耶鲁大学-南京信息工程大学大气环境中心
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Discussion on: Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China

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Atmospheric Chemistry and Physics

Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China

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Outline

- Introduction
- Methods
- Results and Discussion
- Conclusions

➢ Introduction

- Global atmospheric emissions of nitrogen oxides (NOx, the sum of NO and NO2) have increased dramatically during the past 150 years.

- Once emitted to the atmosphere, NO_x is oxidized via several pathways to form highly soluble nitric acid (HNO_3).

- The N stable isotopic composition of atmospheric deposition has often been viewed as reflecting NO_x source.

- $\delta^{18}O$ of atmospheric is considered to be mostly related to oxidation pathways in the atmosphere.

➢ Introduction

- $\delta^{18}O$ of atmospheric NO_3^- is consideredto be mostly related to oxidation pathways in the atmosphere.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R1)}$$

$$NO_2 + h\nu \rightarrow NO + O \quad \text{(R2)}$$

$$NO_2 + OH \rightarrow HNO_3 \quad \text{(R3)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R4)}$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \quad \text{(R5)}$$

$$N_2O_5 + H_2O_{(surface)} \rightarrow HNO_3 \quad \text{(R6)}$$

➢ Methods

- Sampling

location： South China Botanical Garden of Guangzhou City

Period： Form 2008 to 2009

Samplers:For the 113 precipitation samples was collected with an open funnel (23 cm in diameter) that was connected to a 5 L sampling bottle with a black polypropylene tube.

➢ Methods

- Water soluble inorganic ions(WSII):IC

- Iostopic:IRMS coupled with a gas chromatograph equipped with a PoraPLOT column (25m×0.32 mm) and GC interfaceIII.

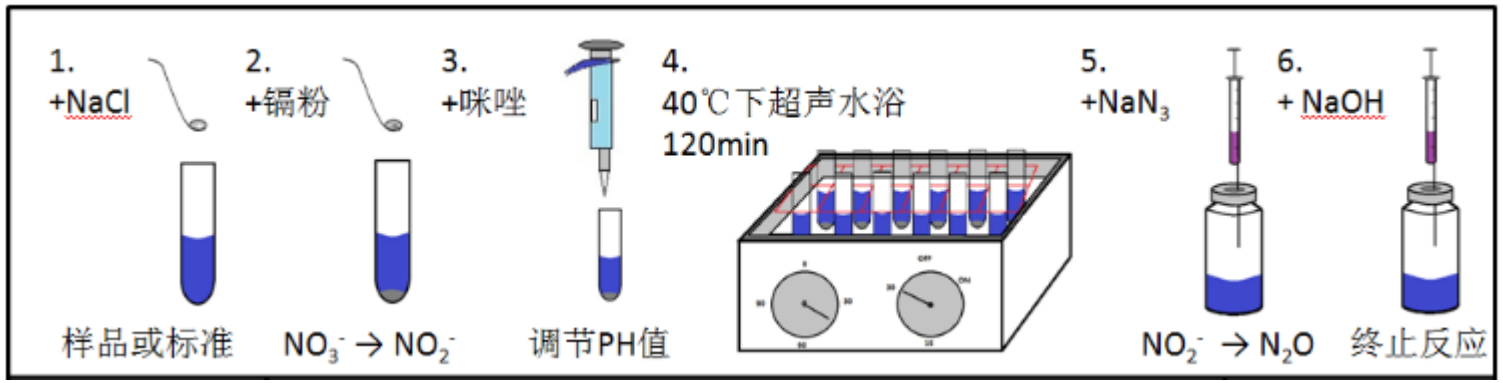
- Backward trajectories:HYSPLIT(72-hour,altitude of 500ma.g.l)

- Calculations and statistical analysis:Arithmetic and volume-weighted means , NO_3^- -flux-weighted mean ,Statistically significant differences were set at P＜0.05.

➢ Methods

- The denitrifying bacterium, Pseudomonas aureofaciens, was used to convert 25 nmol of NO_3^- into gaseous N_2O in 20mL vials prior to isotope analysis.

- In our lab.



➢ Results and Discussion

- Precipitation NO_3^- input

1. NO_3^- concentration ranged : 6 ~256 μmol L^{-1}

	Range	NO_3^- con. (μmol L^{-1}) Mean[a]	Mean[b]	Range	δ^{15}N-NO_3^- (‰) Mean[a]	Mean[b]	Mean[c]
2008	6 to 406	63	53	−3.9 to +7.9	+3.9	+3.7	+4.2
2009	9 to 256	77	68	−4.9 to +10.1	+3.3	+3.0	+3.5

[a] arithmetic mean.
[b] volume-weighted mean.
[c] NO_3^--flux-weighted mean.

Table.1.Ranges of NO_3^- con.

2.Isotope results were not anomalous

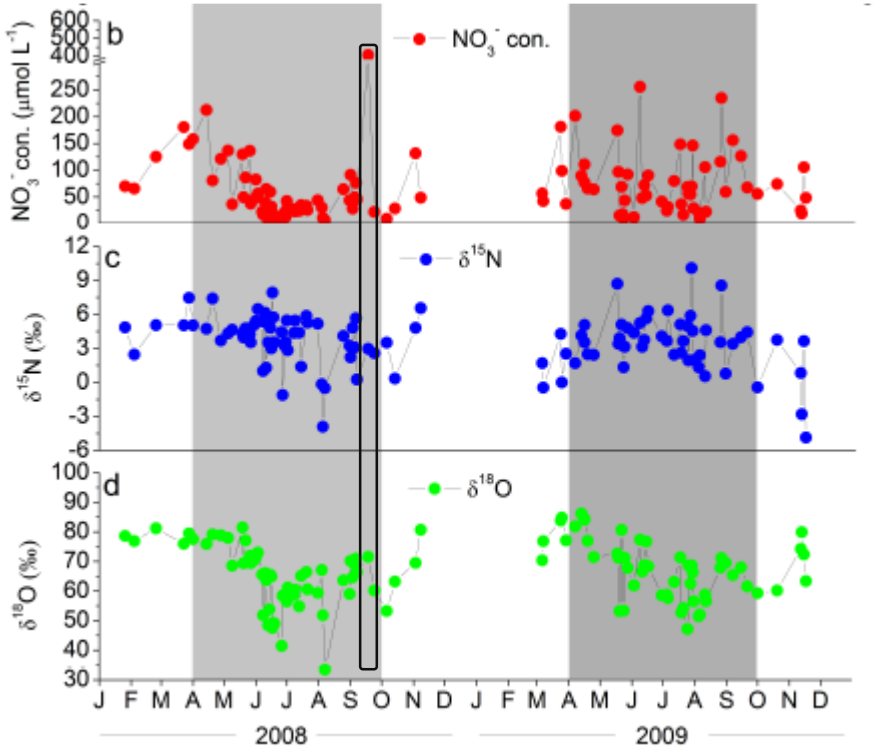


Fig.1. values of $\delta^{15}N$,$\delta^{18}O$ and NO_3^- con.

➢ Results and Discussion

- Precipitation NO_3^- input

3.Mean NO_3^- concentration was higher during the cool season than warm season in 2008, but the reverse was true in 2009 .

4.The annual NO_3^- input in precipitation : 16.0 and 18.5kg N ha^{-1} . 74% and 80% falling in the warm season.

Year	Season	*n*	Precipitation (mm)	NO_3^- input (kg N ha^{-1} a^{-1})	NO_3^- con. (μmol L^{-1})	$\delta^{15}N\text{-}NO_3^-$ (‰)
2008	Cool	9	491	4.1	89.9 (9 to 181, 19.6)	+4.5 (+0.3 to +7.5, 0.7)
	Warm	50	1670	11.9	57.7 (6 to 406, 9.4)	+3.8 (−3.9 to +7.9, 0.3)
	P value				0.18	0.41
2009	Cool	11	411	3.7	67.6 (19 to 181, 14.5)	+0.7 (−4.9 to +4.3, 0.9)
	Warm	43	1520	14.8	78.8 (10 to 256, 9.1)	+4.1 (+0.5 to +10.1, 0.3)
	P value				0.57	<0.001

Table.2.Seasonal comparison of NO_3^- con.and NO_3^- input

➢ Results and Discussion

- Nitrogen deposition
- The total inorganic N input:30.9 (2008)and 40.3 kg (2009)N ha^{-1} a^{-1}

- Compared with the small measured N deposition of 1.8–3.2 kg N $ha^{-1}a^{-1}$ in some remote areas in China and 0.9 kg$Nha^{-1}a^{-1}$ in Hawaii.

- Such high bulk N deposition is mainly caused by increased human activities associated with industrialization and urbanization.

➢ Results and Discussion

N isotopes of NO_3^-

1. $\delta^{15}N$ over the study period varied between −4.9‰ and +10.1‰.

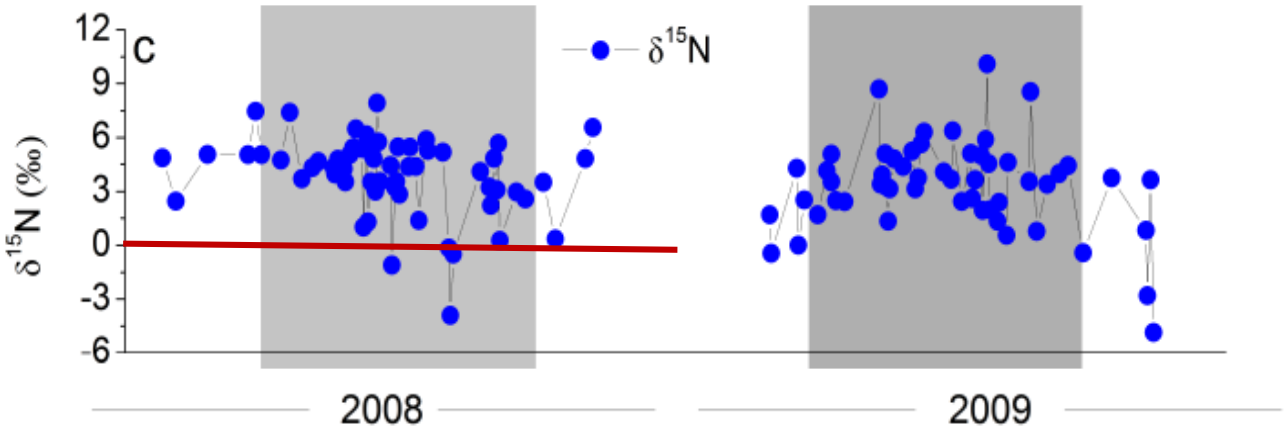


Fig.2. Ranges of $\delta^{15}N$ values

2.Positive $\delta^{15}N$ values were observed in 2008, but some negative values or near zero values were observed in the summer .

3. Annual mean values: +3.9‰(2008)and +3.3‰ (2009).

	$\delta^{15}N$-NO_3^- (‰)			
	Range	Mean[a]	Mean[b]	Mean[c]
2008	−3.9 to +7.9	+3.9	+3.7	+4.2
2009	-4.9 to +10.1	+3.3	+3.0	+3.5

Table.3 Annual mean of $\delta^{15}N$ - NO_3^-

➢ Results and Discussion

- N isotopes of NO_3^-

4.The seasonal difference between the warm and cool seasons was not significant in 2008 . In 2009, $\delta^{15}N$ of NO_3^- in the warm season was higher than that in the cool season.

5.There was also no significant difference in $\delta^{15}N$ values between continental and marine sources.

Year	Season	*n*	I	δ^{15}N-NO_3^- (‰)
2008	Cool	9		+4.5 (+0.3 to +7.5, 0.7)
	Warm	50		+3.8 (−3.9 to +7.9, 0.3)
	P value			0.41
2009	Cool	11		+0.7 (−4.9 to +4.3, 0.9)
	Warm	43		+4.1 (+0.5 to +10.1, 0.3)
	P value			<0.001

Table.4 Seasonal comparison of concentration $\delta^{15}N$

Year	Season	*n*	P1	δ^{15}N-NO_3^- (‰)
2008	Continental	21		+3.4 (-3.9 to +7.4, 0.6)
	Marine	38		+4.2 (−1.1 to +7.9, 0.3)
	*P*value			0.22
2009	Continental	19		+1.9 (−4.9 to +8.7, 0.7)
	Marine	35		+4.1 (+1.1 to +10.1, 0.3)
	P value			0.002

Table.5. Sources comparison of concentration $\delta^{15}N$

➢ Results and Discussion

- Seasonal pattern of N isotopes of NO_3^-

- Seasonality has been commonly reported for isotopic composition of atmospheric,The seasonal pattern of $\delta^{15}N$ seems to vary from site to site.

- In the present study, $\delta^{15}N$- NO_3^- was correlated with temperature only in 2009.

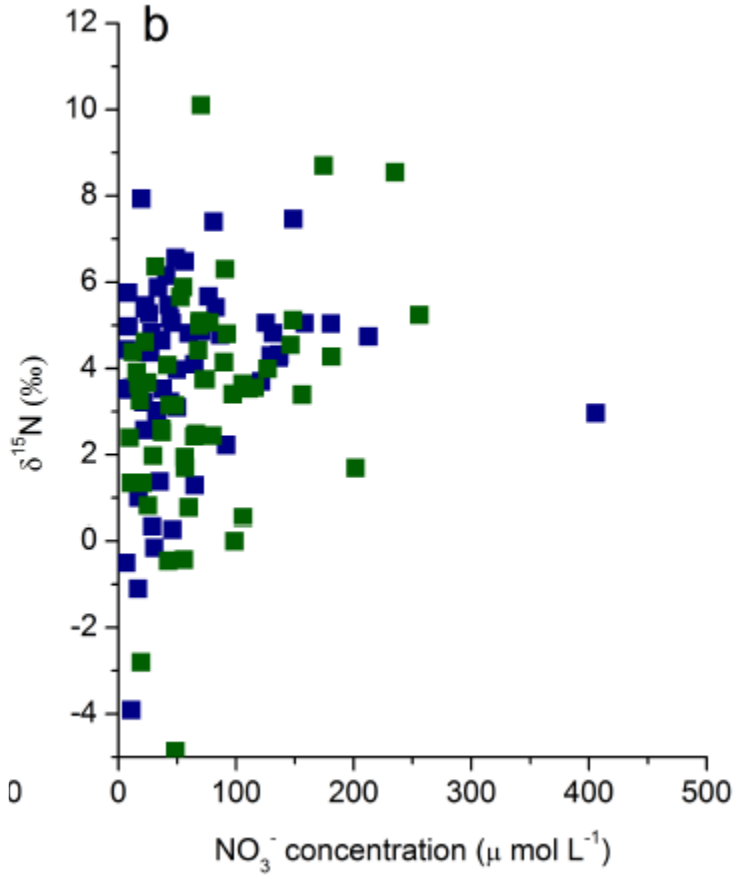


Fig.3. $\delta^{15}N$- NO_3^- vs. NO_3^- con. and R^2 =0.24, P <0.001 in2009.

➢ Results and Discussion

- Seasonal pattern of N isotopes of NO_3^-

- The $\delta^{15}N$ values of precipitation NO_3^- were higher in the summer than in other seasons in 2009.

- In 2009 monthly mean NO_2/NO_x and O3 concentration were lower in the summer than in the winter.

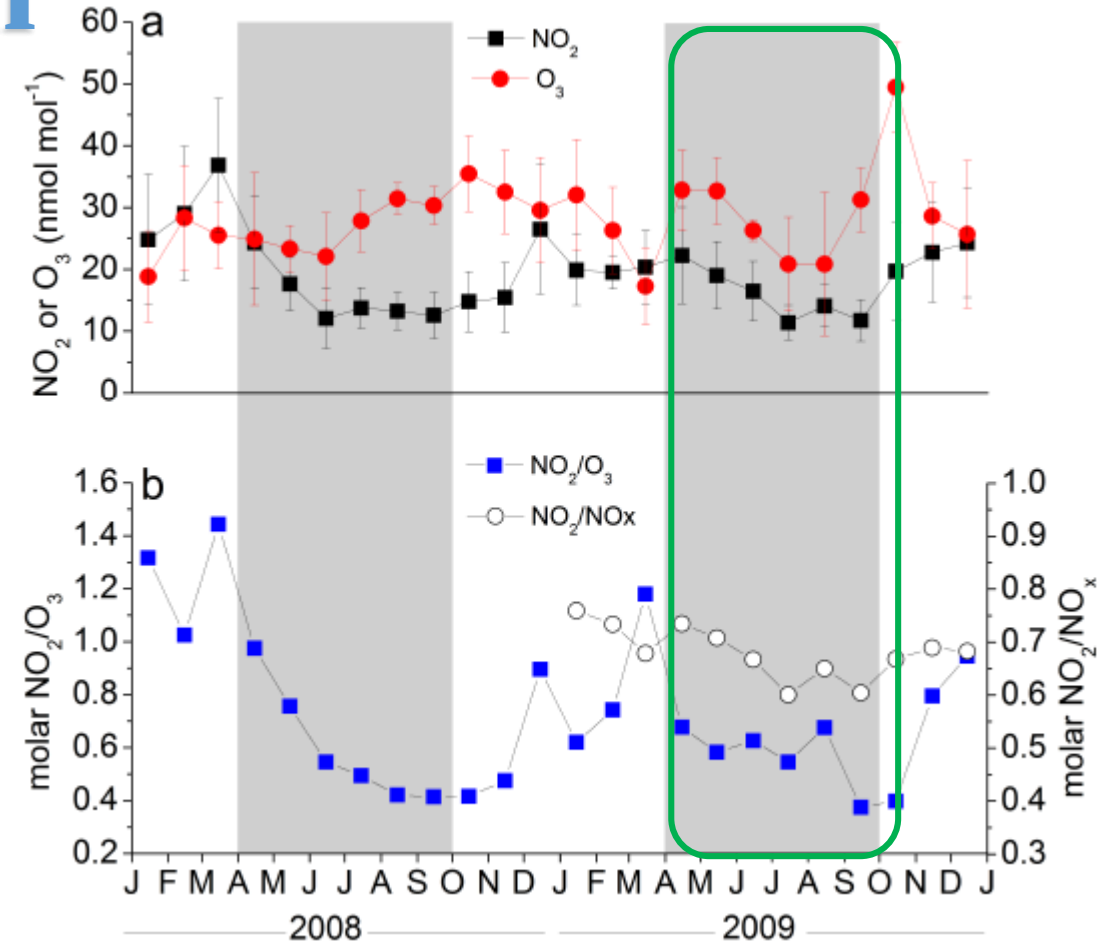


Fig.4. Seasonal changes in NO2 and O3 concentrations (a), monthly mean of three monitoring sites), molar ratios of NO_2/O_3 and NO_2/NO_x (b) during the study course in Guangzhou City. The shaded areas denote the warm seasons from April to September

➢ Results and Discussion

Seasonal pattern of N isotopes of NO_3^-

In 2008,higher $\delta^{15}N$ values the winter, although the seasonal pattern was not as distinct as in 2009.

Year	Season	*n*	Precipitation (mm)	NO_3^- input (kg N ha^{-1} a^{-1})	NO_3^- con. (μmol L^{-1})	$\delta^{15}N$-NO_3^- (‰)	$\delta^{18}O$-NO_3^- (‰)
2008	Cool	9	491	4.1	89.9 (9 to 181, 19.6)	+4.5 (+0.3 to +7.5, 0.7)	+73.2 (+53.3 to +81.2, 3.2)
	Warm	50	1670	11.9	57.7 (6 to 406, 9.4)	+3.8 (−3.9 to +7.9, 0.3)	+63.5 (+33.4 to +81.5, 1.4)
	P value				0.18	0.41	0.01
2009	Cool	11	411	3.7	67.6 (19 to 181, 14.5)	+0.7 (−4.9 to +4.3, 0.9)	+73.0 (+59.3 to +84.4, 2.7)
	Warm	43	1520	14.8	78.8 (10 to 256, 9.1)	+4.1 (+0.5 to +10.1, 0.3)	+66.4 (+47.2 to +86.2, 1.5)
	P value				0.57	<0.001	0.05

The *P* values were obtained by one-way ANOVA performed for each study year. Range (minimum and maximum) and one standard error of mean are given in parentheses.

➢ Results and Discussion

- Seasonal pattern of N isotopes of NO_3^-
- The high values in coincidence with the high temperatures observed in 2009 might be caused by the high demand for fossil fuel because of the intense preparations forthe 16th Asian（2010）.

Year	Season	*n*	Precipitation (mm)	NO_3^- input (kg N ha^{-1} a^{-1})	NO_3^- con. (μmol L^{-1})	δ^{15}N-NO_3^- (‰)	δ^{18}O-NO_3^- (‰)
2008	Cool	9	491	4.1	89.9 (9 to 181, 19.6)	+4.5 (+0.3 to +7.5, 0.7)	+73.2 (+53.3 to +81.2, 3.2)
	Warm	50	1670	11.9	57.7 (6 to 406, 9.4)	+3.8 (−3.9 to +7.9, 0.3)	+63.5 (+33.4 to +81.5, 1.4)
	P value				0.18	0.41	0.01
2009	Cool	11	411	3.7	67.6 (19 to 181, 14.5)	+0.7 (−4.9 to +4.3, 0.9)	+73.0 (+59.3 to +84.4, 2.7)
	Warm	43	1520	14.8	78.8 (10 to 256, 9.1)	+4.1 (+0.5 to +10.1, 0.3)	+66.4 (+47.2 to +86.2, 1.5)
	*P*value				0.57	<0.001	0.05

The *P* values were obtained by one-way ANOVA performed for each study year. Range (minimum and maximum) and one standard error of mean are given in parentheses.

➢ Results and Discussion

Seasonal pattern of N isotopes of NO_3^-

The difference in seasonal pattern of $\delta^{15}N$ of NO_3^- precipitation between 2008 and 2009 may have mainly resulted from two factors:

- 1.different precipitation regime.There was a larger amount of precipitation in 2008 than in 2009.

- 2. human activities. a.global financial crisis starting from 2007.

  b.the intensive preparations for the 16th Asian Games.

➢ Results and Discussion

- Partitioning of NO_x sources using N isotopes of NO_3^-
- Assuming that the precipitation NO_3^- at has only two sources,anthropogenic and natural,Calculations show that on average 59% in 2008 and 55% in 2009 were from an anthropogenic source,may be an underestimation.

- First, the assumed $\delta^{15}N_{anthropogenic}$ value be higher than the actual one.

- Second,the $\delta^{15}N_{natural}$ value used in the estimation may be higher than the actual value.

- Thirdly, the $\delta^{15}N$ signature of thermal NO_x might have failed to be recorded by our precipitation samples

➢ Results and Discussion

- Partitioning of NO_x sources using N isotopes of NO_3^-
- The $\delta^{15}N$ values of fuel NO_xhave been reported to be much more positive than those from natural sources,the fuel NO_x are generally more enriched in ^{15}N than the thermal NO_x.

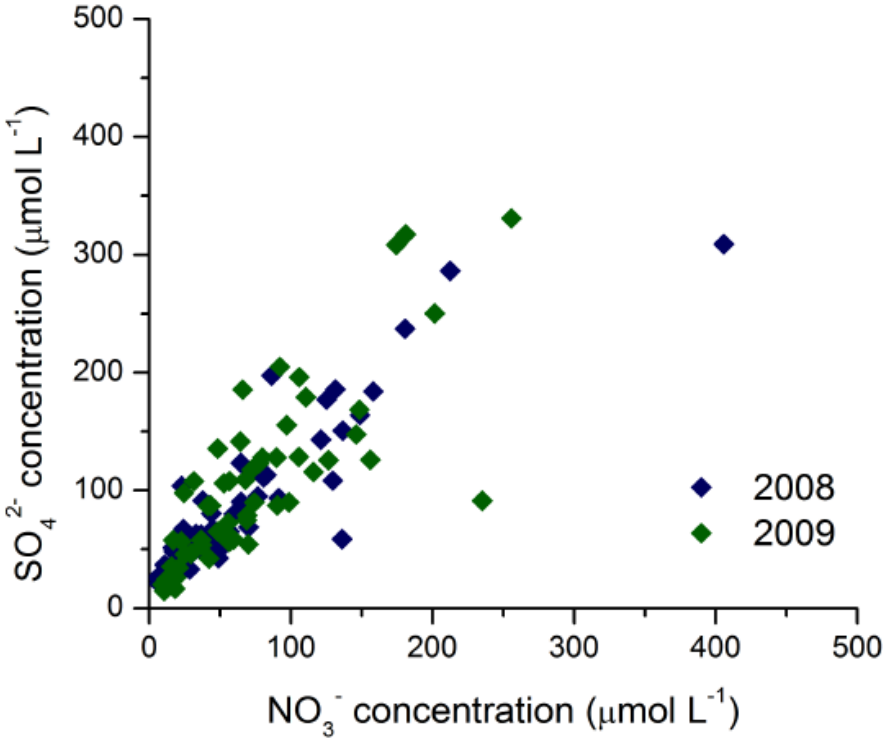


Fig.5. NO_3^- concentration vs. SO^{2-}_4concentration in precipitation collected in 2008 to 2009 in Guangzhou City. R2 =0.80, P <0.001 in 2008; R2 =0.77, P <0.001 in 2009.

➢ Results and Discussion

- O isotopes of NO_3^-

1.The $\delta^{18}O$ values : +33.4 ~+86.2‰.

2. The $\delta^{18}O$ annual mean values:
+65.0‰ (2008) and +67.7‰ (2009).

The NO_3^--flux-weighted $\delta^{18}O$ values :
+71.8‰ (2008) and +70.6‰ (2009).

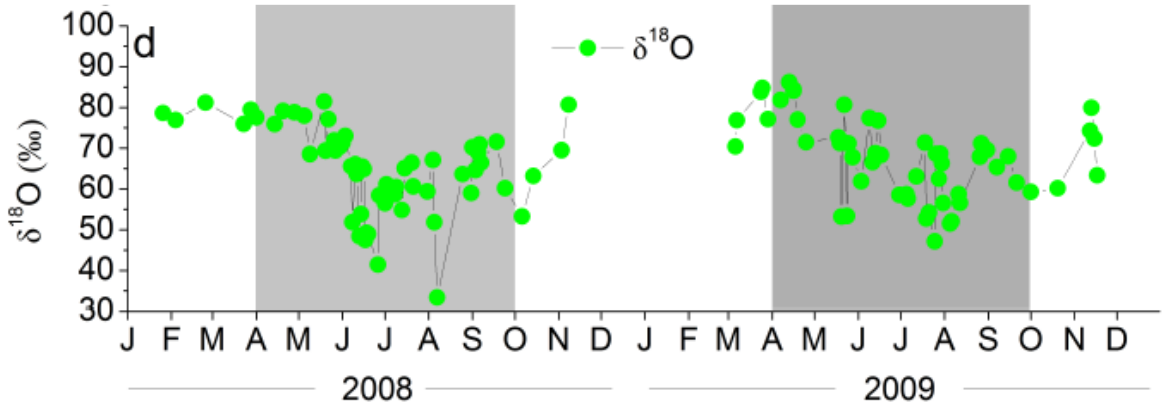


Fig.6 Ranges and values of $\delta^{18}O$

	Range	$\delta^{18}O$-NO_3^- (‰) Mean[a]	Mean[b]	Mean[c]
2008	+33.4 to +81.5	+65.0	+64.9	+71.8
2009	+48.2 to +86.2	+67.7	+66.5	+70.6

Table.6 Annual mean of $\delta^{18}O$

➢ Results and Discussion

- O isotopes of NO_3^-

3.The seasonal pattern of $\delta^{18}O$ of NO_3^- was clear, with values reaching a minimum in July or August.

4.The $\delta^{18}O$ values of NO_3^- were significantly higher inthe cool season than in the warm season.

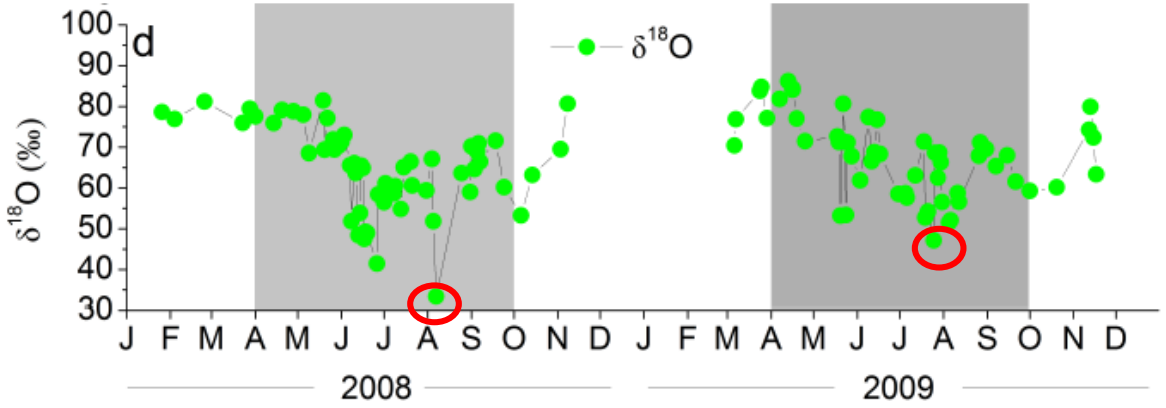


Fig.6 Ranges and values of $\delta^{18}O$

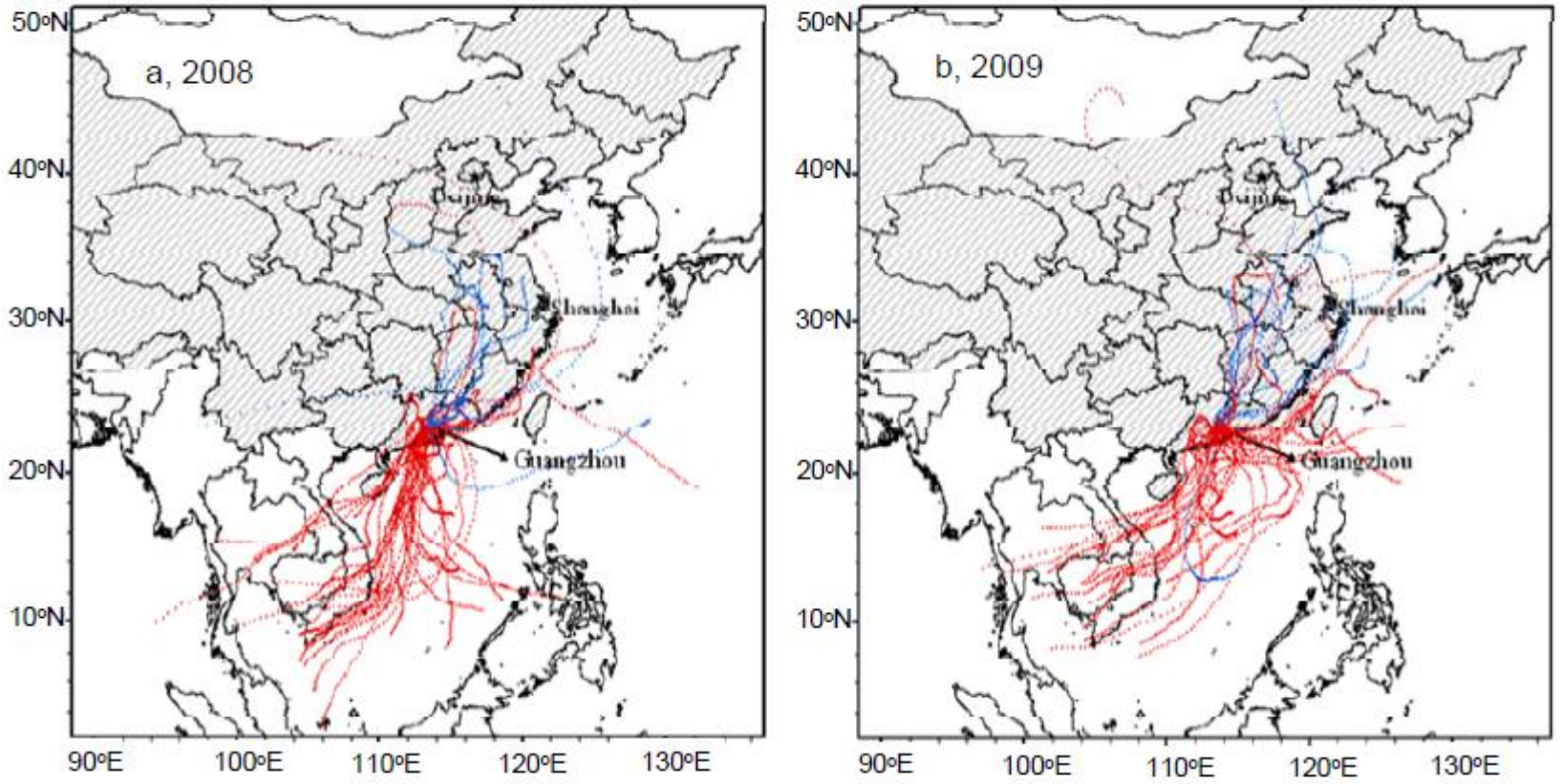
Year	Season	*n*	$\delta^{18}O$-NO_3^- (‰)
2008	Cool	9	+73.2 (+53.3 to +81.2, 3.2)
	Warm	50	+63.5 (+33.4 to +81.5, 1.4)
	P value		0.01
2009	Cool	11	+73.0 (+59.3 to +84.4, 2.7)
	Warm	43	+66.4 (+47.2 to +86.2, 1.5)
	P value		0.05

Table.7.Seasonal pattern of $\delta^{18}O$-NO_3^-

➢ Results and Discussion

- O isotopes of NO_3^-

The continental source precipitation had higher $\delta^{18}O$ of than the marine source precipitation; the continental source precipitation mainly occurred in the cool season that had shorter daytime.



Year	Season	$\delta^{18}O$-NO_3^- (‰)
2008	Continental	+71.6 (+51.8 to +81.5, 1.9)
	Marine	+61.3 (+33.4 to +79.5, 1.6)
	P value	<0.001
2009	Continental	+71.6 (+58.8 to +84.8, 1.9)
	Marine	+65.5 (+47.2 to +86.2, 1.7)
	P value	0.06

Table.8.Sources comparison of $\delta^{18}O$ concentration

Fig.7. 72-hour air mass backward trajectories in Guangzhou City Lines in blue occurring in the cool season,red in the warm season

➢ Results and Discussion

- Oxygen isotopes of NO_3^-
- $\delta^{18}O$ average of +66.3‰,fell in the low end of the reported range of the world.The relatively low $\delta^{18}O$ values in our study suggest the importance of the OH radical pathway in forming atmospheric NO_3^- .

- The seasonality of these formation pathways is a function of both temperature (N_2O_5 is thermally decomposed)and solar radiation (OH is photolytically produced).

➢ Results and Discussion

- Oxygen isotopes of NO_3^-
- 18 samples had $\delta^{18}O$ values being lower than +55‰.After the correction of NO^-_2 interference , still find that 12 values being lower than the expected minimum.

- One possibility for the lower than usual $\delta^{18}O$ values of NO_3^- is oxygen isotopic fractionation, which can induce large variations in $\delta^{18}O$ values between the reactants and the products.

➢ Results and Discussion

- Oxygen isotopes of NO_3^-
- The other possible explanation is the reaction of NO with peroxy radicals , which can compete with O_3 to convert NO into NO_2

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \qquad (R7)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R8)$$

The $\delta^{18}O$ of peroxy radicals is expected to be much lower than that of O3 as the O atoms should come from atmospheric O2

Conclusions

1. Positive nitrate $\delta^{15}N$ values indicating the importance of NO_x emissions from coal combustion.Different seasonal patterns of $\delta^{15}N$-NO_3^- might reflect the global financial crisis and the intensive preparations for the 16th Asian Games.

2. The anthropogenic NO_x source :59% (2008)and 55%(2009) of the total input may be an underestimation.

3. $\delta^{18}O$-NO_3^- values :+33.4‰ — +86.5‰ was lower than reported (the importance of OH radicals in the formation of atmospheric) 16% of $\delta^{18}O$ values that were lower than the expected likely resulted from the reaction of NO with HO_2.

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Thank you for listening!