Isotopic constraints on heterogeneous production of nitrate in extreme haze in Beijing

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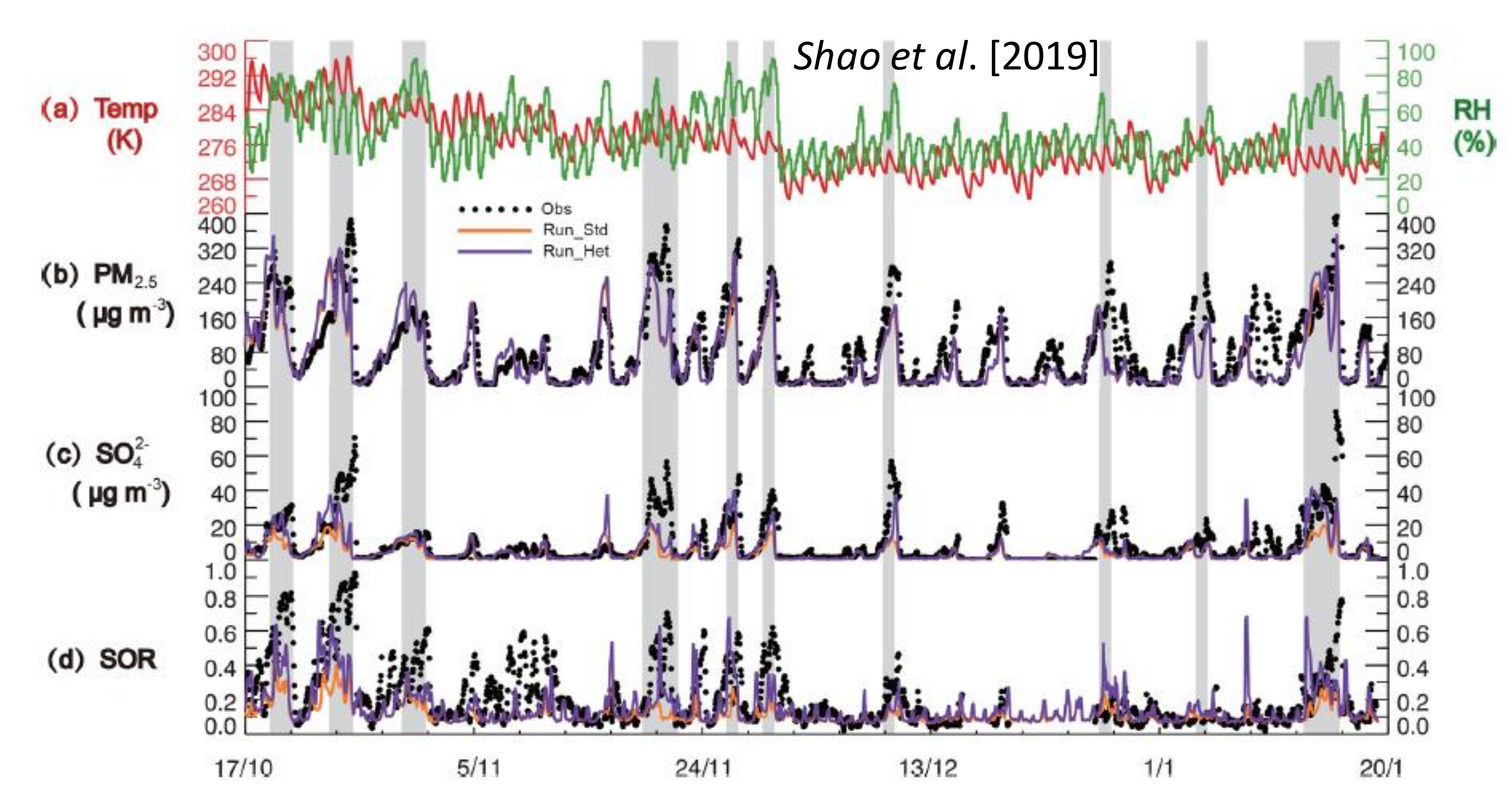
China $PM_{2.5}$ is underestimated in air quality models



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.

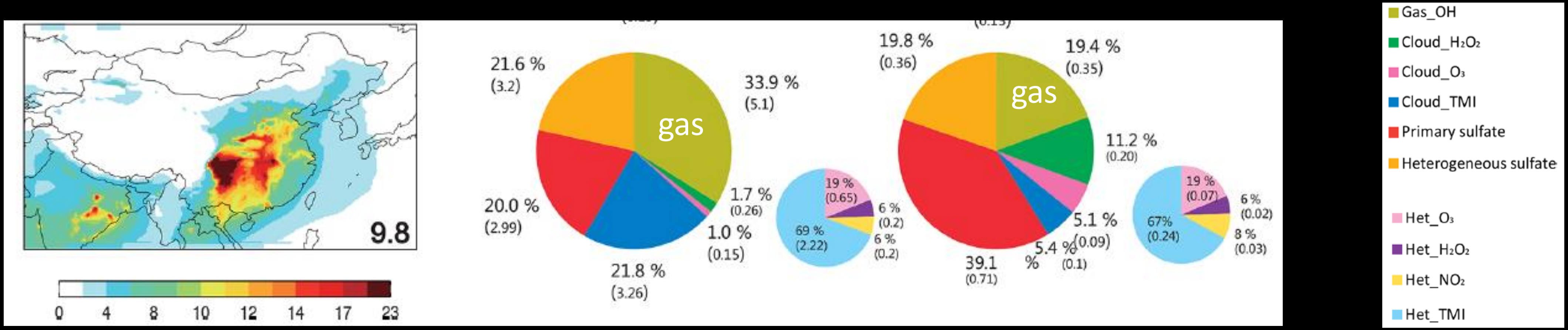
Importance of nitrate formation in Beijing air

- 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.
- Many models have issues in reproducing the observed nitrate levels (high bias).
- 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 [$\mu g\ m^{-3}$] **Polluted** **Clean**



Shao et al. [2019]

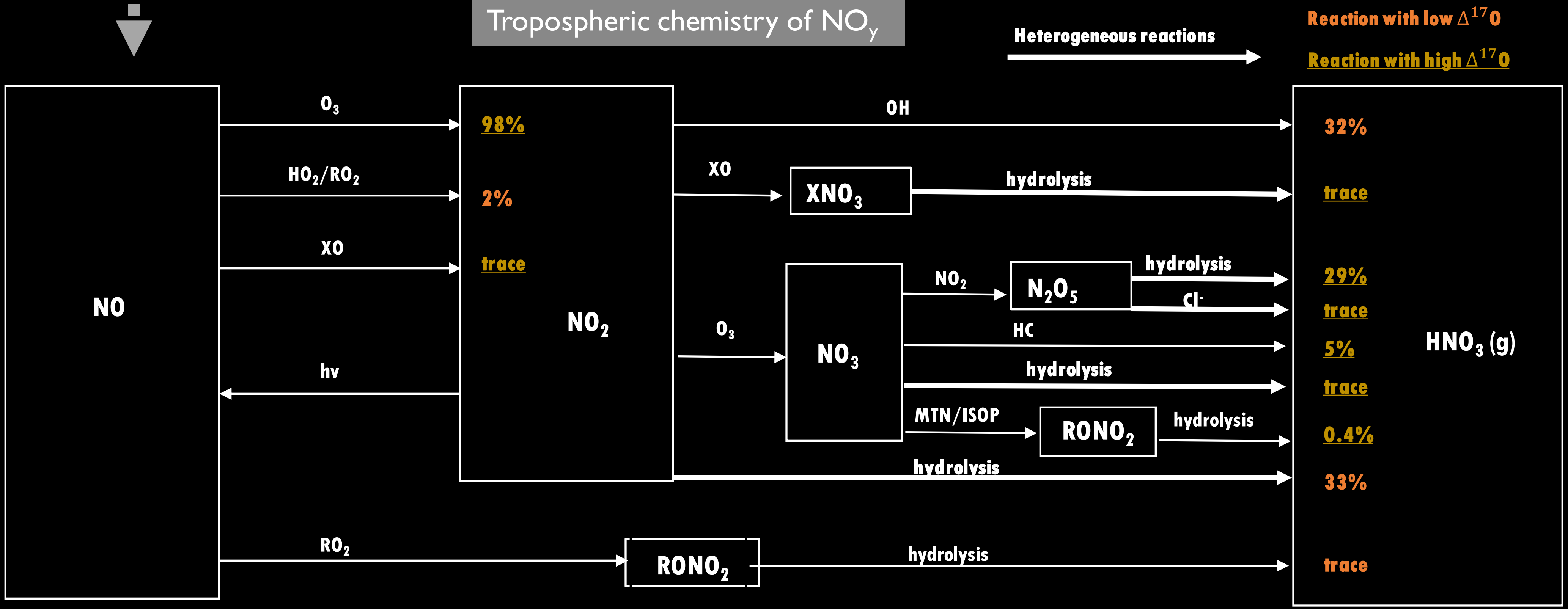
Increase in gas-phase sulfate production (SO_2 + OH) from clean (19%) to polluted (34%) conditions due to increase in OH resulting from production of HONO from heterogeneous uptake of NO_2 in the model.

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

$$NO_2 + NO_3 \rightarrow N_2O_5 \xrightarrow{H_2O} 2HNO_3$$

$\Delta^{17}O$(nitrate) = 31.2‰

$$N_2O_5 \xrightarrow{Cl^-} HNO_3$$

$\Delta^{17}O$(nitrate) = 33.8‰

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$$NO_2 + NO_3 \xrightarrow{H_2O} HNO_3 + HONO$$

$\Delta^{17}O$(nitrate) = 25.5‰

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

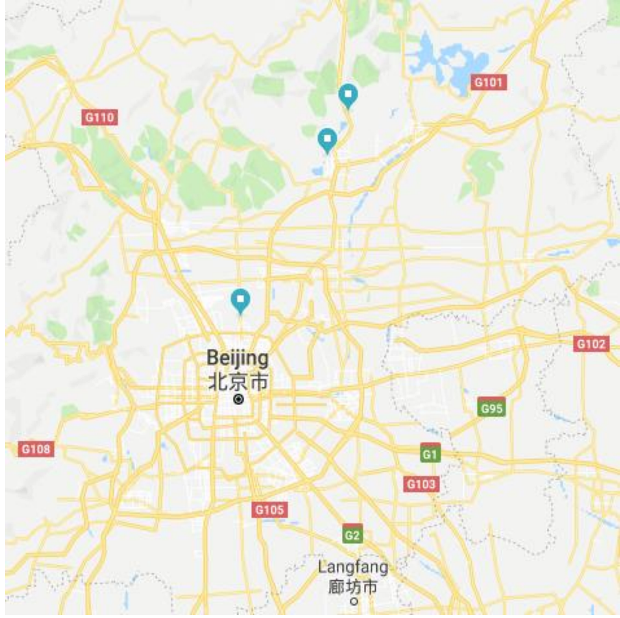
Measurements and observations

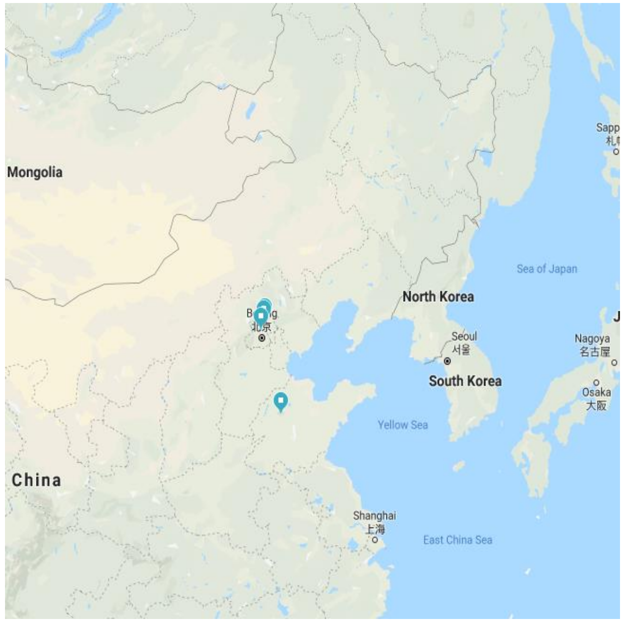
- Two independent datasets of $\Delta^{17}O(NO_3^-)$ measurements for aerosol sampled in Beijing conducted at UW IsoLab:

    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 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)



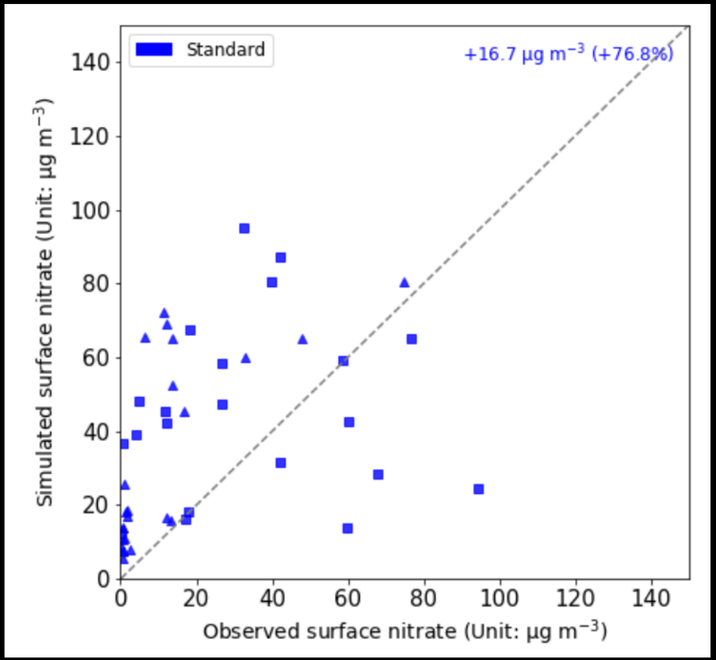


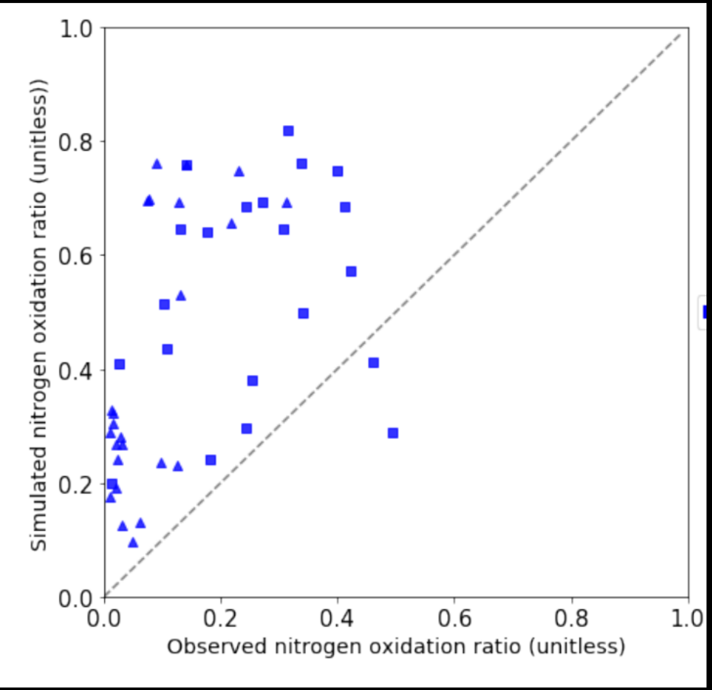
How does the standard GC model perform?

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

- Overestimates nitrogen oxidation ratio (+0.29), suggesting too high nitrate production rates (or underestimates other NO_x loss processes)

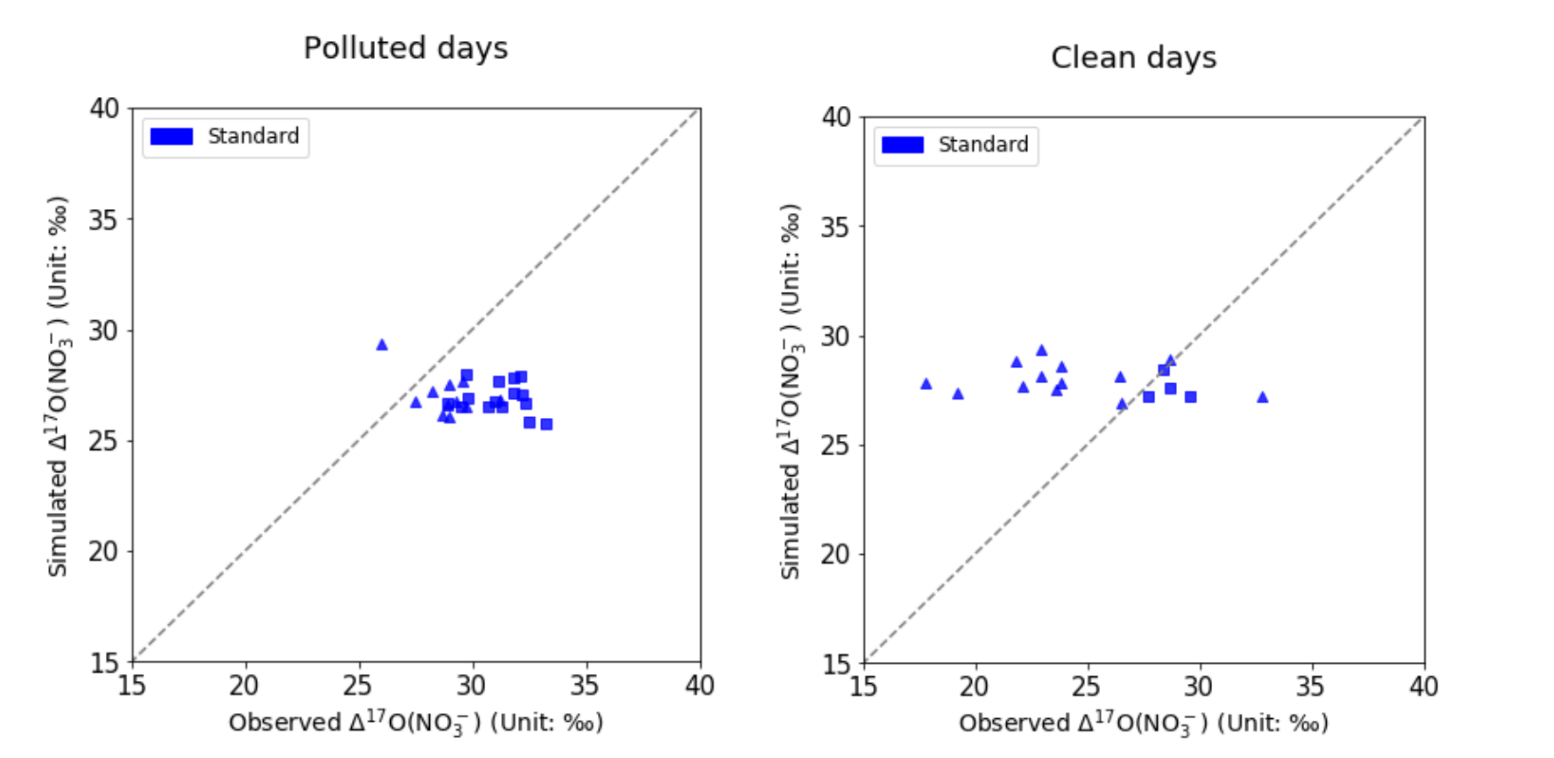
$$\frac{[\mathrm{HNO_3(g)}] + [\mathrm{p{-}NO_3}^-]}{[\mathrm{HNO_3(g)}] + [\mathrm{p{-}NO_3}^-] + [\mathrm{NO_2}]}$$

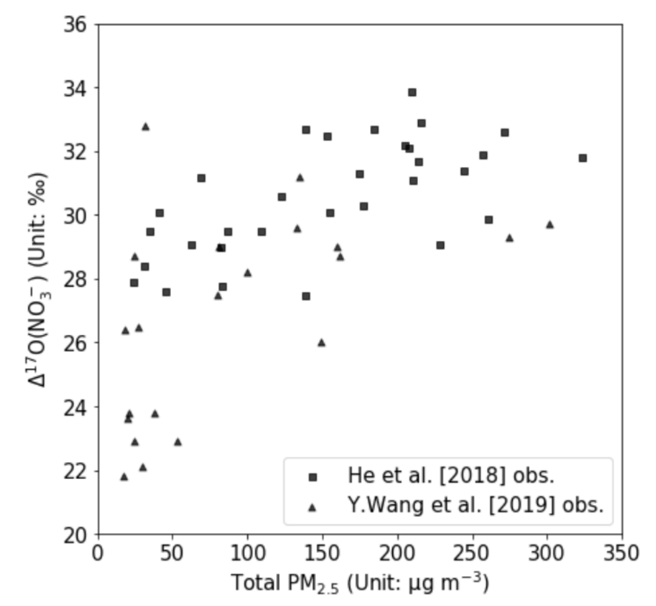


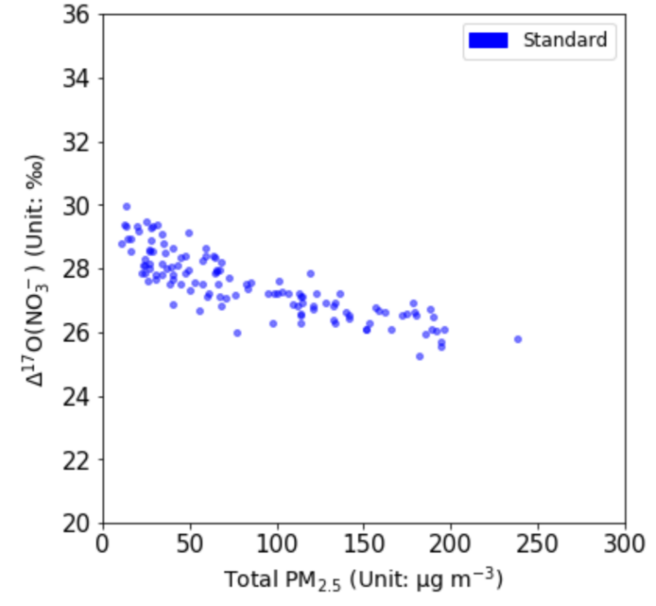


How does the standard GC model perform?

- Underestimates the variability of $\Delta^{17}O(NO_3^-)$ ($\pm 0.9‰$ versus $\pm 3.8‰$)
- 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 $PM_{2.5}$.

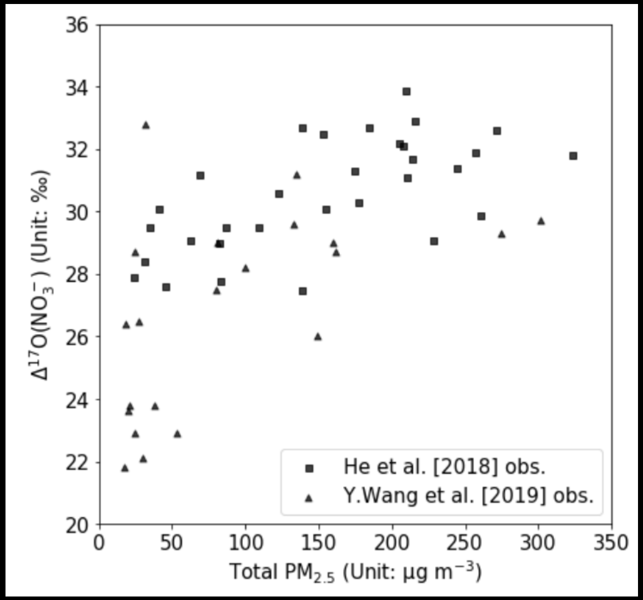




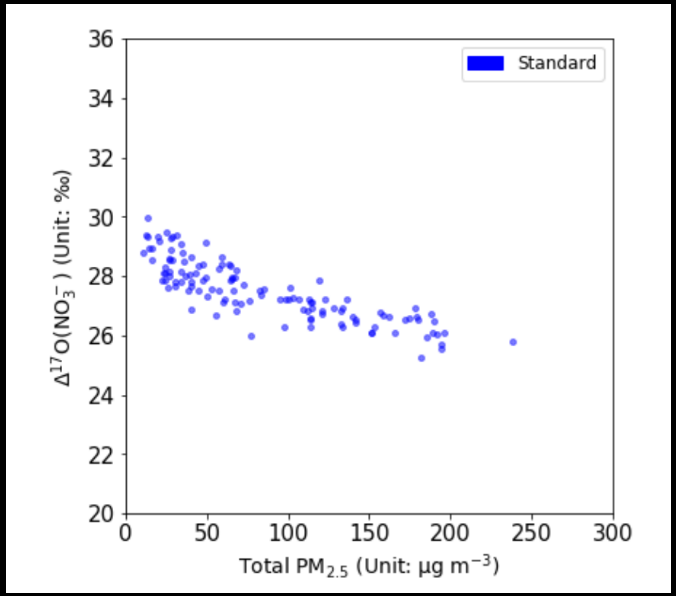


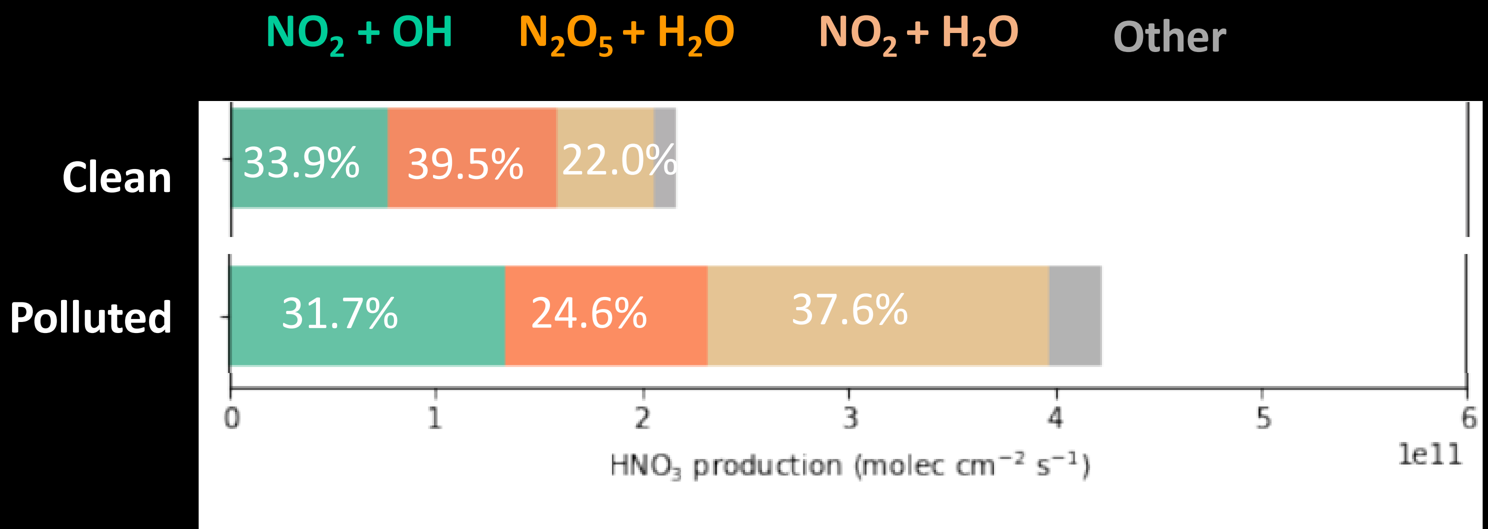
Relationship between $PM_{2.5}$ and $\Delta^{17}O$(nitrate)

Observations



Model





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)

+ NO_2 deposition → HONO

- More detailed treatment of NO_2 deposition
- NO2 deposition to surfaces yields HONO

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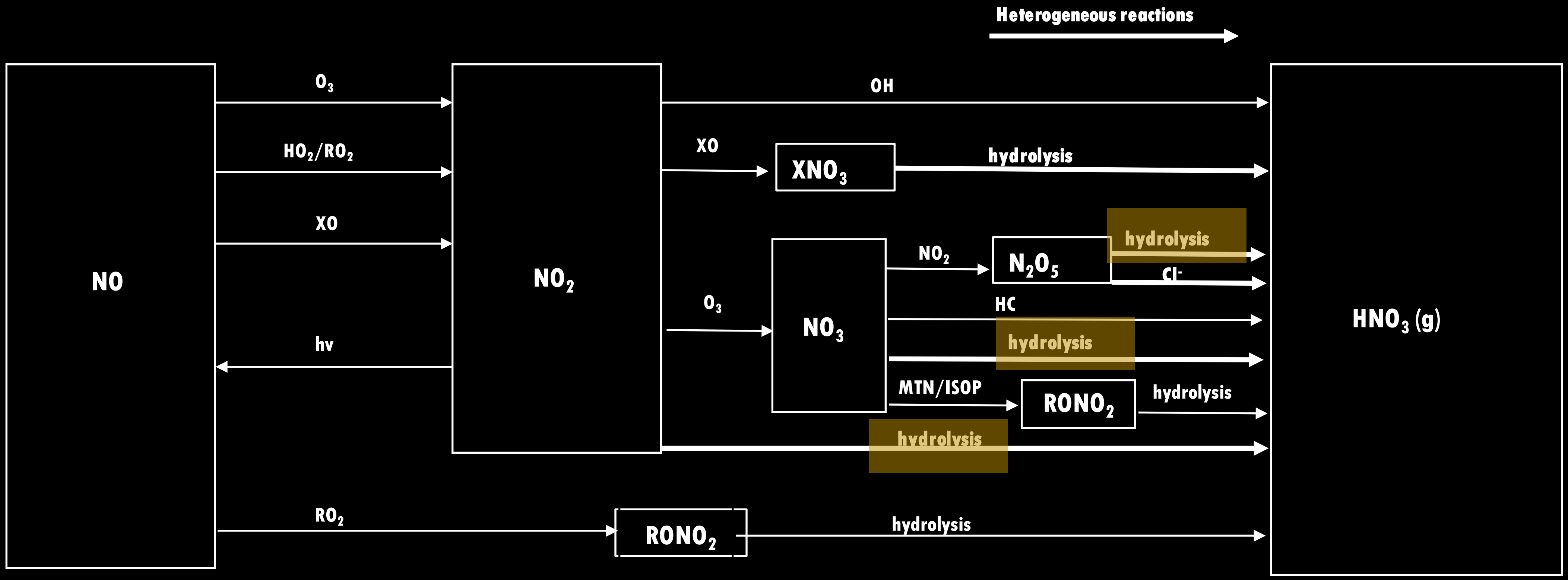
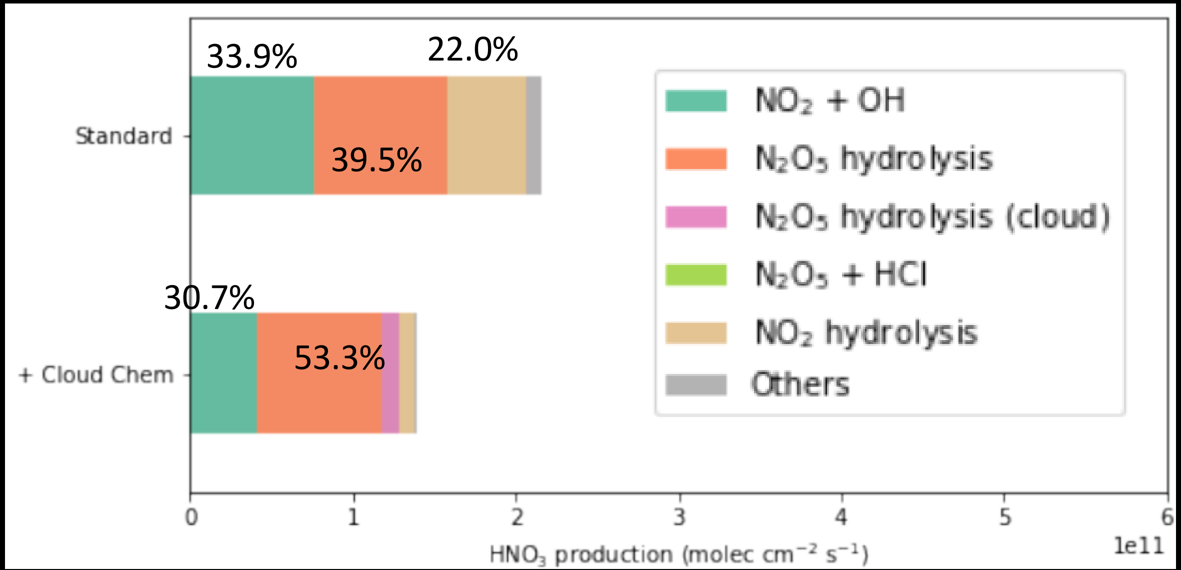
Reactions affected by the model updates

+ Cloud Chem

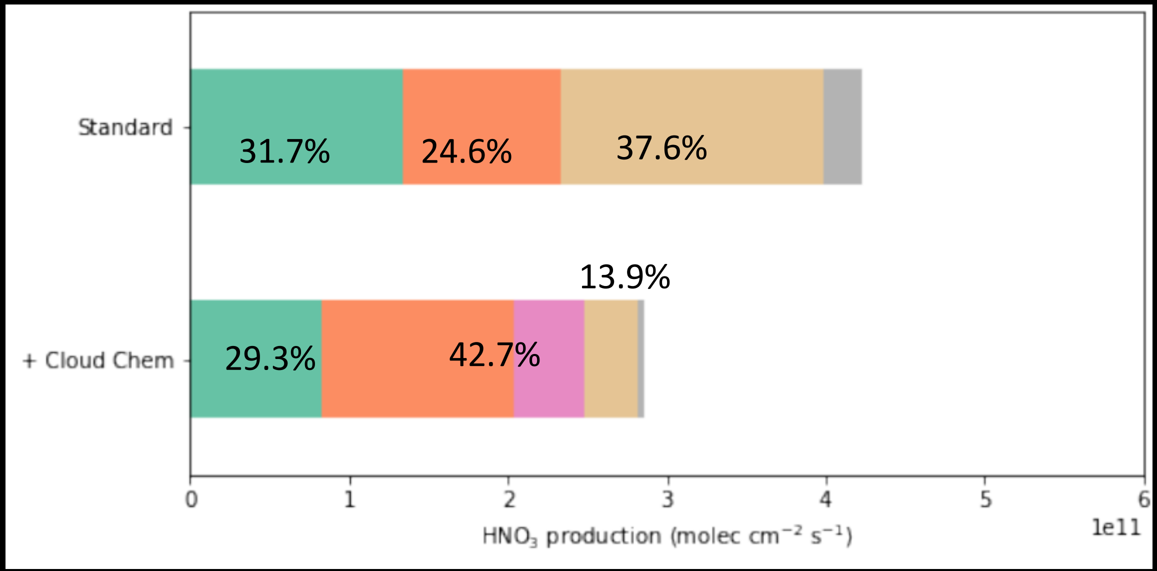


Nitrate production mechanisms: +Cloud chemistry

Clean

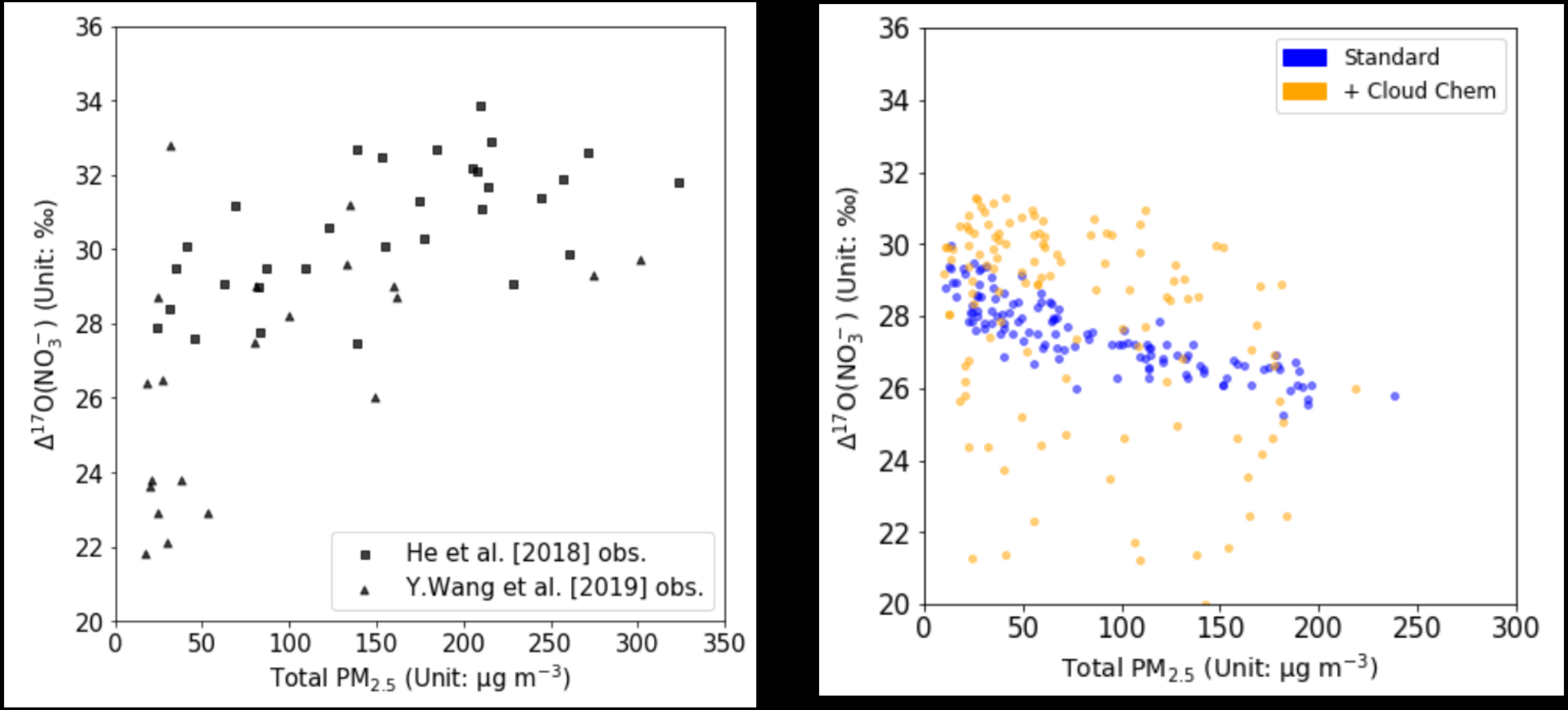


Polluted



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.

Δ^{17}O(nitrate): +Cloud chemistry

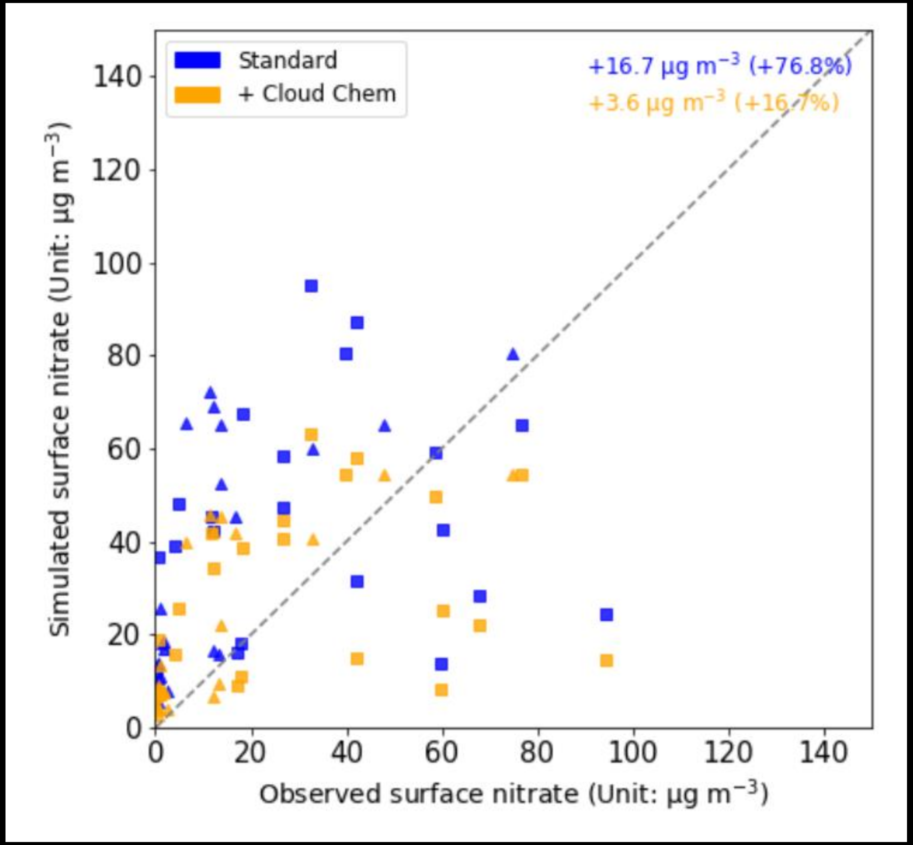


+Cloud chem increases mean Δ^{17}O(nitrate) slightly (by 0.3‰), but does not reproduce relationship between observed Δ^{17}O(nitrate) and $PM_{2.5}$

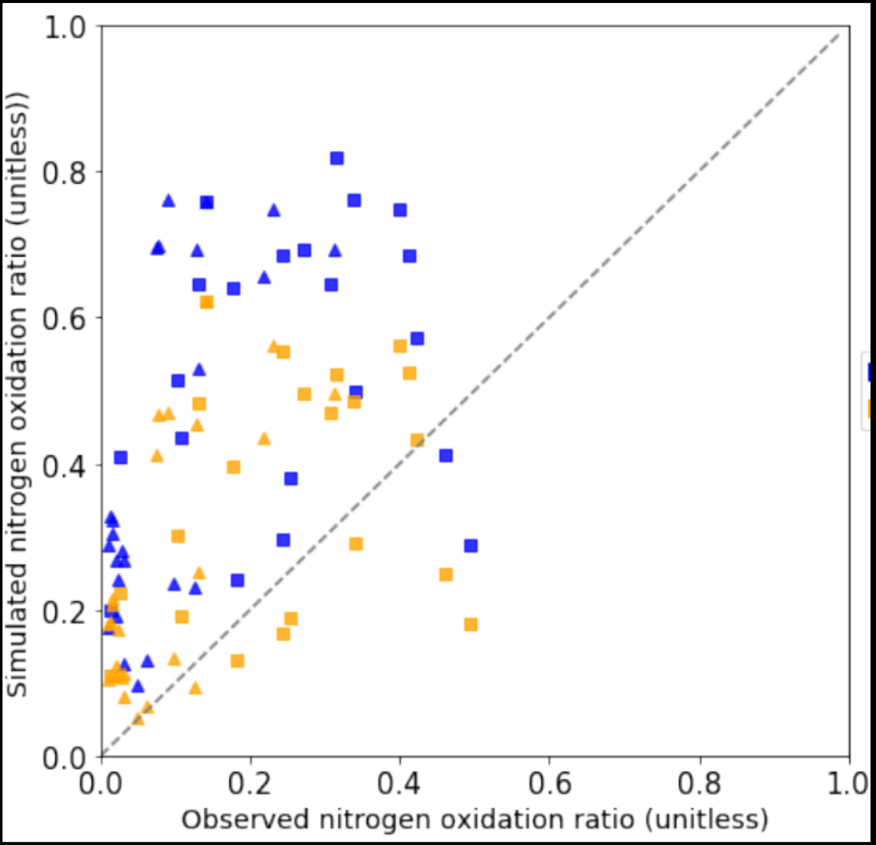
Nitrate concentrations and NOR

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

Nitrate Concentration



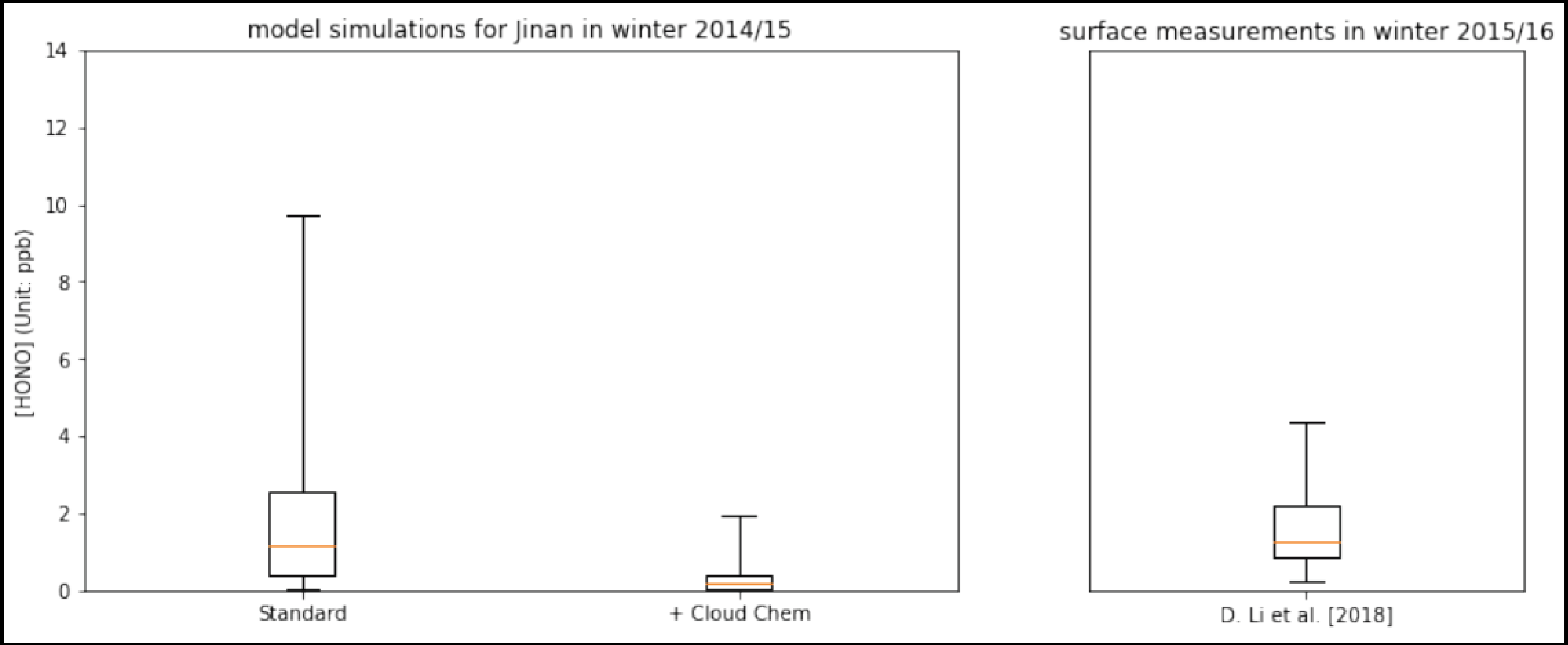
Nitrogen Oxidation Ratio (NOR)



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.

Model **Observations**



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

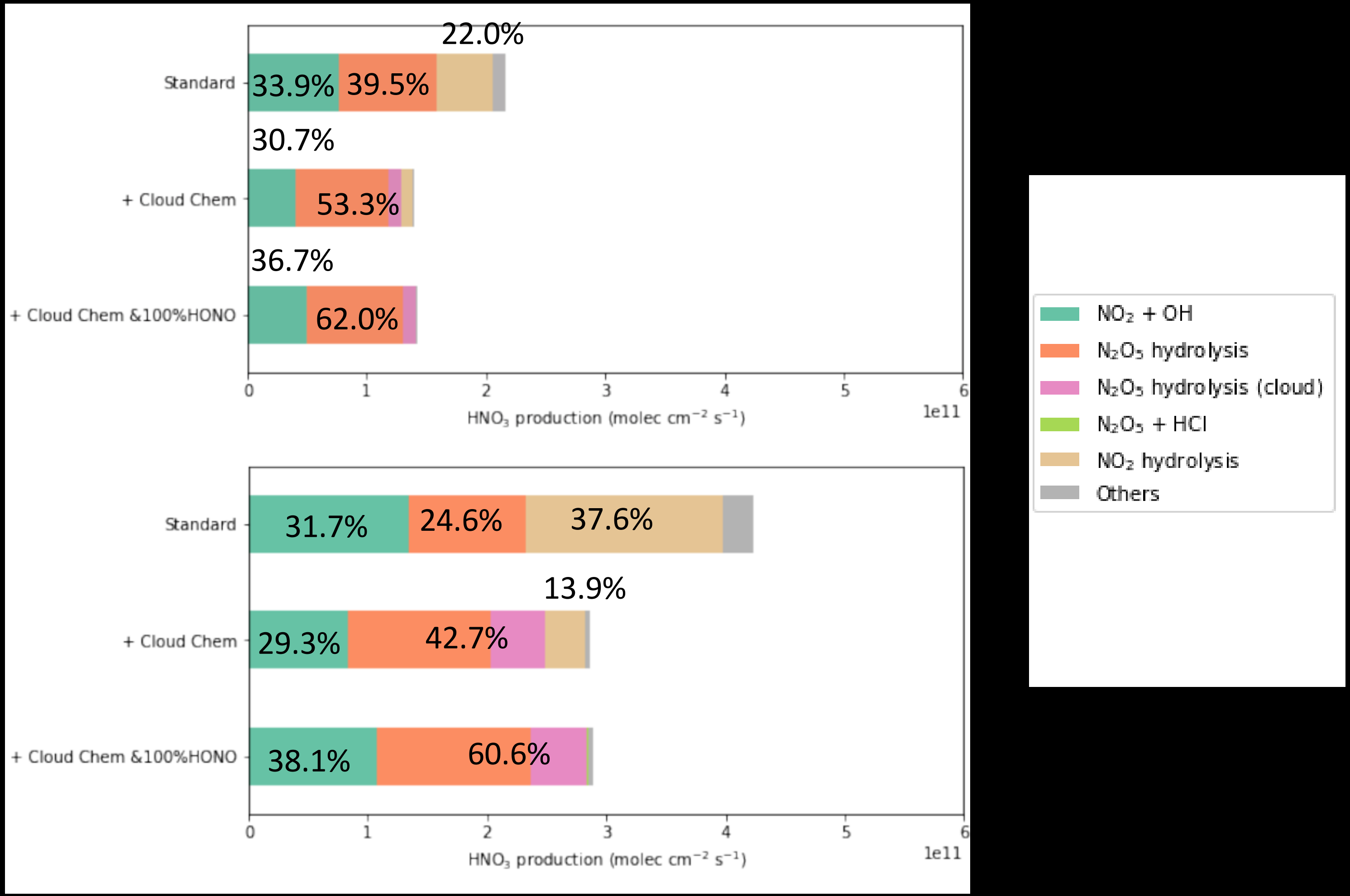
+ Cloud Chem + 100% HONO (+ updates to γ_{N2O5} and γ_{NO2})

- 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.

Applications to AQUARIUS

- $\Delta^{17}O$(nitrate) sensitive to relative importance of nitrate production mechanisms. Observations in Beijing suggest too high NO_2 + OH, NO_2 + H_2O in model.

- $\Delta^{17}O$(nitrate) is a unique method because it's not sensitive to physical processes (e.g., deposition)

- $\Delta^{17}O$(nitrate) complements concurrent observations of NO_x, nitrate, HONO, N_2O_5, $ClNO_2$, etc