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Yale-NUIST Center on Atmospheric Environment

Study on the characteristic of water-soluble ion in PM2.5 of Nanjing based on on-line monitoring

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Outline

- Introduction
- Experimental
- Results and discussion
- Conclusions

Introduction

- Haze pollution caused by particulate matter suspended in the air remains a major environmental issue because of its substantial impacts on climate, air quality, and human health.
- Water soluble inorganic ions (WSII) were found to be the major components of $PM_{2.5}$, especially secondary inorganic ions (sulfate, nitrate and ammonium) , which accounted for one third or more of $PM_{2.5}$ (Cao et al.,2012; Kong et al., 2014).
- The most commonly used procedures for collecting aerosols are filter-based methods, but because of their low accuracy it is not simple to quantify ambient aerosols.
- Online analyzer with highly temporal resolution for monitoring aerosols and gases (MARGA) have been developed to solve the problems related to filter-base methods (Acker et al., 2005) . The characteristics of water soluble ions in Nanjing based on the results of MARGA were analyzed in this study.

Experimental

- Site： Meteorological observation field, NUIST
- Samples: $PM_{2.5}$

Table 1 Summary of data and corresponding instruments

Parameter	Duration	Instruments
1. Gases(NH_3、HNO_2、HNO_3、HCl、SO_2) 2. Aerosols ions(NH_4^+、Na^+、K^+、Ca^{2+}、Mg^2 、Cl^- 、NO_3^-、SO_4^{2-})	Sring:2016.3.3-2016.5.16 Summer:2016.7.11-2016.9.14 Winter:2017.1.15-2017.2.28	MARGA(ADI 2080, Applikon Analytical B. B. Corp., The Netherlands)
Mass concentration of $PM_{2.5}$	2016.3.1-2017.2	THERMO (TEOM1405-DF, Thermo Scientific, USA)
Meteorological parameters (T, RH, WD,WS, P, visibility)	2016.3.1-2017.2	Vaisala (Meteorological observation field, NUIST)

Results and discussion

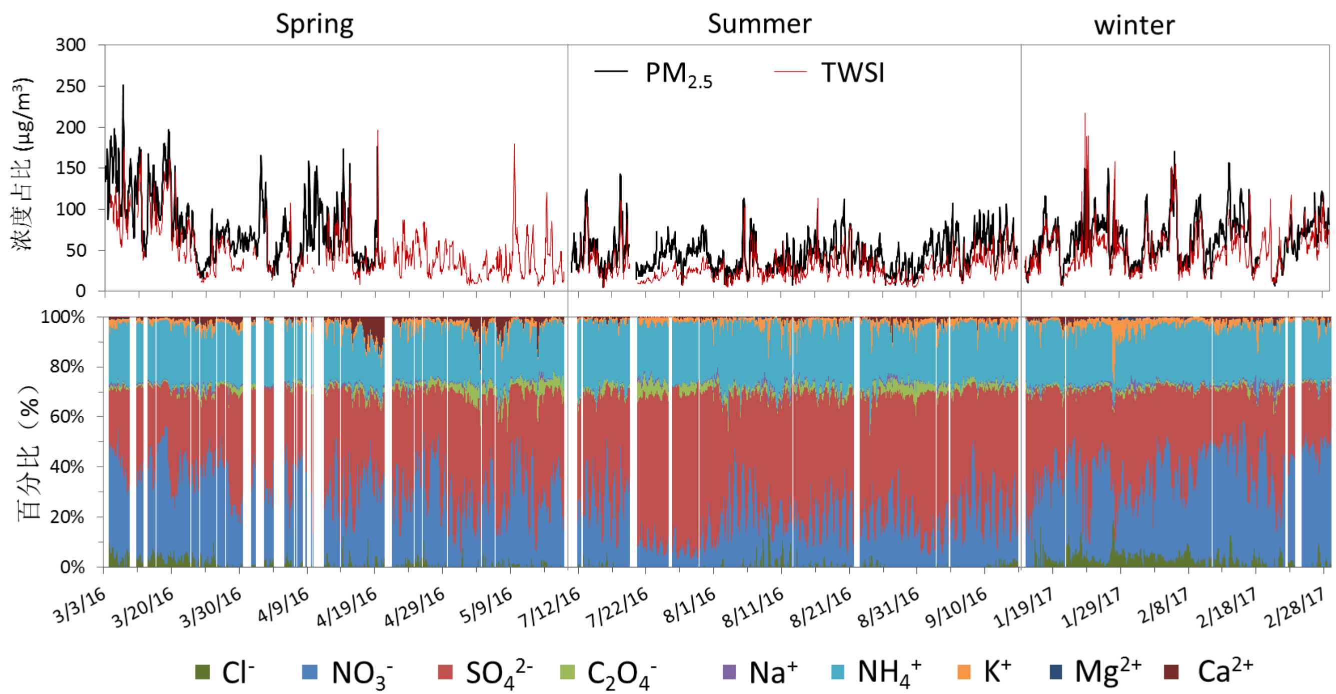


Fig 1. Time series of mass concentration (μg/m3) of $PM_{2.5}$, total water-soluble ions(TWSI) and the proportion of water-soluble ions

Results and discussion

- Seasonal variation

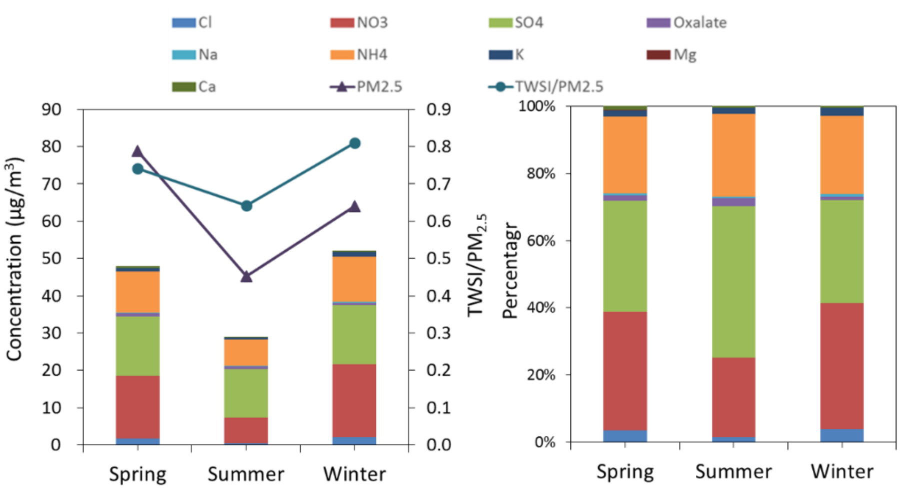


Fig 2. water-soluble ions in $PM_{2.5}$ in different seasons

Table 2. Statistics of ions in different seasons

参数	春季（2016）		夏季（2016）		冬季（2017）	
	浓度 (μg/m³)	占比	浓度 (μg/m³)	占比	浓度 (μg/m³)	占比
Cl^-	1.70	3.54%	0.42	1.47%	2.01	3.87%
NO_3^-	16.89	35.21%	6.83	23.63%	19.80	38.23%
SO_4^{2-}	15.87	33.09%	13.10	45.31%	15.52	29.97%
Oxalate	0.78	1.62%	0.65	2.26%	0.51	0.99%
Na^+	0.28	0.59%	0.14	0.48%	0.38	0.73%
NH_4^+	11.01	22.95%	7.08	24.48%	11.97	23.11%
K^+	0.88	1.84%	0.53	1.83%	1.22	2.35%
Mg^{2+}	0.07	0.15%	0.02	0.09%	0.08	0.16%
Ca^{2+}	0.58	1.20%	0.13	0.46%	0.24	0.47%
TWSI	47.96		28.91		51.79	
TWSI/$PM_{2.5}$（%）	74.16		64.12		81.96	
HCl	0.01		0.20		0.00	
HNO_2	2.33		2.98		2.90	
HNO_3	0.85		1.04		0.92	
SO_2	17.50		16.23		12.49	
NH_3	13.95		18.08		9.91	
T（℃）	16.8		29.1		5.6	
RH（%）	64		68		62	

Introduction

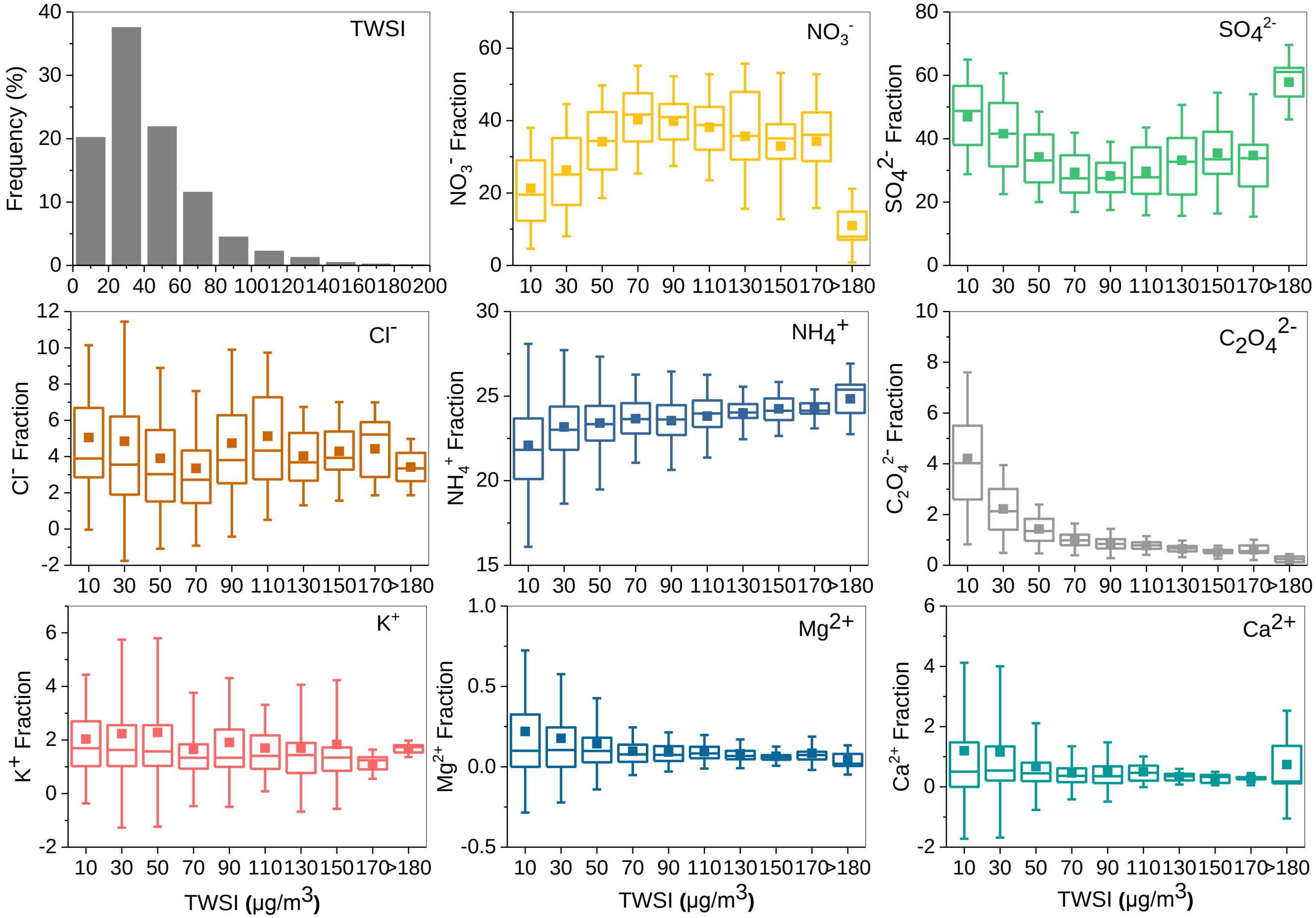


Fig.3 The variability of water-soluble ion fraction (%) and probability of total mass concentration (%)

Results and discussion

- Diurnal variations

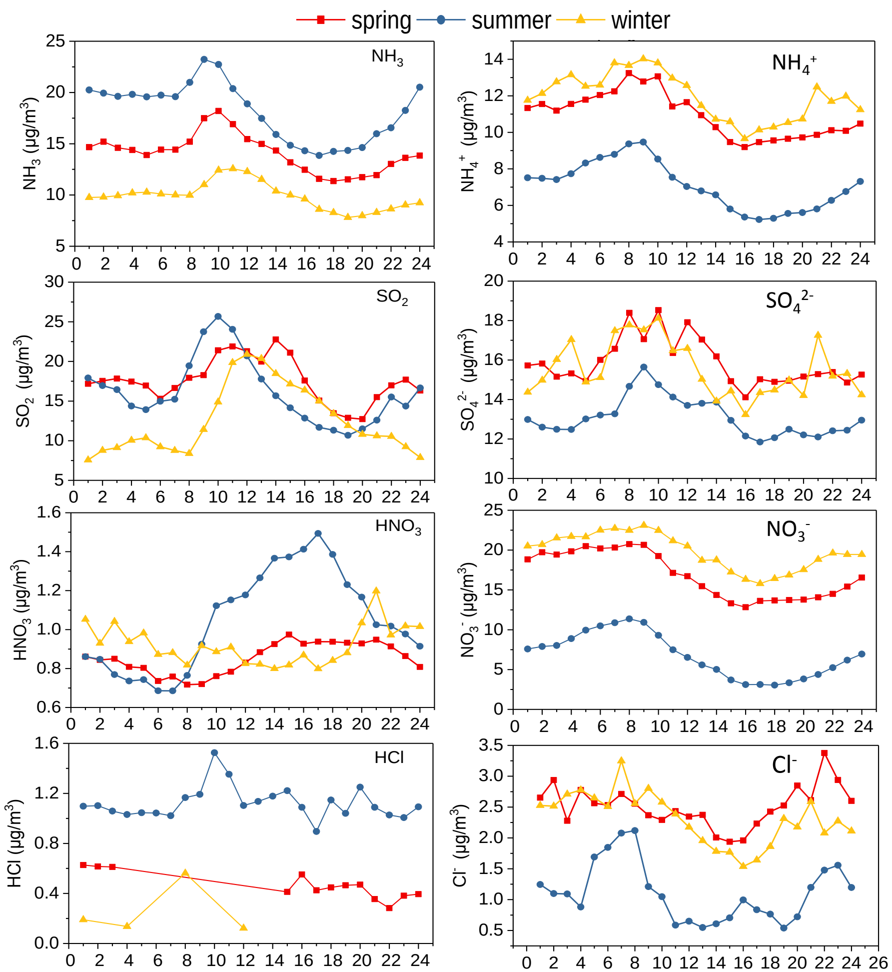


Fig 4. Diurnal variations of NH3, SO2, HNO3, and HCl and major ionic constituents in PM2.5

Results and discussion

- Diurnal variations

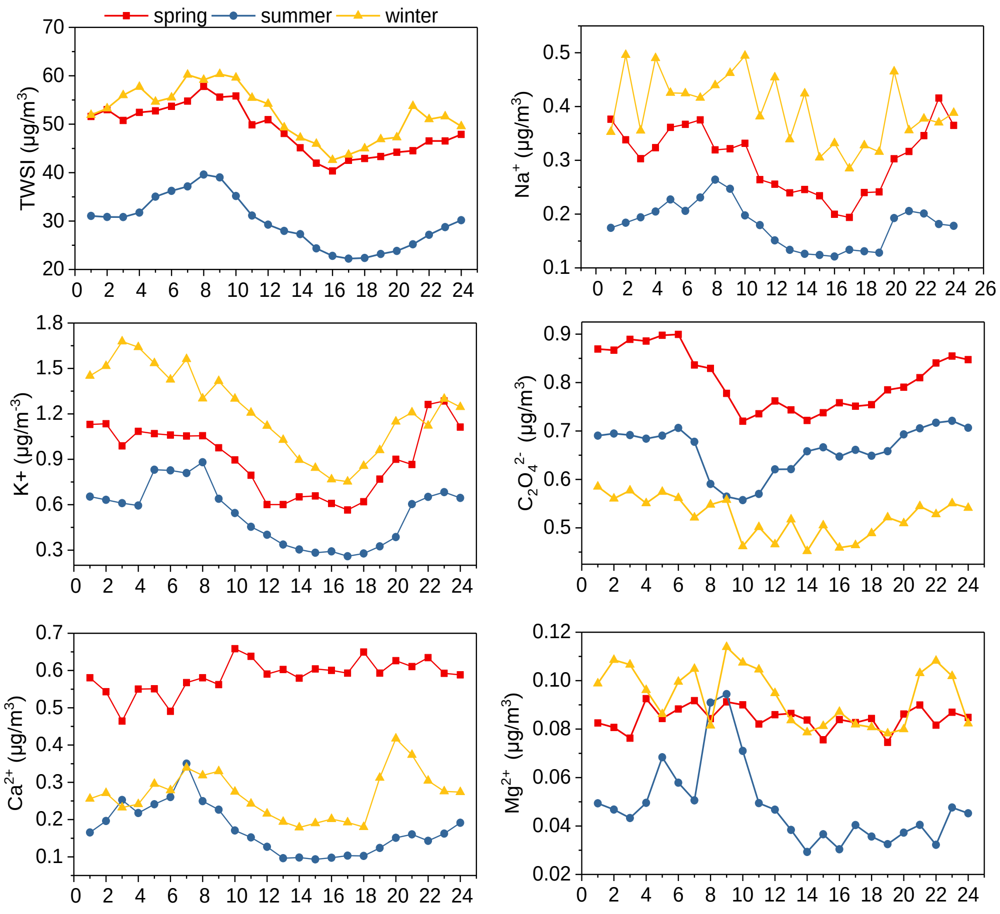


Fig 5. Diurnal variations of TWSI, and other ionic constituents in PM2.5

Results and discussion

- Backward trajectory Cluster analysis

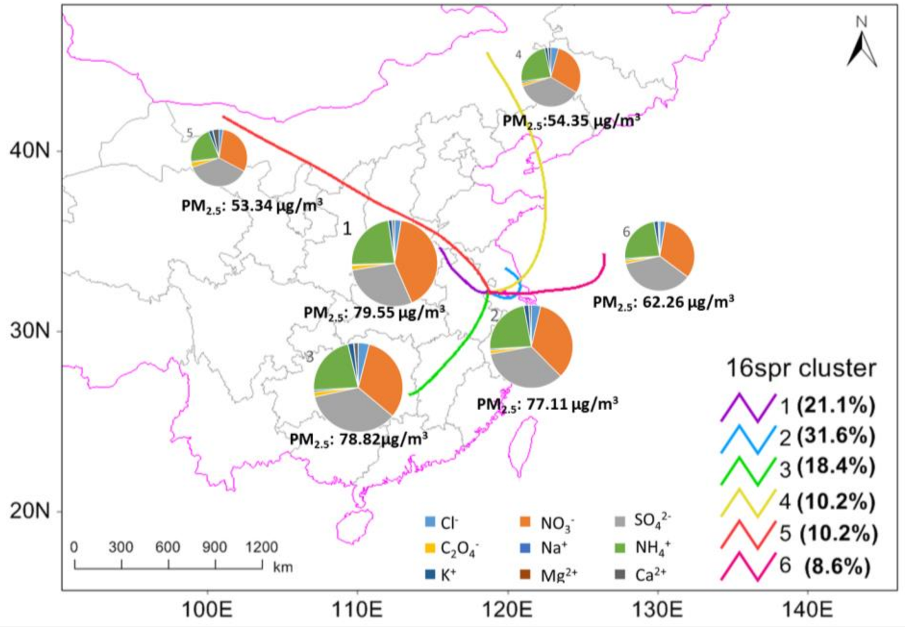


Fig 6. Backward trajectory Cluster analysis in Spring

Table 3. Characteristics of source air mass in Spring

	Cluster1	Cluster2	Cluster3	Cluster4	Cluster5	Cluster6
Ratio	21.10%	31.60%	18.40%	10.20%	10.20%	8.60%
Cl-	1.21±1.92	1.86±2.75	1.81±2.36	1.52±1.82	0.73±1.22	1.04±0.95
NO3-	19.94±16.19	17.56±11.75	14.62±10.77	10.89±11.35	9.68±7.50	12.79±6.85
SO42-	14.14±6.03	17.89±13.31	16.22±10.58	13.45±10.11	11.76±7.09	14.25±4.94
C2O4-	0.83±0.35	0.70±0.38	0.77±0.26	0.65±0.30	0.87±0.25	0.60±0.30
Na+	0.17±0.15	0.30±0.28	0.33±0.20	0.34±0.50	0.22±0.23	0.30±0.35
NH4+	11.26±7.46	11.89±8.18	10.11±7.23	8.81±7.20	6.63±4.22	9.23±2.73
K+	0.69±0.59	0.96±1.09	0.94±0.72	0.61±0.50	0.70±0.63	0.76±0.79
Mg2+	0.05±0.04	0.07±0.07	0.06±0.05	0.09±0.06	0.09±0.08	0.03±0.03
Ca2+	0.42±0.35	0.46±0.55	0.70±0.92	0.56±0.48	1.14±1.33	0.26±0.29
PM2.5	79.55±39.89	77.11±37.91	78.82±35.49	54.35±35.35	53.34±19.37	62.26±23.02

Results and discussion

- Backward trajectory Cluster analysis

Table 4. Characteristics of source air mass in Summer

	Cluster1	Cluster2	Cluster3	Cluster4
Ratio	47.00%	26.10%	12.10%	14.80%
Cl-	0.52±1.18	0.10±0.29	0.40±0.81	1.18±2.12
NO3-	9.30±7.94	5.52±7.56	4.62±3.28	4.45±3.83
SO42-	14.84±6.15	12.30±5.21	9.26±5.99	12.36±6.12
C2O4-	0.69±0.23	0.71±0.33	0.60±0.15	0.53±0.18
Na+	0.12±0.12	0.07±0.07	0.11±0.10	0.25±0.18
NH4+	8.64±4.49	3.36±4.30	4.95±3.66	6.04±3.60
K+	0.58±0.52	0.39±0.27	0.43±0.61	0.68±1.15
Mg2+	0.02±0.04	0.01±0.03	0.03±0.03	0.04±0.07
Ca2+	0.17±0.23	0.11±0.21	0.16±0.35	0.08±0.11
PM2.5	50.63±22.31	43.63±17.83	31.68±14.15	38.06±13.42

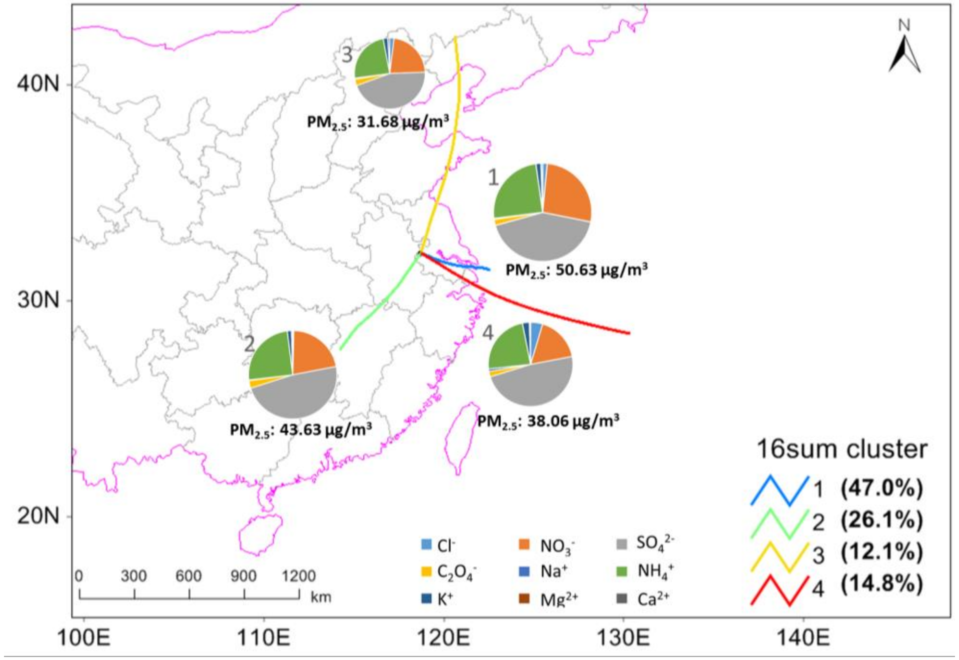


Fig 7. Backward trajectory Cluster analysis in Summer

Results and discussion

- Backward trajectory Cluster analysis

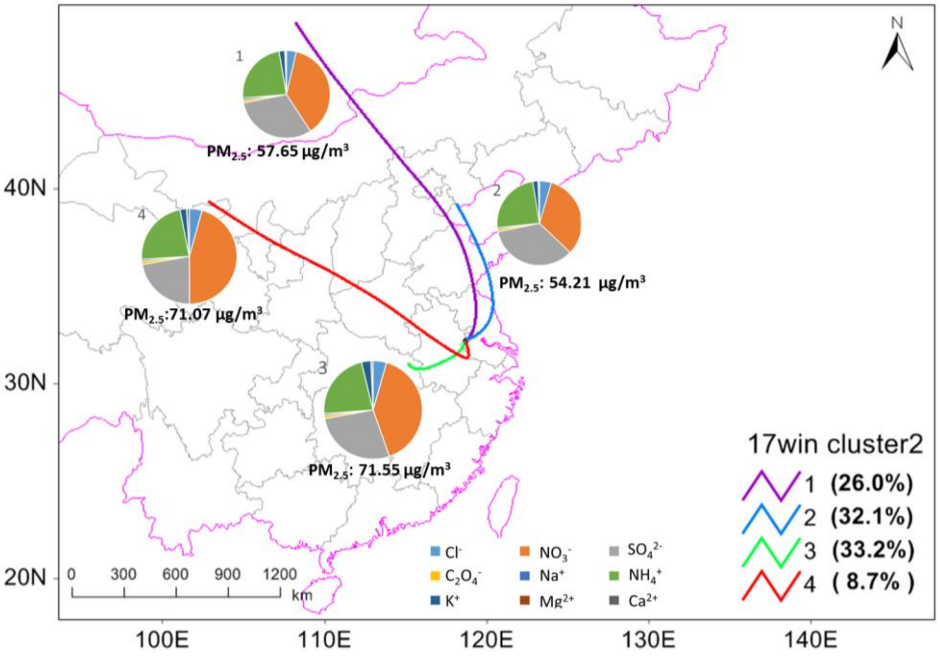


Fig 8. Backward trajectory Cluster analysis in Winter

Table 5. Characteristics of source air mass in Winter

	Cluster1	Cluster2	Cluster3	Cluster4
Ratio	21.10%	31.60%	18.40%	10.20%
Cl-	1.75±1.51	2.13±1.56	2.51±3.09	2.32±1.82
NO3-	17.97±14.51	15.35±9.40	22.98±10.82	24.49±11.35
SO42-	15.07±11.91	16.23±10.54	15.74±12.47	11.98±10.11
C2O4-	0.50±0.32	0.46±0.26	0.55±0.27	0.59±0.30
Na+	0.38±0.24	0.29±0.20	0.36±0.23	0.35±0.50
NH4+	11.41±8.7	11.36±6.14	12.79±5.34	12.26±7.20
K+	1.02±0.76	0.96±0.73	1.77±2.08	1.20±0.50
Mg2+	0.09±0.08	0.07±0.07	0.09±0.1	0.08±0.06
Ca2+	0.02±0.19	0.17±0.16	0.32±0.36	0.41±0.48
PM2.5	57.65±35.84	54.21±21.80	71.55±23.88	71.07±35.35

Results and discussion

- Acidity of particles

$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39.1} + \frac{2 \cdot Mg^{2+}}{243} + \frac{2 \cdot Ca^{2+}}{40}$$

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

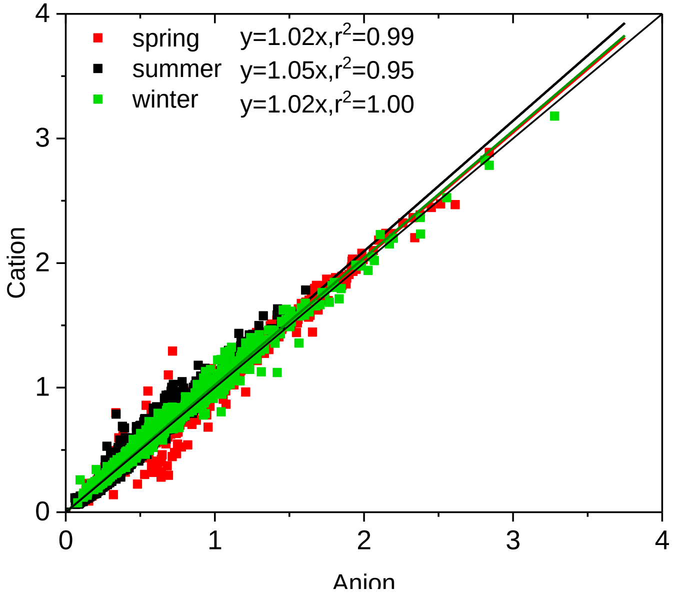


Fig 9. Backward trajectory Cluster analysis in Winter

Results and discussion

- Backward trajectory Cluster analysis

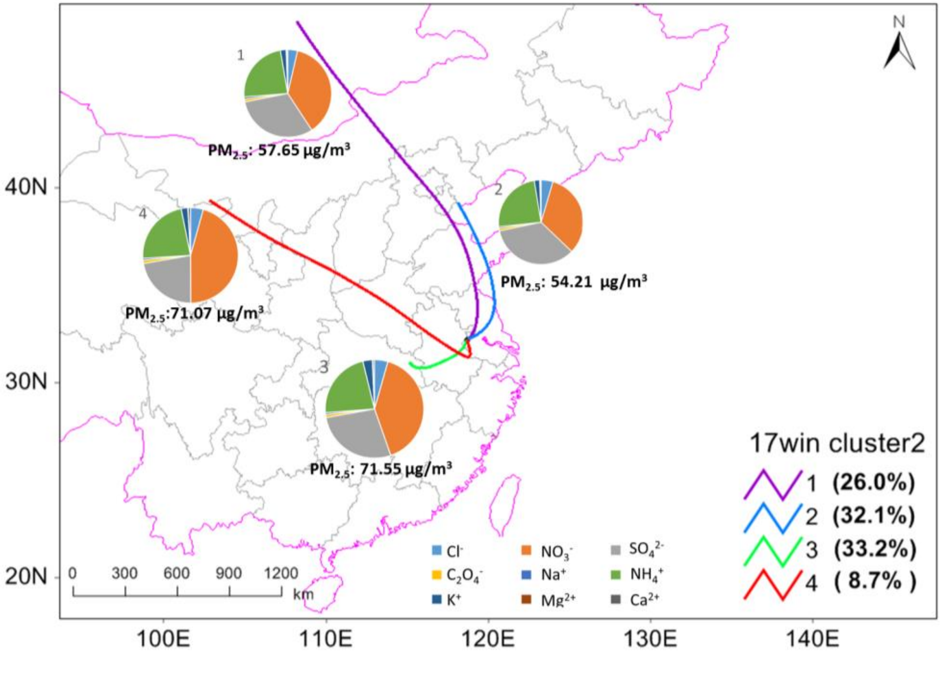


Fig 10. Backward trajectory Cluster analysis in Winter

Table 5. Characteristics of source air mass in Winter

	Cluster1	Cluster2	Cluster3	Cluster4
Ratio	21.10%	31.60%	18.40%	10.20%
Cl-	1.75±1.51	2.13±1.56	2.51±3.09	2.32±1.82
NO3-	17.97±14.51	15.35±9.40	22.98±10.82	24.49±11.35
SO42-	15.07±11.91	16.23±10.54	15.74±12.47	11.98±10.11
C2O4-	0.50±0.32	0.46±0.26	0.55±0.27	0.59±0.30
Na+	0.38±0.24	0.29±0.20	0.36±0.23	0.35±0.50
NH4+	11.41±8.7	11.36±6.14	12.79±5.34	12.26±7.20
K+	1.02±0.76	0.96±0.73	1.77±2.08	1.20±0.50
Mg2+	0.09±0.08	0.07±0.07	0.09±0.1	0.08±0.06
Ca2+	0.02±0.19	0.17±0.16	0.32±0.36	0.41±0.48
PM2.5	57.65±35.84	54.21±21.80	71.55±23.88	71.07±35.35

Results and discussion

- Generation and Evolution of SO_4^{2-}

(1) Gas-phase oxidation reaction

$$SO_2+OH+M \rightarrow HOSO_2\cdot+M$$
$$HOSO_2\cdot+O_2 \rightarrow HO_2\cdot+SO_3$$
$$SO_3+H_2O+M \rightarrow H_2SO_4+M$$
$$H_2SO_4+NH_3 \rightarrow (NH_4)_2SO_4/NH_4HSO_4$$

(2) Liquid chemical reaction

$$SO_2+H_2O \rightarrow HSO_3^-+H^+$$
$$HSO_3^-+H_2O_2 \rightarrow SO_2OOH^-+H_2O$$
$$SO_2OOH^-+H^+ \rightarrow H_2SO_4$$
$$H_2SO_4+NH_3 \rightarrow (NH_4)_2SO_4/NH_4HSO_4$$

(3) The sulfur oxidation ratio (SOR): are available indicators used to quantitatively characterize the secondary transformation reactions of SO_2.(Yang Shi,2012)

$$SOR=n\text{-}[SO_4^{2-}]/n\text{-}[SO_4^{2-}+SO_2]$$

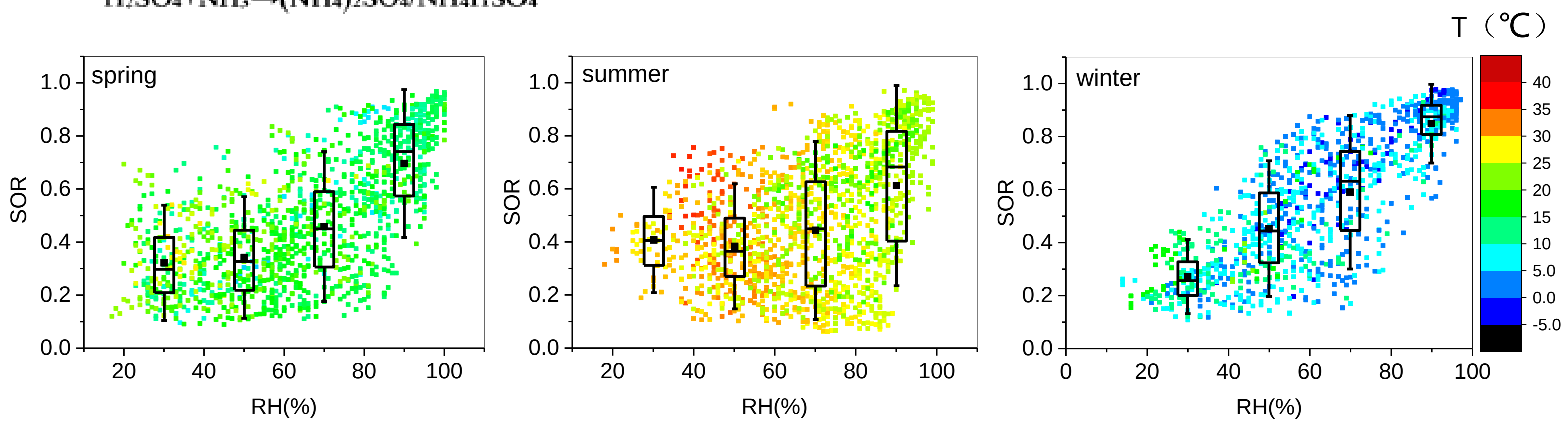


Fig 11. The relationship between SOR and RH/ T in each season

Results and discussion

- Generation and Evolution of SO_4^{2-}

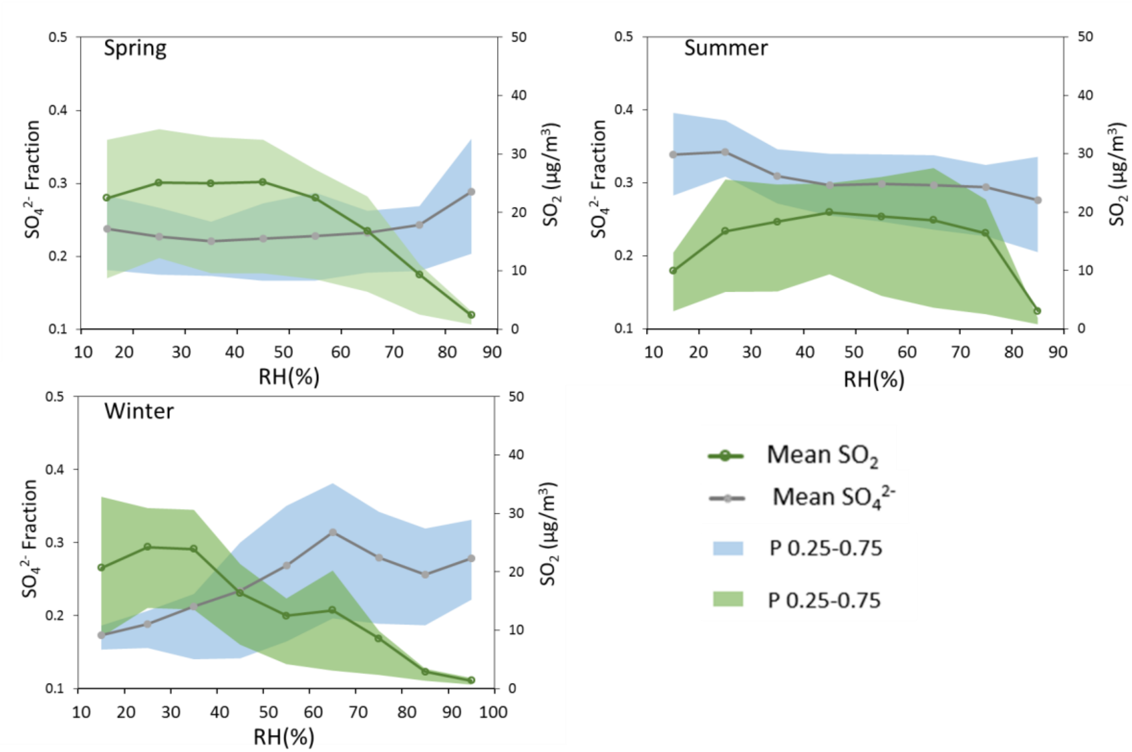


Fig 12. The relationship between fraction of SO_4^{2-} in $PM_{2.5}$, the concentration of SO_2 and RH

Results and discussion

- Effect of *T* and RH on NH4NO3 Gas-Particle Distribution

(1) Gas-phase oxidation reaction

Daytime：

$$RO_2 + NO \rightarrow RO + NO_2$$

$$O_3 + NO \rightarrow O_2 + NO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + OH \xrightarrow{M} HNO_3$$

Nighttime：

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

(2) Heterogeneous reaction：Mainly occurs at the sea salt surface

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

Results and discussion

- $[NO_3^-]/[SO_4^{2-}]$ / $[NH_4^+]/[SO_4^{2-}]$

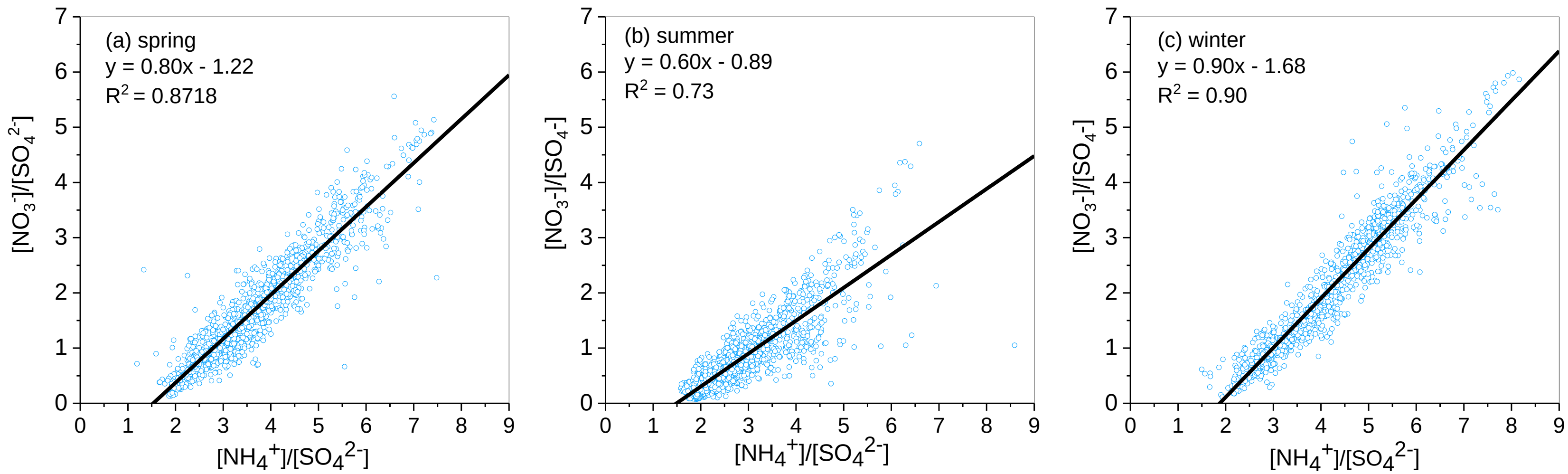


Fig 13. Relationship between $[NO_3^-]/[SO_4^{2-}]$ and $[NH_4^+]/[SO_4^{2-}]$

Total fitting result :Y=0.81x-1.37, R^2=0.88

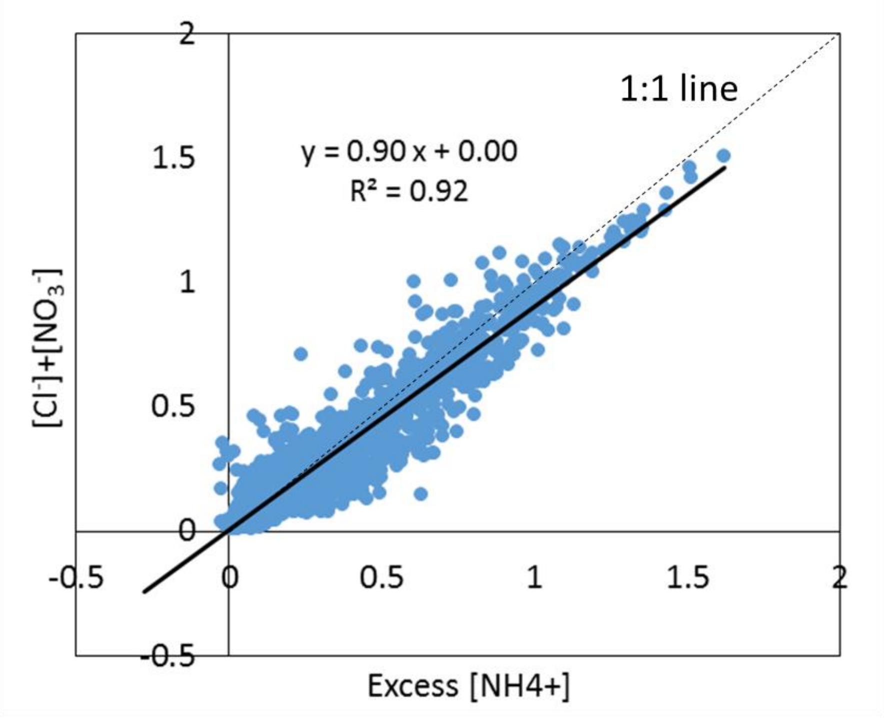
Assume $[NO_3^-]/[SO_4^{2-}] = 0$, $[NH_4^+]/[SO_4^{2-}]$= 1.69 as a critical value to determine a rich or poor NH_4^+ environment.

city	value	author
Guangzhou	1.50	X Huang,2011
Shanghai	1.61	Y Shi,2012
Beijing	1.66	K He,2012

Results and discussion

- Excess[NH_4^+]

$$Excess[NH_4^+]=([NH_4^+]/[SO_4^{2-}]-1.69)*[SO_4^{2-}]$$



city	slope	author
Chongqing	0.65	K He,2012
Shanghai	0.86	Y Shi,2012
Beijing	0.95	K He,2012

Fig 14. Relationship between [NO_3^-]/[Cl^-] and Excess [NH_4^+]

Results and discussion

- NH4NO3 Gas-Particle Distribution

The mass concentration ratios of $HNO_3/(HNO_3 + NO_3^-)$ and $HCl/(HCl + Cl^-)$ can be evaluated to understand phase partitioning of these semi-volatile species (Du et al., 2010; Mehlmann and Warneck,1995; Poschl et al., 2007). The higher $HNO_3/(HNO_3 + NO_3^-)$ and $HCl/(HCl + Cl^-)$ indicate that the semi-volatiles are more favored to exist as gas phase.

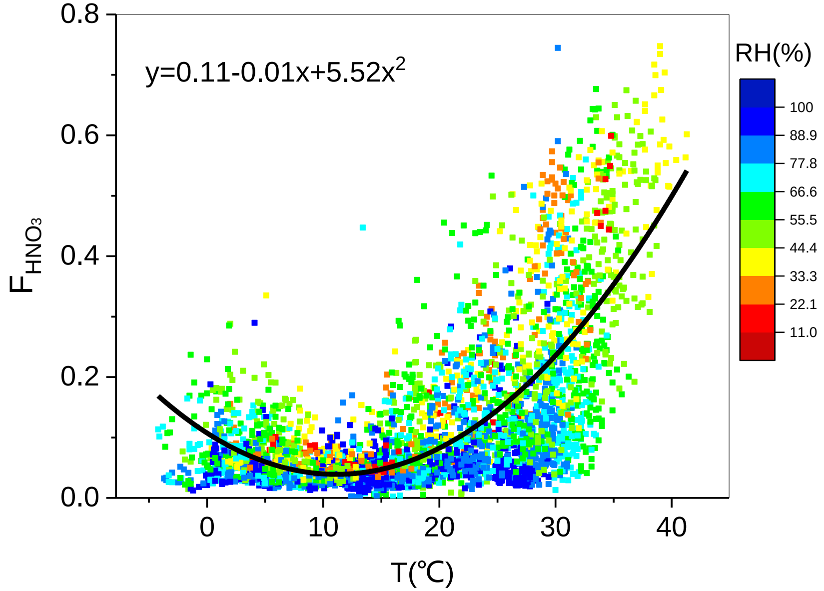


Fig 15. Relationship between F_{HNO3} and T,RH

Results and discussion

- Diurnal variations

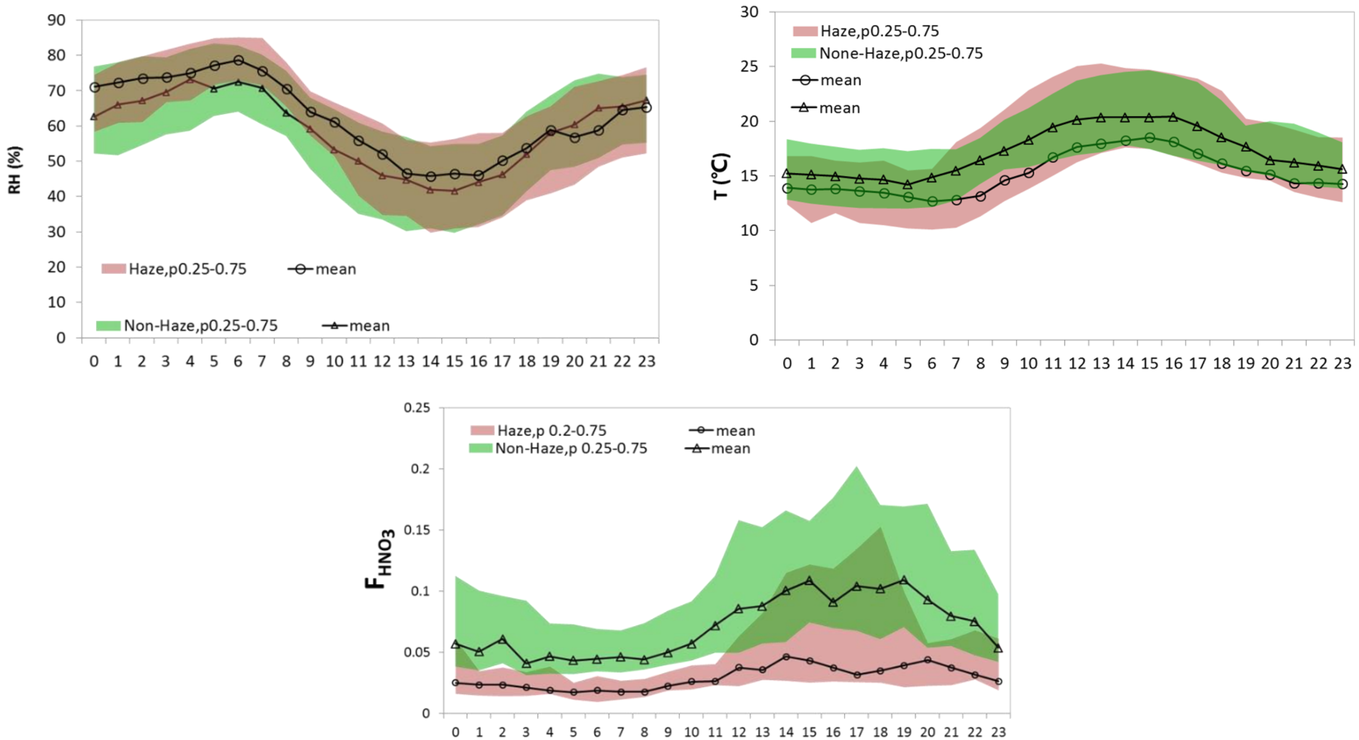


Fig 16. Diurnal variations of $F_{HNO3}$and T, RH in haze and non-haze day

Conclusions

- NH_4^+、SO_4^{2-}、NHO_3^- were the major ions accounting for 23.41%, 35.17% and 33.31% of TWSI, respectively.
- Seasonal variation of $PM_{2.5}$ mass loading was winter>spring>summer. TWSI was the main component in $PM_{2.5}$ in each season, with the average ranging from 64.12-81.96μg/m3, contribution of NO_3^- showed an increase trend with the ascending $PM_{2.5}$ mass concentration, exceeding that of SO_4^{2-} and become the major WSI in $PM_{2.5}$.
- SOR increased with elevated RH, indicating the important role of aqueous phase oxidation for SO_4^{2-} formation.
- NO_3-and Cl- mainly existed as NH_4NO_3 and NH4Cl in $PM_{2.5}$,wich are semi-volatile. High temperature also facilitated the particle to gas partitioning, especially when T >20℃， F_{HNO3} is rapidly increased.