

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 participated 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..

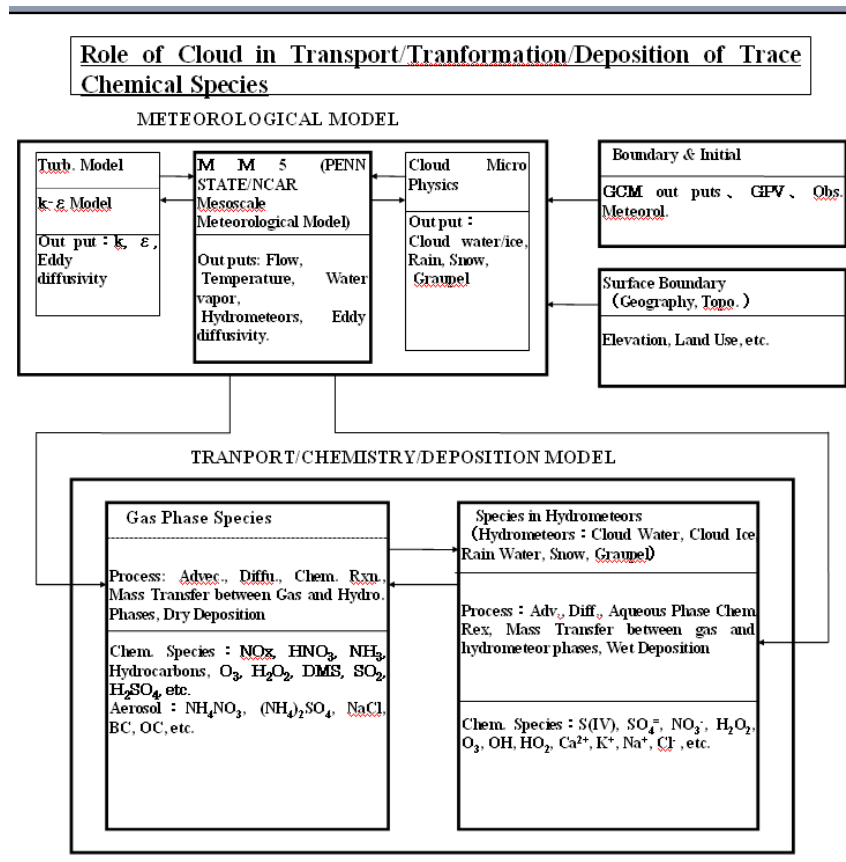


Figure 1. Comprehensive model of transport/transformation/deposition of atmospheric trace chemical species.

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_x (SO₂, and SO₄²⁻) and NO₃⁻ can occur among the phases of gas (aerosol), cloud

water, rain water, cloud ice, and snow. For example, mass transfer and transformation of SO_x may be written as in Fig. 3. In addition, aqueous phase chemical reactions such as oxidation of SO₂ (aq) in cloud and rain water take place as listed, for example, in Table 1 and 2.

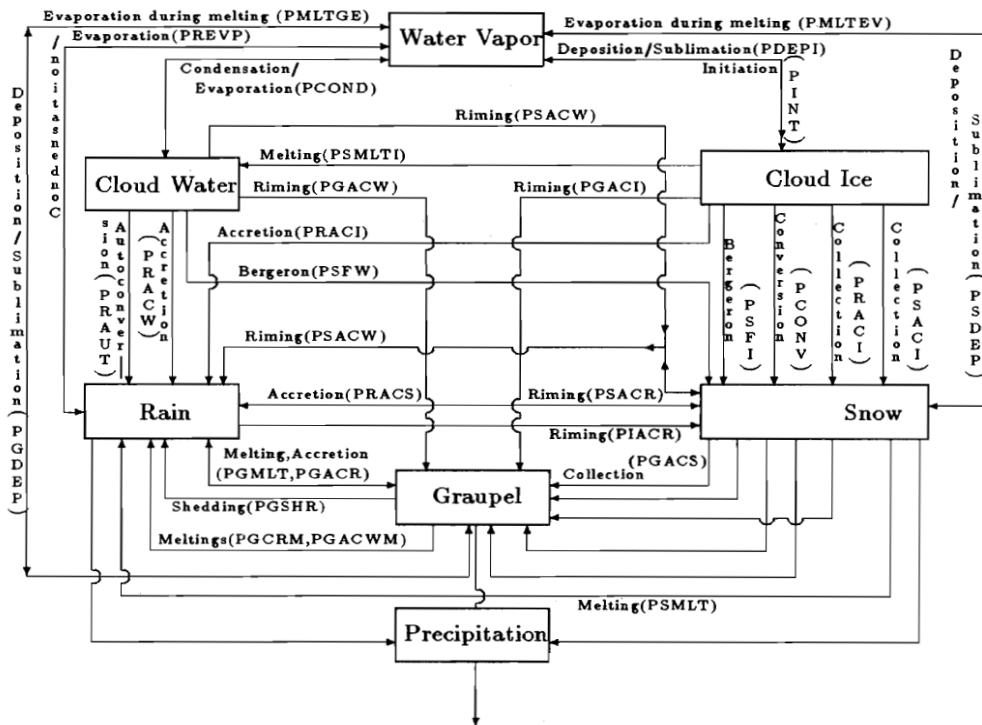


Figure 2. Diagram of inter-hydrometeor-transfers of water substance of the cloud microphysics model after Rutledge and Hobbs, 1984 [4, 5, 10].

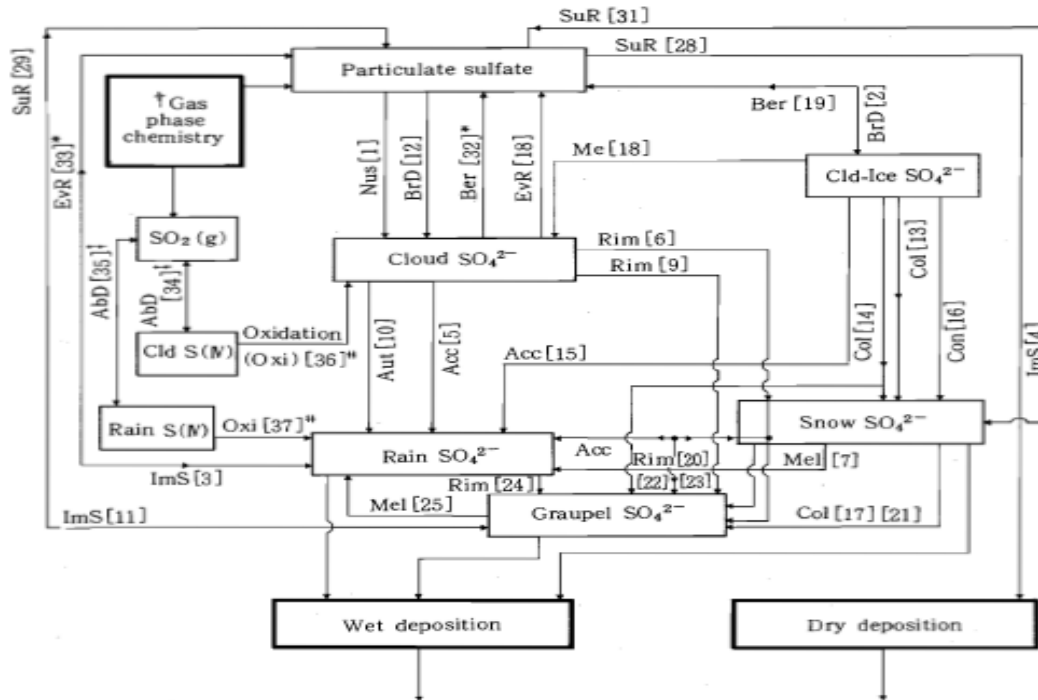


Figure 3. Schematic showing gas-hydrimeteor inter-phase transfers of SO_x [4, 8]. † The gas phase chemistry model includes the following reactions for SO₄²⁻ production as main mechanism: SO₂+OH→SO₄²⁻ (lumped mechanism), SO₂+RO₂→SO₄²⁻ (lumped mechanism), SO₂→SO₄²⁻ (oxidation reaction on the surface of 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.

Table 1. Aqueous phase equilibrium reactions [5]

Reactions	Equilibrium constants M or M (atm.) ⁻¹	Source
EQ1 SO ₂ (g) ⇌ SO ₂ (aq)	1.23 exp[3120 · f(T)*]	PS
EQ2 SO ₂ (aq) ⇌ H ⁺ + HSO ₃ ⁻	1.23 × 10 ⁻² exp[1960 · f(T)]	PS
EQ3 HSO ₃ ⁻ ⇌ H ⁺ + SO ₃ ²⁻	6.61 × 10 ⁻⁸ exp[1500 · f(T)]	PS
EQ4 NH ₃ (g) ⇌ NH ₃ (aq)	75 exp[3400 · f(T)]	PS
EQ5 NH ₃ (aq) ⇌ NH ₄ ⁺ + OH ⁻	1.75 × 10 ⁻⁵ exp[-450 · f(T)]	PS
EQ6 HNO ₃ (g) ⇌ H ⁺ + NO ₃ ⁻	2.6 × 10 ⁶ exp[8700 · f(T)]	C
EQ7 CO ₂ (g) ⇌ CO ₂ (aq)	3.4 × 10 ⁻² exp[2420 · f(T)]	PS
EQ8 CO ₂ (aq) ⇌ HCO ₃ ⁻ + H ⁺	4.46 × 10 ⁻⁷ exp[-1000 · f(T)]	PS
EQ9 HCO ₃ ⁻ ⇌ CO ₃ ²⁻ + H ⁺	4.68 × 10 ⁻¹¹ exp[-1760 · f(T)]	PS
EQ10 O ₃ (g) ⇌ O ₃ (aq)	1.13 × 10 ⁻² exp[2300 · f(T)]	PS
EQ11 H ₂ O ₂ (g) ⇌ H ₂ O ₂ (aq)	7.45 × 10 ⁴ exp[6620 · f(T)]	PS
EQ12 HO ₂ (g) ⇌ HO ₂ (aq)	2 × 10 ³ exp[6640 · f(T)]	PS
EQ13 OH(g) ⇌ OH(aq)	25 exp[5280 · f(T)]	PS
EQ14 H ₂ O ⇌ H ⁺ + OH ⁻	1 × 10 ¹⁴	PS

*f(T) ≡ $\frac{1}{T} - \frac{1}{298}$ where T is temperature in K.

PS: Pandis and Seinfeld (1989).

C: Chameides (1984).

Table 2. Aqueous phase chemical reactions [5].

Reactions	Rates s ⁻¹ , M ⁻¹ s ⁻¹ or M ⁻² s ⁻¹	Source
R1 H ₂ O ₂ $\xrightarrow{h\nu}$ 2 · OH	1.0 × 10 ⁻⁶	ES
R2 OH + HO ₂ → H ₂ O + O ₂	1.1 × 10 ¹² exp[-1500/T]	PS
R3 OH + H ₂ O ₂ → H ₂ O + HO ₂	8.1 × 10 ⁹ exp[-1700/T]	PS
R4 HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.4 × 10 ⁹ exp[-2365/T]	PS
R5 S(IV) + O ₃ → S(VI) + O ₂	for SO ₂ (aq): 2.4 × 10 ⁶ for HSO ₃ ⁻ : 4.2 × 10 ¹³ exp[-5530/T]	
R6 S(IV) + H ₂ O ₂ → S(VI) + H ₂ O	for SO ₂ (aq): 7.4 × 10 ¹⁶ exp[-5280/T] 3.7 × 10 ¹² exp[-4430/T]	PS PS
R7 S(IV) + $\frac{1}{2}$ · O ₂ $\xrightarrow{Fe^{3+}, Mn^{2+}}$ S(VI)	*	M

$$* \text{pH} \leq 5: -4.6 \times 10^{23} \exp\left[-\frac{13,700}{T}\right] [\text{Mn}^{2+}] [\text{HSO}_3^-] \\ - 8.8 \times 10^{15} \exp\left[-\frac{11,000}{T}\right] [\text{Fe}^{3+}] \left(\frac{[\text{SO}_2(\text{aq})] + [\text{HSO}_3^-]}{[\text{H}^+]}\right).$$

$$\text{pH} > 5: -4.6 \times 10^{23} \exp\left[-\frac{13,700}{T}\right] [\text{Mn}^{2+}] [\text{HSO}_3^-].$$

PS: Pandis and Seinfeld (1989).

M: Martin (1984).

ES: estimated for noon time in Jan. at 40°N.

Hence governing equations for chemical species in gas (and aerosol) and hydrometeors are summarized as follows:

For gas and aerosol phase species,

$$\rho \frac{\partial C_i}{\partial t} + \rho \bar{V} \cdot \nabla C_i = \nabla \cdot \rho \bar{K} \cdot \nabla C_i + R_i + S_i - G_i^j, \quad i = 1, 2, \dots, I_1 \quad (1)$$

where C_i is the non-dimensional concentration of the i th chemical species in gas phase, ρ is the air density, R_i is the chemical reaction rate, S_i is the non-flux-type emission source, and G_i^j is

the mass transfer rate between gas and the j th hydrometeor phases; the rate consists of the relevant processes, for example, for SO_x shown in Fig. 3.

For chemical species in hydrometeors,

$$\frac{\partial C_i^j q_j}{\partial t} + u \frac{\partial C_i^j q_j}{\partial x} + v \frac{\partial C_i^j q_j}{\partial y} + W_j \frac{\partial C_i^j q_j}{\partial z} - \frac{q_i \partial \rho V_j}{\rho \partial z} C_i^j = \frac{(R_i^j + {}_k T_i^j + G_i^j)}{\rho}, \quad i = I_1+1, \dots, I_2 \quad (2)$$

where C_i^j 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],

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

$N_{D,j}$ 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 ρ_j is the density of the j th hydrometeor. R_i^j is the chemical reaction rate of the i th species in the j th hydrometeor, and ${}_k T_i^j$ 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_i^j 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.

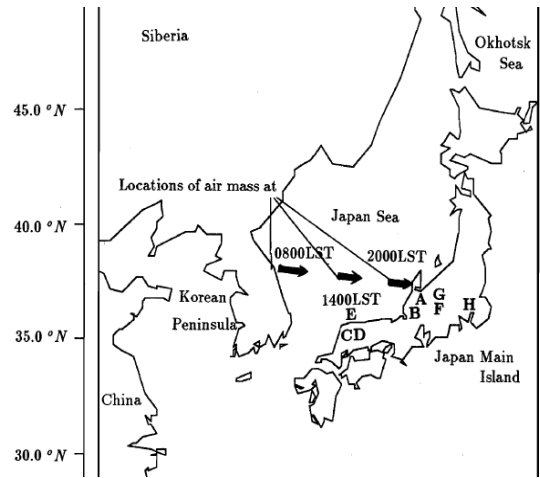


Figure 4. Typical traveling course of the continental air mass moving over the Sea of Japan in winter; formation of cloud and formation of acidic species associated with the cloud were simulated along the course. The locations of the air mass at 0800, 1400, and 2000LST are indicated with thick solid arrows. The symbols from “A” to “H” represent observation points for acid deposition.

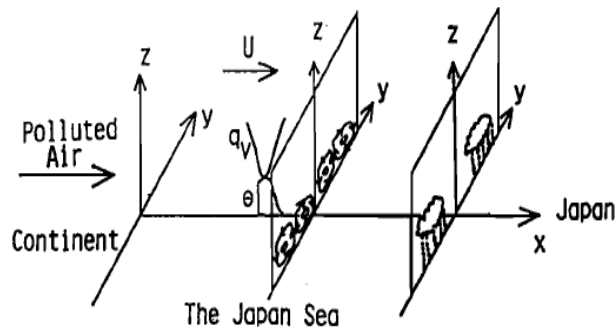


Figure 5. Schematic diagram of the 2-D calculation domain for convective cloud streets over the Japan Sea in winter, where q_v denotes water vapor mixing ratio, and θ the potential temperature [4, 5, 8].

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 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.

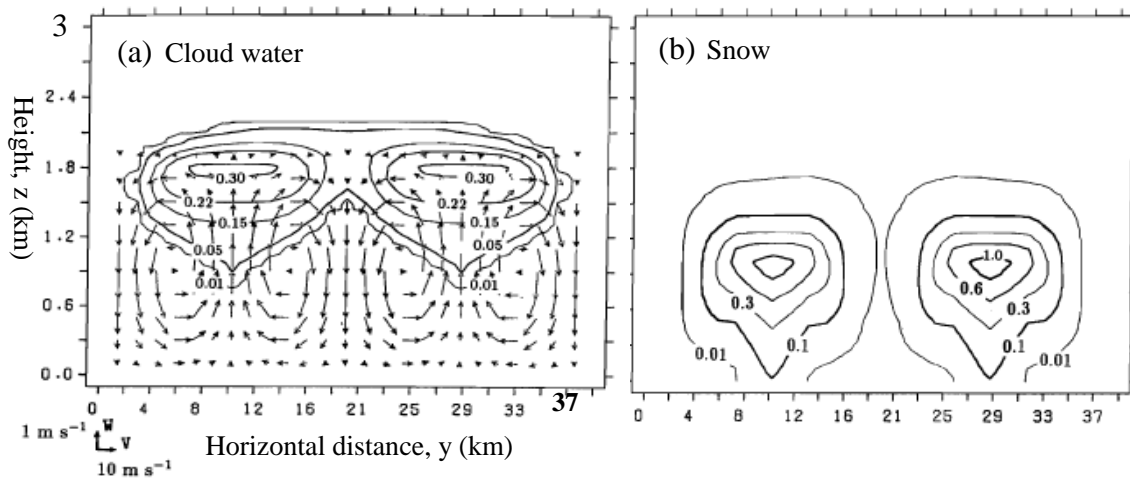


Figure 6. Vertical cross sections of calculated (a) cloud water, and (b) snow at 2000LST; unit in g kg^{-1} [4, 5].

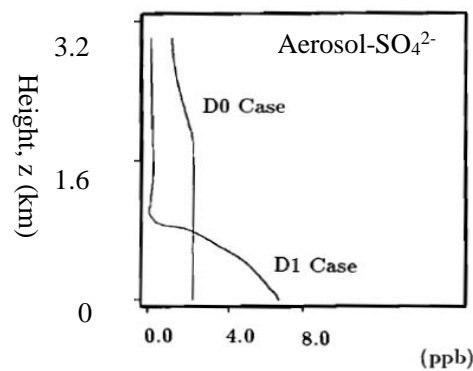


Figure 8. Vertical profiles of calculated aerosol- SO_4^{2-} : the cases of D0 (no-cloud) and D1 (cloud) at 2000LST along $y=10.5$ km [4, 5, 8].

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:

$$C \frac{\partial X_i}{\partial t} + CU \frac{\partial X_i}{\partial x} + CV \frac{\partial X_i}{\partial y} + C\dot{\sigma} \frac{\partial X_i}{\partial \sigma} = \frac{\partial}{\partial x} \left(CE_\phi \frac{\partial X_i}{\partial x} \right) + \frac{1}{\cos \theta} \frac{\partial}{\partial y} \left(C \cos \theta E_\theta \frac{\partial X_i}{\partial y} \right) + \frac{\rho g^2}{\pi^2 r^2} \frac{\partial}{\partial \sigma} \left(C \rho r^2 E_\sigma \frac{\partial X_i}{\partial \sigma} \right) + R_i - \Lambda CX_i, \quad i = 1, 2, \dots, I \quad (3)$$

where $dx = r \cos \theta d\phi$, $dy = r d\theta$, $\sigma = (P - P_T)/\pi$ is the normalized pressure coordinate,

$$\pi = P_s - P_T, \quad \dot{\sigma} = \left\{ \left(\frac{\partial z}{\partial t} \right)_\sigma + \vec{V} \cdot \nabla_\sigma z - W \right\} \frac{\rho g}{\pi},$$

X_i is the non-dimensional concentration of the i th chemical species, C and ρ are the air density in kmol m^{-3} and kg m^{-3} , respectively, θ and ϕ 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 σ surface, U , V , and W are the wind velocity for ϕ , θ , and z directions, respectively, $\dot{\sigma}$ is the vertical velocity in σ 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; Λ 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],

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

and for that by snow [12],

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

where P is the precipitation intensity in mmhr^{-1} , η_r is the collection efficiency of aerosol particle by rain and was assumed to be 0.3~0.5, η_s is the same but by snow and is summarized in Slinn [13], ρ_w and ρ_a are the density of water and air in kgm^{-3} , respectively, and V_t is the average settling velocity of snow flake in ms^{-1} , and $V_t = (102 + 51 \log_{10} d_c)/100$ 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 ($=0.082$



$\ell \text{ atmK}^{-1} \text{ mol}^{-1}$), T is the air temperature in K, and H_{eff, SO_2} is the inverse of the effective Henry's law constant for SO_2 in $\text{mol} \ell^{-1} \text{ atm}^{-1}$ (see [5] and [6] for detail), and β 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; β is 1 for SO_2 , 0.38×10^{-8} for HNO_3 , and 0.055 for H_2O_2 .

APPLICATION OF NON CLOUD-RESOLVING MODELING

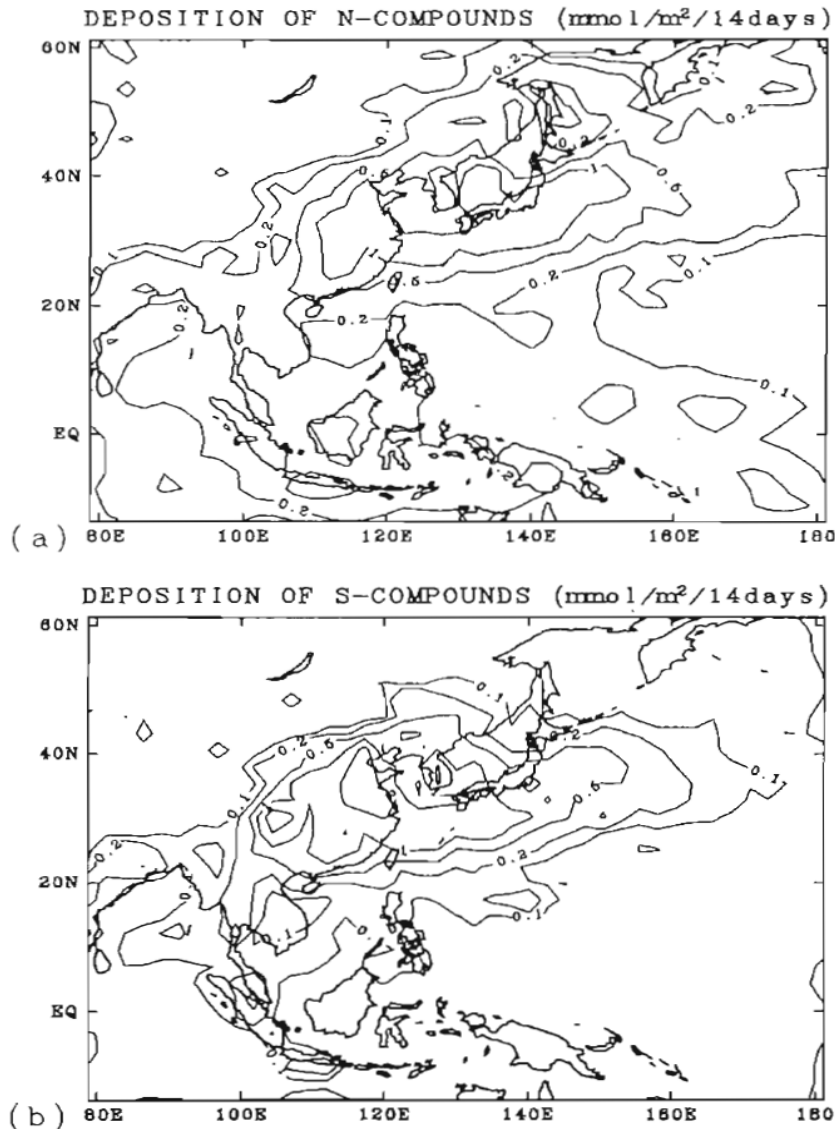
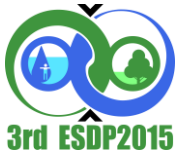


Figure 9. Calculated total deposition (dry + wet) in BASE case: (a) N- and (b) S-compounds in $\text{mmol m}^{-2} (14 \text{ day})^{-1}$. The calculation was performed from 00GMT March 1 to 00GMT March 15, 1994. Contour lines are drawn for 0.1, 0.2, 0.5, 1.0, and 2.0 in $\text{mmol m}^{-2} (14 \text{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

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].

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- [14] International workshop on dispersion and deposition modeling for nuclear accident releases -Transfer of science from academic to operational models- (2015)
<http://venus.iis.u-tokyo.ac.jp/english/workshop/newE.htm>