

Harvard wet deposition scheme for GMI

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(with many useful comments from P.J. Rasch, NCAR)

Meteorological data used as input to GMI must provide two types of information for wet scavenging of soluble tracers: wet convective mass fluxes and precipitation fluxes. We use this information to implement two types of scavenging: (1) scavenging in subgrid wet convective updrafts, and (2) first-order rainout and washout in precipitating columns. The scavenging is applied to aerosols and to soluble gases of interest to tropospheric O₃ chemistry including HNO₃, H₂O₂, CH₃OOH, and CH₂O. The methodology is readily extendable to other soluble gases.

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1. SCAVENGING IN WET CONVECTIVE UPDRAFTS

This scavenging is applied within the convective mass transport algorithm in order to prevent soluble tracers from being transported to the top of the convective updraft and then dispersed on the grid scale. The transport model must provide wet convective air mass fluxes through each grid level in the updraft. As air is lifted a distance Δz from one level to the next, it loses a fraction F_i of soluble tracer i to scavenging. This fraction depends on (1) the rate constant k (s⁻¹) for conversion of cloud condensate (including

liquid and ice) to precipitation; (2) the fraction $f_{i,L}$ of tracer present in the liquid cloud condensate; (3) the fraction $f_{i,I}$ of tracer present in the ice cloud condensate; and (4) the retention efficiency R_i of tracer in the liquid cloud condensate as it is converted to precipitation ($R_i < 1$ accounts for volatilization during riming). Thus the rate constant k_i (s^{-1}) for loss of tracer from the updraft is given by [Mari et al., 2000]

$$k_i = (R_i f_{i,L} + f_{i,I})k \quad (1)$$

and the fraction F_i of tracer scavenged as the air is lifted by Δz is

$$F_i = 1 - \exp\left[-k_i \frac{\Delta z}{w}\right] \quad (2)$$

where w is the updraft velocity. The scavenged tracer is directly deposited to the surface; there can be no re-evaporation.

In the absence of better information provided by the convection model we use $k = 5 \times 10^{-3} \text{ s}^{-1}$ [Mari et al., 2000] and $w = 10 \text{ m s}^{-1}$ (continents) or 5 m s^{-1} (oceans)

1.1 Aerosols and HNO_3

Aerosols and HNO_3 are 100% in the cloud condensate phase ($f_{i,L} + f_{i,I} = 1$), and we assume $R_i = 1$, therefore $k_i = k$ [Liu et al., 2000; Mari et al., 2000].

1.2 Gases other than HNO_3

For gases other than HNO_3 a significant fraction of tracer may be in the gas phase so that $k_i < k$. The phase partitioning of the tracer depends on the cloud liquid water content L ($\text{cm}^3 \text{ water cm}^{-3} \text{ air}$) and the cloud ice water content W ($\text{cm}^3 \text{ ice cm}^{-3} \text{ air}$). If L and W are not available from the convection model we assume the following:

$$\begin{aligned} L &= 2 \times 10^{-6} & T &\geq 268 \text{ K} \\ L &= 2 \times 10^{-6} \frac{T - 248}{20} & 248 < T < 268 \text{ K} \\ L &= 0 & T &\leq 248 \text{ K} \\ W &= 2 \times 10^{-6} - L \end{aligned} \quad (3)$$

Let $C_{i,G}$, $C_{i,L}$, $C_{i,I}$, $C_{i,T}$ represent the atmospheric mixing ratios of tracer in the gas, liquid cloud condensate, ice cloud condensate, and all phases, respectively, so that

$$C_{i,T} = C_{i,G} + C_{i,L} + C_{i,I} \quad (4)$$

$$f_{i,L} = \frac{C_{i,L}}{C_{i,T}} = \frac{\frac{C_{i,L}}{C_{i,G}}}{1 + \frac{C_{i,L}}{C_{i,G}} + \frac{C_{i,I}}{C_{i,G}}} \quad (5)$$

$$f_{i,I} = \frac{C_{i,I}}{C_{i,T}} = \frac{\frac{C_{i,I}}{C_{i,G}}}{1 + \frac{C_{i,L}}{C_{i,G}} + \frac{C_{i,I}}{C_{i,G}}} \quad (6)$$

The ratio $C_{i,L}/C_{i,G}$ is obtained from Henry's law:

$$\frac{C_{i,L}}{C_{i,G}} = K_i^* LRT \quad (7)$$

where K_i^* (M atm^{-1}) is the effective Henry's law constant including contributions from dissociated species in fast equilibrium with the dissolved tracer, $R = 8.32 \times 10^{-2} \text{ atm M}^{-1} \text{ K}^{-1}$ is the ideal gas constant, and T is the local temperature in K. We calculate K_i^* from the van't Hoff equation:

$$K_i^* = K_{i,298}^* \exp \left[-\frac{\Delta H_{i,298}^0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (8)$$

where $T_0 = 298 \text{ K}$. Values of $K_{i,298}^*$ and $-\Delta H_{i,298}^0/R$ for the gases of interest are listed in Table 1.

Table 1. Effective Henry's law constants for soluble gases [Jacob, 2000]

Species	$K_{i,298}^*$ (M atm^{-1})	$\Delta H_{i,298}^0/R$ (K)	C_I/C_G	R_i $248 < T < 268 \text{ K}$
H_2O_2	8.3×10^4	-7400	co-condensation	0.05
CH_3OOH	3.1×10^2	-5200	0	0.02
CH_2O	3.0×10^3 [$\text{CH}_2\text{O}(\text{aq}) + \text{H}_2\text{C}(\text{OH})_2(\text{aq})$]	-7200	0	0.02

The retention efficiency R_i is unity for all gases in a warm cloud ($T \geq 268 \text{ K}$). Values of R_i in a mixed cloud ($248 < T < 268 \text{ K}$) are given in Table 1 [Mari et al., 2000].

The ratio $C_{i,I}/C_{i,G}$ for H_2O_2 is obtained by assuming scavenging by co-condensation

[Mari et al., 2000]:

$$\frac{C_{i,I}}{C_{i,G}} = \frac{W}{C_{H_2O}} \left(\frac{\alpha_{H_2O_2}}{\alpha_{H_2O}} \right) \left(\frac{M_{H_2O_2}}{M_{H_2O}} \right)^{\frac{1}{2}} \quad (9)$$

where C_{H_2O} is the water vapor mixing ratio (to be calculated from saturation over ice at the local temperature), $\alpha_{H_2O_2}/\alpha_{H_2O} = 0.6$ is the ratio of sticking coefficients on the ice surface, and $M_{H_2O_2}/M_{H_2O} = 1.9$ is the ratio of molecular weights.

For CH_3OOH and CH_2O scavenging by co-condensation is inefficient and we assume $C_{i,I}/C_{i,G} = 0$ [Mari et al., 2000].

2. RAINOUT AND WASHOUT

Rainout and washout are first-order losses applied to precipitating columns. *Rainout* refers to in-cloud scavenging by precipitation of cloud droplets or ice crystals. *Washout* refers to below-cloud scavenging by precipitation. For each grid square the model must provide information on the vertical distribution of precipitation rates, separately for stratiform and for convective precipitation. Stratiform and convective columns in each grid square are subgrid in horizontal areal extent. We assume that they do not overlap. The column top is the first level where precipitation occurs; the column bottom is either the Earth's surface or a level where complete evaporation of precipitation from overhead takes place. Within each column we apply first-order rainout loss to the levels where new precipitation forms ($P_{bottom} > P_{top}$) and washout to the levels where precipitation evaporates ($P_{bottom} \leq P_{top}$). Evaporation results in fractional or total release of tracer in the evaporating gridbox. We start the scavenging calculation at the top of each precipitating column and progress downward level by level, applying rainout or washout/reevaporation as appropriate. Scavenged tracer is carried downward from level to level and stored in a "scavenged tracer" array which may accumulate by further rainout/washout and be depleted by evaporation.

2.1 Rainout

Rainout is applied to any level where new precipitation forms. Let Q (cm^3 water cm^{-3} air s^{-1}) represent the rate of new precipitation formation in the corresponding gridbox. The fraction F_i of a soluble tracer in the gridbox scavenged by rainout over a time step Δt is

$$F_i = f(1 - \exp[-k_i \Delta t]) \quad (10)$$

where f is the horizontal areal fraction of the gridbox experiencing precipitation and k_i (s^{-1}) is a first-order loss rainout rate constant. From knowledge of the rate constant k

(s^{-1}) for rainout of condensed water, we calculate k_i for any given tracer using equation (1) and the same procedure as in section 1. Values of f and k may be supplied as part of the hydrological information from the driving meteorological model. If not they are estimated following the Giorgi and Chameides [1986] scheme. Let $L+W$ ($cm^3 cm^{-3}$) represent the condensed water content (liquid + ice) within the precipitating cloud. The fractional area of the gridbox where new precipitation forms is $Q/k(L+W)$. The actual fractional area f experiencing precipitation may be larger because of precipitation forming at higher levels. We assume that precipitation formed overhead extends the fractional cloudy area in the gridbox and scavenges soluble tracers from the cloud in the same manner as rainout. In order to account for this effect in the calculation of f , the calculation must begin at the top of the precipitating column and work downwards.

For *stratiform precipitation*, f and k are given by

$$f = \max\left(\frac{Q}{k(L+W)}, f_{top}\right) \quad (11)$$

$$k = k_{min} + \frac{Q}{L+W} \quad (12)$$

where f_{top} is the value of f in the layer overhead ($f_{top} = 0$ at the top of the precipitating column), k_{min} is a minimum value for k , and the second term on the right-hand side of (12) ensures that $f \leq 1$. We use $k_{min} = 1 \times 10^{-4} s^{-1}$ and $L+W = 1.5 \times 10^{-6} cm^3 cm^{-3}$.

For *convective precipitation* we assume following Giorgi and Chameides [1986] that $k = 1.5 \times 10^{-3} s^{-1}$ and that f cannot exceed a maximum value $f_{max} = 0.3$. In that case f is given by

$$f = \max\left(\frac{f_{max} Q \min\left(\frac{\Delta t}{\tau}, 1\right)}{Q \min\left(\frac{\Delta t}{\tau}, 1\right) + f_{max} k(L+W)}, f_{top}\right) \quad (13)$$

where $\tau = 30$ min is the duration of the rainout event and $L+W = 2 \times 10^{-6} cm^3 cm^{-3}$.

2.2 Washout and reevaporation

Washout applies to any level within a precipitating column where there is no formation of new precipitation and where precipitation is liquid ($T \geq 268$ K). It applies over the areal fraction f of the lowest rainout level overhead. Reevaporation applies to any level where there is net evaporation of precipitation (solid or liquid). For aerosols and HNO_3 , washout and reevaporation are modeled as kinetic processes (collision-limited for aerosols, mass-transfer-limited for HNO_3). For other gases mass transfer may not be limiting, in which case washout and reevaporation are modeled from Henry's law.

2.2.1 Aerosols and HNO₃

The fraction F_i of tracer within a gridbox that is scavenged by washout over a time step Δt is

$$F_i = f \left(1 - \exp \left[-k'_i \frac{P}{f} \Delta t \right] \right) \quad (14)$$

where P (cm³ water cm⁻² surface s⁻¹) is the grid-scale precipitation rate through the bottom of the gridbox and k'_i (cm⁻¹) is a first-order washout loss rate constant. For washout of aerosols we use $k'_i = 1$ cm⁻¹ [Liu et al., 2000]. For washout of HNO₃ we also coincidentally use $k'_i = 1$ cm⁻¹ (Table 2 of Levine and Schwartz [1982]).

When *partial reevaporation of precipitation* takes place in a gridbox, the fraction of tracer precipitating from above that is reevaporated within the gridbox is equal to half the relative evaporation rate of water. “Half” is because part of the evaporation is by shrinking of large raindrops or snowflakes (which doesn’t release aerosols or HNO₃) and part is by total evaporation. When *total reevaporation of precipitation* takes place in a gridbox, all tracer precipitating from above is released in the gridbox.

2.2.2 Gases other than HNO₃

For gases other than HNO₃, we calculate the equilibrium fractionation $f_{i,L}$ of the gas into the rainwater as determined by Henry’s law (equations (5) and (7)):

$$f_{i,L} = \frac{K_i^* L_p RT}{1 + K_i^* L_p RT} \quad (15)$$

where L_p is the rainwater content in the gridbox:

$$L_p = \frac{P \Delta t}{f \Delta Z} \quad (16)$$

and ΔZ (cm) is the thickness of the gridbox. We then compare $f_{i,L}$ to the scavenged fraction F_i/f calculated from equation (14) with $k'_i = 1$ cm h⁻¹:

- If $f_{i,L} > F_i/f$, scavenging is limited by mass transfer and we follow exactly the same procedure as for aerosols and HNO₃ (section 2.2.1).
- If $f_{i,L} < F_i/f$, scavenging is limited by Henry’s law equilibrium. Let m_i represent the mass of tracer in the gridbox and $\Delta m_{i,top}$ represent the mass of scavenged tracer brought *into* the gridbox by precipitation overhead. The total mass $\Delta m_{i,bottom}$ of scavenged tracer transported out through the bottom of the gridbox is then

$$\Delta m_{i,bottom} = f_{i,L} (f m_i + \Delta m_{i,top}) \quad (17)$$