耶鲁大学-南京信息工程大学大气环境中心

Yale-NUIST Center on Atmospheric Environment

Review on atmospheric nitrate formation pathways: Insights from $\Delta^{17}O$ in aerosol

Wenqi Zhang

2018/5/24

Content

- Review

Introduction

Methods

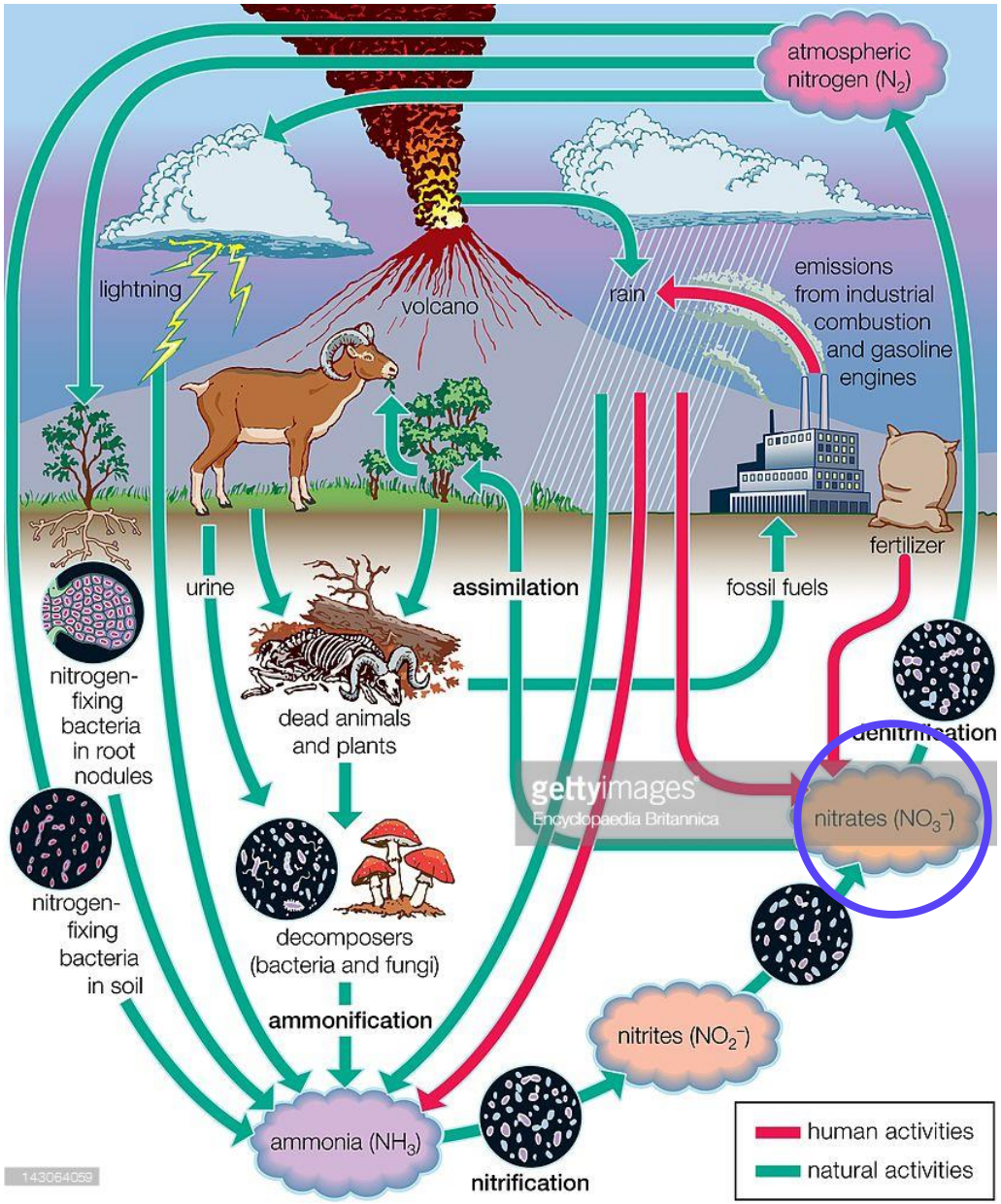
Observations

Reaction mechanism

Modeling $\Delta^{17}O$ in atmospheric nitrate

- Case study (Hangzhou)

Introduction: Why nitrate?



(Photo by encyclopaedia britannica/UIG via Getty Images)

Introduction: Why nitrate?

Increasing anthropogenic NOx emissions

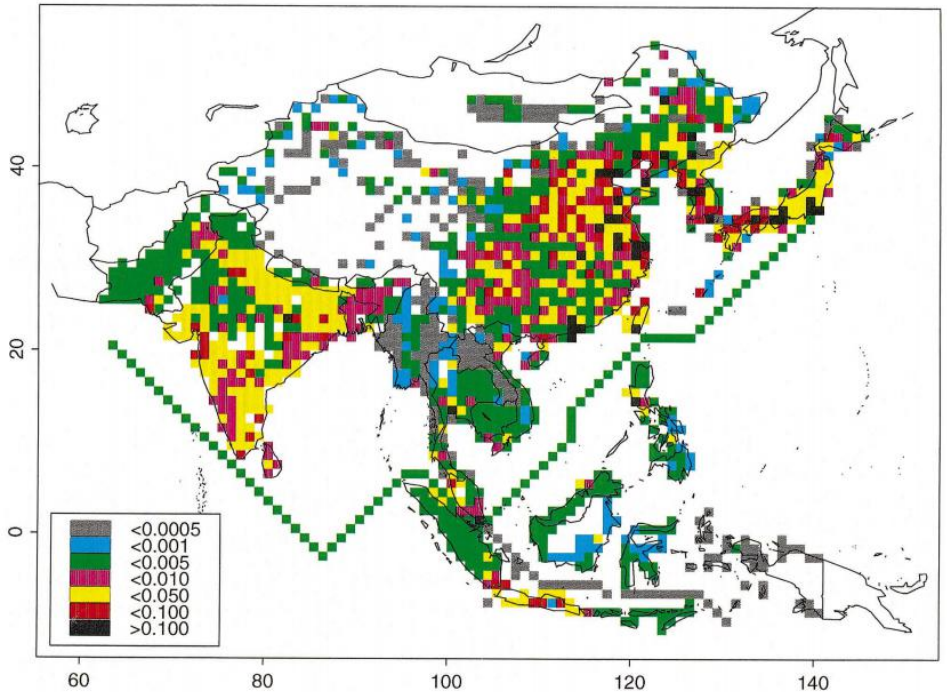


Fig 1. 1990 emissions on 1*1 grid (Tg NO_2 per grid)

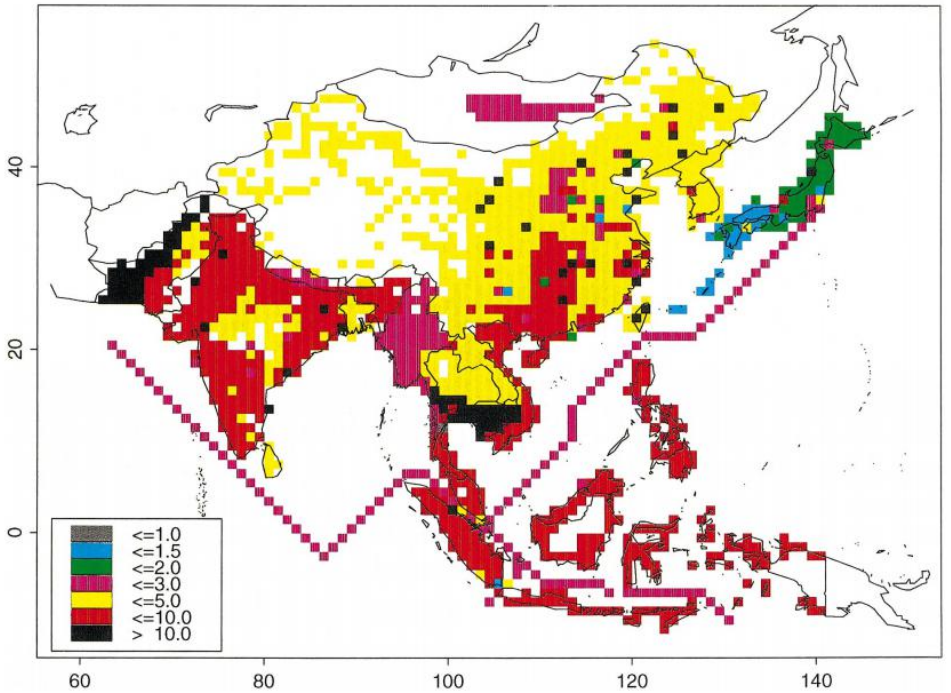


Fig 2. Ratio between 2020 and 1990 emissions on 1*1 grid

Introduction: Why nitrate?

Larger contribution in haze days !

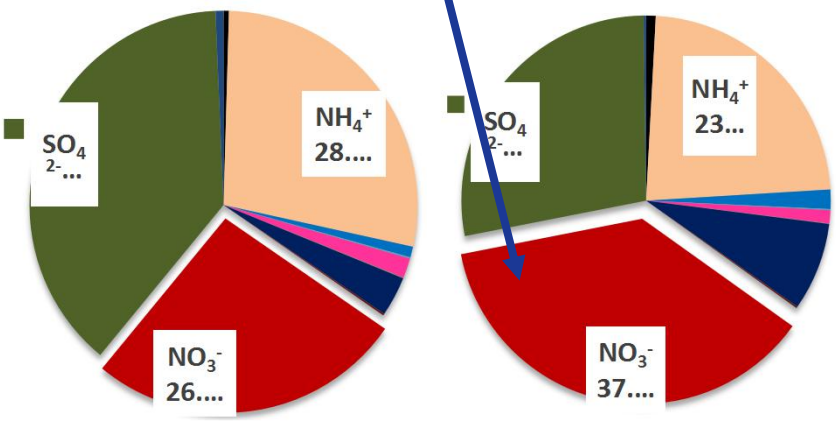
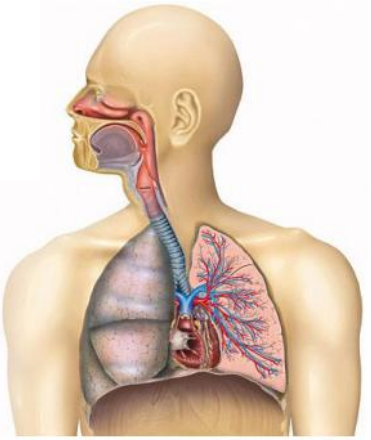


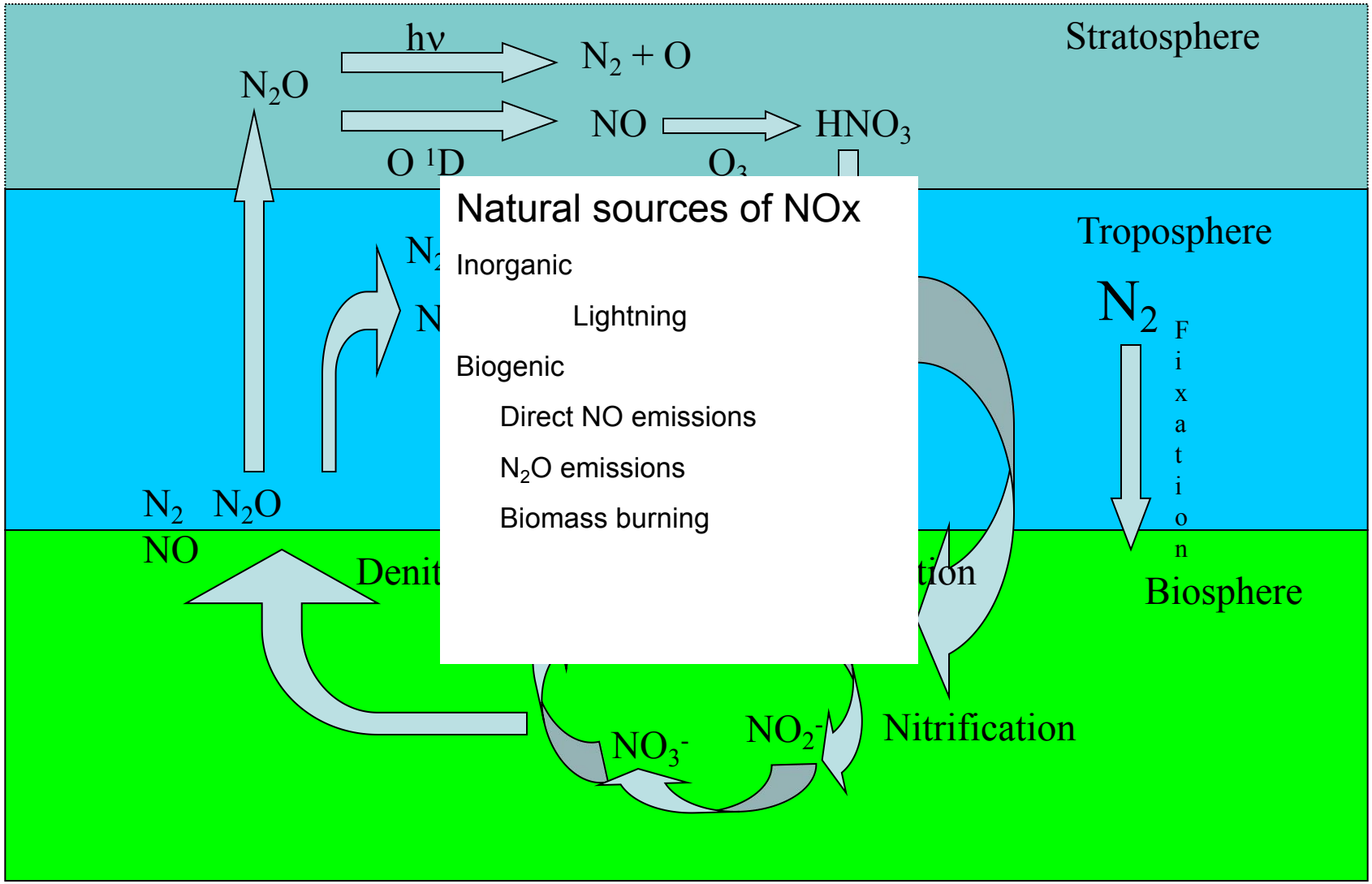
Fig 3. Average ion composition in $PM_{2.5}$ during a clean period (left) and a haze period (right) in Nanjing, 2015.1.

Acid rain

Health effects



Natural sources of NOx



from G. Michalski, 2016

Anthropogenic sources of NOx

Direct NOx emissions by agriculture

NOx emissions by agriculture by burning

Notice NOx emissions are expected to double between now and 2050

Table 1. Global atmospheric emissions of NH_3 and NOx, Tg N yr^{-1}

	1860		1993		2050		Note
	NO_x	NH_3	NO_x	NH_3	NO_x	NH_3	
Food							A1
Sav	0.9	0.2	2.9	1.8	3.8	2.2	
Agl	0.0	–	2.6	–	5.1	–	
Agr	0.9	0.6	2.4	1.4	5.0	3.1	
Def	0.2	0.2	1.1	1.4	0.9	1.1	
Fer							
Anr							
Lan							
Cro							
Sub							
Energ							
E1*							
Nrt							
Air							
His	0.0	0.0	1.5	0.2	3.6	0.2	
Bf3	0.4					1.7	
Subtotal	0.6					2.1	
Natural							A3
Aglnat	2.9					–	
Lightning*	5.4					–	
Firenat	1.6					0.8	
Strat	0.6					–	
Soil and veg	–					3.6	
Ocean	–					5.6	
Subtotal	10.5	1				10.0	
Emission, total	13.1	20.6	45.9	58.2	81.5	118	
Deposition, total	12.8	18.8	45.8	56.7	78.5	116	B1

Introduction: Why pathways?

- Identifying the mechanisms that transform NOx into nitrate is key to understanding the natural and human impacted nitrogen cycles from local to regional and global scales.
- Atmospheric chemistry
- Contribution to models

Introduction: Why $\Delta^{17}O$?

- Oxygen isotopes:

^{16}O(0.9976), ^{17}O(0.0004) and ^{18}O(0.0020)

$$\delta^{18}O_{\text{sample}} = \frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{standard}}{{}^{18}O/{}^{16}O_{standard}} \times 1000$$

- International reference material (standard): V-SMOW Vienna Standard Mean Ocean Water

$^{18}O/^{16}O$:$2.0052*10^{-3}$ $^{17}O/^{16}O$:$3.827*10^{-4}$

- Mass dependent fractionation (MDF)

$$\delta^{18}O = 0.5 * \delta^{17}O$$

- Dual isotope ($\delta^{18}O$ and $\delta^{17}O$) ratio plot: terrestrial fractionation line (TFL)

From Kaiser, 2009

Introduction: Why $\Delta^{17}O$?

- Mass independent fractionation (MIF):

Same enrichment in both ^{18}O and ^{17}O

$$\Delta^{17}O = \delta^{17}O - 0.52 * \delta^{18}O$$

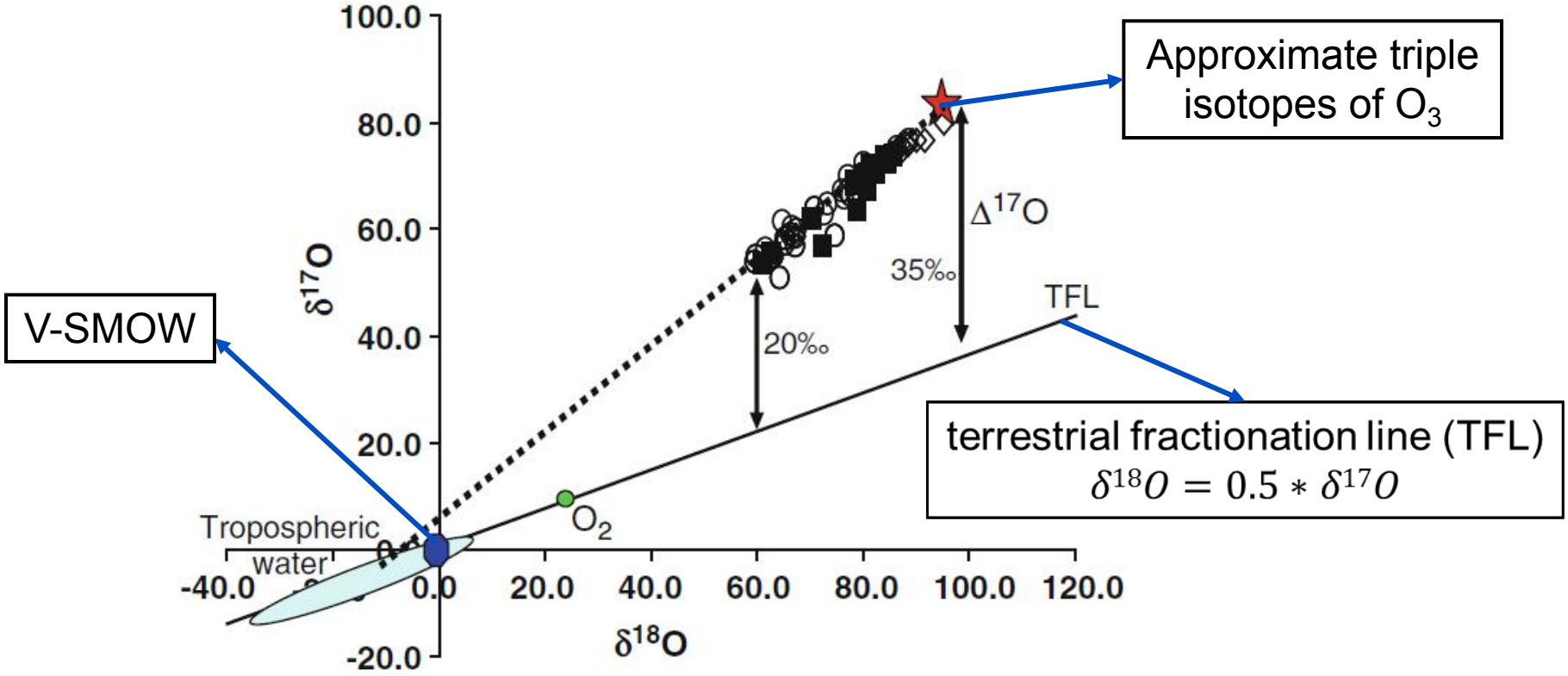


Fig 4. The range of oxygen isotopes atmospheric nitrate from mid-latitude.

Source: G. Michalski 2010

Methods: Isotope measurement

Table 2. The development of the oxygen isotope measurement in nitrate

Year	Approaches	Test system	Advantages /Disadvantages	precison	Citations
1987	KNO_3+$Hg(CN)_2$→550℃→CO_2	Offline	Toxicity risks of $Hg(CN)_2$	$\delta^{18}O$	(Amberger and Schmidt, 1987)
1995	Nitrate salts +graphite→800℃→CO_2 (quartz reaction vessels)	Offline	Oxygen exchanges	$\delta^{18}O$	(Revesz et al. 1997; Silva et al. 2000; Wassenaar 1995).
1999	KNO_3→1400℃→CO_2 (graphite/ glassy carbon reaction tube)	CF-IRMS	No O exchange Automated	±0.7‰ ($\delta^{18}O$)	(Kornexl et al.,1999)
2002	$AgNO_3$→520℃→O_2 (pretreated quartz reaction tube) USGS-35: only available $\Delta^{17}O$ reference material, $NaNO_3$ from Atacama Desert	CF-IRMS	High detection limit (10^{-5}mol) Need purify environmental samples	±0.3‰ ($\Delta^{17}O$)	(Michalski et al. 2002; Chang et al. 1999; Michalski 2009)
2002	NO_3^-→Pseudomonas aureofaciens bacteria→N_2O	CF-IRMS	Nanomolar amounts and limited sample preparation.	±0.5‰ ($\delta^{18}O$)	(Casciotti et al., 2002)
2007	NO_3^-→Pseudomonas aureofaciens bacteria→N_2O→gold tube at 960℃→O_2 +N_2	CF-IRMS		±0.6‰ ($\Delta^{17}O$)	(Kaiser et al., 2007) (Cliff and Thiemens 1994)
2005	NO_3^- + Cd →NO_2^- + azide →N_2O	CF-IRMS	Oxygen exchange with water Toxicity risks of azide	±0.5‰ ($\delta^{18}O$)	(McIlvin and Altabet , 2005)
2008	NO_3^- + Cd →NO_2^- + azide →N_2O→gold tube at 960℃→O_2 +N_2	CF-IRMS		±0.2‰ ($\Delta^{17}O$ and $\delta^{18}O$)	(Komatsu et al., 2008)

GEOPHYSICAL RESEARCH

First measurements and mo

Greg Michalski, Zack Scott, Melanie
University of California, San Diego Department of

JOURNAL OF GEOPHYSIC

Isotopic analysis of aeroso Determination of different particle size

N. Patris,[1,2] S. S. Cliff,[3] P. K. Quir

Anal. Chem. **2007**, *79*, 599–607

Triple Oxygen Is the Denitrifier M of N_2O

Jan Kaiser,*,†,‡ Meredith G. Hasti Daniel M. Sigman†

Department of Geosciences, Princeton U Max Planck Institute for Nuclear Physics

Atmospheric Environment 179 (2018) 1–11

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Summertime diurnal variations in the isotopic composition of atmospheric nitrogen dioxide at a small midwestern United States city

Wendell W. Walters[a,*,1], Huan Fang[a], Greg Michalski[a,b]

[a] Department of Earth, Atmospheric, and Planetary Sciences Purdue University, 550 Stadium Mall Drive, West Lafayette, IN, 47907, United States
[b] Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN, 47907, United States

Atmos. Chem. Phys., 18, 6381–6392, 2018
https://doi.org/10.5194/acp-18-6381-2018

Atmospheric Chemistry and Physics Open Access EGU

Atmos. Chem. Phys., 16, 2659–2673, 2016
www.atmos-chem-phys.net/16/2659/2016/
doi:10.5194/acp-16-2659-2016

Atmospheric Chemistry and Physics Open Access EGU

Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign

Joël Savarino[1,2], William C. Vicars[1,2,a], Michel Legrand[1,2], Suzanne Preunkert[1,2], Bruno Jourdain[1,2], Markus M. Frey[3], Alexandre Kukui[4,5], Nicolas Caillon[1,2], and Jaime Gil Roca[4,5]

[1]Université Grenoble Alpes, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), 38000 Grenoble, France

Reaction mechanism

- How to interpret the nitrate formation pathways with $\Delta^{17}O$?

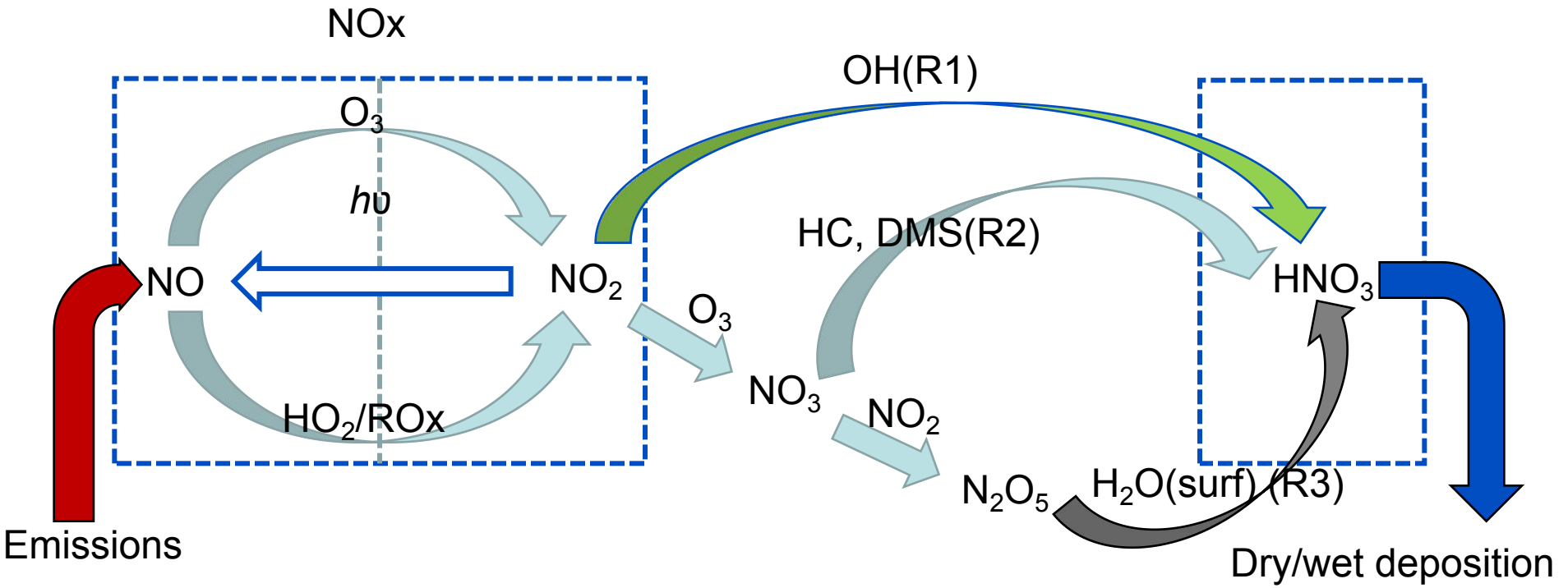


Fig 7. Atmospheric nitrate formation pathways.

Reaction mechanism

NO_3^- formation pathways (NO_2 sink reactions)

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad (R1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (R2a)$$

$$NO_3 + HC, DMS \rightarrow HNO_3 + products \quad (R2b)$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5 \quad (R3a)$$

$$N_2O_5 + H_2O(surf) \rightarrow 2HNO_{3(aq)} \quad (R3b)$$

NO / NO_2 equilibrium

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R4)$$

$$NO + HO_2\ (ROx) \rightarrow NO_2 + OH\ (RO) \quad (R5)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (R6)$$

$$O(^3P) + O_2 + M \rightarrow O_3 \quad (R7)$$

Isotopic mass balance

$$\Delta^{17}O_{sample} = \sum_{i=1}^{3} \Delta HNO_3(Ri) \times f(Ri)$$

Δ^{17}O (oxidant)

Tropospheric HO_2(ROx): 1-2‰

(Rockmann et al., 2001)

$$\Delta^{17}O(NO_2) = \alpha\Delta^{17}O(O_3)$$

Tropospheric O_3: 35‰

(Johnson et al., 2000; Lyons, 2001)

Tropospheric water: 0‰

Tropospheric OH: 0‰

(Dubey et al.,1997, Lyons, 2001)

Reaction mechanism

NO_3^- formation pathways (NO_2 sink reactions)

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad (R1)$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (R2a)$$
$$NO_3 + HC, DMS \rightarrow HNO_3 + products \quad (R2b)$$
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NO / NO_2 equilibrium

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R4)$$
$$NO + HO_2\,(ROx) \rightarrow NO_2 + OH\,(RO) \quad (R5)$$
$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (R6)$$
$$O(^3P) + O_2 + M \rightarrow O_3 \quad (R7)$$

Isotopic mass balance

$$\Delta^{17}HNO_3 = \sum_{i=1}^{3} \Delta^{17}HNO_3(Ri) \times f(Ri)$$

$$\Delta^{17}NO_2 = \alpha\Delta O_3$$

$$\Delta^{17}HNO_3(R1) = {}^2/_3\,\alpha\Delta^{17}O_3 \quad (1)$$

$$\Delta^{17}HNO_3(R2) = {}^2/_3\,\alpha\Delta^{17}O_3 + {}^1/_3\,\Delta^{17}O_3 \quad (2)$$

$$\Delta^{17}HNO_3(R3) = {}^1/_3\,\alpha\Delta^{17}O_3 + {}^1/_2\,({}^2/_3\,\alpha\Delta^{17}O_3 + {}^1/_3\,\Delta^{17}O_3) \quad (3)$$

$$\Delta^{17}O_3 = 1.18 \pm 0.07 \times \Delta^{17}O(O_{3\ atm}) + 6.6 \pm 1.15$$

$$\Delta^{17}HNO_3 = \beta\Delta^{17}HNO_3(\mathrm{R1}) + \chi\,\Delta^{17}HNO_3(\mathrm{R2}) + \varepsilon\Delta^{17}HNO_3(\mathrm{R3})$$

$\Delta^{17}O$ of oxygen sources

- P/T model: $\Delta^{17}O = (78.8P^{-0.122}) + 0.06 \bullet (T(K) - 321)$

Experiments demonstrated $\delta^{18}O$ and $\Delta^{17}O$ varies with different pressure and temperature conditions under which the ozone is formed *(Guenther et al. 2000; Thiemens and Jackson 1990).*

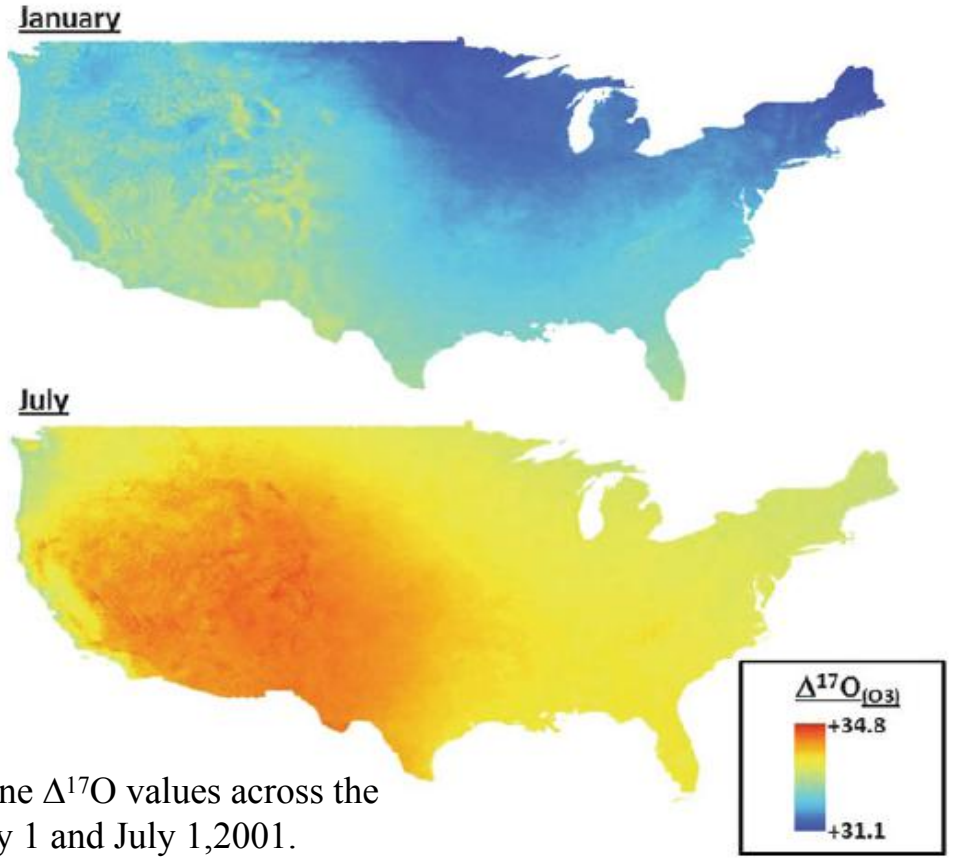


Fig 6. Modeled ozone $\Delta^{17}O$ values across the US for January 1 and July 1,2001.

from G. Michalski, 2010

Modeling $\Delta^{17}O$ in atmospheric nitrate

- Zero dimensional photochemical box model

GEOPHYSICAL RESEARCH LETTERS, VOL. 30, NO. 16, 1870, doi:10.1029/2003GL017015, 2003

First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate

Greg Michalski, Zack Scott, Melanie Kabiling, and Mark H. Thiemens
University of California, San Diego Department of Chemistry and Biochemistry, USA

Received 29 January 2003; revised 22 April 2003; accepted 18 June 2003; published 30 August 2003.

Coupled a secondary $\Delta^{17}O$ isotope fractionation model to a photochemical box model for a polluted marine boundary layer

Tracing the Origin and Fate of NO_x in the Arctic Atmosphere Using Stable Isotopes in Nitrate

Samuel Morin,[1,2]* Joël Savarino,[1,2] Markus M. Frey,[1,2]† Nicolas Yan,[1,3] Slimane Bekki,[1,3] Jan W. Bottenheim,[4] Jean M. F. Martins[1,5]

CiTTyCAT (Cambridge Transport Trajectory model of Chemistry And Transport), a photochemical box model used to examine the origin of polluted layer.

Isotope modeling of nitric acid formation in the atmosphere using ISO-RACM: testing the importance of NO oxidation, heterogeneous reactions, and trace gas chemistry

G. Michalski and F. Xu

Department of Chemistry, Earth and Atmospheric Sciences, Purdue University 550 Stadium Mall Dr. West Lafayette, West Lafayette, IN, USA

Received: 14 January 2010 – Accepted: 9 February 2010 – Published: 11 March 2010

Correspondence to: G. Michalski (gmichals@purdue.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

ISO-RACM (Isotope Regional Atmospheric Chemistry Mechanism) assess changes in $\Delta^{17}O$ over a wide range of atmospheric parameters.

Modeling $\Delta^{17}O$ in atmospheric nitrate

- 3D modeling

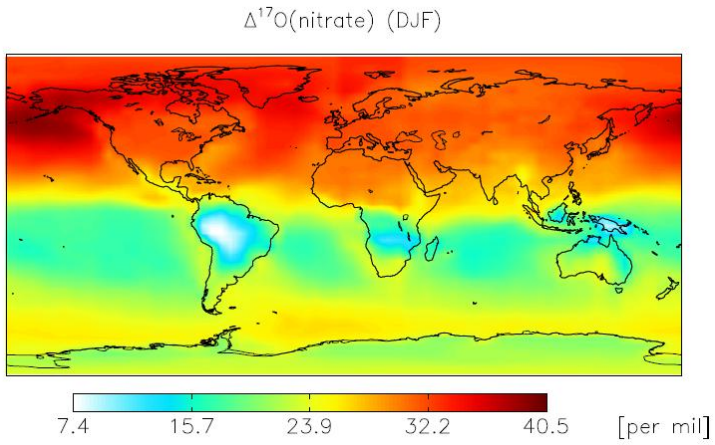
Atmos. Chem. Phys., 9, 5043–5056, 2009
www.atmos-chem-phys.net/9/5043/2009/

Atmospheric Chemistry and Physics

Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}O$) of atmospheric nitrate

B. Alexander[1], M. G. Hastings[2], D. J. Allman[1], J. Dachs[3], J. A. Thornton[1], and S. A. Kunasek[4]
[1]Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA
[2]Department of Geological Sciences and Environmental Change Initiative, Brown University, Providence, RI, USA
[3]Department of Environmental Chemistry, Institute for Environmental Assessment and Water Studies (IDAEA-CSIC), Consejo Superior de Investigaciones Científicas, Barcelona, Spain
[4]Department of Earth and Space Sciences, University of Washington, Seattle, WA, USA

3D chemical transport model GEOS-Chem.
Mass balance approach to calculate $\Delta^{17}O$.
Include vertical and horizontal transport, and incorporates spatial variations in surface fluxes of important primary pollutants.



$\Delta^{17}O$ in nitrate: 7~41‰
Similar seasonal variation as observations.

Fig 7. December-January-February average nitrate $\Delta^{17}O$ (‰) values 0–200m above the surface in .

Importance of each nitrate formation pathways

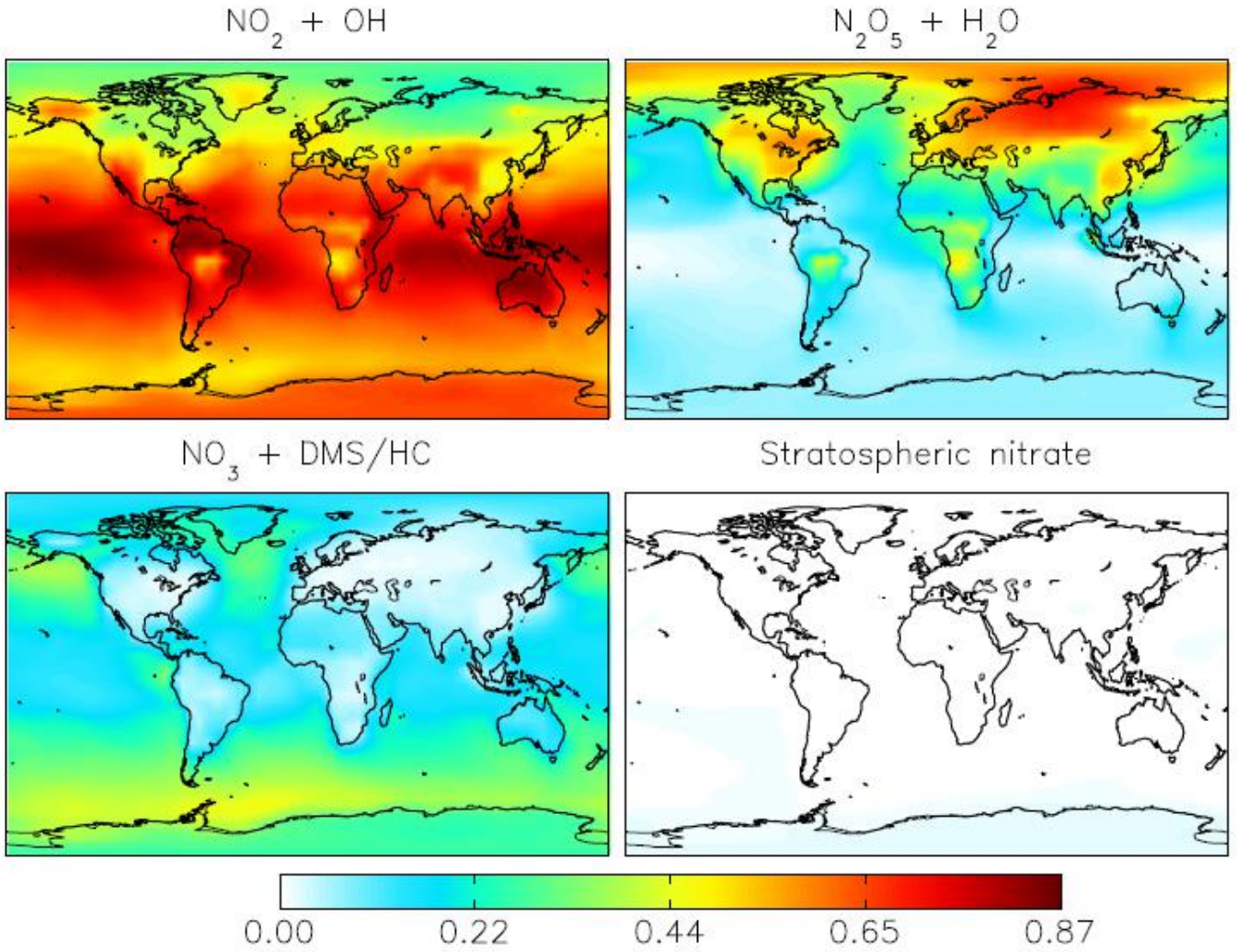


Fig. 8. Annual-mean fractional importance of each nitrate production pathway leading to total inorganic nitrate at the surface in 3D model.

(Alexander et al. 2009)

Summary

- $\Delta^{17}O$ is a potential method to help us understand the nitrate formation pathways.
- Normally, $\Delta^{17}O$ of atmospheric nitrate ranged from 20‰ to 35‰.
- Input information has a great influence of the calculated value.
- Lack of $\Delta^{17}O$ (NO_3^-) observation in urban areas.

Content

- Review
- Case study (Hangzhou)

Experimental

Method

Results and discussion

Conclusions

Outlook

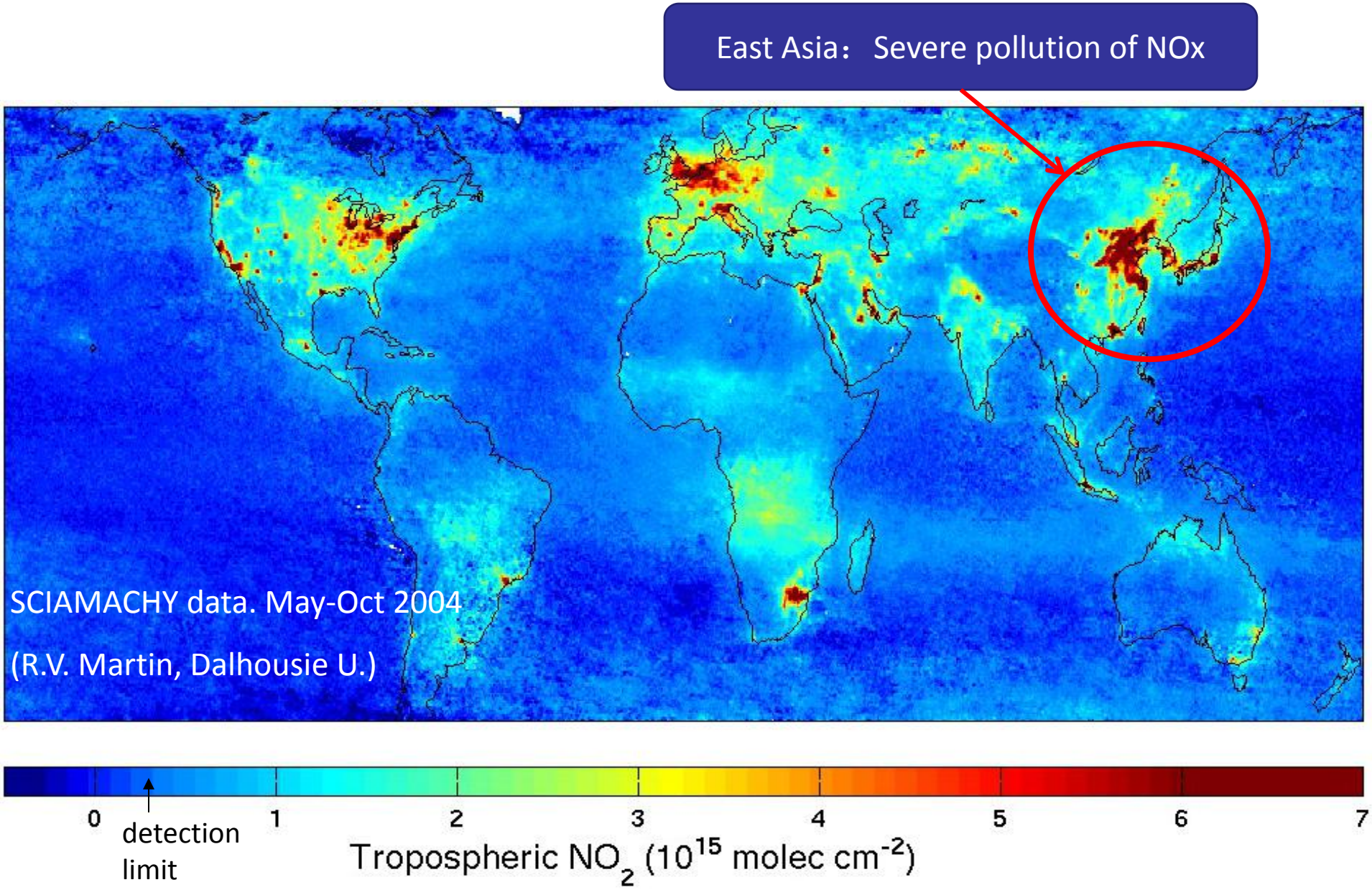


Fig 9. Using satellite observations of NO_2 to monitor NOx emissions.

Experimental

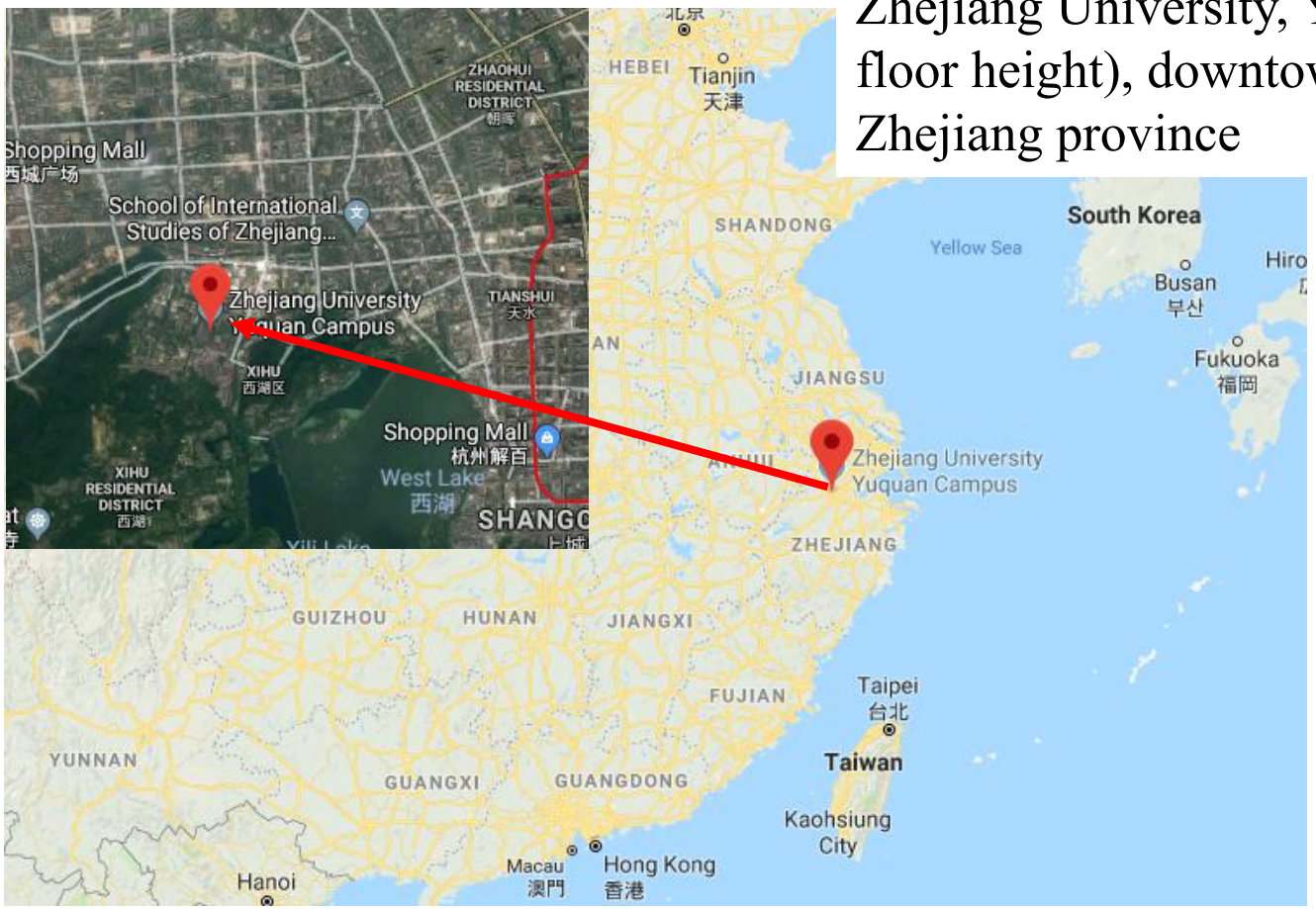


Fig 10. sampling site.

Sampling site:

Zhejiang University, Yuquan campus (7 floor height), downtown of Hangzhou, Zhejiang province

High volume sampler:

NC1000, 1m^3/min

24h / 6 days

2015.9.6-2016.10.24

Data:

nitrate concentration

$\delta^{15}N$, $\delta^{18}O$, $\Delta^{17}O$ in nitrate

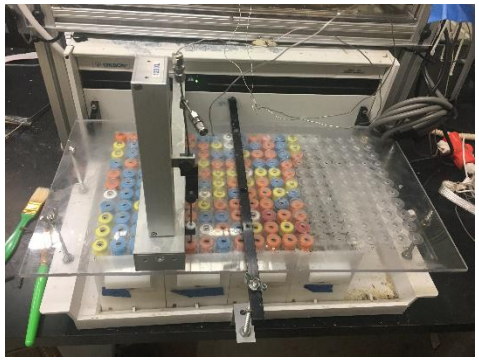
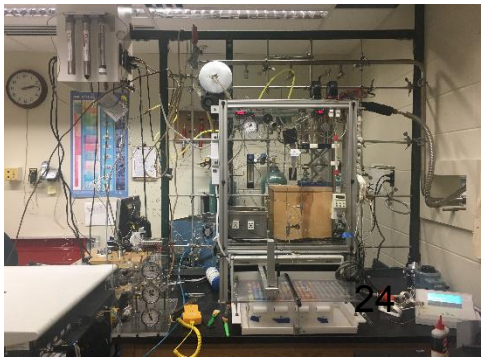
$NO_2/O_3/PM_{2.5}$

Meteorological data

Method: bacteria

- Prep the bacteria：Centrifuge bacteria, rinse for 3 times, bubble rinse solution with helium for 2 hours, sealed to sitting overnight.
- Inject the samples：Bubble rinse solution with helium for 2 hours, flush the vials with helium, sample injection, store upside down overnight.
- On IRMS ： Lyse the bacteria, auto sampler, water trap, CO_2 trap, two liquid nitrogen traps, gold tube at 960 centigrade, GC column, IRMS.



Method: model

- RACM: Gas-phase chemical mechanism for the modeling of regional atmospheric chemistry, the "Regional Atmospheric Chemistry Mechanism"(RACM)
- First presented by William R. Stockwell in 1997.
- Box model
- Valid from remote to polluted conditions, from the Earth's surface to the upper troposphere.
- Based on the Regional Acid Deposition Model, version 2 (RADM2) mechanism and the more detailed Euro-RADM mechanism.
- 17 stable inorganic species, 4 inorganic intermediates, 32 stable organic species, 24 organic intermediates.
- 237 reactions.

Reaction mechanism

- How to interpret the nitrate formation pathways with $\Delta^{17}O$?

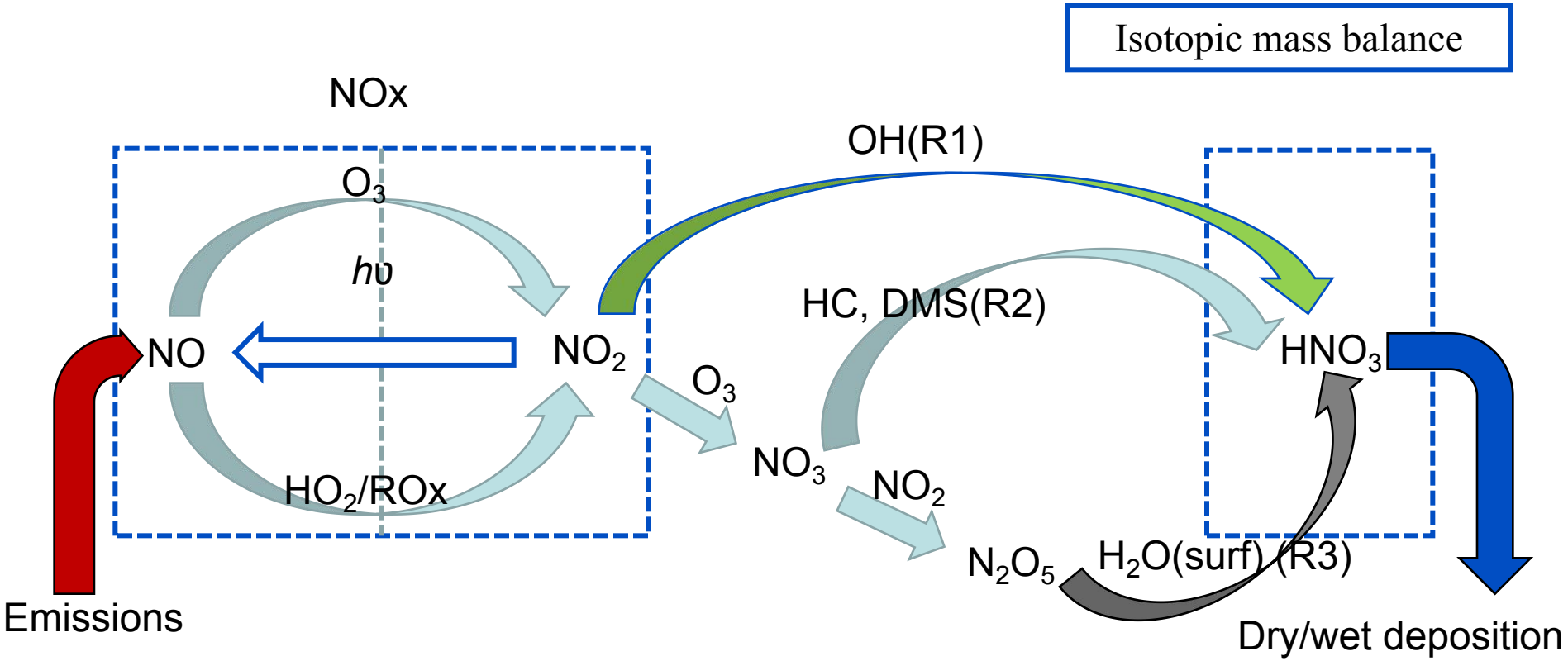


Fig 7. Atmospheric nitrate formation pathways.

Method: model

- Two steps:

Calculate j, photochemical constant

Calculate the product concentration (5 tracers)

- Tracers:

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

$NO + HO_2(ROx) \rightarrow NO_2 + OH(RO) +$ RNOX

R1: $NO_2 + HO + M \rightarrow HNO_3 + M +$ ANOY

R2: $NO_3 +$ HC,DMS $\rightarrow HNO_3 +$ products + BNOY

R3: $N_2O_5 + H_2O(surf) \rightarrow 2HNO_3(aq) +$ CNOY

$$\alpha = \frac{QNOX}{QNOX + RNOX}$$

$$\beta = \frac{ANOX}{ANOX + BNOY + CNOY}$$

$$\chi = \frac{BNOX}{ANOX + BNOY + CNOY}$$

$$\varepsilon = \frac{CNOX}{ANOX + BNOY + CNOY}$$

$$\Delta^{17}NO_3^- = \beta * \Delta^{17}NO_3^-(R1) + \chi * \Delta^{17}NO_3^-(R2) + \varepsilon * \Delta^{17}NO_3^-(R3)$$

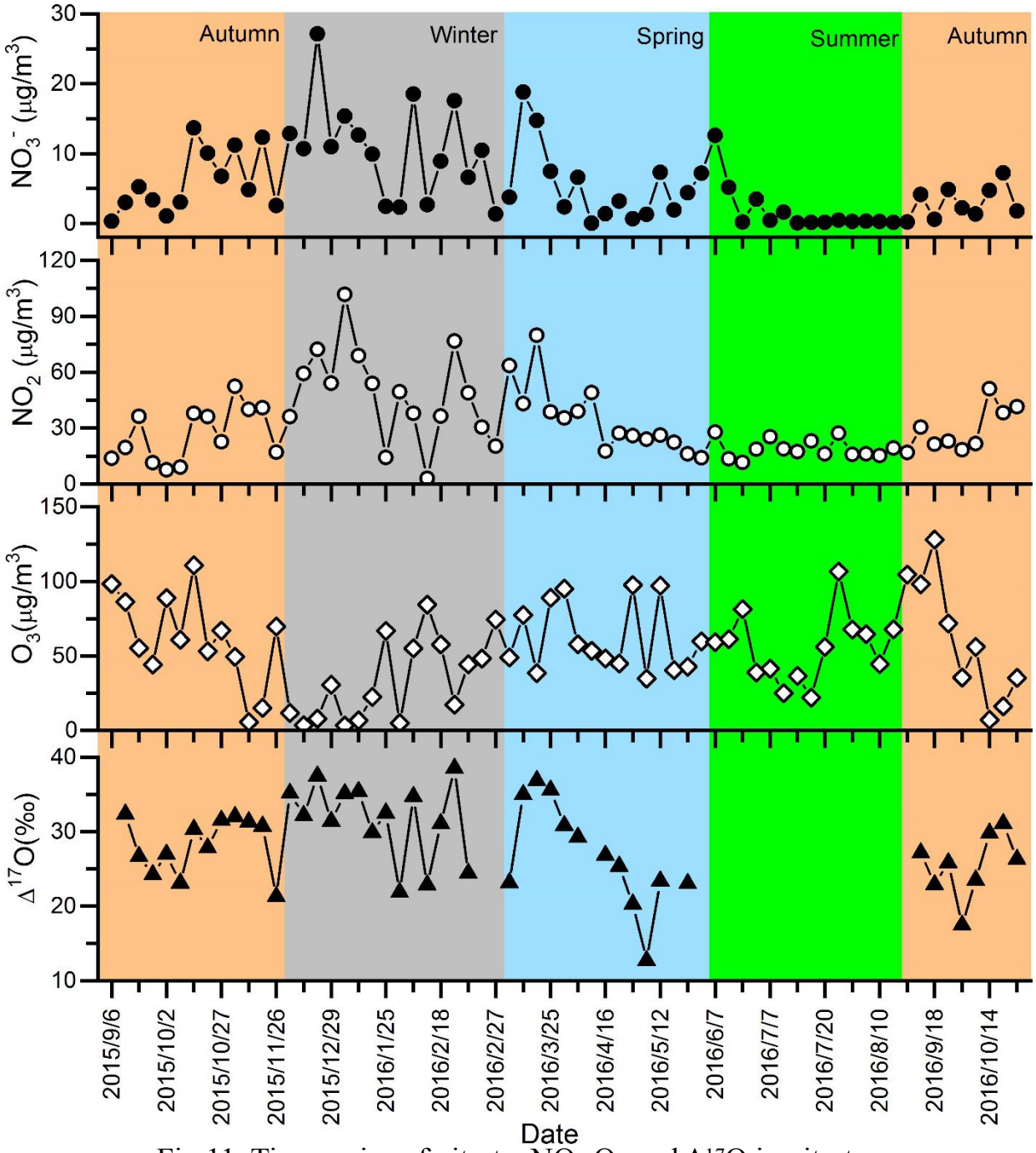


Fig 11. Time series of nitrate, NO_2,O_3 and $\Delta^{17}O$ in nitrate.

- Contribution of O_3 in winter
- $\Delta^{17}O$ is higher in cold seasons and lower in warmer seasons.

Results and discussion

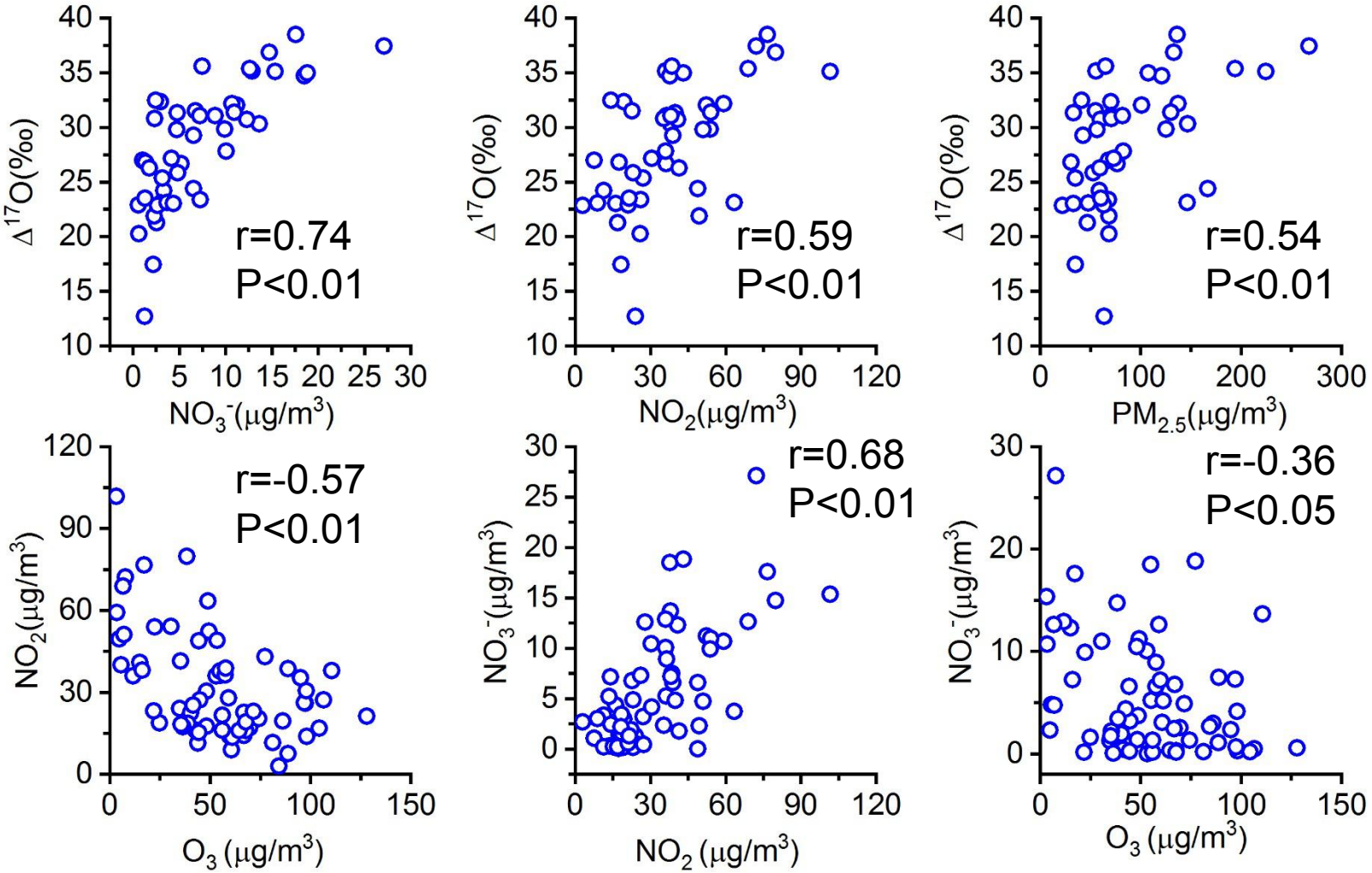


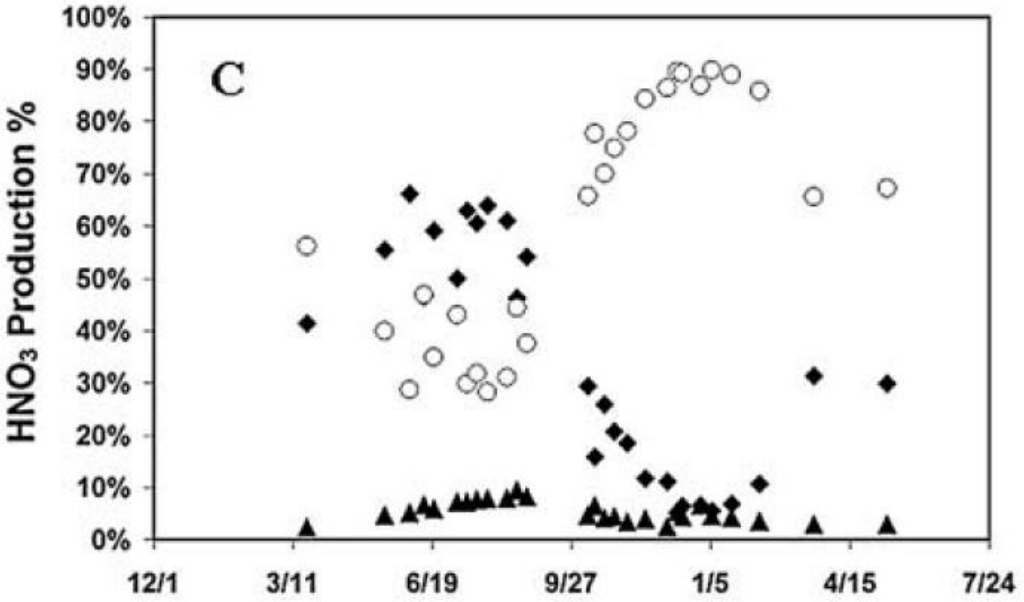
Fig 12. correlation between $\Delta^{17}O$, nitrate, NO^2, nitrate and O^3 in Hangzhou.

Results and discussion

- RACM results:

Winter(2.19) : 6% NO_2+OH; 94% N_2O_5

Spring(3.12) : 37%NO_2+OH; 63% N_2O_5



Attentions

Basic hypothesis:
OH period N_2O_5 period
Ignore HC,DMS

Boundary of daytime/nighttime

Fig 13. HNO_3 production by NO_2+OH, NO_3+HC/DMS and N_2O_5

From G. Micalski 2003

Conclusions

- Seasonal trend of $\Delta^{17}O$ in Hangzhou downtown.
- High value of $\Delta^{17}O$ suggested ozone's contribution as oxidant in winter.

Outlook

- Lab work

Fill the blank of summer data and finish the measurement of the rest samples: Beijing, Xuelong, Tibetan

- Paper work

Review about $\Delta^{17}O$ in nitrate (Chinese)

Finish WSOC paper

Start writing paper about $\Delta^{17}O$ of atmospheric nitrate

- Learning

Atmospheric chemistry, isotope, RACM model

Thanks for your time!

References:

- Tracing the Origin and Fate of NOx in the Arctic Atmosphere Using Stable Isotopes in Nitrate.
- Determination of the Total Oxygen Isotopic Composition of Nitrate and the Calibration of $\Delta^{17}O$: A Nitrate Reference Material.
- Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}O$) of atmospheric nitrate.
- A new mechanism for regional atmospheric chemistry modeling.
- First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate.
- Oxygen Isotope Dynamics of Atmospheric Nitrate Chapter and Its precursor molecules