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On the origin of tropospheric ozone and NO_x over the tropical South Pacific

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Abstract. The budgets of ozone and nitrogen oxides (NO_x = NO + NO₂) in the tropical South Pacific troposphere are analyzed by photochemical point modeling of aircraft observations at 0–12 km altitude from the Pacific Exploratory Mission-Tropics A campaign flown in September–October 1996. The model reproduces the observed NO₂/NO concentration ratio to within 30% and has similar success in simulating observed concentrations of peroxides (H₂O₂, CH₃OOH), lending confidence in its use to investigate ozone chemistry. It is found that chemical production of ozone balances only half of chemical loss in the tropospheric column over the tropical South Pacific. The net loss is 1.8×10^{11} molecules cm⁻² s⁻¹. The missing source of ozone is matched by westerly transport of continental pollution into the region. Independent analysis of the regional ozone budget with a global three-dimensional model corroborates the results from the point model and reveals the importance of biomass burning emissions in South America and Africa for the ozone budget over the tropical South Pacific. In this model, biomass burning increases average ozone concentrations by 7–8 ppbv throughout the troposphere. The NO_x responsible for ozone production within the South Pacific troposphere below 4 km can be largely explained by decomposition of peroxyacetylnitrate (PAN) transported into the region with biomass burning pollution at higher altitudes.

1. Introduction

Ozone in the tropical troposphere is a major global source of OH radicals and hence plays an important role in maintaining the oxidizing power of the atmosphere [Thompson, 1992]. Ozone is produced in the troposphere by photochemical oxidation of CO and hydrocarbons in the presence of nitrogen oxide radicals (NO_x = NO + NO₂). NO_x is in general a limiting precursor for ozone production [Chameides et al., 1992]. Loss of ozone is principally by photolysis and by chemical reactions with OH and HO₂. Several aircraft campaigns of the NASA Global Tropospheric Experiment (GTE) program have

focused on improving our understanding of ozone chemistry and the resulting ozone budget in different regions of the tropical troposphere [Harriss et al., 1988, 1990; Hoell et al., 1996, 1997; Fishman et al., 1996]. The latest of these campaigns, the Pacific Exploratory Mission-Tropics A (PEM-Tropics A), surveyed the distributions of ozone, NO_x, CO, hydrocarbons, and related species over the tropical South Pacific in September–October 1996 [Hoell et al., this issue]. We present here a photochemical model analysis of the PEM-Tropics data aimed at constructing a budget of ozone and NO_x for the South Pacific troposphere and understanding the links to other regions of the tropical troposphere.

The South Pacific is the region of the tropical troposphere most remote from human activity. Tropospheric ozone columns are the lowest in the world, with values as low as one third those found in polluted regions of the tropics [Fishman et al., 1990; Kirchhoff et al., 1991; Fishman and Brackett, 1997]. The timing of PEM-Tropics corresponded to the end of the dry season in the southern tropics, when considerable biomass burning takes place in South America, Africa, and Oceania. The GTE/Transport and Atmospheric Chemistry Near the Equatorial Atlantic (TRACE A) campaign conducted in September 1992 [Fishman et al., 1996] demonstrated that biomass burning in southern Africa and Brazil causes seasonal enhancements in tropospheric ozone by a factor of 2 over the tropical South Atlantic [Olson et al., 1996; Thompson et al., 1996]. The TRACE A observations confirmed previous evidence of large-scale biomass burning pollution over the tropical South Atlantic from satellite observations of ozone and CO [Fishman et al., 1990; Watson et al., 1990]. Fishman et al. [1991] proposed that long-range transport of

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biomass burning pollution would affect ozone on a hemispheric scale. A major objective of PEM-Tropics A was to determine the extent of seasonal biomass burning influence over the South Pacific.

In addition to biomass burning, natural sources of NO_x from soils and lightning contribute to ozone formation in the tropical troposphere. Using the first aircraft observations of NO_x over the South Pacific, *Liu et al.* [1980] proposed a self-sustaining model for ozone in the tropical troposphere where net production of ozone in the upper troposphere balances net loss in the lower troposphere. Ozone production in their model was sustained by transport of NO_x from the stratosphere, which is now known to be negligibly small [*Kasibhatla et al.*, 1991; *Penner et al.*, 1991; *Lamarque et al.*, 1996]. More recent aircraft observations of NO_x in the tropical troposphere have demonstrated major primary sources from lightning [*Drummond et al.*, 1988; *Smyth et al.*, 1996; *Crawford et al.*, 1997], soils [*Jacob and Wofsy*, 1988, 1990], and biomass burning [*Andreae et al.*, 1988; *Singh et al.*, 1996b; *Smyth et al.*, 1996]. A notable feature of these three NO_x sources is that they are all continental (lightning over the oceans is extremely infrequent).

A photochemical model analysis of the TRACE A observations [*Jacob et al.*, 1996] indicated a chemical balance for ozone on the scale of the tropospheric column. On the basis of this analysis, *Jacob et al.* [1996] proposed a schematic for the ozone budget in the tropical troposphere where NO_x pumped convectively over the tropical continents (upwelling branches of the Walker circulation) promotes ozone production in the upper troposphere, to be balanced by ozone depletion in the lower troposphere after the air subsides over the subtropical anticyclones (downwelling branches of the Walker circulation). A global three-dimensional model analysis by *Wang et al.* [1998c] finds a close balance between zonal mean production and loss of ozone in the tropical troposphere, suggesting that the tropical troposphere is self-sustaining with respect to ozone, at least on a zonal scale.

The budget of ozone in the troposphere is strongly linked to that of NO_x. Considering that the lifetime of NO_x with respect to oxidation to HNO₃ is only of the order of 1 day, one would expect NO_x concentrations to decay rapidly downwind of the continents. However, observations over the tropical oceans indicate free tropospheric NO_x concentrations of typically 10-50 parts per trillion by volume (pptv) [*Carroll and Thompson*, 1995; *Emmons et al.*, 1997], which play a major role in ozone production and are much higher than would be expected from direct transport of primary NO_x from the continents. It has been proposed that chemical recycling of NO_x from HNO₃ and other non-radical reservoirs, including in particular peroxyacetyl nitrate (PAN), could play a major role in maintaining NO_x concentrations over the oceans [*Singh*, 1987]. However, previous photochemical model analyses of observations in the tropical marine troposphere concluded that chemical recycling based on known reactions was insufficient to maintain NO_x concentrations at their observed levels, and speculated on the possibility of fast conversion of HNO₃ to NO_x in aerosols [*Chatfield*, 1994; *Hauglustaine et al.*, 1996; *Jacob et al.*, 1996; *Lary et al.*, 1997].

2. Data Summary

Two aircraft participated in the PEM-Tropics A campaign, a DC-8 and a P-3B. Both carried instrumentation for measurement of ozone, NO, CO, hydrocarbons, peroxides, and a

number of other species. The DC-8 included measurements of PAN and HNO₃ and had a higher ceiling (12 km altitude, as compared to 7 km for the P-3B). The analysis here focuses on the DC-8 data.

The DC-8 operated from four bases: Tahiti, Easter Island, Christchurch (New Zealand), and Fiji. Sorties out of these bases examined the chemical composition of the South Pacific troposphere over a domain stretching from the warm pool of the equatorial Pacific to the subsiding region of the tropical eastern Pacific, and from the intertropical convergence zone (ITCZ) to high southern latitudes (Figure 1). The ITCZ was found in transit flights to be located at 7°-9°N.

Tables 1a and 1b list median concentrations of ozone, NO_x, PAN, HNO₃, peroxides, CO, and selected hydrocarbons observed at different altitudes in the equatorial and tropical South Pacific. We divide the data into two latitude bands, 0°-10°S and 10°S-30°S, because of the pronounced differences in ozone and CO concentrations (Figure 2) [see also *Gregory et al.*, this issue]. Figure 3 compares the observations from PEM-Tropics A in the latitude band 0°-30°S to previous tropical data collected in the same season over the northwestern Pacific (Pacific Exploratory Mission-West Phase A) (PEM-West A) [*Hoell et al.*, 1996] and over the South Atlantic (TRACE A) [*Fishman et al.*, 1996]. While the vertical profiles of ozone and PAN (both photochemical products) from PEM-West A fall on the low end of the PEM-Tropics data, the profiles of CO and ethane (tracers for urban/industrial pollution or biomass burning) are shifted to somewhat higher concentrations. The data from TRACE A exhibit higher concentrations for several observed species. The largest differences are found for PAN: above 2 km, the TRACE A PAN concentration is at least a factor 4 higher than in the other two data sets.

The statistical distribution of ozone and CO at 4-8 km during PEM-Tropics A is displayed in Figure 2 for the five geographical regions defined in Figure 1. Both species follow similar patterns. The cleanest air was observed over the western equatorial Pacific and north of the subtropical convergence zone (SPCZ). Here, median mixing ratios were 27-32 ppbv for ozone and 56-58 ppbv for CO. The variability is also very small: the central 50% of the data span a range of less than 10 ppbv. The highest median values for both species were found over the western tropical Pacific (south of the SPCZ), with values of 61 ppbv for ozone and 78 ppbv for CO. These data also show a large variability, indicating the influence of episodic pollution events. During PEM-Tropics A, several layers with continental pollution were encountered in westerly air flow which originated from biomass burning in Africa or South America [*Talbot et al.*, this issue; *Fuelberg et al.*, this issue]. Figure 2 shows occasional ozone and CO mixing ratios in excess of 100 ppbv for the tropical western Pacific south of the SPCZ. Almost 25% of the data from this region had ozone mixing ratios above 80 ppbv. This pollution influence decreased from west to east, reflecting dispersion and photochemical decay.

3. Model Description

We use the Harvard photochemical point model to reconstruct the photochemical environment along the DC-8 flight tracks. The model calculates diurnal steady-state concentrations of radicals and chemical intermediates using as constraints the ensemble of observations from the aircraft. Diurnal steady state is defined by repeatability of concentrations over

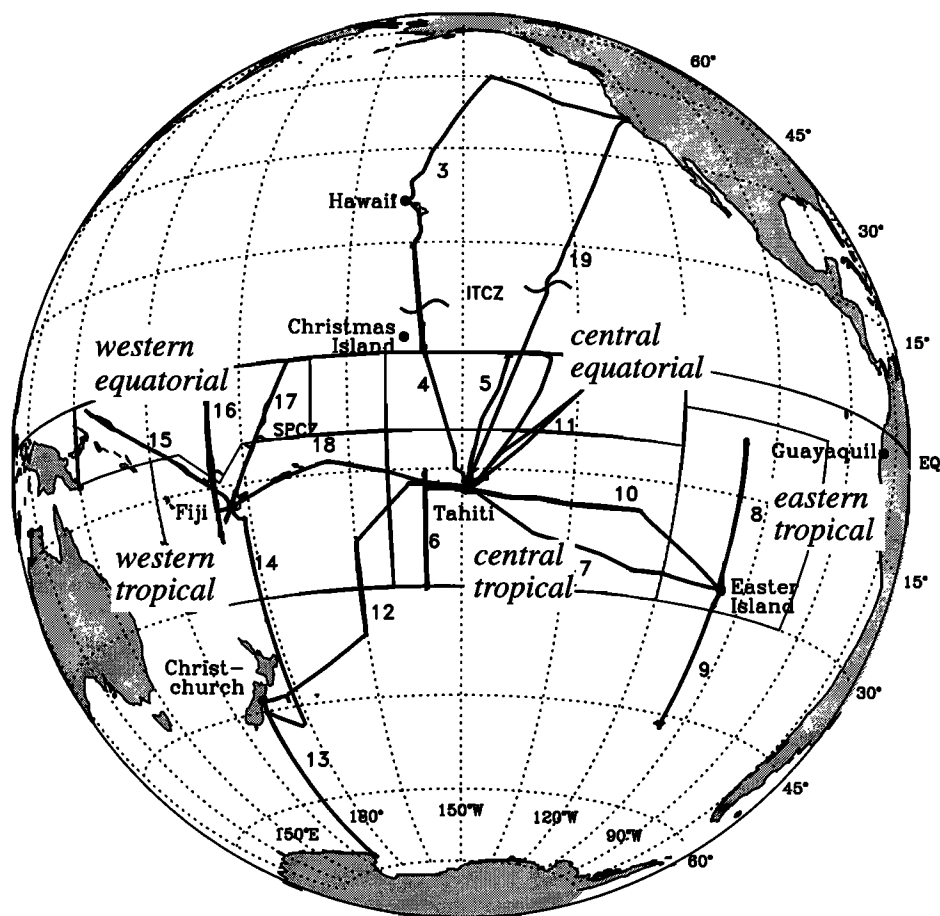


Figure 1. Flight tracks of the DC-8 aircraft during PEM-Tropics A. Thin solid lines delineate the regions discussed in the text. Aircraft crossings of the intertropical convergence zone (ITCZ) and the South Pacific convergence zone (SPCZ) are indicated by tilde symbols.

a 24-hour cycle. The chemical mechanism is based on the compilations of *DeMore et al.* [1997] and *Atkinson et al.* [1997] with updates (e.g. pressure-dependent quantum yields for acetone photolysis [*McKeen et al.*, 1997]). All model results were submitted to the NASA Langley Distributed Active Archive Center (DAAC) archive and are also available from the GTE web site <http://www-gte.larc.nasa.gov>.

Actinic fluxes are calculated with a six stream discrete ordinate radiative transfer model for the Rayleigh scattering atmosphere [*Logan et al.*, 1981]. The overhead ozone column for the radiative transfer calculation is specified from daily total ozone mapping spectrometer (TOMS) observations of total ozone columns, subtracting the ozone column below the aircraft as measured by the differential absorption laser (DIAL) instrument and interpolating when necessary. In order to account for cloud scattering and absorption, we scaled the actinic flux for each individual data point with the ratio of observed to clear-sky modeled photolysis frequencies in two wavelength regimes: for wavelengths up to 310 nm a correction factor for $j(\text{O}^1\text{D})$ was applied, above 310 nm we used a correction factor for $j(\text{NO}_2)$. Median correction factors were 1.21 for $j(\text{NO}_2)$ and 1.03 for $j(\text{O}^1\text{D})$.

For model input the observations were merged over 60 s time intervals. Measurements with a higher sampling frequency were averaged. An observation was considered valid only when all mandatory species (O_3 , NO_x , H_2O , CO , HNO_3 , PAN, peroxides) covered at least 25% of the interval. Observations of water vapor, CO , CH_4 , HNO_3 , PAN, peroxides, and

non-methane hydrocarbons were interpolated for a maximum of 5 min when necessary; remaining gaps in CH_4 , HNO_3 , PAN, and nonmethane hydrocarbons were substituted by median values from Table 1b. For the analysis of the NO_x budget (section 6) we used the time resolution of the HNO_3 measurements which had the longest integration times, and we only considered time intervals with observations of both PAN and HNO_3 .

For water vapor we used measurements from the differential absorption CO measurement (DACOM) instrument (available in 70% of all cases) and from the cryogenically chilled mirror. Although both measurements agree on average within 20%, for mixing ratios below 100 ppmv the cryogenically chilled mirror tends to be lower by a factor of 2 to 5. This can be explained partly by the fact that the chilled mirror has a longer response time and seems to undershoot when the aircraft encounters dry air (*J. Barrick*, personal communication, 1997). The DACOM data appear to be more reliable especially in the upper troposphere. However, the relative humidity derived from the DACOM data often exceeds 100% below 220 K, which would indicate a positive bias.

Acetone can act as the major primary source for hydrogen oxide radicals ($\text{HO}_x = \text{OH} + \text{peroxy species}$) in the upper troposphere [*Singh et al.*, 1995; *Jaeglé et al.*, 1997; *McKeen et al.*, 1997; *Arnold et al.*, 1997]. Since there were no measurements of acetone, we prescribed a constant acetone mixing ratio of 0.4 ppbv as a typical value for the southern tropics [*Wang et al.*, 1998b].

Except for NO , all input variables to the model calculation

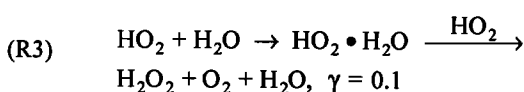
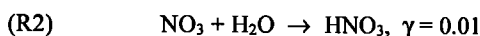
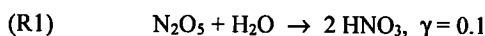
Table 1a. Median Concentrations Over the Equatorial South Pacific (0°-10°S) in PEM-Tropics A

| | Altitude Band, km | | | | | |
|---|-------------------|------|------|------|------|-------|
| | 0-2 | 2-4 | 4-6 | 6-8 | 8-10 | 10-12 |
| Observed quantities | | | | | | |
| Ozone, ppbv | 12 | 23 | 38 | 32 | 37 | 31 |
| NO _x , pptv | 4 | 7 | 15 | 19 | 37 | 28 |
| PAN, pptv | <1 | 2 | 19 | 23 | 32 | 19 |
| HNO ₃ , pptv | 23 | 59 | 74 | 52 | 59 | 27 |
| H ₂ O ₂ , pptv | 1410 | 1270 | 670 | 530 | 200 | 270 |
| CH ₃ OOH, pptv | 1170 | 840 | 360 | 250 | 80 | 110 |
| CO, ppbv | 55 | 53 | 53 | 57 | 61 | 57 |
| Ethane, pptv | 245 | 265 | 290 | 280 | 300 | 290 |
| Propane, pptv | 13 | 16 | 17 | 17 | 18 | 19 |
| Acetylene, pptv | 16 | 18 | 25 | 28 | 31 | 34 |
| Point model results | | | | | | |
| OH, 10 ⁶ molec./cm ³ | 1.64 | 1.76 | 1.11 | 1.35 | 0.91 | 0.66 |
| HO ₂ , 10 ⁶ molec./cm ³ | 139 | 129 | 86 | 77 | 39 | 34 |
| CH ₃ O ₂ , 10 ⁶ molec./cm ³ | 234 | 166 | 69 | 37 | 13 | 11 |
| HNO ₄ , pptv | <0.1 | 0.1 | 1 | 5 | 19 | 16 |
| CH ₂ O, pptv | 340 | 220 | 130 | 100 | 50 | 40 |

Data collected in September-October 1996 over the equatorial regions shown in Figure 1. Model values are 24-hour averages. This table contains 1430 values for species with 60 s sampling time or less, 380 hydrocarbon samples, and 620 model runs.

are assumed constant over the diurnal cycle. Because of the rapid cycling between NO and NO₂, we specify instead total NO_x¹ (= NO + NO₂ + NO₃ + 2•N₂O₅ + HNO₄ + HONO) as constant and calculate the concentrations of the NO_x¹ components as time-dependent variables over the diurnal cycle [Jacob *et al.*, 1996]. The concentration of NO_x¹ is adjusted iteratively to match the observed NO concentration at the local time of the observation. Observations of NO₂ are not used to constrain the model and serve instead for model evaluation (section 4).

The chemical mechanism contains three heterogeneous reactions:



The reaction probabilities γ follow the recommendations of Jacob [1998] with the upper limit for (R2). The aerosol surface area was estimated from the condensation nuclei (0.004-1 μm) measurements using mean correlations between surface area

and number density of aerosols (0.007-6 μm) measured aboard the P-3 aircraft in two altitude regimes.

Because of the requirement of concurrent measurements of NO, peroxides, and CO, model results are available only for about 40% of the PEM-Tropics A flight period. We checked the representativeness of the model data set in various regions of the South Pacific by comparing plots of the frequency distribution of the key species NO, O₃, H₂O, H₂O₂, and CH₃OOH from both the complete observational and the model data set in altitude bands of 2 km. Most species compare well in all regions except above 10 km where sampling of some species is relatively sparse: in that altitude range the model data have significant low biases for NO (factor 0.48) over the central tropical Pacific, and for ozone (factor 0.55) over the western tropical Pacific south of the SPCZ. There are no model data above 10 km in the eastern tropical Pacific.

A different aspect of representativeness is the question of whether the PEM-Tropics observations represent average conditions for the southern Pacific troposphere in September. While the meteorological data indicate that temperatures and flow patterns in 1996 were close to the climatological mean [Fuelberg *et al.*, this issue], the ozonesonde data from Christchurch and Tahiti exhibit some record high values during the

Table 1b. Median Concentrations Over the Tropical South Pacific (10°S–30°S) in PEM-Tropics A

| | Altitude Band, km | | | | | |
|---|-------------------|------|------|------|------|-------|
| | 0-2 | 2-4 | 4-6 | 6-8 | 8-10 | 10-12 |
| Observed quantities | | | | | | |
| Ozone, ppbv | 28 | 50 | 59 | 43 | 44 | 45 |
| NO _x , pptv | 3 | 22 | 26 | 18 | 58 | 98 |
| PAN, pptv | 1 | 19 | 89 | 43 | 48 | 42 |
| HNO ₃ , pptv | 18 | 145 | 155 | 60 | 65 | 47 |
| H ₂ O ₂ , pptv | 930 | 1040 | 620 | 560 | 240 | 130 |
| CH ₃ OOH, pptv | 880 | 480 | 250 | 310 | 90 | < 35 |
| CO, ppbv | 58 | 68 | 70 | 59 | 63 | 58 |
| Ethane, pptv | 310 | 380 | 400 | 340 | 350 | 360 |
| Propane, pptv | 22 | 22 | 24 | 22 | 26 | 27 |
| Acetylene, pptv | 52 | 67 | 68 | 51 | 52 | 53 |
| Point model results | | | | | | |
| OH, 10 ⁶ molec./cm ³ | 1.47 | 1.27 | 1.17 | 0.94 | 1.04 | 0.96 |
| HO ₂ , 10 ⁶ molec./cm ³ | 121 | 115 | 78 | 61 | 39 | 22 |
| CH ₃ O ₂ , 10 ⁶ molec./cm ³ | 217 | 90 | 49 | 33 | 13 | 5 |
| HNO ₄ , pptv | < 0.1 | 0.7 | 3 | 5 | 28 | 29 |
| CH ₂ O, pptv | 280 | 200 | 125 | 80 | 65 | 50 |

Data collected in September–October 1996 over the tropical regions shown in Figure 1. Model values are 24-hour averages. This table contains 3780 values for species with 60 s sampling time or less, 1182 hydrocarbon samples, and 1387 model runs.

time of the expedition (J. Logan, personal communication, 1997).

4. Cycling of NO and NO₂

Comparisons between modeled and observed NO₂/NO concentration ratios have been used previously to evaluate NO_x photochemistry in models and to assess the quality of the NO₂ measurements [e.g., Chameides *et al.*, 1990; Davis *et al.*, 1993; Schultz, 1995; Crawford *et al.*, 1996]. Many previous studies found that model-calculated NO₂/NO ratios are systematically lower than observed ratios by a factor of about 1.5. This discrepancy showed a tendency to increase for cleaner air, that is, closer to the limit of detection (LOD) for the NO_x measurements [Schultz, 1995; Crawford *et al.*, 1996]. In PEM-West A, Crawford *et al.* [1996] found a median ratio of experiment to theory of 3.3. Their analysis led to the conclusion that the measurement of NO₂ which was made with an older version of the two photon laser induced fluorescence (TP-LIF) instrument [Bradshaw *et al.*, 1985; Sandholm *et al.*, 1990] was prone to interferences with other photolabile NO_y compounds. For PEM-Tropics A the TP-LIF technique was improved by installing two new lasers with enhanced power

and by increasing the airflow. For the photodissociation of NO₂ the previously used Xenon lamp was replaced by a pulsed laser. All three improvements were expected to reduce wall losses and interference effects on the NO₂ measurement (S. Sandholm, personal communication, 1997).

Figure 4 displays the ratio of the modeled versus observed NO₂/NO ratio in PEM-Tropics A as a function of altitude. Only data with NO₂ photolysis frequencies $j(\text{NO}_2)$ greater than $7 \times 10^{-3} \text{ s}^{-1}$ were used in order to prevent a possible bias from incorrect NO_x estimates in the point model. The model-calculated NO₂/NO ratios are generally too high by about 10%. This is well within the stated uncertainties of the measurements of NO₂ and $j(\text{NO}_2)$ (20–30% and 10%, respectively).

Below 2 km a systematic negative bias of about 20% is observed which is still within the stated uncertainties, especially since NO_x concentrations were very low. However, halogen chemistry in the marine boundary layer could also cause this bias. We were able to reconcile the modeled NO₂/NO ratio with the observations below 2 km by introducing a chlorine atom concentration of $10^5 \text{ molecules cm}^{-3}$ as suggested from observations of hydrocarbon ratios over the tropical western Pacific [Singh *et al.*, 1996a]. Under these conditions the ClO + NO reaction is a significant pathway

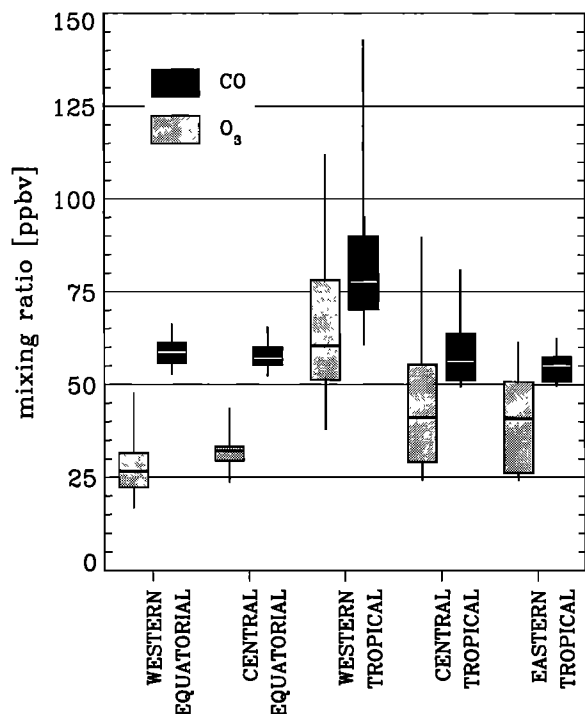


Figure 2. Statistical distributions of ozone and CO mixing ratios at 4–8 km altitude in the five PEM-Tropics A regions defined in Figure 1. Horizontal lines are median values, boxes span the central 50% of the probability distribution, and the vertical lines cover the central 90%. The individual data are 1 min. averages.

converting NO to NO₂. Sensitivity calculations with BrO levels of 10^7 molecules cm⁻³ [Vogt *et al.*, 1996] or I_x (= HOI + HI + IO + I + minor components) concentrations of 3.8×10^7 molecules cm⁻³ [Davis *et al.*, 1996b] showed no significant effect on the NO₂/NO ratio.

5. Peroxides

The peroxides H₂O₂ and CH₃OOH are produced by recombination of peroxy radicals and have lifetimes of 1–2 days with respect to photolysis and reaction with OH for the PEM-Tropics A conditions. One would therefore expect H₂O₂ and CH₃OOH to be in general near chemical steady state, and the ability of the model to reproduce this steady state provides a test for the peroxy radical concentrations and hence the ozone production rates calculated by the model. In our calculations we use the observed peroxide concentrations as model constraints and examine the resulting imbalance between photochemical loss and photochemical production as diagnostic of departure from steady state. This approach has the advantage of not imposing the assumption of steady state for peroxides on the calculation of HO_x concentrations.

Figure 5 shows the balance of simulated 24-hour-averaged chemical loss and production rates for H₂O₂ and CH₃OOH as a function of altitude. Between 2 and 8 km the balance is generally within 10% for H₂O₂ and 15% for CH₃OOH. Below 2 km the agreement is still within 10% for CH₃OOH, but results for H₂O₂ indicate a missing sink of magnitude comparable to chemical loss. This missing sink can be attributed to wet and dry deposition, which is not included in the point model. Above 8 km the scatter increases substantially, and the model

underestimates the source of CH₃OOH by 40–130%, while the H₂O₂ budget remains balanced within 10–40% on average. Deep convection elevates CH₃OOH in the upper troposphere above chemical steady state, while having little impact on H₂O₂ due to scavenging by the convective precipitation [Prather and Jacob, 1997; Jaeglé *et al.*, 1997]. During PEM-Tropics A, Cohan *et al.* [this issue] found that CH₃OOH concentrations in deep convective outflow at 8–12 km altitude were elevated by a factor of 6 relative to background, while H₂O₂ concentrations were elevated only by 50%. Using CH₃I as a chemical clock, they estimated a timescale of 2–3 days for the decay of the convective enhancement of peroxides in the upper troposphere; this timescale is still relatively short compared to the 10 day turnover time for the upper troposphere [Prather and Jacob, 1997].

Therefore it does not appear that convective transport alone can explain the imbalance in the CH₃OOH budget in Figure 5. Another contributing factor could be an underestimate of the rate constant for the CH₃O₂ + HO₂ reaction which is uncertain by about a factor of 3 at temperatures around 220 K [DeMore *et al.*, 1997].

Previous studies of the PEM-West and TRACE A data [Davis *et al.*, 1996a; Jacob *et al.*, 1996; Crawford, 1997] calculated peroxide concentrations from chemical steady state and compared these to the observations. Jacob *et al.* [1996] report a significant underestimate of H₂O₂ model concentrations (median ratios of model/observed of 0.99, 0.87, and 0.57 in the altitude bins 0–4, 4–8, and 8–12 km), and an even worse imbalance for CH₃OOH (ratios are 0.59, 0.79, and 0.28). For PEM-West B the model of Crawford [1997] typically overestimates H₂O₂ by about 30% in the equatorial region below 10 km, except for the surface layer where deposition plays a role. On the other hand, CH₃OOH is generally predicted within about 20% up to 8 km, and it is underpredicted by a factor of 2.4 and 5 in the altitude bins of 8–10 and 10–12 km, respectively. For PEM-West A, Davis *et al.* [1996a] give only one median value for the ratio of observed to modeled peroxide concentrations above 1 km (0.92 for H₂O₂ and 0.62 for CH₃OOH). With the exception of Jacob *et al.* [1996] all these studies indicate that a photochemical steady-state model can successfully simulate H₂O₂ in the free troposphere, whereas CH₃OOH is systematically underestimated by the models above 8 km.

6. Sources and Sinks of NO_x

The lifetime of NO_x with respect to photochemical loss, as calculated by our photochemical model for PEM-Tropics A conditions, is 1–5 days for most of the tropical South Pacific troposphere (Table 2). The PEM-Tropics study region is sufficiently far from most known primary sources of NO_x (fossil fuel combustion, biomass burning, soil emissions, lightning) that we would expect NO_x to be generally near chemical steady state, maintained by recycling of HNO₃ and PAN.

Figure 6 displays mean modeled NO_x budgets for the equatorial and tropical regions, constrained with observations of NO, PAN, and HNO₃. The chemical mechanism of the model takes into account the cycling between NO, NO₂, HNO₃, PAN, and HO₂NO₂. Methyl nitrate is also included as NO_x source because observations of several pptv even above 6 km suggested it might be important under conditions of very low HNO₃ and PAN (F. Flocke, personal communication, 1997).

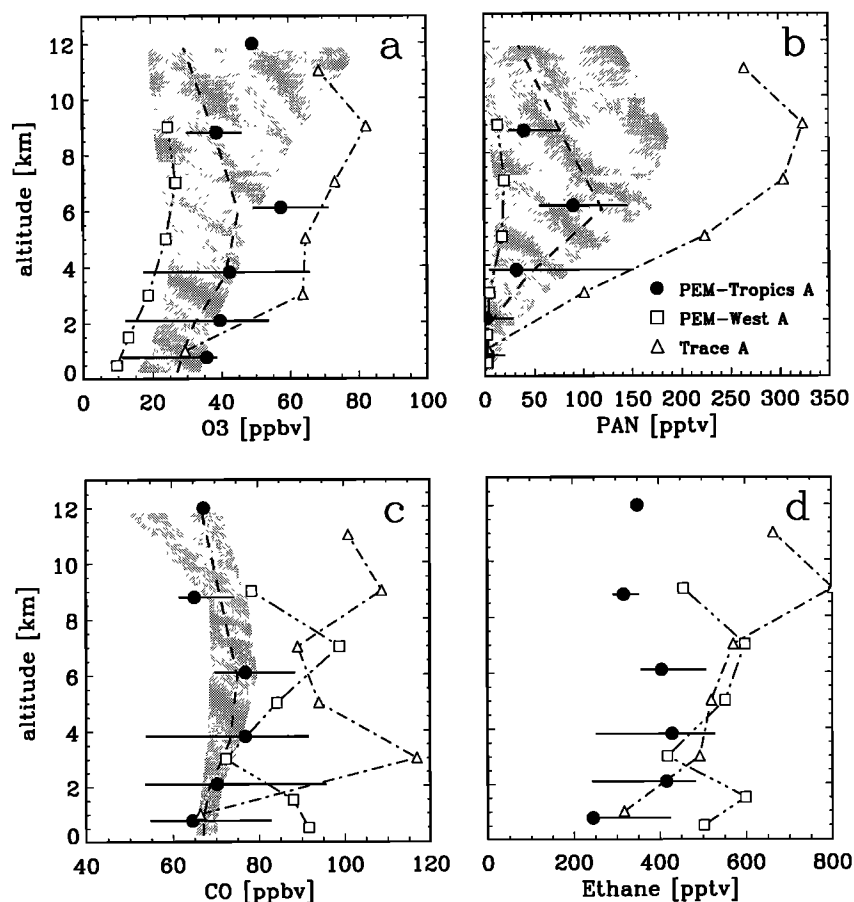


Figure 3. Median vertical profiles of mixing ratios for (a) ozone, (b) PAN, (c) CO, and (d) ethane observed over the equatorial and tropical South Pacific (0° - 30° S, 170° E- 120° W) during PEM-Tropics A, over the tropical north-western Pacific (0° - 18° N, 120° E- 170° E) during PEM-West A, and over the tropical South Atlantic (0° - 25° S, 30° W- 10° E) during TRACE A. Also shown (dashed lines) are monthly mean September values from a global 3-D model simulation [Wang *et al.*, 1998a] for the PEM-Tropics A region. Error bars for the PEM-Tropics A observations denote the central 50% range of the data, and the grey shading represents the central 90% range of monthly mean 3-D model concentrations for the ensemble of grid boxes over the equatorial and tropical South Pacific.

We corrected the rates for production and loss of PAN at every time step as described by [Jacob *et al.*, 1996].

Thermal decomposition of PAN is the dominant production term for NO_x below 4 km, closely balancing the loss of NO_x (Figure 6). We conclude that PAN provides the main source of NO_x at these altitudes. Long-range transport of biomass burning pollution was a major source of PAN over the tropical South Pacific during PEM-Tropics A, as shown in Figure 7 by the correlation between PAN and C₂H₂ at 4-8 km.

Above 4 km we find that the chemical source of NO_x is insufficient to balance the loss of NO_x from oxidation, implying a large missing source for NO_x. Such a chemical imbalance in the upper troposphere has been found in previous missions [e.g., Davis *et al.*, 1996a; Jacob *et al.*, 1996]. Recent studies by Jaeglé *et al.* [1998], Prather and Jacob [1997], and Wang *et al.* [1998b] suggest that this imbalance is mostly caused by convective injection and primary production of NO_x from lightning. However, Wang *et al.* [1998b] find evidence of a missing chemical source of NO_x in tropical regions where biomass burning is of importance. Further analysis of the PEM-Tropics A data (M. Schultz *et al.*, Reconciliation of the chemical budget of NO_x in the upper troposphere over the tropical South Pacific, submitted to *J. Geophys. Res.*, 1998)

suggests that large amounts of ammonia emitted by biomass burning may slow down the loss of NO_x by dehydrating the aerosol, while also providing an additional chemical source of NO_x, thus correcting most of the NO_x budget imbalance apparent from Figure 6.

7. Ozone Formation and Loss Rates

Figure 8 displays median production and loss rates of odd-oxygen ($O_x = O_3 + O + NO_2 + HNO_4 + 2 \cdot NO_3 + 3 \cdot N_2O_5 + HNO_3 + PAN + PPN$) as a function of altitude for the equatorial and tropical South Pacific. The chemical budget analysis must be applied to O_x, rather than to O₃, because of the fast chemical cycling within the O_x family. Considering that ozone makes up more than 90% of O_x for the PEM-Tropics A conditions, we will use both terms interchangeably. During PEM-Tropics A the lower 4 km of the troposphere over the tropical South Pacific exhibit net destruction rates of about 2 ppbv d⁻¹ for ozone, while there is about 1 ppbv d⁻¹ net production above 8 km. The crossover at 6 km is similar to results from PEM-West A and B [Davis *et al.*, 1996a; Crawford, 1997].

The geographical distribution of ozone production (Plate 1) shows highest values over the western tropical Pacific

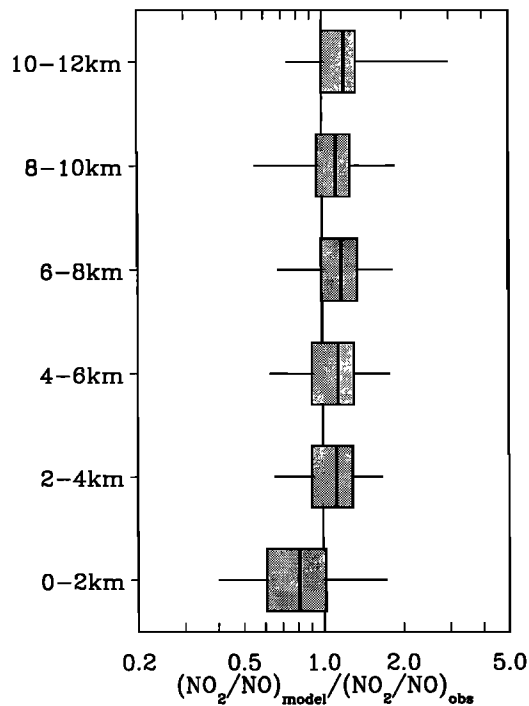


Figure 4. Modeled versus observed NO₂/NO ratios in PEM-Tropics A (0°-30°S) as function of altitude. For explanation of the boxes and whiskers, see caption of Figure 2. Only data with NO₂ photolysis frequencies greater than $7 \times 10^{-3} \text{ s}^{-1}$ are displayed.

where biomass burning influence is strongest (Figure 2). As shown in Table 3, chemical production of ozone balances only about half of the chemical loss for the 0-12 km column over the South Pacific; the column-integrated net loss amounts to about $1.2 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ which is equivalent to

0.35-0.7 Dobson units (DU) per day. This result does not change significantly when we extrapolate the data to the tropopause height of about 16 km (Table 3).

Above 4 km the rates of ozone production and loss over the South Pacific are similar to those computed for the northern tropical Pacific during PEM-West A (Figure 8). Compared to the troposphere over the tropical South Atlantic during TRACE A, production and loss rates over the tropical Pacific are a factor of 2-5 lower.

Our analysis of the photochemical budget for hydrogen peroxides (section 5) revealed some uncertainty regarding the HO_x budget in the upper troposphere. In order to investigate the implications on the calculated budget of ozone, we performed a series of sensitivity simulations, using as reference a simulation constrained by median observed values in the tropical latitude band for the altitude bins of 8-10 km and 10-12 km (Table 1b). In these calculations, water vapor was varied by a factor of 2, the rate coefficient for the HO₂ + CH₃O₂ reaction was varied by a factor of 3, and the acetone concentration was varied from 400 to 50 pptv. From the combination of effects the maximum deviations for P_{O₃} and L_{O₃} were ±35%. The deviation of (P - L)_{O₃} was smaller (-22 to +9%).

Let us now investigate whether the advection of continental air can balance the large observed ozone loss in the South Pacific troposphere. Layers of continental air sampled during PEM-Tropics A contained elevated CO due to pervasive biomass burning on the south tropical continents. The mean enhancement ratio $\Delta\text{O}_3/\Delta\text{CO}$ in these layers was 1.8 mol/mol (*J. Logan*, personal communication, 1997), reflecting the fact that NO_x from continental sources (including biomass burning, lightning, and soil emissions) allowed considerable ozone production. Let us take $\Delta\text{O}_3/\Delta\text{CO} = 1.8 \text{ mol/mol}$ as a general characteristic of continental air advected over the South Pacific; then

$$\nabla F_{\text{O}_3} = \nabla F_{\text{CO}}(\Delta\text{O}_3/\Delta\text{CO}) \quad (1)$$

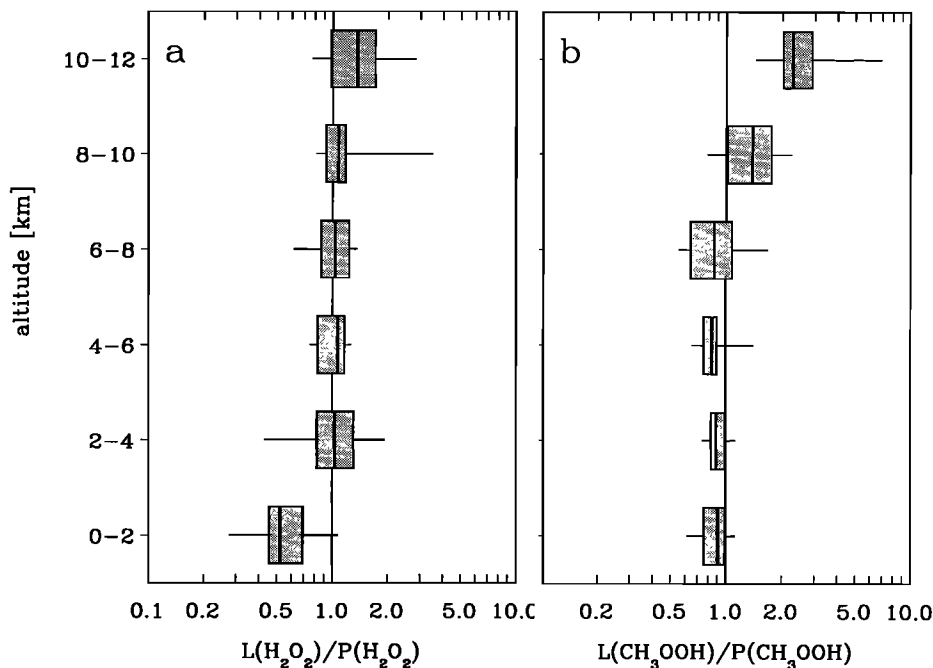


Figure 5. Ratio of 24-hour average point model calculated chemical loss to chemical production rates for (a) H₂O₂ and (b) CH₃OOH in PEM-Tropics A (0°-30°S) as a function of altitude. See caption of Figure 2 for explanation of boxes and whiskers.

Table 2. Median 24-Hour Average Lifetimes for Ozone and NO_x in PEM-Tropics A

| | Altitude Band, km | | | | | |
|--------------------------------|-------------------|-----|-----|-----|------|-------|
| | 0-2 | 2-4 | 4-6 | 6-8 | 8-10 | 10-12 |
| Ozone lifetime, days | | | | | | |
| 0°-10°S | 5 | 7 | 31 | 31 | 110 | 147 |
| 10°S-30°S | 11 | 27 | 48 | 66 | 110 | 201 |
| NO _x lifetime, days | | | | | | |
| 0°-10°S | 0.9 | 1.0 | 1.4 | 1.8 | 5.0 | 7.4 |
| 10°S-30°S | 0.7 | 1.0 | 1.1 | 2.1 | 4.2 | 5.4 |

where ∇F_{O_3} and ∇F_{CO} are the flux divergences of O₃ and CO over the South Pacific, that is, the net influx into the region. The net influx of CO is exclusively from continental pollution. We write a mass balance equation for CO in the tropospheric column over the South Pacific,

$$\nabla F_{CO} + (P - L)_{CO} = 0 \quad (2)$$

where $(P - L)_{CO}$ is the net production of CO over the South Pacific as determined from our photochemical model analysis (Table 3). In equation (2) we have ignored the CO tendency term, which is negligibly small. Equation (2) yields $\nabla F_{CO} = 1.6 \times 10^{11}$ molecules cm⁻² s⁻¹ (Table 3, results for 0-16 km); replacing into equation (1), we obtain $\nabla F_{O_3} = 2.9 \times 10^{11}$ molecules cm⁻² s⁻¹. Comparing to the net column loss of ozone over the South Pacific computed from our photochemical

model analysis, $(L - P)_{O_3} = 0.9 \times 10^{11}$ molecules cm⁻² s⁻¹, we conclude that advection of continental air can readily account for the net influx of tropospheric ozone over the tropical South Pacific. The $\Delta O_3/\Delta CO$ ratio used in our calculation is certainly too high because the aircraft undersampled continental air advected in the lower troposphere from South America, which had a low $\Delta O_3/\Delta CO$ ratio due to fast chemical loss of ozone. A mean $\Delta O_3/\Delta CO$ ratio of 0.6 mol/mol for continental air advected over the South Pacific would close the ozone budget and is in the range of expected values.

Our analysis above indicates that ozone production over the South Pacific driven by influx of PAN and direct influx of ozone from tropical continental regions both provided major sources for ozone in the South Pacific troposphere during PEM-Tropics A. It appears likely that biomass burning made a

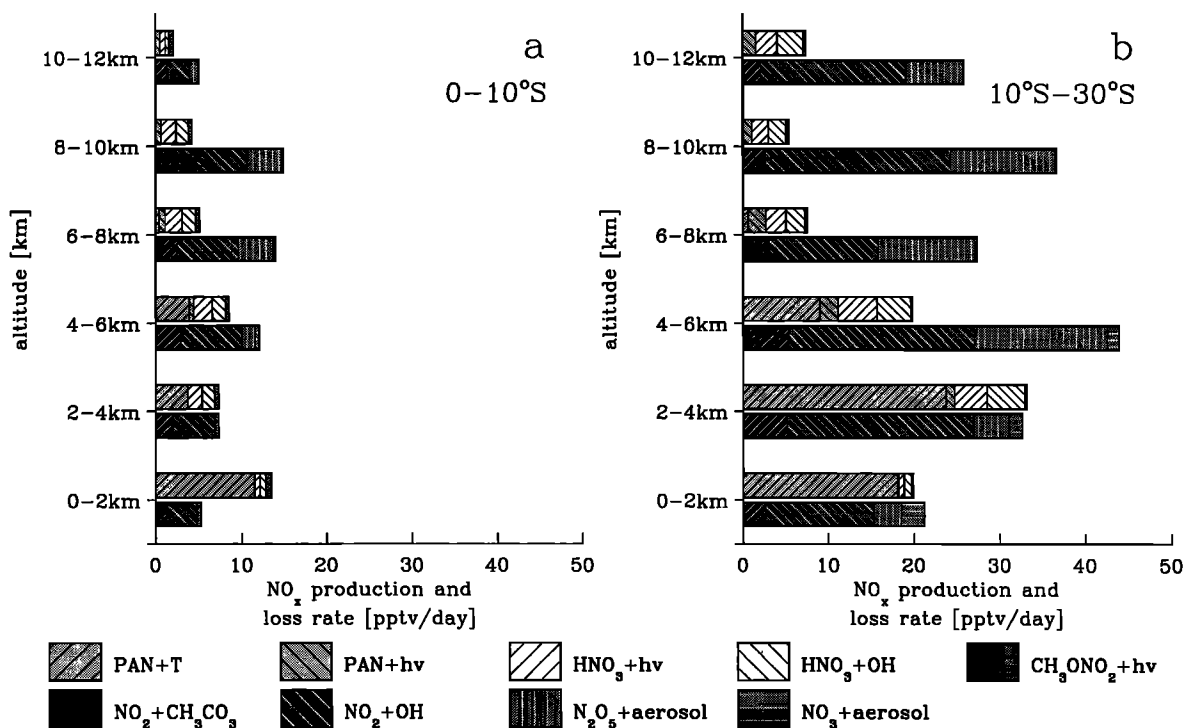


Figure 6. Mean chemical production and loss rates of NO_x calculated over the equatorial and tropical South Pacific during PEM-Tropics A: (a) 0°-10°S and (b) 10°S-30°S. Values are 24-hour averages. The model was constrained with concurrent observations of NO, HNO₃, and PAN. Rates of interconversion between NO_x and PAN are corrected for PAN-CH₃COO₂ cycling as described in the text.

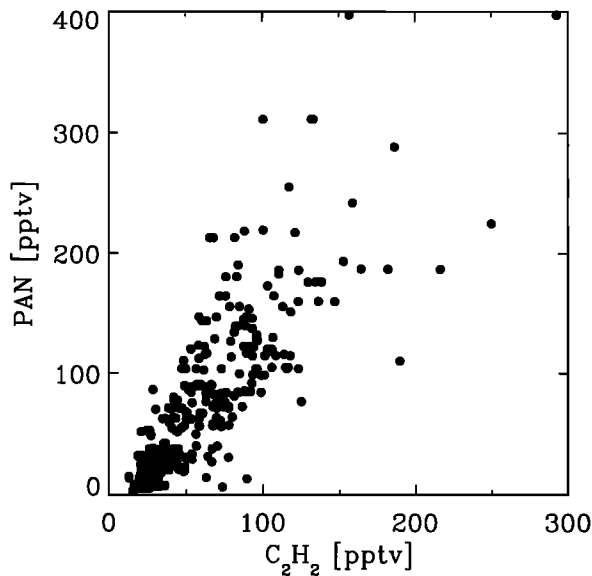


Figure 7. Correlation between PAN and acetylene in the tropical South Pacific (10°S-30°S) during PEM-Tropics A at 4-8 km altitude.

dominant contribution to both of these sources. Ozone and PAN concentrations measured in the free troposphere over Brazil and Africa during TRACE A were considerably higher than in PEM-Tropics A (Figure 3) and were due unambiguously to biomass burning [Singh *et al.*, 1996b; Thompson *et al.*, 1996]. Zonal transport at both tropical and subtropical latitudes [Fuelberg *et al.*, this issue] would supply this biomass burning ozone and PAN to the South Pacific troposphere. As mentioned previously, PAN in PEM-Tropics A was correlated positively with tracers of biomass burning (Figure 7). Although lightning could also have contributed to long-range transport of NO_x over the Pacific, year-round ozonesonde measurements at South Pacific sites (S. Oltmans *et al.*, personal communication, 1997) argue against a major contribution of lightning to ozone in PEM-Tropics A. The ozonesonde data show a pronounced seasonal maximum of ozone in austral spring, during the biomass burning season, consistent with ozonesonde data in the TRACE A region [Olson *et al.*, 1996]. In contrast, lightning peaks in austral summer [Turman and Edgar, 1982].

8. Global 3-D Model Simulation

In order to provide an additional perspective on the large-scale regional budget of ozone over the tropical South Pacific, we analyzed results from the Harvard/Goddard Institute for Space Studies (GISS) global 3-D model [Wang *et al.*, 1998a]. The model uses meteorological fields from the GISS Global Climate Model (GCM) and has 4° × 5° horizontal resolution with nine vertical layers, seven of which are in the troposphere. A suite of 15 chemical tracers including O₃, NO_x, PAN, HNO₃, CO, H₂O₂, and five primary hydrocarbons is simulated, with parameterizations for tracer production and loss derived from point model simulations with a detailed mechanism over a wide range of conditions. Fossil fuel combustion, woodburning, and biomass burning emissions are from J. Logan (manuscript in preparation, 1998). Biogenic

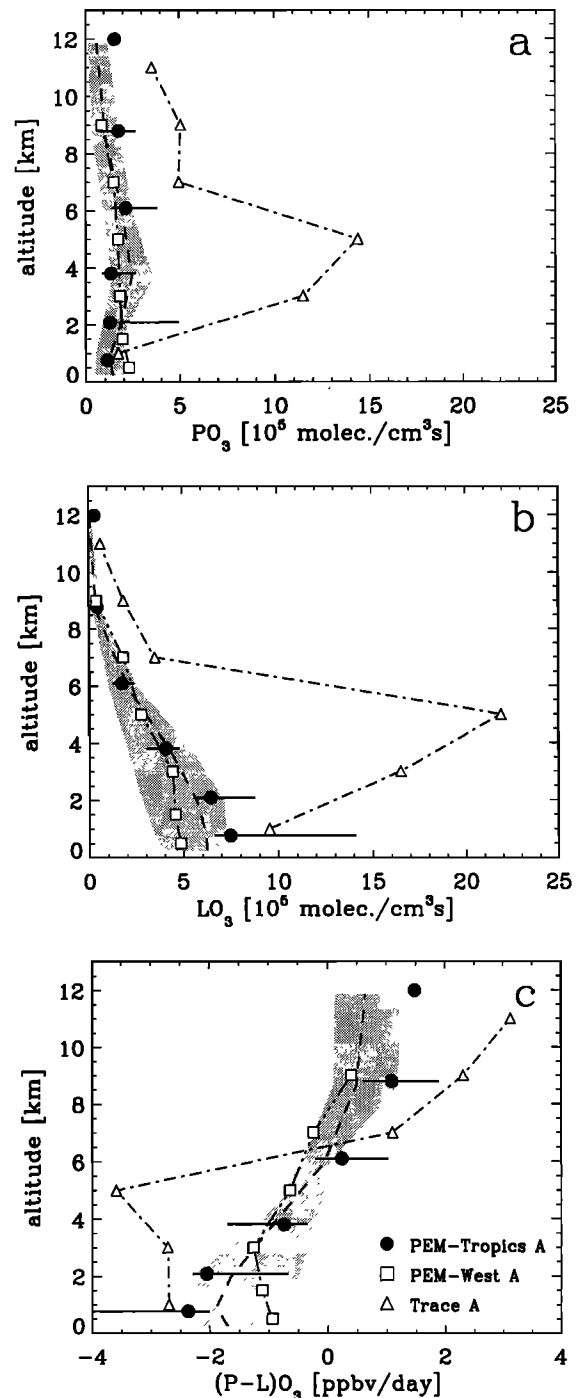


Figure 8. Median profiles of (a) the chemical production rate, (b) the chemical loss rate, and (c) the net production rate (P-L) of ozone over the equatorial and tropical South Pacific during PEM-Tropics A. Values for the northwestern tropical North Pacific during PEM-West A [Davis *et al.*, 1996a] and the tropical South Atlantic during TRACE A [Jacob *et al.*, 1996] are shown for comparison. All values are 24-hour averages. See caption in Figure 3 for region boundaries.

emissions are parameterized similar to Guenther *et al.* [1995], and soil emissions are formulated according to Yienger and Levy [1995] and Jacob and Bakwin [1991]. The model has been extensively evaluated with observations [Wang *et al.*, 1998b].

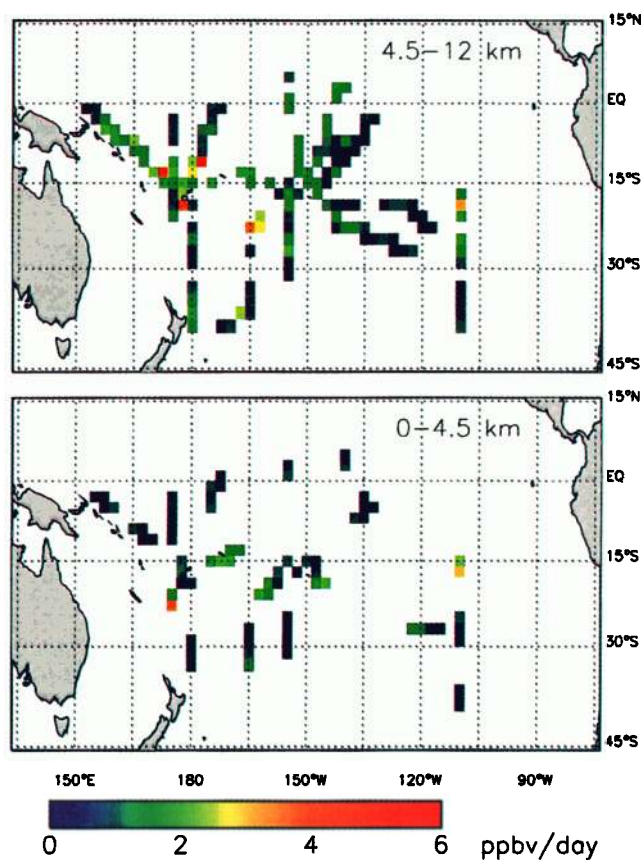


Plate 1. Geographical distribution of chemical production rates of ozone from the PEM-Tropics A data at 0–4.5 km and 4.5–12 km. Values are 24-hour averages and are displayed on a $2^\circ \times 2.5^\circ$ grid.

Figure 3 compares model results (dashed lines) with the PEM-Tropics A observations (solid circles) for median concentrations of ozone, CO, and PAN. Ozone concentrations in the 3-D model are lower than the observations below 3 km by 7 ppbv (30%), and they show a smaller enhancement near 6 km (the 25 percentile of the observations is close to the 95 percentile of the model). However, the general tendency is reproduced: median concentrations of ozone are largest

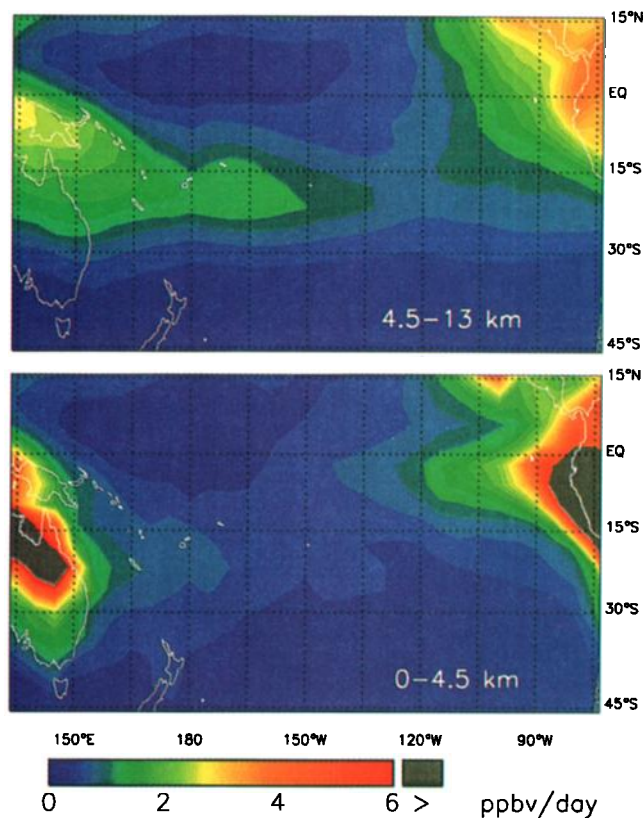


Plate 2. Mean ozone production rates in September calculated by the Harvard/GISS global 3-D model.

around 6 km. The simulated vertical profile of CO agrees with the observations within 5 ppbv. As in the case of ozone, the variability of the observations is significantly larger than the variability in the 3-D simulation below 4 km. The vertical profile of PAN is also predicted within one standard deviation of the observations; the model concentrations are about 20% higher.

The rates of photochemical ozone formation and loss calculated with the global model agree with those from the point model within 20% (Figure 8). Ozone loss below 2 km and production above 6 km are somewhat higher in the point model. The geographical distribution of ozone production

Table 3. Median 24-Hour Average Column Budgets of O_x and CO in PEM-Tropics A

| | P _{O₃} | L _{O₃} | (P-L) _{O₃} | P _{CO} | L _{CO} | (P-L) _{CO} |
|----------------|----------------------------|----------------------------|--------------------------------|-----------------|-----------------|---------------------|
| 0–12 km column | | | | | | |
| 0°–10°S | 1.36 | 3.20 | -1.84 | 1.59 | 2.66 | -1.07 |
| 10°S–30°S | 1.82 | 3.05 | -1.23 | 1.24 | 2.68 | -1.44 |
| 0–16 km column | | | | | | |
| 0°–10°S | 1.72 | 3.24 | -1.52 | 1.61 | 2.88 | -1.27 |
| 10°S–30°S | 2.18 | 3.09 | -0.91 | 1.26 | 2.90 | -1.64 |

Column rates of production (P) and loss (L) are in units of 10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$. At 12–16 km, rates are computed by linearly extrapolating median concentration profiles above the 12 km ceiling of the aircraft. The extrapolated profiles for NO_x, ozone, and CO agree within 30% with observations from the Stratospheric Tracers of Atmospheric Transport (STRAT) campaign in August 1996 (P. Wennberg, personal communication, 1997).

rates (Plate 2) is similar in both models. Both show enhanced ozone production above 4 km in the western Pacific around 15°S due to advection of continental air. The global model also predicts enhanced ozone production over the eastern equatorial Pacific (Plate 2), indicating outflow of pollution from South America. Data from the P-3B aircraft flights along the western coast of South America indicate that easterly continental outflow can have biomass burning as a major component (N. Blake, personal communication, 1997).

Table 4 lists the individual terms that contribute to the 3-D model budget for ozone over the tropical South Pacific in September. The two altitude regimes (0–4.5 km and 4.5–13 km) reflect the transition from southeasterly trade winds to predominant westerly flow [e.g., *Fuelberg et al.*, this issue]. In the lower part of the troposphere the ozone budget is dominated by advection from the east together with vertical downward transport, and by photochemical loss inside the region. In situ formation of ozone balances only one third of the photochemical loss. Above 4.5 km, ozone is advected predominantly from the west; this term is about twice as large as the advection from the east in the lower part. The net downward vertical flux of 0.53×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ amounts to about 17% of the lateral outflux above 4.5 km to the east and south. For the entire 0–13 km column over the South Pacific, we find in the 3-D model that 55% of the ozone originates from within the region and 45% is transported in the flux divergence term. This result is consistent with our point model analysis, where column-integrated chemical production balanced 50% of the chemical loss (Table 3). Although not apparent from Table 4, a tracer analysis in the 3-D model indicates that 20% of tropospheric ozone over the tropical South

Pacific (0°–30°S) originates from cross-tropopause transport in the extratropical Southern Hemisphere [*Wang et al.*, 1998c].

In order to assess the impact of biomass burning on the ozone budget over the tropical South Pacific, we conducted a 3-D model simulation without biomass burning emissions. Ozone mixing ratios from both simulations are compared in Figure 9. September mean ozone mixing ratios over the tropical South Pacific (0°–28°S; 165°E–100°W) are on average higher by 7 and 8 ppbv (~20%) for altitudes below and above 4.5 km, respectively. Without biomass burning, influx from the east at lower altitudes decreases by almost a factor of 2, while the advection from the west above 4.5 km decreases by 30% (Table 4). Photochemical production above 4.5 km now exceeds loss by almost a factor of 2, but the absolute difference between these two terms remains about the same. In general, the chemical terms decrease proportionally to the advection terms, supporting our finding that biomass burning pollution affects advection of ozone as well as in situ production over the South Pacific.

At first sight, these simulations suggest that biomass burning in South America impacts ozone below 4.5 km, whereas source regions to the west (Africa and South America) contribute to ozone advection and formation above. However, as discussed in section 6, the abundance of NO_x in the lower troposphere is controlled by thermal decomposition of PAN which is advected above 4 km as part of the biomass burning pollution. Because of the warm temperatures and the availability of UV radiation, the lifetimes of NO_x and PAN are too short to allow significant transport of these species in the trade winds at lower altitudes. This implies that the chemical

Table 4. September Mean Ozone Budget Over the Tropical South Pacific from the Harvard/GISS Global 3-D Model.

| Process | Base Simulation | | No Biomass Burning | |
|---|-----------------|--------------------|--------------------|--------------------|
| | 0–4.5 km | 4.5–13 km | 0–4.5 km | 4.5–13 km |
| Mean O ₃ mixing ratio, ppbv | 31 | 44 | 24 | 36 |
| Budget terms, 10 ¹¹ molecules cm ⁻² s ⁻¹ | | | | |
| Advection from west | -0.33 | +3.84 | -0.26 | +2.70 |
| from east | +1.81 | -2.51 | +1.03 | -1.85 |
| from south | -0.14 | -0.92 | -0.07 | -0.65 |
| from north | -0.19 | +0.04 | -0.08 | +0.04 |
| Total (flux divergence) | +1.14 | +0.46 | +0.62 | +0.24 |
| Vertical transport | +0.53 | -0.49 ^a | +0.50 | -0.46 ^a |
| Chemical production | +0.98 | +0.92 | +0.52 | +0.74 |
| Chemical loss | -2.61 | -0.71 | -1.63 | -0.48 |
| Dry deposition | -0.27 | 0 | -0.20 | 0 |
| Residual ^b | -0.23 | +0.18 | -0.19 | +0.04 |

The budget was computed for the region 0°–28°S, 165°E–100°W. Fluxes are normalized to horizontal surface area. Positive transport terms indicate net inflow.

^a Includes direct input from the stratosphere.

^b Diffusive transport and tendency term.

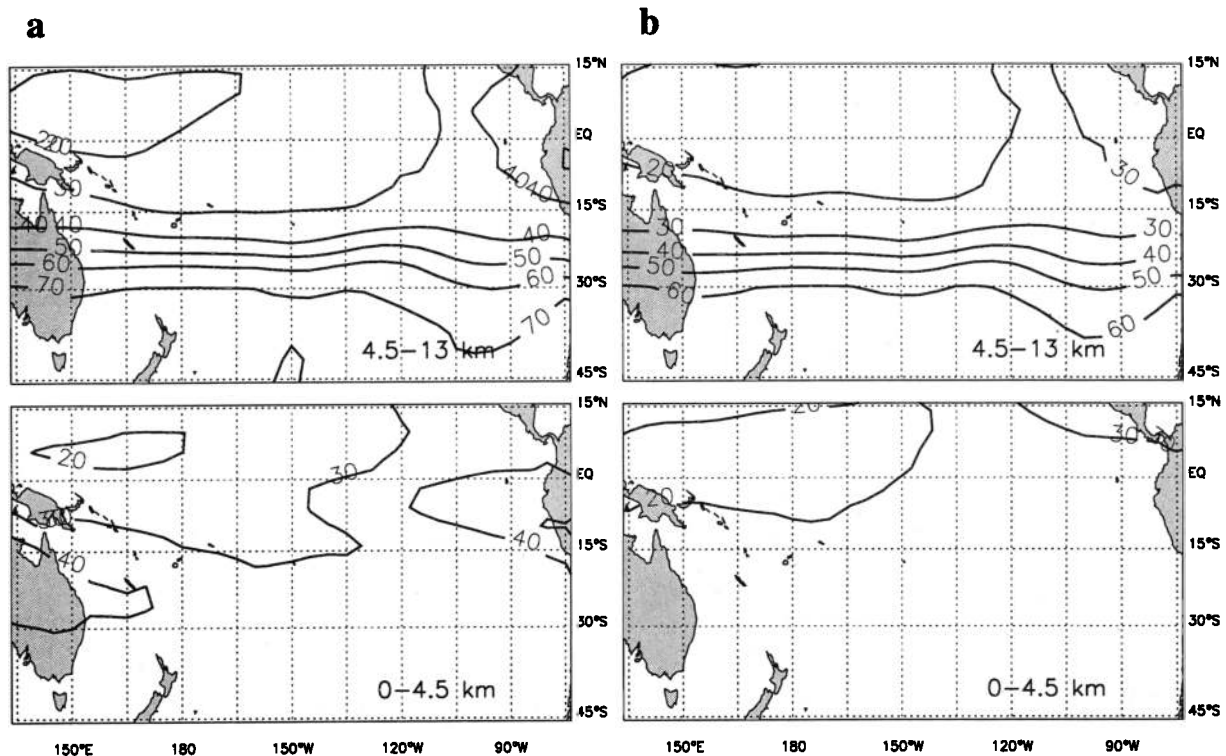


Figure 9. Mean ozone mixing ratios in ppbv over the tropical South Pacific for the month of September calculated by the Harvard/GISS global 3-D model; (a) standard simulation and (b) simulation without biomass burning.

ozone formation in the lower troposphere is controlled by downward transport of precursors that have been advected from the west. This is supported by the difference in subsidence fluxes of PAN between the two simulations: without biomass burning emissions this flux is a factor of 3 lower. Adding the vertical transport of ozone to the chemical formation of ozone in the lower troposphere, we find that the sum is comparable in magnitude with the horizontal advection of ozone from the east (Table 4). Hence biomass burning pollution advected from the west can account for all the biomass burning ozone enhancement above 4.5 km and for half of the increase at lower levels. Biomass burning pollution advected from the east affects ozone only in the lower troposphere over the eastern South Pacific.

9. Summary

The model analysis of the PEM-Tropics A data from the DC-8 revealed the important contribution of biomass burning to the ozone budget over the tropical South Pacific. PEM-Tropics A took place during the burning season, and it will be interesting to compare these results to the data of PEM-Tropics B which is scheduled for the rain season in February–March 1999. Both, the point model and the Harvard/GISS global 3-D model, calculate a photochemical column net loss for ozone of about 1.5×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ during PEM-Tropics A. Photochemical production of ozone balances about half of the chemical loss; the ozone budget can be closed with advection of continental air. The turnover from net photochemical loss to net photochemical production takes place around 6 km, as was previously found for the tropical South Atlantic in TRACE A and for the tropical North Pacific in PEM-West A and B.

The ozone budget in the lower 4 km of the South Pacific troposphere is largely affected by PAN that is advected in biomass burning pollution layers at higher altitudes. Below 4 km the thermal decomposition of PAN can account for most of the NO_x production, and it therefore controls chemical ozone formation. Subsidence of ozone from above and photochemical production contribute as much to the ozone budget in the lower troposphere as advection of biomass burning pollution from South America in easterly trade winds. The comparison of a global 3-D simulation with and without biomass burning emissions showed that biomass burning caused an increase in ozone concentrations over the tropical South Pacific of 7–8 ppbv at all altitudes.

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