

Factors controlling tropospheric O₃, OH, NO_x, and SO₂ over the tropical Pacific during PEM-Tropics B

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Abstract. Observations over the tropical Pacific during the Pacific Exploratory Mission (PEM)-Tropics B experiment (March-April 1999) are analyzed. Concentrations of CO and long-lived nonmethane hydrocarbons in the region are significantly enhanced due to transport of pollutants from northern industrial continents. This pollutant import also enhances moderately O₃ concentrations but not NO_x concentrations. It therefore tends to depress OH concentrations over the tropical Pacific. These effects contrast to the large enhancements of O₃ and NO_x concentrations and the moderate increase of OH concentrations due to biomass burning outflow during the PEM-Tropics A experiment (September-October 1996). Observed CH₃I concentrations, as in PEM-Tropics A, indicate that convective mass outflux in the middle and upper troposphere is largely independent of altitude over the tropical Pacific. Constraining a one-dimensional model with CH₃I observations yields a 10-day timescale for convective turnover of the free troposphere, a factor of 2 faster than during PEM-Tropics A. Model simulated HO₂, CH₂O, H₂O₂, and CH₃OOH concentrations are generally in agreement with observations. However, simulated OH concentrations are lower (~25%) than observations above 6 km. Whereas models tend to overestimate previous field measurements, simulated HNO₃ concentrations during PEM-Tropics B are too low (a factor of 2–4 below 6 km) compared to observations. Budget analyses indicate that chemical production of O₃ accounts for only 50% of chemical loss; significant transport of O₃ into the region appears to take place within the tropics. Convective transport of CH₃OOH enhances the production of HO_x and O₃ in the upper troposphere, but this effect is offset by HO_x loss due to the scavenging of H₂O₂. Convective transport and scavenging of reactive nitrogen species imply a necessary source of 0.4–1 Tg yr⁻¹ of NO_x in the free troposphere (above 4 km) over the tropics. A large fraction of the source could be from marine lightning. Oxidation of DMS transported by convection from the boundary layer could explain the observed free tropospheric SO₂ concentrations over the tropical Pacific. This source of DMS due to convection, however, would imply in the model free tropospheric concentrations much higher than observed. The model overestimate cannot be reconciled using recent kinetics measurements of the DMS-OH adduct reaction at low pressures and temperatures and may reflect enhanced OH oxidation of DMS during convection.

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1. Introduction

The Pacific Exploratory Mission (PEM) - Tropics B experiment took place during March-April 1999 [Raper *et al.*, this issue]. The mission was conducted using two aircraft, DC-8 and P-3B. Flights of the DC-8 surveyed areas around Hawaii, Fiji, Tahiti, and Easter Island from the boundary layer up to 12-km altitude, whereas the P-3B flights with an emphasis on sampling the tropical lower troposphere surveyed below 6 km mostly between Hawaii and Tahiti. Previously, the PEM-Tropics A experiment sampled similar regions over the tropical Pacific in September-October 1996 [Hoell *et al.*, 1999]. One prominent feature observed during PEM-Tropics A was the prevalent influence of biomass burning plumes over the tropical Pacific [Blake *et al.*, 1999; Schultz *et al.*, 1999; Talbot *et al.*, 1999]. Wang *et al.* [2000] analyzed the effects of biomass burning outflow using a one-dimensional (1-D) model. Observations in the tropics were binned into three equally divided groups (tertiles) by C₂H₂ concentrations. The upper tertile data group showed clear chemical signatures of biomass burning outflow with high concentrations of O₃, NO_x (NO+NO₂), and CO, whereas the lower tertile group was much cleaner with

low concentrations of pollutants. The PEM-Tropics B experiment sampled over the tropical Pacific in March-April, when biomass burning is not expected to be significant in the tropics. Nevertheless, high-concentration pollutant plumes were encountered [Blake *et al.*, this issue]. We will compare the chemical signatures observed during the two PEM-Tropics missions in different seasons and examine the likely sources of the pollutant inflow into the tropical Pacific and their effects. We will examine, in particular, the effects of pollutants on tropical OH concentrations, which constitute a substantial portion of the oxidizing power of the atmosphere [Intergovernmental Panel on Climate Change (IPCC), 1996].

Convection can have profound impact on chemistry in the tropics. One aspect examined by Prather and Jacob [1997] is the HO_x (OH+HO₂) source enhancement in the upper troposphere due to photolysis of CH₃OOH transported convectively from the lower troposphere. Müller and Brasseur [1999] estimated that this source dominates other primary HO_x sources in the tropical upper troposphere. During PEM-Tropics A, Wang *et al.* [2000] found that its effects on O₃ and OH concentrations are generally too small to compare with those of biomass burning outflow. The PEM-Tropics B experiment, which sampled air much cleaner than that in PEM-Tropics A, offers a better opportunity to examine this and other aspects of the effects on tropical trace gas composition by convection. Furthermore, four key species (OH, HO₂, CH₂O, and acetone), not measured during PEM-Tropics A, were measured during PEM-Tropics B and can be used to better constrain HO_x chemistry.

In addition to the O₃-HO_x-NO_x chemistry over the tropical Pacific, examined by Wang *et al.* [2000] for PEM-Tropics A, we will investigate sources of SO₂ in the free troposphere. Thornton *et al.* [1999] reviewed 1991-1996 aircraft SO₂ measurements over the Pacific. They suggested that anthropogenic activities along the North Pacific rim and volcanic sources along the western Pacific rim contribute significantly to free-troposphere SO₂ concentrations. The contribution from DMS, emitted by oceans, appears to dominate in the boundary layer. Quantifying the link between oceanic DMS and free troposphere SO₂ is, however, important because of the implications on climate feedback [Charlson *et al.*, 1987]. We will investigate how much free-troposphere SO₂ during PEM-Tropics B may be attributed to DMS oxidation. The widely adopted rate constants for the DMS-OH adduct reaction by Hynes *et al.* [1986] were derived from experiments conducted for atmospheric conditions near surface. We will derive rate constants more appropriate for free tropospheric conditions on the basis of recent low-temperature and low-pressure measurements by Hynes *et al.* [1995] and Barone *et al.* [1996].

We will analyze observations of 15°S-15°N from the DC-8 flights to understand chemistry over the tropical Pacific; a large number of industrial plumes observed north of 15°N are therefore excluded. During the return flights from Easter Island to NASA Dryden Flight Research Center, highly polluted continental outflow was sampled. We excluded these last two flights from our analysis. Instruments used on board DC-8 are described by perspective investigators in this issue. We will take into account instrument sensitivities in our analysis. We describe in section 2 the 1-D model applied in the analysis. In section 3, we compare the chemical characteristics between PEM-Tropics A and B and examine the effects of long-range transport of pollutants over the tropical Pacific. In section 4, we analyze using the 1-D model the convective turnover timescale constrained by CH₃I observations and the impact of convection on O₃, HO_x, NO_x, DMS, and SO₂ concentrations. Conclusions are given in section 5.

2. One-Dimensional Model

Concentrations of chemical species often change rapidly with altitude. This rapid change reflects in part the changing photochemical environment with altitude and in part the relatively slow transport in the vertical compared with that in the horizontal. The vertical distribution of chemical species often provides a sensitive test for our understanding of chemistry and transport. A 1-D model is suited for such analysis. The 1-D model used in this work is described by Wang *et al.* [2000]. It is based on the model by Trainer *et al.* [1987, 1991] and McKeen *et al.* [1997]. The vertical transport of the model was originally computed using a diffusion scheme, in which the rate of tracer transport depends on the diffusion coefficient K_z and the vertical gradient of the tracer [e.g., Liu *et al.*, 1984]. The diffusion scheme alone, however, cannot represent vertical mixing of the tropospheric column in the tropics [Wang *et al.*, 2000], where convection dominates. During convection, air in the lower troposphere is lifted by updrafts into the free troposphere and air in the free troposphere is brought by subsidence to the lower troposphere. This direction-oriented transport differs from the underlying assumption of random motions in all directions in diffusion transport. Wang *et al.* [2000] implemented an explicit scheme of convective transport using specified convective mass fluxes. A diffusion coefficient is specified in the model to reproduce the observed vertical gradient of CH₃I concentrations below 2 km (section 4). Soluble species H₂O₂ and HNO₃ are scavenged during convective transport [Wang *et al.*, 2000].

The model extends to 16 km with decreasing vertical resolutions from 10 m near the surface to 1 km at the ceiling of the DC-8 aircraft (12-km altitude). The time step for transport and chemistry is 30 s. The model is run for 60 days to obtain steady state results. The kinetics data are taken from DeMore *et al.* [1997] and Atkinson *et al.* [1997], with updates from Sander *et al.* [2000]. The rate constants for the DMS-OH adduct reaction are uncertain, particularly for free tropospheric conditions [DeMore *et al.*, 1997]. We derive new rate constants from more recent kinetics measurements by Hynes *et al.* [1995] and Barone *et al.* [1996] and compare those to the widely adopted rate constants from Hynes *et al.* [1986] in section 4.4. We did not include hydrolysis of N₂O₅ on aerosols due in part to the uncertainties in the calculation of aerosol surface areas [Schultz *et al.*, 2000]; its implications on the budget of NO_x in the model are discussed in section 4.3. The total ozone column is specified to 262 Dobson Unit (DU), the average observed by the Total Ozone Mapping Spectrometer during PEM-Tropics B. The oceanic surface albedo is specified to 0.1. Model calculated photolysis rates of J(O¹D) and J(NO₂) agree within ±15% to the observed medians (binned in 1-km intervals) for solar zenith angle <50°, when the value of J(NO₂) is insensitive to solar zenith angle. Soluble species HNO₃ and H₂O₂ deposit to water at 1 cm s⁻¹ [Wang *et al.*, 1998a]. We constrain the model using observed median profiles of O₃, NO, CO, and hydrocarbons up to 12-km altitude. Concentrations of these species above 12 km are specified as the medians at 11-12 km. Concentrations of H₂O decrease with temperature to 6 ppmv at 16 km.

3. Pollutant Import: PEM-Tropics B Versus PEM-Tropics A

3.1. Sources of Pollutant Inflow

The Pacific Ocean covers more than one third of the Earth's surface. Its vast size allows long-term evolution of pollutant outflow from the continents without too much interference

from fresh emissions. During PEM-Tropics A in austral spring, chemistry over the southern tropical Pacific was strongly perturbed by pollutants from biomass burning [Blake *et al.*, 1999; Schultz *et al.*, 1999; Talbot *et al.*, 1999; Wang *et al.*, 2000]. Using C₂H₂ as a tracer, Wang *et al.* [2000] estimated that biomass burning outflow enhances O₃ concentrations, O₃ production, and concentrations of NO_x and OH by 60, 45, 75, and 7%, respectively.

Air masses with enhanced concentrations of C₂H₂ were also observed during PEM-Tropics B in austral fall [Blake *et al.*, this issue]. However, this enhancement shows distinctively different chemical characteristics from those of PEM-Tropics A indicating a different origin from biomass burning. Figure 1 compares the correlation of C₂H₂ and C₂Cl₄ at 15°S–15°N between PEM-Tropics A and B. Tetrachloroethene is emitted from dry cleaning and industrial usage [McCulloch and Midgley, 1996] and is therefore a good industrial tracer. Its chemical lifetime is ~3 months in the tropics. Acetylene is emitted from either fossil fuel combustion and industry or biomass burning and has a lifetime of a few weeks in the tropics. Figure 1 shows a positive C₂H₂–C₂Cl₄ correlation during PEM-Tropics B, implying that C₂H₂ originated from northern industrialized continents. The scattering in the data reflects the difference in the production processes of C₂H₂ and C₂Cl₄. Their industrial origin is further supported by decreasing concentrations of C₂H₂ and C₂Cl₄ as well as CO, C₃H₆, and C₃H₈ with latitude from north to south [Blake *et al.*, this issue]. In contrast, C₂H₂ concentrations in the northern tropics were close to background levels and much lower than in the southern tropics during PEM-Tropics A [Wang *et al.*, 2000]. Furthermore, concentrations of C₂H₂ were mostly independent of comparatively low C₂Cl₄ concentrations during PEM-Tropics A, consistent with a biomass burning origin of C₂H₂ in austral spring.

We use C₂H₂ as a tracer for industrial pollutant outflow and group PEM-Tropics B observations into three equally divided tertiles to analyze further air chemical characteristics in the region. Figure 2 shows the vertical profiles of median concentrations of C₂H₂, CO, acetone, O₃, OH, and NO for the lower, middle, and upper tertiles of C₂H₂. The median concentrations of C₂H₂ in the lower tertile are only ~10 pptv, about factors of

2 and 4 lower than medians in the middle and upper tertiles, respectively. Concentrations of CO show a similar trend. The median concentrations of CO in the lower tertile of C₂H₂ is ~45 ppbv, only a few ppbv above the background CO concentration of 40 ppbv from CH₄ oxidation. Median CO concentrations in the middle and upper tertiles of C₂H₂ are significantly higher than the 40-ppbv level expected from CH₄ oxidation. The grouping of observations by C₂H₂ concentrations therefore separates air masses strongly influenced by pollutant outflow from those relatively clean and can be used to estimate the impact of pollutant outflow. The concentrations of CO and C₂H₂ exhibit generally decreasing concentrations with altitude, which was not observed during PEM-Tropics A [Wang *et al.*, 2000], implying that the lower troposphere is an important conduit for the long-range transport of northern industrial plumes but not for southern biomass burning plumes.

The median concentrations of acetone are moderately higher in higher tertiles of C₂H₂ (Figure 2) reflecting in part production of acetone from oxidation of anthropogenic hydrocarbons such as propane, the concentrations of which correlate well with C₂H₂ [Blake *et al.*, this issue]. However, the observed enhancements of 0–200 pptv due to pollutant import over a background of 400 pptv are marginal considering that standard deviations are ~100 pptv (not shown). These measurements suggest that the sources of acetone are located largely in the tropical region, most likely of biogenic origin [Singh *et al.*, 1994, 2001; Wang *et al.*, 1998b].

3.2. Timescale of Transport and Its Effects on Tropical OH Concentrations

During PEM-Tropics A, biomass burning outflow was observed to enhance significantly not only reduced compounds like C₂H₂ and CO but also O₃ and NO concentrations; model simulations indicated that it also enhanced tropical OH concentrations [Wang *et al.*, 2000] (OH was not measured on the DC-8 during PEM-Tropics A). Despite of the large enhancements in C₂H₂ and CO concentrations due to outflow from northern industrial continents, PEM-Tropics B observations (Figure 2) show only some enhancements in O₃ concen-

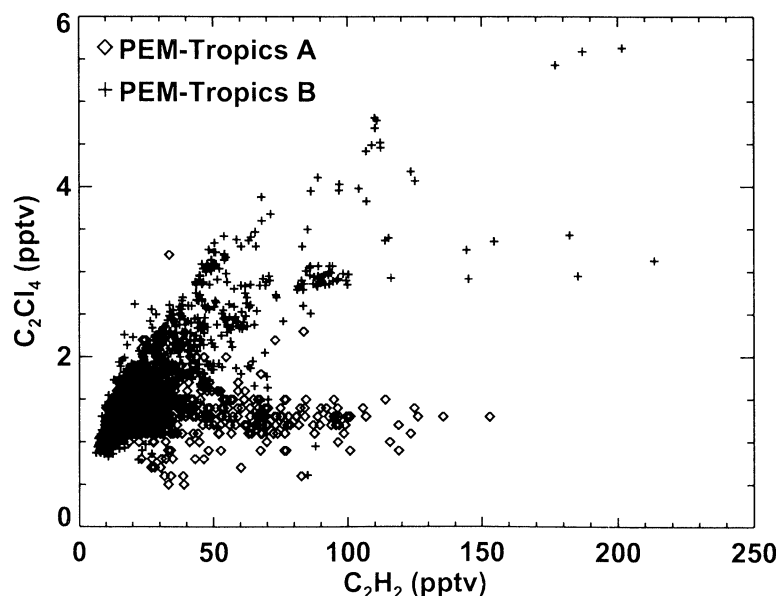


Figure 1. Distribution of C₂Cl₄ concentrations as a function of C₂H₂ concentrations over the tropical Pacific (15°S–15°N) during PEM-Tropics A and B.

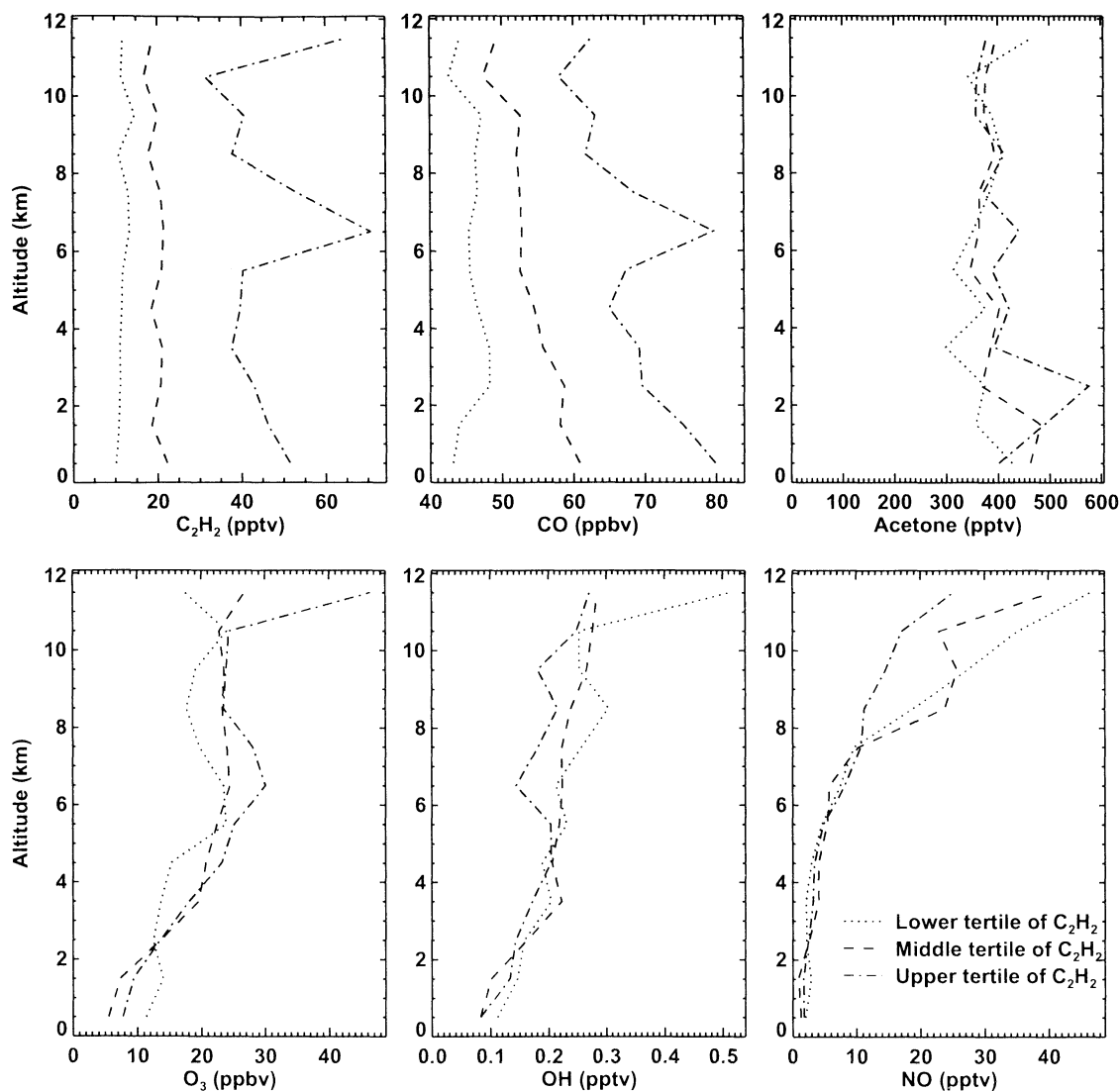


Figure 2. Observed median profiles of C₂H₂, CO, acetone, O₃, OH, and NO concentrations for the three tertiles of C₂H₂. The observations are binned vertically in 1-km intervals.

trations from lower to higher tertiles of C₂H₂. In contrast to PEM-Tropics A, concentrations of NO and OH during PEM-Tropics B were higher in the lower tertiles of C₂H₂, which represent air masses not strongly influenced by pollutant outflow.

We examine this comparison quantitatively in Table 1 by listing median column concentrations of observed O₃ and OH, as well as model computed column production of O₃, and concentrations of NO_x (NO+NO₂), NO_t (NO_x + 2xN₂O₅ + HNO₄ + PAN + HNO₃), and daytime and 24-hour average OH. The corresponding values for PEM-Tropics A are given in parenthesis. Column production and concentrations of O₃ and column NO_x more than doubled from the lower to upper tertile of C₂H₂ during PEM-Tropics A. In comparison, there is only a small increase in tropospheric O₃ column and actually a 15% decrease in O₃ production during PEM-Tropics B. The O₃ production decrease is closely related to that of NO_x (30%). The former decrease is smaller in part because column integrated O₃ production is weighted by mass favoring lower and middle troposphere, where the decrease of NO_x is not as much as in the upper troposphere (Figure 2).

Fresh pollutant outflow from northern industrial continents is enriched in CO, hydrocarbons, and NO_x as the biomass

burning outflow. We believe that the drastically different effects on the air chemical composition over the tropical Pacific by pollutant outflow during PEM-Tropics A and B reflects a much longer timescale of transport from northern industrial continents than that of biomass burning outflow. Short-lived NO_x is depleted in the long-range transport during PEM-Tropics B but longer-lived NO_t, CO, and C₂H₂ are not. During PEM-Tropics A, on the other hand, the timescale of transport of biomass burning outflow is short enough that NO_x concentrations were also enriched. Quantitative assessments of transport timescales from available observations require a more rigorous treatment that we will undertake in a subsequent study. We will suggest in section 4.3 that NO_x observed during PEM-Tropics B is mainly from lightning.

Concentrations of OH in general depend strongly on concentrations of NO_x, CO, and hydrocarbons. Higher NO_x concentrations shift HO₂ towards OH and tend to increase OH concentrations. Carbon monoxide and hydrocarbons have the opposite effects. *Davis et al.* [this issue] examined the distributions of OH and its precursors in detail. We examine here the effects of pollutant transport on OH concentrations. During PEM-Tropics B the longer transport timescale for pollutants

Table 1. Column O₃, OH, NO_x, NO_t, and Production of O₃^a

Tertile of C ₂ H ₂	O ₃ ^b	P(O ₃) ^c	NO _x ^d	NO _t ^e	Observed OH ^f	Model OH ^g	24-hour OH ^h
Lower	10 (14)	1.3 (1.4)	2.1 (2.0)	10	2.87	2.55	1.27 (1.4)
Middle	11 (20)	1.2 (1.7)	2.0 (3.1)	12	2.59	2.25	1.12 (1.5)
Upper	12 (34)	1.1 (3.1)	1.6 (5.4)	14	2.30	1.94	0.96 (1.6)

^a Integrated over the air column of 0–12 km (15°S–15°N). Observations are for solar zenith angle <85° excluding the return flights from Easter Island to California. Numbers in parenthesis are the corresponding values for PEM-Tropics A [Wang *et al.*, 2000]. The model is constrained by observed median concentrations of O₃, NO, CO, and hydrocarbons for the perspective tertiles of C₂H₂ (section 2).

^b Observed medians in Dobson Unit (DU).

^c Model computed 24-hour averages in 10¹¹ molecules cm⁻³ s⁻¹.

^d Model computed daytime averages constrained by observed NO concentrations in 10¹⁴ molecules cm⁻³.

^e Reactive nitrogen NO_t = NO_x + PAN + HNO₃ + 2xN₂O₅ + HNO₄, in 10¹⁴ molecules cm⁻³. Column PAN and HNO₃ are measured medians. Daytime N₂O₅ and HNO₄ concentrations, ~5% of column NO_t, are from the model.

^f Observed medians. Concentrations of OH are in 10⁶ molecules cm⁻³.

^g Computed daytime averages.

^h Computed 24-hour averages.

from northern industrial continents leaves only the imprints of long-lived CO and hydrocarbons but not so much in short-lived NO_x concentrations. The net effect is a significant decrease of observed OH concentrations from lower to upper tertiles of C₂H₂ during PEM-Tropics B (Table 1), suggesting that the long-range transport of pollutants depressed tropical OH concentrations (particularly in the southern tropics). Model results show a similar trend but simulated column concentrations are 15% lower than observations. The underestimate is due to that in the upper troposphere (section 4.2). Concentrations of OH were not measured during PEM-Tropics A; we use model results here. Table 1 shows a small increase of 7% from the lower to upper tertile of C₂H₂. The shorter transport timescale during PEM-Tropics A allowed concurrent increases of short-lived NO_x with longer-lived CO and hydrocarbons in air masses influenced by biomass burning outflow. These two factors have offsetting effects resulting in a small enhancement of OH concentrations.

4. Convective Transport and Its Effects on Photochemistry

4.1. Convective Turnover Timescale

A good chemical tracer for convection over the tropical ocean is CH₃I [Davis *et al.*, 1996; Cohan *et al.*, 1999; Wang *et al.*, 2000]. Emitted from the ocean, CH₃I has a short lifetime of ~3 days against photolysis in the tropics. The observed vertical profile of CH₃I in the free troposphere reflects a balance between the supply by convective transport and the loss by photolysis and offers good constraints on the rate of convective transport from the boundary layer into the free troposphere. Wang *et al.* [2000] analyzed the vertical distribution of CH₃I during PEM-Tropics A using the 1-D model (section 2). Two findings are noteworthy in light of the observations from PEM-Tropics B.

Wang *et al.* [2000] adopted convective mass fluxes from a general circulation model (GCM), which has strong outflow in

the upper troposphere but little in the middle troposphere. The 1-D simulation of CH₃I using the GCM convective statistics shows a C-shaped profile with higher concentrations in boundary layer (due to emission) and in the upper troposphere (due to convective transport). Observations of CH₃I during PEM-Tropics A, in comparison, show little altitude dependence in the free troposphere, suggesting that oceanic convective outflow distributes evenly with altitude. Figure 3 shows the median profile of CH₃I observed during PEM-Tropics B. Observed CH₃I concentrations again show little altitude dependence in the free troposphere corroborating with our finding from PEM-Tropics A.

We estimated a 20-day turnover timescale during PEM-Tropics A on the basis of observed CH₃I observations. Figure 3 shows that the diffusion transport ($K_2 = 10 \text{ m s}^{-1}$, the same as for PEM-Tropics A) alone captures the vertical gradient in the boundary layer but grossly underestimates CH₃I concentrations in the free troposphere. The mass fluxes adjusted to simulate PEM-Tropics A observations lead to large underestimates of CH₃I concentrations in the free troposphere. A doubling of the mass fluxes is necessary to explain PEM-Tropics B CH₃I observations. It implies a 10-day turnover timescale of the free troposphere due to convection during PEM-Tropics B.

With rapid turnover by convection and away from fresh pollutant outflow (section 3), PEM-Tropics B observations promise a good case for studying the effects of convective transport on air chemistry over the tropical Pacific. The 1-D model is constrained by observed median concentrations of O₃, NO, CO, hydrocarbons, and boundary layer DMS and SO₂. We compare with observations model simulations of OH, HO₂, CH₂O, peroxides, HNO₃, PAN, DMS, and SO₂ concentrations. The discrepancies between model and observations found in section 4.2 (hydrogen oxides and O₃) are largely independent of the C₂H₂ tertiles, as are the concentrations of free tropospheric DMS and SO₂ in section 4.4. We show therefore the model comparison with observed medians. Only in section 4.3 (nitrogen oxides) do we compare model results

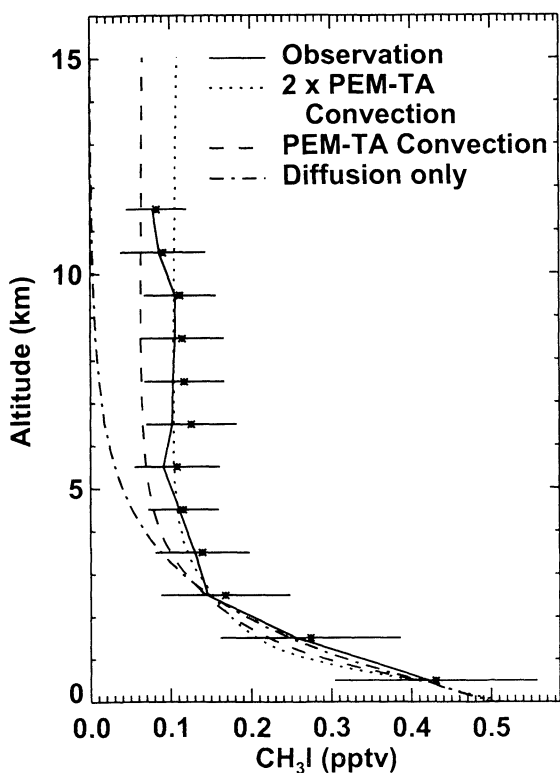


Figure 3. Observed and simulated daytime concentrations of CH₃I as a function of altitude. The solid line represents median concentrations in 1-km intervals; asterisks and horizontal bars represent means and standard deviations, respectively. Three model simulations are shown (see text for details). The concentration of CH₃I at 500 m is specified in the model as the observed median value at 0–1 km.

with observations for the three tertiles of C₂H₂ separately because observed HNO₃ and PAN concentrations vary with C₂H₂ tertiles.

4.2. Hydrogen Oxides and O₃

Hydroxyl radicals are the key species for the oxidation of reduced compounds such as CO and hydrocarbons in the troposphere [IPCC, 1996]. During oxidation, OH is converted to HO₂, which is recycled back to OH by reacting with NO. A key intermediate product of hydrocarbon oxidation is CH₂O. The lifetime of CH₂O is relatively short (5–10 hours) in the tropics. Its concentration therefore serves as a good gauge for photochemical activities. However, previously large discrepancies have been found between model simulated and observed CH₂O concentrations [e.g., Fried *et al.*, 1997].

Figure 4 compares simulated daytime OH, HO₂ and CH₂O concentrations with observations. The model is well within the range of observed HO₂ concentrations, but underestimates OH concentrations by ~25% above 6 km. Similar results were found in point model calculations [Olson *et al.*, this issue; Tan *et al.*, this issue; J. M. Rodriguez *et al.*, manuscript in preparation, 2001]. The discrepancy is within the instrument uncertainty of ±40% [Faloona *et al.*, 2000]; the reason for the altitude dependence of the bias is unclear.

Most of CH₂O is produced from CH₄ oxidation during PEM-Tropics B. A substantial fraction of data points are below the limit of detection (LOD) of 50 pptv. The LOD fraction increases from 30% at 7 km to 50% at 12 km (Figure 5). When the LOD fraction is >30%, we show only the median values. When the LOD fraction is >50% at 9–10 km, we use the LOD limit of 50 pptv for the median of the data bin, which is an upper limit. Model simulated CH₂O concentrations generally agree with observations but with a consistent high bias of ~25 pptv. The agreement between the model and observations are substantially better than previous missions [e.g., Fried *et al.*, 1997]. Although the lifetime of CH₂O is only a few hours, model results indicate that convection decreases CH₂O concentrations by 10–30 pptv in the lower troposphere and increases CH₂O concentrations by similar amounts in the upper troposphere. Inclusion of convection improves model comparison with observed CH₂O concentrations in the lower and middle troposphere.

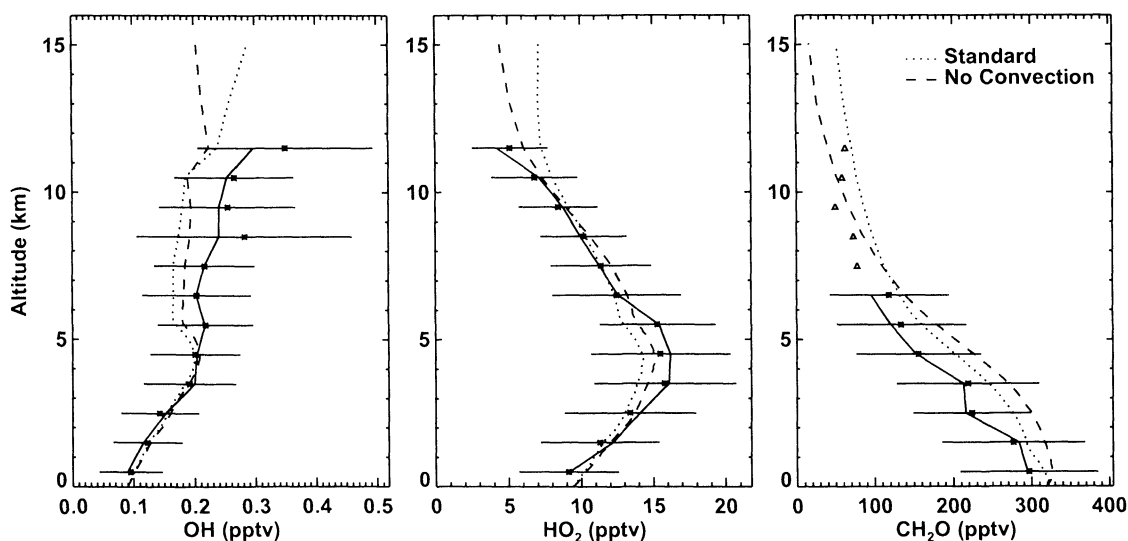


Figure 4. Observed and simulated daytime concentrations of OH, HO₂, and CH₂O as a function of altitude. Symbols for the observations are the same as in Figure 3. Observed medians, means, and standard deviations are shown for data bins with a LOD fraction <30% (the LOD limit (50 pptv) is assumed for LOD data); only median points (open triangles) are shown for data bins with a larger LOD fraction. When the LOD fraction is >50%, the LOD limit is used as the median. Model results are shown with and without convection.

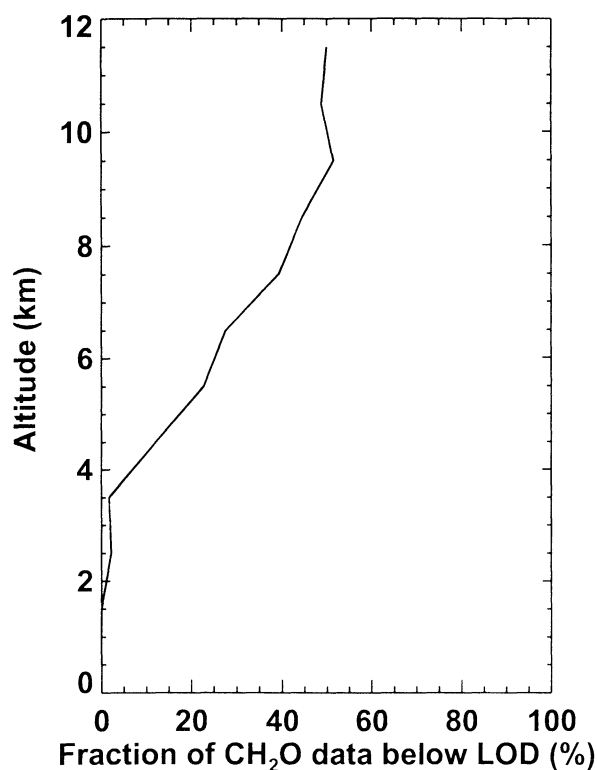


Figure 5. The percentage fraction of observed CH₂O data points below the LOD as a function of altitude.

During PEM-Tropics A, OH, HO₂, and CH₂O were not measured. Model simulations of HO_x were constrained by its longer-lived reservoirs, H₂O₂ and CH₃OOH. Wang *et al.* [2000] showed that model simulated H₂O₂ and CH₃OOH concentrations agree well with observations except some underestimates in the lower troposphere for the upper tertile of C₂H₂, associated with dry and polluted air. Figure 6 illustrates these comparisons for PEM-Tropics B and shows reasonable agreement between the model and observations for H₂O₂ concentra-

tions but a consistent overestimate of 100–200 pptv for CH₃OOH concentrations. Including convective transport improves both simulations. The observed 3-km H₂O₂ maximum and a large drop of CH₃OOH concentrations at 0–1 km compared to higher altitudes are inconsistent with the observations of PEM-Tropics A [Wang *et al.*, 2000], which may reflect the uncertainties of ±30% in the measurements [Hoell *et al.*, 1999].

Convective transport of CH₃OOH into the upper troposphere boosts the production of HO_x in the region [Prather and Jacob, 1997]. Figure 7 shows simulated primary HO_x sources. Compared to a similar figure by Wang *et al.* [2000] for PEM-Tropics A, the crossover point at which photolysis of CH₃OOH from convective transport begins to dominate moves down from 11 km during PEM-Tropics A to 10 km due to the faster convective turnover during PEM-Tropics B. Model results suggest an enhancement of H₂O₂ concentrations above 13 km despite convective scavenging of H₂O₂ as a result of increased primary HO_x production from photolysis of convected CH₃OOH (Figure 6). Convective transport also more than doubles upper tropospheric CH₃OOH concentrations in the model.

This boost to the primary HO_x source from convective transport of CH₃OOH is offset by the scavenging loss of H₂O₂, a reservoir of HO_x radicals. The latter factor dominates in the middle atmosphere. Both OH and HO₂ concentrations are lower below 9 km with convection, as are the production rates of HO_x and O₃ (Figure 8). The effects of convection on the production of O₃ should be considered over the whole tropospheric column since the convective turnover timescale of 10 days is shorter than the lifetime of O₃ above 4 km [Wang *et al.*, 2000]. Column (0–16 km) O₃ production (1.3 × 10¹¹ molecules cm⁻² s⁻¹) is 4% more, but column HO_x production (6.2 × 10¹¹ molecules cm⁻² s⁻¹) and OH concentration (1.1 × 10⁶ molecules cm⁻³) are 7 and 4% less, respectively, in the convective than nonconvective case. These results obviously depend on our assumptions of convective mass fluxes and species concentrations above 12 km, which could not be constrained due to the lack of observations. They nonetheless imply relatively small effects by convection on column O₃ and OH concentra-

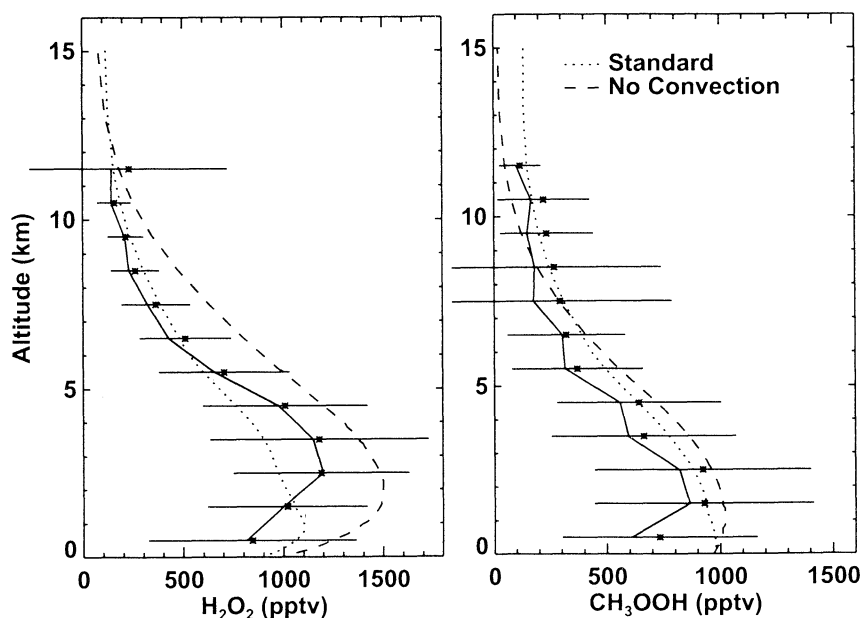


Figure 6. Same as Figure 4 but for H₂O₂ and CH₃OOH concentrations.

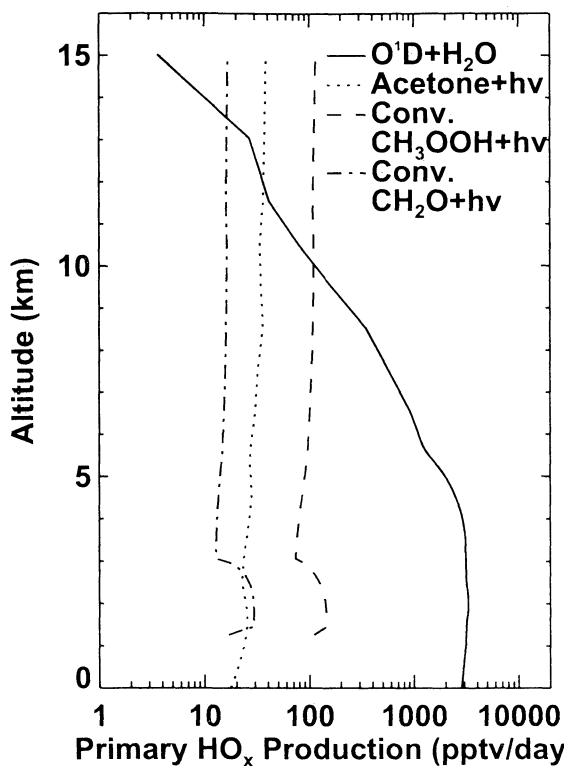


Figure 7. Simulated (24-hour average) primary HO_x sources as a function of altitude from O(¹D)+H₂O, photolysis of acetone, and photolysis of CH₃OOH and CH₂O transported from the lower troposphere by convection. The HO_x yield of CH₂O photolysis is computed on line.

tions due to the offsetting effects of convective transport of CH₃OOH and scavenging of H₂O₂. One convective effect not taking into account here is the convective transport of H₂O, which is reflected in the observed H₂O concentrations. Its effect on the HO_x primary sources is unlikely to be significant

above 12 km due to the large contribution by convectively transported CH₃OOH. However, convective transport of H₂O and subsequent moistening of the atmosphere could substantially boost the primary HO_x production in the middle and lower troposphere because of the dominance of the O(¹D)+H₂O reaction (Figure 7). Our model, however, is inadequate to assess this effect.

Figure 9 shows model diagnosed median O₃ production and loss rates and a deficit in the O₃ budget. Column O₃ production at 0–16 km is 1.3×10^{11} molecules cm⁻² s⁻¹ only ~50% of the column loss (2.5×10^{11} molecules cm⁻² s⁻¹) during PEM-Tropics B. Previous O₃ budget studies over the tropical Pacific also showed large deficits during PEM-West A [Davis *et al.*, 1996], PEM-West B [Crawford *et al.*, 1997], and PEM-Tropics A [Schultz *et al.*, 1999; Wang *et al.*, 2000]. The ubiquitous O₃ budget deficit over the tropical Pacific is not unexpected since the region is away from major sources of O₃ precursors. The lifetime of O₃ is long above 5 km (> 3 months) [Wang *et al.*, 2000]. Long-range transport from continents, where emissions of O₃ precursors are abundant, can make up for the column budget deficit [Schultz *et al.*, 1999; Wang *et al.*, 2000; Browell *et al.*, this issue]. Direct transport of large amounts of O₃ from the stratosphere in the tropics is unlikely [Holton *et al.*, 1995]. Additional observations are required to quantify contributions from different O₃ transport pathways. The comparisons between PEM-Tropics A and B in Table 1 offer some hints worth mentioning. Concentrations of O₃ and NO_x are similar among C₂H₂ tertiles during PEM-Tropics B despite large differences in CO and long-lived hydrocarbon concentrations (Figure 2). They are also close to the values in the lower tertile during PEM-Tropics A. These similarities imply that the sources and transport of O₃ and NO_x are largely located within the tropics, a feature simulated in a global 3-D model [Wang *et al.*, 1998c].

4.3. Nitrogen Oxides

Model simulations of HNO₃ concentrations generally overestimate field measurements [e.g., Chatfield, 1994; Fan *et al.*, 1994; Jacob *et al.*, 1996; Wang *et al.*, 1998b; Lawrence and

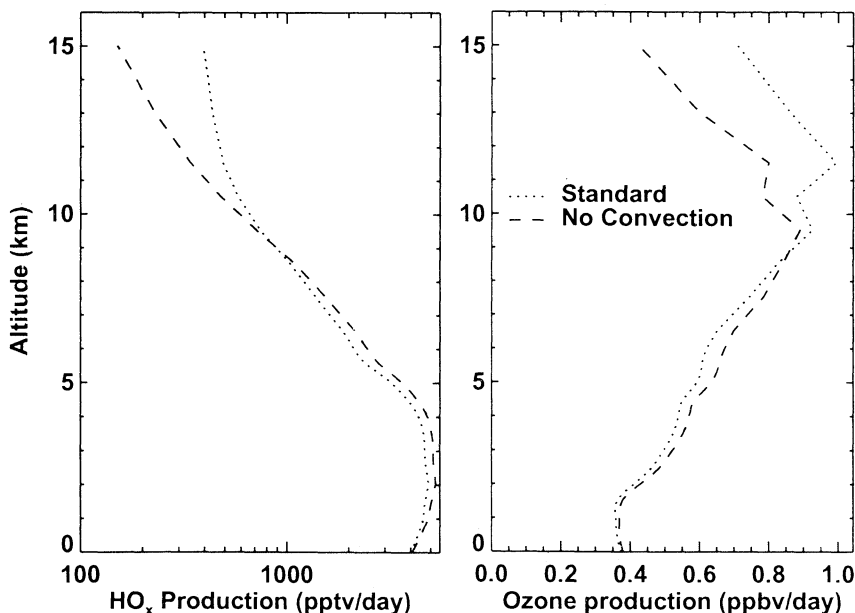


Figure 8. Simulated (24-hour average) production rates of HO_x and O₃ as a function of altitude with and without convection.

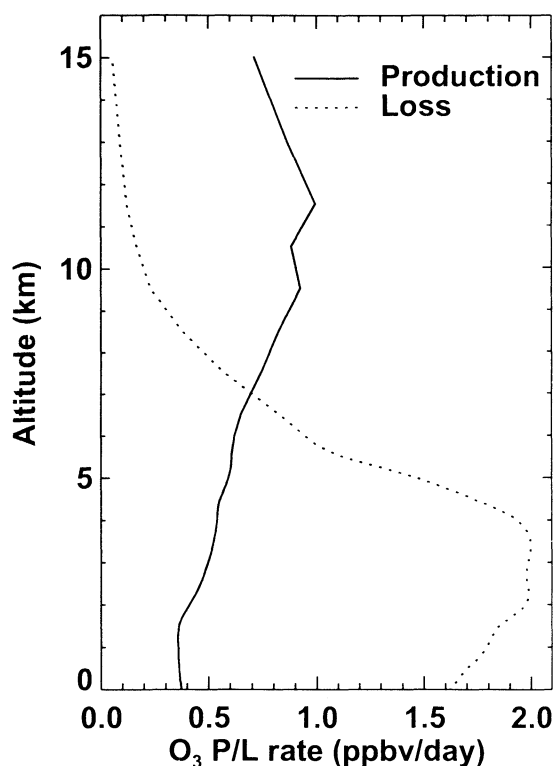


Figure 9. Simulated (24-hour average) chemical production and loss rates of O₃ as a function of altitude.

Cruzen, 1998; Hauglustaine et al., 1998]. During PEM-Tropics A, however, good agreement was obtained for the lower and middle tertiles of C₂H₂ with some model overestimates in the upper tertile of C₂H₂ [*Wang et al., 2000*]. Figure 10 compares simulated and observed HNO₃ for the three tertiles of C₂H₂ for PEM-Tropics B. Unlike in the previous cases, simulated HNO₃ concentrations are much lower (by a factor of 2 or more) than the observed medians. Median concentrations of HNO₃ measured on the P-3B using the same type of instrument [*Talbot et al., 1999*] are generally lower than those on the DC-8 but are still higher than model simulations. Furthermore,

observed HNO₃ concentrations increase from the lower to upper tertile of C₂H₂ but simulated HNO₃ has an opposite trend because of NO_x and OH concentrations are lower in the upper tertile (Table 1, Figure 2). An obvious possibility is the hydrolysis of N₂O₅ in aerosols, not simulated in the model. However, aerosol observations do not show a discernible trend in surface area from the lower to upper tertile of C₂H₂. Aerosol NH₄⁺ and SO₄⁻² concentrations during PEM-Tropics B are also similar to PEM-Tropics A (*J. Dibb, personal communication, 2000*), when hydrolysis of N₂O₅ was not necessary to explain the observed HNO₃ concentrations [*Schultz et al., 2000; Wang et al., 2000*].

Model comparison with observations for PAN (Figure 11) shows similar results to those by *Wang et al. [2000]* for PEM-Tropics A. The model generally reproduces PAN concentrations in the lower and middle tertiles of C₂H₂, but underestimates the concentrations in the upper tertile of C₂H₂, implying long-range transport of PAN into the region. The concentrations of PAN during PEM-Tropics B are much lower than during PEM-Tropics A in the upper tertile of C₂H₂ but are similar in the lower tertile of C₂H₂. The overestimate of HNO₃ is unlikely caused by long-range transport for the lower and middle tertiles of C₂H₂ because the chemical lifetime of PAN is longer than HNO₃ in the upper troposphere.

Nitric acid and PAN are longer lived than NO_x. Their decomposition to NO_x is very slow in the upper troposphere. The loss of these reservoirs is not due to chemistry but downward transport associated with the subsidence branch of convection. The loss of HNO₃ and PAN in the upper troposphere cannot be compensated for by convective updrafts, in which HNO₃ is scavenged and PAN concentrations are very low. This loss of HNO₃ and PAN, and to a much smaller extent HNO₄ and N₂O₅, must be compensated for by chemical production from NO_x. Convective transport therefore dictates an upper tropospheric source of NO_x to make up for the loss. Figure 12 shows the simulated chemical production and loss rates of HNO₃ and PAN. Chemical production of HNO₃ exceeds loss throughout the troposphere reflecting wet scavenging of HNO₃. The net production of PAN above 5 km is compensated for by downward transport into the lower troposphere where PAN readily decomposes by thermolysis at warm temperatures and produces a large source of NO_x. In the model the source of

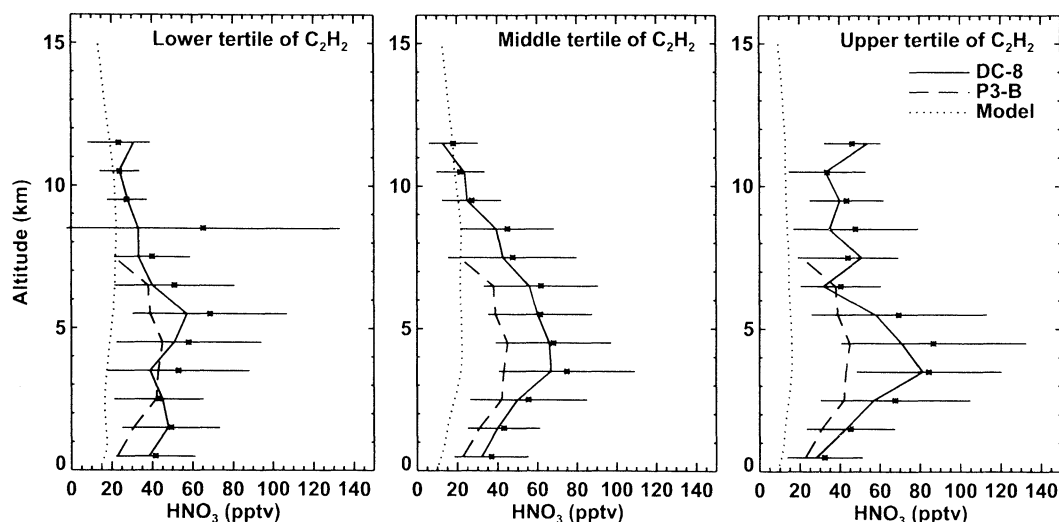


Figure 10. Observed and simulated daytime concentrations of HNO₃ as a function of altitude for the three tertiles of C₂H₂. Symbols for the observations are the same as in Figure 3. The dotted line shows the results from the standard model. Median concentrations from P-3B measurements are shown by the long dashed line.

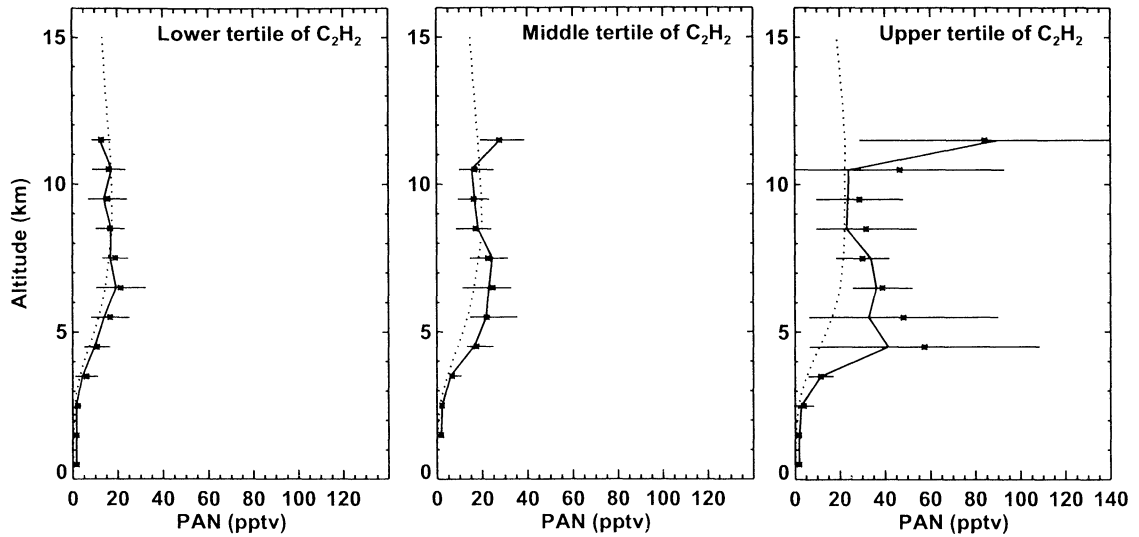


Figure 11. Same as Figure 10 but for PAN.

NO_x from PAN decomposition in the lower troposphere is able to compensate for the loss due to wet and dry deposition of HNO₃ in the region. It is in the upper and middle troposphere (above 4 km) that a large source of NO_x of 4×10^8 molecules cm⁻² s⁻¹ is needed to account for the surplus in the chemical budgets of PAN and HNO₃. Extending this source over the tropics (20°S–20°N) yields a net source of 0.4 Tg N yr⁻¹. If we assume that N₂O₅ hydrolysis in aerosols or another NO_x to HNO₃ pathway is necessary to correct the underestimate of HNO₃ concentrations in the model, this tropical source of NO_x is at least 1 Tg N yr⁻¹.

Three possible venues could contribute to the needed NO_x sources, lightning over the oceans, transport of lightning NO_x from tropical continents, and long-rang transport of NO_x reservoirs (PAN and HNO₃). We have discussed previously that the third possibility may have contributed to PAN and HNO₃ con-

centrations in the upper tertile of C₂H₂ but not the lower tertiles. Given the inefficient decomposition rates in the upper troposphere (Figure 12), the source is unlikely to be significant. The lightning sources over the tropical ocean and land are difficult to distinguish on the basis of anthropogenic chemical tracers because fossil fuel and industrial emissions are weak in the tropics. Examination of high-NO_x encounters during PEM-Tropics B often leads to oceanic cumulus clouds in GEOS satellite images a few days back along the air trajectories calculated by *Fuelburg et al.* [this issue]. Even if only half of the source (0.2–0.5 Tg N yr⁻¹) is due to marine lightning, it is significantly large considering that the global lightning sources have been estimated to be as small as 3 Tg N yr⁻¹ in 3-D models [e.g., *Levy et al.*, 1996; *Wang et al.*, 1998a]. The lightning parameterization in global 3-D models [e.g., *Price and Rind*, 1992] generally predicts lightning frequencies

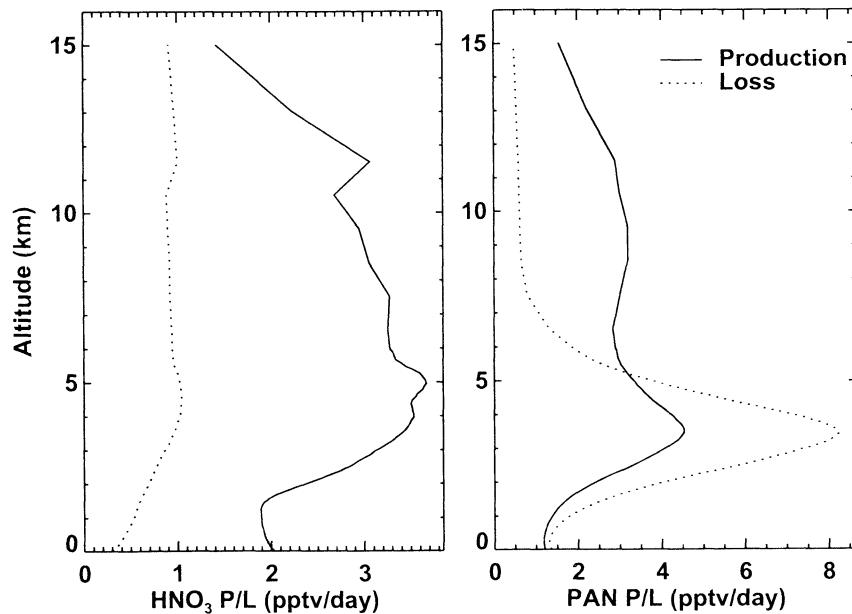
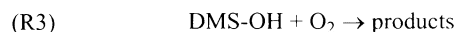


Figure 12. Same as Figure 9 but for HNO₃ and PAN.

orders of magnitudes smaller over the ocean than over land. Future studies on the NO_x source from marine lightning are warranted.

4.4. Free Tropospheric DMS and SO₂

Dimethylsulfide in the atmosphere is oxidized mostly by OH and to a lesser extent by NO₃ [Berresheim *et al.*, 1995]. Whereas the rate constants for H abstraction reaction by the radicals are reasonably known, kinetics data for the adduct reaction of DMS and OH are uncertain [DeMore *et al.*, 1997]. While the former reaction is bimolecular, the latter reaction involves the DMS-OH adduct that either decomposes or reacts with O₂ and hence is more complex. The bulk rate constants for the adduct reaction were derived by Hynes *et al.* [1986] for near surface atmospheric conditions. Their empirical fitting function has since been widely adopted [e.g., Atkinson *et al.*, 1997]. Hynes *et al.* [1995] and Barone *et al.* [1996] undertook two more recent experiments that probed elementary reactions at low pressures and temperatures. For DMS oxidation in the free troposphere the recent works are more pertinent. We derive new rate constants for the adduct reaction on the basis of Hynes *et al.* [1995] and Barone *et al.* [1996]. The reaction sequence is



The equilibrium constant for reactions (R1) and (R2) is

$$K_c = k_1/k_2. \quad (1)$$

Hynes *et al.* [1995] and Barone *et al.* [1996] derived K_c values from their measurements at 250–267 and 228–234 K, and 30–100 and 100 Torr, respectively. Fitting these data, we obtain

$$K_c = 2.7 \times 10^{-26} \exp(5133/T) \text{ cm}^3 \text{ molecule}^{-1}. \quad (2)$$

There is a slight temperature dependence of k_1 [Barone *et al.*, 1996]. We apply a generic formulation $k_1 = A_1 \exp(200/T)$ [DeMore *et al.*, 1997] to fit the experimental data and obtain

$$k_1 = 3.2 \times 10^{-12} \exp(200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

and hence

$$k_2 = 1.2 \times 10^{14} \exp(-4933/T) \text{ s}^{-1}, \quad (4)$$

where T is in Kelvin. Barone *et al.* [1996] also showed pressure dependence of k_1 and k_2 . We include this uncertainty by assuming a linear pressure dependence to compute another set of rate constants k' , i.e., $k'_1 = k_1 \cdot (P/100)$ and $k'_2 = k_2 \cdot (P/100)$, where P is in Torr.

For the value of k_3 , Hynes *et al.* [1995] and Barone *et al.* [1996] found it to be independent of T and P at 8×10^{-13} and $10 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. We adopt $k_3 = 9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We therefore derive a rate expression for the adduct channel,

$$k_{ad} = \frac{2.4 \times 10^{-38} \exp(5133/T)}{1 + 7.5 \times 10^{-27} \exp(4933/T) [\text{O}_2]} \quad (5)$$

and with a linear pressure dependence of k'_1 and k'_2 ,

$$k'_{ad} = \frac{2.4 \times 10^{-38} \exp(5133/T)}{1 + 7.5 \times 10^{-25} \exp(4933/T) ([\text{O}_2]/P)} \quad (6)$$

where k_{ad} and k'_{ad} are in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, T is in Kelvin, and P is in Torr.

Figure 13 compares these rate constants to those for the abstraction channel and the addition reaction rate constants by Hynes *et al.* [1986]. The H-abstraction rate constant decreases with altitude while the addition rate constant generally increases; the latter channel is more important or even dominant in the free troposphere. The DMS-OH adduct reaction accounts for 20, 30, and 40% in boundary layer and 75, 60, and 75% at 8 km, respectively, for the rate constants by Hynes *et al.* [1986] and of (5) and (6). Equation (6) with the pressure dependence is expected to give faster rate constants than (5). The relatively good agreement between that from Hynes *et al.* [1986] and (6) in the free troposphere is fortuitous since the rate expression given by Hynes *et al.* [1986], strictly speaking, applies only for 1 atmosphere pressure whereas (6) is pressure dependent. The new measurements at low pressures and temperatures imply higher branching ratios for the addition channel in the boundary layer than predicted by Hynes *et al.* [1986]. Our primary interest is in DMS and SO₂ concentrations in the free troposphere. We will adopt in our 1-D simulations equations (5) and (6) to bracket the range of addition rate constants.

In the simulation of DMS we specify its concentration at 500 m as observed. The resulting DMS concentrations in the free troposphere reflect the source from convective transport compensated for by oxidation by OH and NO₃. Figure 14 shows that 50–90% of the observations are below the LOD at altitudes above 3 km, where the model predicts concentrations of 5–10 pptv. The observed medians in the free troposphere are lower than plotted values since we used the LOD value as an upper limit for data bins with LOD fraction > 50%. To narrow

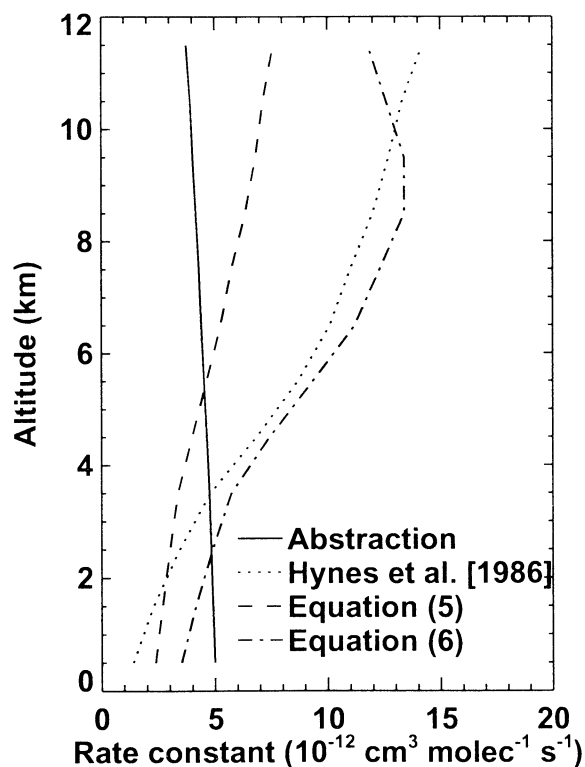


Figure 13. Rate constants for the abstract and addition channels of the DMS+OH reaction as a function of altitude. Three rate constants are calculated for the addition channel (see text for details).

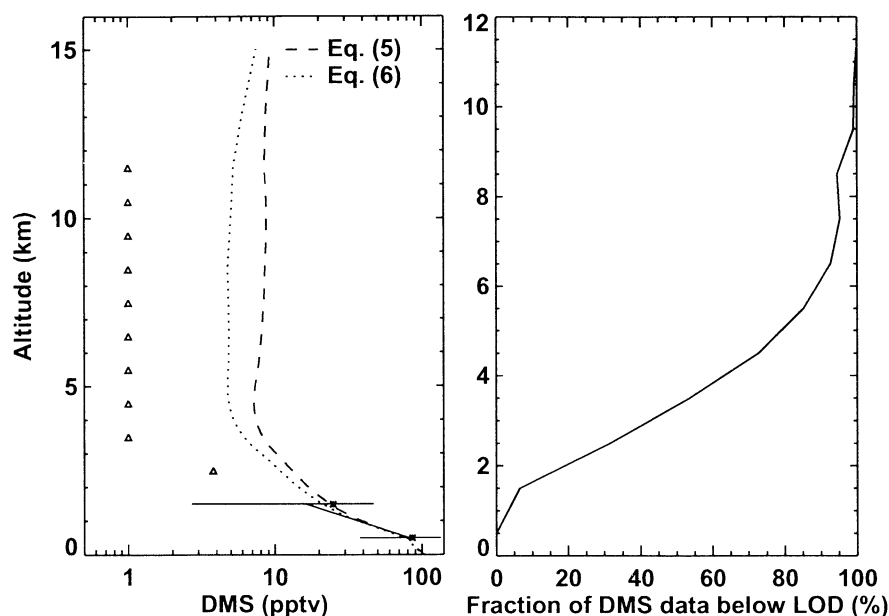


Figure 14. Observed and simulated daytime concentrations of DMS and the percentage fraction of observed DMS data points below the LOD (1 pptv) as a function of altitude. Symbols for the observations are the same as in Figure 3. As in Figure 4 for CH₂O, only median points (open triangles) are shown for data bins with >30% of data points below the LOD; when the LOD fraction is >50%, the LOD limit is used as the median. Two model results are shown using (5) and (6), respectively, for the rate constants of the DMS-OH adduct reaction. The concentration of DMS at 500 m is specified in the model as the observed median value at 0–1 km.

the possible causes for the large model overestimates, further measurements on the kinetics of DMS+OH adduct reaction are necessary. The chemical lifetime of DMS is less than 1 day in the upper troposphere. The concentrations of DMS are therefore more susceptible to sometimes highly elevated OH concentrations observed around convective systems [e.g., Jaeglé *et al.*, 1997]. It is also possible that DMS is oxidized in the free troposphere by processes other than reactions with OH and NO₃.

The virtually unobservable level of DMS in the free troposphere, at first sight, implies that DMS cannot be a major source of SO₂ outside the boundary layer. This issue is further masked by other sources apparently making contributions to free tropospheric SO₂ including anthropogenic and volcanic sources [Thornton *et al.*, 1999]. However, convection can transport into the free troposphere large amounts of insoluble DMS. It is reasonable to assume that SO₂ is produced from transported DMS in the free troposphere. The yields of SO₂ from DMS oxidation are yet another uncertainty [e.g., Davis *et al.*, 1999]. We adopt oxidation yields of 1 for OH and NO₃ abstraction reactions and 0.6 for the DMS-OH adduct reaction [Davis *et al.*, 1999; Koch *et al.*, 1999]. Figure 15 shows the observed median SO₂ profile and model results using the rate expressions of (5) and (6), respectively. To simplify the interpretation of the model results, we assume a complete scavenging of SO₂ during convective transport and specify the SO₂ concentration at 500 m as observed. The latter led to the kink at 500 m in the model results. These measures ensure that free tropospheric SO₂ simulated in the model are produced from DMS oxidation. The difference in the yield of SO₂ between the abstraction and addition channels is reflected in the general decrease of model simulated SO₂ concentrations with altitude as the addition channel becomes more important (Figure 13). It is also reflected in the lower SO₂ concentrations obtained using the faster rate expression of (6) than using that of (5) for

the addition channel. Model results suggest that convective transport of DMS from the boundary layer could explain the observed level of SO₂ concentrations in the free troposphere over the tropical Pacific.

5. Conclusions

We analyzed observations from PEM-Tropics B to investigate factors controlling O₃-HO_x-NO_x and SO₂ chemistry over the tropical Pacific. Interesting comparisons can be made with PEM-Tropics A observations, which were strongly influenced by biomass burning outflow. During PEM-Tropics B, C₂H₂ correlated well with C₂Cl₄, an industrial tracer, reflecting long-range transport of pollutants from northern industrial continents. No such correlation was found for biomass-burning dominated PEM-Tropics A. The degree of influence, for which we examined data groups categorized by tertiles of C₂H₂, varied drastically between the two missions. Whereas CO concentrations were enhanced significantly from the lower to upper tertile of C₂H₂ in both missions, enhancements in O₃ and NO_x concentrations were hard to find during PEM-Tropics B in contrast to the large increases observed during PEM-Tropics A. Concentrations of NO_x, in fact, showed a decrease from the upper to lower tertiles of C₂H₂ during PEM-Tropics B. The differences reflect longer timescales of transport during PEM-Tropics B than A, resulting in the depletion of shorter-lived O₃ and NO_x. The large enhancements in longer-lived CO and hydrocarbons but not in O₃ and NO_x depressed OH concentrations in air masses influenced by industrial outflow over the tropical Pacific. In contrast, OH concentrations over the tropical Pacific were enhanced in air masses influenced by biomass burning outflow during PEM-Tropics A because the shorter timescale of transport allowed for enhanced O₃ and NO_x concentrations. Transport of pollutants from different source regions during PEM Tropics A and B therefore showed

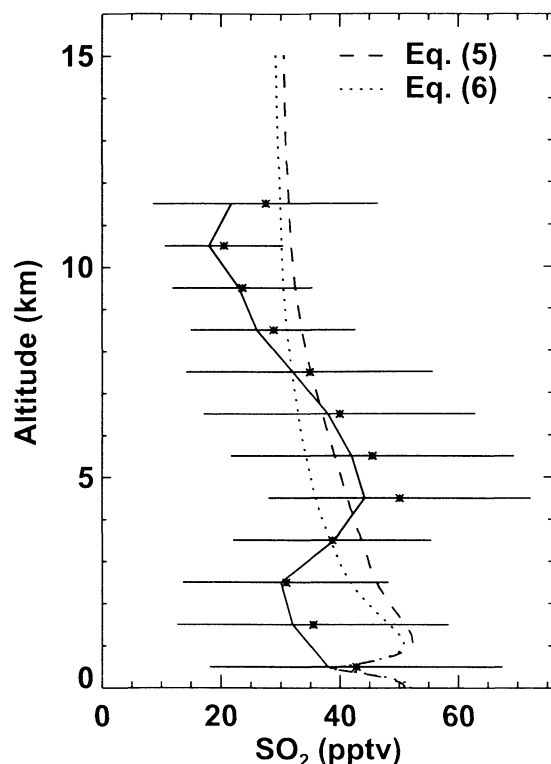


Figure 15. Same as Figure 14 but for SO₂. The concentration of SO₂ at 500 m is specified in the model as the observed median value at 0–1 km.

opposite effects on the oxidizing capacity of the atmosphere (defined largely by OH concentrations) over the tropical Pacific. The observed tendency of pollutant outflow to enhance OH concentrations near the source regions and reduce OH concentrations afar is consistent with the global 3-D model result by Wang and Jacob [1988] that fossil fuel and industrial emissions in general boost OH concentrations in the northern hemisphere while depressing OH in the southern hemisphere.

Convection during PEM-Tropics B was more vigorous than during PEM-Tropics A. Using CH₃I as a tracer for convective transport in a 1-D model, we found a turnover timescale of 10 days by convection during PEM-Tropics B, twice as fast as during PEM-Tropics A. Observations of CH₃I from PEM-Tropics A and B suggest that convective outflow in the tropics is evenly distributed with altitude up to the DC-8 flight ceiling of 12 km, implying stronger outflow in the middle troposphere than predicted in a general circulation model [Wang *et al.*, 2000]. Observations of CH₃I above 12 km are necessary to examine if such a distribution profile of convective outflow extends into the top layer of the tropical troposphere.

Model simulated HO₂, CH₂O, H₂O₂, CH₃OOH, and PAN concentrations showed reasonable agreement with the observations. Although simulated CH₂O concentrations are consistently higher by ~25 pptv than observed medians, this level of agreement is still noteworthy in light of large discrepancies found in previous field campaigns. Proper care needs to be taken to account for CH₂O data below the LOD. Despite of the good agreement for HO₂, model simulated OH concentrations were consistently lower (~25%) than observations above 6 km. The agreement between simulated and observed peroxides is not as good as that for PEM-Tropics A; model simulated CH₃OOH are consistently higher by ~100 pptv. The discrepan-

cies between simulated and observed OH and peroxides are, however, within the measurement uncertainties. Unlike the model overestimates of HNO₃ in previous studies, simulated HNO₃ concentrations during PEM-Tropics B were much lower than observations. Invoking N₂O₅ hydrolysis in aerosols could mitigate the underestimates. It is, however, difficult to reconcile the difference between PEM-Tropics A and B. During PEM-Tropics A the model predicted concentrations of HNO₃ close to or moderately higher than the observations without invoking N₂O₅ hydrolysis in aerosols.

The comparatively faster convective transport and less influence from long-range transport of pollutants during PEM-Tropics B than A makes PEM-Tropics B a good case for studying the effects of convection on chemistry over the tropics. Convective transport of CH₃OOH was the dominant primary HO_x source above 10 km. The corresponding increase in HO_x and O₃ production in the upper troposphere was offset by the decrease in the lower and middle troposphere due to convective scavenging of another HO_x reservoir, H₂O₂. Convective transport increased column O₃ production by 4% but decreased column HO_x production and OH concentrations by 7 and 4%, respectively. We could not analyze the effect of convection on enhancing H₂O concentrations in our model. Convection could in this sense be a primary driver for HO_x chemistry in the tropical troposphere since the reaction of O(¹D) and H₂O provides the dominant primary HO_x source in the middle and lower troposphere.

The column budget of O₃ had a large deficit; column production was only half of the loss. The deficit is likely compensated for by transport of O₃ from other regions of the tropics since transport from northern industrial continents had little impact on O₃ and NO_x concentrations. Convective transport of reactive nitrogen also imposed a budget deficit of NO_x. The loss of upper tropospheric HNO₃ and PAN due to the subsiding branch of convection could not be compensated for by the ascending branch because of convective scavenging of HNO₃ and very low concentrations of PAN in the lower troposphere. In the lower troposphere, thermal decomposition of PAN transported by subsidence provided the necessary NO_x source to account for scavenging and deposition of HNO₃. The implied NO_x source in the free troposphere (above 4 km) is 0.4–1 Tg N yr⁻¹ over the tropics (20°S – 20°N). The likely sources are in situ marine lightning or transport of NO_x from continental lightning. The former source is supported by GEOS observations of marine cumulus clouds along the calculated back trajectories of high NO_x encounters. The magnitude of this source highlights the need to understand NO_x production by marine lightning.

Concentrations of DMS were barely detectable in the free troposphere with 60%–100% observational data below the LOD (1 pptv). The widely adopted rate constants by Hynes *et al.* [1986] were measured for atmospheric conditions near the surface. For free tropospheric studies, we derived new rate constants for the DMS–OH adduct reaction on the basis of recent kinetics data at low pressures and temperatures by Hynes *et al.* [1995] and Barone *et al.* [1996]. A large uncertainty in the new rate constants is the pressure dependence of *k*₁. We adopted one pressure-independent rate expression and one with a linear pressure dependence between 100 and 760 Torr as the lower and upper limits, respectively. Convective transport supplied far higher DMS concentrations in the free troposphere in the model than were observed. Either abnormal enhancements of OH concentrations around convective events observed in previous field campaigns or oxidation mechanisms other than reaction with OH and NO₃ are necessary to explain the observed low DMS concentrations in the tropical

free troposphere. Our results suggest that caution must be exercised when using observed very low concentrations of DMS as evidence of little contribution by DMS to free tropospheric SO₂. Although more work is needed to clarify potential DMS oxidation pathways, it is clear that the amount of DMS transported by convection was large enough to explain observed SO₂ concentrations in the free troposphere over the tropical Pacific.

Acknowledgments. We thank Anthony Hynes for helpful comments on sulfur chemistry and William Grant and Gao Chen for their suggestions. We thank Francois Ravetta and Daniel Jacob for providing the merged data files used in this work and anonymous reviewers for their comments. This work was supported in part by the National Aeronautics and Space Administration Global Tropospheric Experiment Program. The contribution of PHW was supported by the National Science Foundation through grant ATM-9910912.

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(Received September 7, 2000; revised January 21, 2001; accepted January 24, 2001.)