MODELING OF WET DEPOSITION IN CHEMICAL TRANSPORT SIMULATION

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Abstract: Transport/chemistry/deposition model for atmospheric trace chemical species is now frequently used as an important tool to assess the effects of various human activities, such as fuel combustion and deforestation, on human health, eco-system, and climate. In the analysis of the serious release of radioactive species from the accident of Fukushima Daiichi Nuclear Power Plant in March, 2011, various models were also applied to estimate the amount of discharged radioactive materials and to understand observed spatial distributions (Sectional Committee on Nuclear Accident, Science Council of Japan, 2014[11]; hereafter abbreviated as SCNA). The SCNA report shows that results of some models and also ensemble average of the calculated results of all the participate models successfully captured main features of horizontal distribution of the accumulated deposition of 137Cs. However, it seems there are still by factors of 5 and 1/5 differences between observed and calculated results at the largest.

Thus in this paper I like to show our previous attempts on wet deposition in chemical transport simulation for reference to think about the phenomena. The chemical transport model is required to reproduce correctly mass balance of various chemical species in the atmosphere with keeping adequate accuracy for calculated concentration distributions of chemical species. For the purpose, one of the important problems is a reliable wet deposition modeling, and here, we introduce two types of methods of “cloud-resolving” and “non-cloud-resolving” modeling for the wet deposition of pollutants.

Keywords: Air pollution, transport modeling, wet deposition, cloud resolving/non-resolving

INTRODUCTION

Historically several models such as RADM[2] and STEM-II [1] included not only gas/aerosol phase chemistry but also aqueous phase chemistry in cloud/rain water in addition to the processes of advection, diffusion, wet deposition (mass transfer between aqueous and gas/aerosol phases), and dry deposition. Software of CMAQ (Community Multi-scale Air Quality model [3]) has been released by EPA for public use of a “comprehensive” model. These models are now frequently used by many people, and show their ability to successfully reproduce some features on atmospheric environment such as high ozone concentration episode by photochemical smog reactions. Figure 1 shows a model system for atmospheric trace chemical species. Meteorological model provides hydrometeors' fields as well as flow, temperature, and eddy diffusivity to the comprehensive model for chemical species. Final target of the “comprehensive” model will be that the model can correctly reproduce mass balance of various chemical species in the atmosphere with keeping adequate accuracy for calculated concentration distributions of chemical species; in this situation life times of various primary and secondary pollutants should be correctly predicted. To do so many problems may be still remained. One of the important problems is reliable wet deposition prediction. There may be two types of attitudes for the modeling of the wet deposition; one considers trans-horizontal-grids transport of aqueous phase chemical species with use of partial differential equations for these
simplified modeling.

In the following sections, we will introduce our previous attempts on these modeling techniques.

### CLOUD-RESOLVING MODELING

Cloud-resolving modeling describes dynamics of chemical species in hydrometeors with unsteady partial differential equations, and allows the chemical species to cross grid cell boundary. It usually treats detailed mass transfer processes of chemical species among gas/aerosol and hydrometeor phases. Let us imagine the situation of the complex mass transfer taking place in the atmosphere. First, aerosol may serve as condensation nuclei to form cloud droplets. Then the cloud droplets either further grow with the processes such as accretion and auto-conversion to rain drop or with the Bergeron process to snow particle, or they may disappear by evaporation. These cloud processes can be summarized as Fig. 2 [4, 5, 10].

Associated with each cloud process shown in Fig. 2, inter-phase transfers of air pollutants such as SO\textsubscript{x} (SO\textsubscript{2}, and SO\textsubscript{4}\textsuperscript{2-}) and NO\textsubscript{3} can occur among the phases of gas (aerosol), cloud
water, rain water, cloud ice, and snow. For example, mass transfer and transformation of SOx may be written as in Fig. 3. In addition, aqueous phase chemical reactions such as oxidation of SO$_2$ (aq) in cloud and rain water take place as listed, for example, in Table 1 and 2.

Figure 2. Diagram of inter-hydrometeor-transfers of water substance of the cloud microphysics model after Rutledge and Hobbs, 1984 [4, 5, 10].
Figure 3. Schematic showing gas-hydrometeor inter-phase transfers of SOx [4, 8]. T The gas phase chemistry model includes the following reactions for SO$_4^{2-}$ production as main mechanism: $\text{SO}_2 + \text{OH} \rightarrow \text{SO}_4^{2-}$ (lumped mechanism), $\text{SO}_2 + \text{RO}_2 \rightarrow \text{SO}_4^{2-}$ (lumped mechanism), $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ (oxidation reaction on the surface of aerosol particle). AbD, Absorption-Desorption; Acc, Accretion; Aut, Autoconversion; Ber, Bergeron process; BrD, Brownian diffusion; Col, Collection; Con, Conversion; EvR, Evaporation; ImS, Impaction scavenging; Mel, Melting; NuS, Nucleation scavenging; Oxi, Oxidation; Rim, Riming; SuR, Sublimational Release.
Hence governing equations for chemical species in gas (and aerosol) and hydrometeors are summarized as follows:

For gas and aerosol phase species,

\[ \rho \frac{\partial C_i}{\partial t} + \mathbf{v} \cdot \nabla C_i = \nabla \cdot (\mathbf{v} C_i) + R_i + S_i - G_i, \quad i = 1, 2, \ldots, I_1 \]

(1)

where \( C_i \) is the non-dimensional concentration of the \( i \)th chemical species in gas phase, \( \rho \) is the air density, \( R_i \) is the chemical reaction rate, \( S_i \) is the non-flux-type emission source, and \( G_i \) is
the mass transfer rate between gas and the jth hydrometeor phases; the rate consists of the relevant processes, for example, for SOx shown in Fig. 3.

For chemical species in hydrometeors,

$$\frac{\partial C_j^i}{\partial t} + u \frac{\partial C_j^i}{\partial x} + v \frac{\partial C_j^i}{\partial y} + W_j \frac{\partial C_j^i}{\partial z} - q_j \rho \frac{\partial V_j}{\partial z} C_j^i = \left( R_j^i + T_j^i + G_j^i \right), \quad i = I_1 + 1, \ldots, I_2 \quad (2)$$

where $C_j^i$ is the concentration of the $i$th chemical species in the $j$th hydrometeor, $q_j$ is the water content of the $j$th hydrometeor, $W_j = w - V_j$, $V_j$ is the gravitational falling velocity of the $j$th hydrometeor such as rain, snow, and graupel, for which prescribed size distributions are assumed; for example, so-called Marshall-Palmer size distribution [9],

$$N_{D,j} = N_{oj} \exp \left( -\lambda_j r_D \right) \text{ and } \lambda_j = \left( \frac{\pi^2 N_{oj}^2}{\rho q_j} \right)^{0.25} \text{ for rain, snow, and graupel;}$$

$N_{D,j}$ stands for the number density of droplets of the $j$th hydrometeor in the diameter range between $D_j$ and $D_j + dD_j$, and $\rho_j$ is the density of the $j$th hydrometeor. $R_j^i$ is the chemical reaction rate of the $i$th species in the $j$th hydrometeor, and $T_j^i$ is the mass transfer rate of the $i$th chemical species between the $j$th and $k$th hydrometeors, the inter-phase mass transfer processes among hydrometeors are shown, for example, in Fig. 3; the term $R_j^i$ is formed with the chemical reactions in Table 1 and 2.

**APPLICATION OF CLOUD-RESOLVING MODELING: ACIDIC SNOW FORMATION OVER THE SEA OF JAPAN**

In winter, cold air mass is accumulated over Siberia, and huge amounts of air pollutants, emitted from East Asian continental countries such as China and Korea, are also injected into the air mass. When this cold and pollutants-rich air mass flows out over the warmer Sea of Japan, thermal convection develops to form organized roll vortices aligned with main wind direction heading toward Japan. Hence the humid air mass, supplied with water vapor from the Sea of Japan, frequently brings heavy snow fall and also acidic deposition in the coastal area of Japan on the Japan Sea side. To analyze how and how much the acidic species are formed in the cloud streets associated with the roll vortices, our cloud-resolving model was used [5].

Figure 4 illustrates relative location of the East Asian countries, the Sea of Japan, and Japan, and also shows typical direction of the cold and polluted air mass movement and typical time required for the air mass’s crossing of the Japan Sea; as an example, approximate time of the passage is written in the figure. Figure 5 is the calculation domain idealized as two-dimensional situation.
Figures 6a,b show the calculated water content maps of cloud water and snow, respectively. They are the results after 12 hours’ advancement of the air mass over the Japan Sea. Similarly, Figures 7a,b,c are the calculated pH and SO$_4^{2-}$ in the cloud water, and SO$_4^{2-}$ in the snow, respectively. Figure 7a suggests (1) the pH value of cloud water over the Japan Sea in winter can be around 4 or less, (2) the pH value is lower where the cloud water content is smaller, thus, pH is low at the edge of the cloud. The contour map of SO$_4^{2-}$ in Fig. 7b indicates (3) SO$_4^{2-}$ is trapped at the cloud base where upward air flow exists and (4) SO$_4^{2-}$ accumulates at the cloud top, in particular, in the interstitial air of the clouds. However, (5) SO$_4^{2-}$ in the snow phase is much larger than in the cloud phase as shown in Fig. 7c. Interestingly, the cloud and...
snow formation sometimes keeps pollutant concentration in the lower atmosphere rather high as suggested in Fig. 8, which compares vertical profiles of $\text{SO}_4^{2-}$ between D1 (with cloud and snow) and D0 (without them) cases; that is, in the cloud and snow case the cloud traps the pollutant and the snowfall returns the pollutant in the cloud again to the below-cloud level, and if the sublimation of the snow occurs, then the pollutant can be backed to gas and aerosol phase in the lower layer; of course, if there is no condition for the snow sublimation, then the pollutant in the snow will deposit onto the earth’s surface without raising atmospheric concentration.

Figure 6. Vertical cross sections of calculated (a) cloud water, and (b) snow at 2000LST; unit in g kg-air$^{-1}$ [4, 5].

Figure 8. Vertical profiles of calculated aerosol-$\text{SO}_4^{2-}$: the cases of D0 (no-cloud) and D1 (cloud) at 2000LST along y=10.5 km [4, 5, 8].

NON CLOUD-RESOLVING MODELING
Non cloud–resolving modeling usually (1) does not use unsteady partial differential equation for chemical species in hydrometeor phases, (2) does not allow the pollutants in
hydrometeor phases to directly cross horizontal grid cell, and (3) is thus a simplified approach; many of the comprehensive models such as RADM [2], STEM-II [1], and CMAQ [3] currently use this non cloud-resolving model.

In this section we will introduce our non cloud-resolving modeling and its application [4, 6]. If we use a spherical coordinate to describe transport/transformation equation for trace chemical species, governing equation can be written as follows:

$$
\frac{\partial X_i}{\partial t} + CU \frac{\partial X_i}{\partial x} + CV \frac{\partial X_i}{\partial y} + C\sigma \frac{\partial X_i}{\partial \sigma} = \frac{\partial}{\partial x} \left( CE_r \frac{\partial X_i}{\partial x} \right) + \frac{1}{\cos \theta \sigma} \frac{\partial}{\partial y} \left( C \cos \theta E_{\theta} \frac{\partial X_i}{\partial y} \right) + \frac{\rho g}{\sigma} \frac{\partial}{\partial \sigma} \left( C \rho r^2 E_{\sigma} \frac{\partial X_i}{\partial \sigma} \right) + R_i - \Lambda C X_i, \quad i = 1, 2, \ldots, I
$$

where $dx = r \cos \theta d\phi$, $dy = r \sigma d\theta$, $\sigma = (P - P_T)/\pi$ is the normalized pressure coordinate, $\pi = P_s - P_T$, $\sigma = \left( \frac{\partial z}{\partial t} \sigma \right) + \vec{V} \cdot \nabla \sigma - W \right) \frac{\rho g}{\pi}$, $X_i$ is the non-dimensional concentration of the $i$th chemical species, $C$ and $\rho$ are the air density in kmol m$^{-3}$ and kg m$^{-3}$, respectively, $\theta$ and $\phi$ are the latitude and longitude, $r$ is the distance from the earth’s center, $P_s$ and $P_T$ are the atmospheric pressure at the earth’s surface and top boundary, respectively, $z$ is the altitude of surface, $U, V,$ and $W$ are the wind velocity for $\phi, \theta,$ and $z$ directions, respectively, $\sigma$ is the vertical velocity in $\sigma$ coordinate, and $R_i$ is the chemical reaction term. In Eq. (3), the last term on the right hand side stands for the wet deposition process; $\Lambda$ is the scavenging coefficient due to cloud water, rain, and snow, and was derived for aerosol particle and gaseous species as follows (see for detail Kitada [4]; Kitada and Nishizawa [6]):

For wet deposition of $SO_4^{2-}$ particle by rain drop [4],

$$
\Lambda_{p, \text{rain}} = 6 \times 10^{-4} \eta_s P^{0.75} \text{ in s}^{-1},
$$

and for that by snow [12],

$$
\Lambda_{p, \text{snow}} = \frac{\rho_w g \eta_s (3.6 \times 10^{-6} P)}{\rho_a V_i^2} \text{ in s}^{-1},
$$

where $P$ is the precipitation intensity in mmhr$^{-1}$, $\eta_s$ is the collection efficiency of aerosol particle by rain and was assumed to be 0.3~0.5, $\eta_s$ is the same but by snow and is summarized in Slinn [13], $\rho_w$ and $\rho_a$ are the density of water and air in kgm$^{-3}$, respectively, and $V_i$ is the average settling velocity of snow flake in ms$^{-1}$, and $V_i = (102 + 51 \log_{10} d_c)/100$ is recommended [7].

For wet removal of gaseous species by rain, the following equation was derived (Kitada [4]; Kitada and Nishizawa [6]):

$$
\Lambda_{SO_2} = \beta \frac{\alpha P}{3.6H} \text{ and } \alpha = 10^{-6} RTH_{eff,SO_2}
$$

where $H$ is the height of the cloud top in m, $R$ is the universal gas constant (=0.082
\( \ell \text{ atm} K^{-1} \text{ mol}^{-1} \), \( T \) is the air temperature in K, and \( H_{\text{eff}, \text{SO}_2} \) is the inverse of the effective Henry’s law constant for \( \text{SO}_2 \) in \( \text{mol} \ell^{-1} \text{ atm}^{-1} \) (see [5] and [6] for detail), and \( \beta \) is an “equilibrium index” and represents the ratio of the real S(IV) concentration to the hypothetical equilibrium S(IV) concentration in rain water; and was determined with a series of numerical experiments in which concentrations of S(IV) etc. in rain drop falling through polluted atmosphere were calculated; \( \beta \) is 1 for \( \text{SO}_2 \), \( 0.38 \times 10^{-8} \) for \( \text{HNO}_3 \), and 0.055 for \( \text{H}_2\text{O}_2 \).
APPLICATION OF NON CLOUD-RESOLVING MODELING

Figure 9. Calculated total deposition (dry + wet) in BASE case: (a) N- and (b) S-compounds in mmol m\(^{-2}\) (14 day\(^{-1}\)). The calculation was performed from 00GMT March 1 to 00GMT March 15, 1994. Contour lines are drawn for 0.1, 0.2, 0.5, 1.0, and 2.0 in mmol m\(^{-2}\) (14 day\(^{-1}\)).

The model described in section 3 was applied for pollutants transport in East Asia. Figure 9 shows, as an example of the results, the calculated total deposition of N- and S-compounds for 14 days [6].
SUMMARY AND CONCLUSION
Two types of the modeling methods for the wet deposition processes, i.e., “cloud-resolving” and “non-cloud-resolving”, were introduced. Examples of their applications were also briefly described. For meso- and micro-scale phenomena such as the formation of acidic fog, the cloud-resolving approach described here should be further investigated. Also in Fukushima Nuclear Power Plant case, to consider transport equations of radioactive materials in cloud and rain phases directly may lead to better agreement with observation. A recent meeting on the modeling of atmospheric transport and deposition of radioactive nuclei in the Fukushima case may be referred in the web site [14].

REFERENCES
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