THE HONG KONG POLYTECHNIC UNIVERSITY
香港理工大學

Persistent winter nitrate pollution driven by increased oxidants in northern China

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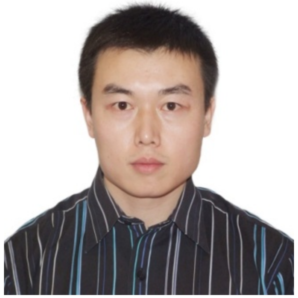

Workshop on Air quality in western US

Salt Lake City, 25-26 September 2019

Acknowledgement

- National Natural Science Foundation of China (91544213)

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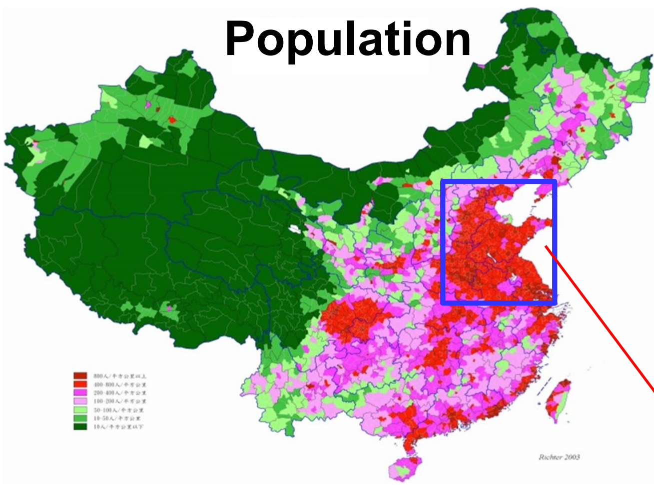
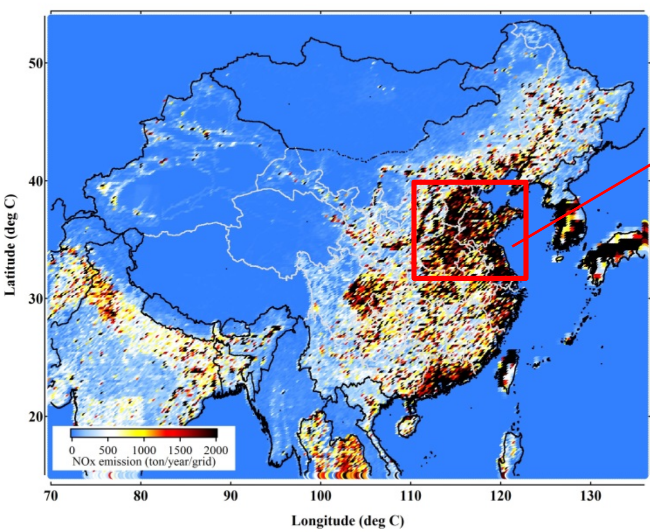
(ANR-RGC Joint research and Theme-based research T24-504/17-N)

Outline

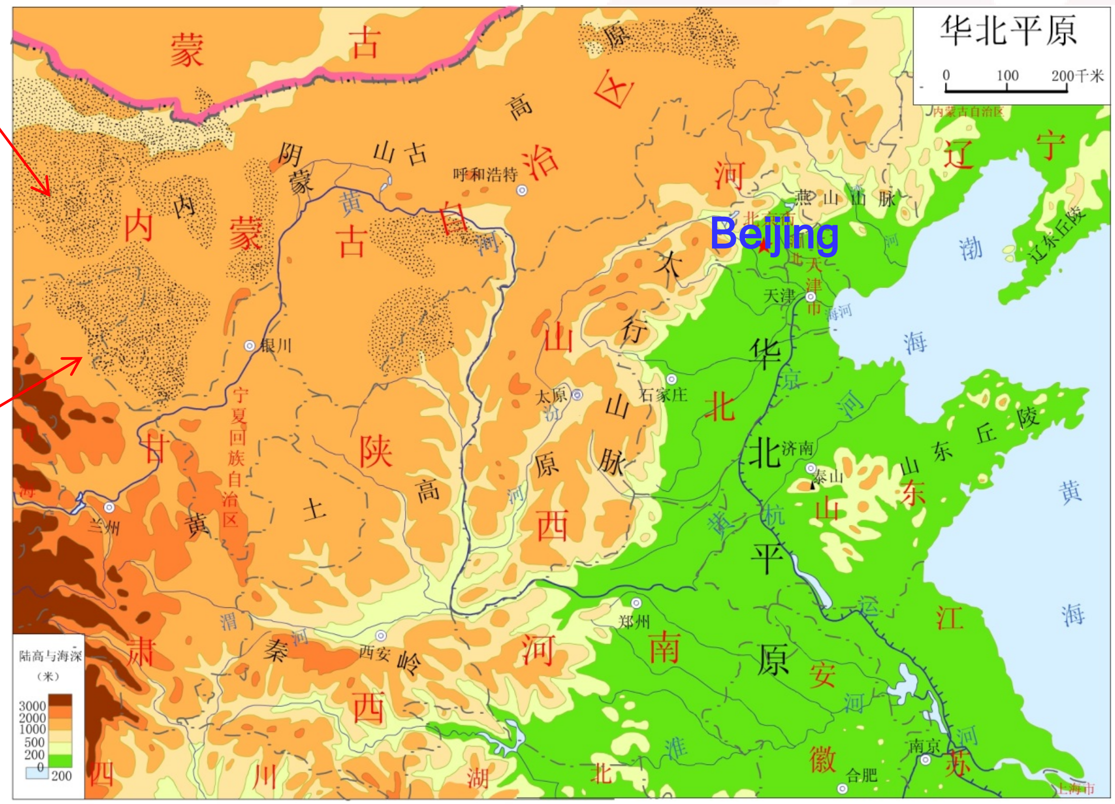
- Winer haze in the North China Plain (NCP)
- Nitrate observations in Dec 2017 in NCP
- Key factors controlling nitrate formation and trend (by model)

The North China Plain (NCP)





- **~0.3** million *km²* and **~1/5 Chinese population**
- Home to Beijing, Tianjin, Shandong, and part of Hebei, Henan, Jiangsu and Anhui



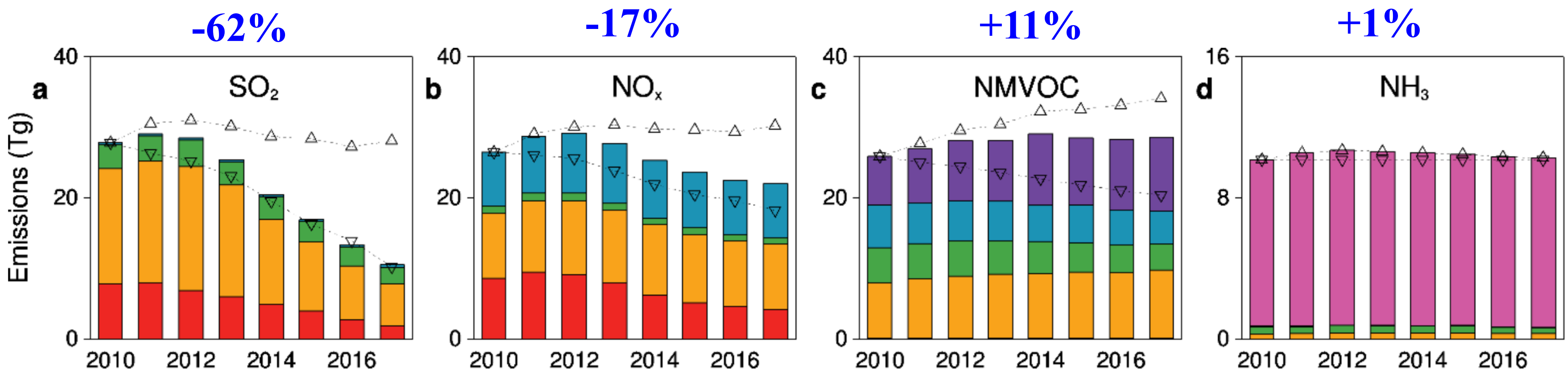
Severe winter haze in NCP

The “Bird Nest” Stadium in Beijing

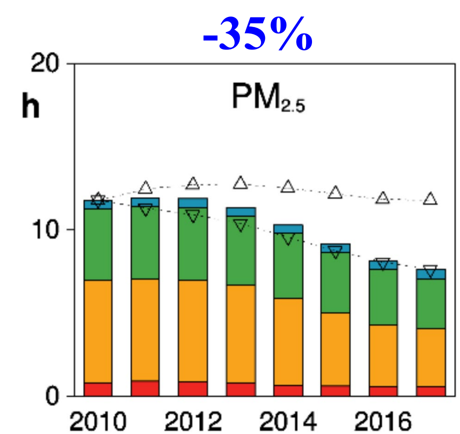
(Photo by Xinhua News Agency on 7 Dec 2015)

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

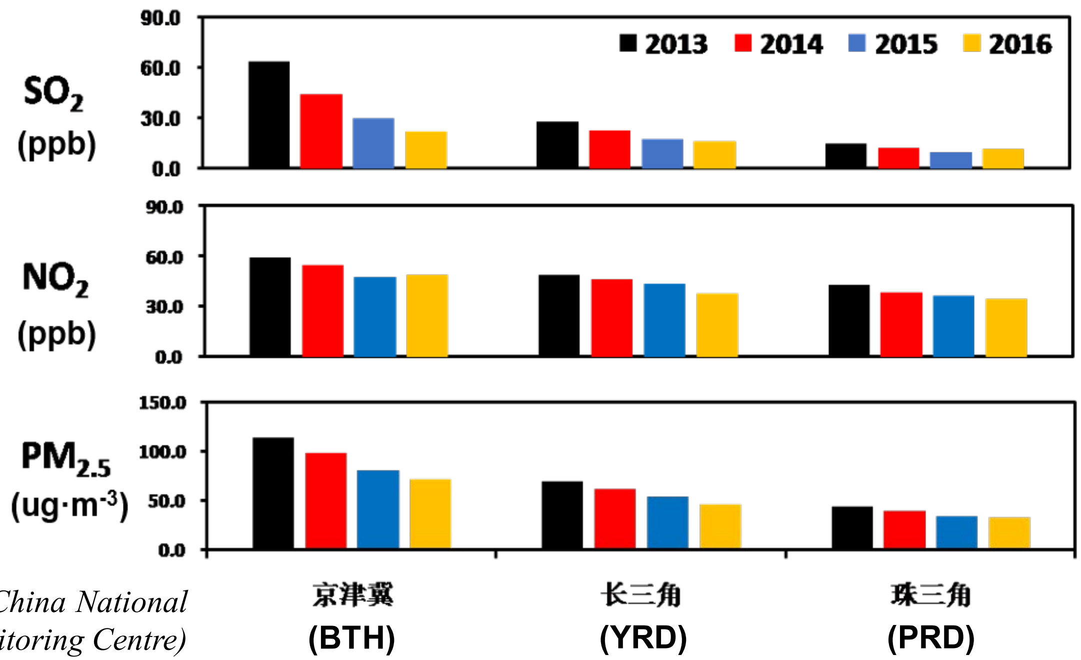
China emission changes (2010-2017)



Zheng et al., 2018

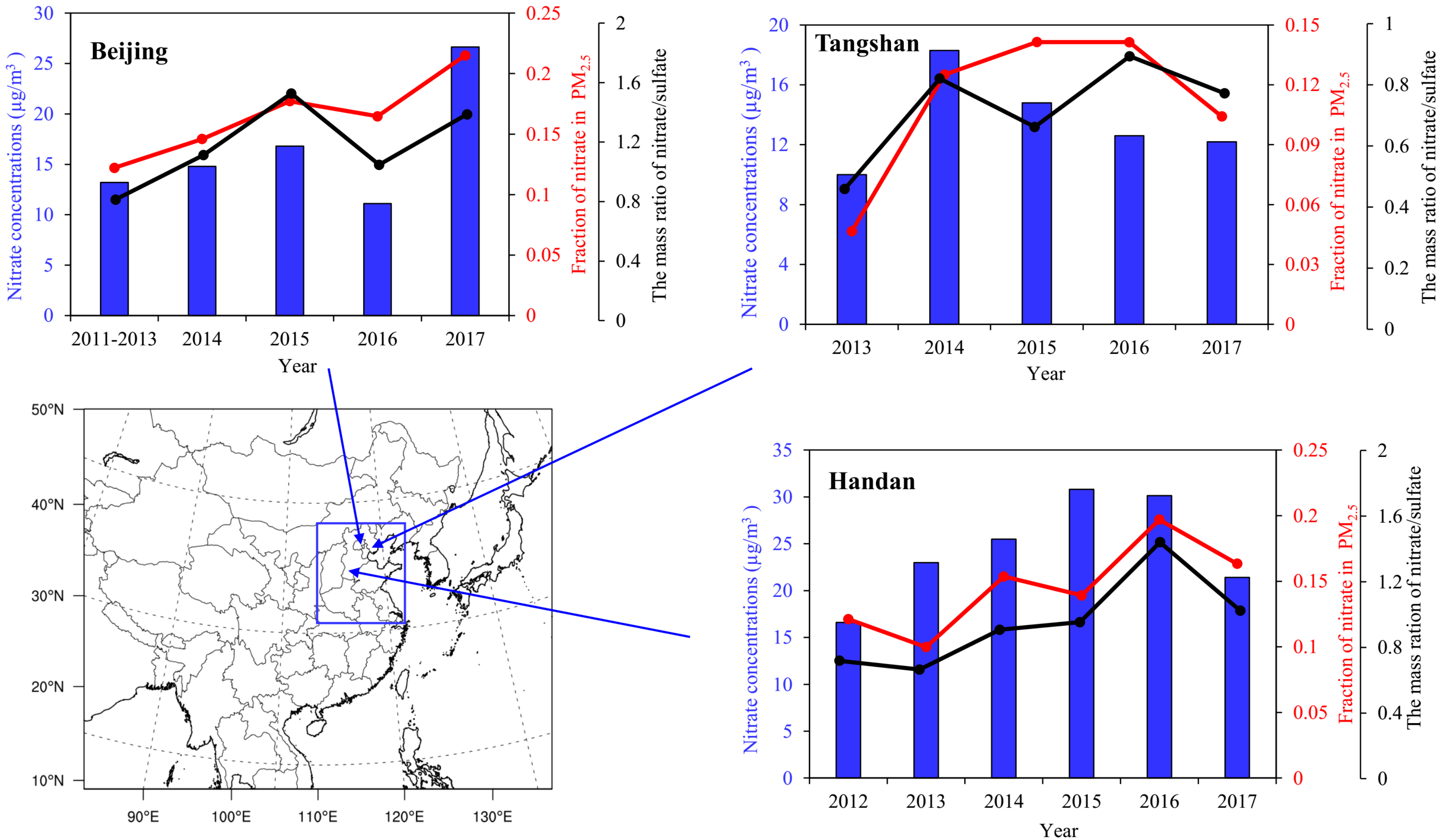


Atmos. conc. changes



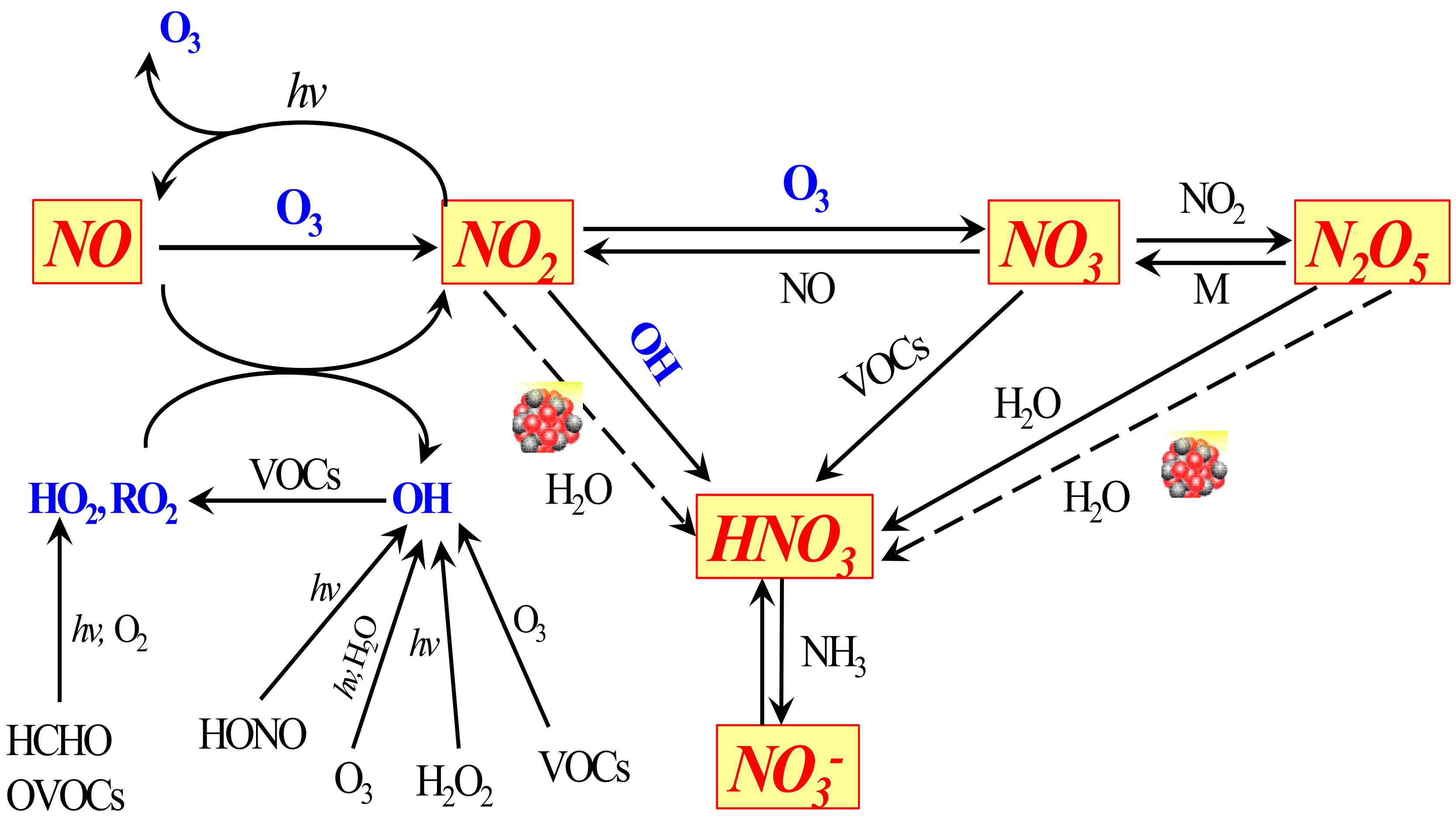
(Data source：China National Environmental Monitoring Centre)

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

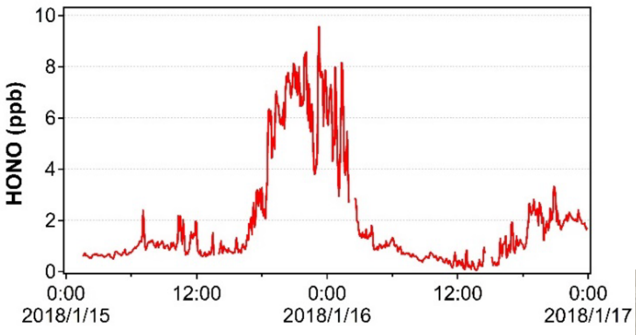


Three key processes: HNO_3 production by $OH+NO_2$ and N_2O_5 hydrolysis followed by reaction with NH_3

Three key ingredients: NO_x, oxidants, &NH_3

Evidence of active winter photochemistry

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



Elevated HONO in Beijing

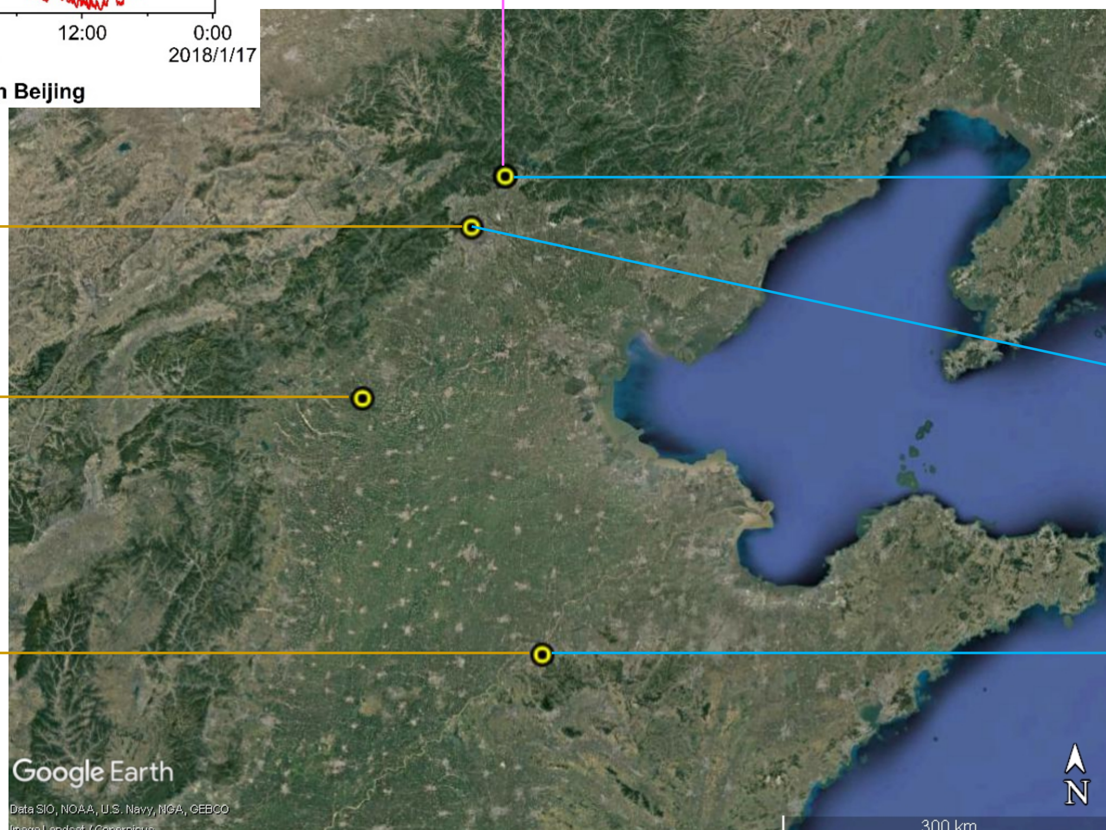
Salt Lake Valley
HONO: <1.5 ppb
(Kuprov et al., 2014)

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)

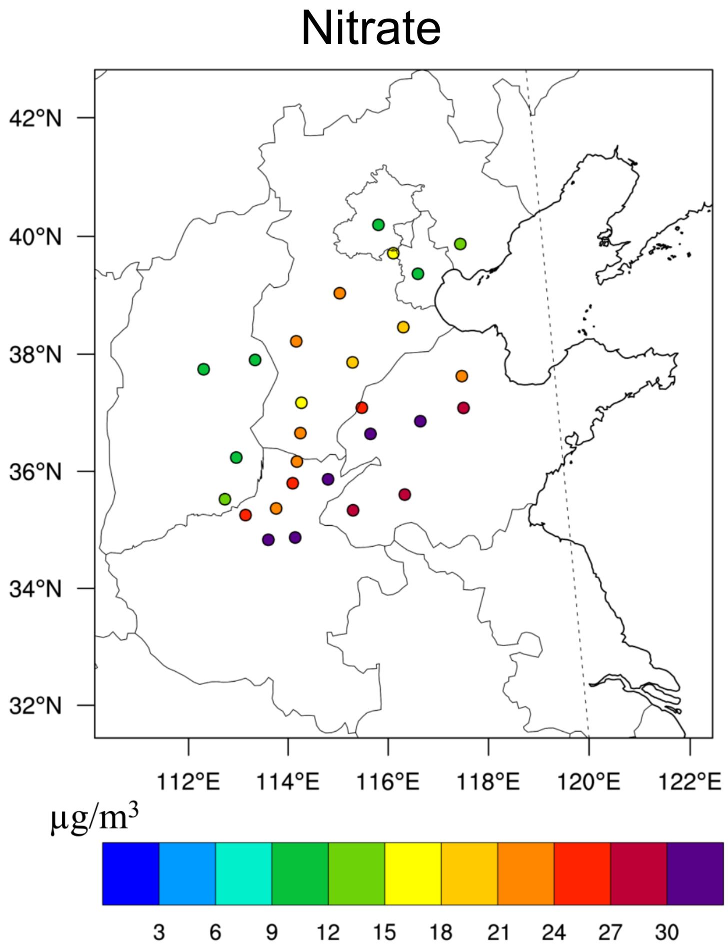


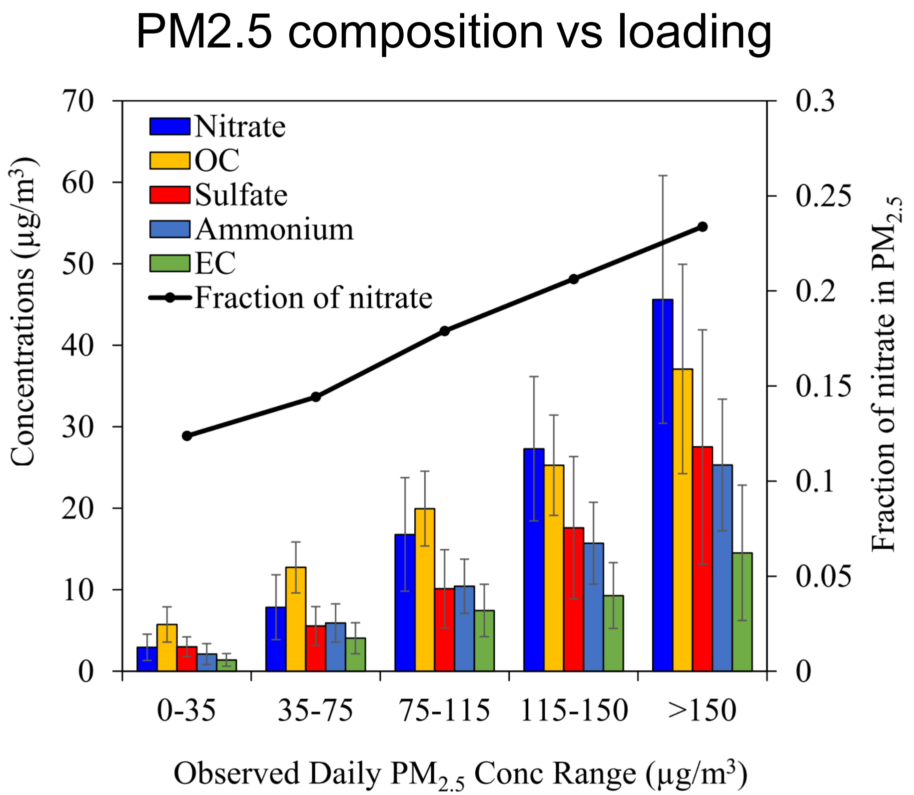
Beijing *(suburban)*
PAN: 6.0 ppb
(Zhang et al., 2019)

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





Salt Lake Valley (Jan-Feb 2009)

Nitrate: Max=50 ug·m-3, PM2.5 max ~100 ug·m-3

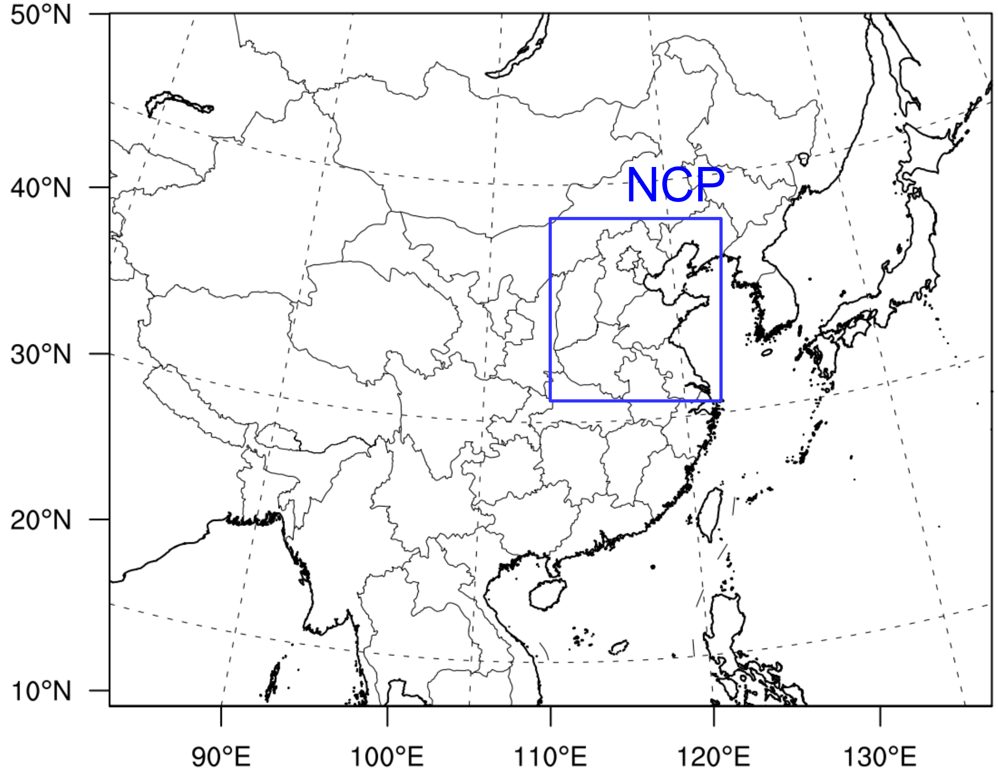
Nitrate percentage: mean=40%, max=69%

(Kuprov et al., 2014)

Model simulations of winter nitrate in Dec 2017

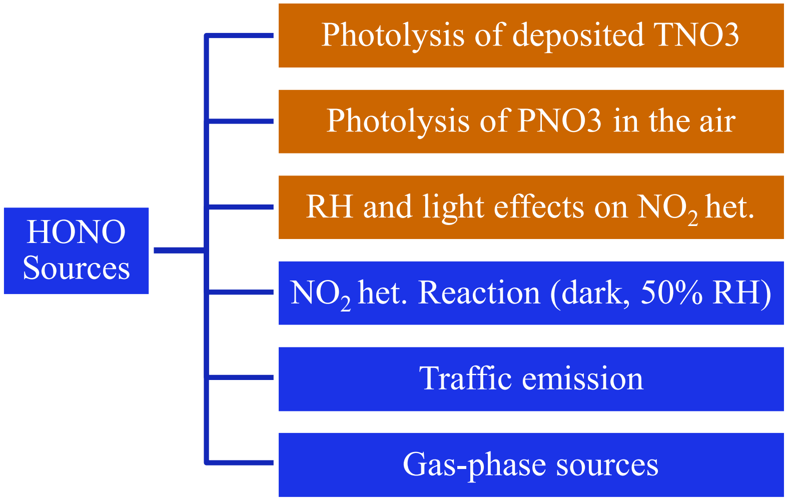
- Model simulation
  - CMAQ5.1 / WRF4.0
  - Domain: 36km, 12km
  - Period: 1-31 Dec. 2017

- 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., submitted)

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

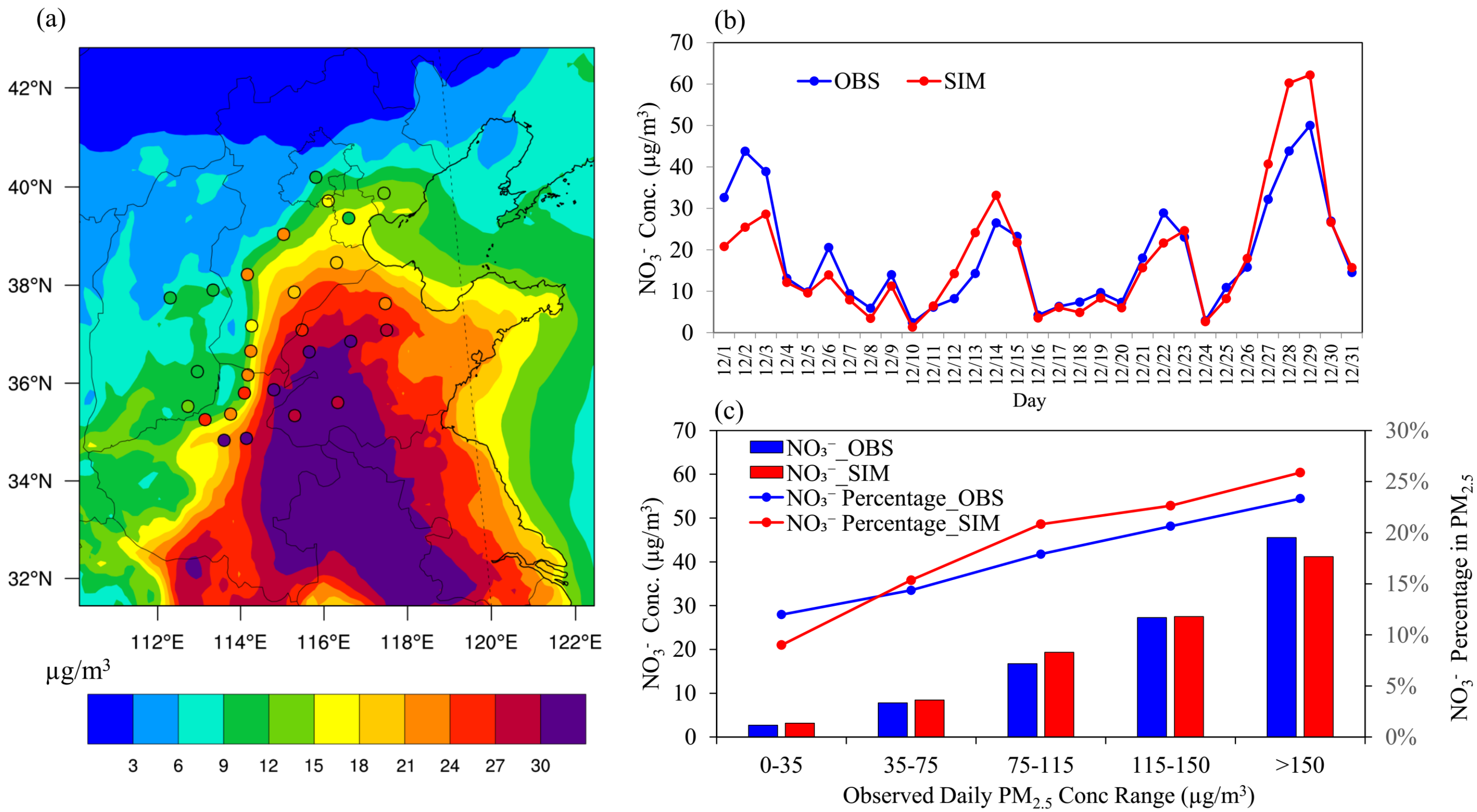
$k_{2f}' = \beta(1-\exp(-\delta[H_2O]))$
$\beta = (11.5\pm3)\times10^5$; $\delta = 0.13\pm0.05$
$k_3/k_{2b} = 0.06\pm 0.01$
$k_4/k_{2b} = 29 \pm 6$

→

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

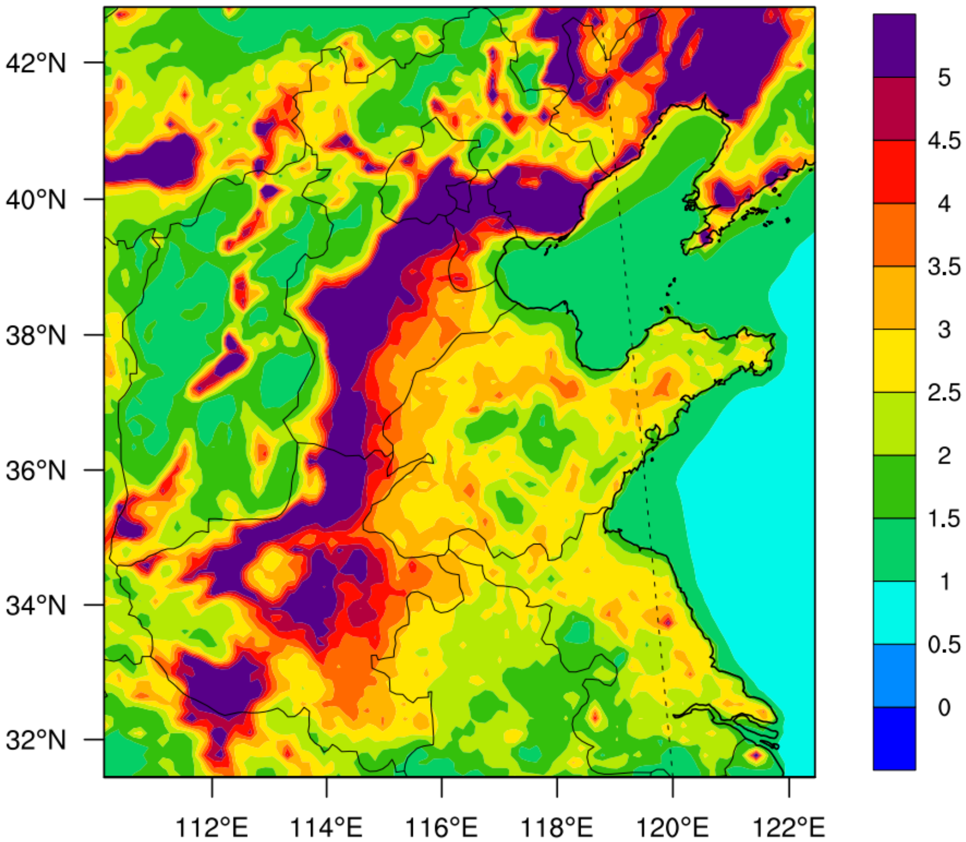
	$\gamma(N_2O_5)$
"Observed"	0.024±0.023
B&T para.	0.046±0.015
Modified	0.023±0.020

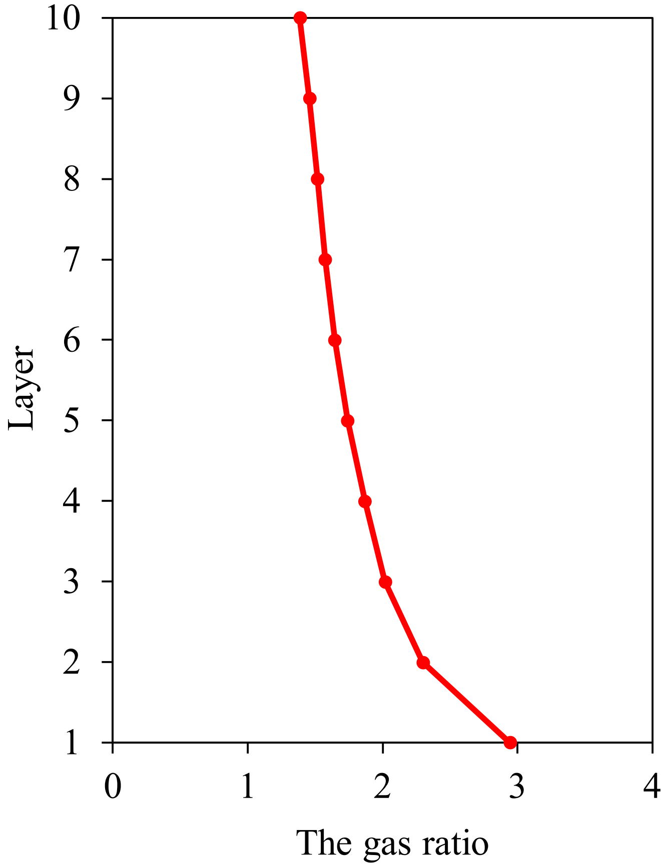
Improved simulations of NO_2 and nitrate in NCP



		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



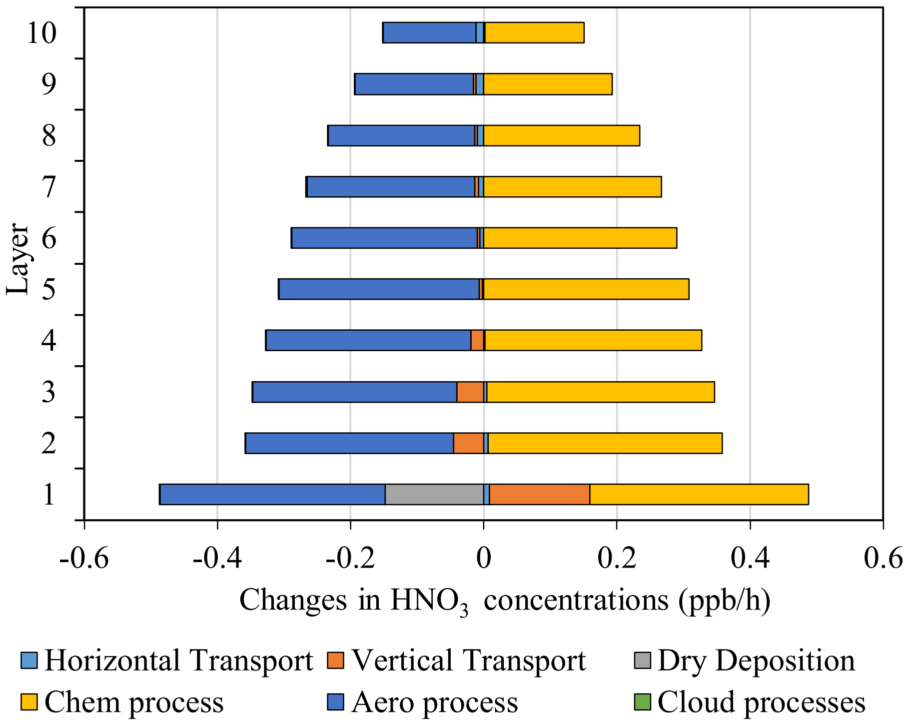


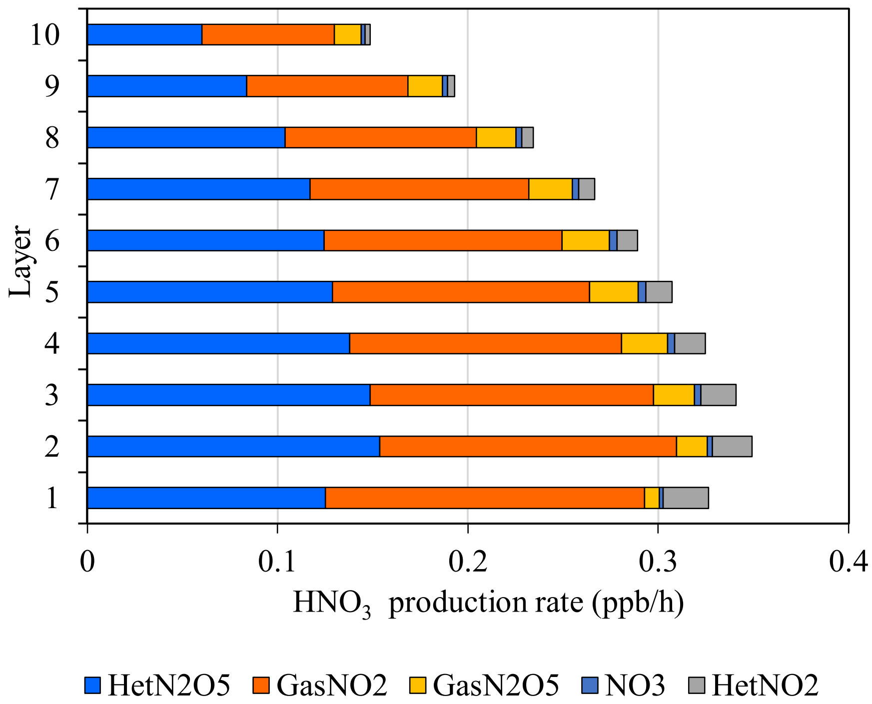
$$GR=\frac{\left([NH_3]+\left[NH_4^+\right]\right)-2\times\left[SO_4^{2-}\right]}{\left[NO_3^-\right]+\left[HNO_3\right]}$$

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



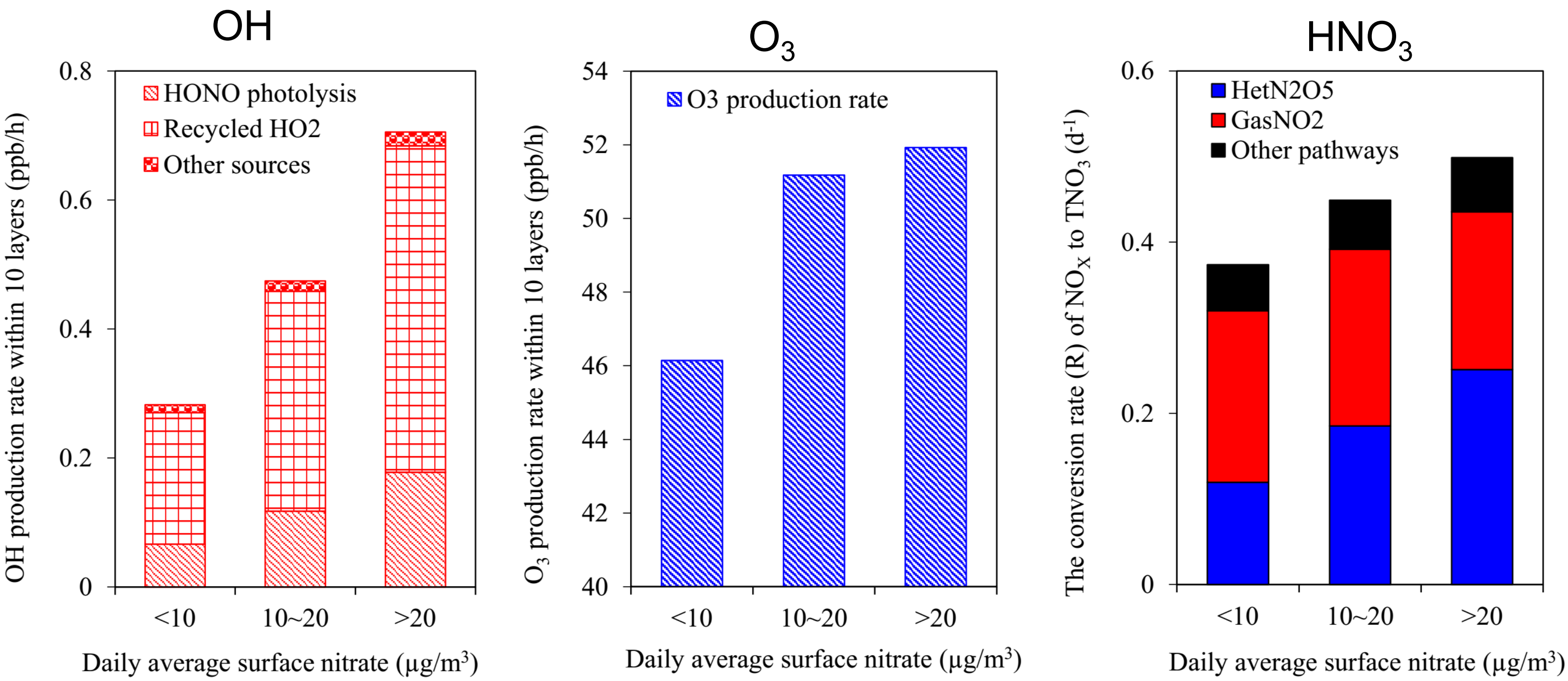


Layer 1=34 m, layer 5 = 322 m, layer 10=1184 m

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

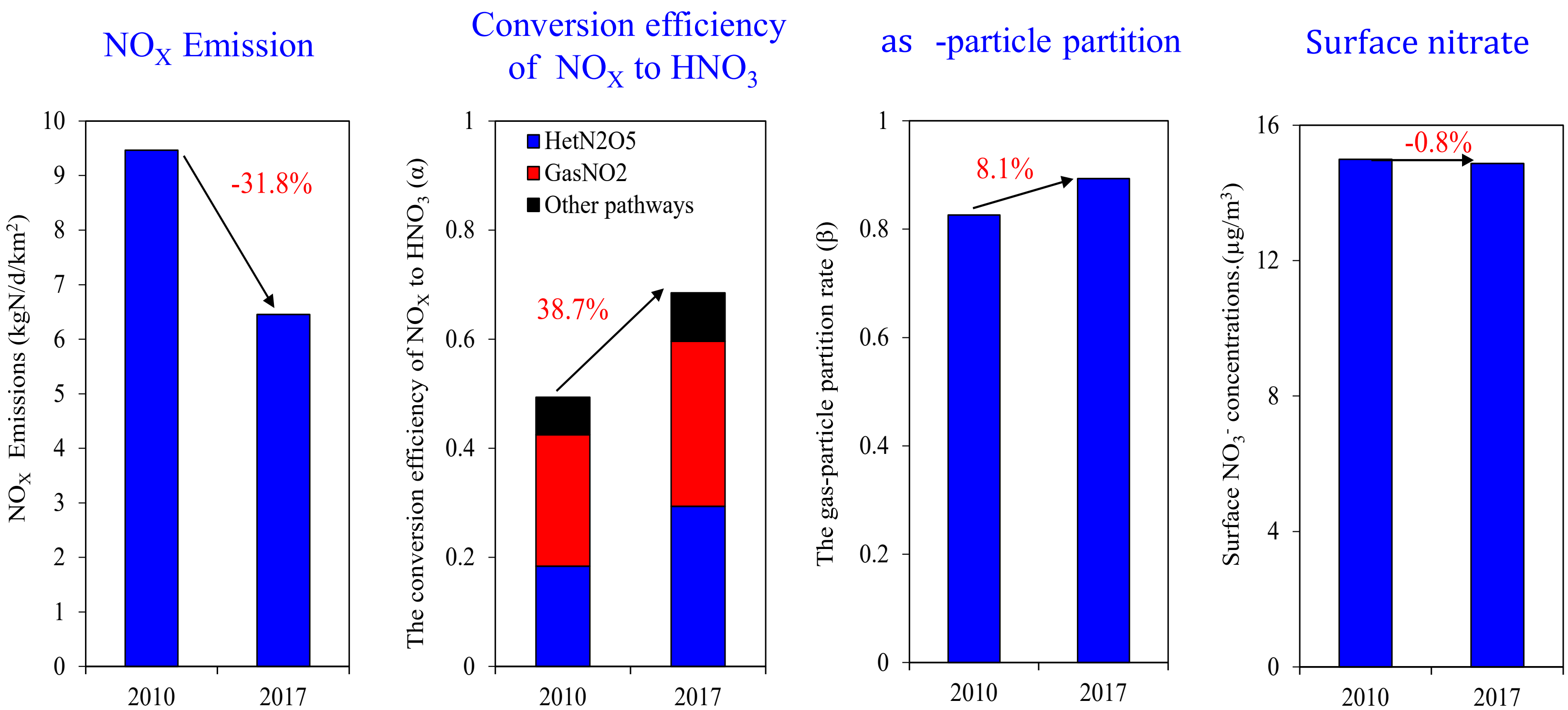


Due to increase in HONO, OVOCs, NOx, RH, despite ~30% reduction in sunlight

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%)



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

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

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 emission control measures (targeting PM) in the past decade increased O_3 and OH, which offset the effectiveness of NO_X emissions reduction.
- Future strategies should also reduce the oxidants, via larger NO_X and VOC emissions reduction. (-20% VOC, -8% nitrate)

Suggestions for AQURIUS

- **Spatial variations of PM composition in the western basins**

  - Integrate continuous (long-term) and intensive measurements

- **Drivers of the observed high nitrate**
  - Measure key oxidants and precursors (especially HONO)
  - Quantify the role of dynamic transport

- **Air quality models better represent HONO and N_2O_5 processes**

  - Incorporate observation-based findings to CTMs

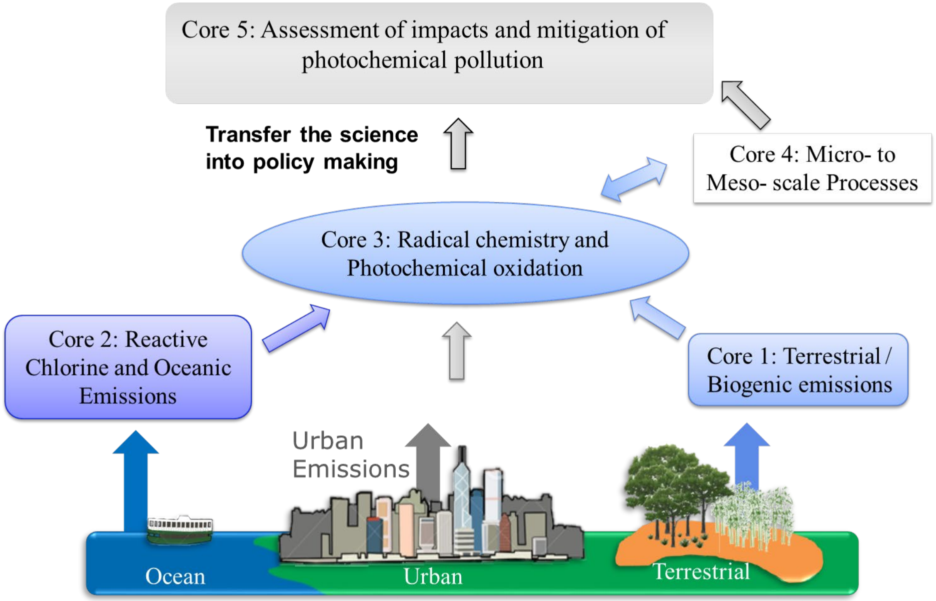

View of Mt Tai in NCP
Thank you!

Photochemical air pollution in highly urbanized subtropical regions

- from micro environ. to urban-terrestrial-oceanic interactions

<u>PC</u>: Tao WANG

<u>Co-PIs</u>: T Wang, G. Brasseur, S.C. Lee, H Guo, K.F. Ho, P. Louie, XM. Wang, Z. Wang



A newly funded Theme-based project of HK Research Grants Council (2018-2022, HK$33.33M, ~US$4.3 M)

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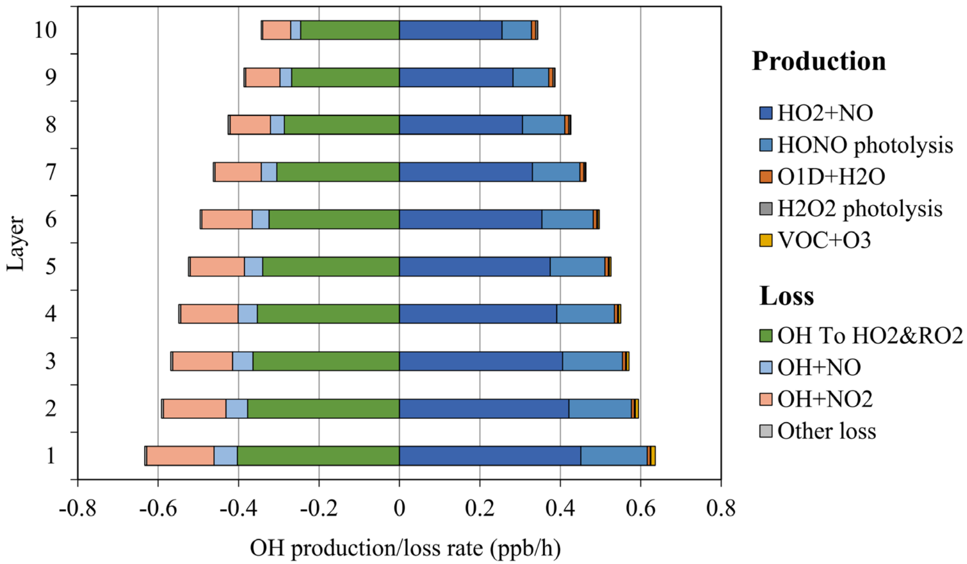
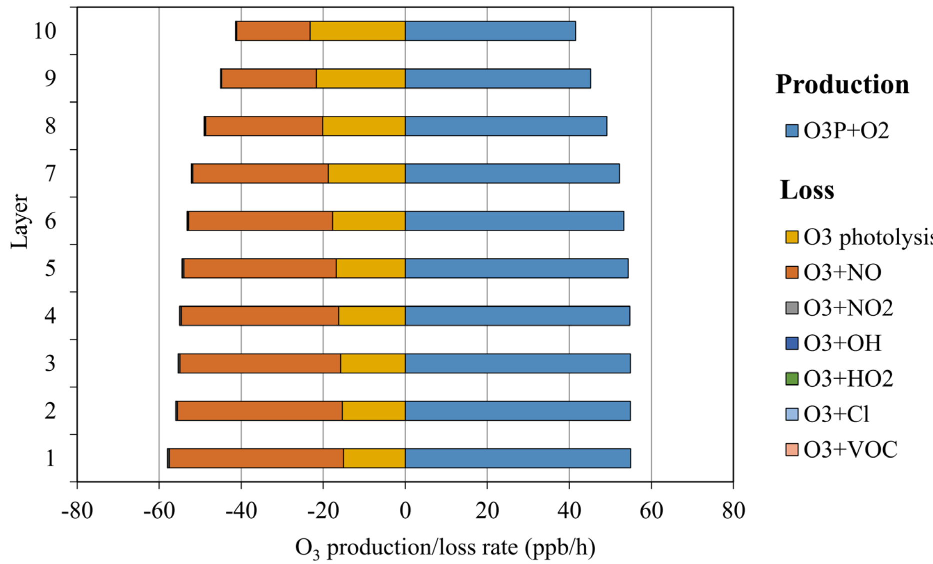
Oxidant sources and sinks (region average)

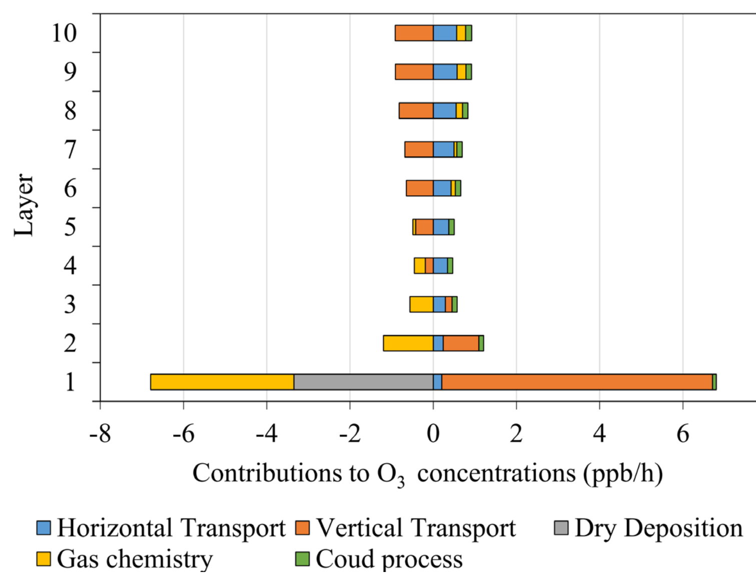




Source: HO_2+NO, HONO photolysis

Loss: OH+NO, OH+NO_2

Large O3 prod and loss rates



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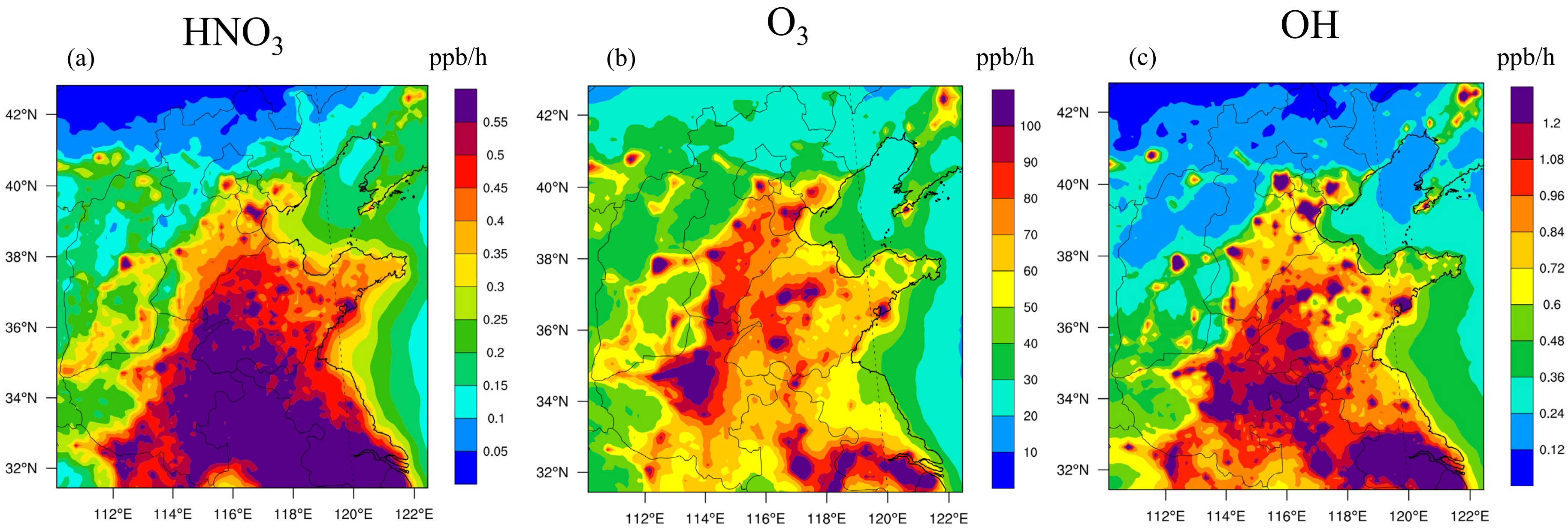
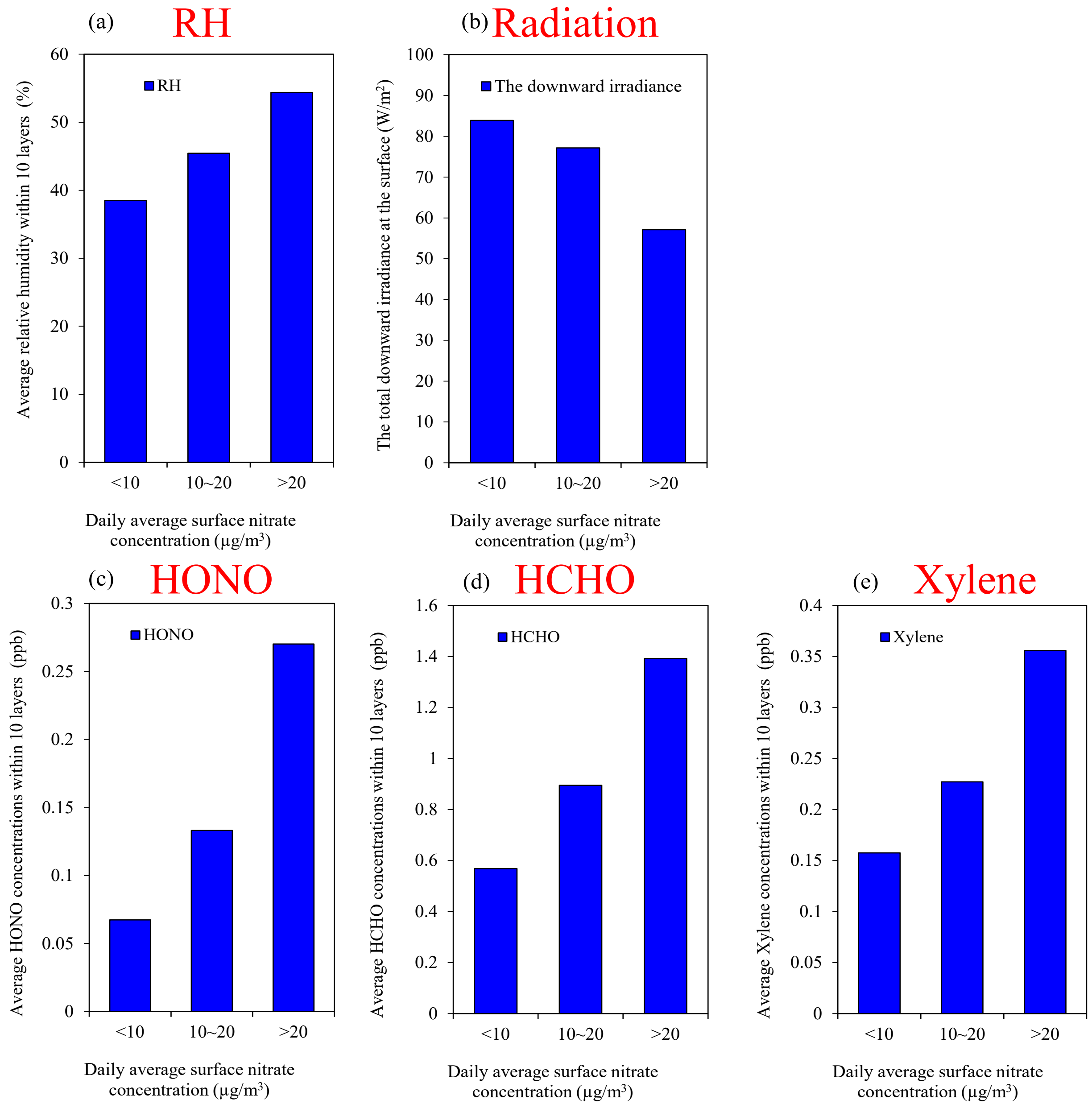
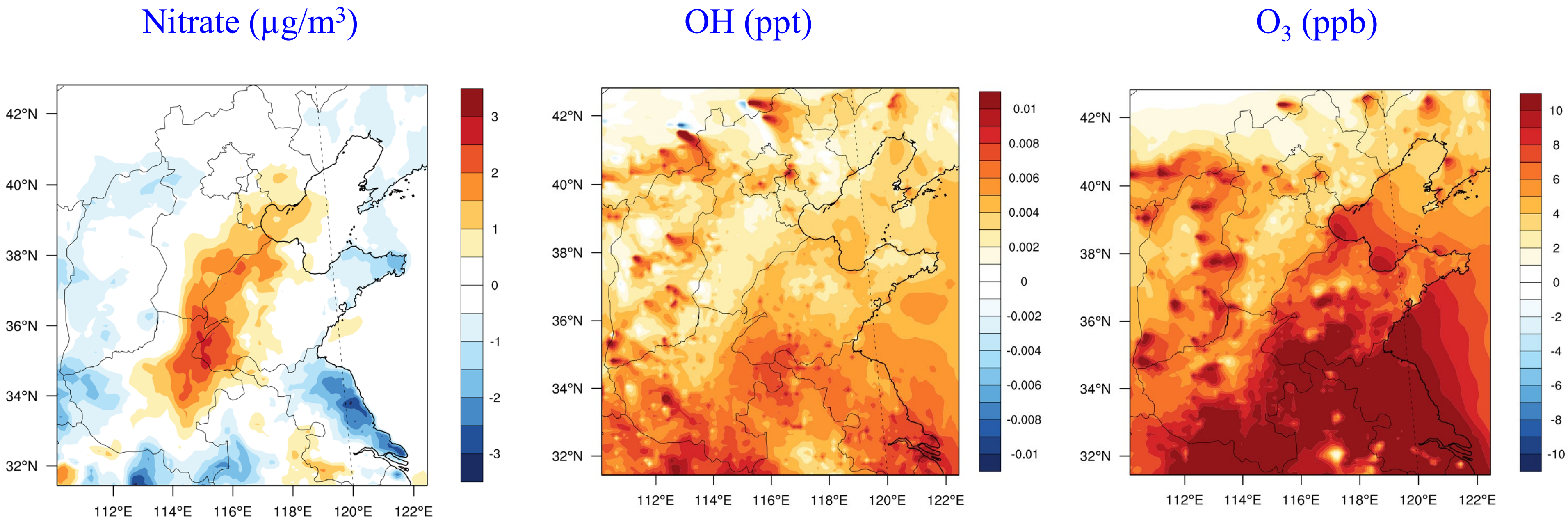
Production rates within 10 layers



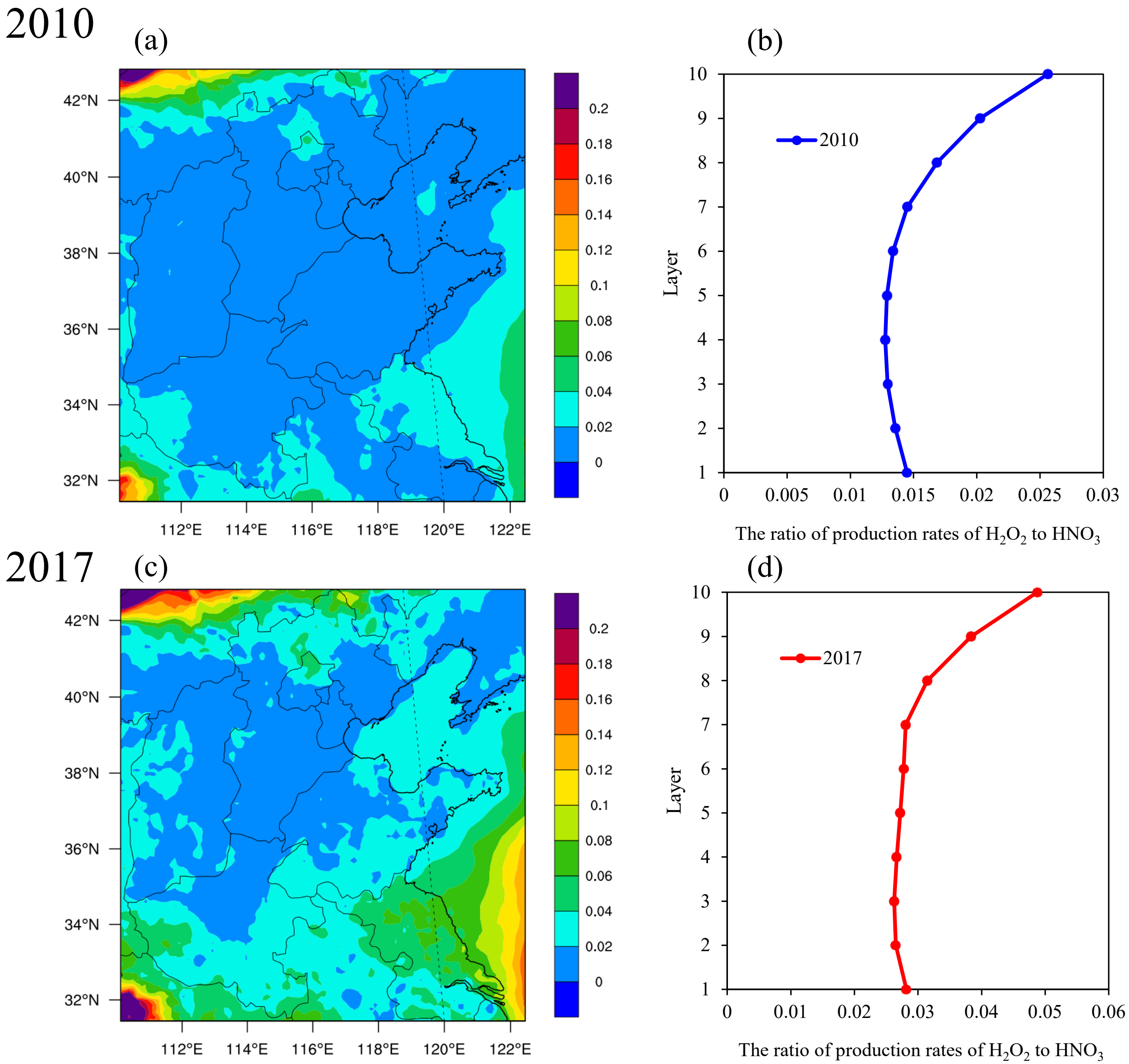
Changes under different nitrate pollution levels



Changes due to emission control from 2010 to 2017



NCP is under VOC-limited in winter



Production rates of H_2O_2 to HNO_3:
<0.06, VOC-limited
0.06–0.2, transition
and >0.2 NOx-limited