The comparison between the wet scavenging ratios of PM2.5 and the wet deposition flux in rainwater samples(RS) in winter at NUIST site(μg/m^2)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
R14	-22.2%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	-40.7%
R14-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R15	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
R15-RS(μg/㎡)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Average scavenging rat [redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	-49.3%

The effect of precipitation [redacted] was：

$F^- > NO_3^- > K^+ > NH_4^+ > SO_4^{2-} > Cl^- > Na^+ > Ca^{2+}$

Table 17 The average of PM2.5 wet scavenging ratios in four seasons at NUIST site

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	雨量
2015-春	-16.7%	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	16.16
2015-夏	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
2015-秋	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	3.33
2015-冬	-31.9%	-57.0%	[redacted]	[redacted]	[redacted]	[redacted]	-41.2%	-67.4%	-49.3%	12.80

The efficiency of ion scavenging in the PM2.5 weather in the four seasons is: winter> spring> summer> autumn 。

Wet scavenging in short-time scale

- The lowest total ions concentration will be compared with the concentration of last hour. The specific formula is as follows：

$$S\ (\%)_{max} = \frac{C_{lowest} - C_{before}}{C_{before}}$$

Where $S\ (\%)_{max}$ indicates the maximum scavenging rate of the corresponding ions during the precipitation period, C_{lowest} represents the concentration of the corresponding ions at the lowest total ion concentration, and C_{before} represents the concentration of the corresponding ions at the time point before precipitation.

Calculation of wet deposition ion flux:

$$\mathrm{Flux(ion)} = C \times P \times \pi \mathrm{r}^2 \times {}^{1}/_{\pi \mathrm{r}^2}$$

Where C is the mass concentration of the corresponding ions, P is the rainfall, and r is the radius of the collector.

Effect of rainfall to scavenging (NH_4^+, SO_4^{2-}, NO_3^-)

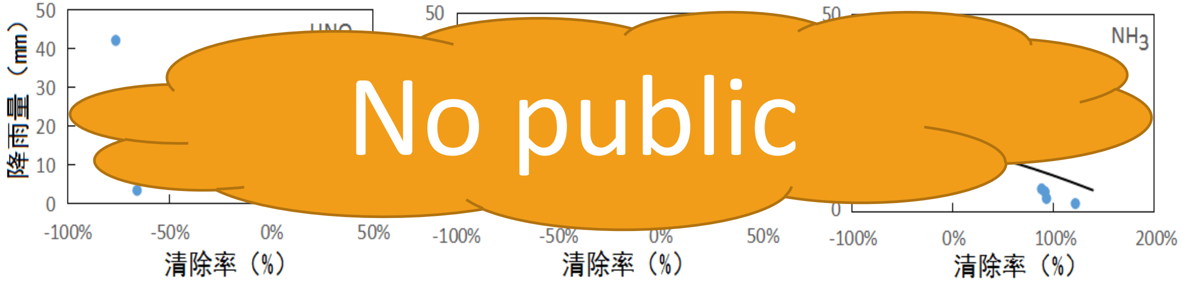


Fig.16 The change features between precipitation and HNO_3, SO_2, NH_3 in PM2.5 during raining

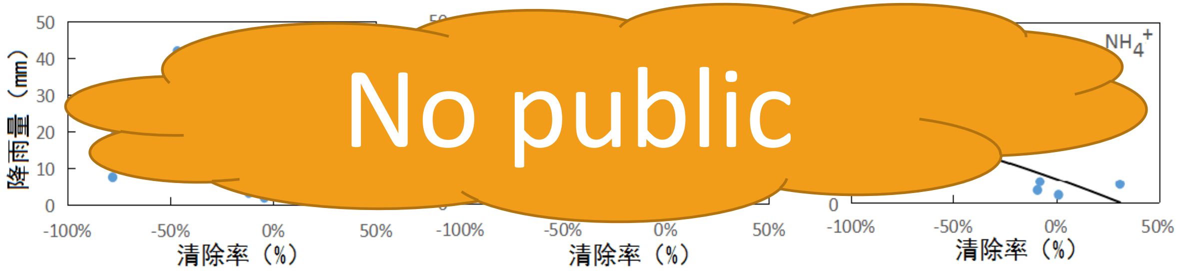


Fig.17 The change features between precipitation and NH_4^+, SO_4^{2-}, NO_3^- in PM2.5 during raining

Table 18 The correlation between the wet scavenging ratios of ions and gas in PM2.5 and the precipitation

	HNO_3	SO_2	NH_3	NO_3^-	SO_4^{2-}	NH_4^+
Rainfall(mm)	-0.572	-0.559	-0.447	-0.413	-0.673*	-0.610*

*： $p<0.05$ showed significant correlation.

Effect of rainfall to scavenging (Na^+, K^+ and Ca^{2+})

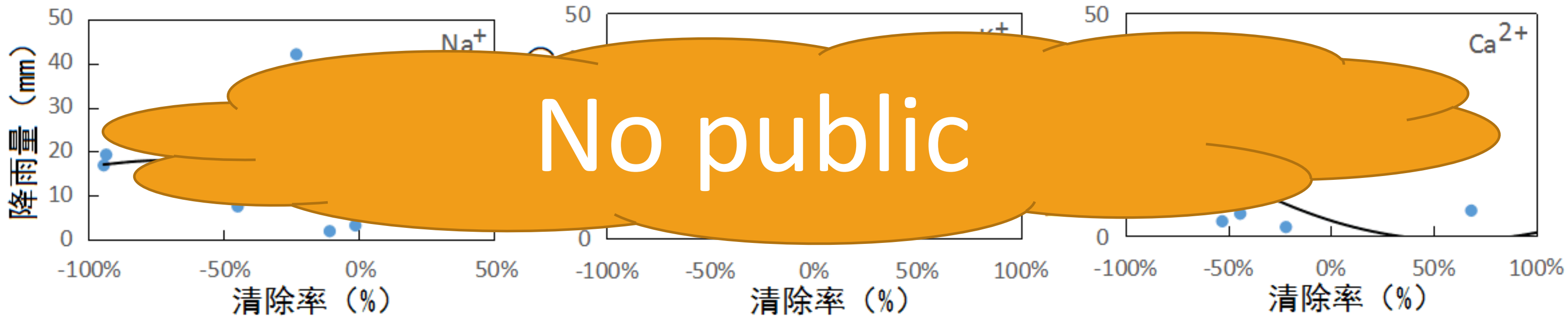


Fig.18 The change features between precipitation and Na^+, K^+, Ca^{2+} in PM2.5 during raining

Table 19 The correlation between the wet scavenging ratios of ions in PM2.5 and the precipitation

	Na^+	K^+	Ca^{2+}
Rainfall(mm)	-0.121	-0.466	-0.089

The relationship between scavenging and flux of ions

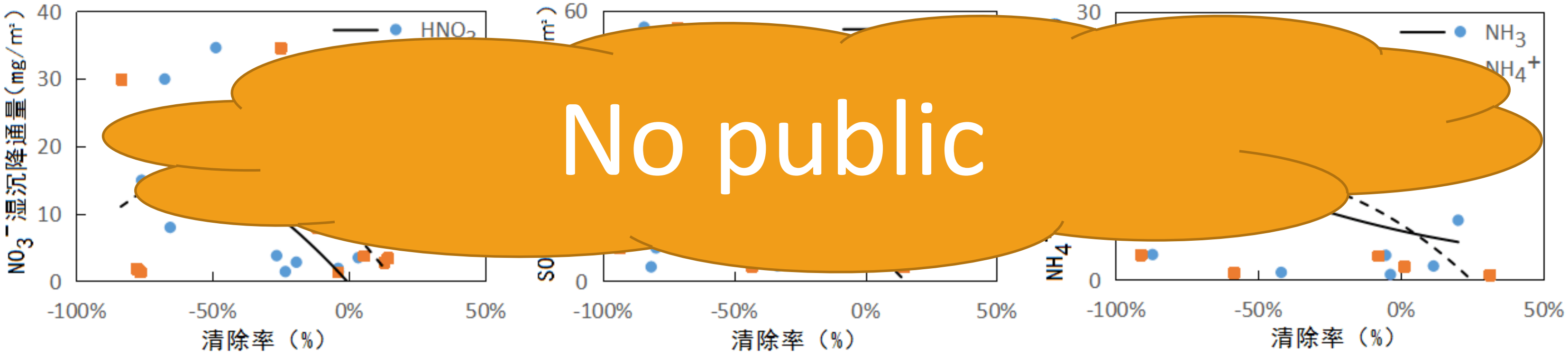


Fig.19 The change features between ions flux in wet deposition and NH_4^+, SO_4^{2-}, NO_3^- with their gas precursor NH_3, SO_2 and HNO_3 in PM2.5 during raining

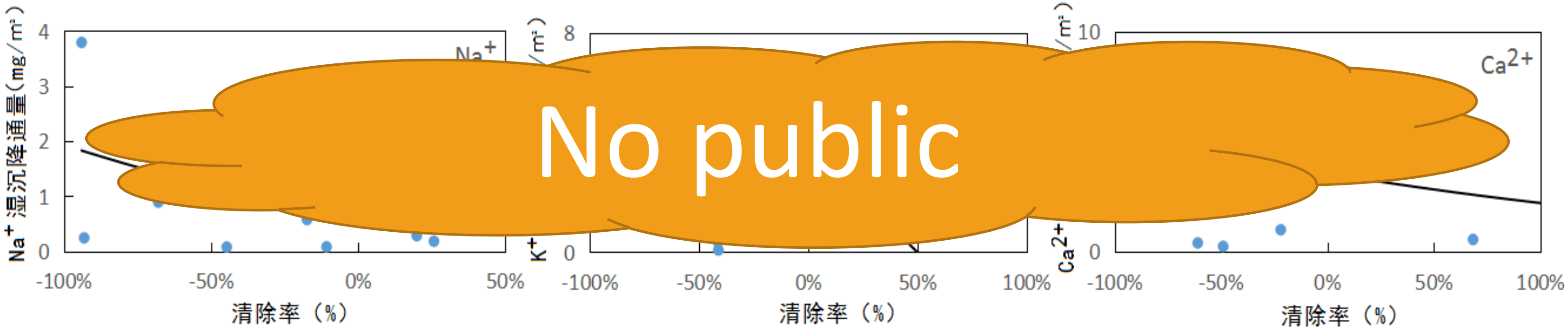


Fig.20 The change features between ions flux in wet deposition and Na^+, K^+, Ca^{2+} in PM2.5 during raining

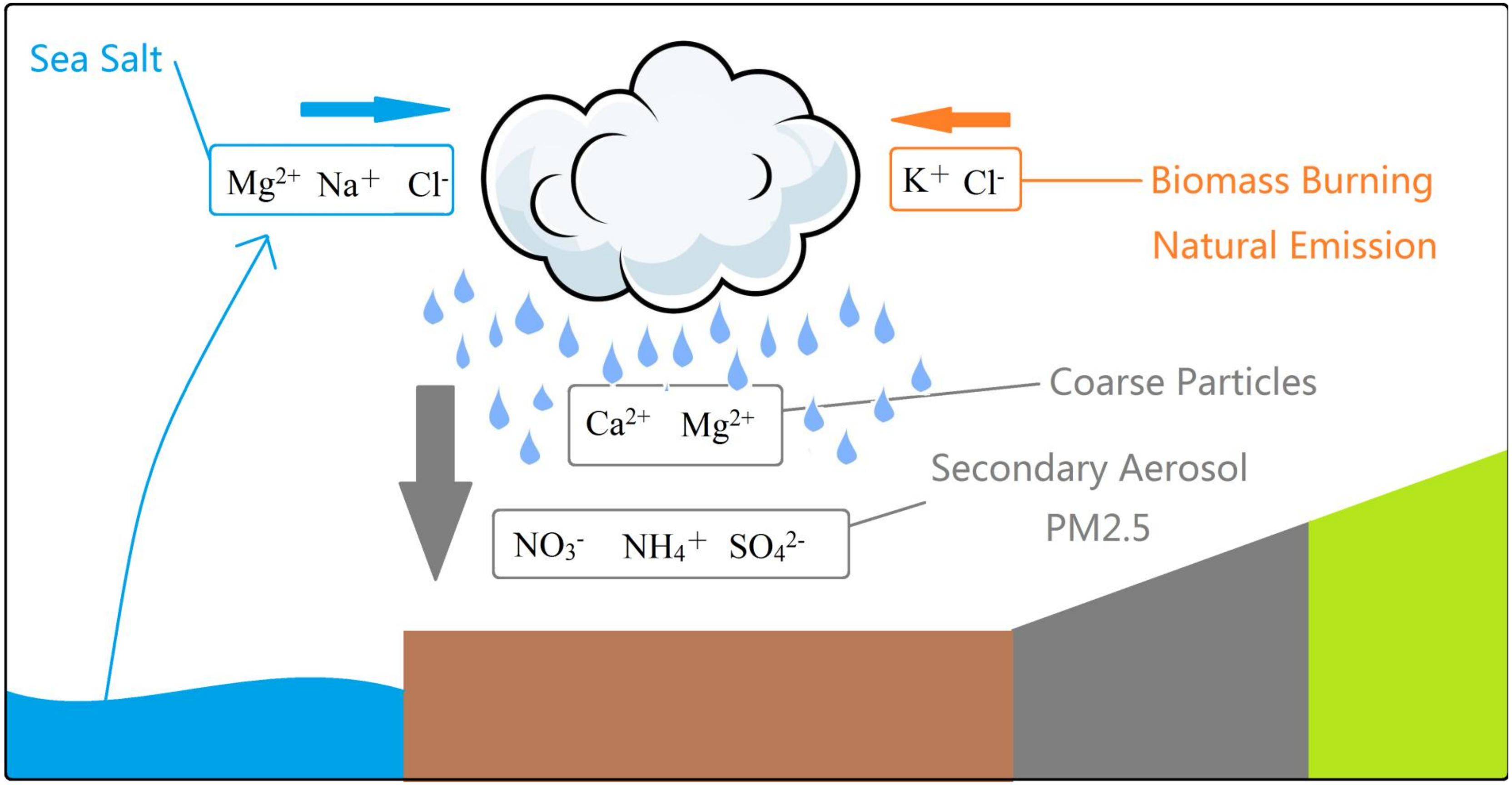
Conclusion

- The concentration of acid in the rainwater was higher, but the pH is not low due to the neutralization of the calcium and ammonium. The secondary aerosol produced by the anthropogenic activities had a great contribution to the chemical composition of rainwater, reaching 51.08%. The K^+, Ca^{2+} and Mg^{2+} sources are mainly from inland emissions, especially K^+ and Ca^{2+}, and the contribution of marine sources is very small. K^+ is mainly biomass. Ca^{2+} is related to dust and coal combustion byproducts. 10% of the contribution, the rest mostly from the crust source. F-content is scarce and comes mainly from by-products from coal. Precipitation in the sample accounted for 13% of the proportion of precipitation, the precipitation of its main role in the dilution of industrial emissions for its main source of inorganic nitrogen samples in the presence of significant changes in seasonal and composition types, including autumn and winter high, spring and summer low; Nitrogen-based, precipitation is also the main role of its dilution.

- The removal efficiency of PM2.5 in different seasons showed different removal characteristics in different seasons. The removal efficiency of precipitation in atmospheric PM2.5 showed winter> spring> summer> autumn. The main components of NH_4^+, SO_4^{2-} and NO_3^- in the second aerosol are obviously different from the corresponding ions in the rainwater after the precipitation weather is removed, but the elimination of other ions, especially Ca^{2+} and Mg^{2+}, The Na^+ and K^+ were obviously removed in the four seasons precipitation weather, but they did not correlate well with the corresponding ions in the rainwater.

- The precipitation of NH_4^+, SO_4^{2-} and NO_3^- with their precursors NH_3, SO_2 and HNO_3 have a clearing effect, while NH_4^+, SO_4^{2-} show the inverse relationship with their corresponding precursors. Precipitation is therefore the main reason for the reduction of polluted gases, but the reduction of pollutants in the precipitation days is also controlled by other factors. In addition, the precipitation of three kinds of metal ions on the removal effect of Ca^{2+} the best, and K^+ followed, Na^+ slightly weaker.

Discussion


Sea Salt
Mg^{2+} Na^{+} Cl^{-}
K^{+} Cl^{-}
Biomass Burning
Natural Emission
Coarse Particles
Ca^{2+} Mg^{2+}
Secondary Aerosol
PM2.5
NO_3^{-} NH_4^{+} SO_4^{2-}

感谢中心!

感谢环科院!

感谢南信大!

Thanks!