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\textsubscript{x} chemistry as a source of HONO?

Fractional contributions of sulfate formation pathways

Increase in gas-phase sulfate production (SO\textsubscript{2} + OH) from clean (19%) to polluted (34%) conditions due to increase in OH resulting from production of HONO from heterogeneous uptake of NO\textsubscript{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$_y$

- NO
  - $O_3$
  - $NO_2/RO_2$
  - $HO_2/RO_2$
  - $XO$
  - hv

- NO$_2$
  - 98% trace
  - $XNO_3$
  - $NO_3^-$
  - $NO_2$
  - $O_3$
  - $NO_2$
  - $N_2O_5$
  - MTN/ISOP
  - RONO$_2$

- RONO$_2$
  - hydrolysis

- Reaction with low $\Delta^{17}O$
  - 32% trace
  - 29% trace
  - 5% trace
  - 0.4% trace
  - 33% trace

- Reaction with high $\Delta^{17}O$
  - 32% trace
  - 29% trace
  - 5% trace
  - 0.4% trace
  - 33% trace

- Heterogeneous reactions
  - $N_2O_5$ hydrolysis
  - $HCl$ hydrolysis
  - $HNO_3$ (g)
Heterogeneous nitrate formation: $\Delta^{17}O$(nitrate)

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

$\text{HNO}_3$

$\Delta^{17}O$(nitrate) = 25.5‰

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

$2\text{HNO}_3$

$\Delta^{17}O$(nitrate) = 31.2‰

$\text{HNO}_3$

$\text{Cl}^-$

$\Delta^{17}O$(nitrate) = 33.8‰
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$\rightarrow 2\text{HNO}_3$

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$\text{HNO}_3 + \text{Cl(NO}_2$

$\rightarrow \Delta^{17}O$ (nitrate) = 33.8‰
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\textsubscript{x}-NO\textsubscript{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 Δ^{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)

\[
\frac{[\text{HNO}_3(\text{g})] + [\text{p-NO}_3^-]}{[\text{HNO}_3(\text{g})] + [\text{p-NO}_3^-] + [\text{NO}_2]} \]
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 $\gamma_{N2O5}$ 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)

+ NO$_2$ deposition $\rightarrow$ HONO

- More detailed treatment of NO$_2$ deposition
- NO2 deposition to surfaces yields HONO
## Model sensitivity simulations

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### + NO$_2$ deposition $\rightarrow$ HONO

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Reactions affected by the model updates

- Heterogeneous reactions

NO → NO₂
NO₂ → NO₃
NO₃ → HNO₃ (g)
NO → NO₂
O₃ → NO₂
HO₂/RO₂ → NO₂
XO → NO₂
hv → NO₂
RO₂ → RONO₂
RONO₂ → hydrolysis
N₂O₅ → hydrolysis
H₂O → hydrolysis
HC → hydrolysis
MTN/ISOP → hydrolysis

Cloud Chem

Becky Alexander
Nitrate production mechanisms: +Cloud chemistry

Cloud NO$_y$ chemistry + updates to $\gamma_{N_2O_5}$ and $\gamma_{NO_2}$ yield relatively more heterogeneous $N_2O_5$ chemistry and less heterogeneous NO$_2$ uptake. $N_2O_5$ hydrolysis dominates nitrate production pathway in polluted and clean atmosphere.
\[ \Delta^{17}O(\text{nitrate}): +\text{Cloud chemistry} \]

+Cloud chem increases mean \[ \Delta^{17}O(\text{nitrate}) \] slightly (by 0.3‰), but does not reproduce relationship between observed \[ \Delta^{17}O(\text{nitrate}) \] and PM\(_{2.5}\).
"+ Cloud Chem" reduces nitrate concentrations (~+17%) and NOR (+0.13) in Beijing in model and brings it closer to the observed levels.
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\textsubscript{2} uptake and HONO

- Polluted conditions increase nitrate formation via heterogeneous uptake of NO\textsubscript{2}, even with updated (reduced) $\gamma_{\text{NO}_2}$. This drives the decrease in $\Delta^{17}\text{O}(\text{nitrate})$ with increasing PM\textsubscript{2.5}, the opposite trend of the observations.
- Yield of NO\textsubscript{2} + H\textsubscript{2}O $\rightarrow$ 0.5HNO\textsubscript{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\textsubscript{2} + H\textsubscript{2}O $\rightarrow$ 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$_2$O 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$_2$O$_5$, ClNO$_2$, etc