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NUMERICAL STUDY OF TROPOSPHERIC OZONE TRANSPORT AND PHOTOCHEMICAL PRODUCTION IN EAST ASIA DURING THE TRACE-P EXPERIMENT

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1. INTRODUCTION

East Asia is a region of the world with large and rapidly increasing anthropogenic emissions of nitrogen oxides (NO_x), carbon monoxide (CO), and other species. *Kato and Akimoto* (1992) estimated that the emissions of NO_x in East Asia have increased by 58% from 1975 (2.05TgN/yr) to 1987 (3.25TgN/yr), and *van Aardenne et al*. (1999) predicted an increase of almost fourfold in NO_x emissions from 1999 to 2020. Gas-phase emissions of NO_x, CO and hydrocarbons from the Asian continent undergo photo-oxidation as air masses are advected eastward over the Pacific. Transport and chemical evolution of trace gases and aerosols from the Asian continent significantly alter the composition of the remote Pacific troposphere (e.g., *Jaffe et al*., 1997; *Crawford et al*., 1997; *Mauzerall et al*., 2000), and there is growing observational evidence for an Asian impact extending to North America (e.g., *Berntsen et al*., 1999; *Yienger et al*., 2000). In this study we use the Models-3 Community Multi-scale Air Quality (CMAQ) modeling system to study the transport and chemical transformation processes of tropospheric ozone (O_3) in the springtime for better understanding the impacts of emissions over East Asia upon ozone production over the Pacific. For evaluating the model performances, model simulated O_3 and some of its closely related species are compared against observations obtained during the Transport and Chemical Evolution over the Pacific (TRACEP; *Jacob et al*., 2003) field campaign.

2. MODEL DESCRIPTION

CMAQ is a Eulerian-type model developed to address tropospheric ozone, acid deposition, visibility, particulate matter and other pollutant issues in the context of a "one atmosphere" perspective where complex interactions between atmospheric pollutants and regional and urban scales are confronted. It is designed to be flexible so that different levels of model configuration can be achieved. The current version of CMAQ uses meteorological fields from the Regional Atmospheric Modeling System (RAMS; *Pielke et al*., 1992) version 4.3 instead of its default meteorological driver - the Mesoscale Modeling System (MM5), and is configured with the chemical mechanism of the Regional Acid Deposition version 2 (RADM2; *Stockwell et al*., 1990), extended to include the four-product Carter isoprene mechanism (*Carter*, 1996), and aerosol processes from direct emissions and production from sulfur dioxide, long-chain alkanes, alkyl-substituted benzene, etc. Other important components to the CMAQ configuration are: (1) advection algorithm with Piece-wise Parabolic Method (*Colella and Woodward*, 1984); (2) horizontal diffusion with scale dependent diffusivity; (3) vertical diffusion with a local scheme based on the semi-implicit K-theory; (4) Mass conservation adjustment (*Byun, 1999*); (5) emissions injected in the vertical diffusion module; (6) deposition flux as bottom conditions for the vertical diffusion; and (7) QSSA gas-phase reaction solver. A general description of CMAQ and its capabilities are given in *Byun and Ching* (1999). CMAQ coupled with RAMS has recently been applied to East Asia to simulate boundary layer ozone in the wintertime (*Zhang et al.,* 2002).

For CMAQ, the anthropogenic emissions of nitrogen oxides, carbon monoxide, and volatile organic compounds (VOCs) were obtained from the emission inventory of $1^{o}x1^{o}$ specially prepared to support TRACE-P (*Streets et al.,* 2003) and from the Emission Database for Global Atmospheric Research (EDGAR; *Oliver et al.,* 1996). NO_x emissions from soils and natural hydrocarbon emissions were obtained from the Global Emissions Inventory Activity (GEIA) 1°x1°

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monthly global inventory (*Benkovitz,* 1996) for the month of March. VOC emissions were apportioned appropriately among the lumped-hydrocarbon categories used in RADM2.

Biomass burning is an important source of CO and NO_x in Asia in the springtime, because spring is the dry season, and there is extensive biomass burning in Southeast Asia and India, mainly due to burning of agricultural waste (rice straw) and deforestation (*Nguyen et al.,* 1994). In this study emissions of CO and NO_x from biomass burning were based on the inventory of a 1^ox1^o spatial resolution and daily temporal resolution estimated using fire count derived from the AVHRR satellite images (*Woo et al.,* 2003).

The model domain is 8000x5600 km^2 (outside region) for RAMS and 6240x5440 km^2 (inside region) for CMAQ on a rotated polar-stereographic map projection centered at (25^oN, 115^oE) with 80 km mesh. RAMS and CMAQ have the same model height. For RAMS there are 23 vertical layers in the σ_z coordinates system unequally spaced from the ground to ~23 km, with about 9 layers concentrated in the lowest 2 km of the atmosphere in order to resolve the planetary boundary layer, while there are 14 levels for CMAQ with the lowest 7 layers being the same as those in RAMS.

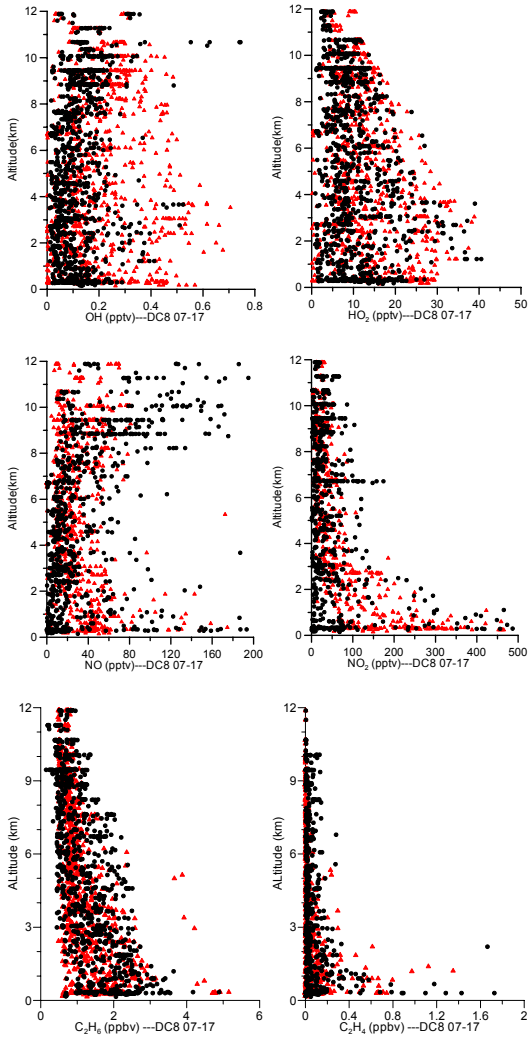
Initial and boundary conditions of species in CMAQ were chosen to reflect the East Asian situation. Recent measurements were used whenever possible. To evaluate the impact of the anthropogenic emissions on the distributions of trace gases and aerosols, the initial and boundary conditions were generally chosen at the lower end of their observed range (e.g., the northern and western boundary conditions for O_3, CO, and NO_2, were 30, 120, and 0.2 ppbv, respectively) so as to allow the emissions and chemical reactions to bring them closer to their actual values during the initialization period.

The upper boundary of CMAQ is located in the lower stratosphere. Stratospheric influence on tropospheric ozone is parameterized by specifying the initial and boundary conditions at the top 3 altitude levels of the model to values proportional to potential vorticity (PV). The proportional coefficient is assumed to be constant. For ozone, 50 ppbv per PV unit is adopted according to the studies by *Ebel et al*. (1991) and *Beekmann et al*. (1994), where the PV unit is 10^{-6} $Km^2kg^{-1}s^{-1}$.

3. RESULTS AND DISCUSSIONS

3.1 Comparison with airborne observations from the TRACE-P mission

CMAQ was run from 22 February to 5 May 2001 with a starting time at 0000 Z on 22 February, i.e., 0900 JST (Japanese Standard Time). In order to evaluate the model's ability in depicting the transport and chemical production processes of tropospheric ozone, we compared the modeled and observed hydroxyl radical (OH), hydroperoxyl radical (HO_2), nitric oxide (NO), nitrogen dioxide (NO_2), ethane (C_2H_6), ethene (C_2H_4), CO, and O_3 with observations obtained onboard of aircrafts DC-8 and P-3B during the TRACE-P mission. In comparing the model results with the aircraft observations, we sampled the model along the flight tracks and with a 1 hour temporal resolution. The observed data were 5 min averaged.



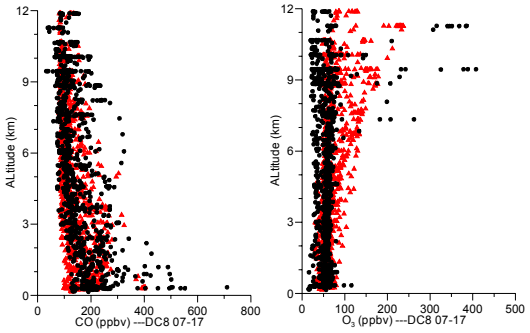


Fig.1 observed (black dots) and modeled (red triangle) vertical variations in OH, HO_2, NO, NO_2, C_2H_6, C_2H_4, CO, and O_3 concentrations for DC-8.

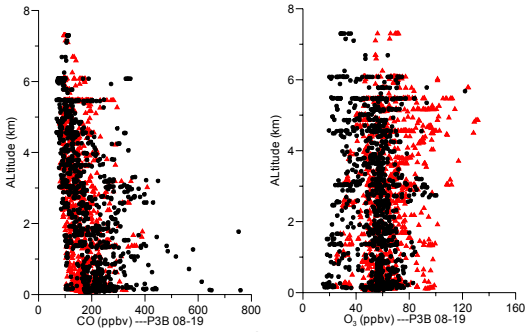
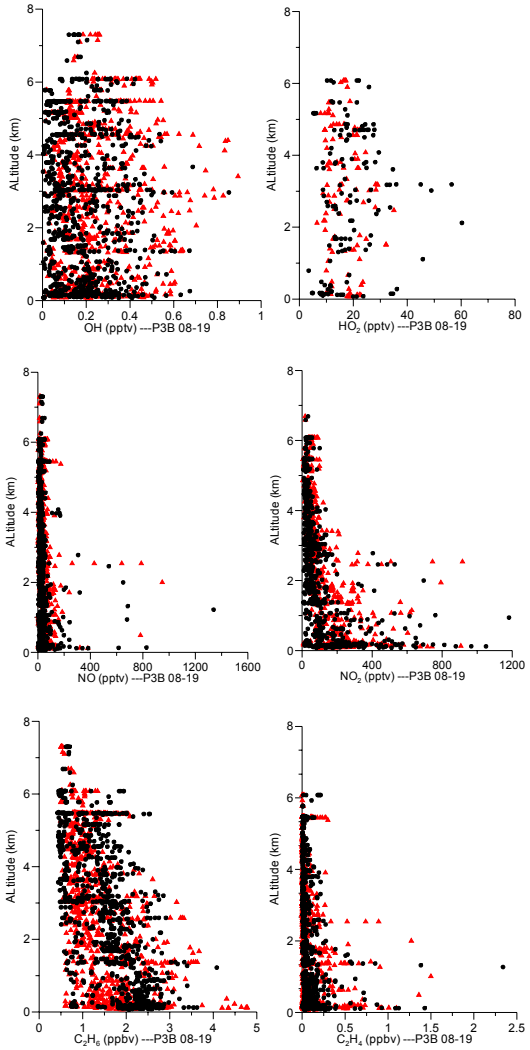


Fig.2 same as Fig.1 but for P-3B



Figures 1 and 2 present vertical variations in the modeled and observed mixing ratios of OH, HO_2, NO, NO_2, C_2H_6, C_2H_4, CO, and O_3 during the period of 07-31 March 2001, when two aircrafts made extensive observations in the western Pacific with bases near Hong Kong, Okinawa and Tokyo, successively.

OH is the primary atmospheric oxidant, and HO_2 defines one of the most important pathways for converting NO to NO_2, and is pivotal to photochemical production of O_3, Their concentrations are strongly dependent on altitude, latitude, season, time of day, and the local environment. From the figures we find that the observed OH and HO_2 concentrations show strong variations, and the modeled distributions of OH and HO_2 are quite similar to the observed ones, while the model tends to overestimate OH values. Statistics indicate that the modeled OH mixing ratios are higher than the observed ones by a factor of 1.38 and 1.18 onboard of DC-8 and P3B, and their correlation coefficients are 0.88 and 0.83, respectively.

Active nitrogen constituents, primarily NO and NO_2, are necessary for the photochemical production of O_3 in the troposphere. Comparison of modeled and observed NO and NO_2 concentrations shows that the model was not able to catch very high NO and NO_2 concentrations, so we show in the figures 1c, 1d, 2c and 2d only observed NO values smaller than 400 and 1600 pptv, and observed NO_2 values smaller than 1000 and 1200 pptv for DC-8 and P-3B, and their coordinated modeled values. The figures show that the modeled and observed values are generally in good agreement, and analysis indicates that the inability of the model to reproduce high NO and NO_2 concentrations is partly due to the coarse resolution and no account of NO_x emissions from lightning and downward transport from stratosphere.

Emissions of CO and hydrocarbons are a key ingredient in O_3 production and we compare

observed and modeled mixing ratios of C_2H_6, C_2H_4 and CO in Figures 1 and 2 to show how the model reproduces the different carbon-containing compounds. The atmospheric budget of C_2H_6, C_2H_4 and CO is controlled by their emissions and by their photochemical reactions with atmospheric oxidants. Form the figures we find that simulated values and vertical distribution patterns are generally agree well and the model treats transport and transformation processes of different non-methane hydrocarbon species properly.

O_3 in the troposphere is supplied by transport from troposphere, and is produced within the troposphere during the oxidation of hydrocarbons and CO catalyzed by NO_x and HO_x. Observations show O_3 mixing ratios have strong time spatial variations (cf. Figures 1h and 2h) and some elevated O_3 levels above ~7 km, which were associated with stratospheric O_3 incursion (cf. Figure 1h). From the figures we find that modeled and observed O_3 concentrations are in good agreement, but the model can not catch these high O3 levels in the upper layers even the model results show stratospheric ozone impacts.

3.2 Comparison with surface observation

3.2 O_3 budget analysis

4. SUMMARY

Models-3 Community Multi-scale Air Quality (CMAQ) modeling system was applied to East Asia to investigate transport and transformation processes of ozone and its precursors in the springtime of 2001. For evaluating the model performance simulated concentrations of ozone and its precursors such as hydroxyl radical, hydroperoxyl radical, nitric oxide, nitrogen dioxide, ethane, ethene, and CO were compared with observations on board of aircrafts. The comparison results indicate that simulated distributions of these species are quite similar to the observed ones, and both simulated and observed concentrations are generally in good agreement. The model system treats transport and transformation processes of different non-methane hydrocarbon species properly, depicts the processes influencing the tropospheric ozone distributions such as photochemical production, stratospheric ozone influx into troposphere, etc. reasonably well.

5. REFERENCES

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