Yale-NUIST Center on Atmosphere Environment

Characteristics of Water Soluble Inorganic Ions in Fine Particulate Matter During Winter in Xuzhou

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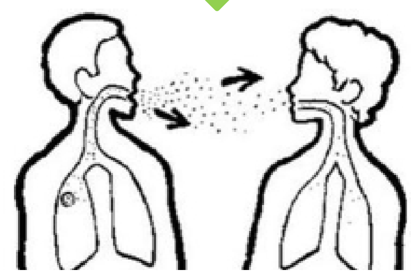
Outline

- Introduction
- Method
- Result and Discussion
- Conclusion
- Future work

Introduction

$PM_{2.5}$ (OC/EC, water-soluble ions, Stable carbon and nitrogen isotopes)



Introduction

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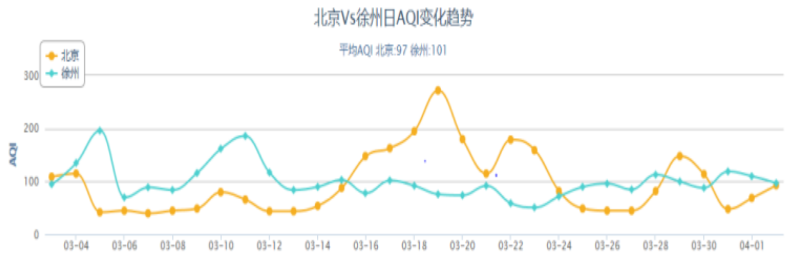
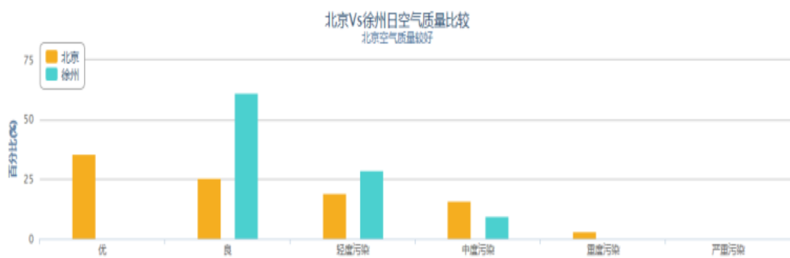
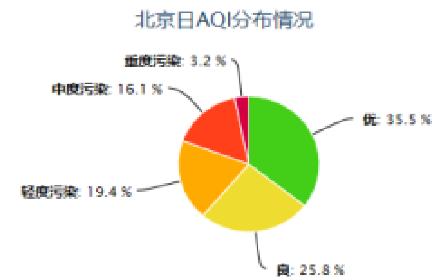
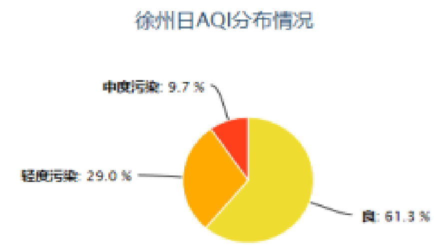
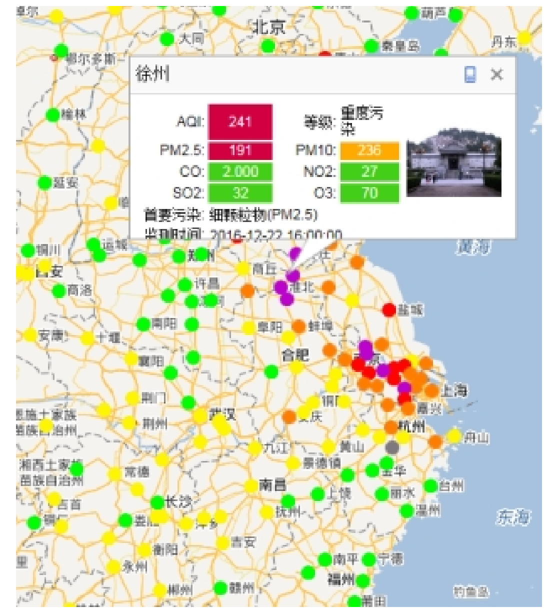






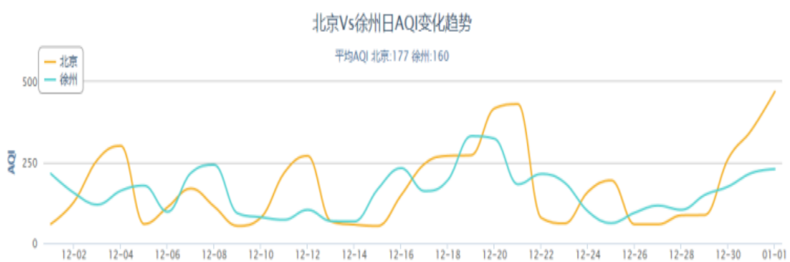


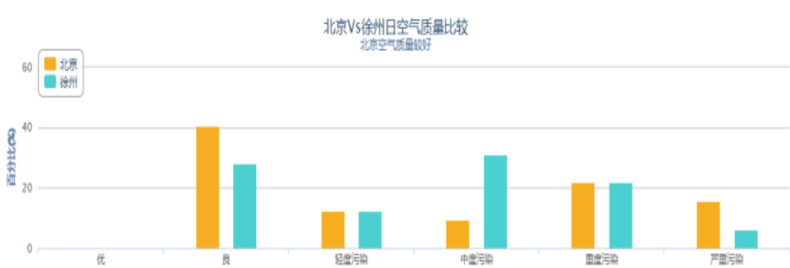


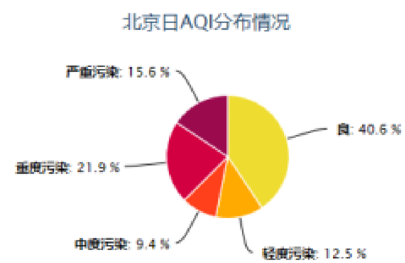
全国空气质量最差城市实时排名

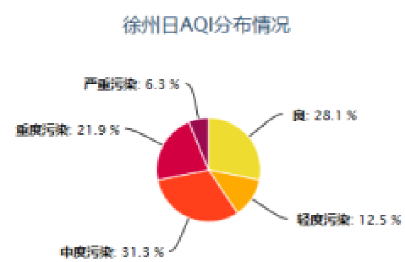
排名	城市	AQI	空气质量等级
1	保定	501	极度污染
2	沧州	456	严重污染
3	宿州	267	重度污染
4	邯郸	261	重度污染
5	淮北	254	重度污染
6	德州	244	重度污染
7	吐鲁番地区	232	重度污染
8	徐州	227	重度污染
9	济宁	226	重度污染
10	菏泽	225	重度污染

冬季：2016.12.01-2017.1.1







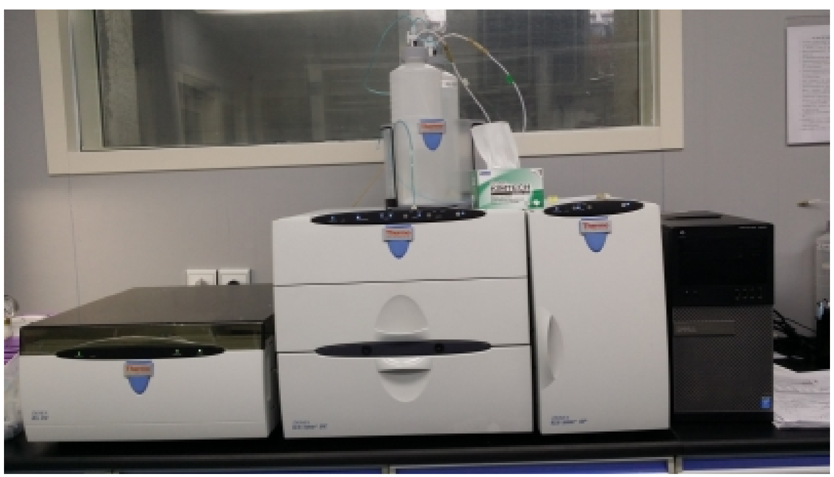


数据来自中国空气质量在线监测分析平台
2016-12-22 16:00

Method

Sampling Information: 23.5h, Continuous Sampling (KC-1000 high volume sampler , $1.05 m^3 \cdot min^{-1}$, LAOSHAN MOUNTAIN ELECTRONIC INSTRUMENT   FACTORY CO., LTD.)

Sample Analysis : Ion chromatography (ICS 5000+,Thermo Scientific);



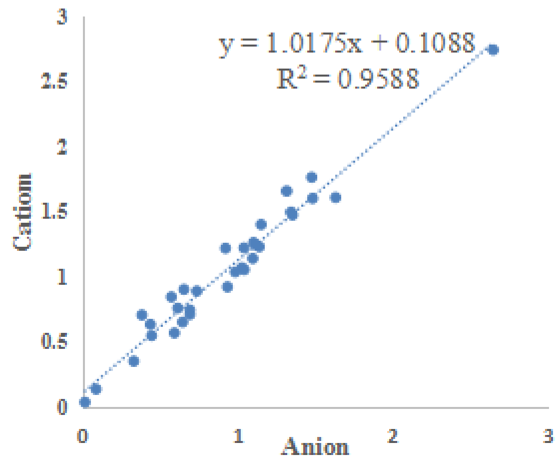
N 34°19'，E117°15'

Result and Discussion

Ion balance（winter）：

$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39.1} + \frac{2 \cdot Mg^{2+}}{24.3} + \frac{2 \cdot Ca^{2+}}{40} \quad (1)$$

$$AE = \frac{Cl^-}{35.45} + \frac{2 \cdot SO_4^{2-}}{96} + \frac{NO_3^-}{62} + \frac{F^-}{19} \quad (2)$$



clear air: visibility>10km，RH<90%;
mild haze: visibility5~10km，RH≤80% or RH80~95%，$PM_{2.5}$>75μg·m^{-3};
severe haze: visibility<5km.

	整体期间	清洁大气	轻度霾	重度霾
CE/AE	1.02	0.99	0.88	0.93
R^2	0.96	0.99	0.84	0.95

Result and Discussion

Concentration of $PM_{2.5}$ and water-soluble ions:

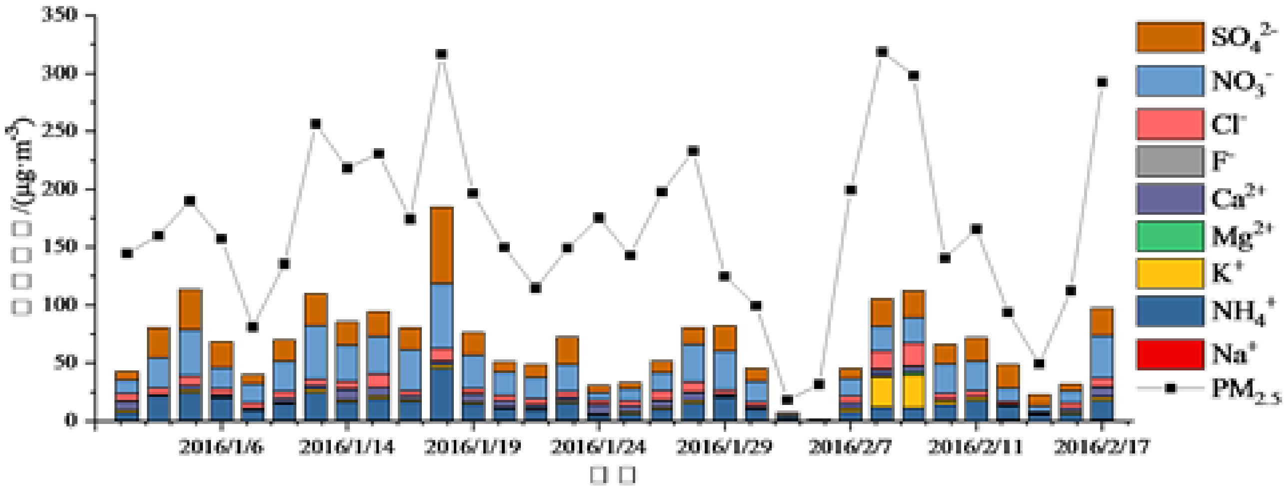


Fig.1 Daily variation of $PM_{2.5}$ and WSIIs mass concentration

Tale1 Mean mass concentration of $PM_{2.5}$ and water-soluble ions in different cities/μg·m^{-3}

城市	时间	样品数	$PM_{2.5}$	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	NO_3^-/SO_4^{2-}
徐州（本研究）	2015-12~2016-2	32	164.8	0.59	13.16	3.34	0.25	3.78	0.20	6.01	22.50	17.52	1.37
苏州[6]	2015-12	21	99.37	1.61	12.53	0.94	0.10	0.38	0.19	3.74	23.19	15.06	1.54
厦门[14]	2014-12	62	77.8	0.19	4.29	0.50	0.03	0.38	0.07	1.47	5.49	3.94	~1.4
台湾[16]	2015-1	30	36.1	0.79	4.54	0.41	0.59	0.95	—	0.96	4.82	4.22	—
上海[18]	2013-12~2014-2	28	138	—[1)]	12.6	—	—	—	—	4.98	29.1	19.5	1.42
南京[17]	2014-8~9	1h	55.1	—	9.02	—	—	0.45	—	—	12.12	16.54	0.74

1）不存在相应数据

Result and Discussion

Characteristics of water-soluble ions in $PM_{2.5}$ under different haze levels:

Table2 Mass concentrations of $PM_{2.5}$, water-soluble ions , NO_3^-/ SO_4^{2-}, and WSIIs/$PM_{2.5}$

项目	总体采样期间	清洁大气	轻度霾	重度霾
样品数	32	3	14	15
$PM_{2.5}$	164.8± 77.3	32.8±15.5	124.9±22.5	228.4±55.5
Na^+	0.59±0.32	0.08±0.07	0.58±0.32	0.70±0.24
NH_4^+	13.16±8.34	2.47±2.57	12.37±5.82	16.03±9.37
K^+	3.34±6.54	0.28±0.22	1.57±0.76	5.59±9.14
Mg^{2+}	0.25±0.42	0.03±0.02	0.12±0.08	0.41±0.57
Ca^{2+}	3.78±2.73	0.50±0.24	2.90±2.21	5.24±2.57
F^-	0.20±0.16	0.02±0.03	0.16±0.13	0.27±0.17
Cl^-	6.01±3.98	0.51±0.36	4.90±1.28	8.15±4.57
NO_3^-	22.50±12.69	2.67±2.40	20.73±8.87	28.11±12.72
SO_4^{2-}	17.52±12.09	4.±4.71	15.69±8.86	21.81±13.74
NO_3^-/ SO_4^{2-}	1.37±0.49	0.79±0.77	1.49±0.45	1.39±0.41
WSIIs	67.50±36.08	±8.76	±22.82	±35.98
WSIIs/$PM_{2.5}$	0.42±0.15	0.37±0.09	0.48±0.19	0.37±0.10

Result and Discussion

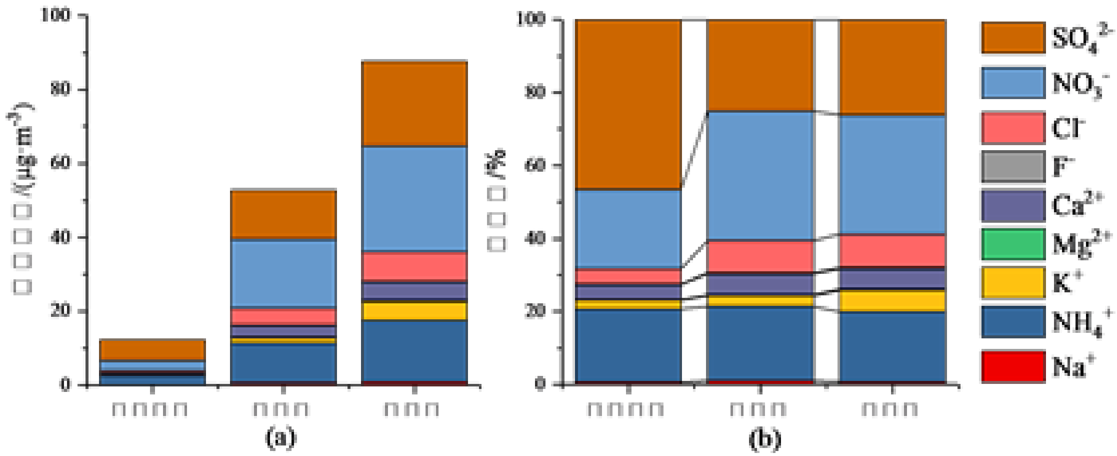


Fig.2 Accumulation of water-soluble ions and its contribution to WSIIs in clear air, mild haze and severe haze

Result and Discussion

Correlation analysis:

Table 3 Matrix of Correlation coefficients between main water-soluble ions in $PM_{2.5}$ during haze period

	NH_4^+	K^+	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
NH_4^+	1					
K^+	-0.11	1				
Ca^{2+}	-0.23	0.08	1			
Cl^-	0.17	0.85**	0.29	1		
NO_3^-	0.89**	-0.02	-0.02	0.24	1	
SO_4^{2-}	0.94**	0.14	-0.19	0.37*	0.82**	1

1）**在0.01水平上显著相关，*在0.05水平上显著相关

$c(NH_4^+)/c(SO_4^{2-})=4.12$, $c(NH_4^+)/c(NO_3^-)=1.86$

Result and Discussion

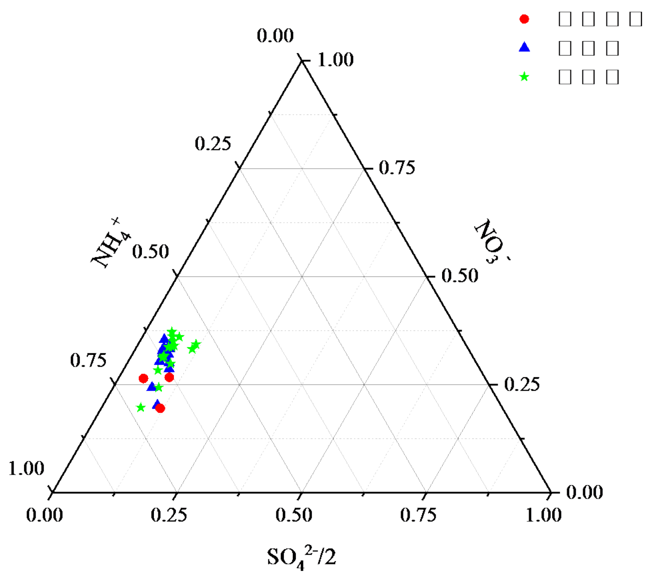


Fig.3 Triangle diagram of SO_4^{2-}-NO_3^--NH_4^+

城市	时间	NO_3^-/SO_4^{2-}
徐州（本研究）	2015-12~2016-2	1.37
苏州[6]	2015-12	1.54
厦门[14]	2014-12	~1.4
台湾[16]	2015-1	—
上海[18]	2013-12~2014-2	1.42
南京[17]	2014-8~9	0.74

项目	总体采样期间	清洁大气	轻度霾	重度霾
NO_3^-/SO_4^{2-}	1.37±0.49	0.79±0.77	1.49±0.45	1.39±0.41

Result and Discussion

PCA:

Table 4 Varimax rotated factor loading matrix for water-soluble ions in $PM_{2.5}$

	因子1	因子2	因子3
Na^+	0.38	0.43	0.14
NH_4^+	0.98	-0.03	-0.08
K^+	-0.02	0.98	0.03
Ca^{2+}	-0.03	0.08	0.95
Cl^-	0.31	0.84	0.33
NO_3^-	0.93	0.03	0.08
SO_4^{2-}	0.94	0.20	-0.09
累积百分比/%	33.26	65.91	87.65
污染源	二次污染源	生物质燃烧、化石燃料	土壤建筑扬尘

Result and Discussion

Backward trajectory analysis:

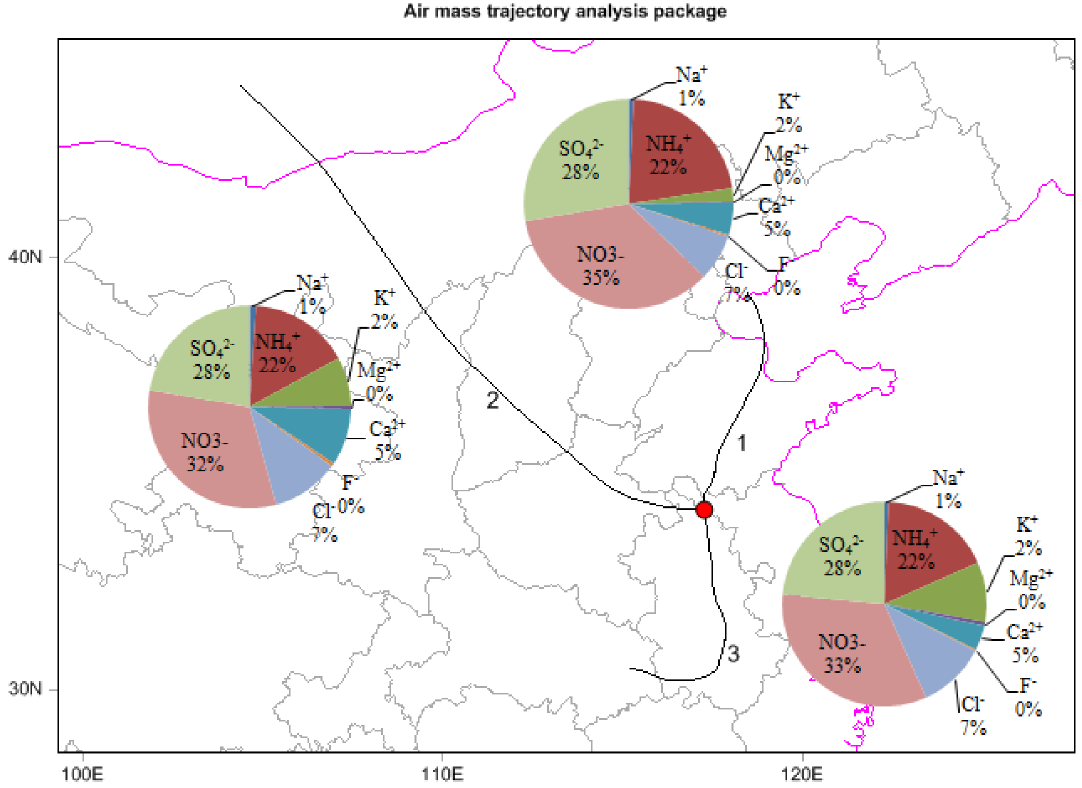


Fig.4 The 72h backward trajectories of air mass arriving Xuzhou and mass percentage of water-soluble ions associated with three air mass trajectory cluster

Conclusion

1. The average concentration of WSIIs in winter is （73.6±40.9）μg·m^{-3}， which accounted for 43.2% of $PM_{2.5}$. NH_4^+, NO_3^- and SO_4^{2-} are the major components of water soluble ions. With the increase of pollution degree,the proportion of Cl^- and NO_3^- increased obviously, conversely, the concentration of NH_4^+ and SO_4^{2-} in WSIIs decreased.
2. The value of NO_3^-/ SO_4^{2-} in haze period(mild haze :1.49 and severe haze:1.39) obviously larger than clear air period(0.79), the results show that the contribution of vehicle exhaust is greater than that of coal combustion during the sampling period, and vehicle emission is the main source of air pollutants during the haze occurrence in Xuzhou.
3. SNA's correlation with each other were significant, NH_4^+、NO_3^- and SO_4^{2-}were in the form of $(NH_4)_2SO_4$ and NH_4NO_3.Secondary formation, biomass burning, fossil fuel combustion and dust were the major sources of the water-soluble ions in $PM_{2.5}$.
4. Air masses arrive at Xuzhou mainly from the northeast, northwest and south through long distance transmission. During the transmission, SO_2 and NO_x are converted into NO_3^- and SO_4^{2-}, and biomass combustion products K^+ and Cl^- are brought to Xuzhou.

Future work

- Data:one year data of water-soluble ions,OCEC,stable carbon and nitrogen isotopes

Result and Discussion

- Fluctuation of $PM_{2.5}$ and TWSIs concentration diurnal variations in winter is greater than in summer.
- The variation trends of the concentration of $PM_{2.5}$ and TWSIs was consistent ,the ratios of TWSIs to PM2.5 during winter and summer were 40.3% and 38.7%.
- SNA(SO_4^{2-}、NO_3^-、NH_4^+) was the main component of $PM_{2.5}$.

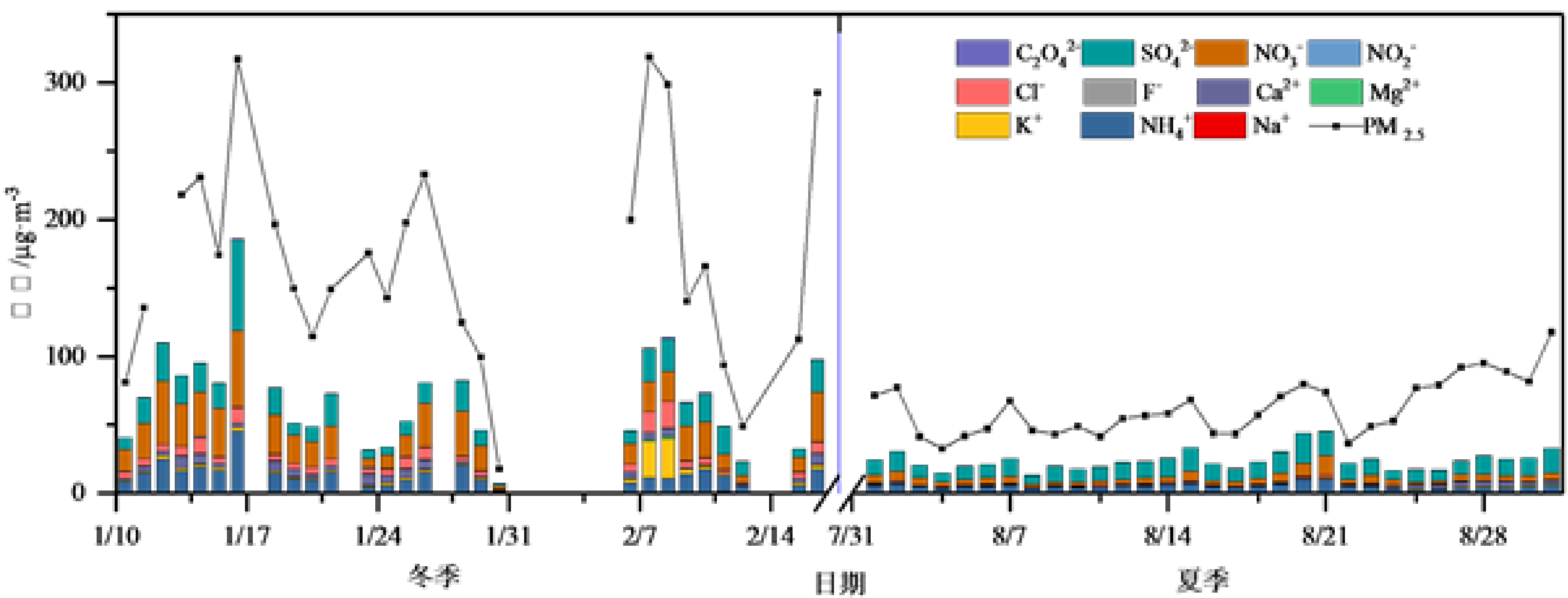


Fig.1 Diurnal variation of $PM_{2.5}$ and total water-soluble ions (TWSIs) concentrations(24h average) in winter and summer

Result and Discussion

- The concentration of SO_4^{2-},NO_3^- and NH_4^+ has the same variation trends. The concentration of K^+ in February 8th and 9th was significantly higher than other dates maybe due to the effects of biomass combustion.

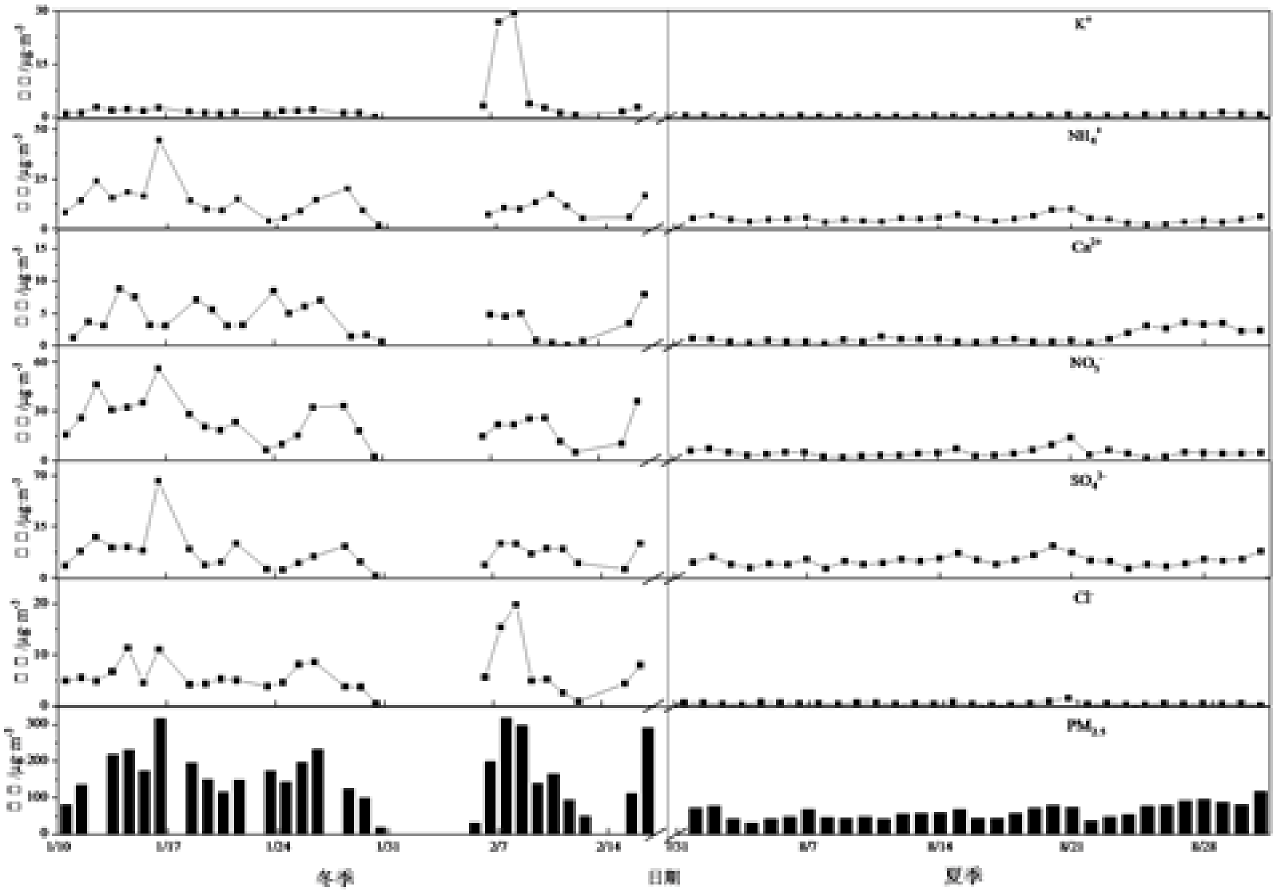


Fig.2 Diurnal variations of major water-soluble ions(Ca^{2+}, Cl^-,K^+,SO_4^{2-},NO_3^-,NH_4^+) in PM2.5.

Result and Discussion

Table 1 The concentration of water-solution ions in $PM_{2.5}$ and the value of SOR,NOR and NO_3^-/SO_4^{2-} in winter and summer/$\mu g \cdot m^{-3}$

	Winter	Summer	Winter/Summer
$PM_{2.5}$	165.21±81.95	62.46±20.38	2.64
Na^+	0.59±0.34	0.17±0.09	3.37
NH_4^+	12.53±8.38	4.88±1.77	2.56
K^+	3.56±6.97	0.45±0.29	7.95
Mg^{2+}	0.26±0.44	0.05±0.03	5.66
Ca^{2+}	3.83±2.71	1.29±1.00	2.96
F^-	0.23±0.15	0.04±0.03	5.75
Cl^-	5.99±4.24	0.46±0.27	12.81
NO_2^-	0.28±0.24	0.20±0.13	1.41
NO_3^-	22.33±12.97	4.69±2.48	4.75
SO_4^{2-}	17.28±12.08	11.79±3.53	1.46
Oxalate（$C_2O_4^{2-}$）	0.37±0.35	0.21±0.12	1.73
TWSIs	66.56±37.84	24.21±7.38	2.75
SOR	0.35±0.15	0.29±0.11	1.18
NOR	0.28±0.09	0.13±0.04	2.19
NO_3^-/SO_4^{2-}	1.46±0.44	0.39±0.14	3.69

The concentration level of water-solution ions was $NO_3^- > SO_4^{2-} > NH_4^+ > Cl^- > Ca^{2+} > K^+ > Na^+ > C_2O_4^{2-} > NO_2^- > Mg^{2+} > F^-$ in winter, was $SO_4^{2-} > NH_4^+ > NO_3^- > Ca^{2+} > Cl^- > K^+ > C_2O_4^{2-} > NO_2^- > Na^+ > Mg^{2+} > F^-$ in summer,

In winter, the main pollution source is Mobile Sources,and its Stationary Source in summer.

Result and Discussion

Table 2 Mean mass concentration of $PM_{2.5}$ and water-soluble ions in different cities/μg·m^{-3}

城市	时间	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-
徐州	2016-1~2	0.59	12.53	3.56	0.26	3.83	0.23	5.99	22.33
	2016-8	0.17	4.88	0.44	0.04	1.29	0.04	0.46	4.69
厦门	2014-8	0.12	1.96	0.23	0.02	0.24	0.06	0.07	0.74
	2014-12	0.19	4.29	0.50	0.03	0.38	0.07	1.47	5.49
苏州	2015-8	2.30	8.00	0.44	0.11	0.44	0.05	0.53	7.88
	2015-12	1.61	12.53	0.94	0.10	0.38	0.19	3.74	23.19

The concentration of water-soluble ions in Xuzhou is higher than in Xiamen and Suzhou in winter , and is higher than in Xiamen and lower than in Suzhou in summer.

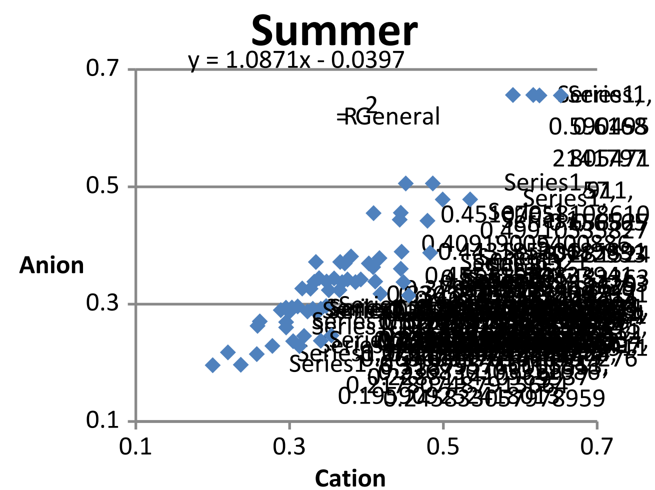
Result and Discussion

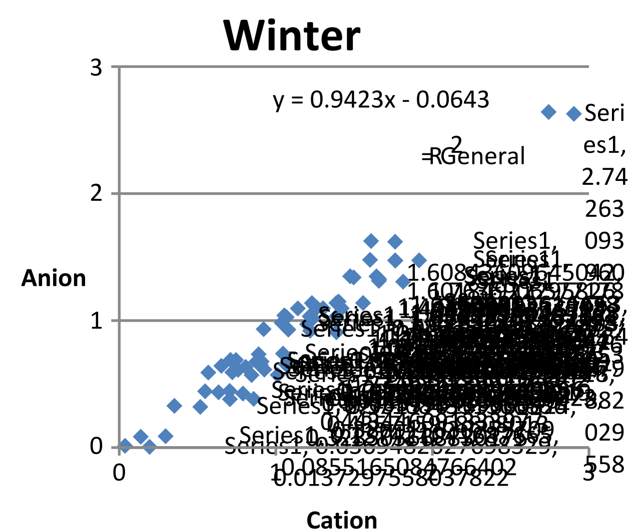
Ion balance in PM2.5:

$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39.1} + \frac{2 \cdot Mg^{2+}}{24.3} + \frac{2 \cdot Ca^{2+}}{40}$$

$$AE = \frac{Cl^-}{35.45} + \frac{NO_2^-}{46} + \frac{NO_3^-}{62} + \frac{2 \cdot SO_4^{2-}}{96} + \frac{2 \cdot C_2O_4^{2-}}{88}$$

Winter:AE/CE<1,particulate matter was weakly alkaline, probably due to excess NH4+ in the atmosphere ;
Summer:Particulate matter is neutral





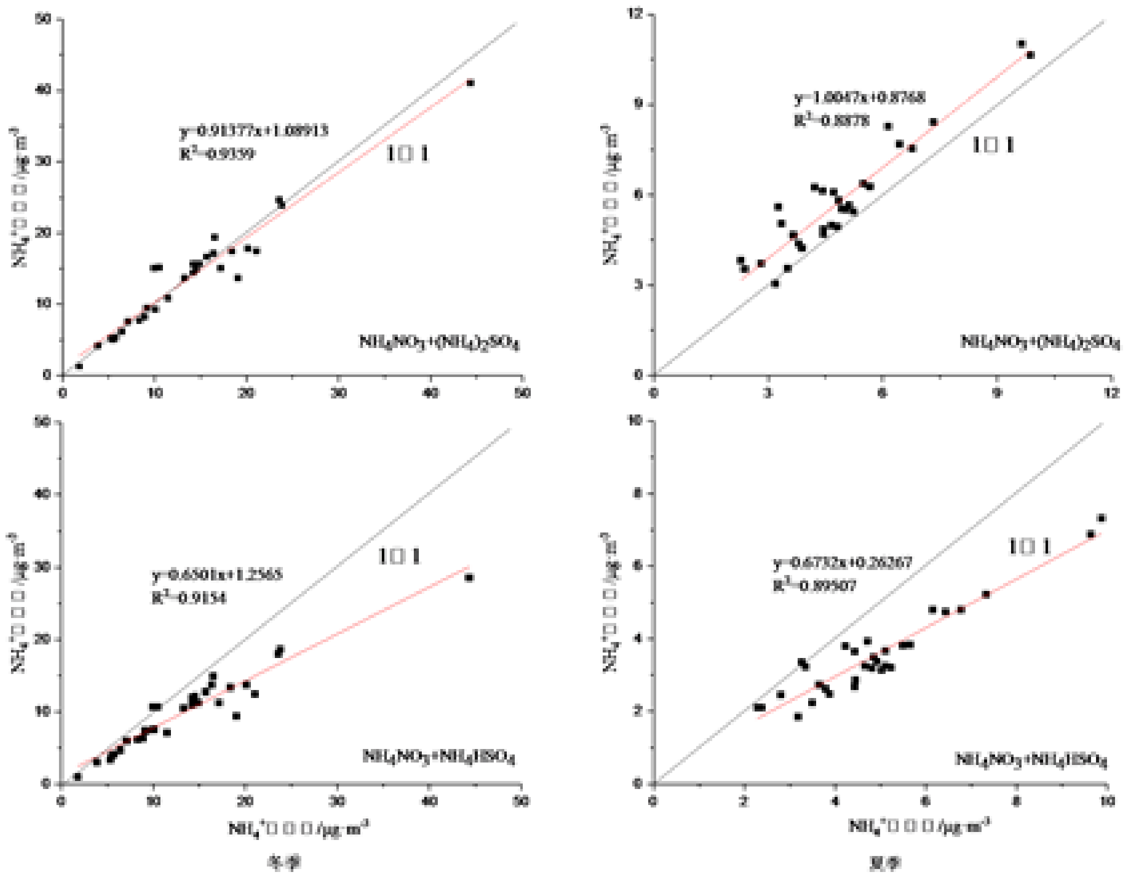
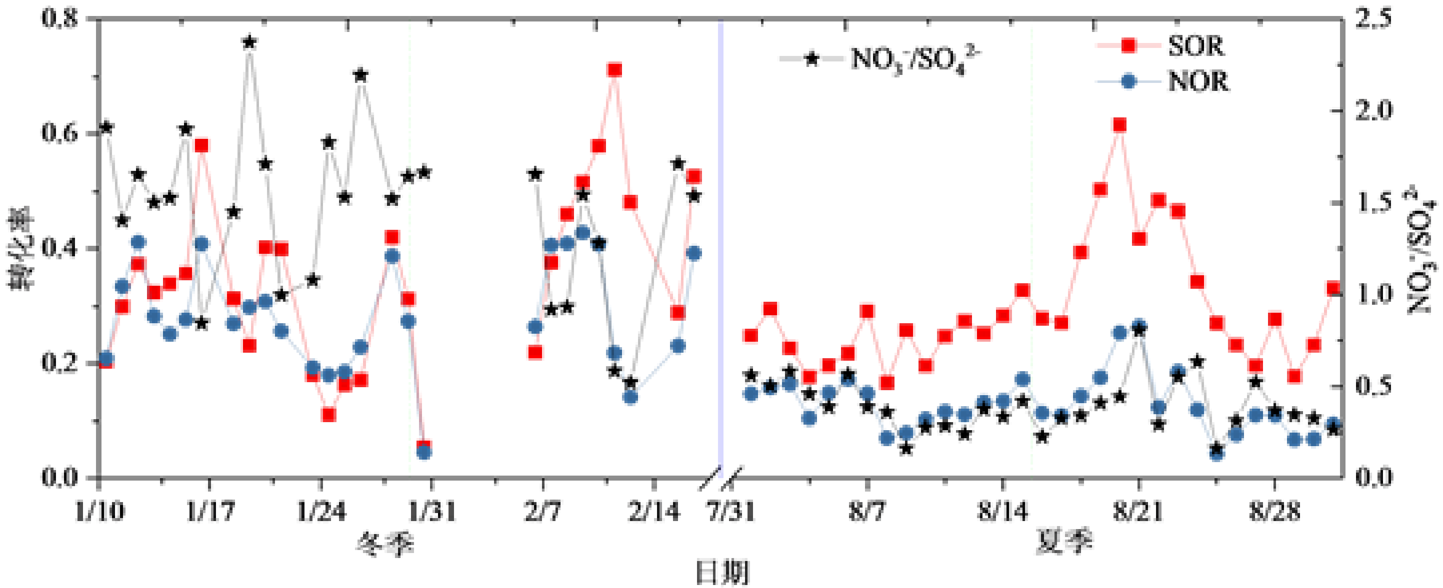


Fig.3 Comparison between measured NH_4^+ and calculated NH_4^+ value

The main forms of NH_4^+ in the atmosphere are $(NH_4)_2SO_4$ and NH_4NO_3

Result and Discussion

Fig.4 Diurnal variations of $[NO_3^-]/[SO_4^{2-}]$,SOR and NOR.



SOR and NOR fluctuated greatly in winter than in summer, the range of SOR in winter is 0.05~0.71,in summer is 0.11~0.62,the average value of SOR in winter is 0.34±0.15, in summer is 0.29±0.11;the average of NOR in winter is 0.28±0.09,in summer is 0.13±0.04.

The $[NO_3^-]/[SO_4^{2-}]$ is higher when SOR decreases and NOR increases, or NOR increases rapidly.

Result and Discussion

PCA:

	冬季			夏季		
	因子 1	因子 2	因子3	因子 1	因子 2	因子 3
Na^{+}	0.38	0.43	0.14	0.25	0.78	0.04
NH_4^{+}	0.98	-0.03	-0.08	0.96	-0.08	-0.18
K^{+}	-0.02	0.98	0.03	0.37	0.82	0.22
Mg^{2+}	-0.03	0.97	0.10	-0.14	0.90	0.09
Ca^{2+}	-0.03	0.08	0.95	-0.23	0.89	0.13
F^{-}	-0.01	0.23	0.93	-0.66	0.21	-0.05
Cl^{-}	0.31	0.84	0.33	0.75	-0.08	0.15
NO_3^{-}	0.93	0.03	0.08	0.96	-0.05	0.15
SO_4^{2-}	0.94	0.20	-0.09	0.85	0.19	-0.34
贡献率（%）	33.26	32.65	21.74	35.19	31.23	11.09

Source:Secondary formation, biomass burning, fossil fuel combustion and dust