

The role of clouds in the tropospheric NO_x cycle: a new modeling approach for cloud chemistry and its global implications

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Introduction

This supplement contains:

- A derivation of the entrainment-limited uptake equations;
- Additional figures showing simulated ozone and NO_x, nitrate deposition, and the accuracy of the approximate entrainment-limited uptake equations;
- A table of reactive uptake coefficients used in this work.

Text S1. Derivation of entrainment-limited uptake in a partly cloudy environment

In a partly cloudy environment, the total mass m of a gas, such as N_2O_5 , is the sum of mass inside cloud (m_i) and outside cloud (m_o): $m = m_i + m_o$. Within the cloud, the gas is susceptible to reactive uptake at a rate k_i determined by its reactivity (γ) and the surface area of condensed water according to Eq. 1. In-cloud air is also detrained to the cloud-free region at a rate k_c , where $\tau_c = 1/k_c$ is the residence time of air in cloud. Over the life cycle of the cloud, entrainment and detrainment of air must be equal, which implies that the mean rate for entrainment of cloud-free air is $k_c f_c (1 - f_c)^{-1}$, where f_c is the cloud fraction. The mass balance equations are, therefore,

$$\frac{dm_o}{dt} = -\frac{f_c}{1-f_c} k_c m_o + k_c m_i \quad \text{S1}$$

$$\frac{dm_i}{dt} = \frac{f_c}{1-f_c} k_c m_o - k_c m_i - k_i m_i. \quad \text{S2}$$

The system of Eqs. S1 and S2 can be solved numerically, but doing this within every grid cell of an atmospheric chemistry model would require doubling the chemical state variables and it is unnecessary, as we show here. Instead, recognize that the mass balance for the entire cell is

$$\frac{dm}{dt} = -k_i m_i. \quad \text{S3}$$

We can eliminate m_i from this equation with the identity

$$m_i = m \left(\frac{m_i}{m_i + m_o} \right) = m \left(\frac{x}{1+x} \right), \quad \text{S4}$$

where $x \equiv m_i/m_o$ is the ratio of mass inside cloud to mass outside cloud. Given time, the system defined by Eqs. S1 and S2 will adjust to a steady decay in which x is constant while m_i , m_o , and m all decrease at the same fractional rate

$$\frac{1}{m_o} \frac{dm_o}{dt} = \frac{1}{m_i} \frac{dm_i}{dt}. \quad \text{S5}$$

Combining S1, S2, and S5 yields the quadratic identity

$$x^2 + (1 + k' - f')x - f' = 0, \quad k' \equiv \frac{k_i}{k_c}, f' \equiv \frac{f_c}{1-f_c} \quad \text{S6}$$

whose solution is

$$x = \frac{1}{2} (f' - k' - 1) + \frac{1}{2} (1 + k'^2 + f'^2 + 2k' + 2f' - 2k'f')^{1/2}. \quad \text{S7}$$

Combining Eqs. S3, S4, and S7, the mass balance equation for the total mass in a partly cloudy environment is

$$\frac{dm}{dt} = -km, \quad k \equiv k_i \left(\frac{x}{1+x} \right). \quad \text{S8}$$

The mean concentration in the grid cell is $c = m/(MV)$, where M is the molecular mass and V is the grid cell volume, so the same k coefficient also describes the concentration loss. This exact expression for k is easily evaluated within a numerical model, but examining solutions under the limits $k_i/k_o \ll 1$ and $k_i/k_o \gg 1$ can provide a deeper understanding of the limiting processes.

In the limit $k_i \gg k_c$, meaning that the residence time of air in cloud is much longer than the characteristic timescale for in-cloud heterogeneous loss, we can neglect the detrainment terms ($k_c m_i$) in Eqs. S1 and S2. In that case, $x = f' k_c (k_i - f' k_c)^{-1}$ and the overall decay rate is $k = f' k_c$. In the opposite limit of $k_i \ll k_c$, meaning that in-cloud heterogeneous loss is slow compared to cloud detrainment, the entrainment and detrainment mass fluxes in Eqs. S1 and S2 are approximately equal, which implies $x = f'$ and $k = f_c k_i$. An approximate solution that reproduces both limits and reasonably describes the intermediate behavior is

$$\tilde{k} = \left(\frac{1}{f_c k_i} + \frac{1}{f' k_c} \right)^{-1} . \quad \text{S9}$$

Figure S3 evaluates the accuracy of the approximate \tilde{k} against the exact solution k over a wide range of k_i/k_c and f_c . The error in \tilde{k} is under 5% for $f_c \leq 0.2$ and never exceeds 50%. For comparison, the median and mean cloud fractions in MERRA-2 are 0.06 and 0.2, respectively. The largest \tilde{k} errors occur when mass is lost quickly anyway, so the maximum errors in simulated mass are only about 15%. The accuracy of \tilde{k} relative to the exact k is similar to the widely used Schwartz (1986) equation for gas-aerosol mass transfer (Eq. 1), which also has errors that approach 40% under some conditions when compared to more accurate expressions (Fuchs & Sutugin, 1971; Sander, 1999). In both cases, the simpler solution may be acceptable when errors due to parameter uncertainty (e.g. γ, r, f_c, k_c) exceed the error of the approximation.

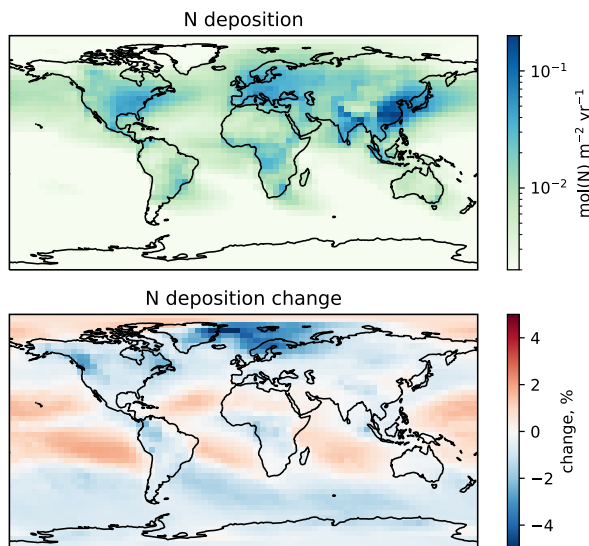


Figure S1. Inorganic nitrate deposition in the control simulation (top) and change due to neglecting cloud heterogeneous chemistry (bottom). Includes wet and dry deposition of gaseous HNO_3 and particulate NO_3^- . Change reported as $(\text{Cloud Off} - \text{Control})/\text{Control} \times 100\%$.

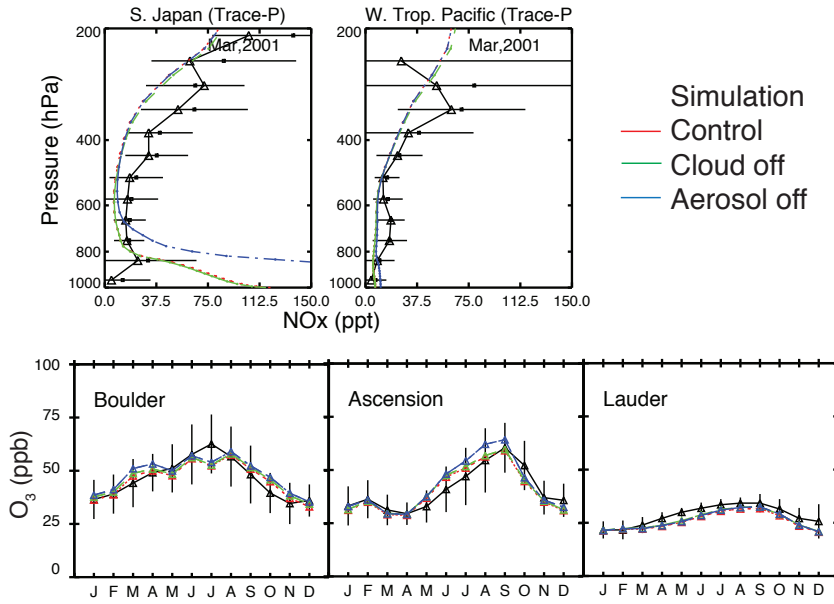


Figure S2. Simulated and observed NO_x (top row) and O₃ (bottom row). NO_x observations are from Trace-P aircraft (Jacob et al., 2003) and O₃ observations are from a sonde climatology at 800 hPa (Logan, 1999; Logan et al., 2012). Simulated values are monthly averages for 2015, not matched to the time of observations, in order to illustrate the modest effects of cloud and aerosol uptake relative to typical environmental variability.

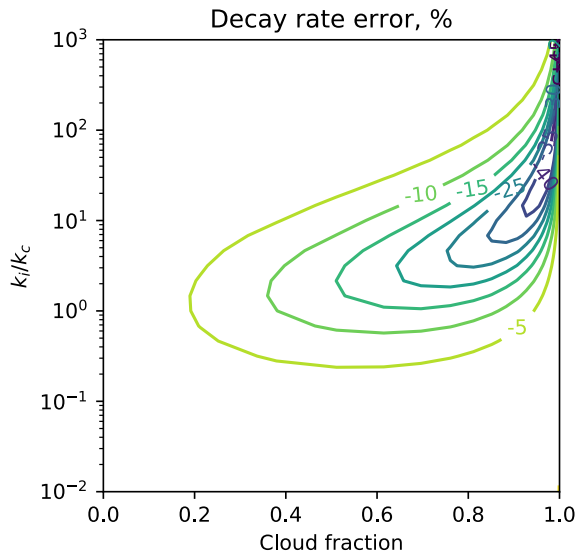


Figure S3. Error in approximate decay rate (\tilde{k} , Eq. S9) expressed as percent difference from the exact numerical solution (k , Eq. S8). Maximum mass errors in 1 hour of simulation are about one-third of the decay rate errors.

Table S1. Reactive uptake coefficients (γ) used in this work for nitrogen gases on tropospheric cloud and aerosol surfaces.

Reaction, Surface	Uptake coefficient, γ^a	Reference
NO₂ + surface → 0.5HNO₃ + 0.5HONO		
Cloud water	10 ⁻⁸	(Ammann et al., 2013) ^b
Cloud ice	0	(Crowley et al., 2010) ^c
Dust	10 ⁻⁸	(Crowley et al., 2010)
Black carbon	10 ⁻⁴	(Burkholder et al., 2015)
Organic carbon	10 ⁻⁶	(Bröske et al., 2003) ^d
Sea salt	10 ⁻⁸ (R < 40%) Interpolated (40% ≤ RH < 70%) 10 ⁻⁴ (RH ≥ 70%)	(Burkholder et al., 2015)
Sulfate	5 × 10 ⁻⁶	(Tan et al., 2016) ^e
NO₃ + surface → HNO₃		
Cloud water	0.002	(Burkholder et al., 2015)
Cloud ice	0.001	(Burkholder et al., 2015)
Dust	0.01	(Crowley et al., 2010)
Black carbon	2 × 10 ⁻⁴ (RH < 50%) 1 × 10 ⁻³ (RH ≥ 50%)	(Burkholder et al., 2015)
Organic carbon	0.005	(Atkinson et al., 2016) ^f
Sea salt	0.05 (RH < 40%) Interpolated (40% ≤ RH < 70%) 0.002 (RH ≥ 70%)	(Ammann et al., 2013; Burkholder et al., 2015) ^g
Sulfate	0.001 (RH < 40%) 0.002 (RH ≥ 40%)	^h
N₂O₅ + surface → 2HNO₃		
Cloud water	$\left(\frac{0.03}{0.019}\right) \exp\left(-a + \frac{b}{T} - \frac{c}{T^2}\right)$, $a = 25.5265, b = 9283.76 \text{ K},$ $c = 851801 \text{ K}^2$	(Burkholder et al., 2015) ⁱ
Cloud ice	0.02	(Burkholder et al., 2015)
Dust	0.02	(Crowley et al., 2010)
Black carbon	0.005	(Evans & Jacob, 2005) ^j
Organic carbon	0.6 × 10 ⁻⁴ (RH < 30%) 1.5 × 10 ⁻⁴ (RH ≥ 30%)	(Escorcia et al., 2010) ^k
Sulfate	$f([\text{NO}_3^-], [\text{H}_2\text{O}])$	(Bertram & Thornton, 2009) ^l
N₂O₅ + surface → HNO₃ + ClNO₂		
Sea salt	0.005 (R < 40%) Interpolated (40% ≤ RH < 70%) 0.02 (RH ≥ 70%)	(Ammann et al., 2013; Thornton & Abbatt, 2005) ^m

^a T is temperature (K). RH is relative humidity (%). Linear interpolation between RH endpoints is used for sea-salt aerosol.

^b Coefficient depends on temperature, [NO₂], and solutes. Value adopted here is the recommendation for dilute water solutions at 273 K and 1 ppb NO₂. Cloud water is not expected to contain solutes at levels that would significantly raise the coefficient value.

^c Upper limit is 10⁻⁴, but this likely reflects a sticking coefficient.

^d Midpoint of the reported range 10⁻⁷ to 10⁻⁵.

^e Value for (NH₄)₂SO₄.

^f Value for pure alkane aerosol, which is similar to values for alcohols and carbonyls.

^g Low RH value from Burkholder et al. (2015); high RH value from Ammann et al. (2013).

^h No measurements on dry or wet sulfate-nitrate-ammonium aerosol are available. High RH value is for pure liquid water. Low RH value is an upper limit based on H₂SO₄ aerosol (Fenter & Rossi, 1997).

ⁱ Value is 0.03 at 298 K. Temperature dependence follows sulfuric acid aerosol.

^j Consistent with the upper limit ≤ 0.02 from Burkholder et al. (2015)

^k Value for α -pinene secondary organic aerosol.

^l Eq. 12 from Bertram & Thornton (2009) with [Cl⁻] = 0 because sea salt aerosol is separate. A lower limit of 0.005 is used for dry aerosol (RH < 40%). Values fall in the range 0.005-0.03.

^m Low RH value from Thornton & Abbatt (2005). High RH value from Ammann et al. (2013). Values are for pure salt aerosol, appropriate for clean marine conditions with low organic content (Ryder et al., 2015).