Influence of convection and biomass burning outflow on tropospheric chemistry over the tropical Pacific

Yuhang Wang,1 Shaw C. Liu, Hongbin Yu, and Scott T. Sandholm
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta

Tai-Yih Chen and Donald R. Blake
Department of Chemistry, University of California, Irvine

Abstract. Observations over the tropics from the Pacific Exploratory Mission-Tropics A Experiment are analyzed using a one-dimensional model with an explicit formulation for convective transport. Adopting tropical convective mass fluxes from a general circulation model (GCM) yields a large discrepancy between observed and simulated CH4 concentrations. Observations of CH4 imply the convective mass outflow to be more evenly distributed with altitude over the tropical ocean than suggested by the GCM. We find that using a uniform convective turnover lifetime of 20 days in the upper and middle troposphere enables the model to reproduce CH4 observations. The model reproduces observed concentrations of H2O and CH3OOH. Convective transport of CH3OOH from the lower troposphere is estimated to account for 40-80% of CH3OOH concentrations in the upper troposphere. Photolysis of CH3OOH transported by convection more than doubles the primary HOx source and increases OH concentrations and O3 production by 10-50% and 0.4 ppbv d-1, respectively, above 11 km. Its effect on the OH concentration and O3 production integrated over the tropospheric column is, however, small. The effects of pollutant import from biomass burning regions are much more dominant. Using C3H8 as a tracer, we estimate that biomass burning outflow enhances O3 concentrations, O3 production, and concentrations of NO2 and OH by 60%, 45%, 75%, and 7%, respectively. The model overestimates HNO3 concentrations by about a factor of 2 above 4 km for the upper one-third quantile of C3H8 data while it generally reproduces HNO3 concentrations for the lower and middle one-third quantiles of C3H8 data.

1. Introduction

Convection is a dominant process for the vertical distribution of chemical species in the troposphere. This distribution process, unlike diffusion, is strongly direction oriented. Uplifts bring up air from the lower troposphere into the free troposphere, and compensating subsidence takes free tropospheric air back down into the lower troposphere. Over industrialized continents, convection leads to efficient export of pollutants into the free troposphere and greatly enhances photochemistry outside the polluted continental lower troposphere [Gidel, 1983; Chatfield and Crutzen, 1984; Dickerson et al., 1987; Pickering et al., 1988, 1992; Jaegle et al., 1998].

Over tropical continents, convection exports large amounts of pollutants from biomass burning [Crutzen and Andreae, 1990]. Fishman et al. [1990] showed widespread high tropospheric O3 columns over the tropical South Atlantic and adjacent continents during the biomass burning season (September-November). Estimated tropospheric O3 column in the region is a factor of 2 higher than over the tropical Pacific. During the Transport and Atmospheric Chemistry Near the Equatorial Atlantic (TRACE A) Experiment in September-October, 1992, elevated concentrations of O3, NO2 (NO+NO2), CO, and hydrocarbons from biomass burning emissions were observed at all altitudes [Fishman et al., 1996]. Transport of these pollutants evidently influences chemistry in the remote tropical Pacific [Jacob et al., 1996; Schultz et al., 1999].

Recent works suggest that local convection in remote tropical regions also has a large impact on chemistry in the upper troposphere [Prather and Jacob, 1997; Jaegle et al., 1997; Cohan et al., 1999]. This effect arises from the large gradient of chemical species between the lower and upper troposphere. Photochemistry driven by radical production from photolysis of O3 and the subsequent reaction of O1D+H2O is active in the lower troposphere due to the abundance of H2O. In the upper troposphere, photochemistry is considerably slower; radical sources, such as photolysis of acetone, become much more important than O1D+H2O [Singh et al., 1995; Arnold et al., 1997; McKeen et al., 1997b; Jaegle et al., 1997; Wennberg et al., 1998; Müller and Brasseur, 1999]. As a result, photochemically produced chemical species tend to have much higher concentrations in the lower than in the upper troposphere. Prather and Jacob [1997] noted the large vertical gradient of CH3OOH in the tropics and suggested that convection of CH3OOH is a dominant radical source in the tropical upper troposphere.
It is, however, not clear to what extent the radical source from convected CH$_3$OOH affects O$_3$ and OH concentrations in the tropical troposphere and how this effect compares with that of biomass burning. Using a one-dimensional model, we analyze tropical DC-8 observations from the Pacific Exploratory Mission-Tropics A (PEM-Tropics A) Experiment in September-October, 1996 [Hoell et al., 1999]. Previous photochemical analyses for PEM-Tropics A [e.g., Schultz et al., 1999; Cohan et al., 1999; Crawford et al., 1999] have used point models, which cannot directly simulate the effect of convection. The vertical transport in our model, which includes an explicit treatment for convective transport, is constrained using the observations of CH$_3$I since the vertical distribution of CH$_3$I is a sensitive indicator for marine convection [Davis et al., 1996b; Cohan et al., 1999]. On the basis of observations of O$_3$, NO, CO, and hydrocarbons, we investigate if the model can simulate observed vertical profiles of other chemical species such as peroxides and use the model to compute the column budget of O$_3$. We will examine the effect of convection on chemistry. We will also use C$_2$H$_2$ as a tracer of outflow from biomass burning regions [Blake et al., 1996, 1999, Andreae et al., 1996] to examine the effect of this pollutant import and compare this effect with that of local convection.

2. Model Description

The model is based on the one-dimensional model by Trainer et al. [1987, 1991] and McKeen et al. [1997a]. We extend the vertical domain to 16 km, the altitude of the tropical tropopause. The vertical resolution of the model decreases from 10 m near the surface to 1 km at 12 km altitude, which is the flight ceiling of the DC-8 aircraft. The top two layers are equally spaced between 12 and 16 km. Chemical species with lifetimes longer than 10 min are transported vertically. The time step for transport and chemistry is 30 s. The model is run for 60 days to obtain a steady state solution.

The mass continuity equation for a one-dimensional model is

$$\frac{\partial n_i}{\partial z} = P_i + L_i + \frac{\partial \Phi_i}{\partial z},$$

where $n_i$ is the concentration of species $i$, $P_i$ is the chemical production rate, $L_i$ is the loss rate by chemical reactions and in the lowest model layer by dry deposition, and $\Phi_i$ is the flux due to vertical transport. We consider two types of vertical transport, diffusion and convection. Diffusion, which is the only transport mechanism used by Trainer et al. [1987], represents mixing by random motion of air parcels. In contrast, convection represents direct transport of the lower tropospheric air into the free troposphere followed by compensating subsidence. The need for invoking convective transport in our model becomes apparent in the simulation of CH$_3$I in section 3. Including convective transport also allows us to explicitly simulate wet scavenging of soluble species in the model. Previous one-dimensional models usually invoke a pseudo first-order loss rate constant to account for wet scavenging of soluble species [e.g., Logan et al., 1981].

The vertical flux $\Phi_i$ is the sum of diffusive and convective fluxes. The diffusive flux $\theta_{diff}$ is a function of the vertical gradient of the chemical species $i$ and the eddy diffusivity coefficient $K_z$.

$$\Phi_i = NK_z \frac{\partial (n_i/N)}{\partial z},$$

where $N$ is the concentration of air. The value of $K_z$ in the surface layer (lower than 800 m altitude) is calculated from similarity theory [Trainer et al., 1987]. The value of $K_z$ above the surface layer will be specified. Convective mass fluxes in the model are from the Goddard Institute for Space Studies (GISS) general circulation model (GCM) (version 1.1) as previously used by Prather and Jacob [1997]. We will discuss the model vertical transport constrained by CH$_3$I observations in section 3.

The chemical mechanisms in the model are updated from the compilations by DeMore et al. [1997] and Atkinson et al. [1997]. Quantum yields and cross sections for photolysis of acetonitrile are from Gierczak et al. [1998]. The reaction rate constants of OH with HNO$_3$ and NO$_2$ are updated from Brown et al. [1999a, b]. The model does not include N$_2$O$_5$ hydrolysis on aerosols [Schultz et al., 2000]. The total ozone column is specified to be 268 Dobson units (DU), the average measured for the tropical region during PEM-Tropics A by the Total Ozone Mapping Spectrometer. A surface albedo of 0.1 is specified for the ocean. We compared model computed photolysis rates of J(0D) and J(0O$_2$) with observations for solar zenith angle <50°, when the value of J(0O$_2$) is largely meaningless to solar zenith angle. The model averages agree to within ±12% with mean and median values of the observations binned in 1-km intervals. Dry deposition velocities to water are specified to be 1 cm s$^{-1}$ for soluble species HNO$_3$ and H$_2$O$_2$ and less than 0.1 cm s$^{-1}$ for other species [Wang et al., 1998a].

3. Vertical Transport Constrained by CH$_3$I Observations

We use observed CH$_3$I concentrations to adjust the parameters of our vertical transport scheme. Methyl iodide is emitted largely from the ocean [Andreae, 1990; Bates et al., 1992; Happell and Wallace, 1996]. It is lost primarily by photolysis. Its photochemical lifetime is about 3 days near the surface and 2 days in the upper troposphere. Its vertical distribution therefore depends critically on the vertical transport of CH$_3$I from the marine lower troposphere. Furthermore, the detection limit of CH$_3$I during PEM-Tropics A is low (0.01 parts per trillion by volume (pptv)) [Cohan et al., 1999], making CH$_3$I observations a valuable constraint on the model transport scheme. Blake et al. [1996] estimated that CH$_3$I emissions from biomass burning during 1RACE-A are much smaller than the oceanic source. The vertical profiles of CH$_3$I sampled for the lower, middle, and upper one-third quantiles of C$_2$H$_2$, a tracer for biomass burning, also do not exhibit enhancements of CH$_3$I associated with upper quantiles of C$_2$H$_2$, suggesting that observed CH$_3$I originates primarily from the ocean. We specified the CH$_3$I concentration at 500-m altitude in the model to the observed value.

Figure 1 shows simulated CH$_3$I concentrations using different vertical transport schemes. The two diffusion-only simulations show the largest discrepancies. For these simulations we specified the values of $K_z$ as 10 and 60 m s$^{-2}$ above the surface layer, respectively. For comparison, values of $K_z$ in the troposphere derived from measurements of $^{222}$Rn in the eastern United States vary from 40 m$^2$ s$^{-1}$ in summer to 20 m$^2$ s$^{-1}$ in
were found in a global simulation of CH$_3$I driven by assimilated meteorological data from the Goddard Earth Observation System Data Assimilation System (M. Schultz, personal communication, 1999).

Observations of CH$_3$I in the tropics therefore argue for a more uniformly distributed profile of the convective mass out

4. Influence of Biomass Burning Outflow

Biomass burning took place in Australia, southern Africa, and South America during the PEM-Tropics A period [Olson et al., 1999]. Its strong influence was reflected in the observations over the tropical Pacific [Blake et al., 1999; Schultz et al., 1999; Talbot et al., 1999]. A good tracer of tropical biomass burning is C$_2$H$_2$ [Blake et al., 1996, 1999; Andrew et al., 1996]; almost all C$_2$H$_2$ data between 0° and 20°N were below 30 pptv, whereas observations in the southern tropics often exceeded this level. We group observations in the tropics (20°S-20°N) on the basis of concurrent measurements of C$_2$H$_2$ to analyze the effect of biomass burning.

Three vertical profiles of observed chemical species (binned in 1-km intervals) are compiled corresponding to the

<table>
<thead>
<tr>
<th>Altitude Range, km</th>
<th>GISS Flux$^a$, g m$^{-2}$ s$^{-1}$</th>
<th>Modified Flux$^b$, g m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-16</td>
<td>1.6</td>
<td>0.88</td>
</tr>
<tr>
<td>7.5-10</td>
<td>0.8</td>
<td>0.76</td>
</tr>
<tr>
<td>5-7.5</td>
<td>0</td>
<td>0.90</td>
</tr>
<tr>
<td>3.5</td>
<td>1.1</td>
<td>0.96</td>
</tr>
<tr>
<td>1.5-3</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>0.7-1.5</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>0-0.7</td>
<td>-2.6</td>
<td>-2.6</td>
</tr>
</tbody>
</table>

$^a$ Convective statistics over the equatorial region (12°S-12°N) in the GISS II' general circulation model between May and August (M. Prather, personal communication, 1999). Positive values are mass fluxes of convection; negative values reflect convergence in the lower troposphere feeding the convection. The upward convective mass transport is compensated for by subsidence as required by mass balance.

$^b$Redistributed uniformly above 3 km by air density to reproduce observed CH$_3$I concentrations (Figure 1).
lower, middle, and upper one-third quantiles of C$_2$H$_2$ concentrations. This simple grouping separates air masses significantly influenced by biomass burning outflow with high C$_2$H$_2$, CO, O$_3$, and NO concentrations from those with much lower concentrations (Figure 2). The median concentration of C$_2$H$_2$ increases from about 20 pptv in the lower one-third quantile to 60-80 pptv in the upper one-third quantile. The chemical lifetime of C$_2$H$_2$ against OH oxidation is only 1-2 weeks in the tropics. The factor of 3-4 enhancement of C$_2$H$_2$ concentrations from the lower to the upper one-third quantile therefore indicates strong influence of biomass burning outflow in the region. Another biomass burning tracer, CO, shows an increase of 20-80% from the lower to the upper one-third quantile of C$_2$H$_2$. This increase is smaller because of background CO concentrations from CH$_4$ oxidation [e.g., Logan et al., 1981]. The small CO vertical gradient is due to its much longer lifetime (about 1 month in the lower troposphere and over 2 months in the upper troposphere) relative to convective turnover, which we estimate to be about 20 days (section 3). If CH$_4$ oxidation were its sole source, the CO concentration would be about 40 ppbv in the tropics. The enhancement of CO over a background of 40 ppbv shows large increases from the lower to the upper one-third quantile of C$_2$H$_2$, which is consistent with the enhancement of C$_2$H$_2$. Biomass burning also emits large amounts of NO that can lead to enhanced O$_3$ concentrations from the increasing in situ production [e.g., Crutzen and Andreae, 1990]. Concentrations of NO in biomass burning outflow may be further enhanced by lightning production [e.g., Wang et al., 1998b]. Observed concentrations of O$_3$ and NO concentrations show corresponding increases with C$_2$H$_2$ (Figure 2). Column O$_3$ and NO$_x$ concentrations (0-12 km) for different quantiles of C$_2$H$_2$ are listed in Table 2.
Table 2. Column O\textsubscript{2} Budget and OH and NO\textsubscript{x} Concentrations

<table>
<thead>
<tr>
<th>One-Third Quantile of C\textsubscript{2}H\textsubscript{5}</th>
<th>O\textsubscript{3}\textsuperscript{a}</th>
<th>P(O\textsubscript{3})\textsuperscript{b}</th>
<th>L(O\textsubscript{3})\textsuperscript{b}</th>
<th>OH\textsuperscript{b}</th>
<th>NO\textsubscript{x}\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>14</td>
<td>1.4</td>
<td>3.5</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Middle</td>
<td>20</td>
<td>1.7</td>
<td>4.5</td>
<td>1.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Upper</td>
<td>34</td>
<td>3.1</td>
<td>5.5</td>
<td>1.6</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Integrated over the air column of 0-12 km (20\degree S-20\degree N). Model values are 24-hour averages.

\textsuperscript{a}Model-computed chemical production of O\textsubscript{3} from reactions of NO and peroxy radicals and loss from the reaction of O\textsubscript{1D}+H\textsubscript{2}O and reactions of O\textsubscript{3} with OH and HO\textsubscript{2} [Davis et al., 1996a]. Column ozone is in Dobson units. Column production (P(O\textsubscript{3})) and loss (L(O\textsubscript{3})) of O\textsubscript{3} are in 10\textsuperscript{11} molecules cm\textsuperscript{-2} s\textsuperscript{-1}.

\textsuperscript{b}Mass-weighted column mean OH concentrations (in 10\textsuperscript{6} molecules cm\textsuperscript{-3}) computed using the one-dimensional model.

\textsuperscript{c}Concentrations of NO\textsubscript{x} are computed using the one-dimensional model constrained to match observed daytime NO concentrations shown in Figure 2. Column NO\textsubscript{x} is in 10\textsuperscript{14} molecules cm\textsuperscript{-2}.

5. Model Simulations: Effects of Convection and Biomass Burning Outflow

We constrain the one-dimensional model by observed median concentrations of O\textsubscript{3}, NO, CO, nonmethane hydrocarbons (NMHCs), and H\textsubscript{2}O for the lower, middle, and upper one-third quantiles of C\textsubscript{2}H\textsubscript{5}. Concentrations of NO\textsubscript{x} are constrained in the model such that simulated daytime mean NO concentrations match the observed NO profiles. Among NMHCs, only long-lived C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{2}H\textsubscript{2} were observed in significant amounts [Blake et al., 1999]. Acetone was not measured during PEM-Tropics A. Observations during the Pacific Exploratory Mission (PEM-West B) show acetone concentrations above 200 pptv and below 400 pptv in the tropics [Singh et al., 1995]. We therefore specify acetone concentrations of 200 and 400 pptv for data groups of the lower and upper one-third quantiles of C\textsubscript{2}H\textsubscript{5}, respectively. We specify for the middle one-third quantile of C\textsubscript{2}H\textsubscript{5} a concentration of 300 pptv based on a global three-dimensional model simulation by Wang et al. [1998a, b]. The concentration of CH\textsubscript{4} is specified at 1.7 ppmv. The DC-8 flight ceiling was at about 12 km; we assume constant mixing ratios above 12 km to be the observed medians at 11-12 km for most species except for water vapor, which decreases with altitude to 6 ppmv at the tropopause.

5.1. Hydrogen Oxides

Concentrations of OH or HO\textsubscript{2} radicals were not measured on the DC-8 during PEM-Tropics A. We evaluate the model simulations using observations of the reservoirs of these radicals, H\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}OOH. In situ chemistry generally plays a central role in determining peroxy concentrations since their lifetimes in the tropics are less than 1 day in the lower troposphere and about 2 days in the upper troposphere. An exception is in the upper troposphere, where convective transport can greatly change their concentrations. In section 3 we have estimated a convective turnover lifetime of 20 days for the ventilation of the upper troposphere. Although this timescale is considerably longer than the lifetimes of peroxides, the peroxy concentrations are about a factor of 10 higher in the lower than in the upper troposphere (Figure 3). As a result, convective transport of air masses from the lower troposphere may provide a source of peroxides similar to in situ production. This effect does not apply to H\textsubscript{2}O\textsubscript{2} since H\textsubscript{2}O\textsubscript{2} is soluble, whereas the solubility of CH\textsubscript{3}OOH is very low [Lind and Kok, 1986]. Cohan et al. [1999] estimated that 50-70% of convected H\textsubscript{2}O\textsubscript{2} is scavenged, suggesting that convection has a small impact on upper tropospheric H\textsubscript{2}O\textsubscript{2} concentrations.

Figure 3 compares observed and simulated H\textsubscript{2}O\textsubscript{2} concentrations. We conducted simulations with wet scavenging coefficients of 50% and 100% for HO\textsubscript{2}. A 100% scavenging coefficient corresponds to a complete removal of H\textsubscript{2}O\textsubscript{2} from the convective air masses. The lower H\textsubscript{2}O\textsubscript{2} concentrations simulated with a scavenging coefficient of 100% are in closer agreement with observations in the upper troposphere. The difference between the two simulations is small in the lower and middle troposphere. Thus we select the scavenging coefficient of 100% as the standard model.

Hydrogen peroxide is produced by the self-reaction of HO\textsubscript{2} and chemically destroyed by photolysis and the reaction with OH. The HO\textsubscript{2} self-reaction is the dominant pathway for HO\textsubscript{2} (OH + peroxy radicals) loss under low NO\textsubscript{x} conditions in the lower troposphere [Kleinman, 1994]. The TIO\textsubscript{2} loss is balanced by the HO\textsubscript{2} production, which is largely photolysis of O\textsubscript{3} followed by the reaction of O\textsubscript{1D}+H\textsubscript{2}O in the lower and middle troposphere [Logan et al., 1981]. Although O\textsubscript{3} concentrations increase by a factor of 2 from the lower to the upper one-third quantile of C\textsubscript{2}H\textsubscript{5} (Figure 2), air masses with high C\textsubscript{2}H\textsubscript{5} concentrations were much drier (Figure 4). The relative humidity for the lower one-third quantile of C\textsubscript{2}H\textsubscript{5} decreases from 80% in the lower troposphere (to 15% in the upper troposphere. It is 50-300% higher than that for the upper one-third quantile of C\textsubscript{2}H\textsubscript{5}. The compensating effects of O\textsubscript{3} and H\textsubscript{2}O on the source of HO\textsubscript{2} are reflected in comparable H\textsubscript{2}O\textsubscript{2} concentrations for the three quantiles of C\textsubscript{2}H\textsubscript{5} simulated in the model.

Observed H\textsubscript{2}O\textsubscript{2} concentrations are similar for the lower and middle one third quantiles of C\textsubscript{2}H\textsubscript{5} but are lower for the upper one-third quantile of C\textsubscript{2}H\textsubscript{5}. The lower H\textsubscript{2}O\textsubscript{2} concentrations (in the lower and middle troposphere) are not reproduced by the model. Comparison of observed and simulated CH\textsubscript{3}OOH concentrations (Figure 3) shows a more pronounced overestimate for the upper one-third quantile of C\textsubscript{2}H\textsubscript{5}. The CH\textsubscript{3}OOH budget for 0\degree-30\degree S by Sula et al. [1999] also shows larger chemical production of CH\textsubscript{3}OOH than loss in the lower and middle troposphere. A possible explanation is that dry, high C\textsubscript{2}H\textsubscript{5} concentration air masses, which originated most likely from the continents, have not reached chemical steady state with respect to peroxides and hence have lower peroxy concentrations.

Convective transport largely enhances CH\textsubscript{3}OOH concentrations in the upper troposphere (Figure 3), as suggested by Prather and Jacob [1997]. Model results with convective
transport agree better with the observations above 10 km than without convection. Figure 5 shows the fraction of CH$_3$OOH attributed to convective transport in our standard model. The fraction is large in the upper troposphere, increasing from 40\% at 10 km up to 80\% at 15 km. Below 6 km the fraction drops to less than 20\%. In this region the increase of CH$_3$OOH from convective transport is not enough to offset the decrease due to subsidence of air with lower CH$_3$OOH concentrations, resulting in lower CH$_3$OOH concentrations compared with the simulation without convection (Figure 3).

Photolysis of CH$_3$OOH convected from the lower troposphere provides a significant primary HO$_x$ source that drives chemistry faster in the upper troposphere. Figure 6 compares primary HO$_x$ sources, O$^1D$+H$_2$O, photolysis of acetone, and photolysis of CH$_3$OOH and CH$_3$O transported from the lower troposphere by convection (for the middle one-third quantile of CH$_2$H$_2$). Photolysis of O$_3$ followed by the reaction of O$^1D$+H$_2$O dominates the primary HO$_x$ sources up to 10 km. The rapid decrease of this source with altitude reflects decreasing H$_2$O levels (Figure 4). The HO$_x$ sources from photolysis of acetone and convected CH$_3$OOH are less variable with altitude and surpass that from O$^1D$+H$_2$O above 11 km. Convective transport of CH$_3$OOH more than doubles the total primary source of HO$_x$ in the upper troposphere. The source from photolysis of convected CH$_3$O is a factor of 5-10 smaller than that from convected CH$_3$OOH.

The total HO$_x$ production is larger than the sum of its primary sources because of photolysis of H$_2$O$_2$ and CH$_3$OOH.
produced in situ and photolysis of CH$_3$OH from CH$_4$ oxidation. Figure 7 compares the total HO$_x$ production with and without convection. The increase of total HO$_x$ production due to convective transport of CH$_3$OOH is apparent above 10 km by up to a factor of 3. Below 8 km, HO$_x$ production with convection tends to be lower than without convection due to lower H$_2$O$_2$ and CH$_3$OOH concentrations in the convective case (Figure 3). The concentration of OH shows corresponding changes but with smaller magnitudes (Figure 7); the maximum increase is less than 50% in the upper troposphere. The increase of HO$_x$ production due to convection of CH$_3$OOH has a negligible effect on the column mean OH concentration.

5.2. Ozone

The additional HO$_x$ source from CH$_3$OOH transported by convection enhances in situ O$_3$ production in the upper troposphere [Prather and Jacob, 1997; Jæger et al., 1997]. Figure 8 compares the O$_3$ production rate between simulations with and without convection for the middle one-third quantile of C$_2$H$_2$. Ozone is produced by reactions of NO and peroxy radicals. The production rate increases by about 0.4 ppbv d$^{-1}$ above 11 km. Integrated over the tropospheric column (0-16 km), the production rate of O$_3$ increases by only 4% from 1.88x10$^{11}$ to 1.96x10$^{11}$ molecules cm$^{-2}$ s$^{-1}$.

The effect of biomass burning outflow is much larger in comparison. Observed ozone columns of 0-12 km are 14, 20, and 34 DU for the lower, middle, and upper one-third quantiles, respectively, of C$_2$H$_2$ (Table 2). Assuming the lower one-third quantile of C$_2$H$_2$ data are not significantly influenced by outflow from biomass burning regions, we estimate an increase of 60% or 9 DU due to enhanced O$_3$ concentrations in

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**Figure 4.** Same as Figure 2 but for relative humidity (over water). Water vapor concentrations measured by the differential absorption CO measurement (DACOM) instrument are used.

**Figure 5.** Fraction of CH$_3$OOH attributed to convective transport as a function of altitude for the lower, middle, and upper one-third quantiles of C$_2$H$_2$.

**Figure 6.** Simulated primary sources of HO$_x$, O$^1$D + H$_2$O, photolysis of acetone, and photolysis of CH$_3$OOH and CH$_3$O transported from the lower troposphere by convection, as a function of altitude for the middle one-third quantile of C$_2$H$_2$. The HO$_x$ yield of CH$_3$O photolysis is computed online.
biomass burning outflow. The column mean OH concentrations are 1.4x10⁹, 1.5x10⁹, and 1.6x10⁹ molecules cm⁻³ for the lower, middle, and upper one-third quantiles, respectively, of C₂H₂, corresponding to a relatively small enhancement of 7% due to biomass burning outflow. The small increase in the OH concentration reflects in part the compensating effects of concurrent increases of NO₂ and CO concentrations with C₂H₂. NO₂ tends to increase OH concentrations, while CO has the opposite effect.

Figure 9 shows simulated production and loss rate and the chemical lifetime of O₃ for the middle one-third quantile of C₂H₂. The production rate of O₃ increases slightly with altitude and is more uniformly distributed vertically than the loss rate. The loss of O₃ occurs primarily in the lowest 5 km. Integrated over the air column of 0-12 km, about 70% of O₃ loss occurs at 0.3 km and 20% occurs at 4-5 km. The column O₃ production (0-12 km) is 1.7x10¹¹ molecules cm⁻² s⁻¹, less than half of the column O₃ loss of 4.5x10¹¹ molecules cm⁻² s⁻¹ (Table 2). About 70% of the O₃ loss is due to the reaction of O¹D+H₂O. The remaining fraction is due to O₃ reactions with OH and HO₂. The chemical lifetime of O₃ increases from 4.5 days near the surface to over 300 days at 15 km.

Air masses with higher concentrations of C₂H₂ have higher concentrations of NO (Figure 2), which is produced most likely from biomass burning and lightning during convection. Higher NO concentrations tend to increase in situ production of O₃. The column O₃ production of 0-12 km are 1.4x10¹¹, 1.7x10¹¹, and 3.0x10¹¹ molecules cm⁻² s⁻¹ for the lower, middle, and upper one-third quantiles, respectively, of C₂H₂ (Table 2). Assuming as previously that the lower one-third quantile of C₂H₂ data represent air masses not significantly influenced by outflow from biomass burning regions, we estimate that the column production of O₃ is increased by 45%, or 6.3x10¹⁰ molecules cm⁻² s⁻¹, due to biomass burning outflow.

Our estimate of the column O₃ production of 1.7x10¹¹ molecules cm⁻² s⁻¹ compares well with 2.0x10¹¹ molecules cm⁻² s⁻¹ over the tropical North Pacific calculated by Davis et al. [1996a] and 1.4-1.8x10¹¹ molecules cm⁻² s⁻¹ over the tropical South Pacific calculated by Schultz et al. [1999]. Our estimated column O₃ loss of 4.5x10¹¹ molecules cm⁻² s⁻¹ is, however, significantly higher than 2.9x10¹¹ molecules cm⁻² s⁻¹ calculated by Davis et al. [1996a] and 3.7x10¹¹ molecules cm⁻² s⁻¹ calculated by Schultz et al. [1999]. Compared with median values compiled by Davis et al. [1996a] (for PEM West A), median O₃ and H₂O₂ concentrations for the middle one-third quantile of C₂H₂ used in our model during PEM-
Figure 9. Simulated O₃ production and loss rate and its chemical lifetime as a function of altitude for the middle one-third quantile of C₂H₂. Tropics A (Figure 2) are both up to a factor of 2 greater at 0-4 km. The difference between our estimate and that of Schultz et al. [1999] largely reflects the difference in the data selection method and the large variability in observed H₂O concentrations. Data shown in Figure 9 correspond to median concentrations for the middle one-third quantile of C₂H₂. Median concentrations of O₃ and H₂O selected in this manner tend to be higher than the median concentrations for all the data. The difference is much larger for H₂O than O₃. For instance, median H₂O concentrations are factors of 2 and 6 higher at 2-3 and 4-5 km, respectively, for the middle one-third quantile of C₂H₂ than for all the data. High H₂O concentrations at these altitudes are reflected in the O₃ loss rate in Figure 9. The uncertainty in the model estimate of the column O₃ loss tends to be larger than that of the column O₃ production since the former estimate relies largely on a subset of observations (below 3 km) that also have large variability.

The net column O₃ deficits (0-12 km) computed in our model are 2.3x10¹¹, 2.8x10¹¹, and 2.4x10¹¹ molecules cm⁻² s⁻¹ for the lower, middle, and upper one-third quantiles, respectively, of C₂H₂. The largest deficit is for the middle one-third quantile of C₂H₂ due to a combination of high relative humidity and relatively high O₃ concentrations (Figures 2 and 4). Schultz et al. [1999] suggested that the large O₃ deficit is supplied mostly by longitudinal transport of O₃ into the region. We conduct a sensitivity simulation; the concentration of O₃ at 11-12 km is specified as observed, below which altitude O₃ concentrations are determined by chemical production and loss and a downward flux of O₃ from the upper troposphere due to subsidence. The resulting O₃ concentrations are much lower than the observations (Figure 10). The O₃ column of 0-12 km in the sensitivity simulation is 50% lower, suggesting large amounts of lateral import of O₃ in the region, in agreement with Schultz et al. [1999].

5.3. Nitrogen Oxides

Simulated HNO₃ concentrations are generally within the range of observations for the lower and middle one-third quantiles of C₂H₂ but are about a factor of 2 higher above 4 km for the upper one-third quantile of C₂H₂ (Figure 11). Using rate constants for reactions of OH with NO₂ and HNO₃ from Brown et al. [1999a, b], instead of those recommended by Demore et al. [1997], decreases HNO₃ concentrations by 5-20
Figure 11. Same as Figure 3 but for HNO$_3$. Model simulations are shown for using reaction rate constants of OH with NO$_2$ and HNO$_3$ from Brown et al. [1999a, b] and DeMore et al. [1997].

The relative reduction of HNO$_3$ concentrations increases with altitude to 20-30% in the upper troposphere. However, only in the case of the upper one-third quantile of C$_2$H$_4$ is the agreement between model and observations markedly improved when using the new rate constants.

Model simulations of HNO$_3$ in the troposphere generally overestimate observations by more than a factor of 2 on a global scale [e.g., Wang et al., 1998b; Lawrence and Crutzen, 1998; Hauglustaine et al., 1998]. A number of hypotheses have been proposed to explain this discrepancy [e.g., Schultz et al., 2000]. As in other models, ours does not resolve fractionation of HNO$_3$ into the aerosol phase. However, Schultz et al. [2000] found that aerosol nitrate concentrations were very low during PEM-Tropics A. The hypothesis that rapid chemical recycling of HNO$_3$ to NO$_2$ in sulfate aerosols or on soot [Chatfield, 1994; Fan et al., 1994; Hauglustaine et al., 1996; Jacob et al., 1996; Lary et al., 1997] is compatible with our results because both sulfur and soot are emitted from biomass burning. Wang et al. [1998b] found some evidence for the chemical recycling in biomass burning outflow over the tropical South Atlantic during TRACE-A. Loss of HNO$_3$ due to deposition to cirrus ice crystals followed by subsequent removal by gravitational settling [Lawrence and Crutzen, 1998] cannot explain the dependence of HNO$_3$ overestimates on high C$_2$H$_4$ concentrations and appears to be inconsistent with our results. Another explanation for our results could be that air masses with high C$_2$H$_4$ concentrations are recently exported from biomass burning regions and have not reached chemical steady state with respect to HNO$_3$.

Observed peroxyacetyl nitrate (PAN) concentrations above 4 km increase from 20 pptv in the lower one third quantile of C$_2$H$_4$ to about 100 pptv in the upper one-third quantile of C$_2$H$_4$ (Figure 12). Concentrations of PAN are much lower below 4 km due in part to its short lifetime (20 min to 1 day) against thermolysis. The rate constant of thermolysis decreases exponentially with decreasing temperature and becomes insignificant above 7 km in comparison with photolysis [Talukdar et al., 1995]. The chemical lifetime of PAN in the upper troposphere, controlled by photolysis, is much longer (about 1 month). Model results compare reasonably well with observations for the lower one-third quantile of C$_2$H$_4$ but tend to be much lower (up to 40 pptv) for the middle and upper one-third quantile of C$_2$H$_4$. The model underestimates likely reflect the influx of relatively long lived PAN similar to the influxes of O$_3$ (section 5.7) and C$_2$H$_2$ (section 4) associated biomass burning outflow. Schultz et al. [1999] suggested that PAN transported from biomass burning regions provides the major source of NO$_2$ in the lower troposphere.

6. Conclusions

We applied a one-dimensional model with an explicit formulation for convective transport to analyze observations over the tropical Pacific during PEM-Tropics A. The vertical transport of the model is constrained by the observations of CH$_3$I, which originates primarily from the ocean and has a short lifetime of 2-3 days in the tropics. Observed CH$_3$I concentrations decrease rapidly with altitude in the lowest 3 km but show little dependence on altitude above 5 km. Using diffusive transport alone in the model cannot reproduce the observed profile. When tropical convective mass fluxes from a GCM (GISS model II') are applied, the model grossly overestimates CH$_3$I concentrations in the upper troposphere but largely underestimates CH$_3$I in the middle troposphere, indicating that convective mass outflow over the tropical ocean is more evenly distributed with altitude than suggested by the GISS statistics. In order to match observed CH$_3$I concentrations, the GISS convective outflux above 3 km is redistributed evenly (by air density), yielding a uniform convective turnover lifetime of 20 days. Observations of CH$_3$I above 12 km, not available during PEM-Tropics A, are necessary to constrain the convective turnover lifetime there.

The model generally reproduces observations of H$_2$O$_2$ and CH$_3$OOH. We find that efficient convective scavenging of
H$_2$O$_2$ by 50-100% is necessary in the model to match observations. Model results indicate that 40-80% of CH$_3$OOH in the upper troposphere is due to convective transport from the lower troposphere. Photolysis of convected CH$_3$OOH more than doubles the primary source of HO$_x$ in the region. The reaction of O$_2$+H$_2$O, which is the dominant primary HO$_x$ source in the lower and middle troposphere, is surpassed by photolysis of convected CH$_3$OOH and photolysis of acetone above 11 km. The latter two sources are also much larger than that from photolysis of convected CH$_3$O. Convection of CH$_3$OOH increases the total HO$_x$ source and OH concentration by up to a factor of 3 and 50%, respectively, in the upper troposphere; it increases the production rate of O$_3$ by about 0.4 ppbv d$^{-1}$ above 11 km. Integrating over the air column of 0-16 km, we find that convection of CH$_3$OOH has a negligible effect on the column mean OH concentration and increases column O$_3$ production by only 4%.

In comparison, the effect of biomass burning outflow is much more significant in changing chemistry over the tropical Pacific. We group observations into three equally divided quartiles of C$_2$H$_2$ concentrations, because C$_2$H$_2$ is a good tracer for biomass burning outflow during PEM-Tropics A. Using the lower one-third quantile of C$_2$H$_2$ data as the air masses least influenced by biomass burning outflow, we estimate that 60% (or 9 DU) of O$_3$ and 75% NO$_x$ enhancements in the air column of 0-12 km are due to import of pollutants from biomass burning regions. The NO$_x$ enhancement increases column O$_3$ production (0 12 km) by 45%. The import of pollutants increases the column mean OH concentration by a moderate 7% due in part to the offsetting effects of concurrent increases in NO$_x$ and CO concentrations.

The effect of pollutant import into the region is reflected in the budget and concentrations of long-lived chemical species. Whereas short-lived H$_2$O$_2$ and CH$_3$OOH concentrations are generally reproduced based on in situ chemistry and local convective transport within the PEM-Tropics A region, the budget of longer-lived O$_3$ shows a column O$_3$ loss a factor of 2 larger than column O$_3$ production. A model sensitivity study indicates that 50% of O$_3$ is supplied by lateral import, similar to the finding by Schulte et al. (1999). Peroxyacetyl nitrate has a lifetime of about 1 month in the tropical upper troposphere. Model simulations are in much better agreement with PAN observations for the lower one-third quantile of C$_2$H$_2$ than those for the middle and upper one-third quantiles of C$_2$H$_2$. The underestimate of PAN concentrations for the middle and upper one-third quantiles of C$_2$H$_2$ is consistent with pollutant import into the region. Nitric acid also has a long chemical lifetime but is removed efficiently by wet scavenging. As a result, significant direct import of HNO$_3$ from biomass burning regions is unlikely. Model results are in reasonable agreement with observations for the lower and middle one-third quantiles of C$_2$H$_2$. However, the model overestimates HNO$_3$ concentrations by about a factor of 2 above 4 km for the upper one-third quantile of C$_2$H$_2$, as observed previously in other regions of the globe. This discrepancy cannot be explained by recent kinetic data for the reactions of OH with HNO$_3$ and NO$_2$ (Brown et al., 1999a, b). There are two likely explanations: (1) the outflow from biomass burning regions has not reached steady state with respect to HNO$_3$; and (2) HNO$_3$ is recycled rapidly back to NO$_2$ by some heterogeneous mechanism in biomass burning outflow.

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Andreae, M. O., E. Atlas, H. Cachier, W. R. Cofer III, G. W. Harris,


D. R. Blake and T.-Y. Chen, Department of Chemistry, University of California, Irvine, CA 92697-2025.

S. C. Liu, S. T. Sandholm, and H. Yu, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332-0340.

Y. Wang, Department of Environmental Sciences, Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901-8551. (yhw@envsci.rutgers.edu)

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