Heterogeneous cloud and aerosol chemistry in the tropospheric NO_y cycle

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N_2O_5 hydrolysis on aerosol surfaces: a large NO_x 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

$$N_2O_5 \xrightarrow{k_i} HNO_3, ClNO_2$$

Surface area
Particle size
Diffusion
Reactive uptake γ

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

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)

- **20-35% of global NO_x sink** (Alexander et al., 2009; Bauer et al., 2004)
- **Reduces global O_3 and OH by 1-4%** (Macintyre and Evans, 2010)

What about clouds?

Clouds have 10^6 times greater surface area than aerosols (Holmes et al., 2019)
…but cloud contact is sporadic, roughly daily (Lelieveld et al., 1989)

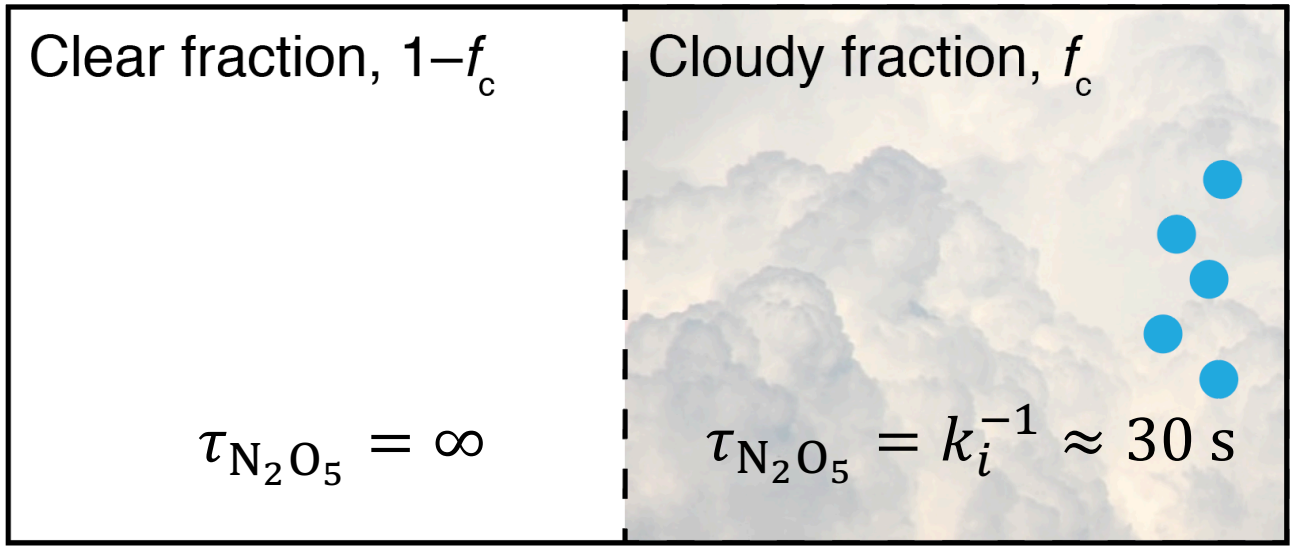
Past studies reported cloud uptake is very small, because they assumed aerosol uptake was very fast ($\gamma = 0.1$)

(Lelieveld and Crutzen, 1990; Dentener & Crutzen, 1993; Jacob, 2000)

Numerical methods for cloud uptake in regional and global models

*that don't resolve clouds

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

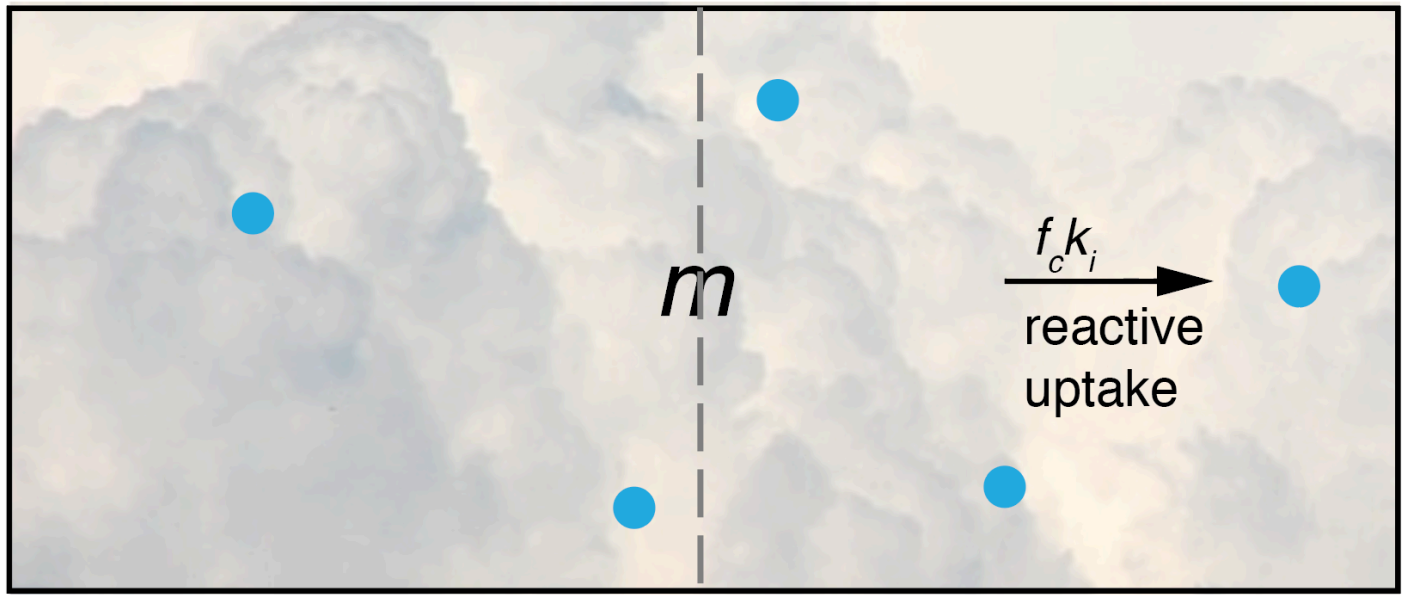


hydrolysis lifetime

Numerical methods for cloud uptake in regional and global models

Existing methods

Thin-cloud approximation

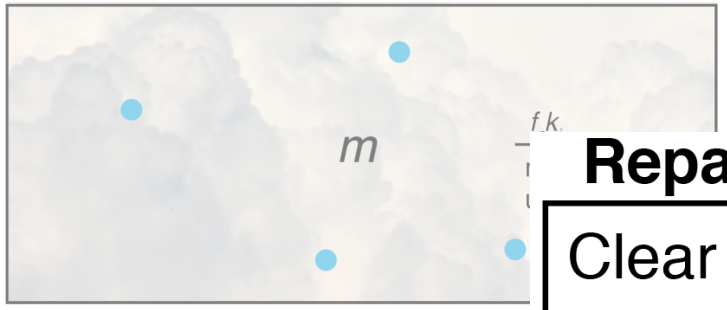


Problem: **uptake much too fast**

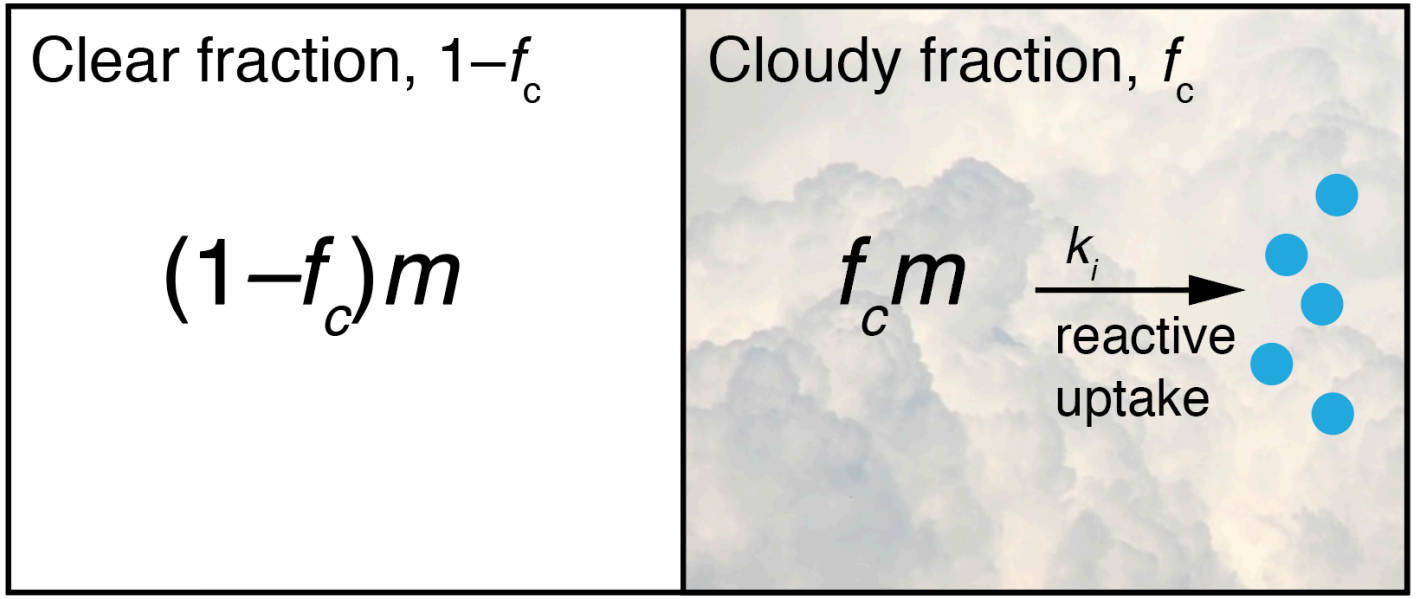
Numerical methods for cloud uptake in regional and global models

Existing methods

Thin-cloud approximation



Repartitioning method



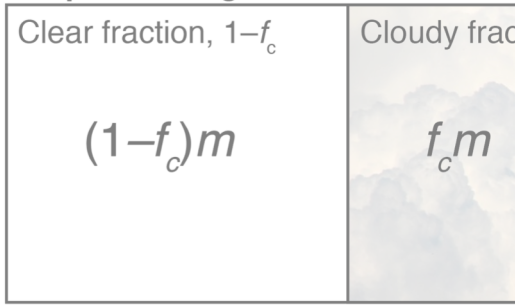
Problem: **sensitive to model time stepping (unphysical)**
converges to thin-cloud approximation

Numerical methods for cloud uptake in regional and global models

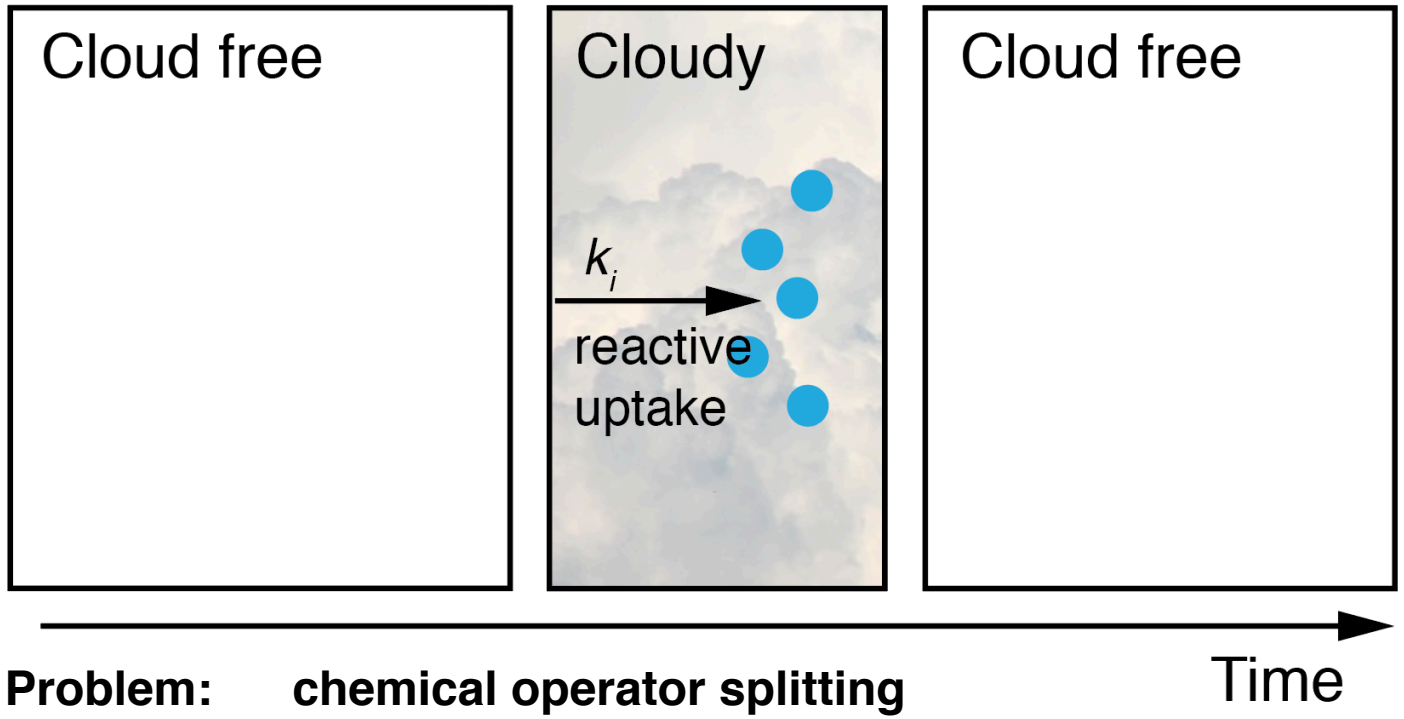
Existing methods

Thin-cloud approximation

Repartitioning method



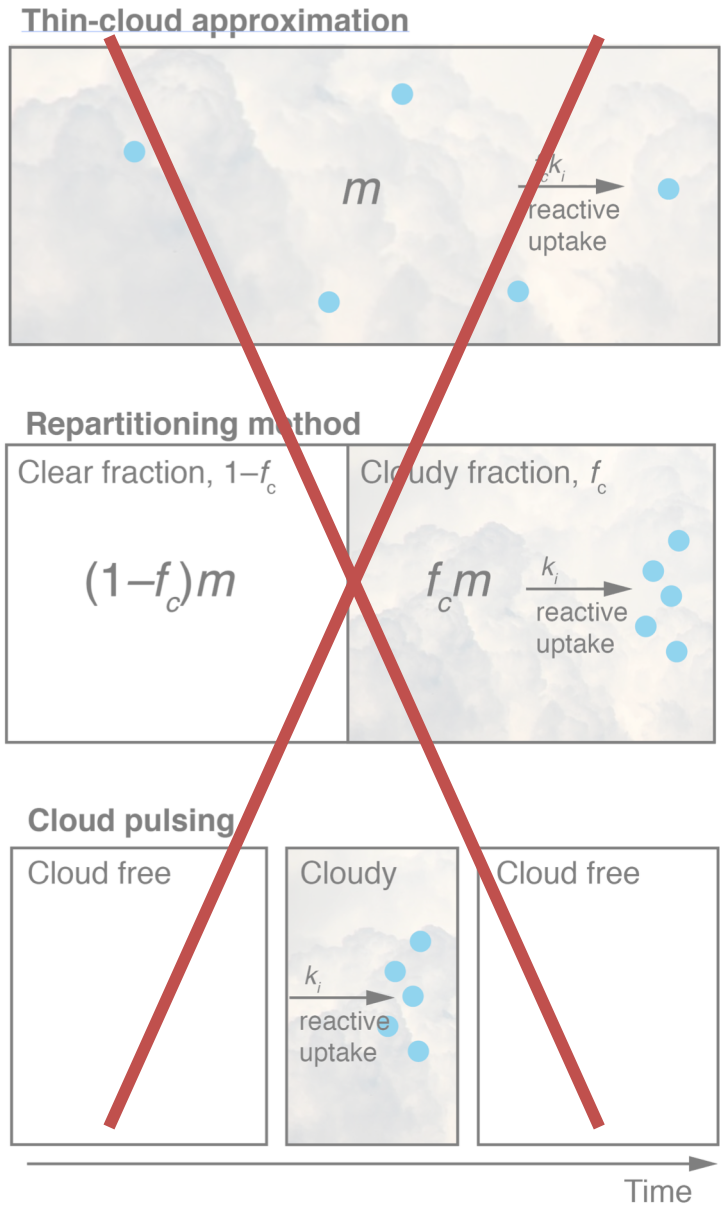
Cloud pulsing



Problem: **chemical operator splitting**
complicated
not used in any current models

Numerical methods for cloud uptake in regional and global models

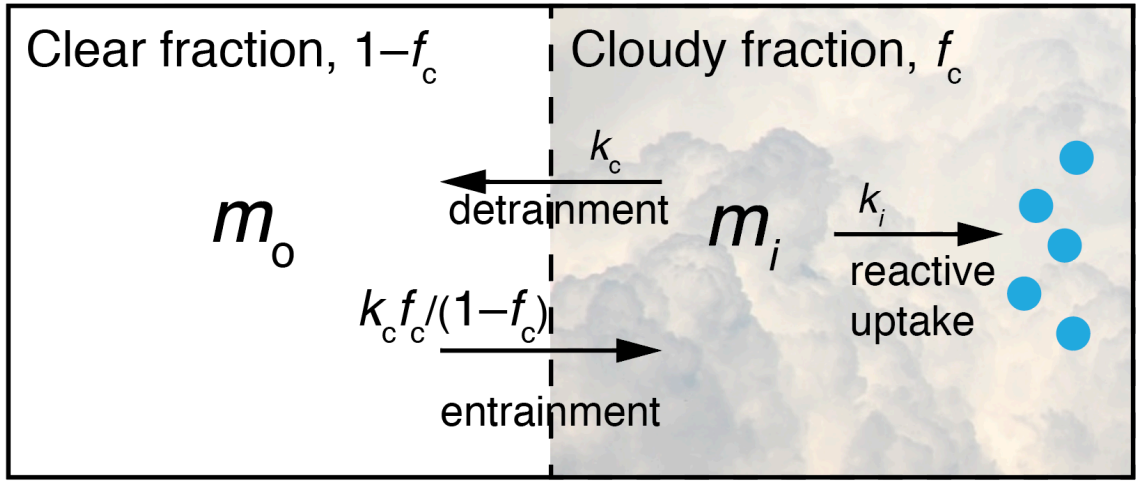
Existing methods



Numerical methods for cloud uptake in regional and global models

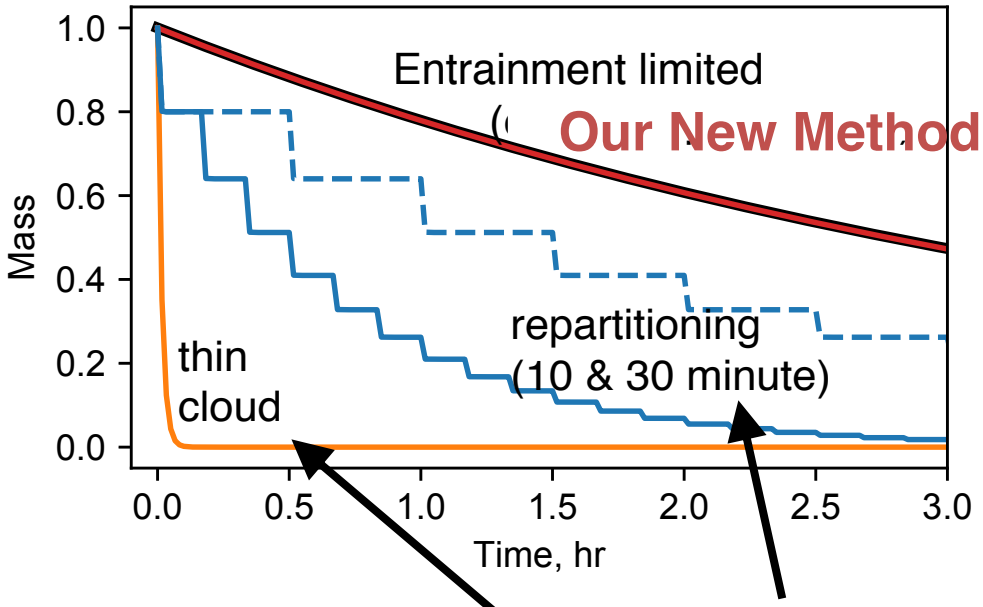
New method

Entrainment-limited uptake



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

Example errors



Methods in current models, including GEOS-Chem

Partly cloudy, entrainment limited (new):

$$\tau_{N_2O_5} \approx \left(\frac{1-f_c}{f_c k_c} + \frac{r}{f_c A D_g} + \frac{4}{f_c A v \gamma} \right) \sim 10 \text{ hr}$$

Entrainment — In-cloud uptake (Schwartz, 1986)

Holmes et al., 2019 GRL

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

Experimental design with GEOS-Chem

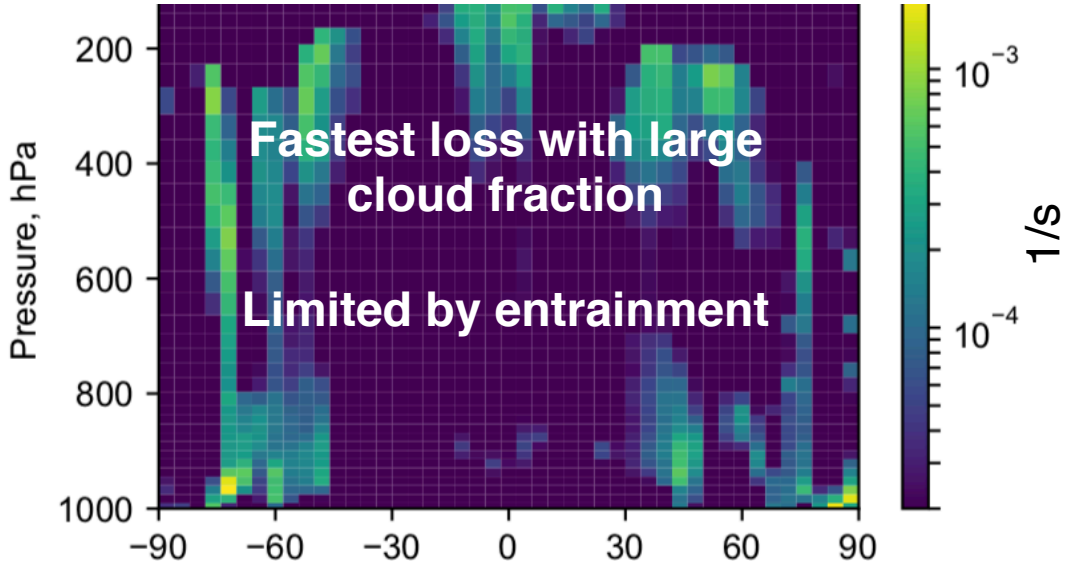
Model configuration, v11-01

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

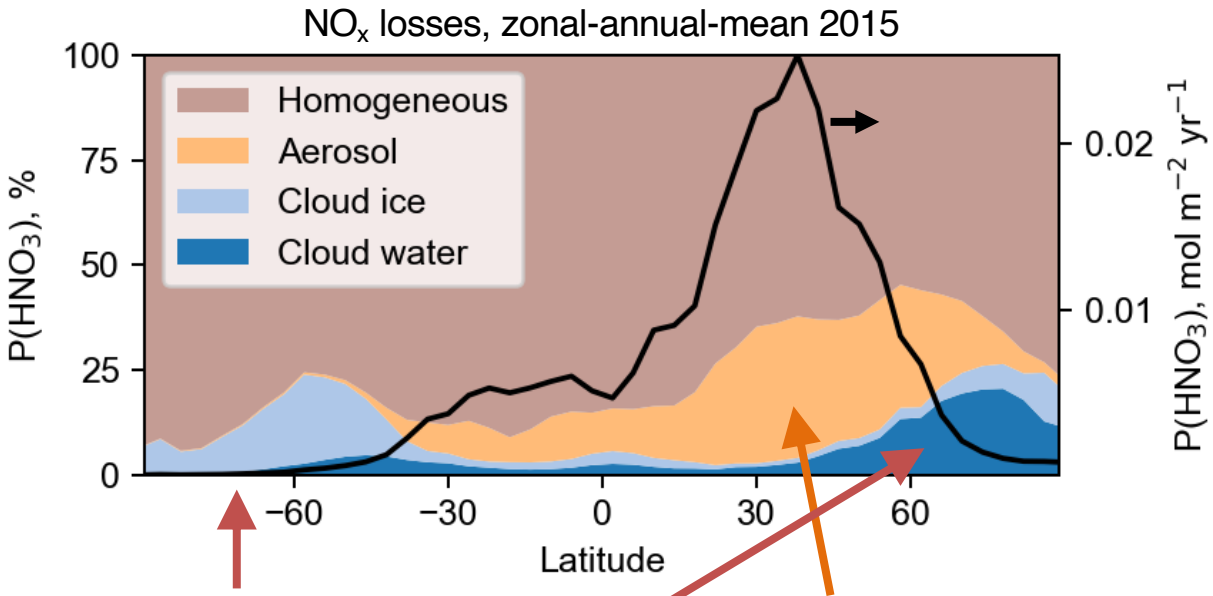
Reassessed γ for a all NO_y species (JPL, IUPAC)
Uptake on SO_4^{2-}–NO_3^-–NH_4^+ aerosol follows
Bertram and Thornton (2009), Shah et al. (2018)
Entrainment-limited cloud uptake

Entrainment-limited, grid-scale N_2O_5 loss



MERRA-2 zonal mean, 2015-04-01

NO_x losses in improved model

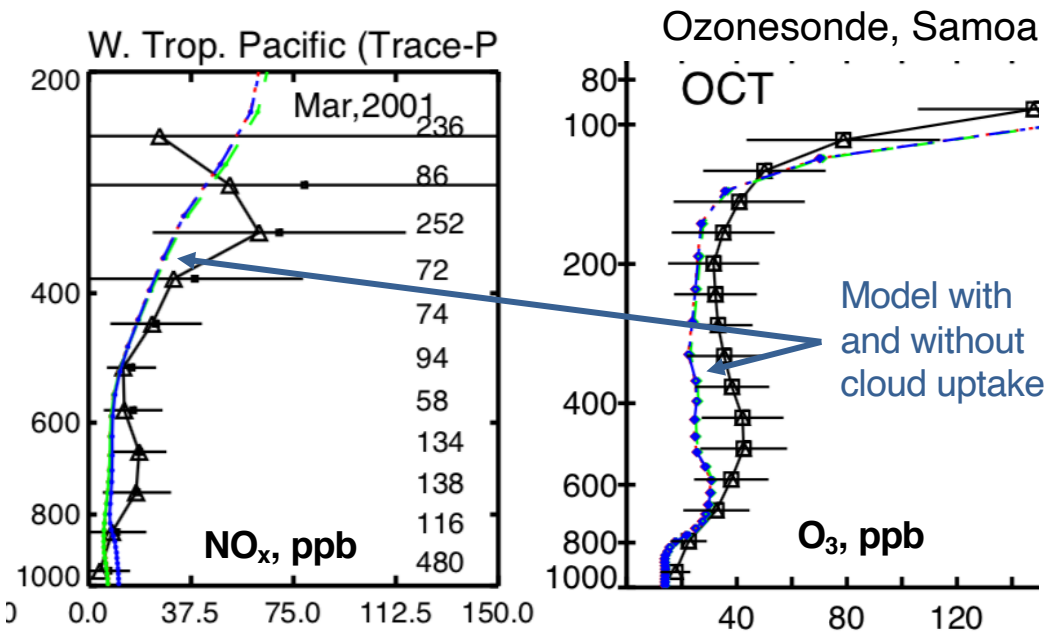


Cloud uptake provides 25% of NO_x loss in high latitudes (new result)

Aerosol uptake provides 30% of NO_x loss in NH mid latitudes (similar to past literature)

Global NO_x losses	**4.1 Tmol(N) yr^{-1}**
Homogeneous	63%
$OH + NO_2 \rightarrow HNO_3$	
$NO_3 + VOC \rightarrow HNO_3$	
Aerosol uptake	25%
Dry deposition	7%
Cloud uptake	**5%**

Model changes are small relative to NO_x, & O_3 environmental variability



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

Chemistry is clear: N_2O_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

Simulation	Control	Cloud Off	Aerosol Off	Both Off
Aerosol reactions	Yes	Yes	No	No
Cloud reactions	Yes	No	Yes	No
NO_x	43 Gmol N	+0.7 %	+3.8 %	
O_3	6.9 Tmol	+2.4 %	+2.5 %	
τ_{CH_4+OH}	8.7 yr	-1.9 %	-3.4 %	

Neglecting cloud uptake of N_2O_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_2O_5

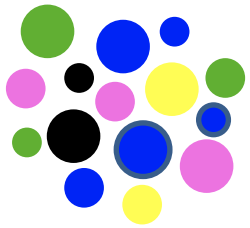
Accounting for clouds makes tropospheric NO_x, O_3, and OH much less sensitive to aerosol γ and surface area.

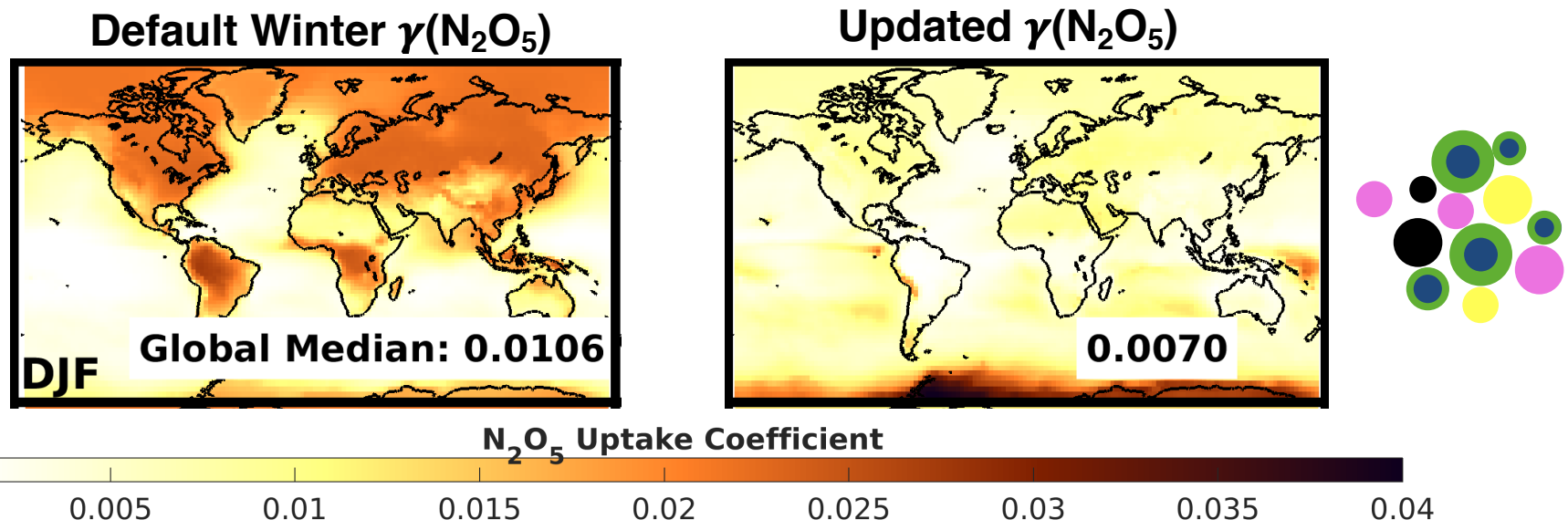
Holmes et al., 2019 GRL

Simulating N_2O_5 uptake on aerosol based on field studies

McDuffie et al. (2018) empirical parameterization of $\gamma(N_2O_5)$

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

Internal mixture of Org+SNA
(McDuffie et al., JGR 2018)

Combined changes in tropospheric composition

GEOS-Chem	12.1	+Holmes 2019	+McDuffie 2018	+Holmes 2019 +McDuffie 2018
Aerosol reactions	Yes	Updated γ	Updated γ Organic coating	Updated γ Organic coating
Cloud reactions	No	Yes	No	Yes
NO_x	41 Gmol N	- 0.9 %	+0.5 %	- 0.6 %
Aerosol nitrate	6.9 Gmol N	-1.2 %	- 0.5 %	-1.7 %
O_3	8.0 Tmol	- 5.2 %	+0.7 %	- 4.9 %
τ_{CH_4+OH}	9.4 yr	- 6.1 % (10.0 yr)		- 5.6 % (9.9 yr)

Cloud and internal mixing updates partially offset each other

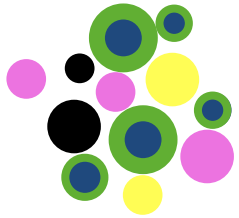
CH_4 lifetime (τ_{CH_4+OH}) now falls within observational constraints: 11.2 ± 1.3 yr
(Prather et al,. 2013)

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.

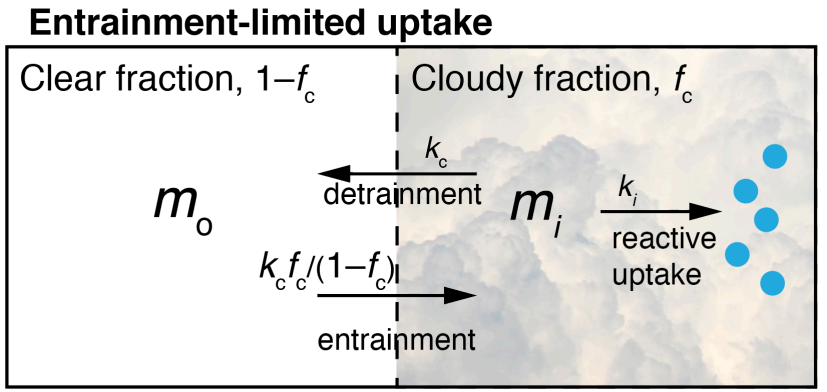
This has been overlooked because early studies overestimated aerosol γ



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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