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SUPPLEMENTARY MATERIAL TO

An aqueous chemistry module for a three-dimensional cloud resolving model: sulfate redistribution

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PS*1 – S(IV) solution in cloud water. PS1* is the source term for S(IV) in cloud water and the sink term for SO_2 from air. It is calculated using the Henry Law (PS1) or using the mass transport approach (PS1K). The total concentration of four-valence S(IV) species predominantly exists in the form of $[HSO_3^-]$ for $2.0 \leq pH \leq 6.0$, which is typical for cloud droplets and raindrops. Thus, the concentration of $[HSO_3^-]$ is given by:

$$[HSO_3^-] = K_{Hs}K_{1s}p_{SO_2}/[H^+],$$

where K_{Hs} is the Henry coefficient, K_{1s} is the first ionic dissociation coefficient, p_{SO_2} is the partial pressure of SO_2 in the air, and $[H^+]$ is the hydrogen ion concentration. The rate for SO_2 leaving the atmosphere (or returning in its gaseous phase) is calculated as:

$$PS1 / SUL1 = \frac{K_{Hs}K_{1s}}{[H_c^+]} p_{SO_2} \frac{M_{SO_2}}{M_{HSO_3}} \frac{dq_c}{dt} \tag{S-1}$$

where dq_c / dt is the condensation rate during one model time step, and M_{SO_2} and M_{HSO_3} are the molecular masses of SO_2 and HSO_3^-, respectively.

The other way to calculate this term is according to Eq. (3) (see the native article):

$$PS1K(t + \Delta t) = A_{SO_2} + (PS1K(t) - A_{SO_2})\exp(B_{SO_2}\Delta t) \tag{S-2}$$

A_{SO_2} and B_{SO_2} are calculated according to Eq. (4) (native article).

PS*2 and* PS*2*hp *– S(IV) oxidation by* O_3 *and* H_2O_2 *to* SO_4^{2-} *in cloud water.* The aqueous-phase conversion of dissolved SO_2 to sulfate is considered the most important chemical transformation in cloud water. Although ozone reacts very slowly with SO_2 in the gas phase, the aqueous-phase reaction:

$$S(IV) + O_3 \rightarrow S(VI) + O_2 \tag{S-3}$$
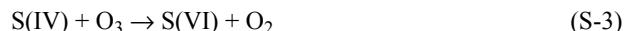
is rapid. The parameterization of this term is performed according to the rate expression:

$$-\frac{d[S(IV)]}{dt} = k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}][O_3] \tag{S-4}$$

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where $k_0 = (2.4\pm1.1)\times10^4$ M^{-1} s^{-1}, $k_1 = (3.7\pm0.7)\times10^5$ M^{-1} s^{-1} and $k_2 = (1.5\pm0.6)\times10^9$ M^{-1} s^{-1} are oxidation rate coefficients. If the assumption that HSO$_3^-$ is the predominant form of S(IV) is applied, then:

$$PS2 = k_1(K_{Hs}K_{1s}p_{SO_2})^{1/2}q_{O_3,c} \tag{S-5}$$

where p_{SO_2} is the partial pressure of SO$_2$ in the air. This reaction plays an important role as a source of cloud water acidification.

Hydrogen peroxide, H$_2$O$_2$, is one of the most effective oxidants of S(IV) in clouds. The rate expression is:

$$-\frac{d[S(IV)]}{dt} = \frac{k[H^+][H_2O_2][HSO_3^-]}{1+K[H^+]}[H_2O_2] \tag{S-6}$$

As H$_2$O$_2$ is a very weak electrolyte, $\left[H^+\right]\left[HSO_3^-\right] = K_{Hs}K_{1s}p_{SO_2}$, and for pH > 2, $1+K\left[H^+\right] \approx 1$, the rate expression can be parameterized by:

$$PS2hp = k_{H_2O_2}K_{Hs}K_{1s}p_{SO_2}q_{H_2O_2,c} \tag{S-7}$$

PS3 – Nucleation scavenging of SO$_4^{2-}$ aerosol by cloud condensation nuclei (CCN). The term for nucleation scavenging of SO$_4^{2-}$ aerosol by CCN simply shows the primary activation of CCN based on numerical integration of the droplet growth equation. Taylor approximated this process with:[3]

$$PS3 = \begin{cases} (\varepsilon_{SO_4^{2-}}q_{SO_4^{2-},a})dq_c/dt, & dq_c/dt > 0 \\ 0, & dq_c/dt \le 0 \end{cases} \tag{S-8}$$

where, dq_c is the condensation of cloud droplets during the current time step in the model and $\varepsilon_{SO_4^{2-}} = 0.55$ is the fractional nucleation efficiency.

PS4cw and PS4ci – SO$_4^{2-}$ scavenging by Brownian diffusion in cloud droplets and cloud ice. Scavenging of SO$_4^{2-}$ by Brownian diffusion was computed using the following equation for continuous collection:

$$-\frac{\partial q_{SO_{4,a}}}{\partial t} = q_{SO_4,a}\int_0^\infty K(a,D)n_c(D)dD \tag{S-9}$$

where $K(a,D)$ is the collection kernel for an aerosol with diameter a and a cloud droplet with diameter D. Assuming a monodisperse cloud droplet spectrum, the term PS4cw can be approximated by:

$$PS4cw = 2\pi D_p N_c D_c q_{SO_4,a} \tag{S-10}$$

where $D_p = 1.56\times10^{-8}$ m^2 s^{-1} is the particle diffusivity,[24 (Reference list in native article)] N_c the cloud droplet concentration, and D_c is the mean cloud droplet diameter. The term *PS4ci* is similar to the term *PS4cw*:

$$PS4ci = 2\pi D_p N_i D_i q_{SO_4,a} \tag{S-11}$$

where N_i is the cloud ice concentration and D_i is the mean cloud ice diameter.

PS5 – Nucleation scavenging of SO$_4^{2-}$ by ice nuclei (IN). The term for nucleation scavenging of SO$_4^{2-}$ by IN is computed in an analogous way to the PS3:

$$PS5 = \varepsilon_{SO_4^{2-}} q_{SO_4,a} \frac{dq_i}{dt} \tag{S-12}$$

dq_i is the cloud ice formation during the current time step in the model.

$PS6$ – *Impact scavenging of SO_4^{2-} aerosol by rain.* This term represents the scavenging of sulfate particles by inertial impaction with raindrops. The impact scavenging of SO_4^{2-} by rain is computed for continuous collection processes:

$$-\frac{\partial q_{SO_4,a}}{\partial t} = \int_0^\infty \frac{\pi}{4} D_r^2 V_r(D_r) q_{SO_4,a} \varepsilon_r N(D_r) dD_r \tag{S-13}$$

where D_r is the mean diameter of raindrops, $V_r(D_r)$ is the terminal velocity of rain, $\varepsilon_r = 0.048$[16] is the aerosol–rain collection efficiency and $N(D_r)$ is the size distribution of rain. Assuming a Marshall–Palmer distribution[15] (Reference list in native article) for the rain drops, $n_r(D) = N_{0r} \exp(-\lambda_r D_r)$, where N_{0r} is the intercept parameter, $N_{0r} = 8 \times 10^6$ m^{-4}, λ_r is the slope parameter of the rain size distribution, and assuming the raindrops terminal velocity:[25] (Reference list in native article)

$$V_r(D_r) = a D_r^b \left(\frac{\rho_0}{\rho}\right)^{1/2} \tag{S-14}$$

where $a = 842$ m^{1-b} s^{-1}, $b = 0.8$, $\rho_0 = 1.225$ kg m^{-3} (the surface air density), $PS6$ is then calculated as:

$$PS6 = \frac{\pi}{4} \frac{\Gamma(3.8)}{\lambda_r^{3.8}} \varepsilon_r a N_{0r} \left(\frac{\rho_0}{\rho}\right)^{1/2} q_{SO_4,a} \tag{S-15}$$

$PS7$ – *SO_4^{2-} impact scavenging by hail.* When a hail particle falls through a field of dry sulfate particles, some of the sulfate particles are removed by impaction with the hail. This removal could be calculated, assuming continuous collection, as:

$$PS7 = \frac{3\pi}{7} \varepsilon_h V_h(D_h) N_h D_h^2 q_{SO_4,a} \tag{S-16}$$

Where $\varepsilon_h = 0.048$ is the collection efficiency for hail,[16] $V_h(D_h)$ is the terminal velocity of the hail, N_h is the hail concentration and D_h is the mean hail diameter.

$PS8$ – *SO_4^{2-} impact scavenging by snow.* This term is computed in a similar way to the terms $PS6$ and $PS7$:

$$PS8 = \frac{\pi}{4} \varepsilon_s V_s(D_s) N_s D_s^2 q_{SO_4,a} \tag{S-17}$$

where $\varepsilon_s = 0.008$[16] (Reference list in native article) is the collection efficiency for snow, $V_s(D_h)$ is the terminal velocity of snow, N_s is the snow concentration and D_s is the mean snow diameter.

$PS9$, $PS9hp$ – *S(IV) oxidation by O_3 and H_2O_2 to SO_4^{2-} in rainwater.* These terms are calculated similarly to $PS2$ and $PS2hp$:

$$\begin{aligned} PS9 &= k_{O_3} (K_{Hs} K_{1s} p_{SO_2})^{1/2} q_{O_3,r} \, dt \\ PS9hp &= k_{H_2O_2} K_{Hs} K_{1s} p_{SO_2} q_{H_2O_2,r} \, dt \end{aligned} \tag{S-18}$$

where dt is the current time model step.

$PS10$ – *Rain evaporation.* This term determines the amount of SO_2 that is returned to the atmosphere during the evaporation of rain. The relation could express the conversion from HSO_3^- to SO_2 in the gas phase:

$$PS10 = \frac{K_{Hs}K_{1s}}{[H_r^+]}\, p_{SO_2}\, \frac{M_{SO_2}}{M_{HSO_3}}\, ern \qquad \text{(S-19)}$$

where *ern* is the evaporation of rain. All microphysical processes used in the paper are described in Table S-I.

TABLE S-I. Microphysical reactions used in the chemistry module

Symbol	Meaning
ern	Rain evaporation
dep	Deposition or sublimation of cloud ice
praut	Autoconversion of cloud water to form rain
pracw	Accretion of cloud water by rain
psacw	Accretion of cloud water by snow; product snow (P_{sacw}) if $T < 273.16$ or rain (Q_{sacw}) if $T > 273.16$
dgacw	Accretion of cloud water by hail
psfw	The Bergeron processes (deposition and riming) - cloud water transfer to snow
pidw	Depositional growth of cloud ice at the expense of cloud water
pihom	Homogeneous freezing of cloud water to form cloud ice
psacr	Accretion of rain or snow; product hail if rain or snow exceed limit value; on the contrary, product snow
dgacr	Accretion of rain by hail
pgfr	Rain freezing to form hail
piacr	Accretion of rain by cloud ice; product snow or hail in dependence on the amount of rain
pgmlt	Hail melting to form rain
pgsub	Hail sublimation
psmlt	Snow melting to form rain
pgaut	Autoconversion (aggregation) of snow to form hail
pgacs	Accretion of snow by hail
pracs	Accretion of snow by rain
pssub	Snow sublimation
psdep	Depositional growth of snow
pgaci	Accretion of cloud ice by hail
praci	Accretion of cloud ice by rain; product snow or hail in dependence of the amount of rain
pimlt	Cloud ice melting and formation of cloud water
psaut	Autoconversion (aggregation) of cloud ice to form snow
psaci	Accretion of cloud ice by snow
psfi	Bergeron process – cloud ice transfer to snow

PS*11 – SO₄²⁻ transfer from cloud water to rain*. This term follows the microphysical transition and transfer of SO_4^{2-} from cloud water to rain:

$$PS11 = \frac{q_{SO_4,c}}{q_c}(praut + pracw + psacw) \qquad \text{(S-20)}$$

Autoconversion is the initial stage of the collision-coalescence process, whereby cloud droplets collide and coalesce to form rain; accretion is the growth of a bigger hydrometeor by collision with super-cooled cloud droplets that freeze wholly or partially upon contact.

$PS12 - SO_4^{2-}$ *transfer from cloud water to hail*. This term represents the action of hail collecting cloud water containing sulfate:

$$PS12 = \frac{q_{SO_4,c}}{q_c} dgacw \tag{S-21}$$

$PS13 - SO_4^{2-}$ *transfer from cloud water to snow*. This term represents the action of snow collecting cloud water that contains sulfate:

$$PS13 = \frac{q_{SO_4,c}}{q_c} (psacw + psfw) \tag{S-22}$$

$PS14 - SO_4^{2-}$ *transfer from cloud water to cloud ice*. Due to the depositional growth of cloud ice at the expense of cloud water and the freezing of cloud water to form cloud ice, there is SO_4^{2-} transfer from cloud water to cloud ice:

$$PS14 = \frac{q_{SO_4,c}}{q_c} (pidw + pihom) \tag{S-23}$$

$PS15 - SO_4^{2-}$ *transfer from cloud water to aerosol*. When cloud water droplets that contain SO_4^{2-} evaporate, some amount of SO_4^{2-} converts to dry sulfate particles. This process is calculated as:

$$PS15 = q_{SO_4,c} \frac{dq_c}{dt} \tag{S-24}$$

$PS16 - SO_4^{2-}$ *transfer from rain to snow*. When raindrops and cloud ice particles collide, initiating snow formation, both the cloud ice sulfate and the rain sulfate must be transferred to the snow sulfate field:

$$PS16 = \frac{q_{SO_4^{2-},r}}{q_r} (piacr + psacr) \tag{S-25}$$

$PS17 - SO_4^{2-}$ *transfer from rain to hail*. Similar to the previous term, $PS17$ follows the microphysical transitions from rain to hail:

$$PS17 = \frac{q_{SO_4^{2-},r}}{q_r} (dgacr + pgfr + piacr + psacr) \tag{S-26}$$

$PS18 - SO_4^{2-}$ *transfer from hail to rain*. When hail melts, the sulfate in hail becomes sulfate in rain at a given proportion:

$$PS18 = \frac{q_{SO_4^{2-},h}}{q_h} pgmlt \tag{S-27}$$

$PS19 - SO_4^{2-}$ *transfer from hail to aerosol*. Owing to the sublimation of hail, the amount of SO_4^{2-} that transfers from hail to aerosol is:

$$PS19 = \frac{q_{SO_4^{2-},h}}{q_h} \, pgsub \tag{S-28}$$

PS*20 – SO₄²⁻ transfer from snow to rain*. Similar to the PS18 term, and owing to snow melt, the sulfate from snow transfers to rain as:

$$PS20 = \frac{q_{SO_4^{2-},s}}{q_s} \, psmlt \tag{S-29}$$

PS*21 – SO₄²⁻ transfer from snow to hail*. Due to the autoconversion of snow to hail the accretion of snow by hail and the accretion of snow by rain, the sulfate transfer from snow to hail given by:

$$PS21 = \frac{q_{SO_4^{2-},s}}{q_s} (pgaut + pgacs + pracs) \tag{S-30}$$

PS*22 – SO₄²⁻ transfer from snow to aerosol*. This term follows microphysical transitions, thus the transfer of sulfate from snow to aerosol fields is given by:

$$PS22 = \frac{q_{SO_4^{2-},s}}{q_s} (pssub + psdep) \tag{S-31}$$

PS*23 – SO₄²⁻ transfer from cloud ice to hail*. Cloud ice sulfate is transferred to hail sulfate when cloud ice and hail collide. This process is represented by:

$$PS23 = \frac{q_{SO_4^{2-},i}}{q_i} (pgaci + praci) \tag{S-32}$$

PS*24 – SO₄²⁻ transfer from cloud ice to cloud water*. When cloud ice melts and forms cloud water, cloud ice sulfate is transferred to cloud water sulfate:

$$PS24 = \frac{q_{SO_4^{2-},i}}{q_i} \, pimlt \tag{S-33}$$

PS*25 – SO₄²⁻ transfer from cloud ice to snow*. This term follows microphysical processes that transfer cloud ice sulfate to cloud water sulfate:

$$PS25 = \frac{q_{SO_4^{2-},i}}{q_i} (psaut + psaci + psfi + praci) \tag{S-34}$$

PS*26 – SO₄²⁻ transfer from cloud ice to aerosol*. This term describes the transfer of cloud ice sulfate to aerosol sulfate during the evaporation of cloud ice:

$$PS26 = \frac{dq_{SO_4^{2-},i}}{dt} \, dep \tag{S-35}$$