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 NOₓ chemistry as a source of HONO?

Fractional contributions of sulfate formation pathways

Increase in gas-phase sulfate production (SO₂ + OH) from clean (19%) to polluted (34%) conditions due to increase in OH resulting from production of HONO from heterogeneous uptake of NO₂ in the model.

Shao et al. [2019]
Nitrate formation in Beijing in GEOS-Chem: $\Delta^{17}O$(nitrate)

Emission of NO$_x$ (NO+NO$_2$)

Tropospheric chemistry of NO$_y$

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

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

Conversion to NO$_3^-$ (aerosol) from HNO$_3$ (g)

Emission of NO$_x$ (NO+NO$_2$)

$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$ (98%)

$\text{NO}_2 + \text{HO}_2 \rightarrow \text{HNO}_3$ (2%)

$\text{NO}_2 + \text{hv} \rightarrow \text{NO}_3 + \text{O}_2$ (trace)

$\text{NO}_2 + \text{RO}_2 \rightarrow \text{RONO}_2$ (trace)

$\text{NO}_2 + \text{NO} \rightarrow \text{NO}_3$ (trace)

$\text{NO}_3 + \text{HO}_3 \rightarrow \text{HNO}_3$ (trace)

$\text{NO}_3 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$ (trace)

$\text{NO}_3 + \text{HC} \rightarrow \text{N}_2\text{O}_5 + \text{H}_2\text{O}$ (trace)

$\text{HNO}_3 (g)$

Conversion to NO$_3^-$ (aerosol) from HNO$_3$ (g)
Heterogeneous nitrate formation: $\Delta^{17}O($nitrate$)$

$$\Delta^{17}O(nitrate) = 25.5\%$$

$$\Delta^{17}O(nitrate) = 31.2\%$$

$$\Delta^{17}O(nitrate) = 33.8\%$$

$$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$$

$$\text{H}_{2}\text{O}$$

$$\text{HNO}_3$$

$$\text{HNO}_3$$

$$2\text{HNO}_3$$

$$\text{H}_2\text{O}$$

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

$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$

$\Delta^{17}O$(nitrate) = 25.5‰

$\text{H}_2\text{O} + \text{HNO}_3 \rightarrow 2\text{HNO}_3$

$\Delta^{17}O$(nitrate) = 31.2‰

$\text{HNO}_3 + \text{ClNO}_2$

$\Delta^{17}O$(nitrate) = 33.8‰
Research questions

1. What is the role of heterogeneous chemistry of reactive nitrogen (NO\textsubscript{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\textsubscript{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

Measurements and observations

• Two independent datasets of $\Delta ^{17}O(\text{NO}_3^-)$ 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$_2$O$_5$ 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)

\[
\frac{[\text{HNO}_3(\text{g})] + [\text{p-NO}_3^-]}{[\text{HNO}_3(\text{g})] + [\text{p-NO}_3^-] + [\text{NO}_2]} \]

Graphs showing modeled and observed surface nitrate and NOR concentrations.
How does the standard GC model perform?

- Underestimates the variability of $\Delta^{17}O(\text{NO}_3^-)$ ($\pm 0.9\%$ versus $\pm 3.8\%$).
- Underestimate the mean of $\Delta^{17}O(\text{NO}_3^-)$ during the wintertime haze events (27‰ versus 30‰).
- Cannot reproduce the observed positive relationship between $\text{PM}_{2.5}$ and $D^{17}O(\text{NO}_3^-)$.
How does the standard GC model perform?

- Underestimates the variability of $\Delta^{17}O(\text{NO}_3^-)$ ($\pm 0.9\%o$ versus $\pm 3.8\%o$)
- Underestimate the mean of $\Delta^{17}O(\text{NO}_3^-)$ during the wintertime haze events ($27\%o$ versus $30\%o$).
- Cannot reproduce the observed positive relationship between and PM$_{2.5}$.

![Graph showing observed vs modeled $\Delta^{17}O(\text{NO}_3^-)$ and PM$_{2.5}$](image-url)
Relationship between PM$_{2.5}$ and $\Delta^{17}$O(nitrate)

Modelled decreasing $\Delta^{17}$O(nitrate) with increasing PM$_{2.5}$ driven by increased nitrate formation from heterogeneous uptake of NO$_2$.

$\text{NO}_2 + \text{OH}$  $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$  $\text{NO}_2 + \text{H}_2\text{O}$  Other

Clean  33.9%  39.5%  22.0%

Polluted  31.7%  24.6%  37.6%

$\text{HNO}_3$ production [cm$^{-3}$ s$^{-1}$]
Model sensitivity simulations

+ Cloud Chem (+ updates to $\gamma_{N2O5}$ and $\gamma_{NO2}$)

- 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 (CINO$_2$) 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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IAMA Conference

2019-12-4
Model sensitivity simulations

+ Cloud Chem (+ updates to $\gamma_{N_2O_5}$, $\gamma_{NO_2}$, and $\gamma_{NO_3}$)
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Nitrate production mechanisms: +Cloud chemistry

Cloud NO\textsubscript{y} chemistry + updates to \(\gamma\text{N}_2\text{O}_5\) and \(\gamma\text{NO}_2\) yield relatively more heterogeneous \(\text{N}_2\text{O}_5\) chemistry and less heterogeneous NO\textsubscript{2} uptake. \(\text{N}_2\text{O}_5\) 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.
$\Delta^{17}O$(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 NO₂ 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) $\gamma_{\text{NO}_2}$. 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$_2$O $\rightarrow$ 0.5HNO$_3$ + 0.5HONO is uncertain and may be pH-dependent

+ Cloud Chem + 100% HONO (+ updates to $\gamma_{\text{N}_2\text{O}_5}$ and $\gamma_{\text{NO}_2}$)

- Same as +Cloud Chem but with NO$_2$ + H$_2$O $\rightarrow$ HONO
Nitrate production mechanisms: +Cloud chemistry + 100%HONO

Clean

Polluted

Cloud NO\textsubscript{y} chemistry + 100% HONO does not change nitrate production rates.
N$_2$O$_5$ uptake limited by N$_2$O$_5$ and ozone abundance

Model underestimates N$_2$O$_5$ because it underestimates ozone.
Heterogeneous \( \text{HO}_2 \) uptake impacts ozone

Laboratory experiments show that:
- \( \gamma_{\text{HO}_2} = 0.1 - 0.3 \) [e.g., Taketani et al., 2012]
- Heterogeneous \( \text{HO}_2 \) uptake catalyzed by Cu-Fe redox:

\[ \gamma_{\text{HO}_2} = 0.2 \] for all aerosol types

Figure from Mao et al. [2013]
Model sensitivity simulations

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**N$_2$O$_5$ and ozone: reduced HO$_2$ uptake**

**N$_2$O$_5$ (ppbv)**

**Modeled**

-32%  
-53%  
-52%  
-40%

**Observed**

Model simulations for Beijing during Nov-Dec 2014

**O$_3$ (ppbv)**

-65%  
-56%

Modeled O$_3$

Observed O$_3$
Conclusions

• \(\Delta^{17}O(\text{nitrate})\) sensitive to relative importance of nitrate production mechanisms. Observations in Beijing suggest too high \(\text{NO}_2 + \text{H}_2\text{O}\) and too low \(\text{N}_2\text{O}_5 + \text{H}_2\text{O}\) in polluted days in the model.

• Overestimate of \(\text{NO}_2 + \text{H}_2\text{O}\) corrected by updating \(\gamma_{\text{NO}_2}\) based on recent literature values. However, underestimate of \(\text{N}_2\text{O}_5\) hydrolysis cannot be reconciled by changes to \(\gamma_{\text{N}_2\text{O}_5}\) because it is limited by \(\text{N}_2\text{O}_5\) abundance. \(\text{N}_2\text{O}_5\) formation in the model is in turn limited by \(\text{O}_3\), which is also underestimated.

• Limiting heterogeneous \(\text{HO}_2\) uptake \((\gamma_{\text{HO}_2} = 0.2)\) to metal-containing aerosol increased modeled \(\text{N}_2\text{O}_5\) and ozone abundance but still underestimates ozone, \(\text{N}_2\text{O}_5\) and observed \(\Delta^{17}O(\text{NO}_3^-)\).
Extra slides
**Nitrate production mechanisms: +Cloud chemistry –γ_{\text{HO}_2}**

![Graph showing nitrate production mechanisms in clean and polluted conditions.](image)

- **Clean**:
  - + Cloud Chem: 31.4% HO2, 30.9% HNO3, 13.6% PM2.5, 13.3% [‰]
  - + Cloud Chem & reduced HO2 uptake: 31.5% HO2, 41.2% HNO3, 14.8% PM2.5, 11.5% [‰]

- **Polluted**:
  - + Cloud Chem: 30.7% HO2, 50.8% HNO3, 7.5% PM2.5, 7.5% [‰]
  - + Cloud Chem & reduced HO2 uptake: 33.8% HO2, 50.7% HNO3, 7.4% PM2.5, 7.2% [‰]
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.

Modeled surface nitrate [µg m$^{-3}$] vs Observed surface nitrate [µg m$^{-3}$]

Modeled NOR vs Observed NOR
Reactions affected by the model updates

- NO
- NO₂
- NO₃
- HNO₃ (g)
- O₃
- HO₂/RO₂
- XO
- hv
- RO₂
- XNO₃
- NO₁
- N₂O₅
- HC
- MTN/ISOP
- RONO₂

Heterogeneous reactions

Cloud Chem +