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Persistent winter nitrate pollution driven by increased oxidants in northern China

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Atmospheric Chemistry Mechanisms Conference
Organized by UC-Davis, Virtual Conference 9-19 November 2020

Acknowledgement

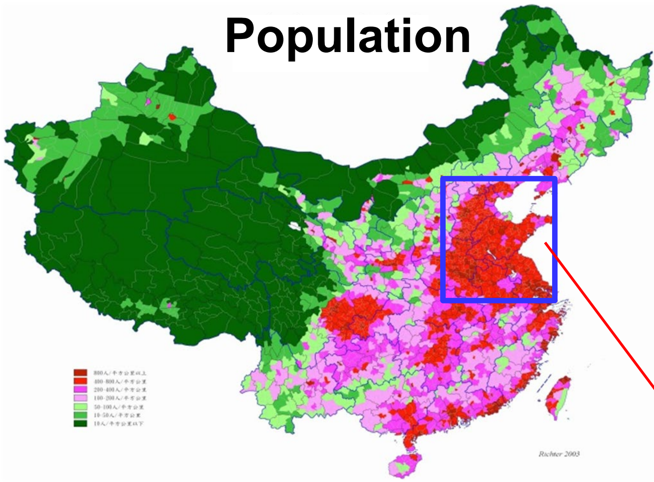
- Prof. Shuxiao Wang of Tsinghua University
- Prof. Likun Xue of Shandong University
- National Natural Science Foundation of China (91544213)
- Hong Kong Research Grant Council

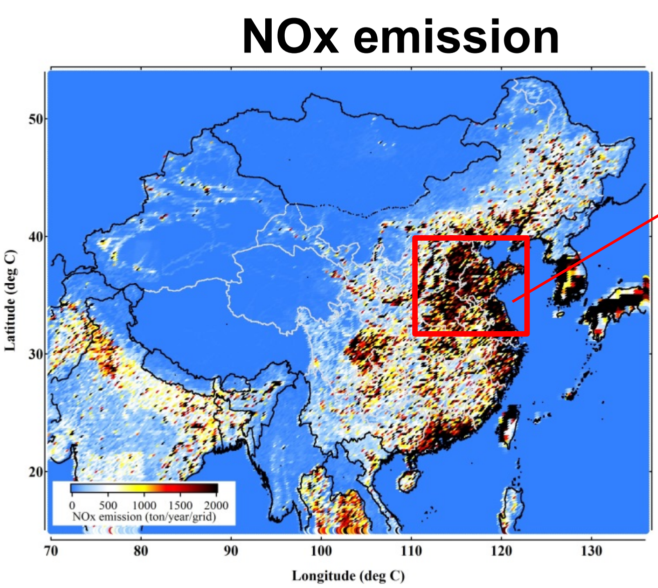
(ANR-RGC Joint research and Theme-based research T24-504/17-N)

Outline

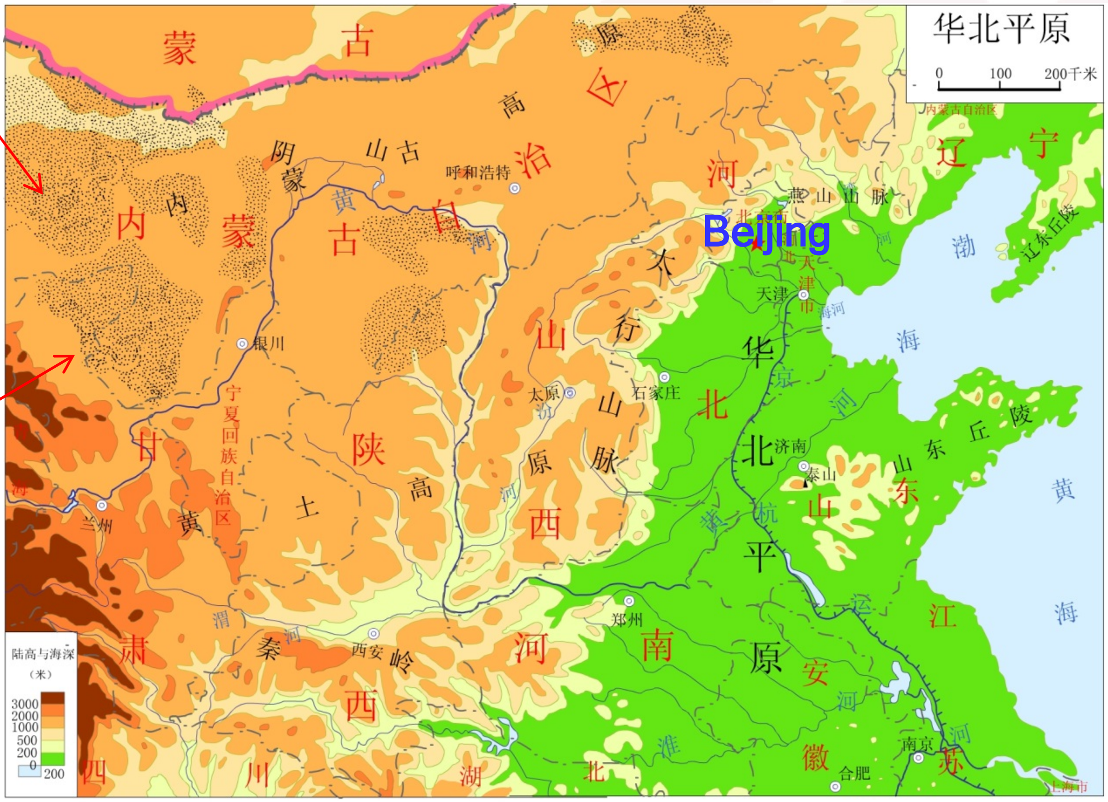
- Winer haze in the North China Plain (NCP)
- Nitrate observations in Dec 2017 in NCP
- Key factors controlling nitrate formation and trend (by model)

The North China Plain (NCP)



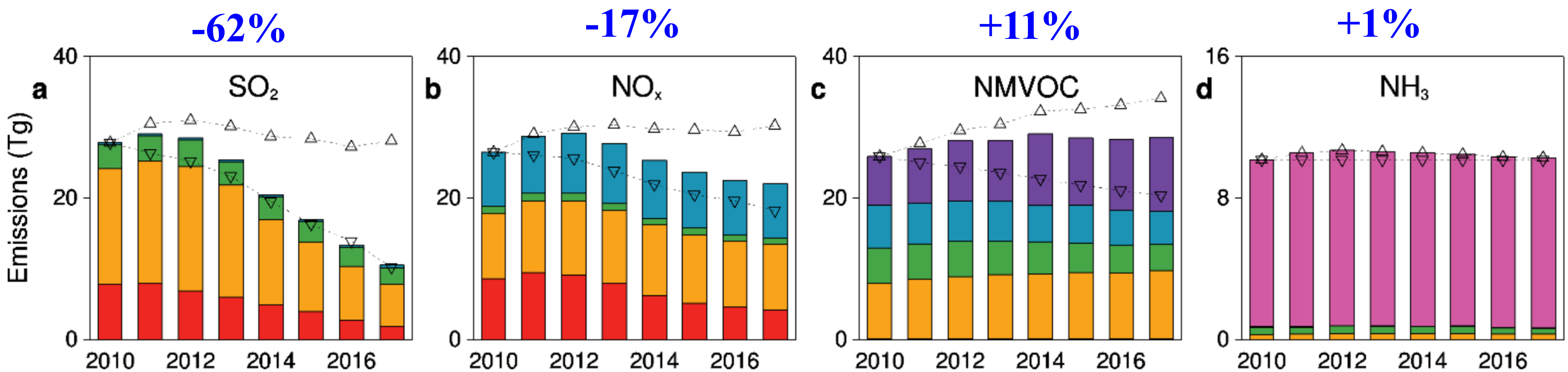


- **~0.3** million *km*^{2} and **~1/5 Chinese population**
- Home to Beijing, Tianjin, Shandong, and part of Hebei, Henan, Jiangsu and Anhui

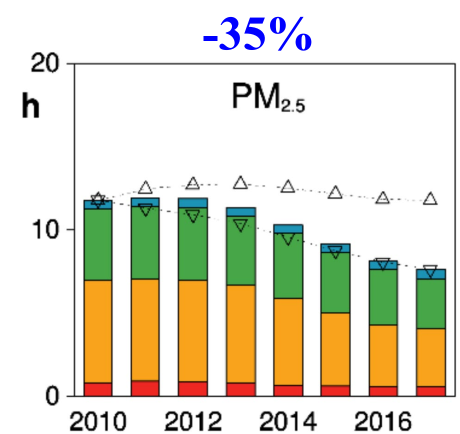


SO_2 & NO_x emissions decreased, so did ambient $PM_{2.5}$ conc.

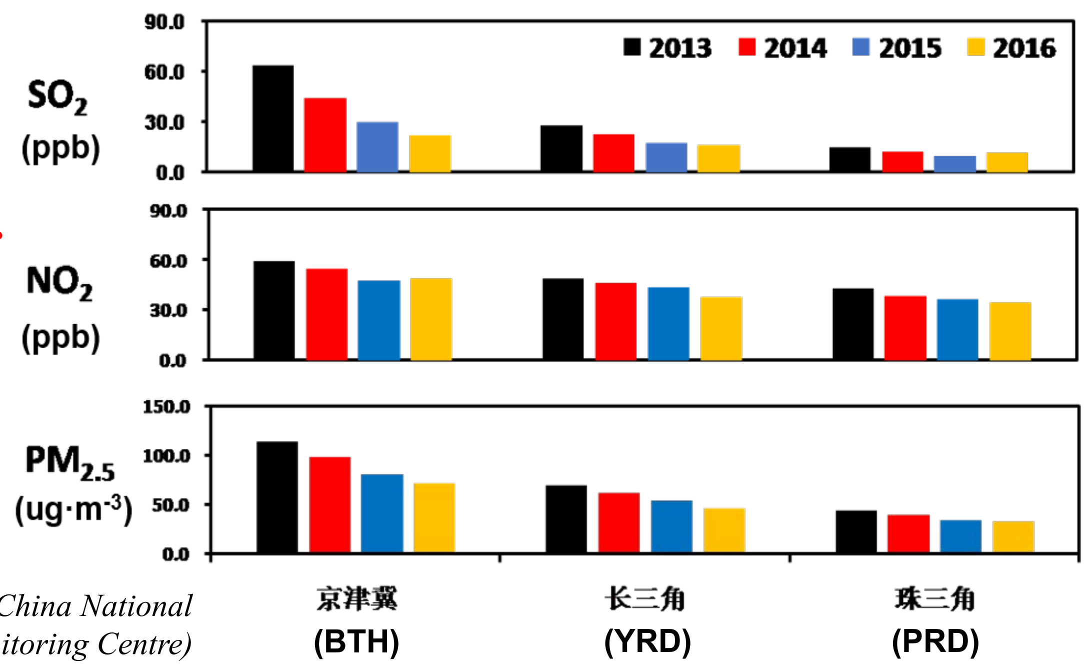
China emission changes (2010-2017)



Zheng et al., 2018

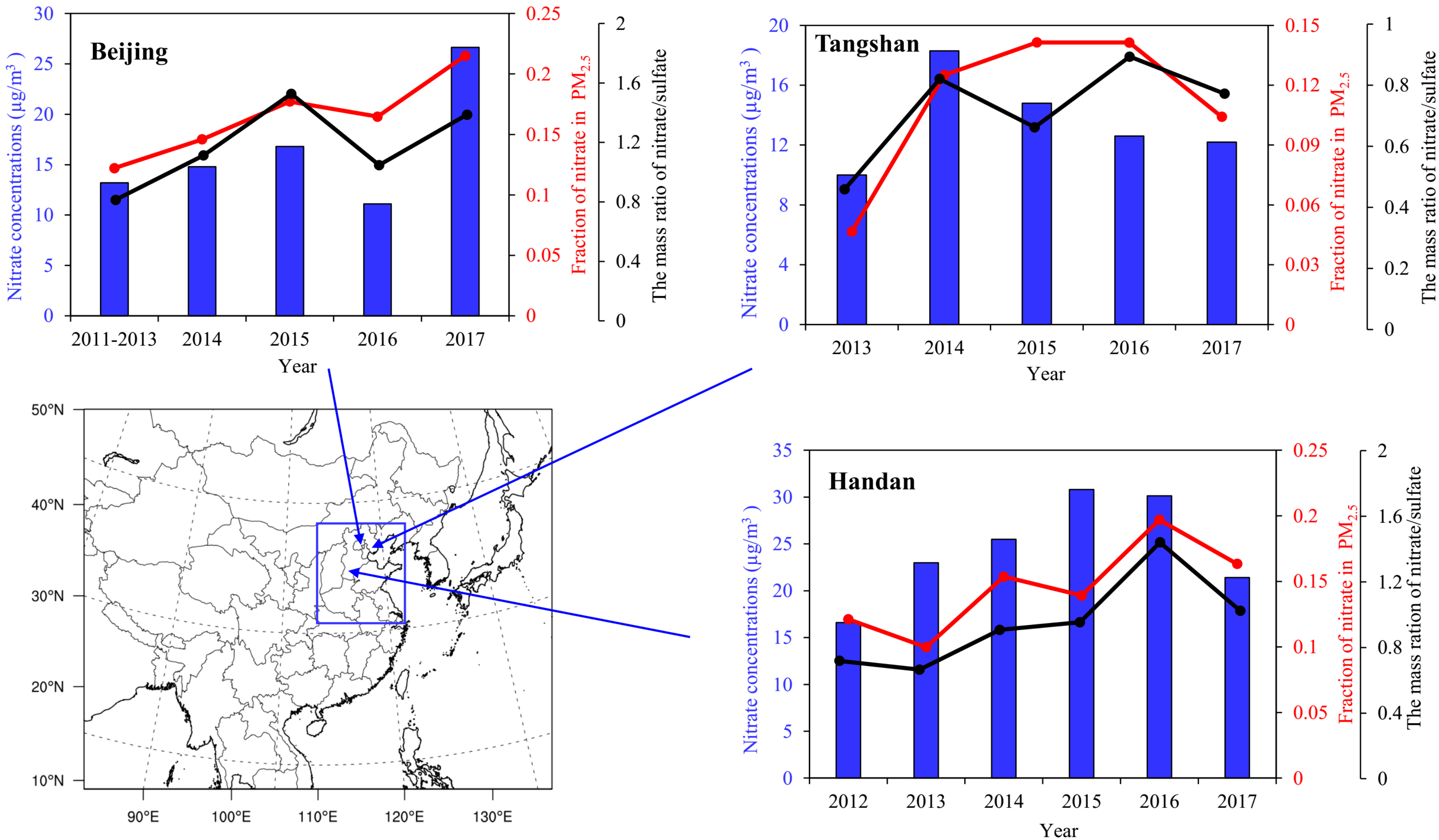


Atmos. conc. changes



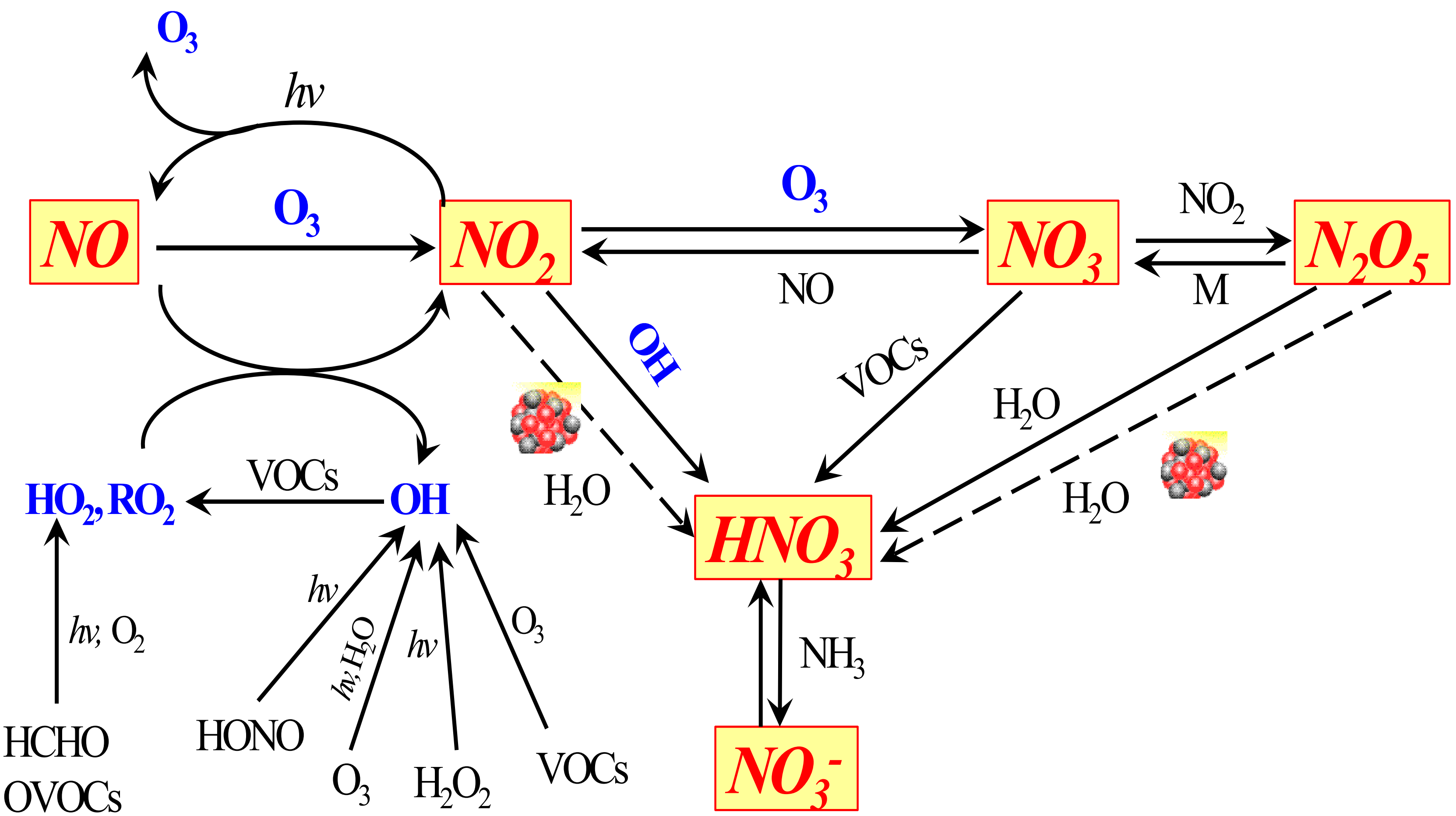
(Data source： China National Environmental Monitoring Centre)

But no obvious decline in fine nitrate in NCP



The trends were composed using the results from Zhao et al., 2019; Meng, 2015; Ma, 2017; Wang et al., 2019; Jia et al., 2018; Zhang et al., 2017; Jia et al., 2018; Wen et al., 2016; Han et al., 2015; Shao et al., 2018.

Nitrate formation pathways

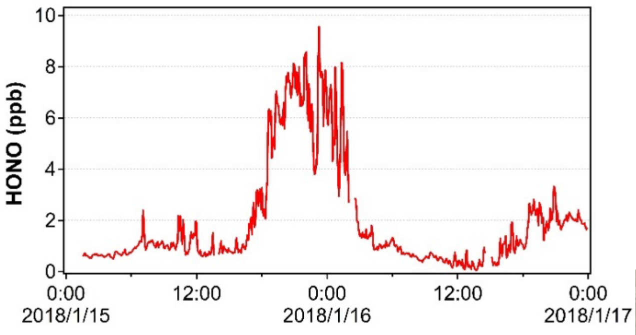


Three key processes: HNO_3 production by $OH+NO_2$ and N_2O_5 hydrolysis followed by reaction with NH_3

Three key ingredients: NO_x, NH_3, &oxidants

Evidence of active winter photochemistry

Peak concentrations of HONO, PAN, and OH observed during wintertime in the NCP



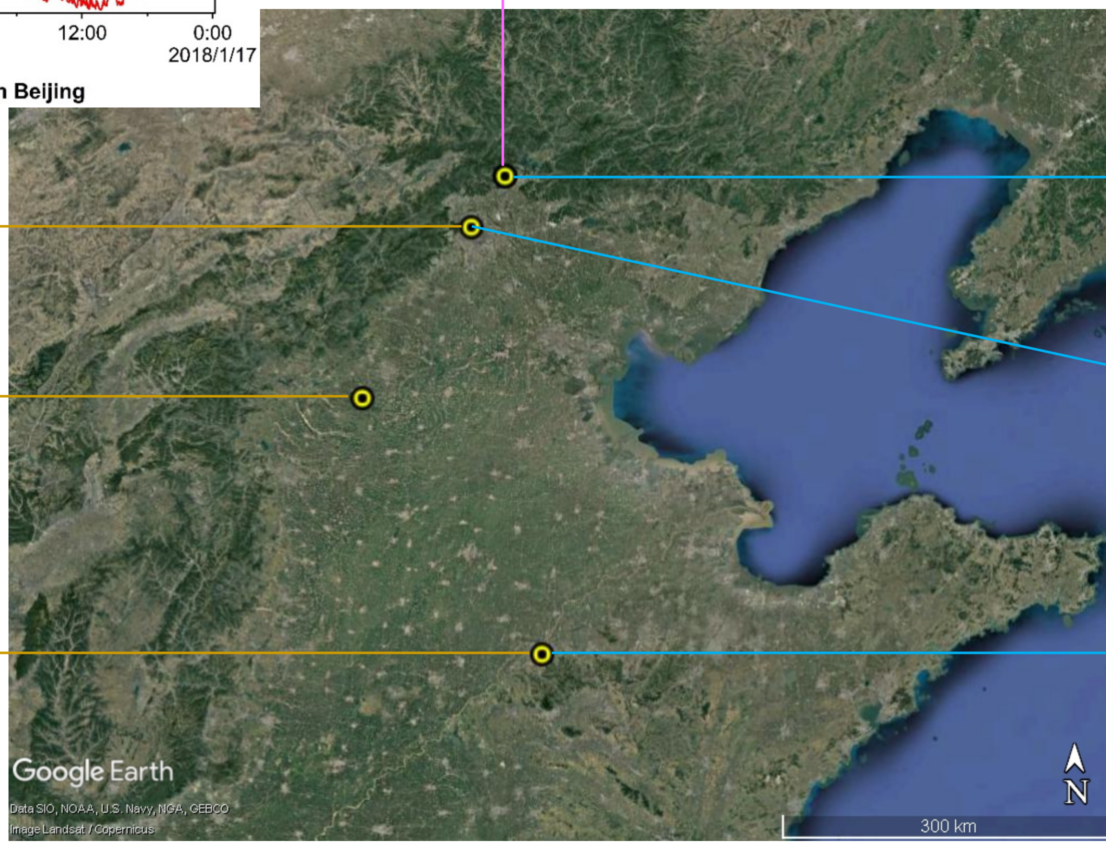
Elevated HONO in Beijing

Beijing *(suburban)*
OH: 1.5×10^{7} molecules·cm^{-3}
(Tan et al., 2018)

Beijing *(urban)*
HONO: 9.7 ppb
(Spataro et al., 2013)

Wangdu *(rural)*
HONO: 10.2 ppb
(unpublished)

Ji'nan *(urban)*
HONO: 8.4 ppb
(Li et al., 2018)



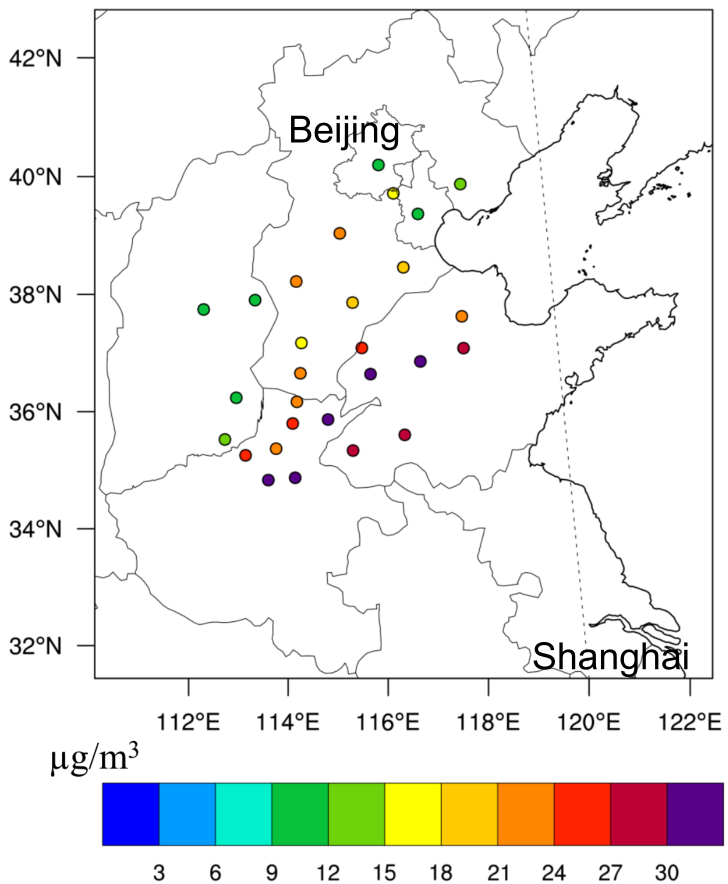
Beijing *(suburban)*
PAN: 6.0 ppb
(Zhang et al., 2019)

Beijing *(urban)*
PAN: 3.5 ppb
(Zhang et al., 2014)

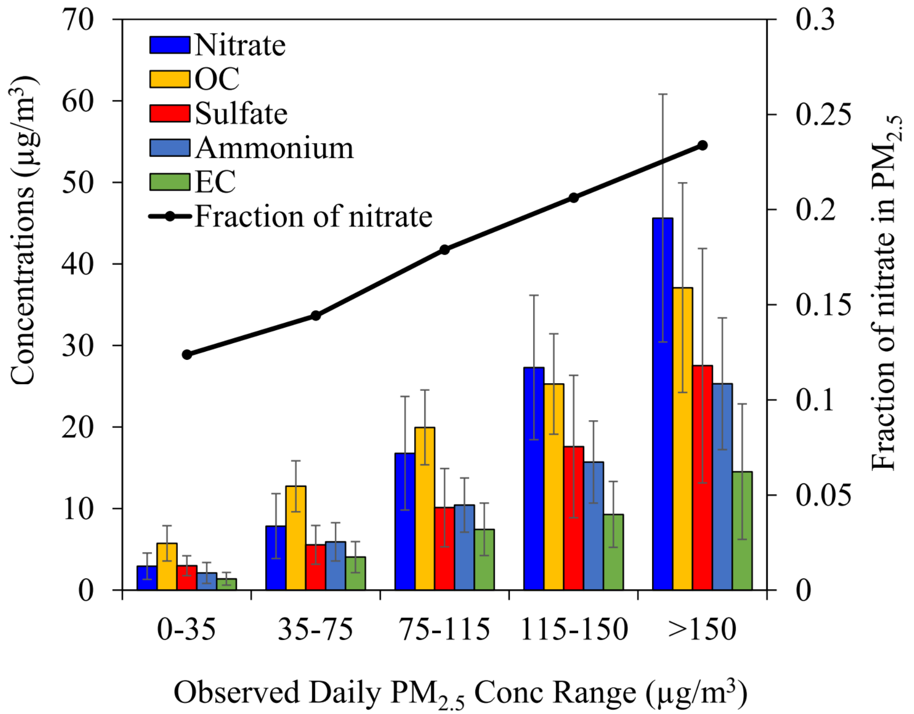
Ji'nan *(urban)*
PAN: 9.6 ppb
(Liu et al., 2018)

Regional observations of PM2.5 in Dec 2017

Nitrate



PM2.5 composition vs loading



Highest pollution occurs south of Beijing

- % of nitrate increases in heavy pollution
- Nitrate is more than sulfate

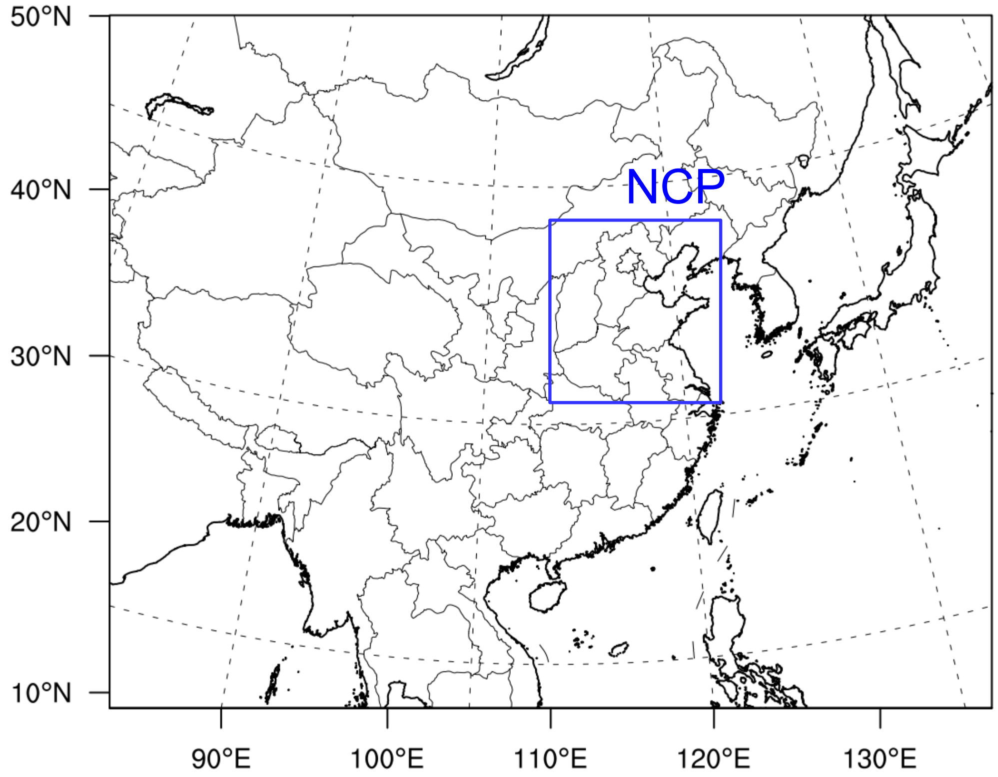
Model simulations of winter nitrate in Dec 2017

- Model simulation
  - CMAQ5.1 / WRF4.0
  - Domain: 36km, 12km
  - Period: 1-31 Dec. 2017

- CMAQ: SAPRC07tic + AERO6i
- WRF: Pleim-Xiu + ACM2 + RRTMG

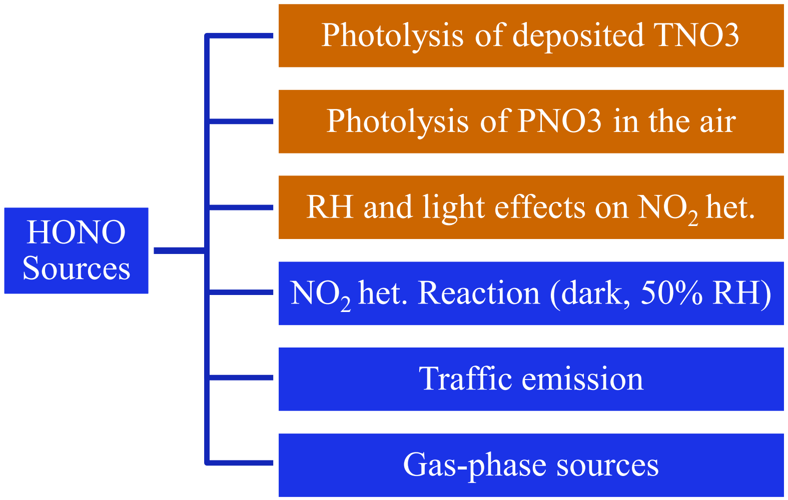
  The first guess fields: ds083.2 from NCEP

  Grid nudging: ds351.0 and ds461.0
- Emission: Tsinghua + MEGAN



Improving the model on reactive nitrogen chem.

HONO sources (Fu et al., 2019)



Location	Obs. period	Obs. average	Sim. average	Reference
ICCAS_Beijing	2014.12	1.34	2.40	Tong et al. (2016)
CEE_Beijing	2016.01	1.05	2.40	Wang et al. (2017)
EPA_Beijing	2015.02-03	1.99	2.40	Zhang et al. (2018)
Jinan_Shandong	2016.12-2017.02	1.75	1.92	Li et al. (2018)
Wangdu_Hebei	2017.12	2.27	0.81	unpublished data

N_2O_5 uptake (Yu et al., ACP, 2020)

$$\gamma(N_2O_5) = A k'_{2f}\left(1 - \frac{1}{\left(\frac{k_3[H_2O(l)]}{k_{2b}[NO_3^-]}\right) + 1 + \left(\frac{k_4[Cl^-]}{k_{2b}[NO_3^-]}\right)}\right).$$

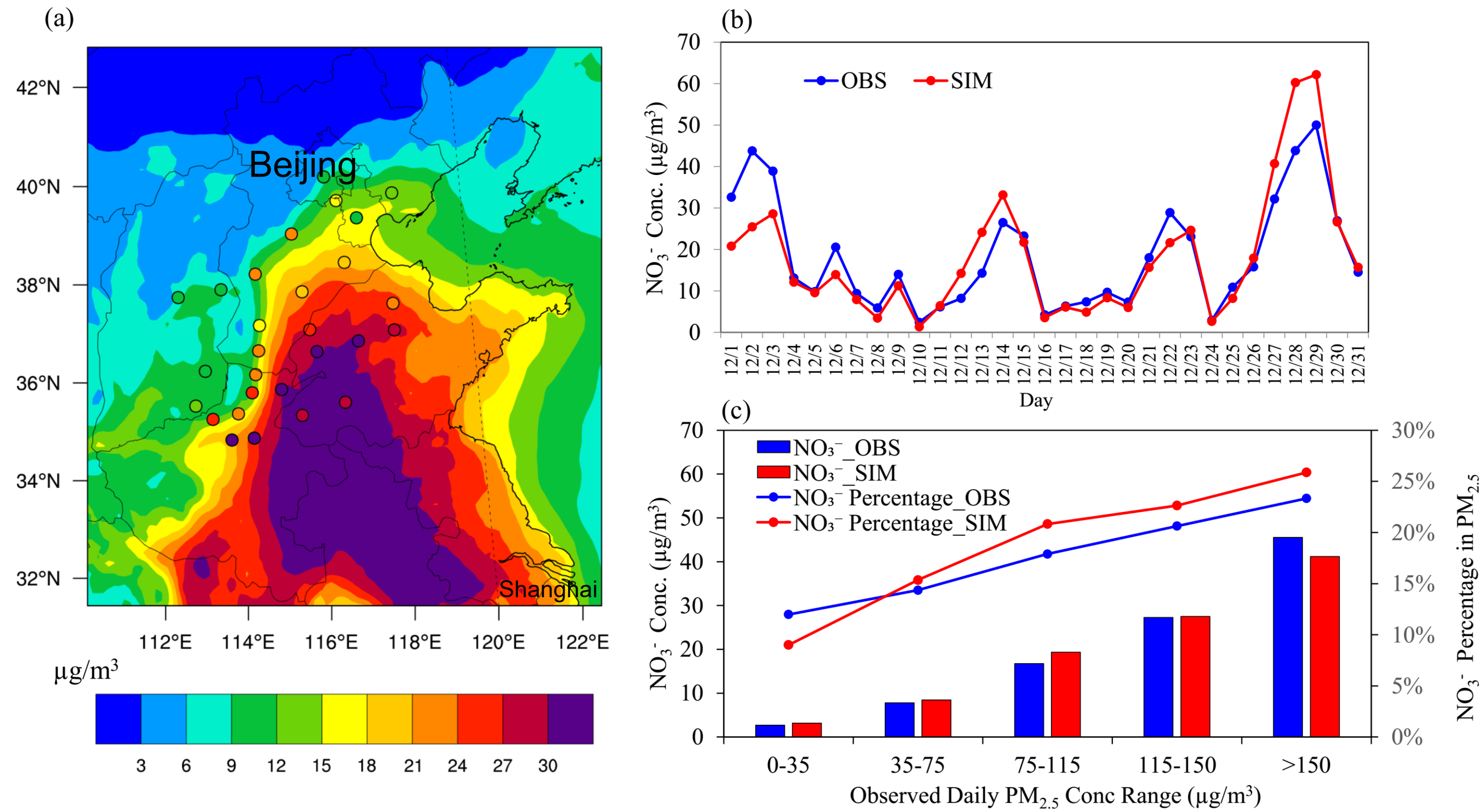
$k_{2f}' = \beta(1-\exp(-\delta[H_2O]))$
$\beta =$ （$11.5\pm3)\times10^5$； $\delta = 0.13\pm0.05$
$k_3/k_{2b} = 0.06\pm 0.01$
$k_4/k_{2b} = 29 \pm 6$

→

$k_{2f}' = k_{2f} * [H2O]$
$k_{2f} = 31823 \pm 5100$
$k_3/k_{2b} = 0.021\pm 0.011$
$k_4/k_{2b} = 2.9 \pm 1.2$

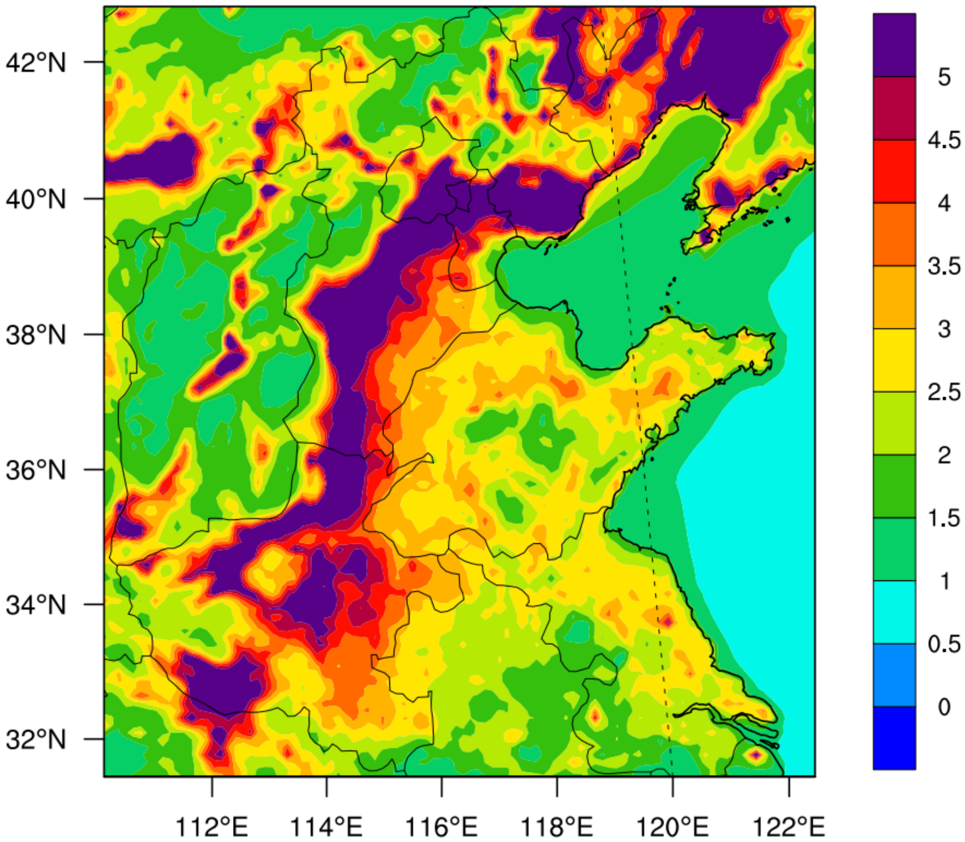
	$\gamma(N_2O_5)$
"Observed"	0.024±0.023
B&T para.	0.046±0.015
Modified	0.023±0.020

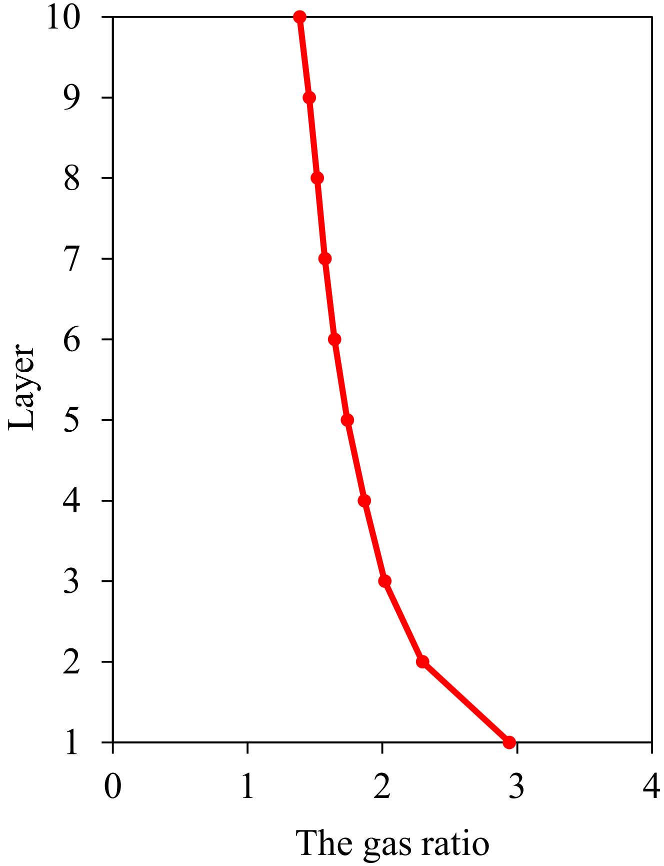
Improved simulations of NO_2 and nitrate in NCP



		OBS (µg m⁻³)	SIM (µg m⁻³)	Bias (µg m⁻³)	NMB (%)	NME (%)	R
NO_3^-	CAMQ default (BT09)	20.94	24.86	3.92	18.72	47.80	0.75
	CAMQ revised (Fitted)		20.98	0.04	0.19	41.70	0.75
NO_2	CAMQ default (BT09)	52.09	45.71	-6.38	-12.25	41.87	0.56
	CAMQ revised (Fitted)		47.89	-4.20	-8.06	41.33	0.58

NCP is a NH_3-rich environment in winter



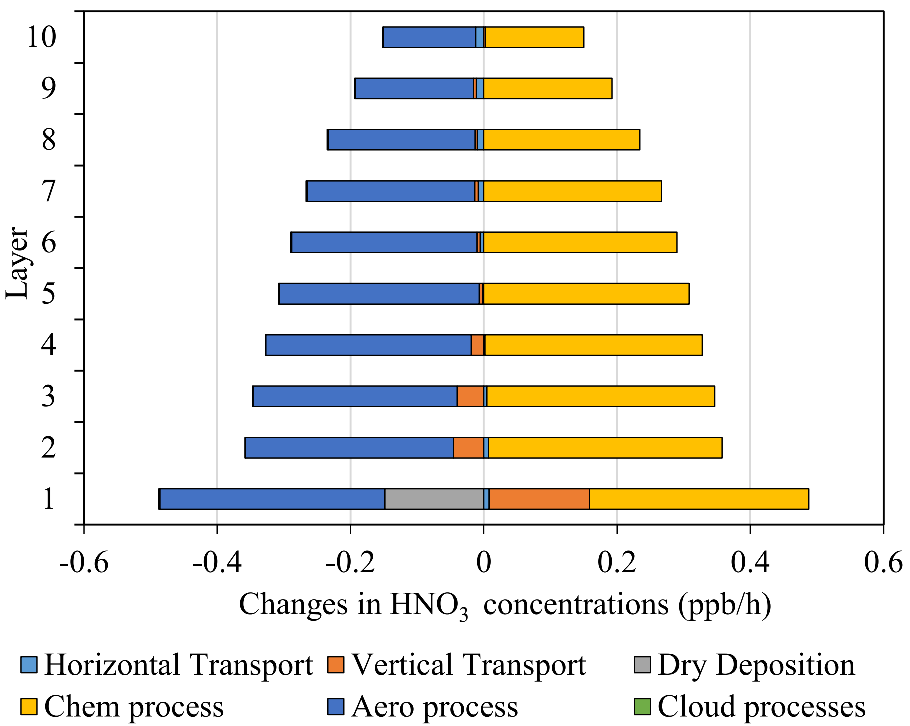


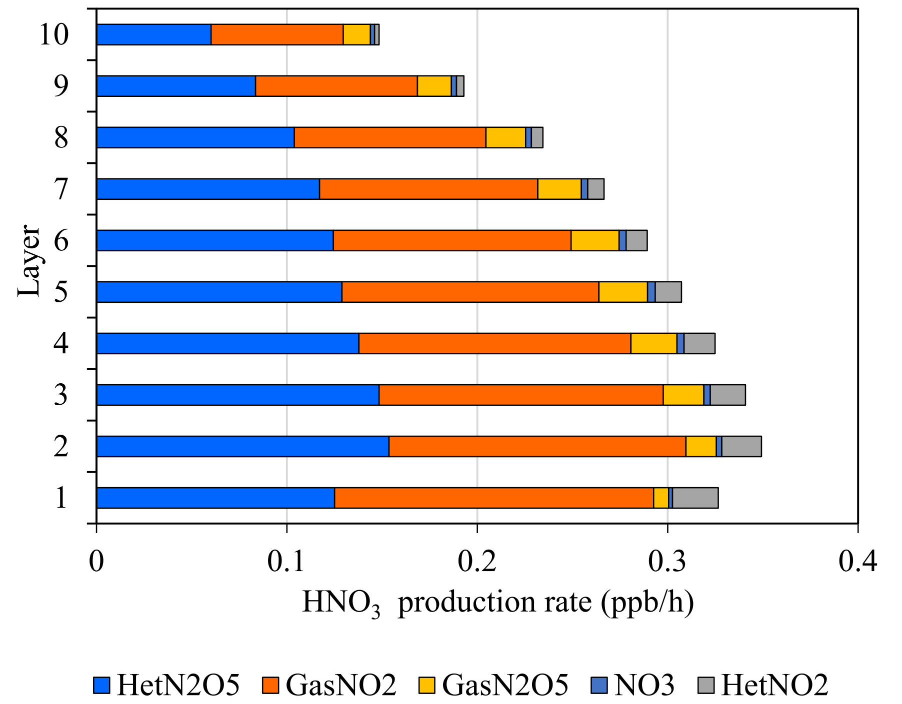
$$GR=\frac{\left([NH_3]+\left[NH_4^+\right]\right)-2\times\left[SO_4^{2-}\right]}{\left[NO_3^-\right]+[HNO_3]}$$

GR>1 indicates NH_3-rich conditions
0<GR<1 indicates NH_3-neutral conditions
GR<0 indicates NH_3-poor conditions

HNO_3 sources and sinks (region average)

Physical & chemical processes



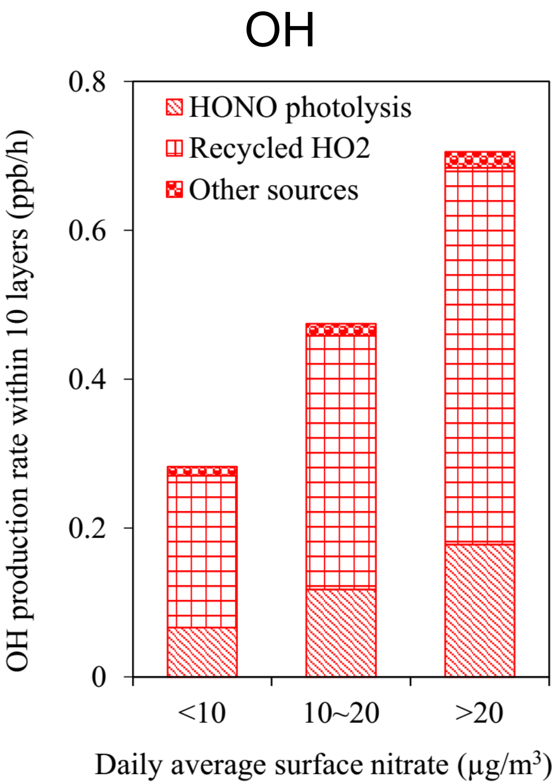


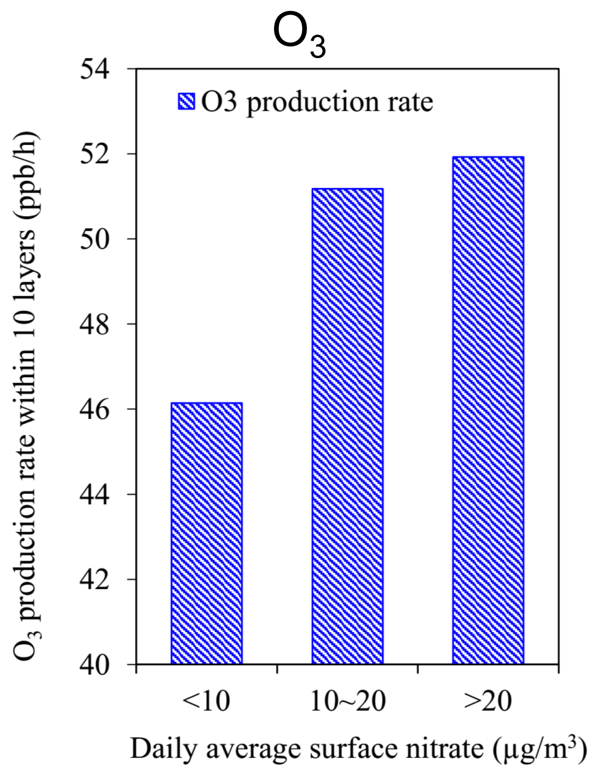
Layer 1=34 m, layer 5 = 322 m, layer 10=1184 m

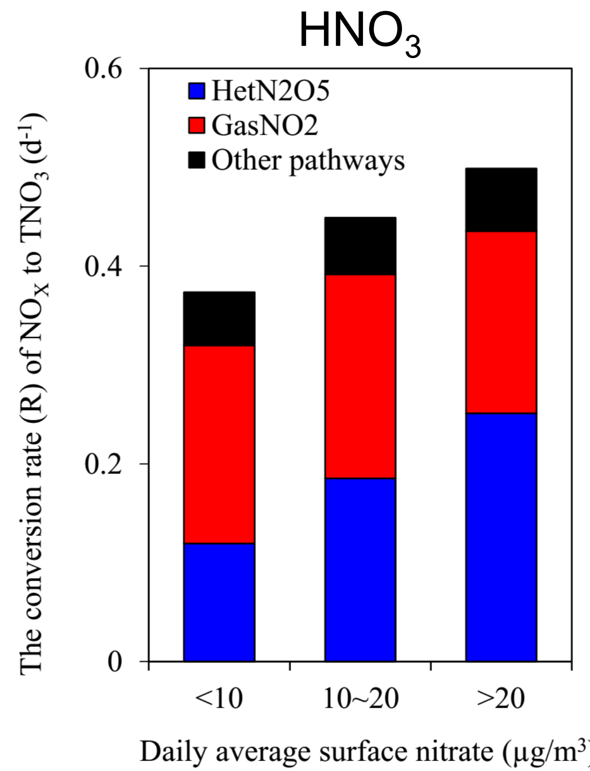
Comparable gas-phase and het. reaction, higher $OH+NO_2$ at surface

Downward contribution to surface nitrate

Increased production of oxidants and HNO_3 in heavy pollution





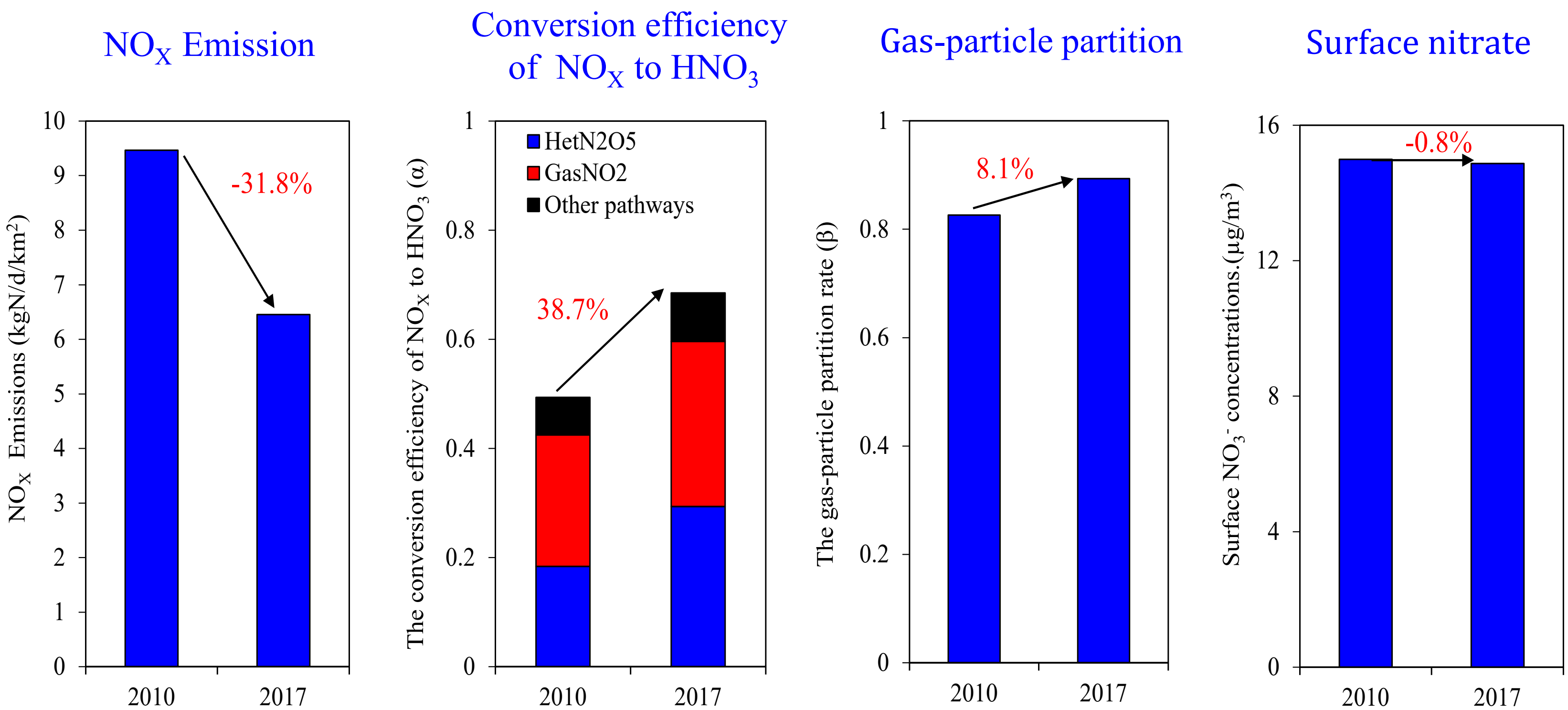


- Due to increase in HONO, OVOCs, NOx, RH, despite ~30% reduction in sunlight
- Increased N_2O_5 hydrolysis in heavy haze

Why no improvement of nitrate from 2010 to 2017?

Emission changes from 2010 to 2017 in the NCP:

SO_2 (-59.7%), NO_X (-31.8%), $PM_{2.5}$ (-38.6%), VOC (4%), NH_3 (0.2%)

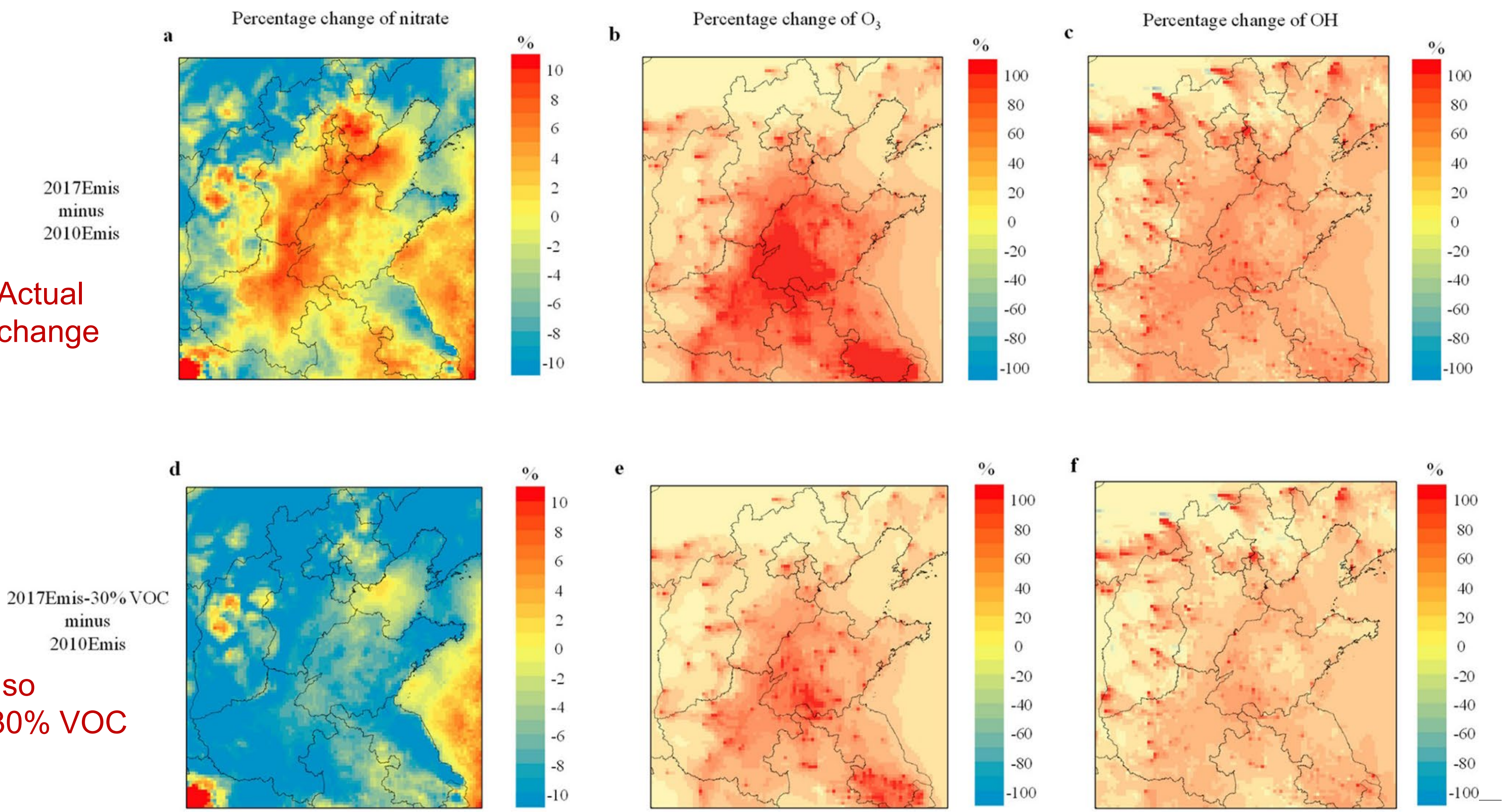


$$\alpha(TNO_3)=\frac{NO_X\ \text{mass converted to}\ HNO_3}{NO_X\ \text{mass emited}} \qquad \beta(NO_3^-)=\frac{[NO_3^-]}{[NO_3^-]+[HNO_3]}$$

$$NO_X \xrightarrow{OH,\ O_3} HNO_3 \longrightarrow ANO_3$$

VOC control would have reduced nitrate

2010-2017 Emission change: NO_x: -32%,SO_2: −60%, $PM_{2.5}$: −39% , VOCs: +4%, NH_3: +0.2%



Actual change

also -30% VOC

DOI: (10.1021/acs.est.9b07248)

Conclusion

- Winter photochemistry in NCP is active enough to drive the formation of nitrate, due to high conc. of oxidant precursors (e.g. HONO, VOC).
- The PM targeting emission control measures in the past decade increased O_3 and OH, offsetting the effectiveness of NO_X reduction.
- Future strategies should also reduce the oxidants, via larger NO_X and VOC control.

View of Mt Tai in NCP

Thank you!

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Article

Persistent Heavy Winter Nitrate Pollution Driven by Increased Photochemical Oxidants in Northern China

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Cite This: *Environ. Sci. Technol.* 2020, 54, 3881−3889

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