The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen in polar regions

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Snow Nitrate Photolysis

\[ \text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2 \rightarrow \text{NO} \rightarrow \text{NO}_3^- / \text{HNO}_3 \]

\[ \lambda = 300-345 \text{ nm} \]

Photolysis Rate Constant

\[ J = \sigma_{\text{NO}_3^-} (\lambda) \cdot \phi_{\text{NO}_3^-} (T, \text{pH}) \cdot I_o (\lambda, z) \]

Images: NASA
Snow Nitrate Photolysis

\[ \text{NO}_3^- + \text{hv}(+\text{H}^+ + \text{OH}) \rightarrow \text{NO}_2 + \text{OH} \]

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Photolysis Rate Constant

Nitrogen recycling influences atmospheric oxidative capacity.
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Photolysis Rate Constant

Nitrogen recycling influences atmospheric oxidative capacity.

Photolysis-driven loss of snow nitrate influences nitrate records in ice cores.
Incorporate snow NO$_3^-$ photolysis into a global chemical transport model to better understand the implications of snow NO$_3^-$ photochemistry for boundary layer chemistry, the recycling and redistribution of nitrogen and its spatial variability, and the preservation of NO$_3^-$ in ice cores.

**Snow-sourced NO$_x$ in GEOS-Chem**

\[ F_{NO_x} = \int_z \int_{\lambda} J(\lambda, T, pH) \cdot [NO_3^-](z) d\lambda dz \]

version: v9-01-01
resolution: 2°x2.5°
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Snowpack actinic flux parameterization
Zatko et al. [2013]

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Snow black carbon concentrations

Bisiaux et al., 2012 (and references within), Chylek et al., 1987, 1992, McConnell et al., 2007

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Snow black carbon concentrations

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Snowpack actinic flux parameterization
Zatko et al. [2013]

Snow nitrate concentrations

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resolution: 2°x2.5°

Snowpack actinic flux parameterization and snow photolysis scheme in GEOS-Chem

Bertler et al., 2005, Burkhart et al., 2009, Bisiaux et al., 2012 (and references within), Chylek et al., 1987, 1992, McConnell et al., 2007
Incorporate snow NO\textsubscript{3} photolysis into a global chemical transport model to better understand the implications of snow NO\textsubscript{3} photochemistry for boundary layer chemistry, the recycling and redistribution of nitrogen and its spatial variability, and the preservation of NO\textsubscript{3} in ice cores.

Flux of Snow-Sourced NO\textsubscript{x} (F\textsubscript{NO\textsubscript{x}})

Modeled F\textsubscript{NO\textsubscript{x}} in general agreement with observations

Baguitte et al., 2012, Honrath et al., 2002, Frey et al., 2013, Jones et al., 2001, Masclin et al., 2013, Oncley et al., 2004
Quantifying the Degree of Nitrogen Recycling

Nitrogen Recycling Factor (NRF\textsubscript{\(\tau_z\)})

\[ \text{NRF}_{\tau_z} = \frac{F_{\text{NOx}}}{F_{\text{PRI}}} \cdot \tau_z \]

The Nitrogen Recycling Factor represents the average number of times that nitrate is recycled between the air and snow before burial below the snow photic zone.
Nitrogen Recycling Factor ($\text{NRF}_{T_z}$)

Nitrate is recycled on average up to 60 times in Antarctica and 3 times in Greenland.
Boundary layer NO\textsubscript{x}, NO\textsubscript{3}^{-}+HNO\textsubscript{3}, OH, and O\textsubscript{3} mixing ratios are increased in Antarctica when snow-sourced NO\textsubscript{x} is present.
Factor increases in boundary layer NO\textsubscript{x}, NO\textsubscript{3}⁻+HNO\textsubscript{3}, OH, and O\textsubscript{3} mixing ratios are smaller across Greenland compared to Antarctica.
Implications for Ice Core Records

Fraction of photolysis-driven loss of NO$_3^-$ from snow ($f$)

Ice-core $\delta^{15}$N(NO$_3^-$) influenced by photolysis-driven loss of NO$_3^-$ in snow.
Implications for Ice Core Records

Fraction of photolysis-driven loss of NO$_3^-$ from snow ($f$)

Ice-core $\delta^{15}$N(NO$_3^-$) influenced by photolysis-driven loss of NO$_3^-$

Ice-core $\delta^{15}$N(NO$_3^-$) is a useful metric to assess model performance.
Summary

- Modeled snow NO\textsubscript{x} fluxes are in rough agreement with observations in Antarctica and Greenland.

Ice core δ\textsubscript{15}N(NO\textsubscript{3}−) can be used to examine the nitrogen recycling in Antarctica.
Summary

- Modeled snow NO$_x$ fluxes are in rough agreement with observations in Antarctica and Greenland.

- Boundary layer abundances of NO$_x$, NO$_3^-$+HNO$_3$, OH, and O$_3$ in these regions are increased.

Ice core $\delta^{15}$N(NO$_3$) can be used to examine the nitrogen recycling in Antarctica.
Summary

• Modeled snow NO\textsubscript{x} fluxes are in rough agreement with observations in Antarctica and Greenland.

• Boundary layer abundances of NO\textsubscript{x}, NO\textsubscript{3}⁻+HNO\textsubscript{3}, OH, and O\textsubscript{3} in these regions are increased.

• Nitrate remains in the snow longer and is recycled more in Antarctica than Greenland.
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• Boundary layer abundances of NO\textsubscript{x}, NO\textsubscript{3}⁻+HNO\textsubscript{3}, OH, and O\textsubscript{3} in these regions are increased.

• Nitrate remains in the snow longer and is recycled more in Antarctica than Greenland.

• The strong relationship between nitrogen recycling and photolysis-driven loss of snow nitrate suggests that ice-core δ\textsuperscript{15}N(NO\textsubscript{3}⁻) can be used to examine the degree of nitrogen recycling.
Extra
Impacts of Snow Photochemistry on Boundary Layer Chemistry

Source of oxidant and oxidant precursors:
- Decreased lifetime of traces gases
- Ozone production and destruction
- Reactive gaseous mercury production

\[ \text{DMS} + \text{OH} \rightarrow \text{DMSO} + x \]
\[ \text{CO} + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]

\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^{(3P)} \]
\[ \text{O}^{(3P)} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \]

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]
\[ \text{NO}_2 + \text{hv(O}_2) \rightarrow \text{NO} + \text{O}_3 \]

\[ \text{Br/BrO} + \text{GEM} \rightarrow \text{RGM} \]

Grannas et al., 2007, Simpson et al., 2007
Nitrate Preserved in Ice Cores

Ice core nitrate records reveal information about NO$_x$ abundances, NO$_x$ sources and the atmospheric oxidant budget in previous climates.

Snow $\delta^{15}\text{N(NO}_3^-)$ profiles provide evidence of snow photochemistry, Ice core $\delta^{15}\text{N(NO}_3^-)$ may be a proxy for the degree of nitrogen recycling in snow.

Isotope calculation

$$\delta = \frac{R_{sample}}{R_{reference}} - 1$$

R is elemental ratio: $^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$, $^{15}\text{N}/^{14}\text{N}$, units: ‰

Freyer et al., 1993, Kendall et al., 2007, Heaton et al., 1997, Alexander et al., 2009
What influences actinic flux in snow?

Developed snowpack actinic flux parameterization
Based on 4-stream radiative transfer model [Grenfell, 1991]

Snowpack actinic flux most sensitive to grain size and impurity content

NonBC material is responsible for roughly 90% of absorption of radiation at 305 nm

Zatko et al. [2013]
Quantifying the Degree of Nitrogen Recycling

Time nitrate in photic zone ($T_z$)

$$T_z = \frac{\text{photic zone}}{\text{annual snow accumulation}}$$

Nitrogen Recycling Factor ($\text{NRF}_{T_z}$)

$$\text{NRF}_{T_z} = \frac{F_{\text{NOx}}}{F_{\text{PRI}}} \cdot T_z$$

Nitrate remains in the photic zone longer and is recycled more before burial in Antarctica.
Quantifying Photolysis-Driven Loss of Snow Nitrate

**Fraction of photolysis-driven loss of NO\textsubscript{3} from snow (f)**

δ\textsuperscript{15}N(NO\textsubscript{3}\textsuperscript{-}) in snow

Ice-core δ\textsuperscript{15}N(NO\textsubscript{3}\textsuperscript{-}) can be used to examine the degree of nitrogen recycling in Antarctica and Greenland.
Implications for Nitrate Ice Core Records

\[ f = \left( 1 - \frac{F_R}{F_{NOx}} \right)^{T_Z} \cdot F_p \]

\[ \delta^{15}\text{N(NO}_3^-) \text{ in snow} \]

\[ \delta^{15}\text{N(NO}_3^-) = \delta^{15}\text{N(NO}_3^-)_{\text{air}} \cdot f(\varepsilon+1) \]

There is strong relationship between NRF\textsubscript{\textit{TZ}} and \textit{f} in Antarctica and Greenland.
Incorporate polar snow nitrate photolysis into GEOS-Chem

- Impact of snow-sourced NO$_x$ on boundary layer chemistry
- Recycling and redistribution of reactive nitrogen
- Preservation of nitrate in ice cores
Incorporate snow NO$_3^-$ photolysis into a global chemical transport model to better understand the implications of snow NO$_3^-$ photochemistry for boundary layer chemistry, the recycling and redistribution of nitrogen and its spatial variability, and the preservation of NO$_3^-$ in ice cores.

Snow-sourced NO$_x$ in GEOS-Chem

$$F_{NO_x} = \int_z \int \lambda J(\lambda, T, pH) \cdot [NO_3^-](z) d\lambda dz$$

Mean Summer UV Photic Zone Depth

Photic zone depth most dependent on snow grain size and light-absorbing impurities in snow
Photochemical Reactions in Snow

In liquid like regions:

\[ \text{NO}_2^- + \text{hv}(+\text{H}^+) \rightarrow \text{NO}_2 + \text{OH} \]
\[ \text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2^- + \text{O}(^3\text{P}) \]
\[ \text{NO}_2^- + \text{hv}(+\text{H}^+) \rightarrow \text{NO} + \text{OH} \]
\[ \text{NO}_2^- + \text{OH} \rightarrow \text{NO}_2 + \text{OH}^- \]
\[ \text{NO}_2^- + \text{H}^+ \rightarrow \text{HONO} \]

Reactions involving:

\[ \text{Br}_y, \text{NO}_2^-, \text{HO}_x, \text{Br}^- \rightarrow \text{Br}_2 \]

Organics + \text{hv} \rightarrow \text{H}_2\text{O}_2, \text{CH}_2\text{O}

Photolysis range: 290-390 nm
Primary and Recycled Nitrogen Fluxes

GEOS-Chem ideal for evaluating recycling and redistribution of nitrogen on large spatial scales.
There is strong relationship between $\text{NRF}_{\tau z}$ and $f$ in Antarctica and Greenland. Ice-core $\delta^{15}\text{N}(\text{NO}_3^-)$ can be used to examine the degree of nitrogen recycling in polar regions.
Quantifying the Degree of Nitrogen Recycling

Time nitrate in photic zone ($T_z$)

Nitrogen Recycling Factor ($NRF_{Tz}$)
Davis et al. [2008]

Nitrate remains in the photic zone longer and is recycled more before burial in Antarctica
There is strong relationship between $NRF_{\tau z}$ and $f$ in Antarctica and Greenland.

Ice-core $\delta^{15}N(NO_3^-)$ can be used to examine the degree of nitrogen recycling in polar regions.
Extra 2
Long range transport of $\text{NO}_3^-$ and stratospheric input

$\text{NO}_2 \xrightleftharpoons{\text{hv}} \text{NO}$

$\text{NO}_3^-/\text{HNO}_3$

$\text{NO}_3^- \rightarrow \text{NO}_x$

$\text{NO}_3^- \xrightarrow{\text{hv}} \text{NO}_x$

$\text{F}_{\text{PRI}}$

$\text{F}_{\text{NOx}}$

$\text{F}_R$

$\text{F}_{\text{NOx}}$

Snow photic zone
Other photochemical reactions in snow

In liquid like regions:

\[
\begin{align*}
\text{NO}_2^- + \text{hv}(+\text{H}^+) & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_3^- + \text{hv} & \rightarrow \text{NO}_2^- + \text{O}^3\text{P} \\
\text{NO}_2^- + \text{hv}(+\text{H}^+) & \rightarrow \text{NO} + \text{OH} \\
\text{NO}_2^- + \text{OH} & \rightarrow \text{NO}_2 + \text{OH}^- \\
\text{NO}_2^- + \text{H}^+ & \rightarrow \text{HONO} \\
\text{organsics} + \text{hv} & \rightarrow \text{H}_2\text{O}_2, \text{CH}_2\text{O} \\
\text{Reactions involving:} & \\
\text{Br}_y, \text{NO}_2^-, \text{HO}_x, \text{Br}^- & \rightarrow \text{Br}_2 \\
\text{Photolysis range: } 290-390 \text{ nm}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{O} + \text{hv(O}_2) & \rightarrow 2\text{HO}_2 + \text{CO} \\
\text{HONO} + \text{hv} & \rightarrow \text{NO} + \text{OH} \\
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{OH} \\
\text{Br}_2 + \text{hv} & \rightarrow 2\text{Br}
\end{align*}
\]