Heterogeneous cloud and aerosol chemistry in the tropospheric NO$_y$ cycle

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**N₂O₅ hydrolysis on aerosol surfaces: a large NOₓ sink**

Field: Platt et al., 1980, 1984; Heikes and Thompson, 1983; Brown et al., 2007
Models: Dentener & Crutzen, 1993; Tie et al., 2001; Evans and Jacob, 2005
*and many more*

![Chemical reaction diagram](image)

- **Surface area**
- **Particle size**
- **Diffusion**
- **Reactive uptake γ**

(A Schwartz, 1986; Sander, 1999; Jacob, 2000)

- **20-35% of global NOₓ sink** (Alexander et al., 2009; Bauer et al., 2004)
- **Reduces global O₃ and OH by 1-4%** (Macintyre and Evans, 2010)

**What about clouds?**

Clouds have 10⁶ times greater surface area than aerosols (Holmes et al., 2019)

…but cloud contact is sporadic, roughly daily (Lelieveld et al., 1989)

Past studies reported cloud uptake is very small, because they assumed aerosol uptake was very fast (γ = 0.1)

(Lelieveld and Crutzen, 1990; Dentener & Crutzen, 1993; Jacob, 2000)
Grid cells are *partly* cloudy, usually $f_c < 0.2$

<table>
<thead>
<tr>
<th>Clear fraction, $1 - f_c$</th>
<th>Cloudy fraction, $f_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{N_2O_5} = \infty$</td>
<td>$\tau_{N_2O_5} = k_i^{-1} \approx 30 \text{ s}$</td>
</tr>
</tbody>
</table>

*hydrolysis lifetime*
Numerical methods for cloud uptake in regional and global models

Existing methods

**Thin-cloud approximation**

Problem: uptake much too fast
Numerical methods for cloud uptake in regional and global models

**Existing methods**

Thin-cloud approximation

**Problem:**
- sensitive to model time stepping (unphysical)
- converges to thin-cloud approximation

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**Repartitioning method**

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<tr>
<th>Clear fraction, $1 - f_c$</th>
<th>Cloudy fraction, $f_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1 - f_c) m$</td>
<td>$f_c m$</td>
</tr>
</tbody>
</table>

- $k_i$ reactive uptake

Problem: sensitive to model time stepping (unphysical) converges to thin-cloud approximation
Numerical methods for cloud uptake in regional and global models

Existing methods

Problem: chemical operator splitting complicated not used in any current models
Numerical methods for cloud uptake in regional and global models

Existing methods

Thin-cloud approximation

Repartitioning method

Cloud free

Cloudy

Cloud free

Cloudy fraction, $f_c$

$
(1-f_c)m
$

Clear fraction, $1-f_c$

$f_c m$

$k r_{reactive uptake}$

$k r_{reactive uptake}$

Cloud pulsing

Time
Numerical methods for cloud uptake in regional and global models

**New method**

**Entrainment-limited uptake**

- Clear fraction, $1-f_c$
- Cloudy fraction, $f_c$

\[
\begin{align*}
\dot{m}_0 &\rightarrow k_c \rightarrow m_c \\
k_c f_c / (1-f_c) &\rightarrow \text{entrainment} \\
 &\rightarrow k_i \rightarrow m_i \\
\end{align*}
\]

A single, 1st order loss rate integrating in-cloud uptake, cloud fraction, and entrainment

**Example errors**

- **Entrainment limited**
- **Our New Method**
- **Repartitioning** (10 & 30 minute)
- **Thin cloud**

\[
\begin{align*}
\tau_{N_2O_5} &\approx \left( \frac{1-f_c}{f_c k_c} + \frac{r}{f_c A D_g} + \frac{4}{f_c A v Y} \right) \sim 10 \text{ hr}
\end{align*}
\]

**Partly cloudy, entrainment limited (new):**

Advantages:
- Physically realistic
- Analogous to Schwartz (1986) mass transfer
- Simple, fast

Applies to *any* irreversible reaction in clouds: $N_2O_5$, S(IV), HO$_2$, Hg(II), halogens, aerosol

Methods in current models, including GEOS-Chem

Holmes et al., 2019 GRL
Experimental design with GEOS-Chem

Model configuration, v11-01

- Tropospheric chemistry (Parrella et al., 2012)
  - includes aerosol heterogeneous chemistry (Evans and Jacob, 2005)

- MERRA-2 meteorology for 2015 at 4° x 5° x 47L

Model improvements

- Reassessed $\gamma$ for all NO$_y$ species (JPL, IUPAC)
- Uptake on SO$_4^{2-}$–NO$_3^-$–NH$_4^+$ aerosol follows
  - Bertram and Thornton (2009), Shah et al. (2018)

- Entrainment-limited cloud uptake

Entrainment-limited, grid-scale N$_2$O$_5$ loss

- Fastest loss with large cloud fraction
- Limited by entrainment

MERRA-2 zonal mean, 2015-04-01
**NO\textsubscript{x} losses in improved model**

**Global NO\textsubscript{x} losses**
- Homogeneous: 4.1 Tmol(N) yr\textsuperscript{-1} (63%)
  - OH + NO\textsubscript{2} → HNO\textsubscript{3}
  - NO\textsubscript{3} + VOC → HNO\textsubscript{3}
- Aerosol uptake: 25%
- Dry deposition: 7%
- Cloud uptake: 5%

Cloud uptake provides 25% of NO\textsubscript{x} loss in high latitudes (new result)
Aerosol uptake provides 30% of NO\textsubscript{x} loss in NH mid latitudes (similar to past literature)

Model changes are small relative to NO\textsubscript{x}, & O\textsubscript{3} environmental variability

Reduces aerosol nitrate bias & improves $\Delta^{17}$O-nitrate (Alexander et al., 2019 ACP)

Chemistry is clear: N\textsubscript{2}O\textsubscript{5} hydrolysis should be included in models regardless of performance benefit

Holmes et al., 2019 GRL
# Effects of clouds and aerosol on global tropospheric chemistry

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Control</th>
<th>Cloud Off</th>
<th>Aerosol Off</th>
<th>Both Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol reactions</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Cloud reactions</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>43 Gmol N</td>
<td>+0.7 %</td>
<td>+3.8 %</td>
<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td>6.9 Tmol</td>
<td>+2.4 %</td>
<td>+2.5 %</td>
<td></td>
</tr>
<tr>
<td>$\tau$$_{CH_4+OH}$</td>
<td>8.7 yr</td>
<td>-1.9 %</td>
<td>-3.4 %</td>
<td></td>
</tr>
</tbody>
</table>

Neglecting cloud uptake of N$_2$O$_5$ and NO$_3$
- Increases tropospheric NO$_x$ by ~1%
- Increases tropospheric O$_3$ by 2.4%
- Decreases CH$_4$ lifetime by 2%

Cloud and aerosol heterogeneous reactions have similar magnitude effects on NO$_x$, O$_3$, and OH

Neglecting both causes larger changes than the sum of their individual effects because clouds and aerosol compete for N$_2$O$_5$

Accounting for clouds makes tropospheric NO$_x$, O$_3$, and OH much less sensitive to aerosol $\gamma$ and surface area.

Holmes et al., 2019 GRL
Simulating $\text{N}_2\text{O}_5$ uptake on aerosol based on field studies

McDuffie et al. (2018) empirical parameterization of $\gamma(\text{N}_2\text{O}_5)$
- Internal mixing of organic and sulfate-nitrate-ammonium aerosol
- Accounts for organic coating (Riemer et al., 2009)
  Surrounding an inorganic core (Bertram and Thornton, 2009)
- Better describes WINTER field observations than existing formulas
- Released in GEOS-Chem 12.6

Default Winter $\gamma(\text{N}_2\text{O}_5)$

Updated $\gamma(\text{N}_2\text{O}_5)$

Global Median: 0.0106

0.005 0.01 0.015 0.02 0.025 0.03 0.035 0.04

$\text{N}_2\text{O}_5$ Uptake Coefficient

Default GEOS-Chem pre-12.6 (Evans & Jacob GRL 2005)

Internal mixture of Org+SNA (McDuffie et al., JGR 2018)
Combined changes in tropospheric composition

<table>
<thead>
<tr>
<th>GEOS-Chem</th>
<th>12.1</th>
<th>+Holmes 2019</th>
<th>+McDuffie 2018</th>
<th>+Holmes 2019 +McDuffie 2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol reactions</td>
<td>Yes</td>
<td>Updated $\gamma$</td>
<td>Updated $\gamma$</td>
<td>Updated $\gamma$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic coating</td>
<td>Organic coating</td>
<td></td>
</tr>
<tr>
<td>Cloud reactions</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\text{NO}_x$</td>
<td>41 Gmol N</td>
<td>- 0.9 %</td>
<td>+0.5 %</td>
<td>- 0.6 %</td>
</tr>
<tr>
<td>Aerosol nitrate</td>
<td>6.9 Gmol N</td>
<td>-1.2 %</td>
<td>- 0.5 %</td>
<td>-1.7 %</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>8.0 Tmol</td>
<td>- 5.2 %</td>
<td>+0.7 %</td>
<td>- 4.9 %</td>
</tr>
<tr>
<td>$\tau_{\text{CH}_4+\text{OH}}$</td>
<td>9.4 yr</td>
<td>- 6.1 % (10.0 yr)</td>
<td>- 5.6 % (9.9 yr)</td>
<td></td>
</tr>
</tbody>
</table>

Cloud and internal mixing updates partially offset each other.

$\text{CH}_4$ lifetime ($\tau_{\text{CH}_4+\text{OH}}$) now falls within observational constraints: $11.2 \pm 1.3$ yr (Prather et al., 2013)
Implications for global atmospheric chemistry

Cloud uptake of NO$_x$ plays a significant role in tropospheric chemistry:
• 20-25% of NO$_x$ loss at high latitudes
• 5% of global NO$_x$ loss.

This has been overlooked because early studies overestimated aerosol γ

After accounting for cloud effects, aerosols have less (half) influence on tropospheric chemistry

Organic coatings on inorganic aerosol decrease global mean aerosol nitrate and increase NO$_x$ by 0.5% each

Entrainment-limited uptake is realistic, simple and suitable for other cloud reactions in regional and global chemistry models: SO$_2$ oxidation, Halogen recycling, HO$_2$ uptake, aerosol processing, aqueous Hg reduction, wet scavenging

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