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1. INTRODUCTION

The tropical marine atmosphere possesses the globally highest UV fluxes and mole fractions of water vapor, and thus arguably the globally highest levels of OH outside of polluted areas (Mauldin et al., 1999). Concentrations of OH and O₃ in these tropical regions are important indicators of the tropospheric oxidizing capacity. Tropical oceanic regions also serve as areas of exchange between air masses from the two hemispheres. Tropospheric chemical processes as well as interhemispheric air transport over tropical oceans are critical to both global and hemispheric budgets of many radiatively and chemically important species (e.g., Prinn et al., 1992; Mahlman, 1997; Prinn et al., 2000). Therefore, understanding tropospheric chemistry over tropical oceans is extremely important to enhancement of our knowledge of not only atmospheric chemistry but also global environmental changes.

Tropical oceans experience frequent deep atmospheric convection that produces deep cloud towers as well as long-lasting anvils. These cloud towers and anvils alter rates of photochemical reactions, provide platforms for aqueous and heterogeneous reactions, and hence possibly play significant roles in determining evolution of chemical species in these regions.

In recent years, many field projects have collected data in the tropical oceanic regions including at the ITCZ. Interesting but puzzling phenomena related to the role of deep convection have been revealed. One of these phenomena is that ozonesondes over tropic oceans show low (sometimes extremely low) ozone in both the planetary boundary layer and, most interestingly, in the upper troposphere associated with deep convection (*e.g.*, Newell and Wu, 1985; Smit *et al.*, 1989; Johnson *et al.*, 1990; Piotrowicz *et al.*, 1991; Kley *et al.*, 1996; Roumeau *et al.*, 2000). However, the results of previous study suggests that the vertical transport might not be the dominant factor in forming the low ozone layer in the upper troposphere (Wang and Prinn, 2000).

Another interesting but puzzling features in upper tropospheric chemistry over remote oceans is that the measured HO_x concentrations (mainly by research aircrafts) appear to be as much as a factor of 2 higher than the predictions of parcel photochemistry model restricted or partially restricted by measured concentrations of chemical species. In addition, calculated ozone production is found to be much lower than the observations, especially from airmass associated with convective outflows (Jaegle *et al.*, 1997; Wennberg *et al.*, 1998; note that this is mainly for the case of aged air and therefore is different than the case of low ozone measured inside ITCZ described before). This reminds the role of peroxy radicals in ozone production, particular in the upper troposphere over remote oceans, and also suggests that additional sources of HO_x are needed to explain the measured features.

This research is a continuation of our previous effort (e.g., Wang et al., 1995; Wang and Prinn, 1998; Wang and Prinn, 2000) to elucidate the various possible impacts of deep convection on tropospheric chemistry over the tropical oceans. An integrated threedimensional model including dynamics, radiative transfer, cloud and aerosol microphysics, gaseous and aqueous chemistry, heterogeneous chemistry, and parameterized lightning and related NO production has been developed for this purpose. Observed trace chemical profiles combined with profiles derived from previous modeling results are used to initialize the model. A number of sensitivity runs are then carried out to understand the net effects of different physical and chemical processes on the redistribution of chemical species during convection and to provide information for handling these processes in large-scale coarseresolution model studies.

2. MODEL AND NUMERICAL EXPERIMENTS

The model used in this study is a three-dimensional cloud-resolving model including interactive dynamics, radiation, and various microphysical as well as chemical processes (Wang and Chang, 1993; Wang *et al.*, 1995; Wang and Prinn, 2000). This integrated model provides the chemistry simulations with 'real-time' values of winds, temperature, turbulent and radiative fluxes, and microphysical conversion rates, and also allows inclusion of aerosols in both the dynamics-physics and chemistry submodels.

The dynamical prognostic equations in this model consist of the nonhydrostatic momentum equations, the continuity equations for water vapor and air mass density, the thermodynamic equation, and the equation of state. Also included are prognostic equations for the mixing ratios as well as number concentrations of four types of hydrometeors.

The microphysical transformations are formulated based on a "two-moment" scheme incorporating the size spectra of particles (Wang and Chang, 1993; Wang *et al.*, 1995). A δ -four-stream radiation module based on Fu and Liou (1993) is incorporated in the model and it uses predicted concentrations of gases (including H₂O and O₃) and hydrometeors to calculate radiative fluxes and heating rates.

The chemistry sub-model currently predicts

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atmospheric concentrations of 25 gaseous and 16 aqueous (in both cloud droplets and raindrops) chemical species, undergoing more than 100 reactions as well as transport, and microphysical conversions. The equilibrium reactions on the surface of liquid particles are calculated using the mass-transfer method described in Wang and Chang (1993). Surface reactions on ice particles involving a group of selected chemical species have also been included as an option. A parameterized lightning scheme based on cloud electricity physics and microphysics, which has been recently improved from Wang and Prinn (2000) in distributions of lightning produced NO_x, is included in the model.

The concentrations of both cloud condensation nuclei (CCN) and ice nuclei (IN) are calculated incorporating transport as well as nucleation and precipitation scavenging in the model. The nucleation rates of cloud droplets and ice crystals are limited by the local concentrations of CNN and IN.

The simulations are initialized using observed profiles of temperature, water vapor concentrations, and horizontal wind velocities from a deep convective event which occurred on March 8, 1993 (see Wang and Prinn, 1998) during the Central Equatorial Pacific Experiment (CEPEX, Ramanathan *et al.*, 1993). This event is a squall line system consisting of several isolated convective storms separated by about 20-50 km from each other. In order to closely simulate this system and to study the redistributions of chemical species in a multiple tower event, three convective towers were initialized with a distance of 50 km. The initial concentration fields for chemical species were derived

from a 6-hour clear-sky integration of the model. These clear-sky calculations were initiated with an observed ozone sounding (Wang *et al.*, 1995) and with vertical profiles for other chemical species based either on observations (e.g., Thornton and Bandy, 1993; Thornton *et al.*, 1996) or on global model results (Wang *et al.*, 1998). They are intended to represent clean atmospheric conditions (Wang and Prinn, 2000). Simulations have been done using three-

Simulations have been done using threedimensional versions of the model with different model settings. These include model runs including/excluding lightning produced NO molecules, including/excluding various chemical reactions, and with/without clouds. They were designed to study the impacts of various physical and chemical processes on the redistributions of chemical species associated with deep convection over tropical oceans.

The spatial resolutions of the model in this study are 2 km horizontally and 0.5 km vertically. The model domain covers 450×400×25 km. Time steps for dynamics, microphysics, and transport of chemicals are all 5 seconds (0.5 second for sound-wave terms, cf. Wang and Chang, 1993). Time steps for radiation are 5 minutes in the first five hours and 10 minutes thereafter. For both gaseous and aqueous chemistry, the time step is 30 seconds. All simulations started from noon local time and lasted 8 hours. Double-periodic lateral boundary conditions are used to maintain mass conservation. All simulations were carried out on a 32node PC cluster using the parallel version of the model. Figure 1 shows the model simulated cloud outlines.



Figure 1. Model simulated outlines of clouds at different stages, defined by the isosurfaces where the mass mixing ratio of total condensed water equals 0.01 g/kg.

3. RESULTS AND CONCLUSIONS

The results of three-dimensional multiple tower runs support several important conclusions of the previous study mainly using the two-dimensional version of the model in sensitivity simulations (Wang and Prinn, 2000). For example, high OH concentration just above the cloud top induced by the increases in H₂O concentration and enhancement of UV flux by upward reflection from the cloud anvils is also found in this study. At the same time, OH concentrations inside or below the cloud are found to be significantly lower than in the case of clear skies. This is also supported by field observations (e.g., Mauldin et al., 1997). In determining the upper tropospheric O₃ concentration, the downward transport of O₃-rich air from the lower stratosphere has been found to be very important while the upward transport of O₃-poor air from the boundary layer does not significantly decrease O₃ concentrations in the upper troposphere. Similar findings to the previous study also include that in the lightning runs, reduced UV fluxes inside and below the convective tower and anvils, as well as during the nighttime, combined with the massive production of NO molecules, leads to reductions of both NO_x and O₃.

The results of this study indicate the enhancement of CH_2O in the upper troposphere induced by deep convection, especially when lightning produced NO are available (through CH_4 oxidation chain). In the runs including lightning produced NO, upper tropospheric mole fraction of CH_2O can be enhanced by at least 50% comparing with runs excluding the lighting influence. The upper tropospheric appearance of CH_2O in several tens of parts per trillion in mole fraction caused by deep convection suggests a possible source of HO_2 .

It has been found that the efficiency of aqueous reactions is greatly reduced by the existence of large amount of ice crystals in the clouds. Although in theory aqueous reactions are very fast in producing sulfates, the results of this study indicate that for the specific remote equatorial convection cases, only a very small faction of the dissolved SO_2 is converted to sulfates, primarily due to the short residence time of liquid phase particles. Due to the same reason, the concentrations of several fast-soluble species including nitric acid are increased in the upper troposphere induced by convection.

Comparing with the single tower simulation in the previous studies, the multiple tower runs in threedimension have revealed much more complicated features of chemical species redistribution, especially in the bordering areas of anvils. Chemical consequences found in these regions often have opposite reaction directions comparing to those inside anvils. The horizontal distribution of chemical species in the upper troposphere demonstrates significant asymmetry. In particularly, downward transport of O_3 from the lower stratosphere is found to influence the O_3 budget in a much larger area than what was suggested in the previous studies (e.g., Wang *et al.*, 1995; Wang and Prinn, 2000). In addition, this downward transport happens in a subtle position (near the end of the anvil), and it implies that when interpreting measured O_3 concentration in the outflow zone of convection or inside the anvil, a special effort must be made to separate the influences of air masses with different origins.

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References

- Fu, Q., and K. N. Liou, 1993: Parameterization of the radiative properties of cirrus clouds. J. Atmos. Sci., 50, 2008-2025.
- Jaeglé, L., *et al.*, 1997: Observed OH and HO₂ in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, 24, 3181-3194.
- Johnson, J. E., R. H. Gammon, J. Larsen, T. S. Bates, S. J. Oltmans, and J. C. Farmer, 1990: Ozone in the marine boundary layer over the Pacific and Indian Oceans: latitudinal gradients and diurnal cycles, *J. Geophys. Res.*, 95, 11847-11856.
- Kley, D., P. J. Crutzen, H. G. J. Smit, H. Vömel, S. J. Oltmans, H. Grassl, and V. Ramanathan, 1996: Observations of near-zero ozone concentrations over the convective Pacific: Effects on air chemistry, Science, 274, 230-233.
- Mahlman, J. D., 1997: Dynamics of transport processes in the upper troposphere, *Science*, 276, 1079-1083.
- Mauldin III, R. L., S. Madronich, S. J. Flocke, F. L. Eisele, G. J. Frost, and A. S. H. Prevot, 1997: New insights on OH: Measurements around and in clouds, *Geophys. Res. Lett.*, 24(23), 3033-3036.
- Mauldin III, R. L., D. J. Tanner, and F. L. Eisele, 1999: Measurements of OH during PEM-Tropics A, J. Geophys. Res., 104, 5817-5827.
- Newell, R. E., and M.-F. Wu, 1985: Simultaneous measurements of carbon monoxide and ozone in the NASA Global Atmospheric Sampling Program (GASP), Atmospheric Ozone, C. S. Zerefos and A. Ghazi (eds.), 548-552, D. Reidel, Dordrecht.
- Piotrowicz, S. R., H. F. Bezdek, G. R. Harvey, M. Springer-Young, and K. J. Hanson, 1991: On the ozone minimum over the equatorial Pacific Ocean, *J. Geophys. Res.*, 96, 18679-18687.

- Prinn, R. G., et al., 1992: Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978-1990, *J. Gephys. Res.*, 97, 2445-2461.
- Prinn, R. G., et al., 2000: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Gephys. Res.*, 105, 17751-17792.
- Ramanathan, V., R. Dirks, R. Grossman, A. Heymsfield, J. Kuettner, and F. P. J. Valero, 1993: Central Equatorial Pacific Experiment Design, Center for Clouds, Chemistry, and Climate, University of California, San Diego, 115 pp.
- Roumeau, S., P. Brémaud, E. Rivière, S. Baldy, J. L. Baray, 2000: Tropical cirrus clouds: a possible sink for ozone, *Geophys. Res. Lett.*, 27, 2233-2236.
- Smit, H., D. Kley, S. McKeen, A. Volz, and S. Gilge, 1989: The latitudinal and vertical distribution of tropospheric ozone over the Atlantic Ocean in the southern and northern hemisphere, Deepak, Hampton, Va., Ozone in the Atmosphere, R. D. Bojkov and P. Fabian (eds.), 419-422, A.
- Thornton, D. C., and A. R. Bandy, 1993: Sulfur dioxide and dimethyl sulfide in the central Pacific Ocean, *J. Atmos. Chem.*, 17, 1-13.
- Thornton, D. C., A. R. Bandy, B. W. Blomquist, D. D. Davis, and R. W. Talbot, 1996: Sulfur dioxide as a

source of condensation nuclei in the upper troposphere of the Pacific Ocean, *J. Geophys. Res.*, 101(D1), 1883-1890.

- Wang, C., and J. S. Chang, 1993: A three-dimensional numerical model of cloud dynamics, microphysics, and chemistry, 1. Concepts and formulation, *J. Geophys. Res.*, 98, 14827-14844.
- Wang, C., P. J. Crutzen, V. Ramanathan, and S. F. Williams, 1995: The role of a deep convective storm over the tropical Pacific Ocean in the redistribution of atmospheric chemical species. J. Geophys. Res., 100(D6), 11509-11516.
- Wang, C., R. G. Prinn, and A. Sokolov, 1998: A global interactive chemistry and climate model: Formulation and testing, *J. Geophys. Res.*, 103, 3399-3417.
- Wang, C., and R. G. Prinn, 1998: Impact of the horizontal wind profile on the convective transport of chemical species, *J. Geophys. Res.*, 103(D17), 22063-22071.
- Wang, C., and R. G. Prinn, 2000: On the Roles of Deep Convective Clouds in Tropospheric Chemistry, J. Geophys. Res., 105(D17), 22269-22297.
- Wennberg, P. O., *et al.*, 1998: Hydrogen radicals, nitrogen radicals, and the production of O_3 in the upper troposphere, *Science*, 279, 49-53.