

Modelling of Sulfur dioxide , Sulfate and Carbonaceous Aerosol in ICTP Regional Climate Model (RegCM3)

A coupled chemistry-climate aerosol module was developed to solve the mixing ratio (χ in unit: kg kg⁻¹ air) of six chemical species: gaseous SO₂, particulate SO₄²⁻, hydrophobic and hydrophilic black carbon (BC_{phobic} and BC_{philic}), and hydrophobic and hydrophilic organic carbon (OC_{phobic} and OC_{philic}) in RegCM3 described as the following prognostic equation:

$$\frac{\partial \chi_i}{\partial t} = -\vec{V} \cdot \nabla \chi_i + F_{H,i} + F_{V,i} + S_i + T_{gas,i} + T_{hetero,i} + T_{ls,i} + T_{conv,i} + T_{below-cloud,i} + T_{dry,i}$$

where i indicates the ith species. The first term on the r.h.s of the above Equation represents the horizontal and vertical advection, F_{H,i} and F_{V,i} are horizontal and vertical turbulent diffusion, S_i is the emission term, T_{gas,i} is the tendency due to gas phase chemical conversion, T_{hetero,i} is the tendency due to heterogeneous reactions, T_{ls,i} and T_{conv,i} are tendencies via large scale and convective cloud processes, respectively, T_{below-cloud,i} is the rate of removal via below cloud scavenging, T_{dry,i} is dry deposition term.

- Sulfur species

The sulfur algorithm is based on that of [Kasibhatla et al. \(1997\)](#) with the revisions and enhancements of Qian et al. (2001) and Tan et al. (2002), where the detailed formulas can be found. A brief description of the terms on the right hand side of Equation (2.2), except for the advection and diffusion terms, is given below. The gas phase oxidation pathway is initiated by the reaction of SO₂ with OH to produce SO₄²⁻

$$T_{gas,so2} = -T_{gas,so4} = -k_{OH,SO2} [OH] \chi_{SO2}$$

where k_{OH,SO_2} is the temperature-dependent reaction rate constant from DeMore et al. (1994) and $[OH]$, the OH concentration, is obtained from the regional chemical transport model simulation of Luo et al. (2000), which used the same domain as the RegCM3 application described here and was driven, in turn, by the meteorological fields calculated by the RegCM3. Following Kasibhatla et al. (1997) and Chameides et al. (2002), an additional pathway to convert SO_2 to SO_4^{2-} is included to account for the effect of heterogeneous reactions of SO_2 with the pre-existing aerosols. The reaction was assumed to only occur within the boundary layer and to have a pseudo 1st order reaction coefficient of $6 \times 10^{-6} \text{ s}^{-1}$,

$$T_{hetero,so2} = -T_{hetero,so4} = -6 \times 10^{-6} \chi_{SO_2}, \text{ within the boundary layer}$$

At pH's typical value of cloud water over your selected region, SO_2 has a relatively low solubility, and in the absence of aqueous-phase chemical conversion, most SO_2 in a cloud would remain in the interstitial air (Chameides, 1984). Hence, the rate of removal of SO_2 in clouds is limited by the rate of aqueous-phase conversion of SO_2 to SO_4^{2-} . This occurs via the dissolution of SO_2 in clouds to form HSO_3^- and SO_3^{2-} ions and then oxidation by dissolved H_2O_2 and O_3 . Previous work indicated that reaction with O_3 only accounts for 10% of the SO_2 oxidation (Rasch et al., 2000), and hence the oxidation by O_3 is neglected in this work. The conversion process is assumed to be limited by the availability of SO_2 and H_2O_2 , and is a function of the cloud liquid water content, cloud fractional cover and cloud lifetime (Giorgi and Chameides, 1986; Rogers and Yau, 1989 and Kasibhatla et al., 1997). As noted above, the RegCM3 simulates two types of clouds: large-scale or resolvable clouds and convective clouds. In large scale clouds, the tendency of SO_2 is given by:

$$T_{ls,so2} = \frac{1}{dt} frc_{ls} [\exp(-\frac{w_L dt}{A}) - 1] \min(\chi_{SO_2}, \chi_{H_2O_2})$$

where frc_{ls} is the fractional cover for the large scale clouds (equal to 1 except where convective clouds are also present, then 0.7), w_L (g m^{-3}) is the liquid water content, which is a prognostic variable calculated by the dynamical portion of the RegCM3, A ($=360 \text{ g m}^{-3} \text{ s}^{-1}$) is a parameter derived from the cloud-chemistry simulation of Chameides (1984), which is related the SO_2 equilibrium dissolution in clouds, dt is the time step ($=200\text{s}$), and the term ' $\min(\chi_{SO_2}, \chi_{H_2O_2})$ ' is used to ensure that the SO_2 conversion is limited by the availability of H_2O_2 whenever $H_2O_2 < SO_2$. The SO_4^{2-} produced by the oxidation of SO_2 in clouds, and the ambient SO_4^{2-} entrained into the clouds, are partially removed

by the precipitation process. Previous observations suggest that SO₄²⁻ particles are entirely dissolved into the cloud water, hence the in-cloud wet removal coefficient is essentially equal to unity (Hegg and Hobbs, 1987; Seinfeld and Pandis, 1998). Therefore, in large scale clouds, the tendency of SO₄²⁻ is given as:

$$T_{ls,so4} = [\exp(-r_{rem} dt) - 1] \left[\frac{1}{dt} frc_{ls} \chi_{so4} - T_{ls,so2} \right]$$

where r_{rem} is the autoconversion frequency for the production of rain water from cloud water (Giorgi and Chameides, 1986; Giorgi et al. 1999), given by the autoconversion rate divided by the cloud water mixing ratio (wL). In addition to chemical conversion and wet removal, convective clouds can affect the horizontal and vertical distribution of tracers through convective entrainment and transport. The treatment of convective transport and wet removal for SO_x tracers in the model closely follows that of water vapor and thus makes use of the pre-existing algorithms within the RegCM3. We first calculate the total amount of SO_x that is entrained into a convective cloud at the k vertical level by assuming that the amount of tracer that enters the cloud is proportional to the amount of water vapor that enters the cloud and the relative concentrations of the tracer and water vapor at that level,

$$En(k)_i = qv_{tendency} \left(\frac{\chi_i}{qv} \right)$$

$$S_i = \sum_{cloudbase}^{cloudtop} En(k)$$

where qv is the mixing ratio of water vapor, and $qv_{tendency}$ is the tendency of water vapor at k level caused by the horizontal convergence, $En(k)_i$ is the rate at which tracer i (i.e. SO₂ and SO₄²⁻, and carbonaceous aerosols) is entrained into the cloud at the k vertical level and S_i is the column integrated amount of tracer i entrained into the cloud from cloud base to cloud top. So the amount of SO₂ and SO₄²⁻ convergence for the k level by cloud entrainment is $En(k)_{SO2}$ and $En(k)_{SO4}$, and the total convergence in the convective column is S_{SO2} and S_{SO4} , respectively.

Next, a fraction of the column integrated entrained SO₂ in the cloud is oxidized to SO₄²⁻. Following the formulation used for large scale clouds, P_{oxid} , the fraction of the entrained SO₂ that is oxidized is given by:

$$P_{oxid} = 1 - \exp(-\tau_{conv} w_L / A)$$

where $\tau_{conv} = 30\text{min}$, the typical lifetime of a mature stage of convective cloud (Rogers and Yau, 1989) and $w_L = 2\text{g m}^{-3}$ is assumed for the liquid water content of a convective cloud (Giorgi and

Chameides, 1986). Thus, $S_{SO_2}P_{oxid}$ and $S_{SO_2}(1-P_{oxid})$ represent the amount of SO_2 entrained in the column that is oxidized to SO_4^{2-} , and not oxidized, respectively. Since SO_2 remains largely in the gas phase, the non-oxidized portion of S_{SO_2} is then returned back to the k vertical layer within the convective column as SO_2 , according to a relative humidity dependent, parabolic vertical weighting factor $w(k)$, which is also used for water vapor detainment for convective clouds in the RegCM3 (Anthes, 1977).

The total amount of SO_4^{2-} in the convective column is the sum of the newly converted SO_4^{2-} from SO_2 (i.e., $S_{SO_2}P_{oxid}$) and the pre-existing SO_4^{2-} entrained into the cloud (i.e., S_{SO_4}). Since virtually all of this SO_4^{2-} resides in the cloud water, a fraction of it will be removed in precipitation and a fraction will be returned to the atmosphere. This fraction is determined using the same approach used in the RegCM3 described to partition between the water in the convective cloud that is removed from the cloud in precipitation and the fraction that is returned to the atmosphere. In the RegCM3, P_{conv} is the fraction of water that is not removed in precipitation; it is dependent on the column averaged relative humidity (RH), and calculated as:

$$P_{conv} = \begin{cases} 2(1 - \overline{RH}), & \text{when } \overline{RH} \geq 0.5 \\ 1, & \text{when } \overline{RH} < 0.5 \end{cases}$$

Thus, the amount of SO_4^{2-} in the column returned to the atmosphere is given by $(S_{SO_2}P_{oxid} + S_{SO_4}) P_{conv}$; and the amount returned to the k level is obtained by multiplying this quantity by the same vertical factor $w(k)$ as in the case of SO_2 .

Therefore, the tendency for SO_x at k vertical level due to the convective cloud processes can be expressed as:

$$T_{conv,SO_2} = -En(k)_{SO_2} + S_{SO_2} (1-P_{oxid}) w(k)$$

$$T_{conv,SO_4} = -En(k)_{SO_4} + S_{SO_4} P_{conv} w(k) + S_{SO_2} P_{oxid} P_{conv} w(k)$$

Below cloud scavenging of SO_2 follows the parameterization of Levine and Schwartz (1982), which is dependent on the precipitation rate and the mixing ratio of SO_2 . The tendency for SO_2 is given as:

$$T_{below-cloud, SO_2} = -k_{scav} Precip^{0.68} \chi_{SO_2}$$

where $Precip$ is the below cloud precipitation rate (in mm hr⁻¹), and k_{scav} is a pseudo 1st order scavenging coefficient of 6.5×10^{-5} s⁻¹. Sulfate aerosols are generally found in the accumulation mode (i.e., submicron to micron in diameter).

- Carbonaceous aerosols

Carbonaceous aerosols mainly arise from combustion processes, i.e. fossil fuel and biomass burning. Following the algorithm of Chameides et al. (2002), they are separated into two modes: a hydrophobic mode and a hydrophilic mode, and two chemical forms: organic carbon (OC) and black carbon (BC). OC and BC are assumed to be primary pollutants, directly emitted into the atmosphere, and when emitted they are assumed to be in hydrophobic form. These primary particles are then allowed to age into hydrophilic form at a rate characterized by a pseudo first-order rate coefficient of k_{age} at $7.1 \times 10^{-6} \text{ s}^{-1}$ (equivalent to a lifetime of 1.6 days) (Cooke et al 1996).

Hydrophilic BC and OC are removed via wet deposition by large scale and convective clouds in the way same as sulfate, while hydrophobic BC and OC are not subject to wet removal. In convective clouds, both hydrophilic and hydrophobic BC and OC are vertically redistributed using the same vertical weighting factor described in the previous section.

The dry deposition velocity for hydrophilic BC and OC is assumed to be 0.2 cm s^{-1} and 0.025 cm s^{-1} over water and land, respectively, while for hydrophobic BC and OC, it is assumed to 0.025 cm s^{-1} everywhere (Ganzeveld et al, 1998). Since no chemical conversion is involved for the carbonaceous aerosols, the prognostic equation is simplified as:

$$\frac{\partial \chi_i}{\partial t} = -\vec{V} \cdot \nabla \chi_i + F_{H,i} + F_{V,i} + S_i + T_{age,i} + T_{ls,i} + T_{conv,i} + T_{dry,i}$$

where i indicates BC and OC hydrophobic and hydrophilic components, $T_{age,i}$ is the aging process converting the hydrophobic mode of BC and CO to hydrophilic mode. The tendencies in the right hand side of the above Equation due to the aging and cloud process are given as:

$$T_{age,phobic} = -T_{age,philic} = -k_{age} \chi_{phobic}$$

$$T_{ls,philic} = (1/dt) \int_{ls} [exp(-r_{rem} dt) - 1] \chi_{philic}$$

$$T_{conv,phobic} = -En(k)_{phobic} + S_{phobic} w(k)$$

$$T_{conv,philic} = -En(k)_{philic} + S_{philic} P_{conv} w(k)$$

where the subscript “phobic” indicates hydrophobic BC or OC, and “philic” hydrophilic BC or OC, all the parameters are assumed to be same as sulfate, if not specified.