

NUMERICAL MODELING OF CUMULUS CLOUD CHEMISTRY —PART II: THE IMPACT OF CUMULUS CLOUD PROCESSES ON OZONE CHEMISTRY*

Zhao Chunsheng (赵春生) and Qin Yu (秦瑜)

Department of Geophysics, Peking University, Beijing 100871

Received October 9, 1995; revised January 19, 1996

ABSTRACT

Ozone chemistry processes are analyzed during a cumulus cloud process with the model (1CCCM) described in Part I. The simulation results show that entire cumulus cloud process can be well described with the development of vertical velocities and liquid water content which are the two most outstanding features of cumulus clouds. Ozone chemistry is strongly influenced by cumulus clouds. NO_x can be transported upwards above 4 km in the first 20 minutes of the convection event and form a relative higher concentration area which enhances the production of ozone. Two areas appear during the convection event: area of net ozone production and area of net ozone depletion. The area of ozone depletion coincides with the area of liquid water within cloud. Results show that the aqueous phase (cloud water and rainwater) can alter gas ozone level through two ways: one is scavenging free radicals (HO_2) from the gas phase and thereby inhibiting the reactions of transformation to NO_2 from NO , which results in reduction of the gas source of ozone; the other is aqueous phase chemical reactions which consume ozone in the aqueous phase. Calculations reveal that the reaction $\text{O}_3 + \text{OH} \rightarrow \text{HO}_2$ is the main pathway of ozone depletion in gas phase during the process of cumulus clouds.

Key words: ozone, cumulus cloud, aqueous chemistry, free radical, scavenging

1. INTRODUCTION

As noted in Part I of our papers (Zhao and Qin 1996), clouds influence troposphere chemistry mainly through three mechanisms: redistributing chemical species vertically by the intensive vertical velocities of clouds, scavenging gaseous and particulate species which may react in liquid water and on the surface of ice water, and altering the photolysis rates of atmospheric photochemistry reactions due to the change of radiation budget.

Recently, several studies have been focused on the interaction of clouds processes and chemical process in the troposphere. One of these studies is the impact of clouds on tropospheric oxidizing capacity (oxidizing efficiency). Chameidies and Divis (1982) studied the aqueous phase chemistry involving hydrogen radicals and the impact of free radicals in cloud drops on the composition of rainwater and cloud water, with a box model. Lelieveld and Crutzen (1990) considered the troposphere as a whole and studied the role of clouds in tropospheric chemistry and its effects on tropospheric ozone. They showed that aqueous phase chemistry is

* This work was supported by the National Natural Science Foundation of China.

a significant sink for troposphere ozone. Johnson and Isaksen (1993) used a two-channel model to test out the effect of clouds and cloud chemistry. Their calculation indicated that ozone level is reduced by 10% to 30% with the largest reductions in the remote middle troposphere.

Studies of whole troposphere chemistry with large-scale models such as global models and channel models can be used to evaluate the roles of the clouds in the whole tropospheric physical and chemical processes. Because of the difference of intensity, lifetime and other physical properties of cumulus clouds, those models have a lot of uncertainties. Thus there is a need to study the physical and chemical processes in a single cumulus cloud process on a relative small time scale. This kind of work, on one hand, may gain insight of the details of chemical processes in the lifetime of cumulus clouds, and on the other hand, might give the parameterization scheme of cumulus cloud chemistry adopted in large scale models.

This paper aims to analyze the impact of clouds on ozone chemistry during a cumulus cloud process with the model we developed in Part I. In the next section, an additional description of the model is given, and the results of this simulation will be discussed in the following section.

II. MODEL DESCRIPTION

The detailed description of the model (ICCCM) can be found in Part I. Here we just give an additional description of the choosing of photolysis rates and the initial condition of the chemical species.

Table 1. Initial Concentrations of Chemical Species

Species	Symbol	Surface concentration (ppb)	Scale height (m)	Species	Symbol	Surface concentration (ppb)	Scale height (m)
Ozone	O ₃	30		Hydrogen peroxide	H ₂ O ₂	1	
Nitric oxide	NO	4	2000	Nitrogen dioxide	NO ₂	1	2000
Nitric acid	HNO ₃	0.01	2000	Ammonium	NH ₃	1.0	1000
Carbon monoxide	CO	100	2000	Carbon dioxide	CO ₂	340000	
Sulfur dioxide	SO ₂	0.1	2000	Methane	CH ₄	1500	
Alkanes	ALK	1.5		Ethene	ETHE	1.0	
Olefins	OLE	0.5		Formaldehyde	HCHO	0.2	
Aldehydes	RCHO	0.1		Toluene	TOLU	0.2	
Dialkylbenzenes	XYLE	0.1					

Since we simulate a cumulus cloud on a time scale of one hour, photolysis rates can be assumed constant over such a short period of time. The data of the photolysis rates are from NCAR model.

The vertical scale of cloud model is 15 km with the increment of 300 m. The time step of

integration is 10 seconds for the cloud physical processes. The model is carried out for one hour.

The initial conditions for chemical species are listed in Table 1. For NO_x , SO_2 , NH_3 , CO and HNO_3 , their concentrations decrease with height exponentially

$$C_i^n(z) = C_i^n(0)\exp\left(-\frac{z}{H_i}\right), \quad (1)$$

where $C_i^n(0)$ is the initial surface concentration of species i , H_i is the scale height, $C_i^n(z)$ is the concentration of species i at height z . Concentrations of other species are vertical homogeneous initially.

III. RESULTS AND DISCUSSIONS

A cumulus cloud process is simulated by calculating the values of temperature, mixing ratios and number concentrations of water substance. Figures 1 and 2 show the evolutions of vertical velocity and the mixing ratios of cloud water and rainwater.

In the first 24 minutes of simulation, the updraft velocity increases rapidly with time and reaches the maximum of 8.1 m s^{-1} at the 24th minute. At this time, the downdraft appears near the surface and then increases with time. The maximum of downdraft is 3.3 m s^{-1} at the 46th minute. Drafts of the falling precipitation particles and the cooling effects of evaporation of rainwater are the main causes that turn the updrafts into downdrafts in the lower part of the cloud. After the 46th minute, downdrafts make the cloud disappear gradually. The evolution of the entire cumulus cloud process can be well described with the evolution of vertical velocities. Intensive updrafts are the main feature of convective events.

Figure 2 shows that in the first 24 minutes, the cloud becomes thicker and thicker while its top rises rapidly. At the 24th minute, the maximum of cloud water mixing ratio is 4.2 g kg^{-1} and the top of cloud reaches 5.5 km . After about half an hour, the development of cloud becomes slow. Then the cumulus cloud goes into a stage of disappearance.

Rainwater first forms in cloud between $3-5 \text{ km}$ in the period when the cumulus cloud

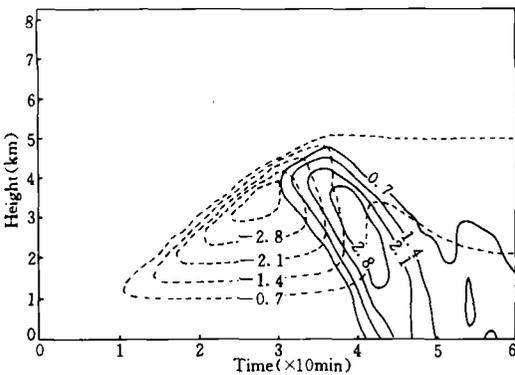


Fig. 1. Evolution of vertical velocity (m s^{-1}).

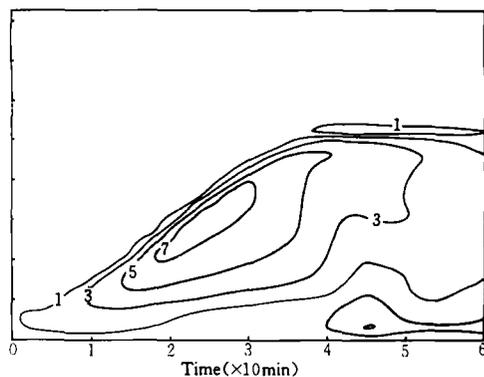


Fig. 2. Evolution of cloud water and rainwater (g kg^{-1}). dashed lines present cloud water; Solid lines present rainwater.

develops fastest. Raindrops appear mostly in the regions of high cloud water content. In these regions they grow up quickly through coagulation with cloud drops. The calculation of micro-process shows that the rates of coagulation of raindrops with cloud drops are in an order of $10^{-2} \text{ g kg}^{-1} \text{ s}^{-1}$. At the 38th minute rain droplets reach the surface. Thereafter the amount of raindrops from cloud drops reduces with the reduction of mixing ratio of cloud water. After the 45th minute, most rainwater is from the melting of graupels.

Figure 3 shows the evolution of ozone in the gas with time and space. In term of ozone concentrations, there are two different areas: ozone net production areas above 5 km and ozone net destruction areas below 5 km. With the expansion of cloud areas the ozone depletion areas expand. After the 45th minute, the vertical distribution of ozone tends to be stable while the cloud turns its development slowly. It can be seen that the area of ozone depletion coincides with the aqueous phase area of the cloud.

In order to compare the roles of vertical transportation and chemical reactions in the determination of ozone vertical distribution, calculations for the instant changes of ozone concentrations of these two processes are made at each time step (see Figs. 4 and 5). The ozone changes due to the vertical transport are defined as $W\Delta t (\partial C/\partial z)$ (ppb), while that due to chemical reactions is the net change of all the chemical reactions (the gaseous and aqueous reactions) in one time step. The calculations show that the magnitude of the changes due to the chemical reactions is one order larger than that due to the vertical transport. Therefore in this simulation the vertical transport does not dominate the ozone vertical distribution. It should be noted that our initial condition for ozone is vertically homogeneous. This lowers the importance of the role of transport in the vertical. Comparing Figs. 1, 2, 4 and Fig. 5, it is found that evolutions of these two processes are similar and they both have a close relationship with the evolution of the cloud.

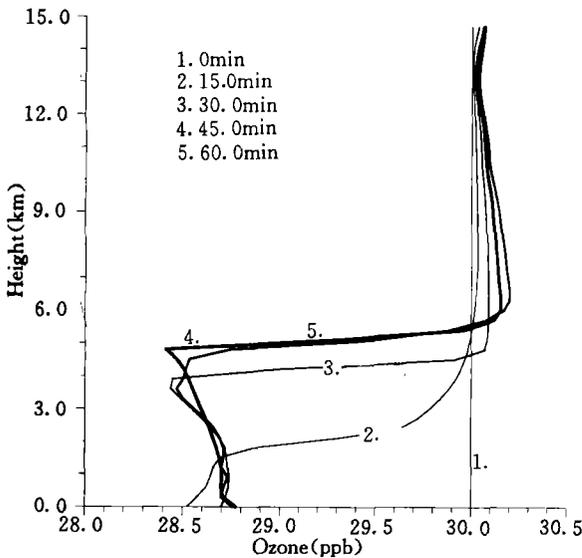


Fig. 3. Evolution of gaseous ozone (ppb).

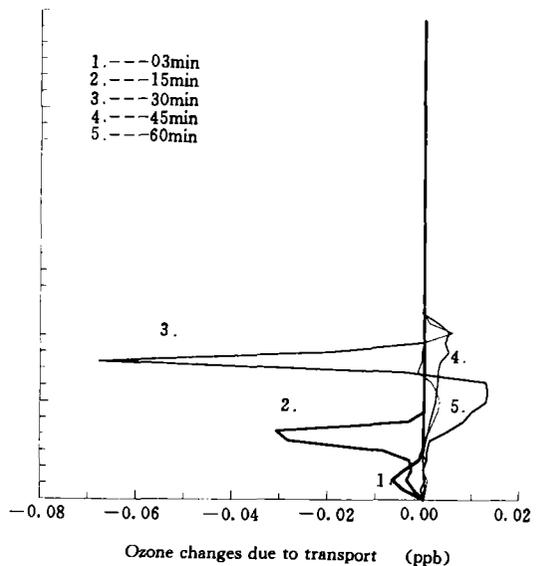


Fig. 4. Ozone changes due to vertical transport (ppb).

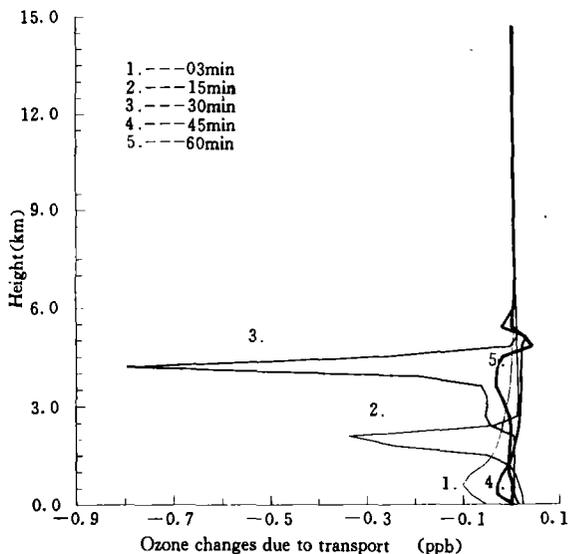
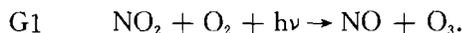


Fig. 5. Ozone changes due to chemical reactions (ppb).

The coincidence of the areas of the ozone depletion and the aqueous phase water indicates that the presence of water enhances the depletion of ozone. A main reason of ozone depletion in cloud areas is the high efficient scavenging of HO_2 by the aqueous phase. Calculations show that concentrations of gas HO_2 in cloud areas (10^{-3} ppt) are about three orders lower than those in cloud-free areas (10^0 ppt). The photolysis of HCHO is the main source of HO_2 in the gas. At the same time, most of HCHO are taken into the aqueous phase for the high solubility of gas HCHO. The scavenging of HCHO lowers the production of gaseous HO_2 in the atmosphere. Most of HO_2 are depleted by the aqueous phase and the minimum is 0.007 ppt within cloud at 4 km height. Reductions of HO_2 inhibit the gas phase ozone production which takes place through the reaction sequence, i. e. ,



NO has a low solubility and remains in the gas phase while most of HO_2 are absorbed into the aqueous phase. Thus the difference of solubility between of these two species makes NO and HO_2 departure. Reductions of gas phase concentrations of HO_2 slow the production of NO_2 and thereby slow the production of ozone in the gas phase within the cloud.

Figures 6 and 7 are the variations of NO and NO_x with time and space. Upward transport of NO is very intense in the first half hour of simulation. As noted before, the scavenging of HO_2 inhibits the reaction G34. The remained NO is transported upwards and forms a rich NO area where the ozone production could be enhanced if there are more peroxide radicals formed through the photochemical reactions of the hydrocarbon. The variation of NO_x is the same as that of NO. It is clear that the concentrations of NO_x from 3 km to 6 km increase rapidly due to the convection.

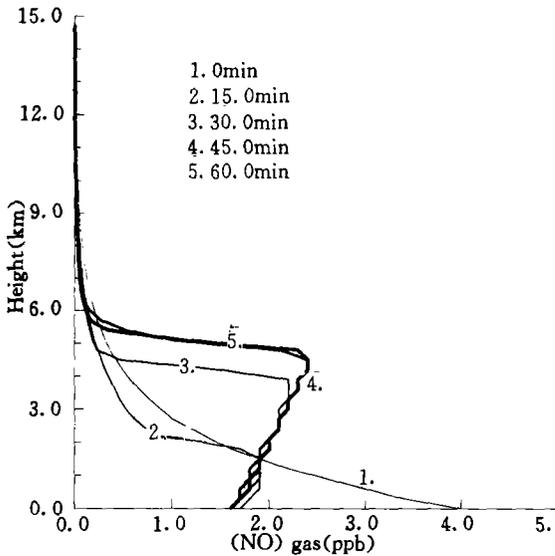


Fig. 6. Variation of gaseous NO with time and space (ppb).

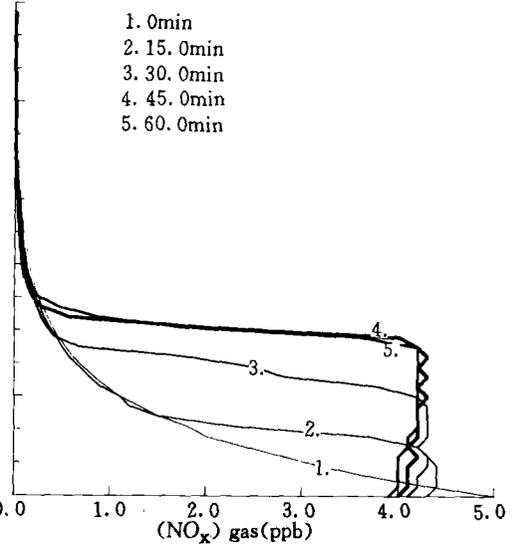
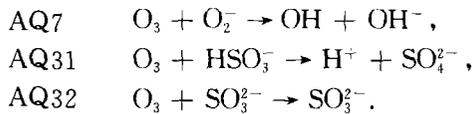


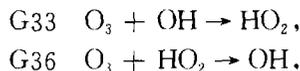
Fig. 7. Variation of gaseous NO_x with time and space (ppb).

In this simulation direct ozone destruction through the aqueous phase reactions is minor. Three main reactions related to ozone in water are



Our calculations show that reaction AQ7 is efficient only at the beginning of the formation of cloud water. Concentrations of O_2^- in water are dependent on ionic equilibrium equation ($\text{HO}_2 = \text{H}^+ + \text{O}_2^-$) (E8 in Table 5 of Part I) and highly dependent on pH value. HO_2 has no initial concentrations and is generated only from the gas phase reactions. Thus there are low concentrations of HO_2 in this simulation. With more SO_2 taken up into the aqueous phase the concentrations of H^+ increase. This makes O_2^- content in water even smaller. At this time, ozone in the aqueous phase is depleted through the oxidation of the aqueous S(IV) (AQ31, AQ32). There is a difference in results of Lelieveld and Crutzen (1990). They reported that the reaction AQ7 is the main process for ozone depletion in aqueous phase. In their simulation the concentrations of HO_2 and pH value are relative high to ours. Furthermore they did not consider SO_2 and the sulfate in their modeling. In our simulation HO_2 has no initial concentration and is generated only from the chemical reactions. Low HO_2 concentrations lower the importance of reaction AQ7.

Figure 8 is the variation of accumulative rates of four gas phase ozone depletion reactions at four sites. 0.3 km (A) for below cloud, 2.4 km and 4.8 km (B, C) for within cloud, and 6.6 km (D) for above cloud. Accumulative rate is the accumulation of productive rates in each time step. Four reactions are



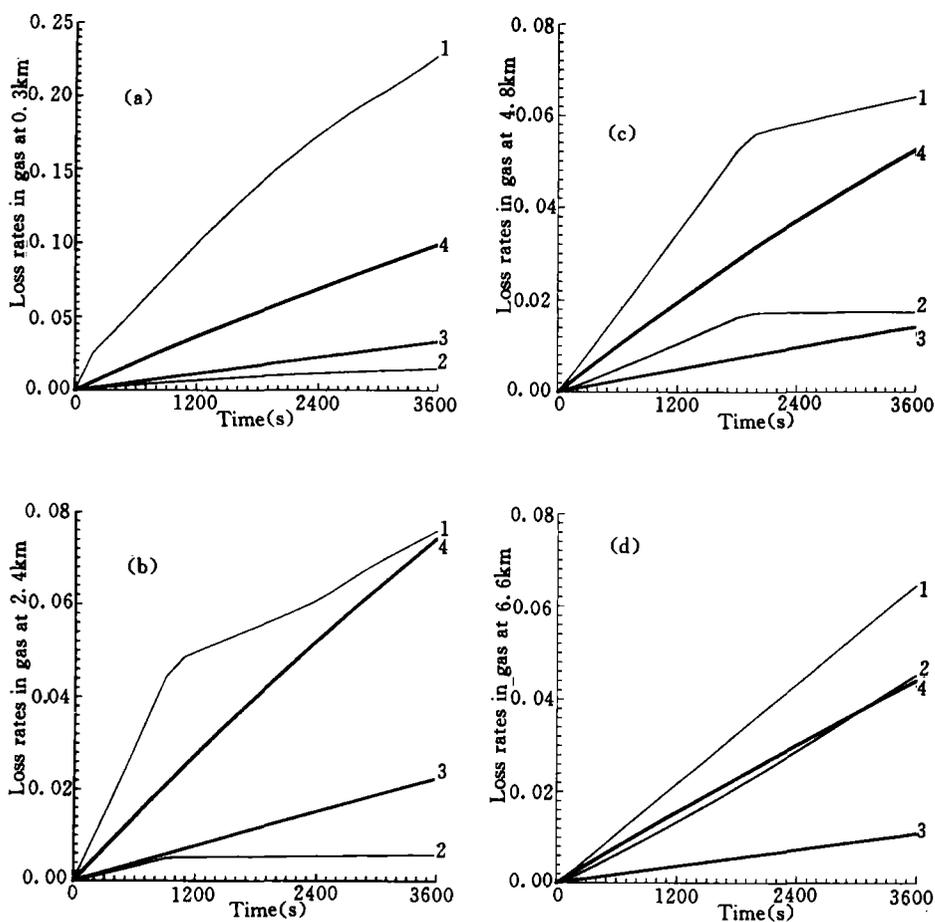
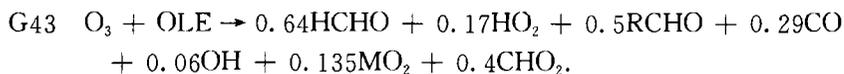
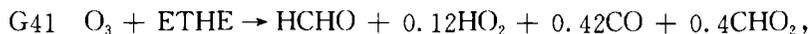
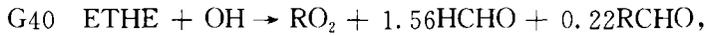


Fig. 8. Relative rates of ozone depletion reactions. The numbers (1, 2, 3, 4) represent four chemical reactions (G33, G36, G41, G43).



It is found that the reaction G33 is the main depletion pathway of ozone from surface to 7 km. Once cloud water appears, rates of reactions G33 decrease (B, C). Just like HO_2 , most of OH are scavenged by the aqueous phase. Reaction G36 becomes more important in the upper areas. As noted before, HO_2 is mainly from the photolysis of HCHO (G6). HCHO has relative higher photolysis rate in the upper areas. Thus the production of HO_2 decreases with the height. Before the presence of cloud water reaction G34 is a significant sink for HO_2 because of the high concentrations of NO near the surface. And once cloud water appears, HO_2 and HCHO are taken up into the aqueous phase. This leads to a rapid reduction of HO_2 in the gas. Figure 8 reveals that the reaction G36 almost stops in the presence of cloud water. It is also found in Fig. 8 that reactions G41 and G43 can not be ignored for ozone depletion in gas phase. Contrary to HO_2 , concentrations of OH below cloud are higher than that above cloud. There

are two other reactions competing with G41. G43 below cloud



These two reactions reduce the effects on ozone depletion in the lower areas.

IV. CONCLUSIONS

With the cumulus cloud chemistry model developed in Part I, ozone chemistry processes are studied during a cumulus convection process. The evolution of the cumulus cloud process can be well described by the evolutions of the vertical velocities and mixing ratios of cloud water and rainwater. Intensive updrafts and large precipitation are two most outstanding features in the life cycle of a cumulus cloud.

Calculations show that cumulus process has a strong influence on ozone chemistry. Vertical velocities not only can redistribute ozone in the vertical directly by transporting ozone but also can alter the ozone level indirectly by transporting the photochemistry-favored species. NO_x can be transported upwards above 4 km in 20 minutes and form a relative higher concentration area. Thereby ozone production processes are enhanced and net production areas of ozone appear. In this simulation ozone vertical distribution is mainly determined by the chemical reactions through comparison of transport process and chemical process.

Large amount of precipitation is generated during the convective event. Soluble gases including some atmospheric free radicals are scavenged by cloud water and rainwater and take part in the aqueous phase reactions. The areas of ozone depletion coincide with the aqueous phase areas of cloud areas. Results show that the aqueous phase (cloud water and rainwater) can alter gas ozone level through two ways: one is scavenging free radicals (HO_2) from the gas phase and thereby inhibiting the reactions of transformation to NO_2 from NO , which results in reduction of the gas source of ozone; the other is aqueous phase chemical reactions which consume ozone in the aqueous phase. In spite of low solubility of ozone, aqueous reactions of oxidation of S(IV) can also make a contribution to the sink for ozone. Comparison of accumulative rates shows that reaction G33 $\text{O}_3 + \text{OH} \rightarrow \text{HO}_2$ is the main pathway of ozone depletion in the process of cumulus cloud.

REFERENCES

- Chamedies, W. L. and Davis, D. D. (1982). The free radical chemistry of cloud droplets and its impact upon the composition of rain. *J. Geo. Res.*, **87** (C7): 4863–4877.
- Jhonson, J. and Isaksen, IVAR, S. A. (1993). Tropospheric ozone chemistry. The impact of cloud chemistry. *J. Atmos. Chem.*, **16**: 99–122.
- Lelieveld, J. and Crutzen, P. J. (1990). Influences of cloud photochemical processes on tropospheric ozone. *Nature*, **343**: 227–232.
- Zhao Chunsheng and Qin Yu (1996). Numerical model of cumulus cloud chemistry—Part I: Model development. *Acta Meteor. Sinica*, **10**: 321–330.