Heterogeneous production of nitrate in extreme haze

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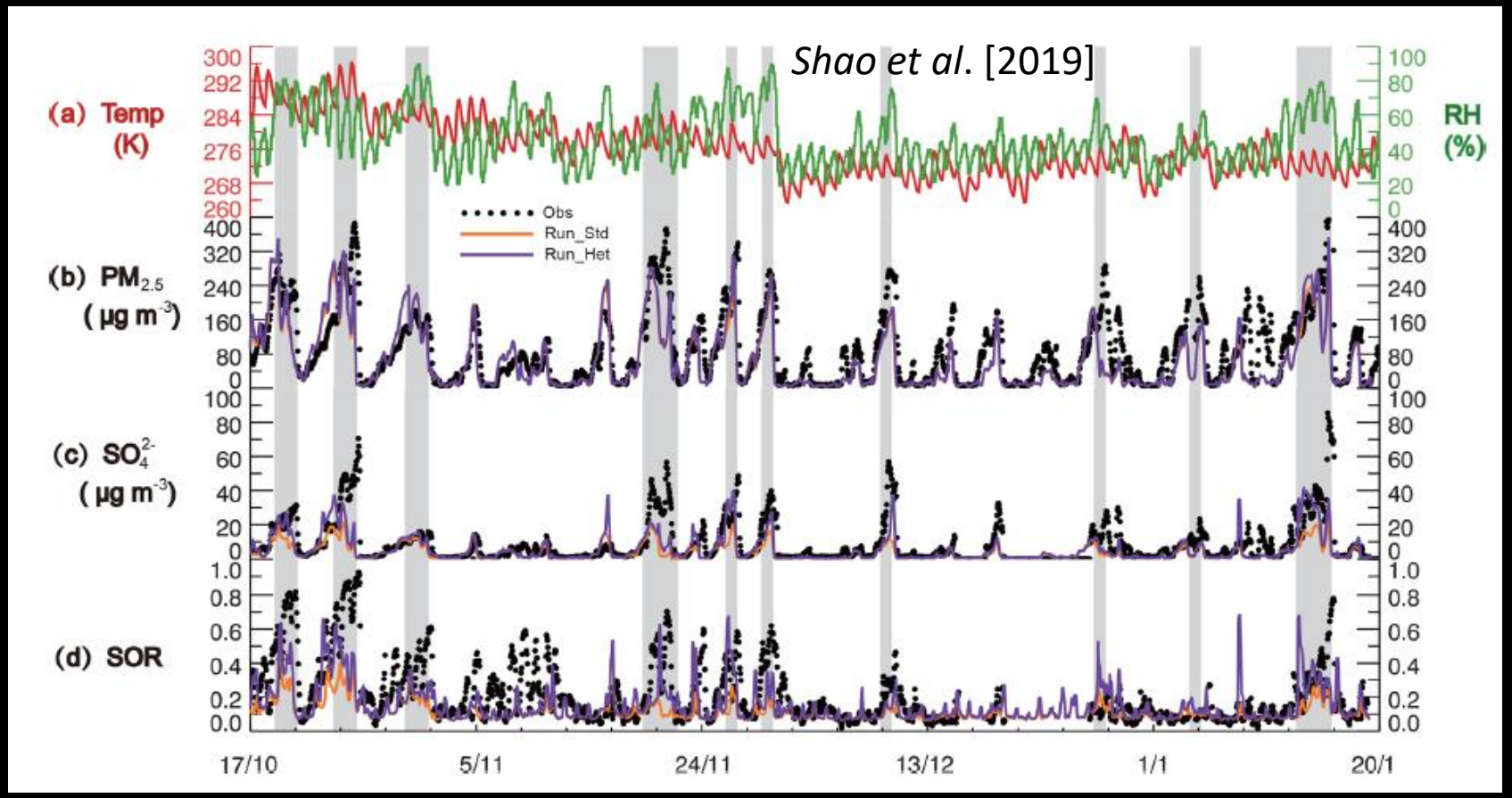
China $PM_{2.5}$ is underestimated in air quality models



Much of this underestimate in $PM_{2.5}$ is thought to be due to a model low bias in sulfate/HMS.

In contrast, the nitrate mass fraction is overestimated in models.

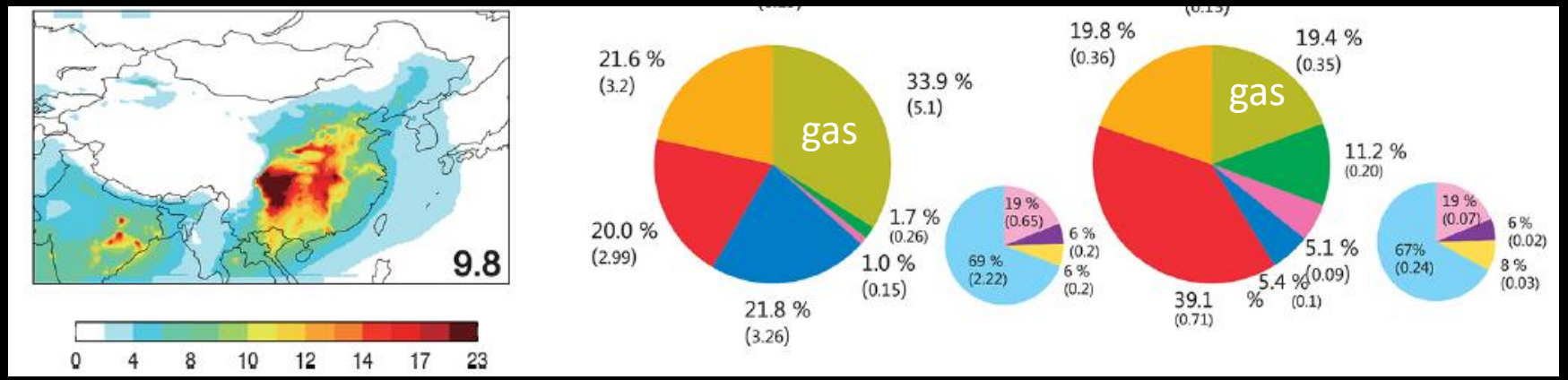
Importance of nitrate formation in Beijing air

- Nitrate is one of the major inorganic aerosol species (10-15% in winter in Beijing).
- Nitrate is becoming more important during wintertime haze events in China after a national regulation of SO_2 emission was introduced.
- Models have high bias relative to observed nitrate concentrations. It is thought that most nitrate forms through heterogeneous chemistry in winter.
- Heterogeneous chemistry of NO_y may influence radical budgets (via HONO and $ClNO_2$ formation)
- …and thus affect the production rate of O_3, organic aerosols and sulfate.

Heterogeneous NO_x chemistry as a source of HONO?

Fractional contributions of sulfate formation pathways

Sulfate [μg m^{-3}] **Polluted** **Clean**



Shao et al. [2019]

Increase in gas-phase sulfate production (SO_2 + OH) from clean (19%) to polluted (34%) conditions due to increase in OH resulting from production of HONO from heterogeneous uptake of NO_2 in the model.

Nitrate formation in Beijing in GEOS-Chem: $\Delta^{17}O$(nitrate)

Emission of NO_x ($NO+NO_2$)

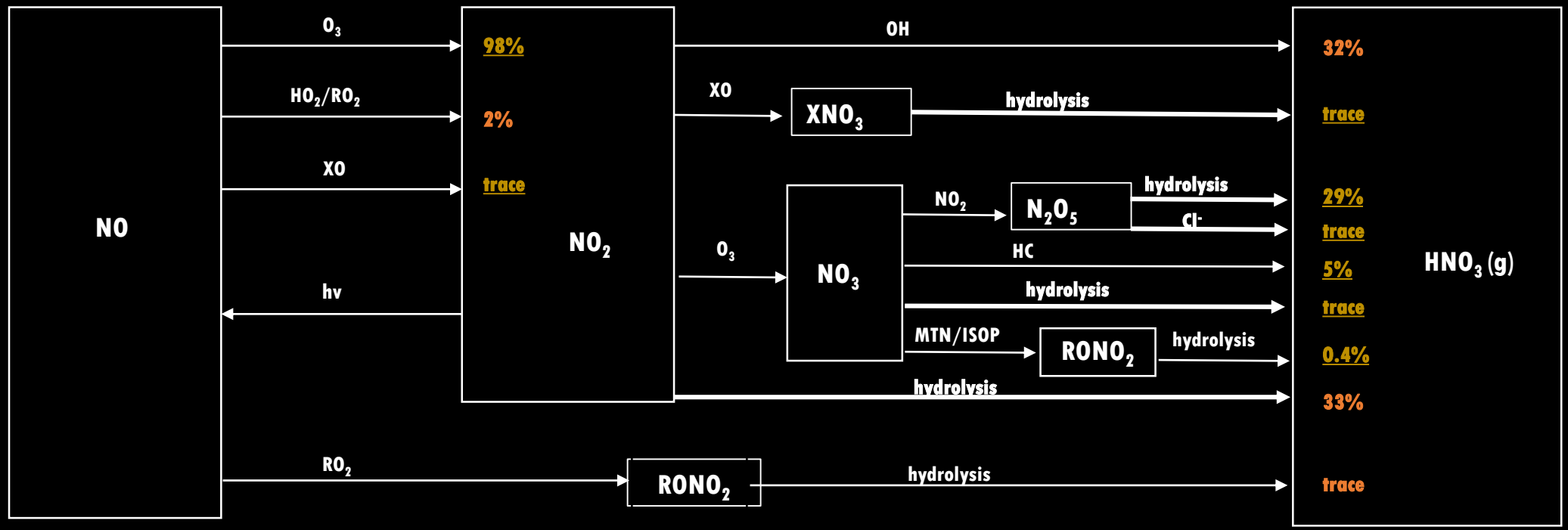
Conversion to NO_3^- (aerosol) from HNO_3 (g)

Tropospheric chemistry of NO_y

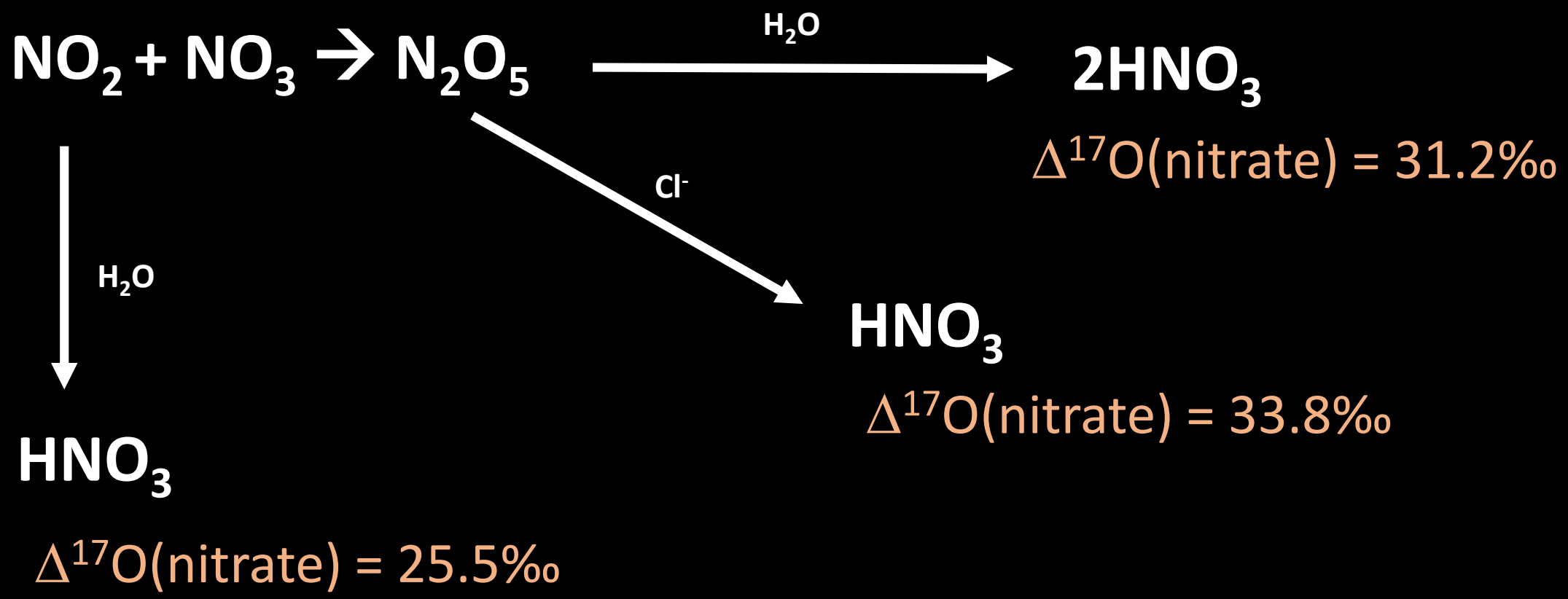
Heterogeneous reactions

Reaction with low $\Delta^{17}O$

Reaction with high $\Delta^{17}O$



Heterogeneous nitrate formation: $\Delta^{17}O$(nitrate)



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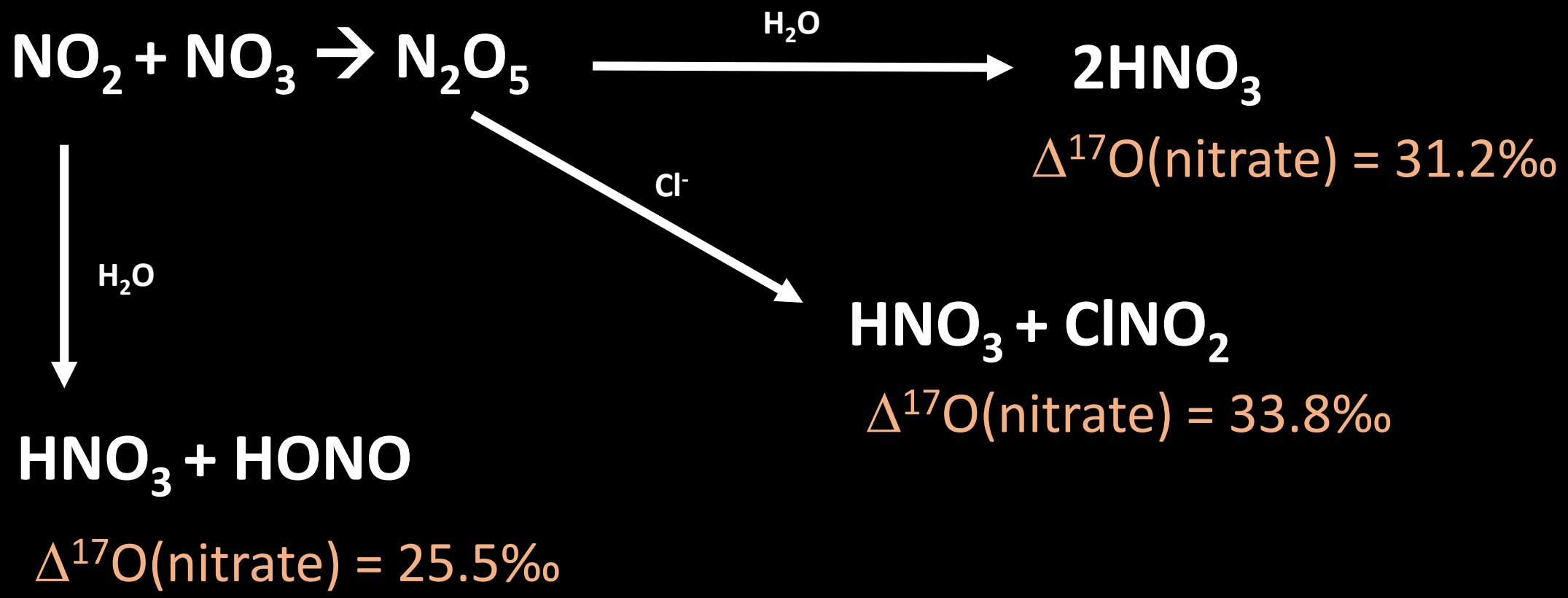


Research questions

1. What is the role of heterogeneous chemistry of reactive nitrogen (NO_y) for nitrate formation during winter extreme haze events in northern China? What is the dominating mechanism?

2. What are the implications of heterogeneous NO_y chemistry for radical formation in polluted, urban air?

3. What are the implications for mitigation strategies for improving air quality in Asian metropolitan regions?

GEOS-Chem (GC) 3D global chemical transport model

- A state-of-the-art numeric global model developed for simulating tropospheric chemistry
- Driven by GEOS-FP meteorological data assimilation products (native resolution: 0.5° latitude x 0.625° longitude x 72 vertical levels)
- Simulates the HO_x-NO_x-VOC-ozone-halogen-aerosol chemistry in the troposphere dynamically
- Calculates aerosol thermodynamical equilibrium using ISORROPIA II module
- Spatial resolution for the GC simulations: 4° latitude x 5° longitude and 47 vertical levels
- Simulation period: Oct 2014 – Jan 2015

GEOS Chem

Measurements and observations

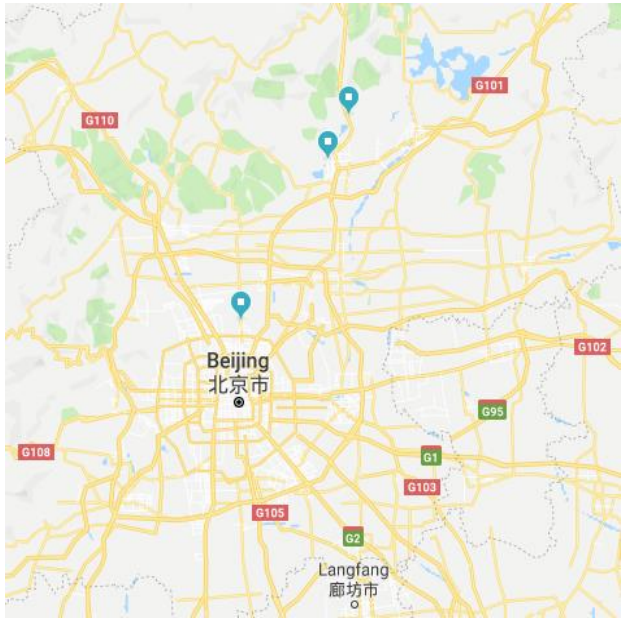
- Two independent datasets of $\Delta^{17}O(NO_3^-)$ measurements for aerosol sampled in Beijing conducted at UW IsoLab:

    1. From *He et al.* (2018); Samples collected during several hazy episodes in Oct 2014 to Jan 2015;
    2. From *Wang et al.* (2019); Samples collected every Wednesday and Sunday in 2014;

- Ground-based measurement of other gas species (e.g., NO_2, ozone) from the same studies above

- Ground-based measurement of HONO concentration in Jinan in 2015-16 winter (another major city in northern China) from *Li et al.* (2018)

- Ground-based measurement of N_2O_5 concentration in Beijing in Nov. – Dec. 2018 (Wei Zhou, CAS, Beijing).

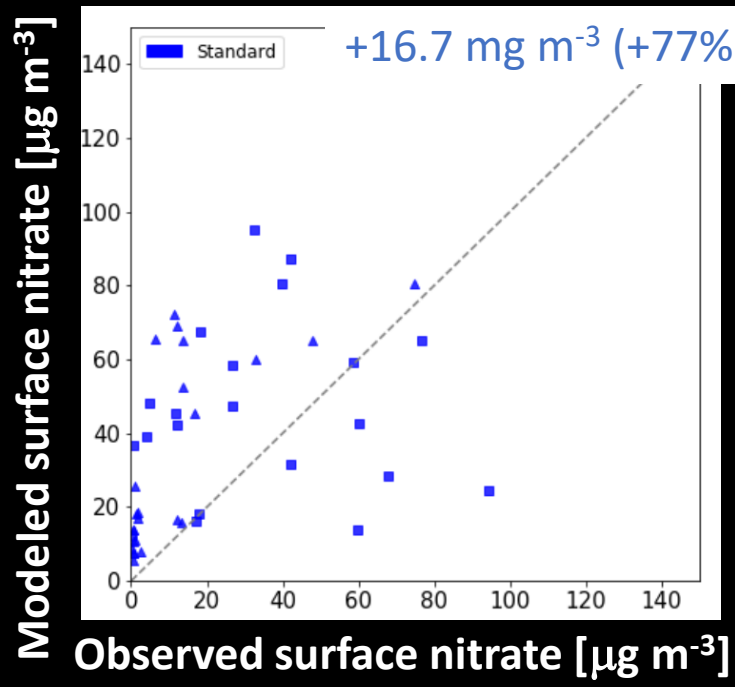


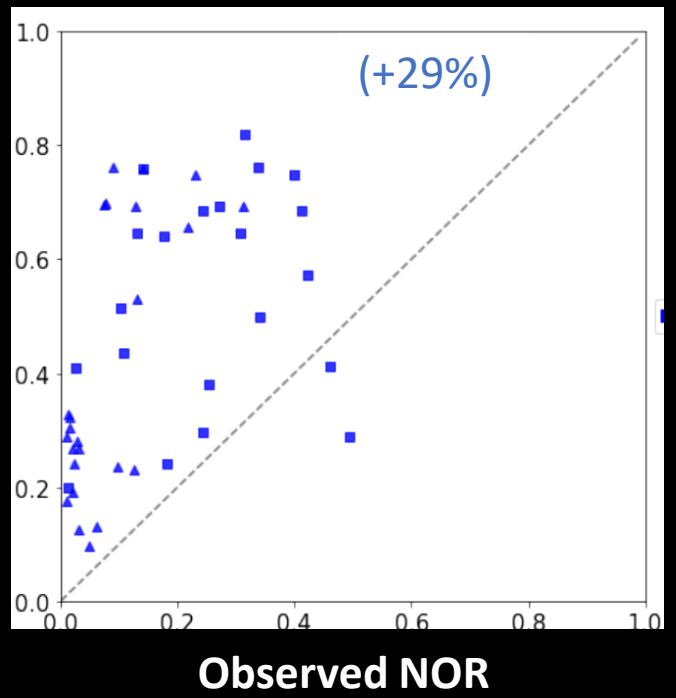
How does the standard GC model perform?

- Overestimates the surface concentration of nitrate in Beijing. (Normalized mean bias: +76.8%)

- Overestimates nitrogen oxidation ratio (NOR, +0.29), suggesting too high nitrate production rates (or underestimates other NO_x loss processes)

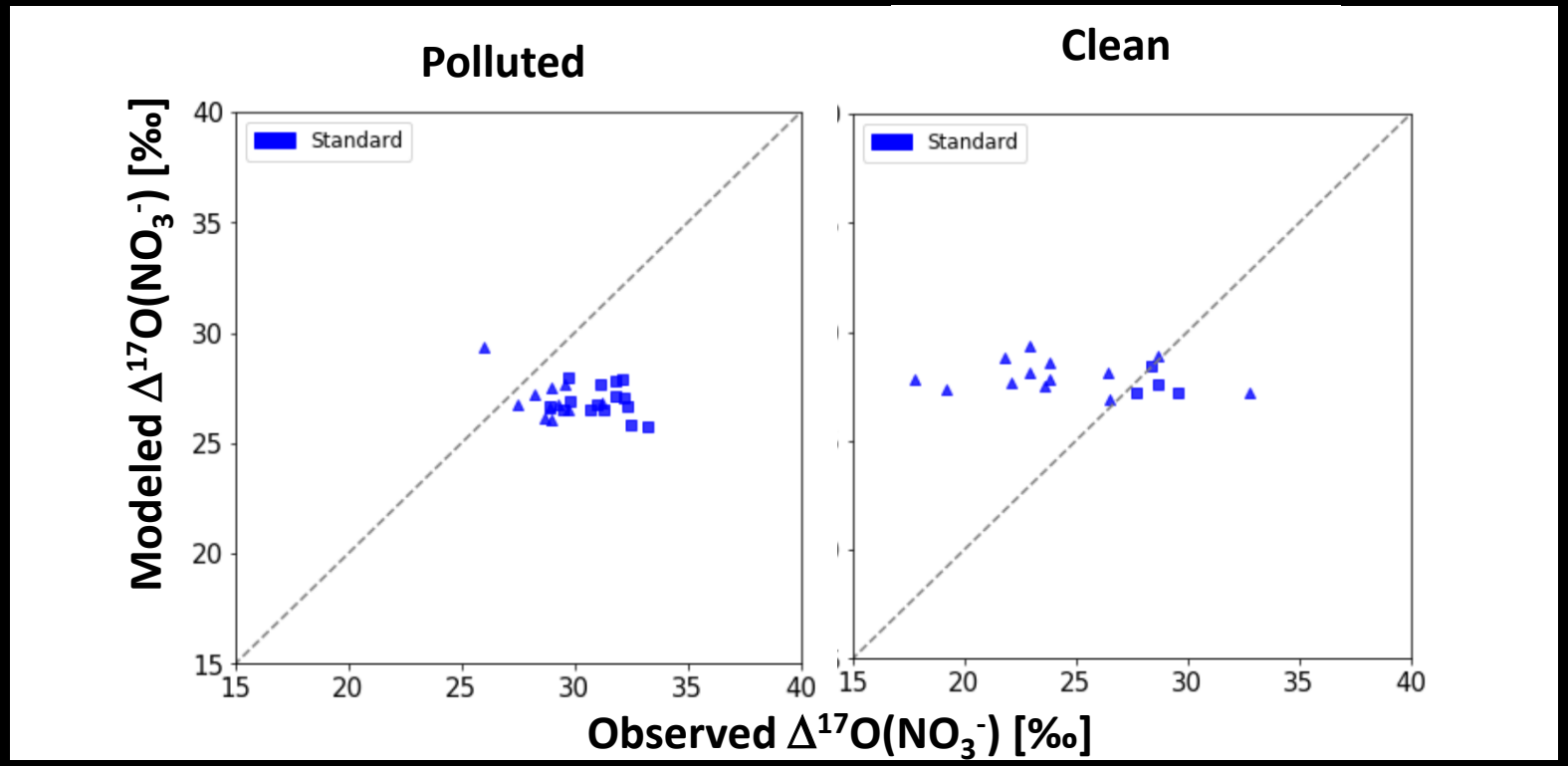
$$\frac{[HNO_3(g)] + [p{-}NO_3^-]}{[HNO_3(g)] + [p{-}NO_3^-] + [NO_2]}$$

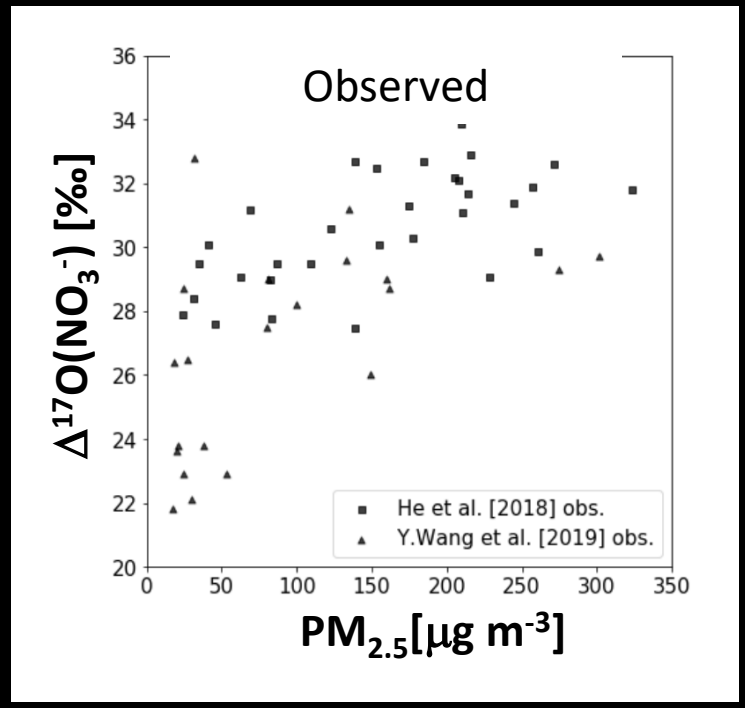




How does the standard GC model perform?

- Underestimates the variability of $\Delta^{17}O(NO_3^-)$ (±0.9‰ versus ±3.8‰)
- Underestimate the mean of $\Delta^{17}O(NO_3^-)$ during the wintertime haze events (27‰ versus 30‰).
- Cannot reproduce the observed positive relationship between and $PM_{2.5}$.





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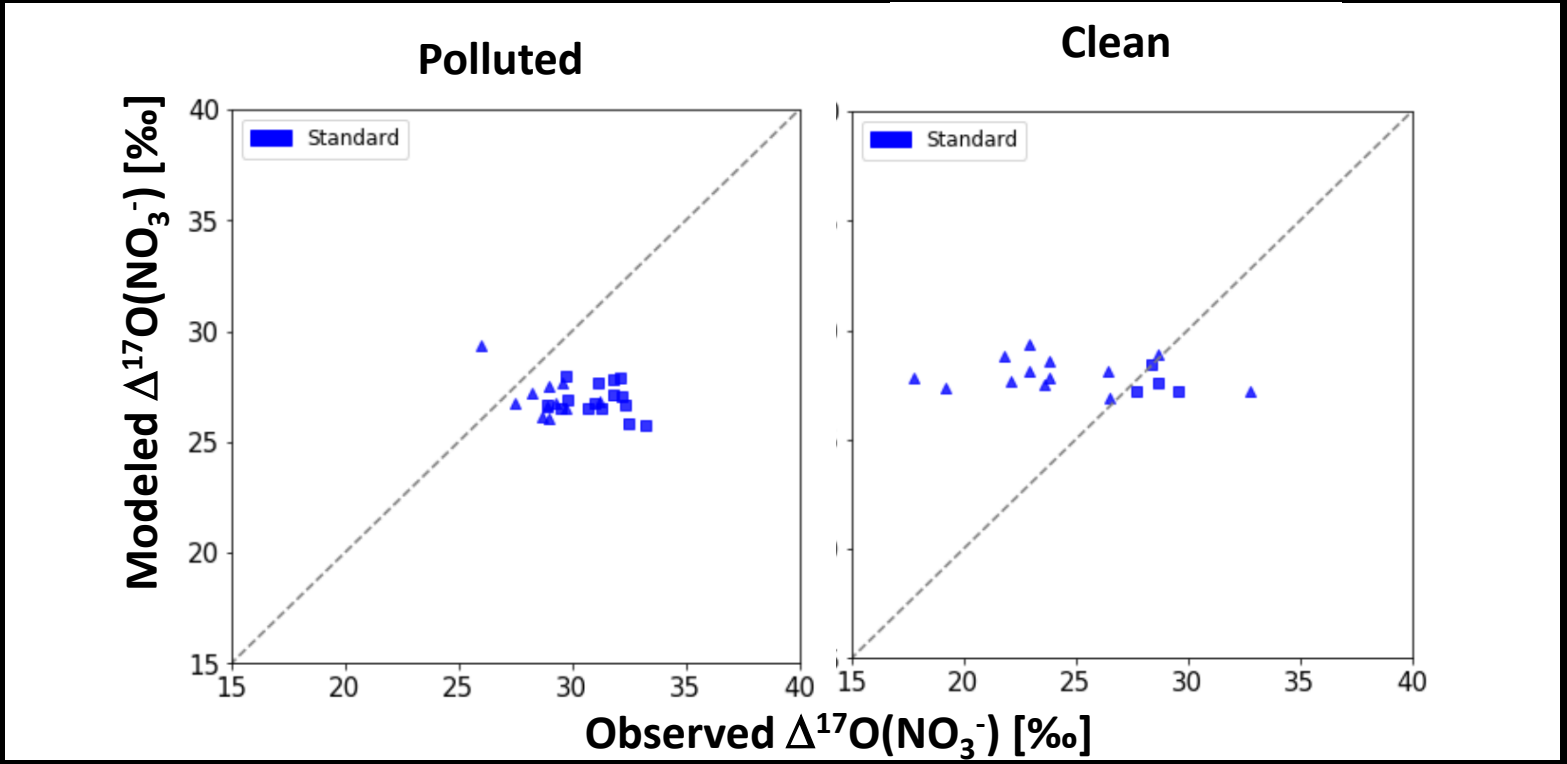
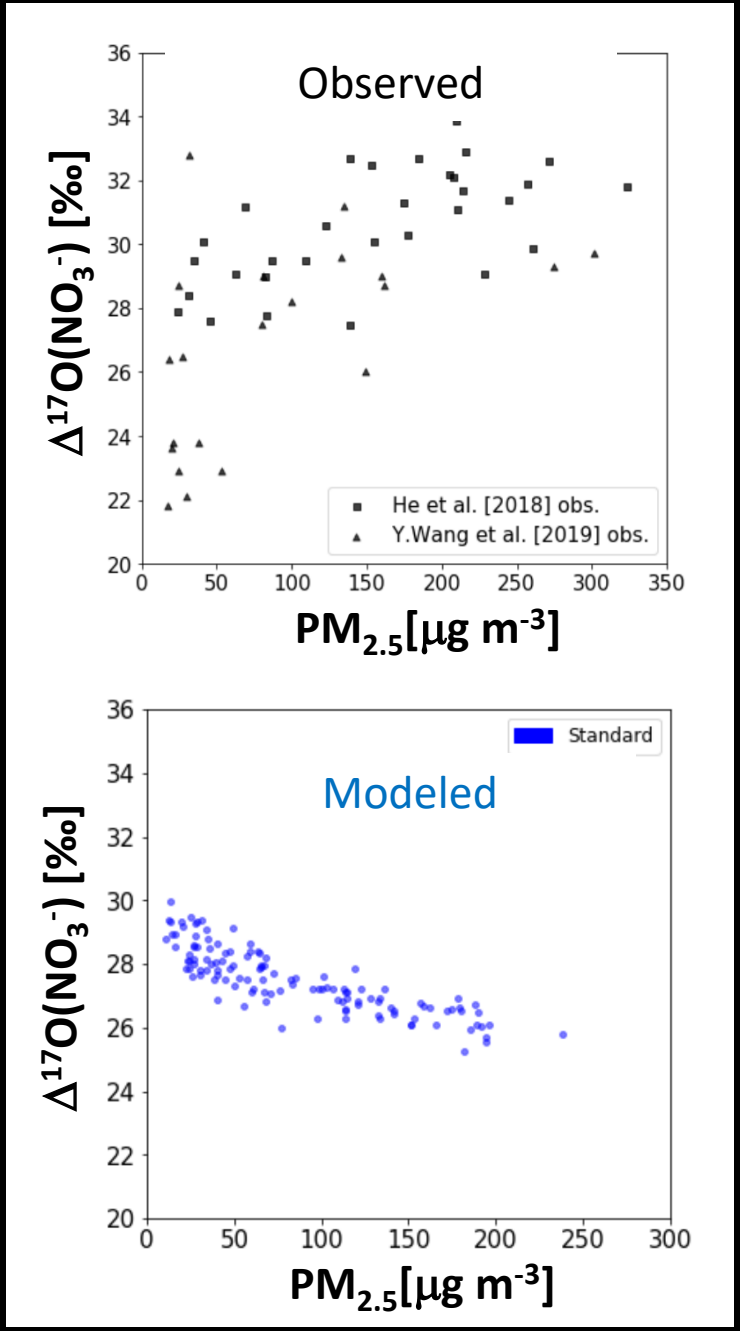
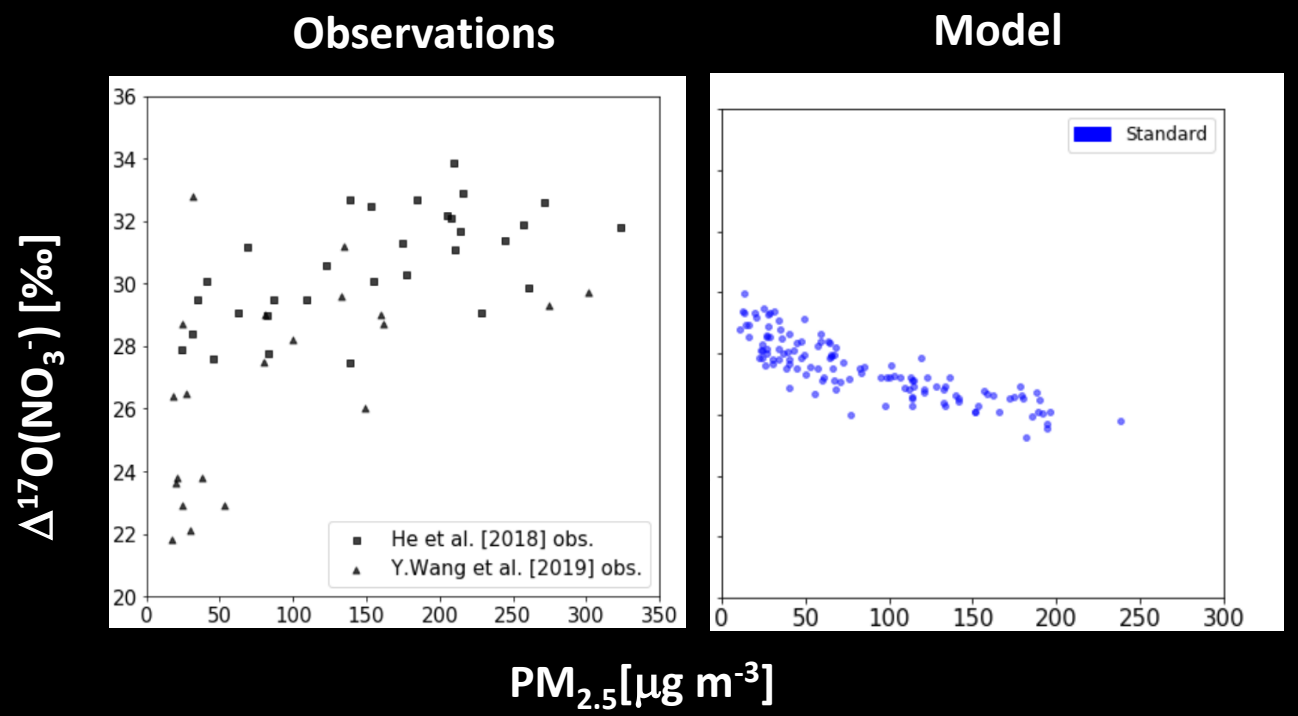
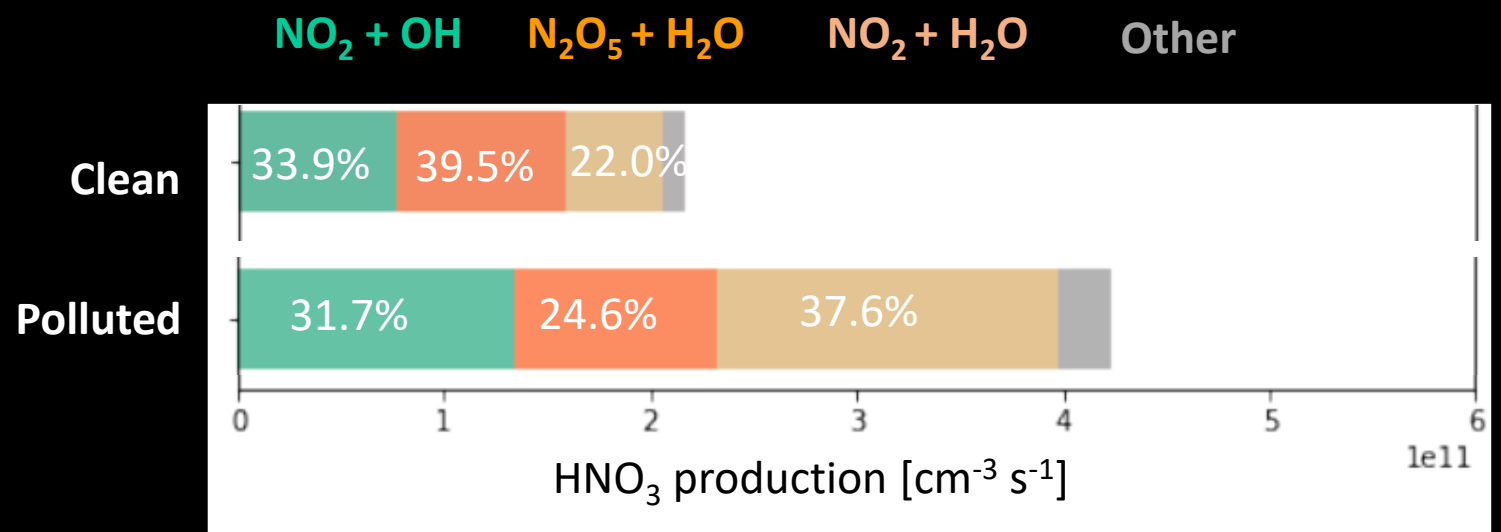




Relationship between $PM_{2.5}$ and $\Delta^{17}O$(nitrate)





Modeled decreasing $\Delta^{17}O$(nitrate) with increasing $PM_{2.5}$ driven by increased nitrate formation from heterogeneous uptake of NO_2

Model sensitivity simulations

+ Cloud Chem (+ updates to γ_{N2O5} and γ_{NO2})

- Current models might have underestimated chemical production of nitrate in cloud while overestimating the contribution from aerosol-phase reactions.
- We follow the proposed corrections from Holmes et al. (2019).

+ Cl Chem

- N_2O_5 update to form nitryl chloride ($ClNO_2$) is a source of nitrate and Cl radical, recycles NOx.
- We adopt the new chlorine chemistry scheme and anthropogenic inventory used in *Wang et al.* (2019).

+ Nitrate photolysis

- Studies found that nitrate in aerosol-phase can photolyze much more quickly than in gas-phase. Model showed that this photolysis reaction can affect NO_y distribution and ozone burden in global scale
–We implement the nitrate photolysis parametrization from *Kasibhatla et al*. (2018)

+ decreased heterogeneous HO_2 uptake

- Restrict aerosol HO_2 uptake to metal-containing aerosol only
- Black carbon + dust / Black carbon only

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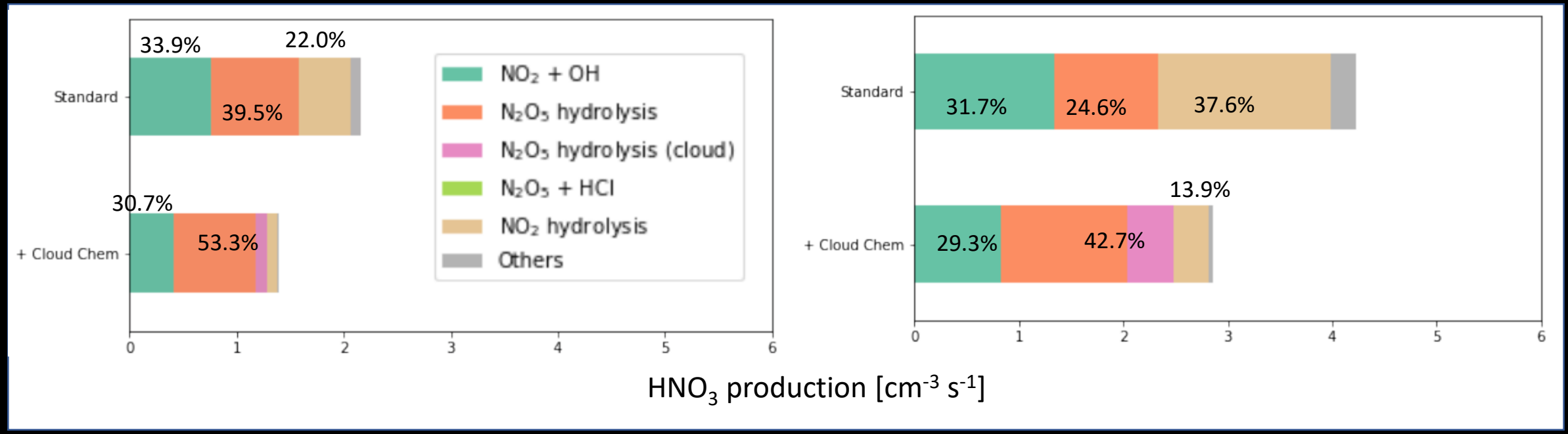
Nitrate production mechanisms: +Cloud chemistry

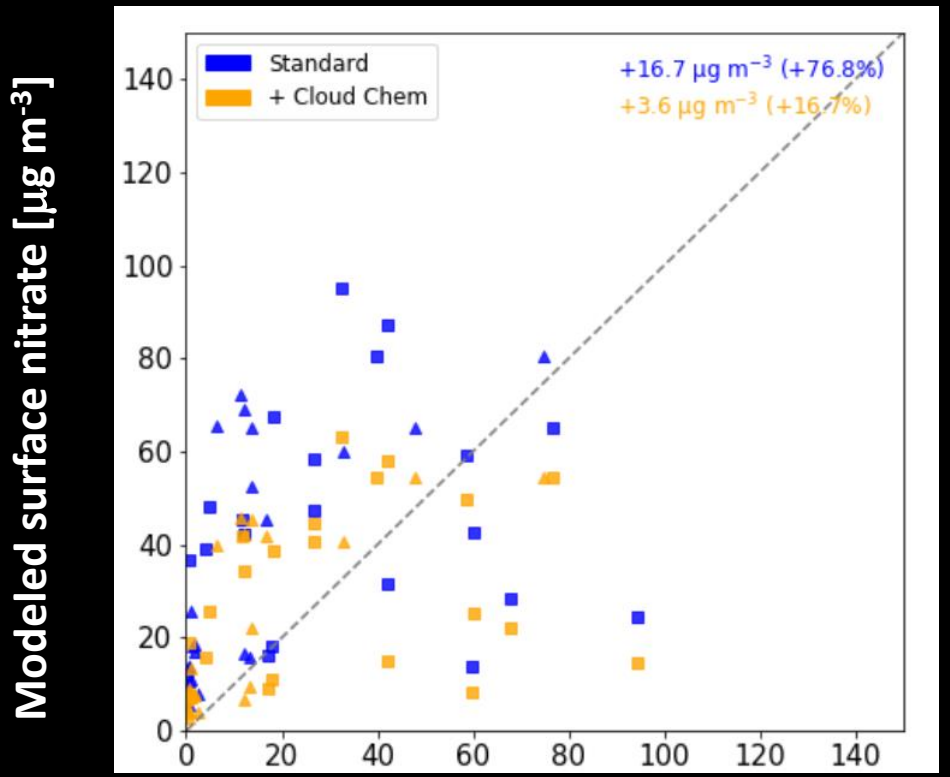


Cloud NO_y chemistry + updates to γ_{N2O5} and γ_{NO2} yield relatively more heterogeneous N_2O_5 chemistry and less heterogeneous NO_2 uptake. N_2O_5 hydrolysis dominants nitrate production pathway in polluted and clean atmosphere.

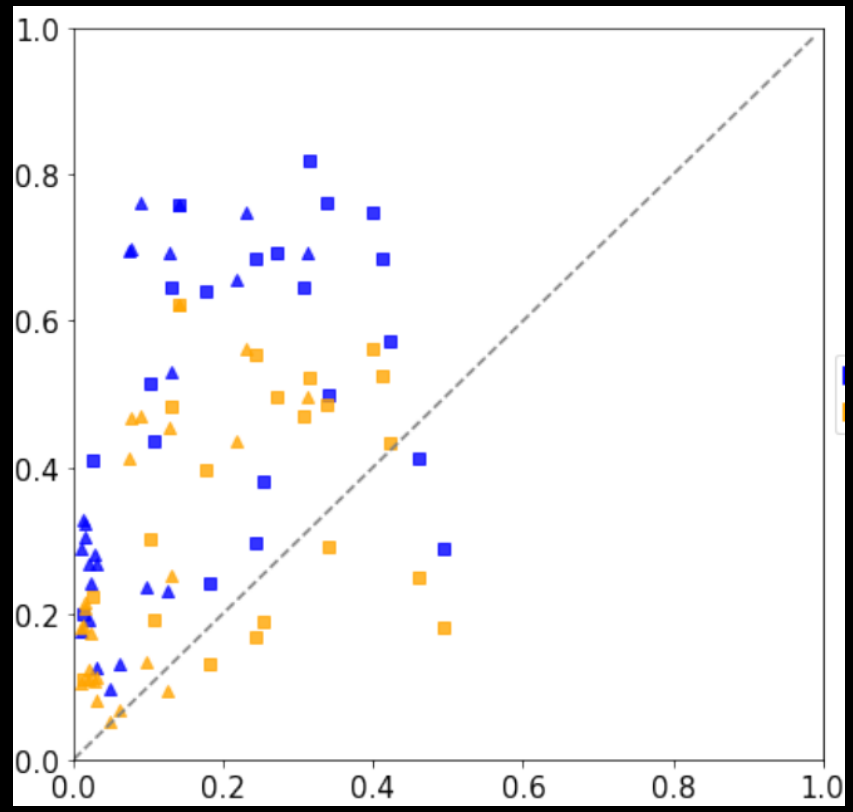
Nitrate concentrations and NOR

"+ Cloud Chem" reduces nitrate concentrations (~+17%) and NOR (+0.13) in Beijing in model and brings it closer to the observed levels

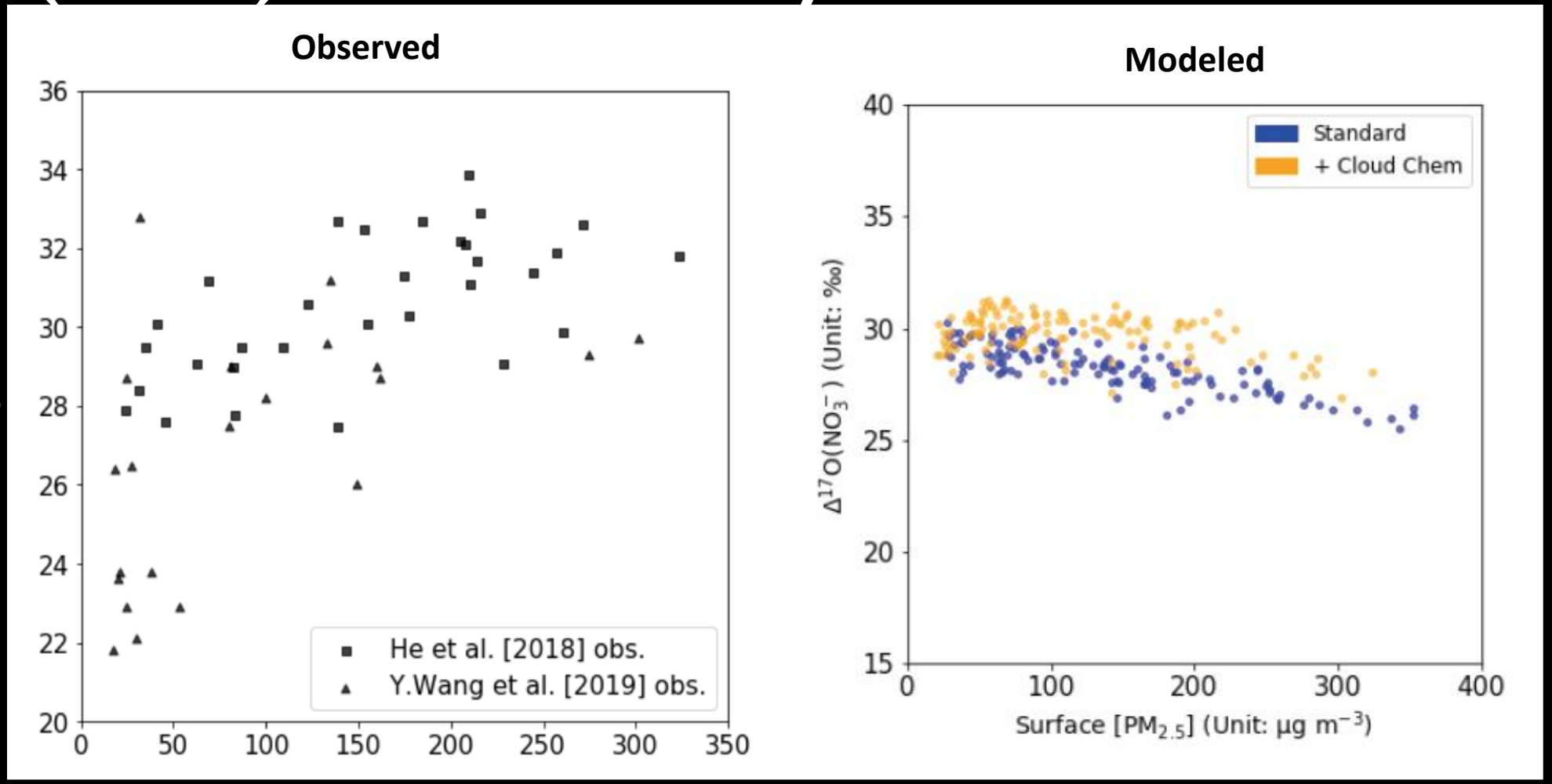
Nitrate Concentration



Nitrogen Oxidation Ratio (NOR)



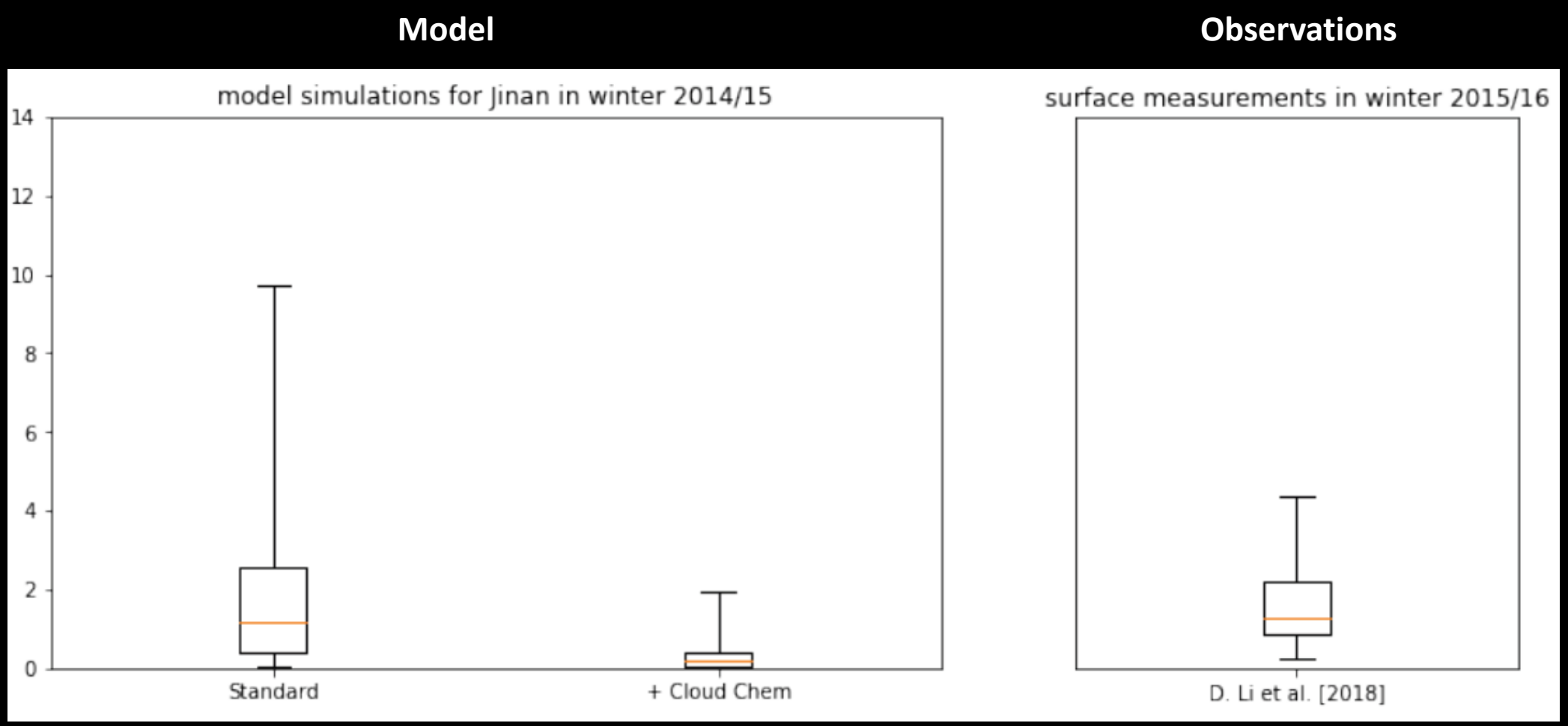
$\Delta^{17}O$(nitrate): +Cloud chemistry



+Cloud chem increases mean $\Delta^{17}O$(nitrate) slightly (by 0.3‰), but does not reproduce relationship between observed $\Delta^{17}O$(nitrate) and $PM_{2.5}$

HONO

- HONO (Nitrous acid) is one of the products of some NO_2 hydrolysis. It readily undergoes photolysis and produces OH radicals, which promotes oxidation of other species.



Heterogeneous NO_2 uptake and HONO

- Polluted conditions increase nitrate formation via heterogeneous uptake of NO_2, even with updated (reduced) γ_{NO2}. This drives the decrease in $\Delta^{17}O$(nitrate) with increasing $PM_{2.5}$, the opposite trend of the observations.
- Yield of $NO_2 + H_2O \rightarrow 0.5HNO_3 + 0.5HONO$ is uncertain and may be pH-dependent

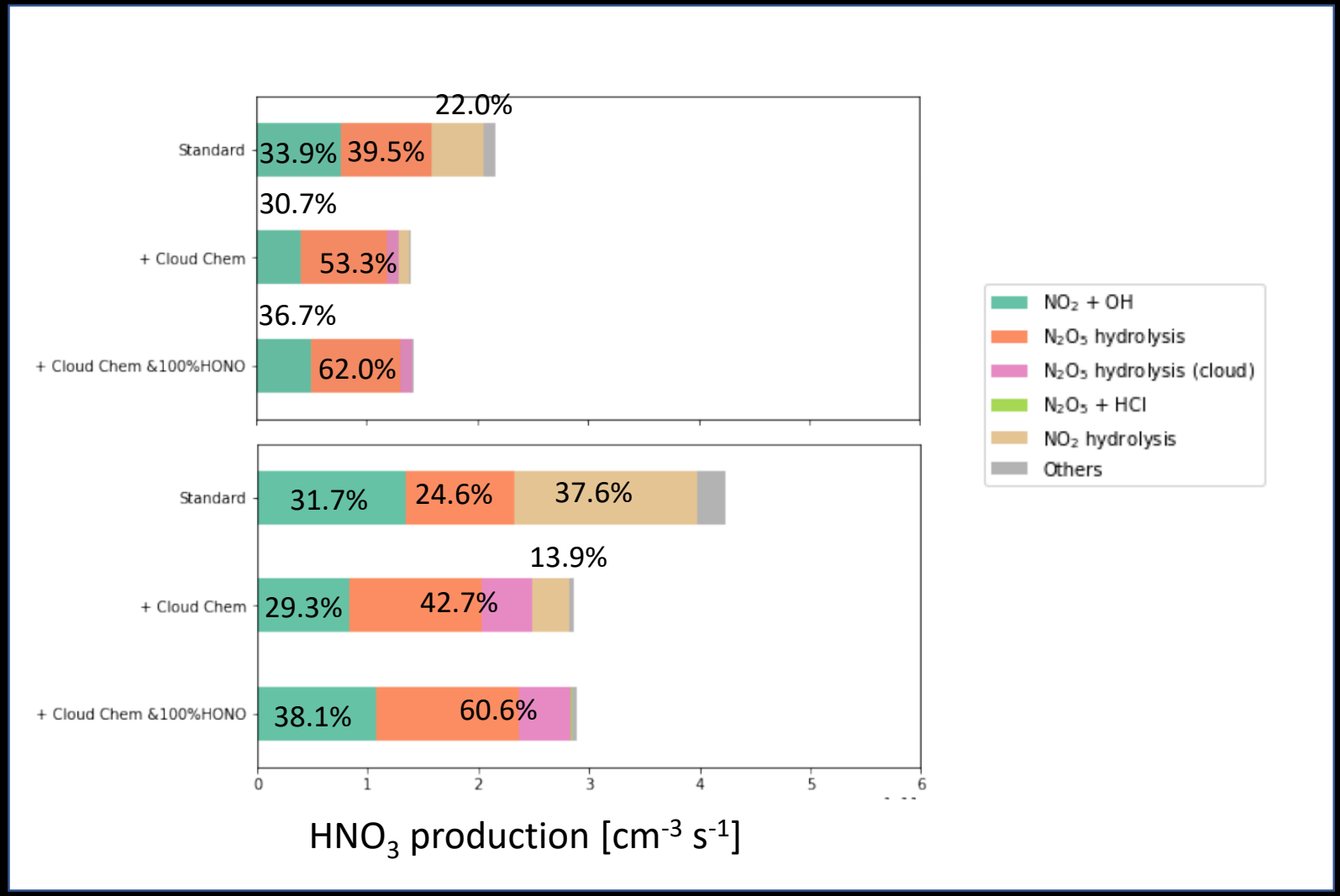
+ Cloud Chem + 100% HONO (+ updates to γ_{N2O5} and γ_{NO2})

- Same as +Cloud Chem but with $NO_2 + H_2O \rightarrow HONO$

Nitrate production mechanisms: +Cloud chemistry + 100%HONO

Clean

Polluted

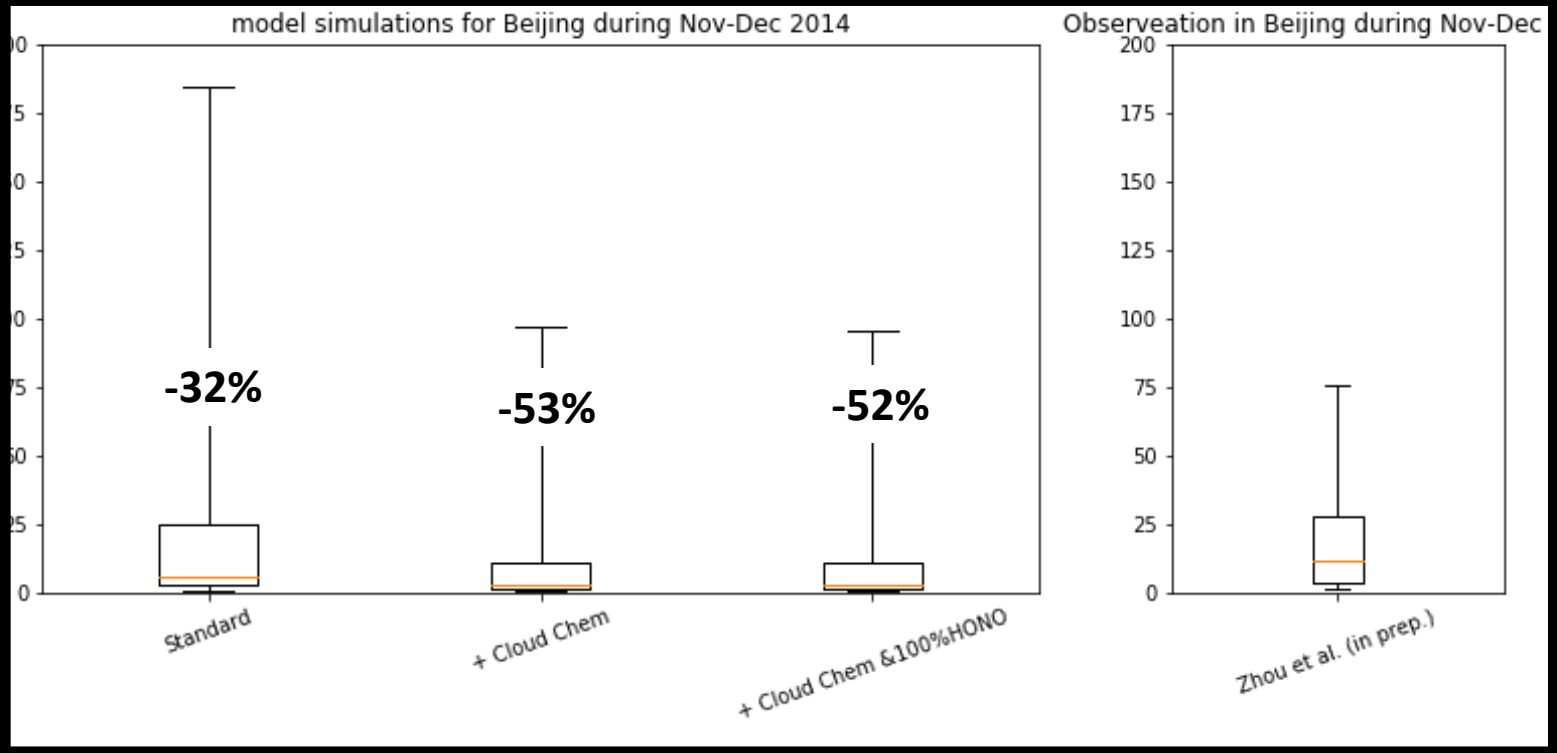


Cloud NO_y chemistry + 100% HONO does not change nitrate production rates.

N_2O_5 uptake limited by N_2O_5 and ozone abundance

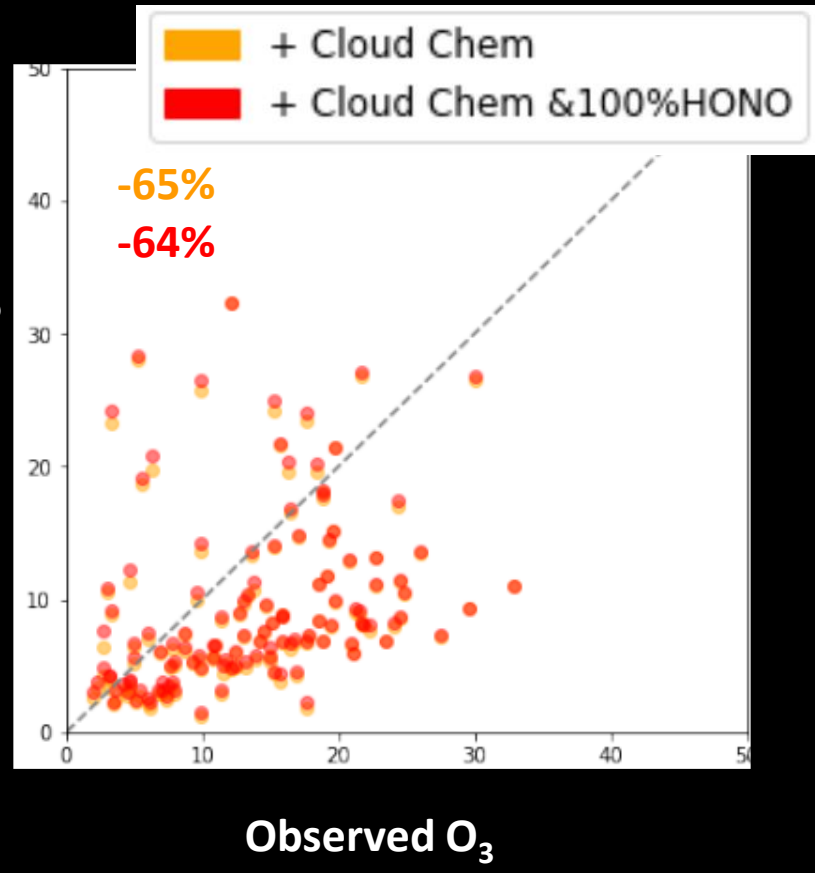
N_2O_5 (ppbv)

Modeled



Observed

O_3 (ppbv)



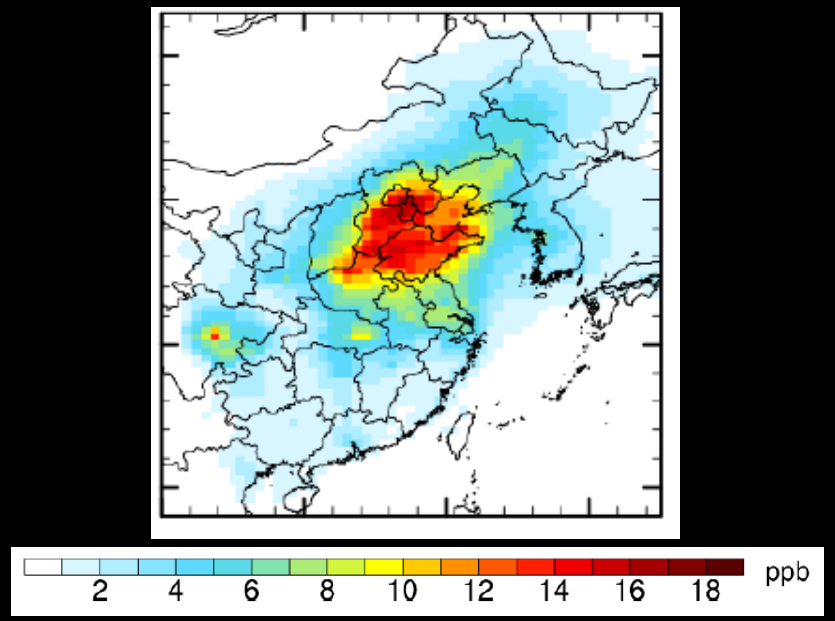
Model underestimates N_2O_5 because it underestimates ozone.

Heterogeneous HO_2 uptake impacts ozone

A two-pollutant strategy for improving ozone and particulate air quality in China [2019]

Ke Li[1,2], Daniel J. Jacob[2*], Hong Liao[3*], Jia Zhu[3], Viral Shah[2], Lu Shen[2], Kelvin H. Bates[2], Qiang Zhang[4] and Shixian Zhai[2]

Modeled O_3 increase after removing heterogeneous HO_2 uptake



γ_{HO2} = 0.2 for all aerosol types

Laboratory experiments show that:

- γ_{HO2} = 0.1 – 0.3 [e.g., Taketani et al., 2012]
- Heterogeneous HO_2 uptake catalyzed by Cu-Fe redox:

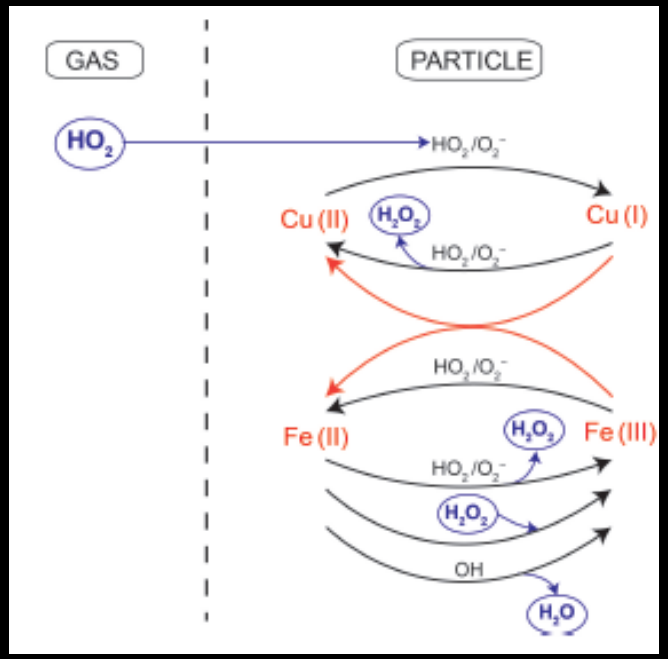


Figure from *Mao et al.* [2013]

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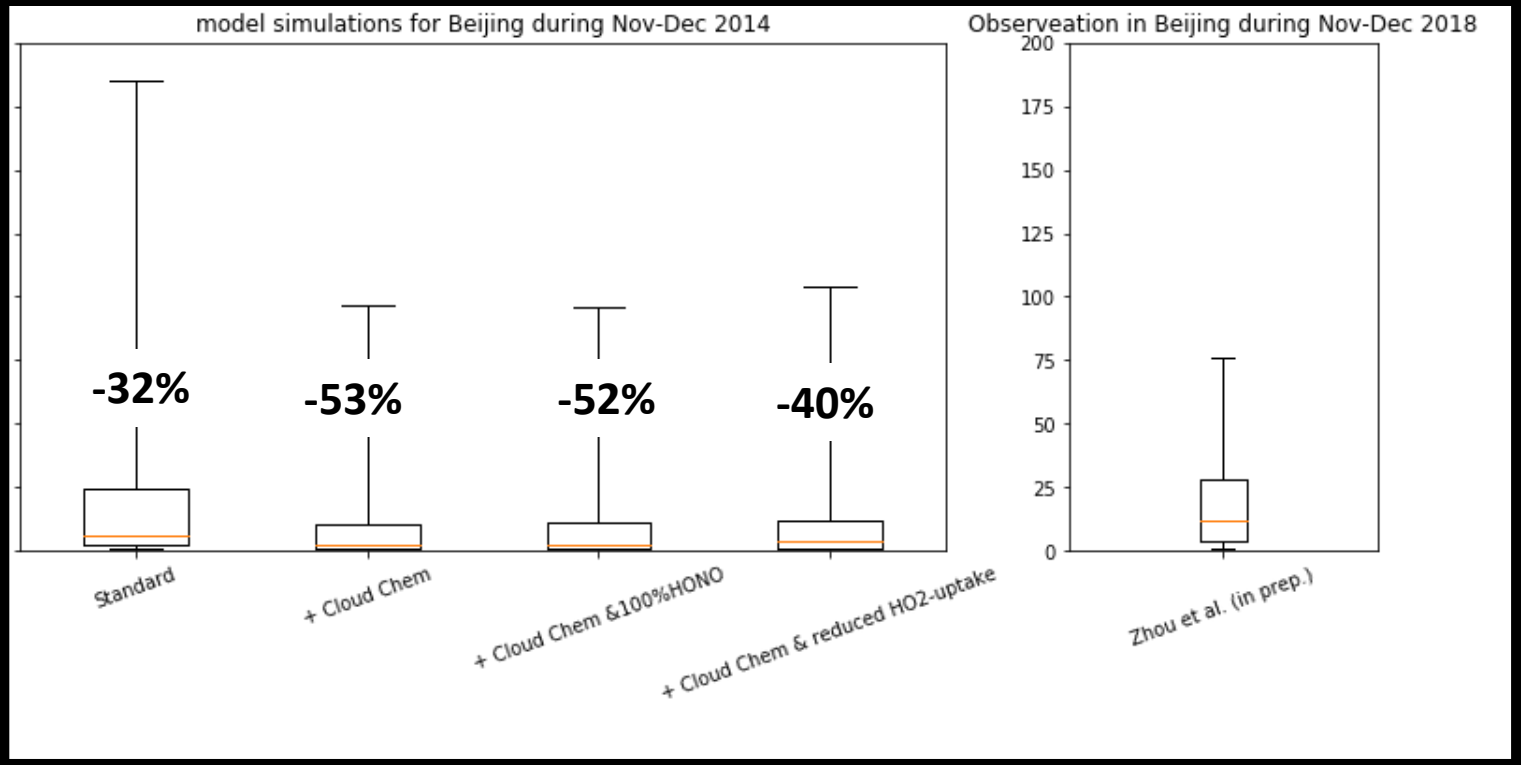
N_2O_5 and ozone : reduced HO_2 uptake

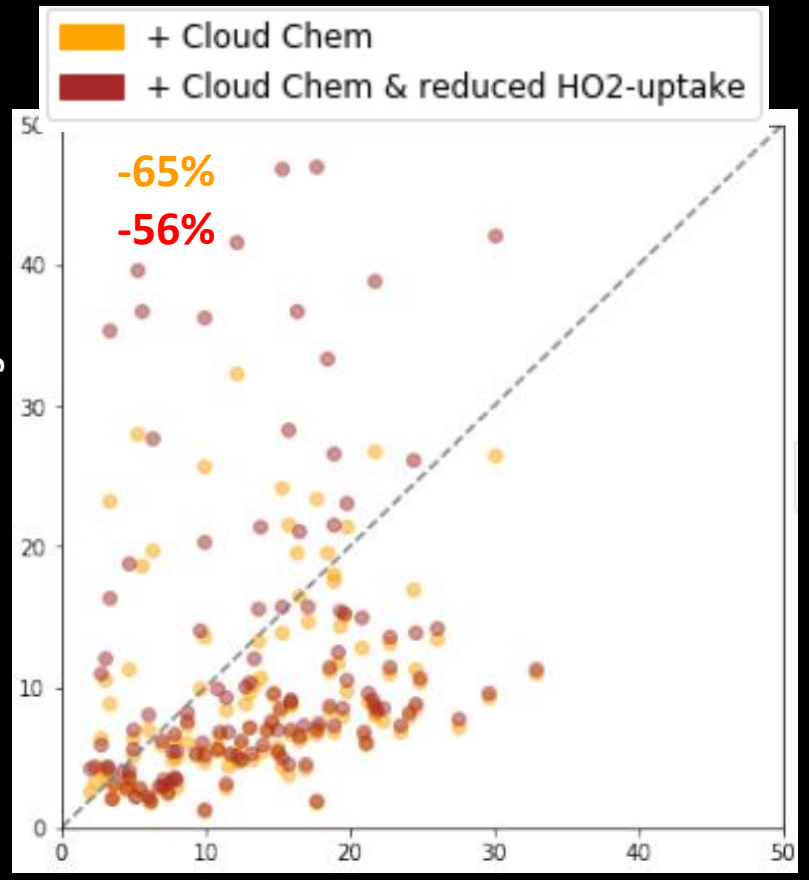
N_2O_5 (ppbv)

Modeled

Observed



O_3 (ppbv)



Conclusions

- $\Delta^{17}O$(nitrate) sensitive to relative importance of nitrate production mechanisms. Observations in Beijing suggest too high $NO_2 + H_2O$ and too low $N_2O_5 + H_2O$ in polluted days in the model.

- Overestimate of $NO_2 + H_2O$ corrected by updating γ_{NO2} based on recent literature values. However, underestimate of N_2O_5 hydrolysis cannot be reconciled by changes to γ_{N2O5} because it is limited by N_2O_5 abundance. N_2O_5 formation in the model is in turn limited by O_3, which is also underestimated.

- Limiting heterogeneous HO_2 uptake ($\gamma_{HO2} = 0.2$) to metal-containing aerosol increased modeled N_2O_5 and ozone abundance but still underestimates ozone, N_2O_5 and observed $\Delta^{17}O(NO_3^-)$.

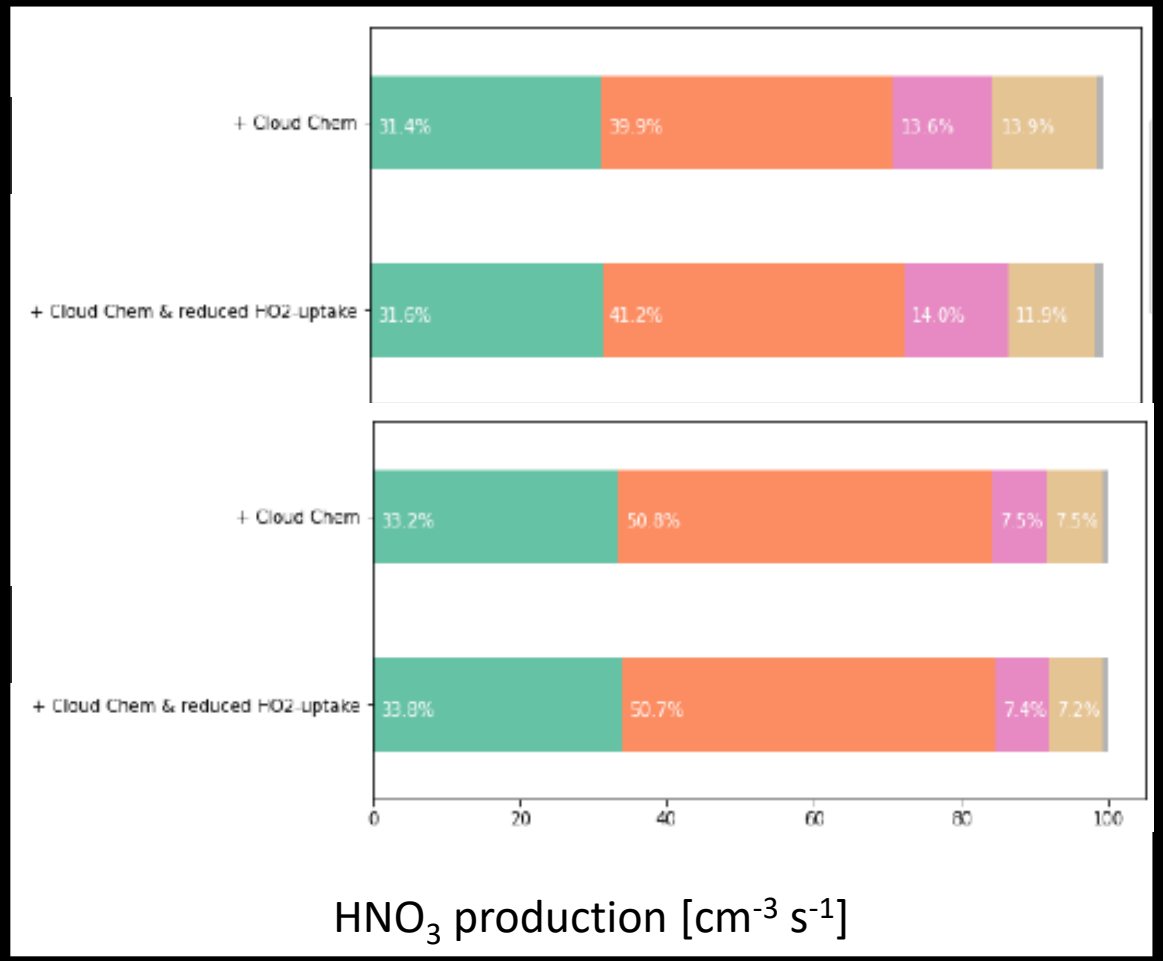
AGS 1644998

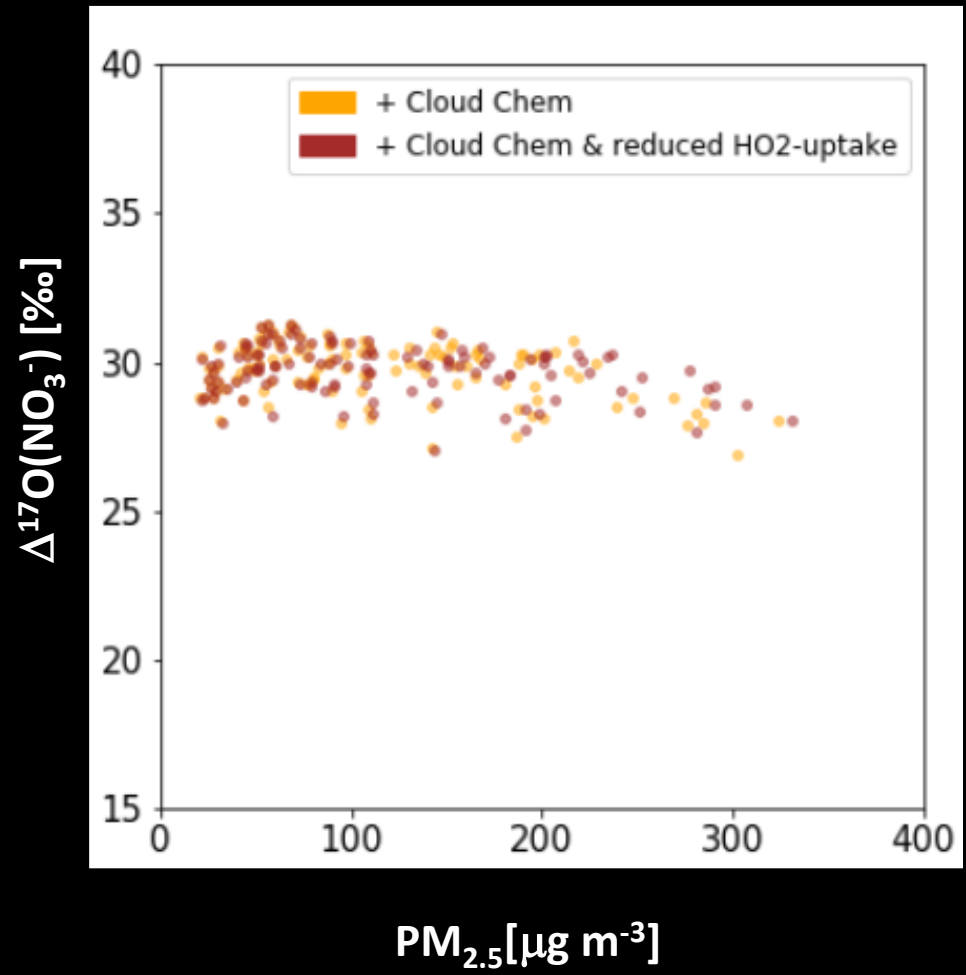
Extra slides

Nitrate production mechanisms: +Cloud chemistry $-\gamma_{HO2}$

Clean

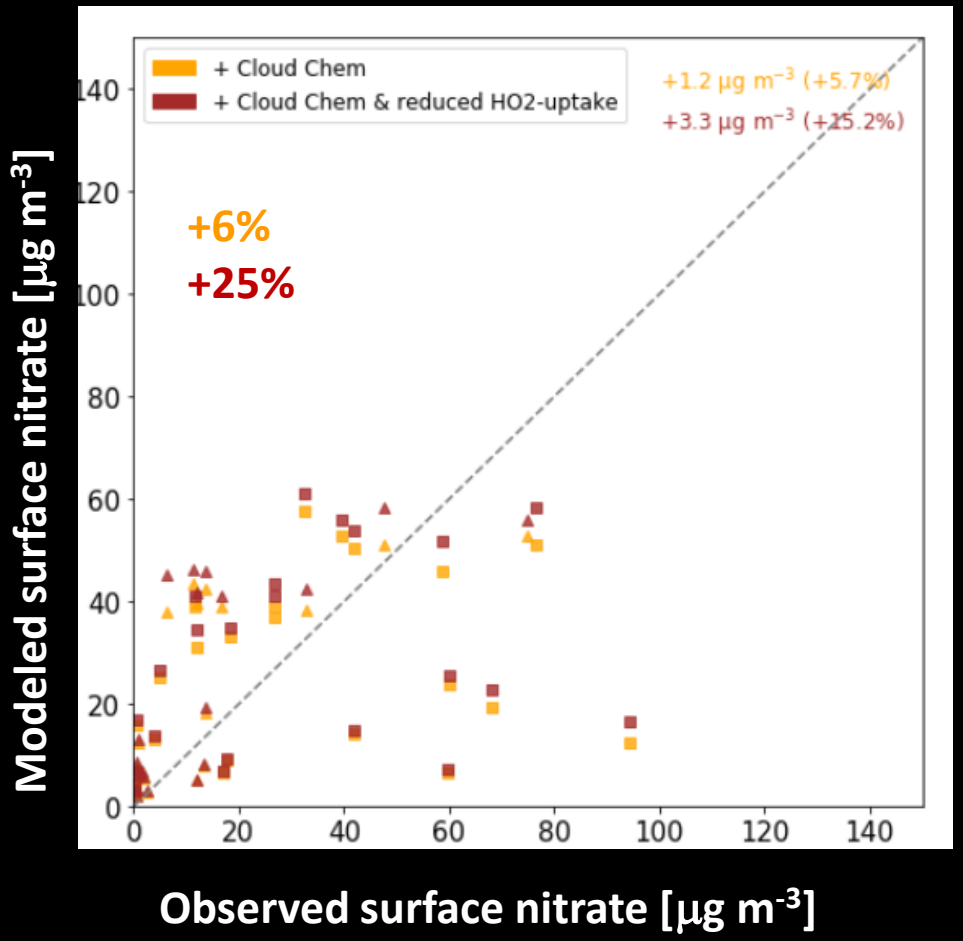
Polluted

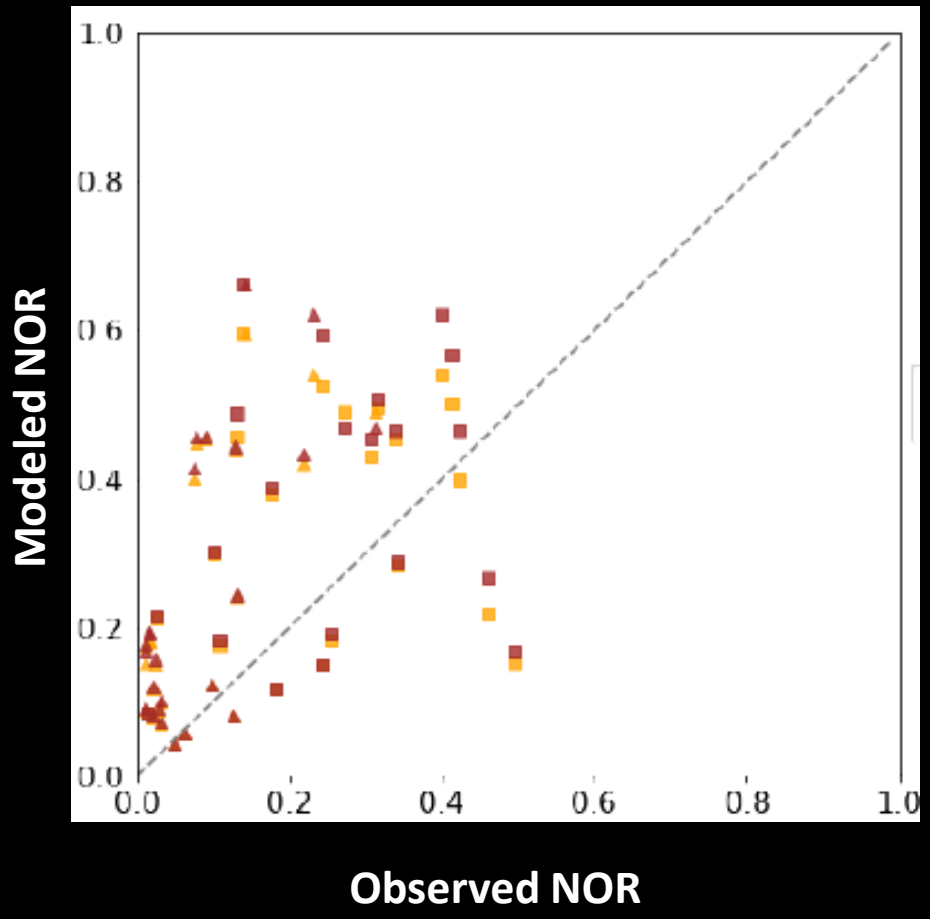




Nitrate concentrations and NOR: reduced HO_2 uptake

"reduced HO_2 uptake" increases nitrate concentrations (~+25%) and NOR (+0.14) in Beijing in model worsening the high bias.





Reactions affected by the model updates

+ Cloud Chem