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Simultaneous online monitoring of inorganic compounds in aerosols and gases during spring in Nanjing Northern Suburb

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2016.7.15

Outline

- Introduction
- Experimental
- Results and discussion
- Conclusions
- Future work

Introduction

- The most commonly used procedures for collecting aerosols are filter-based methods. Filter measurements may have become routine but because of their low accuracy it is not simple to quantify ambient aerosols.
- Furthermore, the atmospheric evaporation of semi-volatile aerosol species and the possible loss of some compounds due to surface reactions due to long time-scale sampling periods have been reported.
- An online analyzer for monitoring for aerosols and gases (MARGA) is one of the latest measurement systems for semi-continuous analysis of gases and soluble ions in aerosols.

Experimental

- MARGA Instrument

On-line Monitor for AeRosols and Gases in ambient Air (MARGA)

- Gases
  - NH_3
  - HNO_2
  - HNO_3
  - HCl
  - SO_2

- Aerosols
  - NH_4^+
  - Na^+
  - K^+
  - Ca^{2+}
  - Mg^{2+}
  - Cl^-
  - NO_3^-
  - SO_4^{2-}

- Time solution
  - 1hour

Experimental

- MARGA Instrument

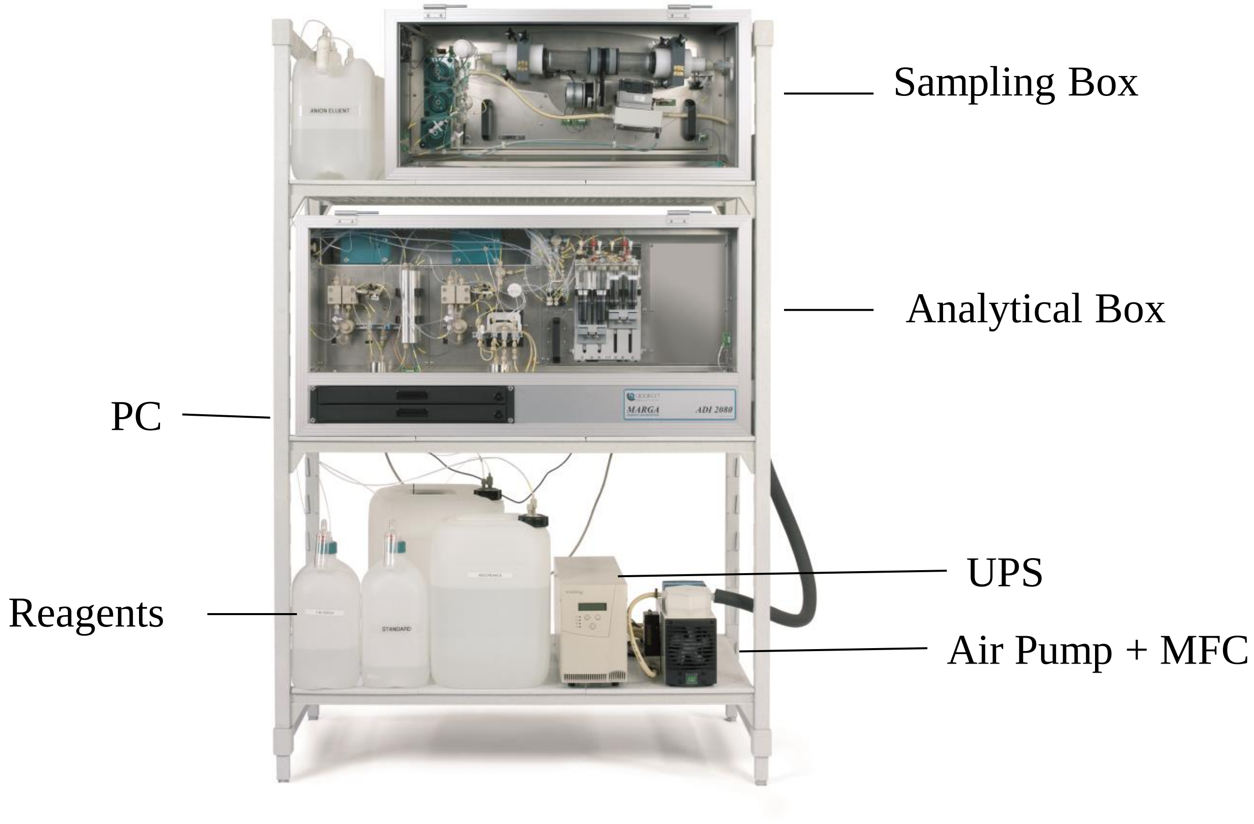

Fig.1 MARGA 1S

Experimental

- Gases

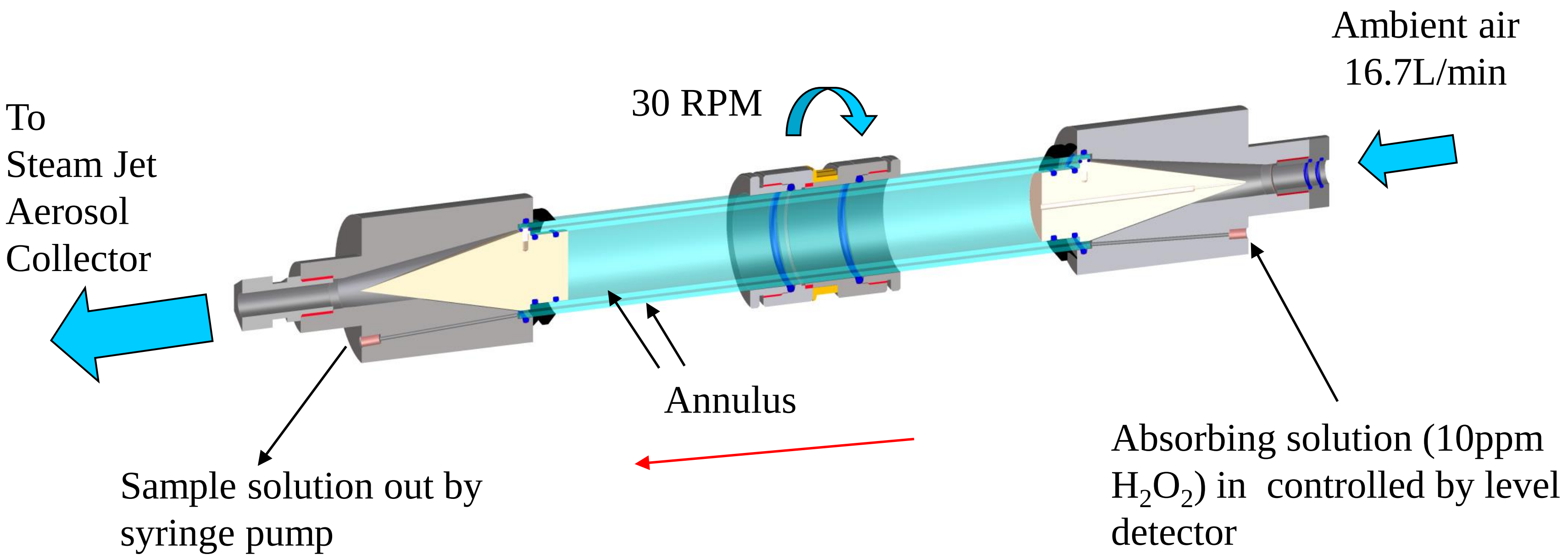

Fig. 2 Gases collector

Experimental

- Aerosols

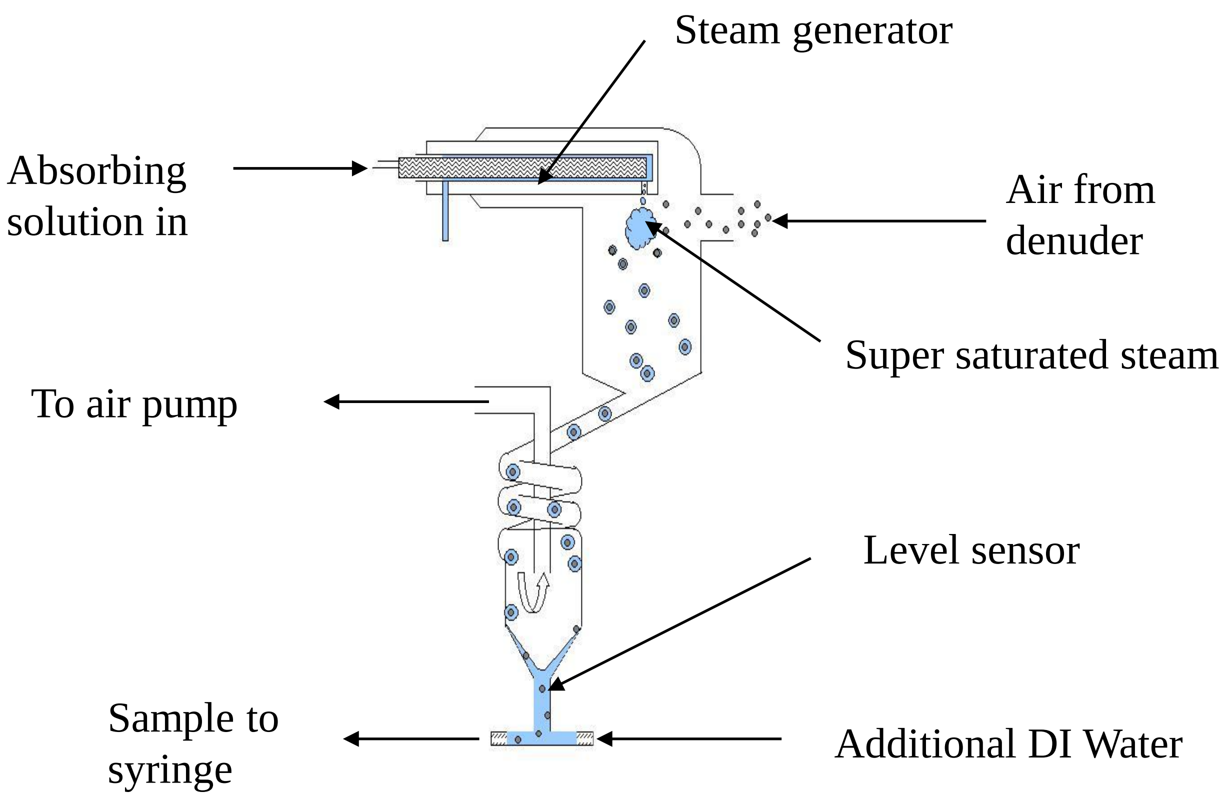

Fig.3 aerosol collector

Experimental

- Sampling time:2016.3.3-2016.5.16
- Sampling place: Meteorological observation field, NUIST
- Samples: $PM_{2.5}$

Table 1 Summary of data derived from instruments

Instruments	**Parameter**	**Data**
MARGA	Gases(NH_3、HNO_2、HNO_3、HCl、SO_2) Aerosols ions(NH_4^+、Na^+、K^+、Ca^{2+}、Mg^2、Cl^-、NO_3^-、SO_4^{2-})	Valid data :1168h Missing data :532h
THERMO	PM2.5	Valid data :2016.3.3-2016.4.19
ENVIS	Meteorological parameters	Valid data :2016.3.3-2016.5.16

Results and discussion

- Variation of PM2.5 chemical compositions

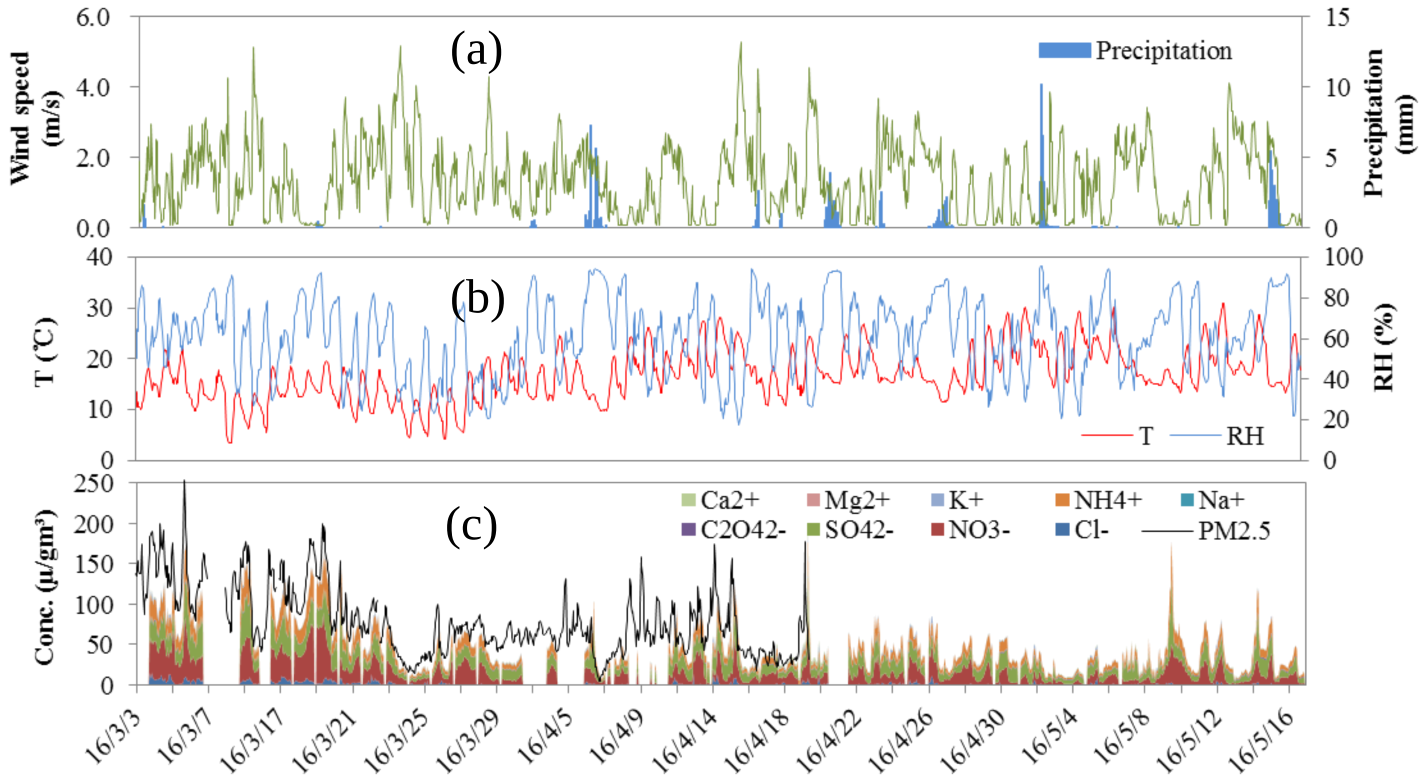

Fig. 4 Time series of (a) wind direction and precipitation (mm), (b) temperature (℃) and RH (%) (c) mass concentration (μg/m3) of PM2.5 and major water-soluble ions during the study period

Results and discussion

- Cation-Anion balance

Cation：

$\sum+ = Na^+/23 + 2 \cdot Mg^{2+}/24.3 +$

$2 \cdot Ca^{2+}/40 + NH4^+/18 + K^+/39.1$

Anion：

$\sum- = Cl^-/35.45 + 2 \cdot SO_4^{2-}/96 +$

$NO_3^-/62$

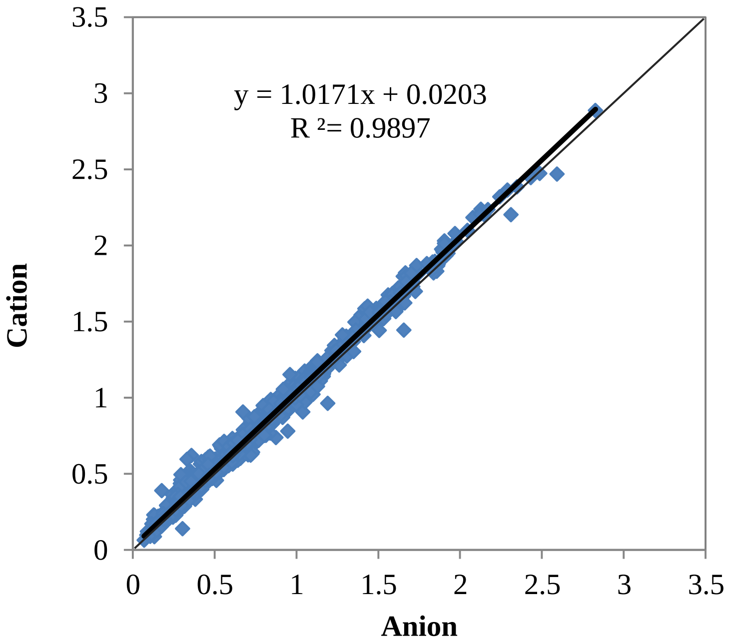

Fig.5 The relationship of cation and anion

Results and discussion

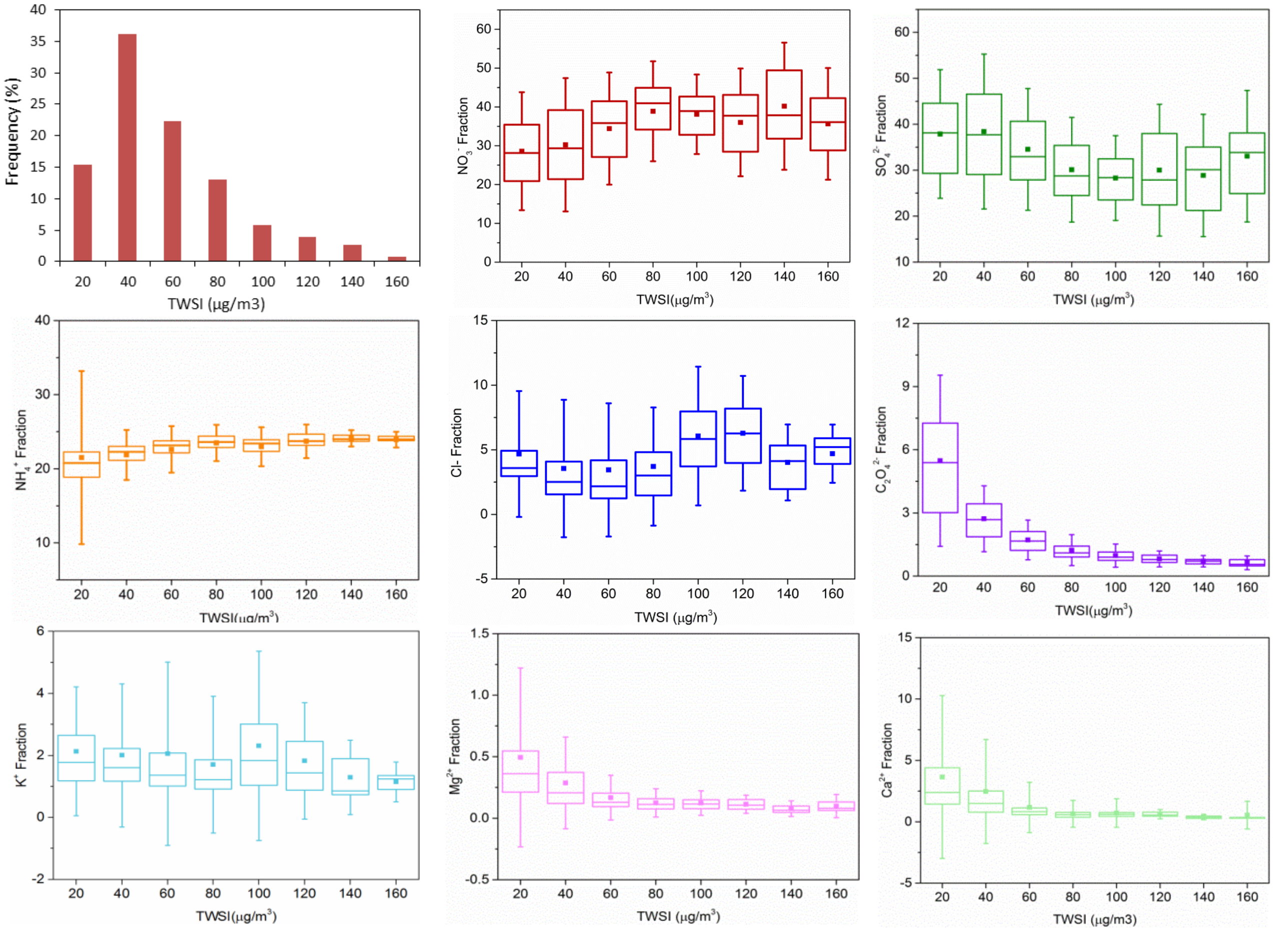

Fig.6 The variability of water-soluble ion fraction (%) and probability of total mass concentration (%)

Results and discussion

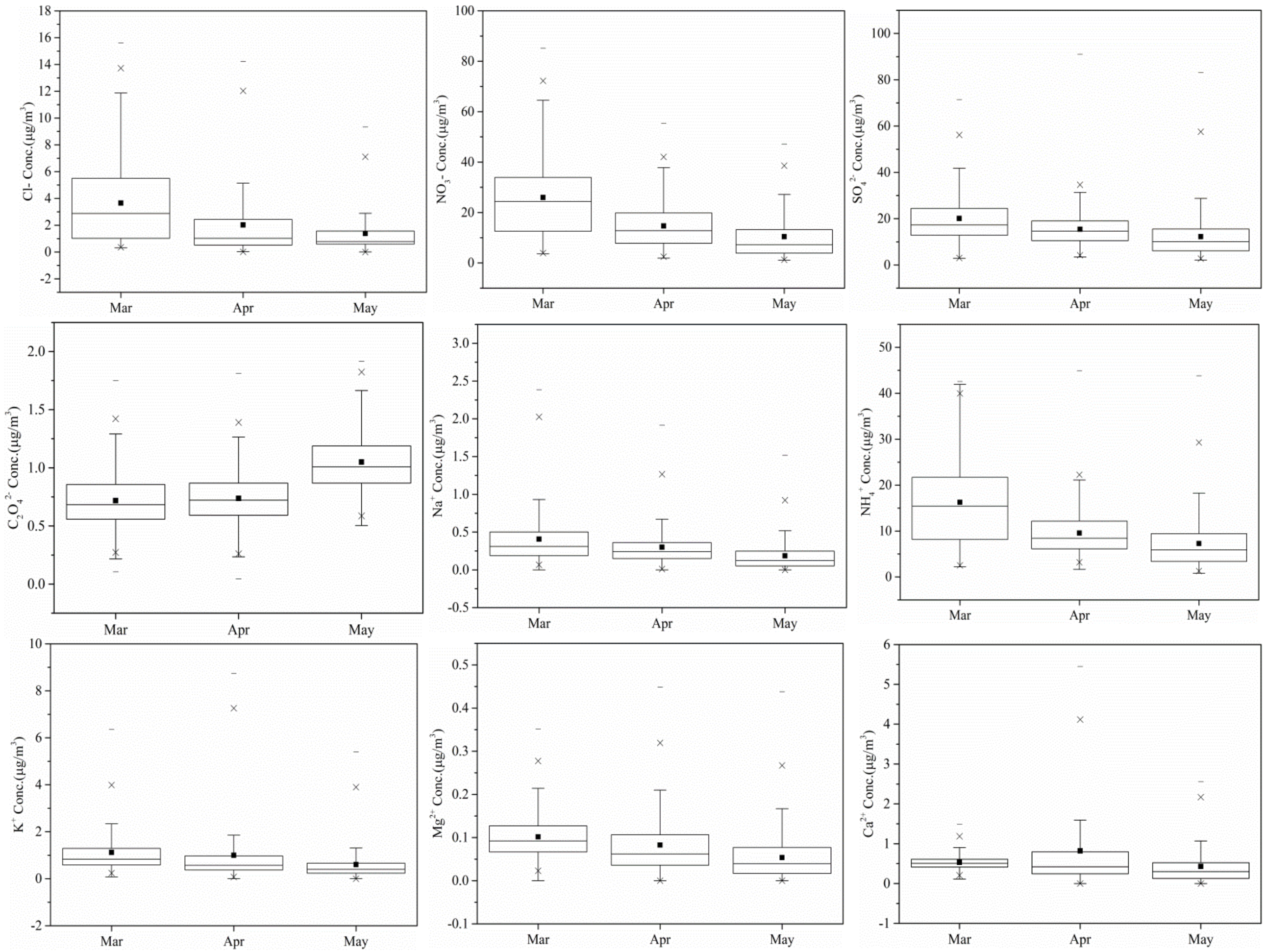

Fig.7 Box-and-whisker plots showing monthly variations of inorganic compounds during sampling period.

Results and discussion

- HNO_2 and HNO_3

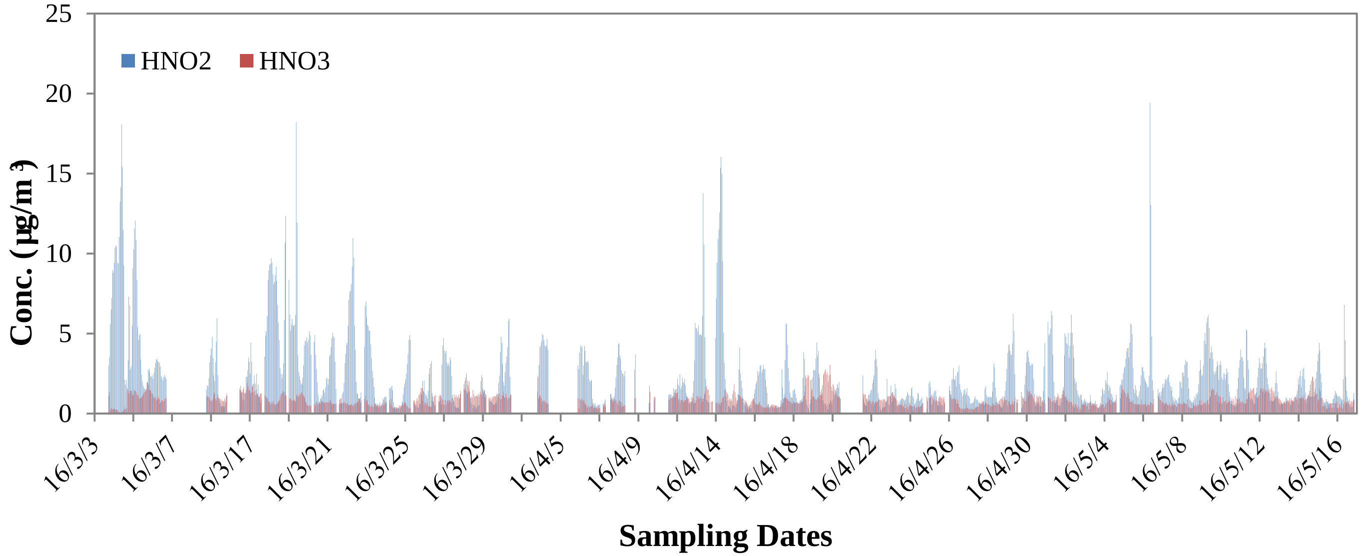

Fig.8 Gaseous HNO2 and HNO3 concentrations measured with MARGA during the whole sampling period (time resolution: 1 h)

Results and discussion

- Transformation of HNO_3

1、gas phase reaction：

$$NO_2(g) + OH(g) + M \rightleftharpoons HNO_3(g) + M$$

$$NO_2 + O_3 \rightleftharpoons NO_3 + O_2$$

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M$$

2、heterogeneous conversion：

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3$$

$$RH/RCO + NO_3 \rightleftharpoons HNO_3 + (R/RCO)$$

Results and discussion

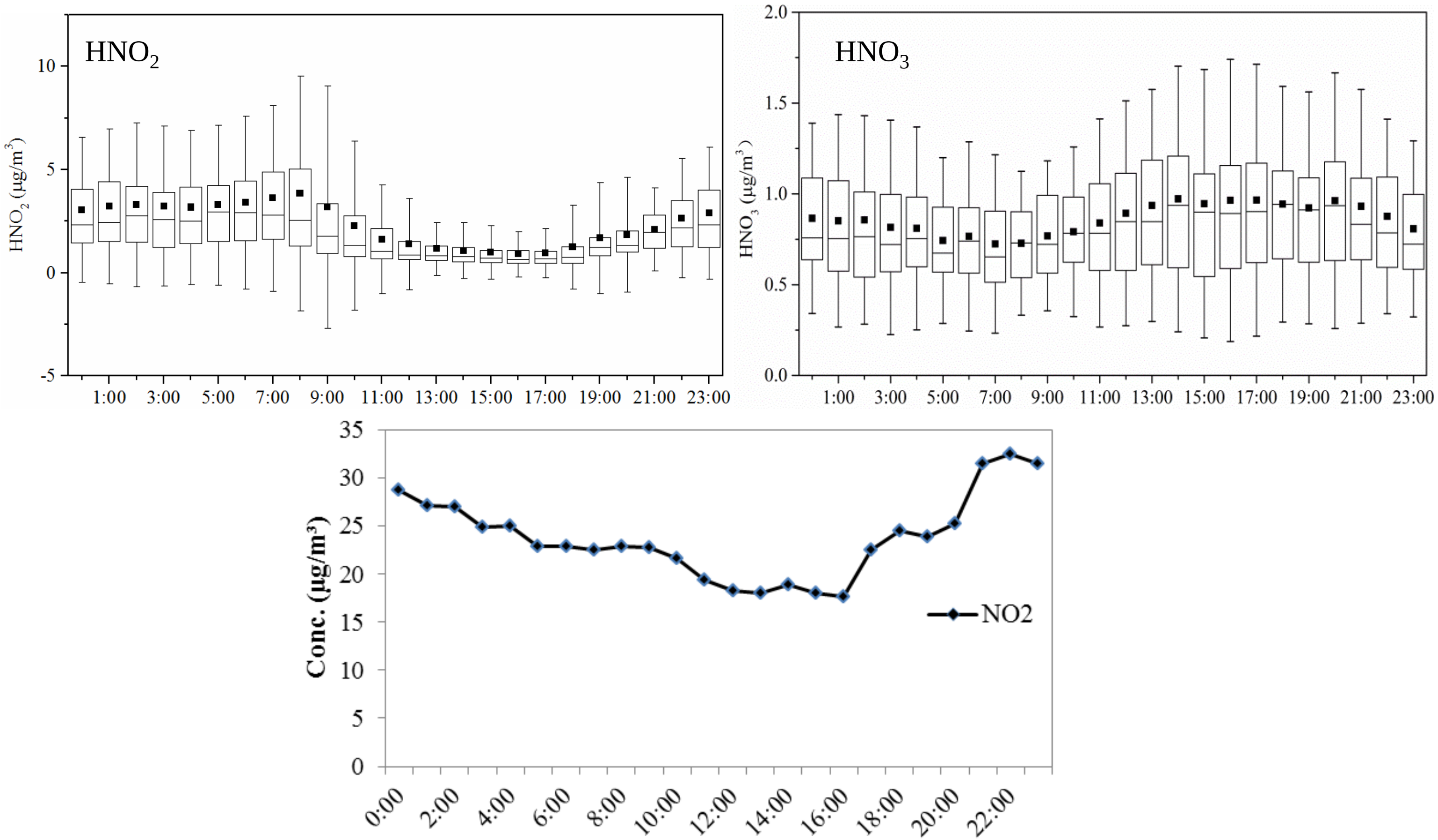

Fig.9 Diurnal variation of Gaseous HNO_2 , HNO_3 and NO_2 concentrations

Results and discussion

- SO_2

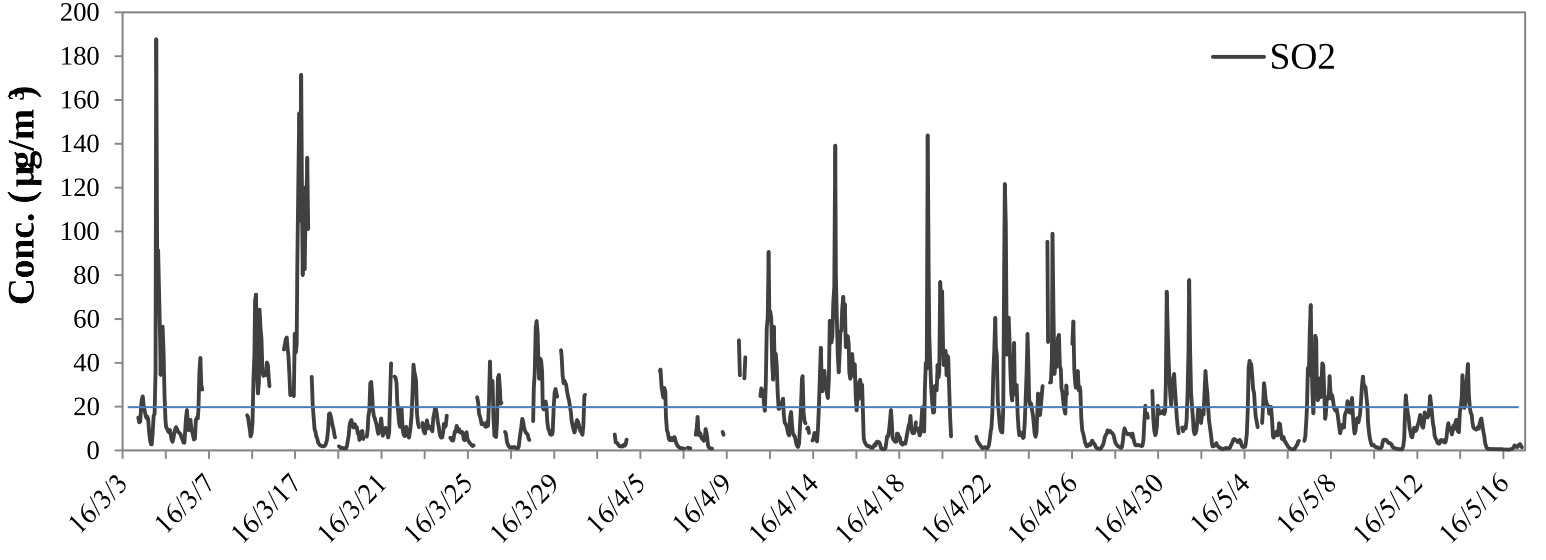

Fig. 10 Time series of mass concentration (μg/m3) of SO_2

Results and discussion

- SO_2

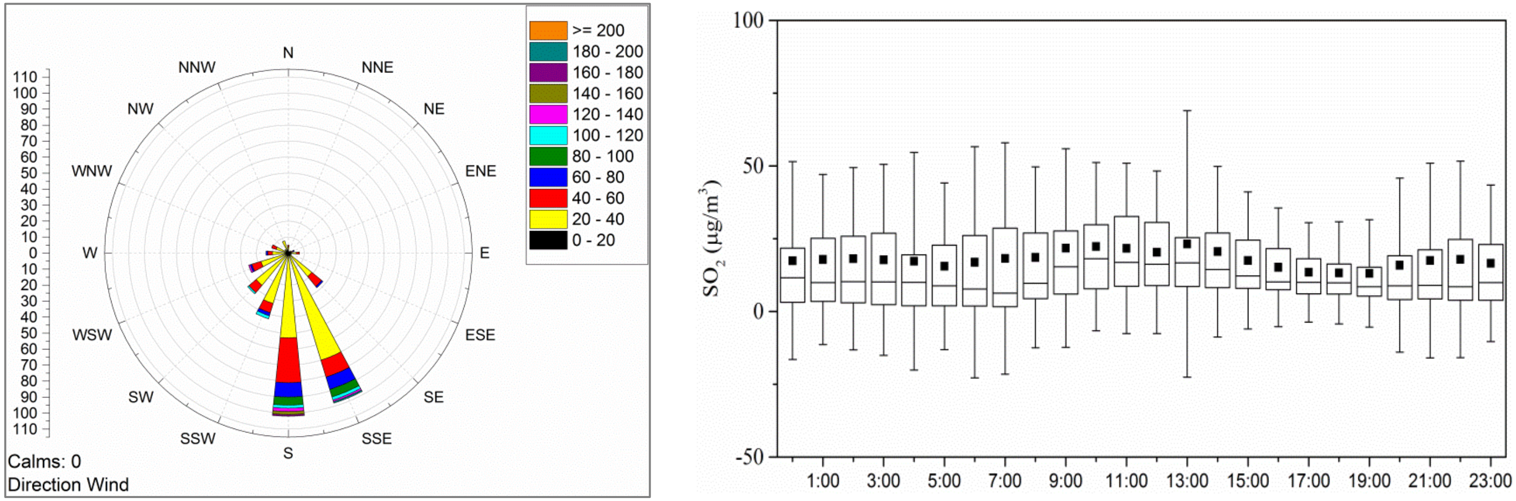

Fig.11 wind rose diagram and diurnal variation of mass concentration (μg/m3) of SO_2

Results and discussion

- Secondary components

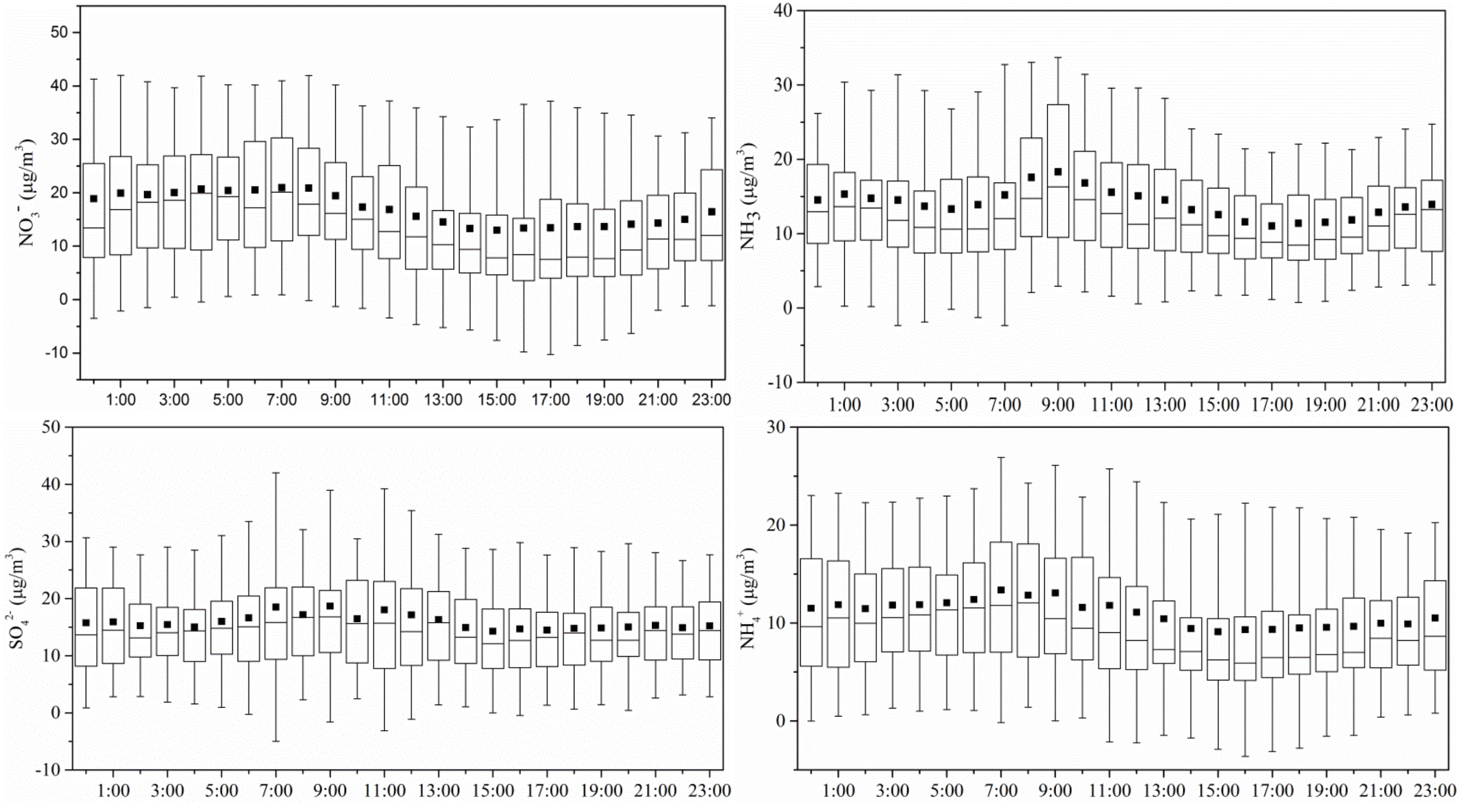

Fig.12 Diurnal variation of Gaseous NH_3 and secondary ions

Results and discussion

- Oxalate

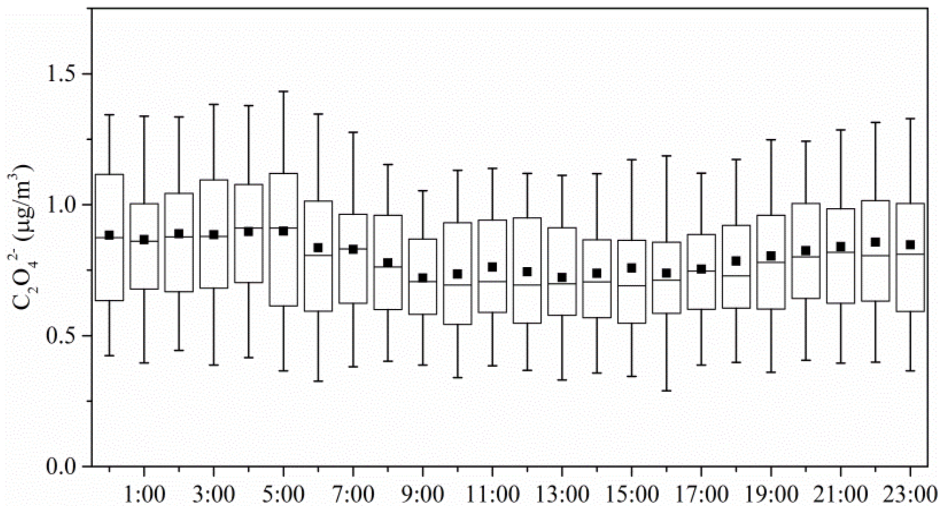

Fig.13 Diurnal variation of $C_2O_4^{2-}$ concentration

Results and discussion

- Other inorganic compounds

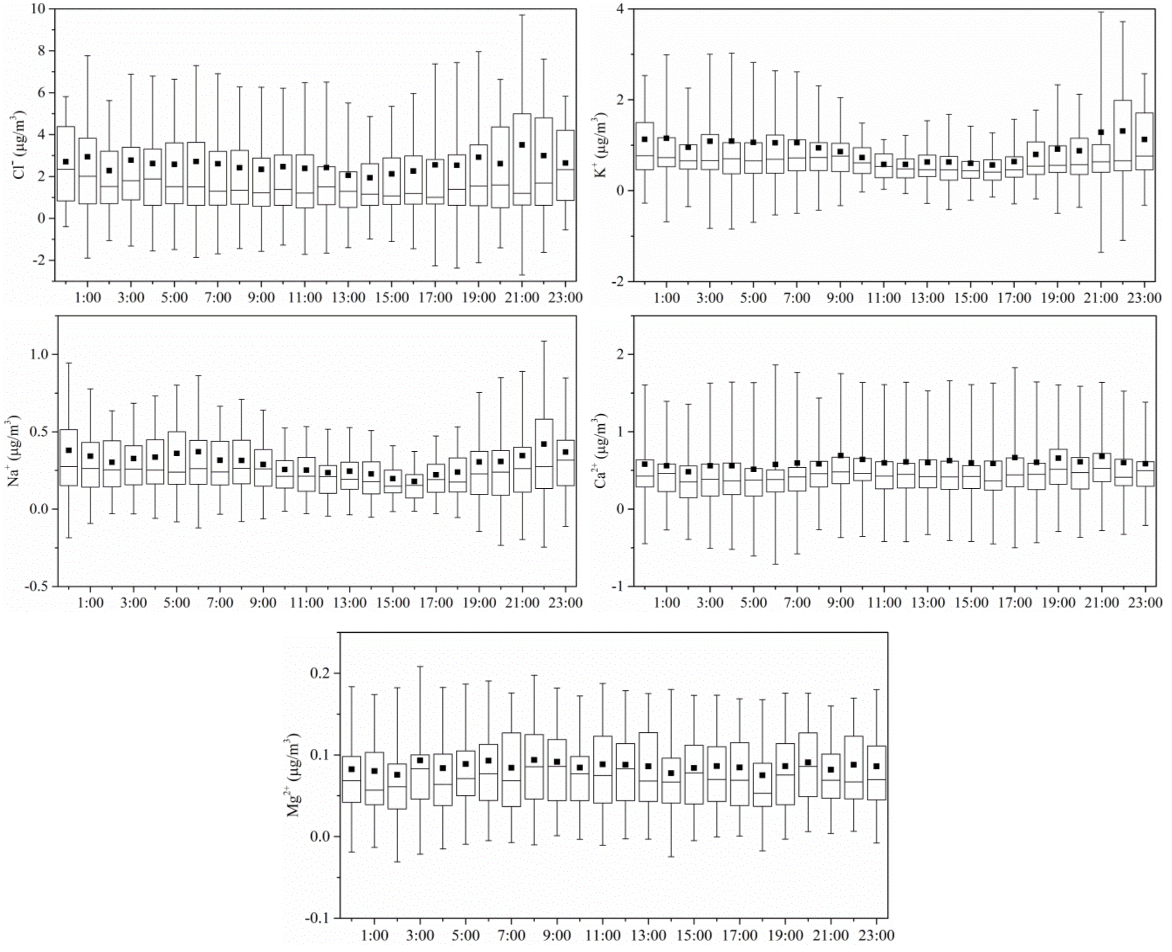

Fig.14 Diurnal variation of the mass concentration of Other inorganic compounds

Results and discussion

- SOR and NOR

The sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) are available indicators used to quantitatively characterize the secondary transformation reactions of SO_2 and HNO_3.

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

$$NOR = [NO_3^-]/[NO_3^- + HNO_3]$$

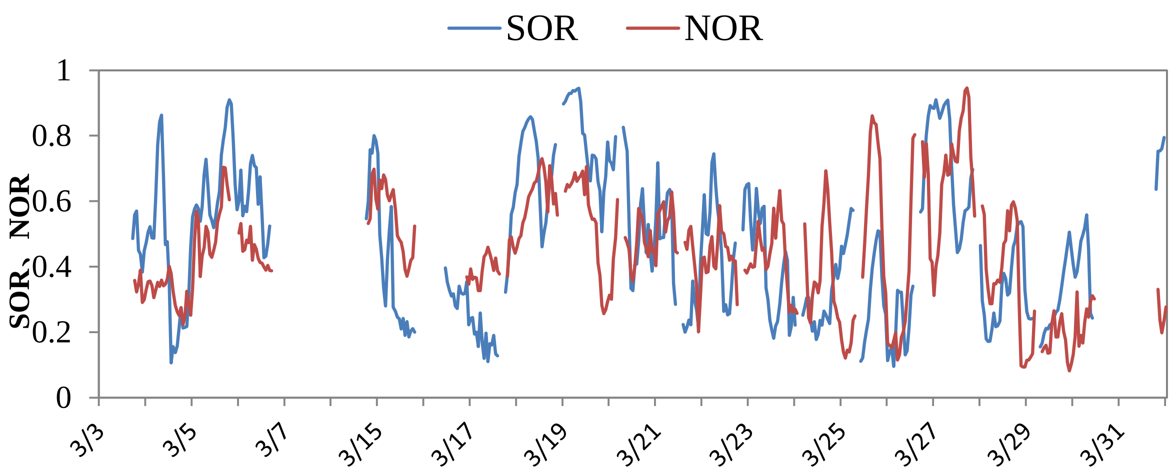

Fig. 15 Time series of mass concentration (μg/m3) of SO_2

Table 2 information of the SOC during the sampling period

	Mar	Apr	May
Mean	0.47	0.44	0.50
Min	0.10	0.09	0.09
MAX	0.94	0.92	0.97
Ratio(>0.1)	0.99	0.99	0.97

Results and discussion

- Acidity of aerosols

The neutralization ratios (NR) were calculated in order to estimate the acidity of atmospheric aerosols. A ratio value of 1.0 would indicate neutralization of HNO_3 and H_2SO_4 by atmospheric NH_3, while NR <1.0 imply the likely presence of acidic aerosols.

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

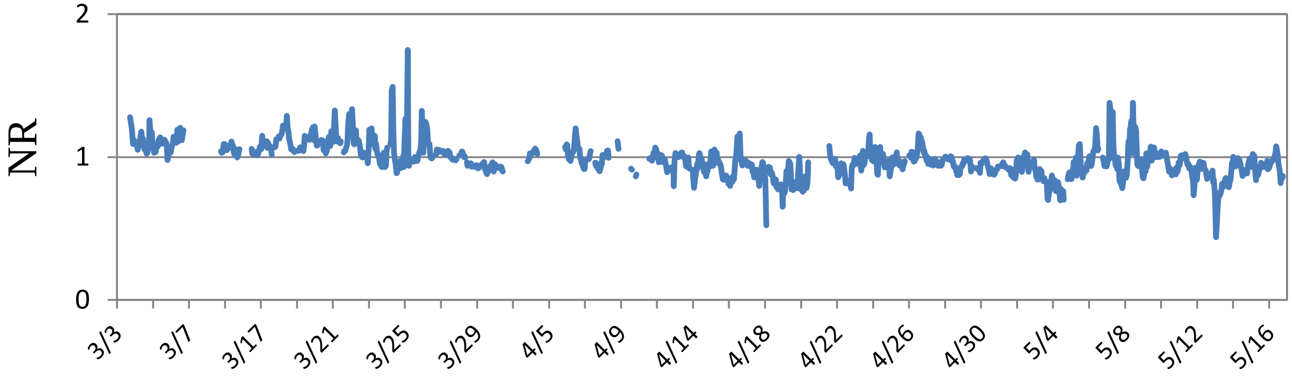

Fig. 16 Time series of NR during the sampling period

Results and discussion

Table 3 Pearson correlation coefficients between major ions during whole field campaign

	Cl^-	NO^{3-}	SO_4^{2-}	$C_2O_4^{2-}$	Na^+	$NH4^+$	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1	.516**	.615**	.345**	.517**	.688**	.781**	.276**	.417**
NO_3^-		1	.584**	.583**	.242**	.885**	.395**	.169**	.249**
SO_4^{2-}			1	.348**	.269**	.884**	.436**	.240**	.242**
$C2O_4^{2-}$				1	.254**	.513**	.463**	.223**	.343**
Na^+					1	.294**	.561**	.239**	.397**
NH_4^+						1	.484**	.237**	.279**
K^+							1	.231**	.489**
Mg_2^+								1	.339**
Ca_2^+									1

*p=0.05;**p=0.01

Wet deposition

Table 4 Variation of the mass concentration(μg/m³)of ions during the whole rainfall events

Date	Duration (h)	precipitation（mm）	event	Cl-	NO3-	SO_4^{2-}	$C_2O_4^{2-}$	Na^+	NH_4^+	K+	Mg^{2+}	Ca^{2+}
5.4	27	30.9	before	1.87	19.15	9.35	0.44	0.33	9.64	0.87	0.07	0.48
			during	1.69	10.42	15.02	0.33	0.28	9.03	0.50	0.03	0.20
			after	0.37	10.97	7.52	0.37	0.06	5.98	0.26	0.05	0.17
			Deposition rate（%）	80.28	42.71	19.57	15.95	80.95	37.89	70.53	36.99	63.75
4.26	35	12.9	before	5.38	33.19	15.91	0.84	0.55	15.79	3.59	0.05	0.28
			during	1.45	12.45	10.45	0.67	0.20	7.66	0.45	0.02	0.15
			after	0.05	15.38	8.39	0.71	0.13	7.24	0.53	0.04	0.15
			Deposition rate（%）	99.14	53.65	47.25	15.91	76.07	54.15	85.33	9.42	46.06
5.2	17	31.2	before	1.74	6.93	11.92	0.89	0.20	6.15	0.80	0.04	0.47
			during	0.29	4.33	6.41	0.70	0.06	3.50	0.32	0.02	0.26
			after	0.29	3.55	4.25	0.91	0.08	2.25	0.18	0.03	0.41
			Deposition rate（%）	83.38	48.69	64.37	-1.75	61.54	63.47	77.26	26.76	11.54
5.15	19	35	before	0.69	22.90	19.93	1.56	0.14	14.15	0.62	0.04	0.06
			during	0.51	7.47	6.20	1.06	0.03	4.19	0.19	0.02	0.04
			after	0. 62	12.20	6.85	1.14	0.02	5.71	0.23	0.02	0.14
			Deposition rate（%）	9.81	46.74	65.63	27.16	85.65	59.65	62.27	55.56	-109.63

Conclusions

- Data analysis showed an average trend of SO_4^{2-}>NO_3^->NH_4^+> Cl^- > K^+ > Na^+ > Ca^{2+}> Mg^{2+} for aerosol species and SO_2 > NH_3 > HNO_2 > HNO_3 > HCl for gases.

- The trend of HNO_2 shows surprisingly significantly higher concentration values compared to HNO_3, lower concentrations of HNO_2 during the day which rises to higher levels during the night.

- Monthly variations of ions concentration are analyzed, that the concentrations of most ions are higher in March and lower in April and May, except for Ca^{2+} and $c_2o_4^{2-}$.

Conclusions

- High SO_2 concentrations and high SOR and NOR values directly resulted in a large amount of secondary sulfate and nitrate particles in the atmosphere at the Nanjing sampling site. However, localized meteorological conditions must also play a main role in the formation processes of these secondary particulate pollutants.

- Most of the time, the aerosols are acidic, this would suggest that all particulate ammonium is of the form ammonium sulfate and bisulfate.

Future work

- Do further analysis on the effect of meteorological elements on inorganic components in aerosols and gases .

- More detailed analysis of gas-particle conversion processes

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Thank you