Cloud chemistry in the tropospheric NO$_x$ cycle: a new modeling approach its global implications

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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

\[
\begin{array}{c}
\text{N}_2\text{O}_5 \quad k_i \quad \text{Surface area} \\
\quad \text{Particle size} \\
\quad \text{Diffusion} \\
\quad \text{Reactive uptake } \gamma
\end{array}
\rightarrow \quad \text{HNO}_3, \text{CINO}_2
\]

Aerosol: \( \gamma \approx 10^{-4} - 0.02 \) (complicated)
Water & Ice: \( \gamma \approx 0.02 - 0.03 \) (well known)

(Crowley et al., 2010; Ammann et al., 2013;
Burkholder et al., 2015)

(\textit{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 \( (\gamma = 0.1) \)

(Lelieveld and Crutzen, 1990; Dentener & Crutzen, 1993; Jacob, 2000)
Numerical methods for cloud uptake in regional and global models

Grid cells are *partly* cloudy, usually $f_c < 0.2$

Clear fraction, $1 - f_c$

Cloudy fraction, $f_c$

$\tau_{N_2O_5} = \infty$

$\tau_{N_2O_5} = k_i^{-1} \approx 30 \text{ s}$

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

New method

Entrainment-limited uptake

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

Partly cloudy, entrainment limited (new):

\[
\tau_{N_2O_5} \approx \left( \frac{1 - f_c}{f_c k_c} + \frac{r}{f_c A D_g} + \frac{4}{f_c A V y} \right) \sim 10 \text{ hr}
\]

Advantages:
- Physically realistic
- Analogous to Schwartz (1986) mass transfer
- Simple, fast
- Applies to any irreversible reaction in clouds: N₂O₅, S(IV), HO₂, Hg(II), halogens, aerosol

Example errors

Methods in current models, including GEOS-Chem
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 γ 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_2O_5 loss

Fastest loss with large cloud fraction
Limited by entrainment

MERRA-2 zonal mean, 2015-04-01
**NO$_x$ losses in improved model**

Global NO$_x$ losses

- Homogeneous: 63%
- OH + NO$_2$ → HNO$_3$
- NO$_3$ + VOC → HNO$_3$
- Aerosol uptake: 25%
- Dry deposition: 7%
- Cloud uptake: 5%

4.1 Tmol(N) yr$^{-1}$

Cloud uptake provides 25% of NO$_x$ loss in high latitudes (new result)

Aerosol uptake provides 30% of NO$_x$ loss in NH mid latitudes (similar to past literature)

Chemistry is clear: N$_2$O$_5$ hydrolysis should be included in models regardless of performance benefit

Model changes are small relative to NO$_x$, & O$_3$ environmental variability

Reduces aerosol nitrate bias & improves $\Delta^{17}$O-nitrate (B. Alexander)

Ozonesonde, Samoa

Model with and without cloud uptake
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 $\gamma$.

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

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.

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Cloud chemistry methods currently used in GEOS-Chem

- **Thin Cloud:**
  - S(IV) oxidation
  - Halogen recycling
  - Everything in gckpp_HetRates

- **Repartitioning:**
  - Hg(II) reduction

- **Entrainment limited:**
  - \( N_2O_5 , \ NO_3 , \ HO_2 \)

**Missing:**
- Aerosol processing?