ABSTRACT

Because many natural occurring chemical reactions can produce compounds that cause health problems as well as affect global climate, it is important to study the processes that affect the chemical compounds in the atmosphere. One major gap in our knowledge of atmospheric chemistry is the effect of clouds on the chemical environment. A recent intercomparison of convective-scale cloud chemistry models has shown that transport of passive tracers from the boundary layer to the upper troposphere in deep convection is simulated consistently among models, while reactive, soluble species are not. Three chemical species of interest are nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and formaldehyde (CH₂O) because they are important chemical reservoir species for both NOx and HOx (precursors for ozone) and because they are reactive and soluble in clouds. In this study, we examine possible reasons for the differences in HNO₃, H₂O₂, and CH₂O mixing ratios among the convective-scale cloud chemistry models. By adding a source of NO to represent its production from lightning, by increasing photolysis rate coefficients to account for increased light scatter by the clouds, and by adding adsorption of different
chemical species by ice, we are able to understand the importance of each of these processes to HNO₃, H₂O₂, and CH₂O mixing ratios. Preliminary results suggest that lightning plays a key role in HNO₃ production, whereas ice adsorption is an important sink for each of the chemical reservoir species. Lastly increased photolysis rates affect only the production of CH₂O.

1. Introduction

Understanding the chemistry of the environment is important because many natural occurring chemical reactions produce compounds that negatively impact human health as well as affect global climate. HOₓ (OH+HO₂) and NOₓ (NO+ NO₂) are two of the main species of interest because of their roles in the production of ozone (O₃) ([Brasseur et al., 1999]). Consequently, it is important to understand the different processes that affect the atmospheric abundance and speciation of both NOₓ and HOₓ. Deep convection acts as a source for chemical species by transporting them from the boundary layer to the upper troposphere, and as a sink for these species through rain out via scavenging into rain droplets. NOₓ and HOₓ both have different reservoir species, while NOₓ can react to form nitric acid (HNO₃) and peroxyacetyl nitrate (PAN), HOₓ can form be stored and transported in the form of formaldehyde (CH₂O) and hydrogen peroxide (H₂O₂). These chemical reservoir species can be both a sink and a source of NOx and HOx because they can later undergo reactions to reproduce the initial chemical compounds.

By taking into account the different chemical reactions that take place in the atmosphere (in both the gas and aqueous phase) as well as convection and other meteorological processes, a model can be made to simulate the processes that would be
expected in a naturally occurring system. These models are important for revealing which processes are critical in determining the concentrations of these important chemical species in and around clouds.

Past studies have been done on cloud modeling and chemistry. In July 1996 the Stratospheric-Tropospheric Experiment, Radiation, Aerosols, and Ozone (STERAO) / Deep Convection Experiment, involving two aircraft and scientists from many different research institutions, was performed in northeastern Colorado. In July 2004 seven different groups came together to compare the ability of their cloud chemistry models to simulate the measurements of the July 10, 1996 STERAO thunderstorm.

In particular, three of these different Cloud Chemistry Models: WRF-AqChem, C.Wang, and U.Md/GCE, were shown to do a good job simulating the transport tracers. As shown in Figure 1, the mixing ratios of CO and O3 predicted by these three models compare well with aircraft observations in the anvil of the July 10 storm (Figure 1).
Figure 1. Comparison of models used to simulate July 10, 1996 stratospheric-tropospheric experiment for CO and O₃ at different distances downwind at different times and comparing them to measured values (Barth et al., 2000).
The model intercomparison study has also examined mixing ratios of CH$_2$O, H$_2$O$_2$, and HNO$_3$ in the anvil. Because there were no measurements of these species in the anvil, we cannot assess the ability of each model to simulate these reservoir species, but we can see how well the models compare with each other. Figure 2 shows how the same models that were used in figure 1 have different values for the chemical reservoir species CH$_2$O, H$_2$O$_2$ and HNO$_3$. Very little agreement between models was found. In order to fully understand the processes of both NO$_x$ and HO$_x$, other convective processes that may be
affecting the chemical reservoir species must be studied to understand the chemistry in the gas-phase.

The focus of this work is to examine the processes affecting the gas-phase concentrations of CH$_2$O, H$_2$O$_2$ and HNO$_3$ such as NO$_x$ being produced by lightning, loss of chemical reservoir species to ice, and enhanced photolysis rates due to cloud scattering.

Lightning is a source for NO. The thermal change in the environment, caused by a flash of lightning, heats up the oxygen to the point of thermal dissociation (DeCaria et al. 2000). Because nitrogen is the most abundant chemical in the atmosphere, the dissociated atomic oxygen will react with nitrogen to form NO.

\[ O_2 \rightleftharpoons O + O \]
\[ O + N_2 \rightleftharpoons NO + N \]
\[ N + O_2 \rightleftharpoons NO + O \]  \hspace{1cm} (1)

Because oxygen is a product of the lightning reaction, the sequence of reactions will keep going until O reacts with something else like O$_2$ to form O$_3$.

The deposition of chemical species onto ice is a process that removes species from the ongoing gas chemistry. Because the chemical reservoir species are being removed from the gas phase into the ice particles, there will be a loss in the sources for NOx and HOx and therefore a reduction in the ability to produce O$_3$.

Chemical reactions initiated by sunlight are critical to the composition of the atmosphere. Cloud particles scatter solar radiation. Because of the solar scatter, greater photochemical dissociation rates are found near the top and sides of the cloud. Reduced
photolysis rates are observed below cloud base due to the decrease in photons transmitted through a cloud.

2. Method

This modeling project was done in both the Atmospheric Chemistry and the Mesoscale and Microscale Meteorology divisions at NCAR. The modeling systems that were used for this project are the Weather and Research Forecast model, coupled with aqueous chemistry and microphysical transfer processes (WRF-AqChem) model, and a simple photochemical box model. The WRF-AqChem model, configured to a 120x120x20 km domain with 121 grid points (1 km resolution) in the horizontal direction and 51 (upwardly decreasing resolution) in the vertical direction, takes into account nonhydrostatic conditions in the cloud system. (Kim et al., 2004). The vertical resolution in the model domain increases from 50 m at the surface to 1200 m at the top of the domain. Because this model takes into account both meteorological and chemical kinetic factors, WRF-AqChem simulates natural occurring conditions and predicts concentrations of chemical species over time. The model is computed on a COMPAQ TR4 with 4 processors. The steady-state photochemical box model represents the chemistry of a system, at a given position, with fixed parameters. It will be used to test the significance of new chemical processes added to the chemical mechanism. This box model uses FORTRAN 90 and was run on a UNIX-based desktop computer. The initial step was to run the WRF-AqChem to mimic conditions in the July 10, 1996 STERAO thunderstorm, allowing a box model to be run at a point where the cloud has affected the chemical concentration for the following species:
<table>
<thead>
<tr>
<th>chemical species</th>
<th>Concentration (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.2028E+02</td>
</tr>
<tr>
<td>O₃</td>
<td>7.6733E+01</td>
</tr>
<tr>
<td>HO</td>
<td>7.6162E-05</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.0103E+03</td>
</tr>
<tr>
<td>CH₃OO</td>
<td>4.2727E-04</td>
</tr>
<tr>
<td>CH₂O</td>
<td>3.6905E-03</td>
</tr>
<tr>
<td>HO₂</td>
<td>1.3071E-03</td>
</tr>
<tr>
<td>NO</td>
<td>2.1656E-01</td>
</tr>
<tr>
<td>NO₂</td>
<td>7.4697E-02</td>
</tr>
<tr>
<td>HNO₃</td>
<td>6.6149E-02</td>
</tr>
<tr>
<td>NH₃</td>
<td>5.7175E-05</td>
</tr>
<tr>
<td>SO₂</td>
<td>1.2418E-01</td>
</tr>
<tr>
<td>SO₄</td>
<td>8.9679E-03</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>9.3017E-02</td>
</tr>
<tr>
<td>HCOOH</td>
<td>7.8722E-04</td>
</tr>
<tr>
<td>CH₃OOH</td>
<td>3.2121E-01</td>
</tr>
</tbody>
</table>

Table 1. This table shows the concentrations of chemical species predicted to be in the July 10, 1996 STERAO experiment by the WRF-AqChem model one hour into the storm.

These concentrations were then put into the box model for quick analysis of just the chemistry of the chemical species over time.

The WRF-AqChem model and the box model both take into account the same gas-phase chemistry listed in Barth et al. (2000). Because the focus of the work was to look at which chemical processes were missing from the mechanism, we will investigate how these new physical and chemical processes affect the in-cloud chemical concentrations of these reservoir species. Three different reactions were first added to the fast box model to determine if they were significant enough to be added into the very time intensive WRF-AqChem model.
2.1 Lightning Reaction

The lightning reaction was the first of the three to be reviewed. A reaction rate was calculated to take into account NO being produced by lightning (DeCaria et al., 2000). This rate was calculated by looking at three different factors; NO produced by each flash,

\[ \text{NO production} = 50 \, \text{mol/flash} \quad (2) \]

the number of flashes, and volume of the region affected by the lightning. The amount of NO and flash where given from measured values.

\[ \text{flashrate} = 80 \, \text{flash/300s} \quad (3) \]

The volume was then calculated by looking at the height and radius of the cloud where lightning occurred in the storm system. The volume was viewed as a cylinder and was calculated as follows

\[ \text{vol} = \pi r^2 h \quad (4) \]

\[ \text{vol} = \pi (7500\,\text{m})^2 (13000\,\text{m}) = 2.3 \times 10^{12} \, \text{m}^3 \quad (5) \]

where 7500 m is the radius of the cloud and 13000 is the height of the storm. Using these factors, the reaction rate was then calculated.

\[
\frac{50 \, \text{mol}}{\text{flash}} \times \frac{80 \, \text{flash}}{300s} \times (2.3 \times 10^{12} \, \text{m}^3)^{-1} \times 10^{-6} \, \frac{\text{m}^3}{\text{cm}^3} \times 6.022 \times 10^{23} \, \frac{\text{molecules}}{\text{mol}} = 3.5 \times 10^6 \, \frac{\text{molecules}}{\text{cm}^3 \, \text{s}}
\]

(Equation 6)

This new rate was then added to the box model to be analyzed.
2.2 Ice Deposition

The deposition of chemical species onto ice depends on three different factors; diffusivity of a chemical, size of the ice crystal, and sticking coefficient of the chemical species (Jacob et al., 2000). This function can be stated as followed

\[
k = \frac{1}{\tau_{Dg} + \tau_i} \quad (7) \quad \tau_{Dg} = \frac{a^2}{3Dg} \quad (8) \quad \tau_i = \frac{4a}{3\gamma} \quad (9)
\]

where \( k \) is the rate of absorption, \( \tau \) is absorption time, \( a \) is the size of the ice crystal, \( Dg=0.1 \text{ cm}^2 \text{ s}^{-1} \) is the diffusivity, and \( \gamma \) is the sticking coefficient. All these factors affect the removal of reservoir species from the atmosphere. The sticking coefficient is determined in laboratory studies (Jacob et al., 2000); the values listed in Table 2 are used in this study.

<table>
<thead>
<tr>
<th>chemical species</th>
<th>Sticking Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OOH</td>
<td>9x10^-3</td>
</tr>
<tr>
<td>O$_3$</td>
<td>1x10^-6</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>0.01</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>8x10^-6</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>0.48</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1x10^-4</td>
</tr>
</tbody>
</table>

Table 2. This table shows the sticking coefficients of the chemical species added to the box model.

Sticking coefficients for other species were changed to 1 x 10^-12 to signify that these chemical were not going to adsorb onto ice. The size of the average ice particle \( a \) was set to a radius of 50 micrometers. It is assumed that there is 0.3 g$_{\text{ice}}$/kg air or 0.084 g/m$^3$. 
2.3 Light Scatter

The third cloud process that was examined was the effect of enhanced light scattering on photodissociation reactions in the anvil of a convective system. Light scattering by cloud droplets or particles increases the actinic flux near the top of the cloud. This effect was added to the model by increasing the clear sky photolysis rates by a constant factor (Table 3).

\[ \text{J}_{\text{cloudy}} = f \times \text{J}_{\text{clear}} \quad (10) \]

\( \text{J}_{\text{cloudy}} \) is the photolysis frequency on a cloudy day and proportional to \( f \times \text{J}_{\text{clear}} \), the photolysis frequency on a clear day multiplied by the cloud enhancement factor.

A box model was used to simulate the upper levels of the storm. The box model is a controlled simulation of the chemistry in the WRF-AqChem without meteorological...
interferences. Each reaction was progressively put into the box model and compared to the control simulation and to the previous sensitivity simulations. After all three of the reactions were added to the box model they were then compared to the control run of the box model.

4. Results and Discussion

Each of the three chemical reservoir's species were looked at with the addition of the new chemical parameters and compared with the original box model system. The reactions were added to the model in order of lightning, ice deposition, and light scatter. Consequently, the ice deposition simulation takes into account the proceeding lightning reactions. However, by the time the light scatter simulation occurs, it has the benefit of being able to take into account both the lightning reactions, and the ice deposition reactions, when modeling the chemical processes in the system, because it is initialized third.
Figure 3 shows the effect that the box model predicts for HNO₃ with the addition of the lightning, ice deposition, and enhanced photolysis. The addition of lightning increases HNO₃ production. While the addition of ice uptake processes results in little change in ambient HNO₃ mixing ratios for the first 10 minutes; however, after 20 minutes the HNO₃ concentration begins to go down compared to the simulation with just lightning NOx production. Enhanced in-cloud photolysis frequencies result in a slight reduction in the HNO₃ concentration over time from the ice deposition model.

The effect of adding lightning NOx production to the model shows that lightning is a source of HNO₃; NO is converted to NO₂, reacting with OH to form HNO₃. In
contrast, the addition of realistic ice HNO$_3$ uptake rates results in a significant reduction for in-cloud interstitial concentrations of HNO$_3$.

Figure 4. Comparison of original box model with the new parameters that were inputted in to the model for CH$_2$O.

Figure 4 shows the effect of these three new processes on CH$_2$O mixing ratios.

The initial effect of the addition of the lightning NOx reaction shows only slight increases compared to the original box model; only after 35 minutes is there a visible difference between those models. The addition of CH$_2$O deposition to ice surfaces in a cloud shows a clear reduction of CH$_2$O in the model within the first 10 minutes. The enhanced in-cloud photolysis rates results in an increase in the production of CH$_2$O much greater then the effect of the ice deposition and lightning NOx processes alone.
The lightning reaction shows little effect on the production of CH₂O, and ice uptake adsorbs only 10-20% of gas phase CH₂O. The photolysis frequencies have the greatest effect on CH₂O mixing ratios in clouds, showing that this enhanced photochemical environment results in a significant increase in net CH₂O production.

Figure 5. Comparison of original box model with the new parameters that were inputted into the model for H₂O₂.

With the addition of the lightning NO production, there appears to be no differences in concentration of H₂O₂ from the original box model (Figure 2). Including the uptake of H₂O₂ onto ice results in a clear reduction of H₂O₂ from the baseline model. Enhanced HOOH [Why not H₂O₂?] photolysis has the net effect of slightly reducing the H₂O₂ mixing ratio.
Because there was no change in concentration of H2O2 when lightning NO was
inserted into this model, it is apparent that NO does not have a significant effect on the
production of H2O2 in this environment. Ice deposition is a significant sink for H2O2;
however, enhanced cloud photolysis frequencies plays only a small role in the net
reduction of H2O2 in the atmosphere.

5. Conclusion

A better understanding of the chemical processes in the atmosphere helps in our
understanding of the whole Earth system. Some fundamental processes are not currently
implemented in cloud chemistry models, such as the impact of lightning NO production,
the uptake of compounds onto ice particle, and the enhancement of photolysis
frequencies in a cloud environment. This study is a first order analysis of the potential
impacts of incorporating these processes in a cloud chemical model.

Each of the chemical processes studied here has a significant impact on the
mixing ratios of the three chemical reservoir species. By including the lightning
production of NO in the model, HNO3 was produced as a result of the increased NO. The
ice deposition served as a major sink to all three chemical reservoir species. The
inclusion of higher photolysis frequencies to the box model did not produce a significant
change in the levels of HNO3 or H2O2, however, the mixing ratios of CH2O significantly
increased by the higher photolysis frequencies.

Further study of the three chemical processes with the WRF-AqChem Model will
give a better understanding of how these processes affect the atmosphere due to the
meteorological factors that it takes into account. The WRF-AqChem is currently being modified to look at the effect of these processes.

Acknowledgements

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References


Jacob, D. J.; “Heterogeneous chemistry and tropospheric ozone” Atmospheric Research vol. 34, 2131-2159, 2000