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Large Scale Atmospheric Chemistry Simulations for 2001: An Analysis of Ozone and Other Species in Central Arizona

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4.3 LARGE SCALE ATMOSPHERIC CHEMISTRY SIMULATIONS FOR 2001: AN ANALYSIS OF OZONE AND OTHER SPECIES IN CENTRAL ARIZONA

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1. INTRODUCTION

A key atmospheric gas is ozone. Ozone in the stratosphere is beneficial to the biosphere because it absorbs a significant fraction of the sun's shorter wavelength ultraviolet radiation. Ozone in the troposphere is a pollutant (respiratory irritant in humans and acts to damage crops, vegetation, and many materials). It affects the Earth's energy balance by absorbing both incoming solar radiation and outgoing long wave radiation. An important part of the oxidizing capacity of the atmosphere involves ozone, through a photolysis pathway that leads to the hydroxyl radical (OH). Since reaction with OH is a major sink of many atmospheric species, its concentration controls the distributions of many radiatively important species.

Ozone in the troposphere arises from both *in-situ* photochemical production and transport from the stratosphere. Within the troposphere, ozone is formed in-situ when carbon monoxide (CO), methane (CH_4), and non-methane hydrocarbons (NMHCs) react in the presence of nitrogen oxides (NO_x = NO + NO_2) and sunlight. The photochemistry of the stratosphere differs significantly from that in the troposphere. Within the stratosphere, ozone formation is initiated by the photolysis of O_2. Stratospheric ozone may be destroyed via catalytic reactions with NO, H (hydrogen), OH, Cl (chlorine) and Br (bromine), or photolysis.

In the past, attempts to simulate the observed distributions of ozone (and other important gases) have focused on either the stratosphere or the troposphere. Stratospheric models either employed simplified parameterizations to represent tropospheric chemical and physical processes, or assumed the troposphere behaved as a boundary condition. Likewise, tropospheric models used simplified stratospheric chemistry and transport.

2. MODEL DESCRIPTION

This work presents results from a global, three-dimensional chemical transport model named IMPACT (Rotman et al., 2002). IMPACT contains both a prognostic troposphere and stratosphere. It simulates the important photochemical production and loss cycles for tropospheric and stratospheric ozone and other species. It also simulates emissions, advection, diffusion, deposition, convection, and gravitational settling.

IMPACT's input meteorological fields are obtained from either a general circulation model (GCM) or assimilated data, such as that available from the Data Assimilation Office (DAO) at NASA-Goddard. IMPACT uses meteorology from a GCM to address historical, future, and climatological average studies. IMPACT uses assimilated data to simulate specific historical time periods, typically for particular regions of interest. The IMPACT grid resolution is dictated by the input meteorological data.

3. Phoenix 2001 Field Campaign

The Department of Energy's Atmospheric Chemistry Program conducted an airborne and field-based campaign during June and July 2001. Previous field and model results for the Phoenix area had shown that, while regional models reproduced peak ozone concentrations, the models under-predicted the amount of ozone formed in the early morning hours after sunrise, and often over-predicted ozone during the night-time hours. Hence, the study in 2001 was conducted to better characterize what chemical and meteorological processes contributed to these phenomena.

The IMPACT model was used in conjunction with assimilated meteorology observed for the June/July 2001 time period to help characterize and analyze the background, upwind, and overhead ozone distributions onto which the local Phoenix photochemistry occurred. It was also used to help quantify the roles of advection, deposition, and local photochemistry on the concentration of ozone in the Phoenix area.

4. MODEL RESULTS AND OBSERVATIONS FOR MAY-JUNE, 2001

Figure 1 shows the hourly concentration of surface ozone measured at the Humboldt Mountain site, which is slightly elevated and downwind of metropolitan Phoenix. Julian Days 120-180 correspond to May 1 through June 29, 2001. Note that Julian Days 165-166 (June 14-15, 2001) shows a local peak in ozone concentrations.

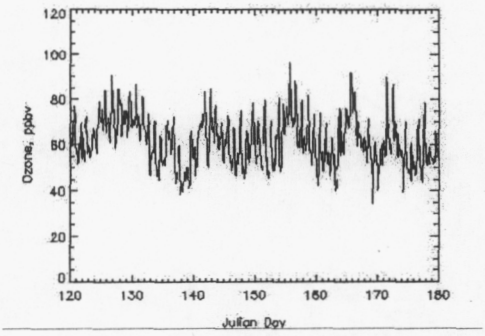

Figure 1. The hourly concentration of surface ozone (ppbv) measured at the Humboldt Mountain site for Julian Days 120-180 (May 1 – June 29, 2001).

Figure 2 shows both IMPACT predicted and observed ozone (from an ozonesonde launched by Pacific Northwest National Laboratory) at 7AM on June 14, 2001. Note that both the model and observations show a local ozone peak at roughly 4km in altitude, indicating that air from aloft may be advecting downward into the Phoenix area.

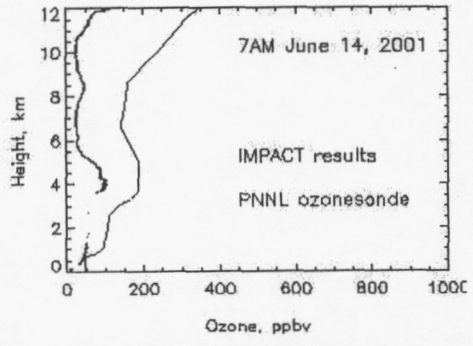

Figure 2. The vertical concentration of ozone (in ppbv) for the Phoenix area at 7AM on June 14, 2001. The red line corresponds to an ozonesonde launched at 7AM by PNNL. The black line is the IMPACT predicted ozone for 7AM June 14, 2001.

Figure 3 shows the concentration of ozone predicted by the IMPACT model for 34N, 247.5E, corresponding to roughly Phoenix's location, for May 1 – June 29, 2001. Concentrations over 100-200 ppbv are commonplace in the stratosphere. Additionally, however, there are several instances during this time period in which the model predicts that ozone concentrations over 100 ppbv extend very close to the surface. This includes the time period mentioned above, corresponding to Julian Days 165-166. Thus, some time periods of elevated surface ozone may correspond to large concentrations of aloft ozone, as well.

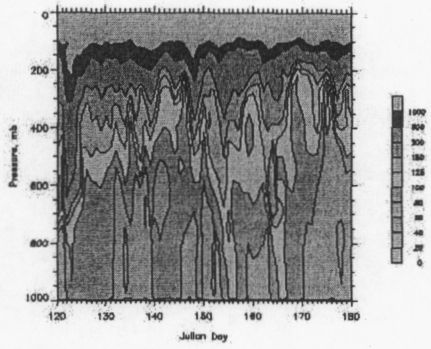

Figure 3. IMPACT predicted vertical ozone concentrations for 34N, 247.5E (corresponding roughly to Phoenix) for Julian Days 120-180 (May 1 – June 29, 2001). The yellow contour represents concentrations between 100 and 150 ppbv, while light orange represents concentrations between 150 and 200 ppbv. Concentrations of ozone over 100 – 200 ppbv are often indicative of air of stratospheric origin. Note that during several periods, concentrations of over 100 ppbv extend from aloft to close to the surface.

Figure 4 shows the IMPACT model predicted change in ozone (in kg) for a three-dimensional box that includes Phoenix for June 1 – 15, 2001. The Phoenix box is defined to extend from 33° to 35°N in latitude, 246.25° to 248.75° in longitude, and from the surface to a pressure of roughly 500 mb (roughly 5.5 km for a standard atmosphere). Shown in Figure 4 are the changes for the Phoenix box due to *net* in-situ photochemical production (green line), *net* advection (black line), and *net* convection (red line). Note that since the box extends from the surface to roughly 500 mb, convection can be quite important at the higher altitudes. There are periods (e.g. June 5 – 10) during which advection, convection, and photochemical production each

contributes significantly to the change in ozone in the "Phoenix box". However, during other periods (e.g. June 11-14), the role of convection appears to dominate the net ozone budget.

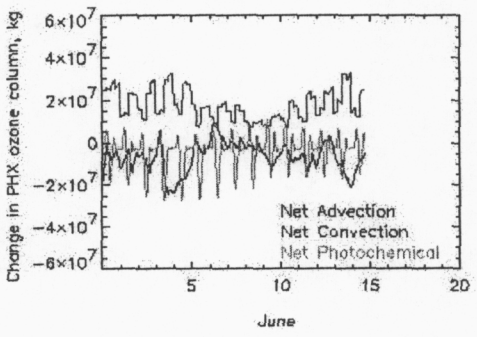

Figure 4. IMPACT predicted changes in the ozone (in kg) for the "Phoenix box" (extending from 33° to 35°N in latitude, 246.25° to 248.75° in longitude, and to a pressure of roughly 500 mb (roughly 5.5 km for a standard atmosphere) due to net advection (black line), convection (red line) and photochemical production (green line).

In the accompanying talk, further information will be presented on the relative importance of these processes on the concentrations of ozone predicted for the full regulatory ozone season (April 1 – October 31, 2001). The concentrations will also be compared with measurements to better characterize the important processes involved when local ozone concentrations are unusually high. This combination of model results and measurements may aid in planning and policy implementation to successfully lower ozone concentrations in Phoenix and other areas.

5. REFERENCES

Fast, JD; Doran, JC; Shaw, WJ; Coulter, RL; and Martin, TJ., 2000: The evolution of the boundary layer and its effect on air chemistry in the Phoenix area, *J. Geophys. Res.*, **105**, 22833-22848.

Rotman, D.A.; C.S. Atherton, D.J. Bergmann, P.J. Cameron-Smith, C.C. Chuang, P.S. Connell, J.E. Dignon, A. Franz, K.E. Grant, D.E. Kinnison, C.R. Molenkamp, D.D. Proctor, and J.R. Tannahill IMPACT, the LLNL 3-D global, troposphere-stratosphere chemical transport model: A model description, submitted to *J. Geophys. Res.*, 2002.

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