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## Citation

Jacob, D. J., E. G. Heikes, S.-M. Fan, J. A. Logan, D. L. Mauzerall, J. D. Bradshaw, H. B. Singh, et al. 1996. "Origin of Ozone and NO<sub>x</sub> in the Tropical Troposphere: A Photochemical Analysis of Aircraft Observations over the South Atlantic Basin ." Journal of Geophysical Research 101 (D19): 24235. doi:10.1029/96jd00336.

## Published Version

doi:10.1029/96JD00336

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# Origin of ozone and $\text{NO}_x$ in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin

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**Abstract.** The photochemistry of the troposphere over the South Atlantic basin is examined by modeling of aircraft observations up to 12-km altitude taken during the TRACE A expedition in September–October 1992. A close balance is found in the 0 to 12-km column between photochemical production and loss of  $\text{O}_3$ , with net production at high altitudes compensating for weak net loss at low altitudes. This balance implies that  $\text{O}_3$  concentrations in the 0–12 km column can be explained solely by in situ photochemistry; influx from the stratosphere is negligible. Simulation of  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ , and  $\text{CH}_2\text{O}$  concentrations measured aboard the aircraft lends confidence in the computations of  $\text{O}_3$  production and loss rates, although there appears to be a major gap in current understanding of  $\text{CH}_2\text{O}$  chemistry in the marine boundary layer. The primary sources of  $\text{NO}_x$  over the South Atlantic Basin appear to be continental (biomass burning, lightning, soils). There is evidence that  $\text{NO}_x$  throughout the 0 to 12-km column is recycled from its oxidation products rather than directly transported from its primary sources. There is also evidence for rapid conversion of  $\text{HNO}_3$  to  $\text{NO}_x$  in the upper troposphere by a mechanism not included in current models. A general representation of the  $\text{O}_3$  budget in the tropical troposphere is proposed that couples the large-scale Walker circulation and in situ photochemistry. Deep convection in the rising branches of the Walker circulation injects  $\text{NO}_x$  from combustion, soils, and lightning to the upper troposphere, leading to  $\text{O}_3$  production; eventually, the air subsides and net  $\text{O}_3$  loss takes place in the lower troposphere, closing the  $\text{O}_3$  cycle. This scheme implies a great sensitivity of the oxidizing power of the atmosphere to  $\text{NO}_x$  emissions in the tropics.

## 1. Introduction

Ozone in the tropical troposphere plays a key role in determining the global oxidizing power of the atmosphere. Most of the oxidation of long-lived gases by OH takes place in the tropics, where high UV and humidity promote the formation of OH from photolysis of  $\text{O}_3$  [Logan *et al.*, 1981; Thompson, 1992]. Ozone is produced within the troposphere by photochemical oxidation of hydrocarbons and CO in the presence of nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) and is also transported down from the stratosphere.

There is continuing controversy as to the relative importance of tropospheric production versus stratospheric influx in controlling  $\text{O}_3$  concentrations in the troposphere, including in the tropics [Liu *et al.*, 1980; Levy *et al.*, 1985; Logan and Kirchhoff, 1986; Krishnamurti *et al.*, 1993; Dibb *et al.*, 1996; Graustein and Turekian, 1996; Browell *et al.*, this issue; Loring *et al.*, this issue]. There is also considerable uncertainty regarding the origin of  $\text{NO}_x$ , the limiting precursor for  $\text{O}_3$  production in the troposphere [Levy and Moxim, 1989; Penner *et al.*, 1991; Kasibhatla *et al.*, 1991, 1993].

We examine here the origin of  $\text{O}_3$  and  $\text{NO}_x$  in the tropical troposphere using observations made during the TRACE A aircraft expedition in September–October 1992 [Fishman *et al.*, this issue]. This expedition provided a detailed survey of  $\text{O}_3$  and its precursors over the tropical South Atlantic and neighboring continents up to 12-km altitude. Its primary objective was to identify the cause of the large-scale  $\text{O}_3$  enhancement observed in the region during the austral spring dry season [Fishman *et al.*, 1990]. Results from TRACE A confirmed earlier suggestions that this enhancement is caused by seasonal biomass burning emissions of  $\text{NO}_x$ , hydrocarbons, and CO from southern Africa and South America [Logan and Kirchhoff, 1986; Fishman *et al.*, 1990; Anderson *et al.*, 1993; Andreae *et al.*, 1994; Gregory *et al.*, this issue; Kirchhoff *et al.*, this issue; Olson *et al.*, this issue; Thompson *et al.*, this issue].

Our goal in the present paper is to explain the total tropospheric  $\text{O}_3$  column observed in TRACE A, not just the biomass burning enhancement, and to draw general inferences regarding the budget of  $\text{O}_3$  in the tropical troposphere. As pointed out by

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Thompson *et al.* [this issue], the tropospheric O<sub>3</sub> column over the South Atlantic during the dry season maximum is only 50% higher than the wet season background when biomass burning influence is minimal. This O<sub>3</sub> background, over the South Atlantic and elsewhere in the tropical troposphere, plays a critical role in determining the oxidizing power of the atmosphere.

Our analysis is based on a combination of photochemical modeling and statistical interpretation of the TRACE A data. The modeling approach is described in section 2 and is evaluated in sections 3 and 4 by simulation of H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, and CH<sub>2</sub>O concentrations measured aboard the aircraft. Regional budgets for O<sub>3</sub> and NO<sub>x</sub> over the South Atlantic basin are derived in sections 5 and 6, respectively. A general representation of the O<sub>3</sub> budget in the tropical troposphere is proposed in section 7. Conclusions are in section 8.

## 2. Modeling Approach

The TRACE A expedition used a DC-8 aircraft with a ceiling of 12-km altitude. The southern hemisphere flight tracks (Figure 1) covered the tropical South Atlantic, eastern Brazil, and southern Africa; we refer to this region as the "South Atlantic basin." Details on the flights and references for the observations are given by Fishman *et al.* [this issue]. Measurements aboard the aircraft included concentrations of O<sub>3</sub>, CO, NO, peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), HNO<sub>3</sub>, speciated hydrocarbons, acetone, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, CH<sub>2</sub>O, and organic acids. Meteorological variables, UV fluxes, and aerosol number

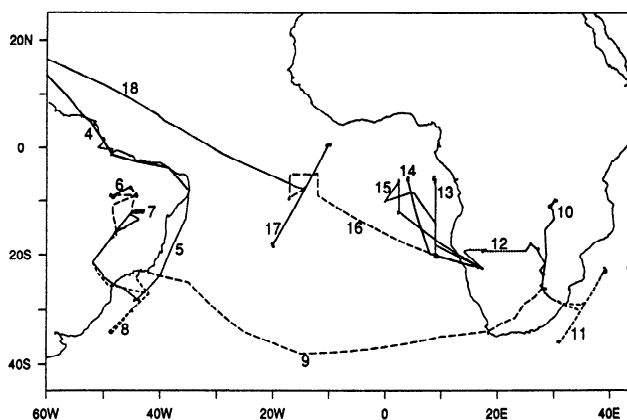


Figure 1. TRACE A flight tracks (September 23 - October 25, 1992). Flight numbers are indicated. The region covered by the southern hemisphere flight tracks is referred to in the paper as the South Atlantic basin.

size distributions were also measured. Table 1 gives median values for the various measurements at different altitudes.

We base our analyses on merged time series of the aircraft data where all measurements have been averaged over a common time interval. The choice of averaging interval must balance the need for high temporal resolution with the danger of misinterpret-

Table 1a. Median Measured Values Over the South Atlantic Basin During TRACE A

	Altitude		
	0-4 km	4-8 km	8-12 km
Temperature, K	284	258	230
Dew point, K	275	244	218
UV flux, <sup>a</sup> mW cm <sup>-2</sup>			
zenith	4.7	5.3	5.8
nadir	0.75	1.5	2.0
O <sub>3</sub> , ppbv	50	69	74
CO, ppbv	112	103	93
CH <sub>4</sub> , ppbv	1695	1707	1715
NO, pptv	25	29	120
PAN, pptv	175	294	223
PPN, pptv	4	3	2
HNO <sub>3</sub> , pptv	390	130	59
Ethane, pptv	590	630	670
Propane, pptv	48	46	58
C <sub>4,5</sub> alkanes, pptv	9	7	8
Ethene, pptv	21	8	9
Propene, pptv	6	4	4
Acetylene, pptv	130	130	110
Benzene, pptv	32	21	15
Toluene, pptv	7	2	<2
Acetone, pptv	750	593	650
Ethanol, pptv	60	<20	<20
HCOOH, pptv	1770	1000	560
CH <sub>3</sub> COOH, pptv	3030	2550	1900
H <sub>2</sub> O <sub>2</sub> , pptv	2800	760	150
CH <sub>3</sub> OOH, pptv	1200	320	60
CH <sub>2</sub> O, pptv	200	<40	<40
Aerosol number, cm <sup>-3</sup>			
0.12 to 0.2-μm radius	181	35	16
0.2 to 0.5-μm radius	310	28	8
0.5 to 2.0-μm radius	0.2	<0.1	0.3

Statistics are for the ensemble of southern hemisphere data collected in TRACE A. The median concentrations of >C<sub>5</sub> alkanes, >C<sub>3</sub> alkenes, xylenes, isoprene, and terpenes were below the detection limit of 2 pptv. Concentrations of NO<sub>2</sub> were measured in TRACE A, but the measurement is considered unreliable [Crawford *et al.*, 1996] and is not used in the paper.

<sup>a</sup> Measured with an Eppley radiometer (Eppley, Inc., Newport, Rhode Island).

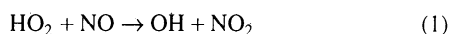
**Table 1b.** Median Model Values Over the South Atlantic Basin During TRACE A

	Altitude		
	0–4 km	4–8 km	8–12 km
OH, $10^5 \text{ cm}^{-3}$	27	16	12
HO <sub>2</sub> , $10^6 \text{ cm}^{-3}$	257	96	22
CH <sub>3</sub> O <sub>2</sub> , $10^6 \text{ cm}^{-3}$	103	34	3
NO <sub>x</sub> =NO+NO <sub>2</sub> , pptv	73	57	145
HNO <sub>4</sub> , pptv	1	10	54

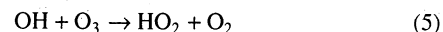
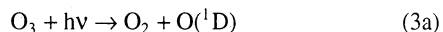
Twenty-four hour average model values computed as described in section 2. The concentration of NO<sub>x</sub> is calculated in the model using as constraint the NO measurement for the time of day of observation.

ing coarse-resolution data. We choose to average the data over the sampling time of the critical variable with the coarsest time resolution. Because this critical variable depends on the problem at hand, we will use over the course of this paper four different merged time series matched to the sampling times of peroxides, CH<sub>2</sub>O, NO, and HNO<sub>3</sub> (Table 2). Ozone columns are included in the merged time series using daily observations with  $1^\circ \times 1.25^\circ$  resolution from the total ozone mapping spectrometer (TOMS). The median O<sub>3</sub> column over the south tropical Atlantic during TRACE A was 281 Dobson units (DU) ( $1 \text{ DU} = 2.687 \times 10^{16} \text{ molecules cm}^{-2}$ ).

A major objective of this paper is to derive a chemical budget for O<sub>3</sub> in the tropospheric column over the South Atlantic basin (section 5). Our approach is to calculate 24-hour average O<sub>3</sub> production and loss rates for individual points in the merged time series of aircraft data and to use statistics from the ensemble of points to infer regionally averaged rates. Rapid chemical cycling takes place between O<sub>3</sub> and other members of the odd-oxygen family ( $\text{O}_x = \text{O}_3 + \text{O} + \text{NO}_2 + \text{HNO}_4 + (2x)\text{NO}_3 + (3x)\text{N}_2\text{O}_5 + \text{peroxyacetylnitrates}$ ), hence the budget analysis must be based on O<sub>x</sub> rather than on O<sub>3</sub>. Considering that O<sub>3</sub> accounts typically for over 99% of O<sub>x</sub>, the budgets of O<sub>3</sub> and O<sub>x</sub> can be viewed as equivalent. Production of O<sub>x</sub> is mainly by reactions (1) and (2):



where RO<sub>2</sub> is any organic peroxy radical (CH<sub>3</sub>O<sub>2</sub> is the most important). Loss of O<sub>x</sub> is principally by reactions (3)–(5):



Calculation of O<sub>x</sub> production and loss rates requires knowledge of the concentrations of HO<sub>x</sub> radicals (OH, HO<sub>2</sub>, RO<sub>2</sub>) along the flight tracks. These species were not measured from the aircraft. We estimate their concentrations for each point in the merged time series by using a zero-dimensional photochemical model constrained with the ensemble of measurements for that point (Table 3). The model is described in Appendix A. It calculates the diel steady state concentrations of HO<sub>x</sub> radicals, short-lived NO<sub>y</sub> species (NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>2</sub>, HNO<sub>4</sub>, organic nitrates), and other photochemical intermediates (peroxides, carbonyls). Production and loss of species are by chemical reactions only (loss by deposition is not considered). "Diel steady state" is defined by reproducibility of concentrations over a 24-hour solar cycle, as obtained in a time-dependent calculation with periodic boundary conditions

$$C_i(t) = C_i(t + T) \quad (6)$$

where  $C_i$  is the concentration of species  $i$ ,  $t$  is time, and  $T = 24$  hours. In this calculation, all input variables in Table 3 except NO are assumed constant over the diel cycle. The concentration of NO must be calculated as a time-dependent quantity because of the strong diel variation driven by photochemical steady state with NO<sub>2</sub>. The few available observations in the remote troposphere indicate little diel variation of NO<sub>x</sub> [Carroll *et al.*, 1992], but some variation might be expected in the upper troposphere due to cycling with HNO<sub>4</sub>. We assume in the model that the concentration of NO<sub>x</sub> (NO + NO<sub>2</sub> + NO<sub>3</sub> + (2x)N<sub>2</sub>O<sub>5</sub> + HNO<sub>2</sub> + HNO<sub>4</sub>) is constant over the diel cycle and calculate its value within the model to match the observed NO concentration at the time of day of the measurement.

**Table 2.** Merged Time Series of TRACE A Data

Matched Species	Time Resolution, min	Number of Points		
		Data	Model	Application
Peroxides	4–5	1254	223	a
CH <sub>2</sub> O	1	1496	61 (926)	b
NO	3	1781	214 (1355)	c
HNO <sub>3</sub>	2–15	721	201	d

Each data point represents one measurement time interval for the matched species. Model points are the subset of data points for which photochemical model quantities can be computed; the computation requires that data for all variables in Table 3 be available for at least a fraction of the time interval. We also give in parentheses the number of model points obtained in the fixed-hydrocarbon approximation, which relaxes the constraint on availability of data for hydrocarbons and acetone (see section 2).

<sup>a</sup> Comparison of simulated and observed peroxide concentrations (section 3).

<sup>b</sup> Comparison of simulated and observed CH<sub>2</sub>O concentrations (section 4).

<sup>c</sup> O<sub>3</sub> production and loss rates and NO<sub>2</sub> concentrations (sections 5 and 6).

<sup>d</sup> Chemical budget of NO<sub>x</sub> (section 6).



**Table 3.** Input Variables for the Photochemical Model Calculation

Variable Type	Variable
Meteorological	pressure, temperature, humidity
Radiation	solar declination, latitude, O <sub>3</sub> column, <sup>a</sup> cloud correction factor CF <sup>b</sup>
Chemical	O <sub>3</sub> , CO, NO <sup>c</sup> , PAN <sup>d</sup> , HNO <sub>3</sub> <sup>d</sup> , methane <sup>c</sup> , ethane, propane, C <sub>4-5</sub> alkanes, C <sub>6-7</sub> alkanes, ethene, propene, C <sub>4-6</sub> alkenes, acetylene, benzene, toluene, xylenes, isoprene, acetone, ethanol, formic acid <sup>c</sup> , acetic acid <sup>c</sup> , aerosol number concentrations in three size classes <sup>c,f</sup>

<sup>a</sup> The total O<sub>3</sub> column is distributed vertically using the mean O<sub>3</sub> profiles measured by ozonesondes at Ascension Island and southern Africa during TRACE A [Thompson *et al.*, 1995].

<sup>b</sup> The cloud correction factor (CF) is calculated from the UV flux observations as described in Appendix A.

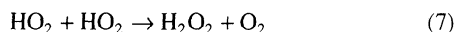
<sup>c</sup> The model calculation assumes a constant concentration of NO<sub>t</sub> (NO<sub>t</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + (2x)N<sub>2</sub>O<sub>5</sub> + HNO<sub>2</sub> + HNO<sub>4</sub>) over the diel cycle and adjusts the concentration of NO<sub>t</sub> to match the observed NO concentration at the time of day of observation.

<sup>d</sup> Data for HNO<sub>3</sub> and PAN are required only for the NO<sub>x</sub> budget calculation of section 6. For other applications, if HNO<sub>3</sub> data are unavailable then a low value is assumed; and if PAN data are unavailable, then PAN concentrations are assumed from chemical steady state. These assumptions greatly increase the number of data points at which model calculations can be done without inducing significant error in the relevant model output quantities.

<sup>e</sup> If data are not available for these variables, default values are used of 1.7 ppbv for CH<sub>4</sub> and zero for formic acid, acetic acid, and aerosol number concentrations.

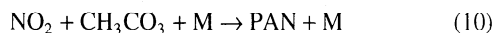
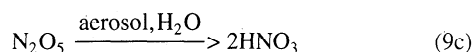
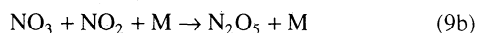
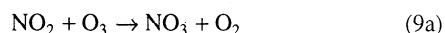
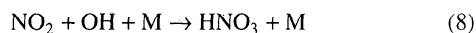
<sup>f</sup> See Table 1a for size class information.

Concentrations of H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, and CH<sub>2</sub>O are calculated in the model, rather than constrained from observations, and comparison of simulated versus observed values serves to test the model (sections 3 and 4). These three species are sensitive to different aspects of HO<sub>x</sub> chemistry [Heikes, 1992; Liu *et al.*, 1992]. Hydrogen peroxide is particularly valuable as a test of O<sub>3</sub> production in the model because its source,

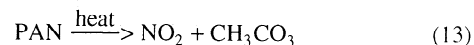
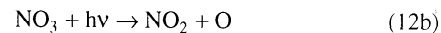
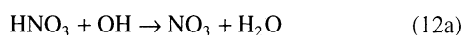
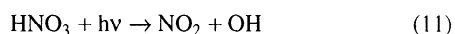


varies quadratically with the concentration of HO<sub>2</sub>, the principal peroxy radical responsible for O<sub>3</sub> production. At low altitudes where H<sub>2</sub>O<sub>2</sub> is the principal sink of HO<sub>x</sub>, the concentration of H<sub>2</sub>O<sub>2</sub> reflects the rate of the O(<sup>1</sup>D)+H<sub>2</sub>O reaction which is the principal source of HO<sub>x</sub> and the principal sink of O<sub>x</sub>.

We will also apply the model to study the chemical cycling of NO<sub>x</sub> over the South Atlantic basin in light of the concurrent measurements of NO, HNO<sub>3</sub>, and PAN made aboard the aircraft (section 6). Oxidation of NO<sub>x</sub> to HNO<sub>3</sub> and PAN takes place on a timescale of the order of 1 day:



Organic nitrates other than PAN are also formed but represent only minor sinks for NO<sub>x</sub> in the model. The species HNO<sub>3</sub> and PAN can act as reservoirs for NO<sub>x</sub>, decomposing to release NO<sub>x</sub> far from its point of origin:



We compute the 24-hour average rates of reactions (8)–(14) in the model at individual points using the observed concentrations of NO, HNO<sub>3</sub> and PAN as constraints, as discussed above. The resulting mass balance between sources and sinks of NO<sub>x</sub> allows us to estimate the degree to which NO<sub>x</sub> concentrations are maintained by chemical recycling from HNO<sub>3</sub> and PAN through the above set of reactions. In such a NO<sub>x</sub> budget calculation it is necessary to correct the rates of conversion between NO<sub>x</sub> and PAN to account for cycling within the (CH<sub>3</sub>CO<sub>3</sub>+PAN) family; the correction is described in Appendix B.

Table 1b gives the median concentrations of OH, HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, NO<sub>x</sub>, and HNO<sub>3</sub> computed in the model for the southern hemisphere TRACE A data set. Diel steady state for these species and for CH<sub>2</sub>O is typically approached to within 10% after 2 days of integration in the model. The peroxides, which have longer lifetimes, require typically 2–3 days at 2 km and 1 week at 8–12 km for approach to steady state. The steady state assumption is prone to large errors in pollution plumes and in the continental boundary layer, where concentrations of the input variables in Table 3 may change greatly over timescales of less than 1 day. It is more adequate in the free troposphere and in the marine boundary layer.

To conduct the model calculation for a given point in the merged time series we require that data be available for all variables in Table 3. Because of lack of temporal overlap in some of the measurements (notably NO, hydrocarbons, acetone), model calculations can be done for only a small fraction of the data points (Table 2). To increase the number of points, we use in certain applications a "fixed-hydrocarbon" version of the model in which we assume 630 parts per trillion by volume (pptv) C<sub>2</sub>H<sub>6</sub> and 650 pptv acetone (mean values in TRACE A) and neglect the other nonmethane hydrocarbons. By relaxing the constraint on the availability of hydrocarbon and acetone data, the number of model points is greatly increased (Table 2). The errors incurred

by the fixed hydrocarbon approximation will be discussed in the context of each application. Data for  $\text{HNO}_3$  and PAN are critical only for the  $\text{NO}_x$  mass balance analysis presented in section 6. For all other applications, when data for  $\text{HNO}_3$  are missing a low value is assumed; and when data for PAN are missing the PAN concentration is assumed from chemical steady state. We verified that these assumptions have a negligible effect on  $\text{HO}_x$  levels and other relevant model results.

### 3. Peroxides

Figure 2 compares simulated and observed concentrations of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  for individual points in the merged time series matched to the peroxide sampling times. Model values were sampled from the diel steady state cycle at the time of day of observation. Two outliers representing fresh fire plumes were excluded from the plots and from the statistics. Also shown on each plot are the least squares correlation coefficient  $r^2$  between model and observations, the slope  $S$  of the linear best fit obtained by the reduced-major-axis method [Hirsch and Gilroy, 1984], and the median ratio  $R$  of simulated-to-observed concentrations.  $S$  and  $R$  offer different measures of model bias.

We find that the model captures 78% of the observed variance of  $\text{H}_2\text{O}_2$  concentrations. This variance is determined strongly by water vapor ( $r^2 = 0.51$  between observed  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  mixing ratios). Median simulated-to-observed concentration ratios are 0.99 at 0–4 km, 0.87 at 4–8 km, and 0.57 at 8–12 km. Although  $\text{H}_2\text{O}_2$  deposition is not included in the model, its effect should be largely limited to the mixed layer and to convective outflows because the lifetime of  $\text{H}_2\text{O}_2$  against photochemical loss is relatively short (1.5 days below 2 km). The underestimate of  $\text{H}_2\text{O}_2$

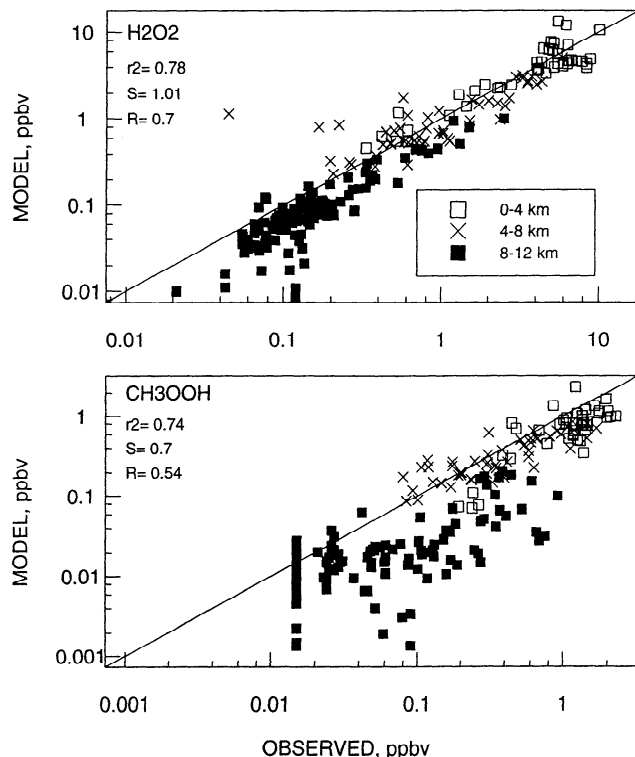


Figure 2. Simulated versus observed  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  concentrations in TRACE A. Also shown are the 1:1 line, the least squares correlation coefficient ( $r^2$ ), the slope of the regression line ( $S$ ), and the median ratio of simulated to observed concentrations ( $R$ ). Observed  $\text{CH}_3\text{OOH}$  concentrations were below the detection limit of 15 pptv for 15% of the points.

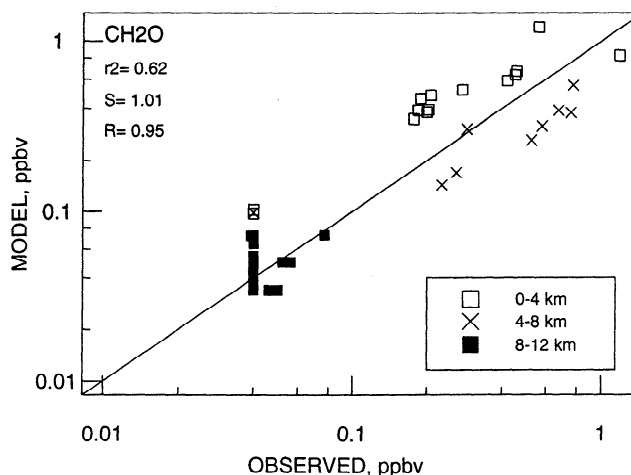


Figure 3. Simulated versus observed  $\text{CH}_2\text{O}$  concentrations in TRACE A. Also shown are the 1:1 line, the least squares correlation coefficient ( $r^2$ ), the slope of the regression line ( $S$ ), and the median ratio of simulated to observed concentrations ( $R$ ). Observed concentrations were below the detection limit of 30–50 pptv for 56% of the points.

in the upper troposphere could reflect a missing  $\text{HO}_x$  source in the model but is also within the low-temperature uncertainties of the rate constants in the mechanism.

For  $\text{CH}_3\text{OOH}$  we find that the model captures 74% of the observed variance but is generally too low, particularly above 8 km. Median simulated-to-observed ratios are 0.59 at 0–4 km, 0.79 at 4–8 km, and 0.28 at 8–12 km. The underestimate is not outside the range of uncertainty of rate constants in the mechanism [Thompson and Stewart, 1991]. The estimated uncertainty on the rate constant for the reaction  $\text{CH}_3\text{O}_2 + \text{HO}_2$ , which is the only  $\text{CH}_3\text{OOH}$  source in the model, is a factor of 2 at 298 K and a factor of 3 at 230 K [DeMore et al., 1994]. Although the underestimate of  $\text{CH}_3\text{OOH}$  could suggest the presence of major hydrocarbon precursors missing from the model, we find no parallel underestimate of  $\text{CH}_2\text{O}$  that would support this hypothesis (see section 4).

The successful simulation of the peroxides below 8-km altitude lends confidence in the  $\text{O}_3$  production and loss rates computed by the model. At 8 to 12-km altitude the  $\sim 40\%$  underestimate of  $\text{H}_2\text{O}_2$  could imply an  $\sim 20\%$  underestimate of  $\text{HO}_2$ . Considering that  $\text{HO}_2$  accounts for  $\sim 90\%$  of total peroxy radicals in that altitude range (Table 1b), we may expect the  $\text{O}_3$  production and loss rates above 8 km to be underestimated by about 20%.

Singh et al. [1995] pointed out the importance of acetone photolysis (included in our model) as a primary source of  $\text{HO}_x$  in the upper troposphere. We conducted a sensitivity calculation without acetone for the point representative of median conditions at 8–12 km (Table 1a). The  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{HO}_2$ , and  $\text{OH}$  concentrations computed for that point decreased by 27%, 36%, 14%, and 16%, respectively, relative to the simulation including acetone. Neglecting acetone as a source of  $\text{HO}_x$  makes the model underestimate of peroxide concentrations in the upper troposphere significantly worse.

### 4. Formaldehyde

Figure 3 compares simulated and observed  $\text{CH}_2\text{O}$  concentrations for individual points in the merged time series matched to the  $\text{CH}_2\text{O}$  sampling times. Again, model values were sampled from the diel steady state cycle at the time of day of observation.

The model captures 62% of the observed variance. Model values tend to be too high in the lower troposphere (0–4 km) and too low in the middle troposphere (4–8 km). Most observations above 8 km are below the detection limit of 40 pptv.

Our ability to interpret model results for  $\text{CH}_2\text{O}$  is evidently hampered by the small number of model points. To address this problem, we turned to the fixed-hydrocarbon version of the model which provides 926 model points for comparison with observations. The fixed-hydrocarbon approximation gives only a lower limit for  $\text{CH}_2\text{O}$ , because it does not allow for the possibility of high hydrocarbon concentrations, but it still allows investigation of model overestimates. We find that the worst overestimate is in the marine boundary layer over the tropical South Atlantic (mean observed conditions 26 parts per billion by volume (ppbv)  $\text{O}_3$ , 66 ppbv  $\text{CO}$ , 3 pptv  $\text{NO}$ , 0.015 vol/vol  $\text{H}_2\text{O}$ ), where the mean observed concentration of  $\text{CH}_2\text{O}$  is 0.11 ppbv (range <0.04–0.25 ppbv) while the corresponding model mean is 0.41 ppbv (range 0.28–0.55 ppbv). The mean observed  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  concentrations in that region are 2.3 ppbv and 1.1 ppbv, respectively, while the corresponding model means are 3.1 ppbv and 1.7 ppbv. The model shows some overestimate for the peroxides, which in the case of  $\text{H}_2\text{O}_2$  could be due to deposition [Heikes *et al.*, this issue], but these discrepancies are small compared to  $\text{CH}_2\text{O}$ . We repeated the model calculation for the marine boundary layer points using observed concentrations of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  as constraints, and assuming a deposition rate constant of  $4 \times 10^{-6} \text{ s}^{-1}$  for  $\text{CH}_2\text{O}$  as representative of a deposition velocity of  $0.4 \text{ cm s}^{-1}$  over the ocean [Thompson and Zafriou, 1983]. The mean  $\text{CH}_2\text{O}$  concentration in this calculation was 0.29 ppbv (range 0.21–0.48 ppbv), still 3 times higher than observed. The root of the discrepancy must therefore lie in the simulation of  $\text{CH}_2\text{O}$  chemistry.

Our model results for  $\text{CH}_2\text{O}$  can be viewed as typical of the current generation of photochemical models. We participated recently in an intercomparison of 20 models organized by the Intergovernmental Panel on Climate Change [Prather *et al.*, 1995]. In a test simulation representative of the remote marine boundary layer we obtained a  $\text{CH}_2\text{O}$  concentration of 0.21 ppbv, while other models obtained values ranging from 0.13 to 0.33 ppbv. The models at the low range had unusually high  $\text{CH}_2\text{O}$  photolysis frequencies.

We compared the marine boundary layer measurements of  $\text{CH}_2\text{O}$  in TRACE A to prior shipboard measurements made over the tropical Atlantic in the same season. Lowe and Schmidt [1983] measured a mean concentration of 0.20 ppbv (range 0.10–0.34 ppbv) at  $30^\circ\text{N}$ – $30^\circ\text{S}$  latitude with no significant latitudinal dependence. These values are higher than observed in TRACE A but still lower than in our model. Harris *et al.* [1992] used tunable diode laser spectroscopy to measure  $\text{CH}_2\text{O}$  concentrations in the northern tropics during the Polarstern cruise and found a mean concentration of 0.37 ppbv at  $10^\circ$ – $20^\circ\text{N}$  (they made no measurements farther south). During the same cruise, Carlier *et al.* [1991] reported mean  $\text{CH}_2\text{O}$  concentrations of 0.4 ppbv and 0.3 ppbv over the north and south tropical Atlantic, respectively. We evaluated our model against the Harris *et al.* [1992] data by taking as constraints the mean Polarstern observations at  $15^\circ\text{N}$ : 30 ppbv  $\text{O}_3$ , 90 ppbv  $\text{CO}$ , 1.3 ppbv  $\text{H}_2\text{O}_2$ , 15 pptv  $\text{NO}_2$ , 0.017 mol/mol  $\text{H}_2\text{O}$ , temperature of 293 K, and actinometer values of  $J_{\text{NO}_2}$  and  $J_{\text{O}^1\text{D}}$  [Platt *et al.*, 1992; Jacob and Klockow, 1992; Brauers and Hofzumahaus, 1992; Hofzumahaus *et al.*, 1992]. We obtained a model  $\text{CH}_2\text{O}$  concentration of 0.42 ppbv, in good agreement with the observations.

Other published measurements of  $\text{CH}_2\text{O}$  concentrations in clean tropical marine boundary layers include 0.4–1.1 ppbv over the Pacific [Zafriou *et al.*, 1980; Arlander *et al.*, 1990] and 0.05–0.4 ppbv over the Indian Ocean [Arlander *et al.*, 1990]. It is not clear why there is such variability in the observations and why models are unable to reproduce the lower range of values. One possibility might be the complexation of  $\text{CH}_2\text{O}$  with organics in

the marine aerosol. To our knowledge, the only concurrent gas phase and aerosol measurements of  $\text{CH}_2\text{O}$  in marine air are those of Klippel and Warneck [1980]. These authors found evidence that  $\text{CH}_2\text{O}$  in the aerosol is predominantly present as  $\text{CH}_2\text{O}$  complexes, but they also found that the aerosol contributes only a small fraction of total atmospheric  $\text{CH}_2\text{O}$ .

In summary, our results point to a major gap in current understanding of  $\text{CH}_2\text{O}$  concentrations in the marine boundary layer. Either some of the  $\text{CH}_2\text{O}$  measurements are flawed or a large  $\text{CH}_2\text{O}$  sink is missing from the models under some conditions. Liu *et al.* [1992] previously noted that  $\text{CH}_2\text{O}$  concentrations measured in free troposphere air at Mauna Loa, Hawaii (3.4-km altitude) were a factor of 3 lower than calculated from a standard photochemical model and attributed the discrepancy to a model overestimate of OH. However, later measurements by Zhou *et al.* [1996] at Mauna Loa indicated that the discrepancy is driven by a model overestimate of  $\text{CH}_3\text{OOH}$  and that  $\text{CH}_2\text{O}$  concentrations calculated in a model constrained with observed  $\text{CH}_3\text{OOH}$  are in good agreement with observations. A global three-dimensional photochemical model study by Brasseur *et al.* [1996] shows, in fact, good simulation of both  $\text{CH}_3\text{OOH}$  and  $\text{CH}_2\text{O}$  at Mauna Loa. We cannot draw a parallel between Mauna Loa and the marine boundary layer in TRACE A, because the discrepancy between model and observations for  $\text{CH}_2\text{O}$  in TRACE A is far greater than for  $\text{CH}_3\text{OOH}$ ; also, as discussed above, there is no evidence in TRACE A for a model overestimate of  $\text{CH}_2\text{O}$  in the free troposphere. We searched the TRACE A data set for conditions that would approximate the Mauna Loa environment described by Liu *et al.* [1992] and Zhou *et al.* [1996], but all TRACE A measurements at that altitude had much lower temperatures and humidities than at Mauna Loa (temperature and humidity are important variables controlling  $\text{CH}_2\text{O}$  concentrations in the model).

## 5. Ozone

Plates 1a and 1b show the horizontal distributions of the 24-hour average gross production rate of odd oxygen,  $P_{\text{O}_x}$ , and the net production rate,  $(P-L)_{\text{O}_x}$ , at different altitudes in TRACE A. The rates were computed for the merged time series matched to the NO sampling time, using the fixed-hydrocarbon approximation in order to maximize the number of model points. The errors on  $P_{\text{O}_x}$  and  $L_{\text{O}_x}$  caused by the fixed-hydrocarbon approximation are small; for those points where the full model (including hydrocarbons) can be applied, the median ratio of  $P_{\text{O}_x}$  calculated in the full versus fixed-hydrocarbon versions of the model is  $1.02 \pm 0.09 (1\sigma)$  when  $P_{\text{O}_x}$  is less than  $20 \text{ ppbv day}^{-1}$ . This regime represents 92% of all observations in TRACE A and all observations outside the continental boundary layer. Plate 1b indicates a broad region of net photochemical loss exceeding  $4 \text{ ppbv day}^{-1}$  at 1.5 to 4-km altitude off the southwestern coast of Africa. This rapid loss is made possible by the albedo of persistent marine stratus decks. Gross photochemical production in the region is also high.

We see from Plate 1 that the gross production of  $\text{O}_3$  decreases on average with altitude while the net production increases with altitude. Median vertical profiles of  $P_{\text{O}_x}$  and  $L_{\text{O}_x}$  for the southern hemisphere TRACE A data are plotted in Figure 4, and a summary  $\text{O}_3$  budget for the 0 to 12-km column is given in Table 4. Both production and loss decrease with altitude, due to decreasing humidity, but production decreases slower than loss above 6 km because of high concentrations of NO. Above 6 km, photochemistry switches from a net sink to a net source of  $\text{O}_3$ . Similar transitions have been reported in previous model studies of the remote troposphere [Liu *et al.*, 1980; Thompson and Cicerone, 1982; Davis *et al.*, 1996]. Figure 4 indicates net production of  $\text{O}_3$  taking place below 2-km altitude, but this portion of the budget is highly uncertain because of the large variability of  $\text{O}_3$  production rates for individual points; there is a sharp contrast between the

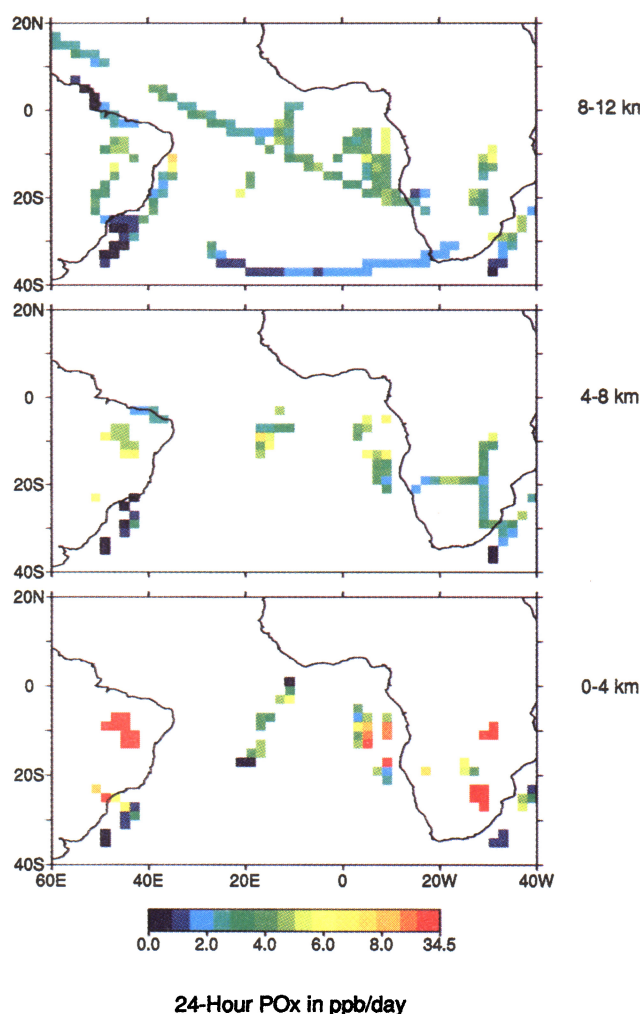


Plate 1a. Twenty-four-hour average gross production rates of odd oxygen ( $O_x = O_3 + O + NO_2 + HNO_4 + (2x)NO_3 + (3x)N_2O_5 +$  peroxyacetylnitrates) computed at 0 to 4-km, 4 to 8-km, and 8 to 12-km altitude in TRACE A.

continental boundary layer, where biomass burning influence can result in rapid  $O_3$  production, and the marine boundary layer, where  $NO_x$  levels are low and  $O_3$  production is slow (Plate 1). The point modeling approach is also most prone to errors in the continental boundary layer, as discussed in section 2.

We take the values in Figure 4 as our best estimates of the regionally averaged rates of  $O_3$  production and loss over the South Atlantic basin. The corresponding integrals of  $P_{O_x}$  and  $L_{O_x}$  for the 0 to 12-km column are both  $1.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ . These values are two orders of magnitude larger than the mean stratospheric influx of  $O_3$  in the southern hemisphere troposphere estimated to be  $1.3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  [Gidel and Shapiro, 1980; Levy *et al.*, 1985]. Even allowing for a slightly higher cross-tropopause flux in spring [Holton, 1990] and for preferential subsidence of air over the south tropical Atlantic [Krishnamurti *et al.*, 1993; Loring *et al.*, this issue], it is clear that stratospheric influx is a negligible contributor to tropospheric  $O_3$  in the region. In situ photochemistry dominates even in the upper troposphere; the 4-km integral of  $P_{O_x}$  at 8 to 12-km altitude is  $1.1 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ .

Deposition has only a small effect on the  $O_3$  budget in the 0 to 12-km column. Heikes *et al.* [this issue] estimated a deposition flux to the Atlantic Ocean of  $1.7 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  during TRACE A. Fan *et al.* [1990] measured a 24-hour average  $O_3$  deposition flux

of  $10 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  to the Amazon forest in the wet season; scaling this flux to the ratio of dry and wet season  $O_3$  concentrations over the forest [Browell *et al.*, 1990] would imply a dry season deposition flux to the Amazon forest of  $17 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ . Another term in the  $O_3$  budget is the time tendency, but this term is also small. Seasonal trends in the tropospheric  $O_3$  column at sites in the South Atlantic basin are of the order of 5 DU per month, or  $5 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$  [Olson *et al.*, this issue].

The close balance between chemical production and chemical loss of  $O_3$  in the 0 to 12-km column implies that the total column amount of  $O_3$  can be explained by in situ photochemistry, with net production above 6-km altitude balancing weak net loss below. To demonstrate this point, we conducted a one-dimensional photochemical steady state model calculation for  $O_3$  in the 0 to 12-km column, fixing as input the median vertical profiles of  $O_3$  precursors and other conditions from Table 1a and adopting a zero-flux upper boundary condition at 12-km altitude. The calculation assumed an  $O_3$  deposition velocity of  $0.05 \text{ cm s}^{-1}$ , a uniform vertical eddy diffusion coefficient  $K_z = 3 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ , and 24-hour average clear-sky photolysis rates. Results in Figure 5 show that it is possible to explain the  $O_3$  concentrations and vertical gradients observed in the 0 to 12-km column in TRACE A without invoking any exogenous  $O_3$  source.

The median lifetime of  $O_x$  against chemical loss over the South Atlantic basin is 6 days at 0-4 km, 25 days at 4-8 km, and

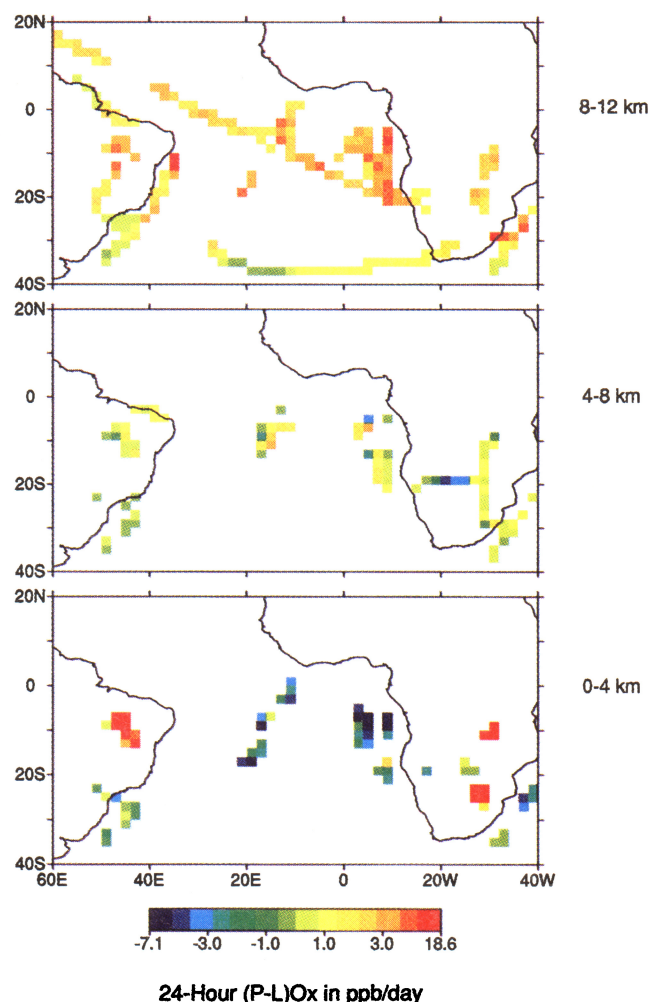


Plate 1b. Twenty-four-hour average net  $O_x$  production rates computed at 0 to 4-km, 4 to 8-km, and 8 to 12-km altitude in TRACE A.

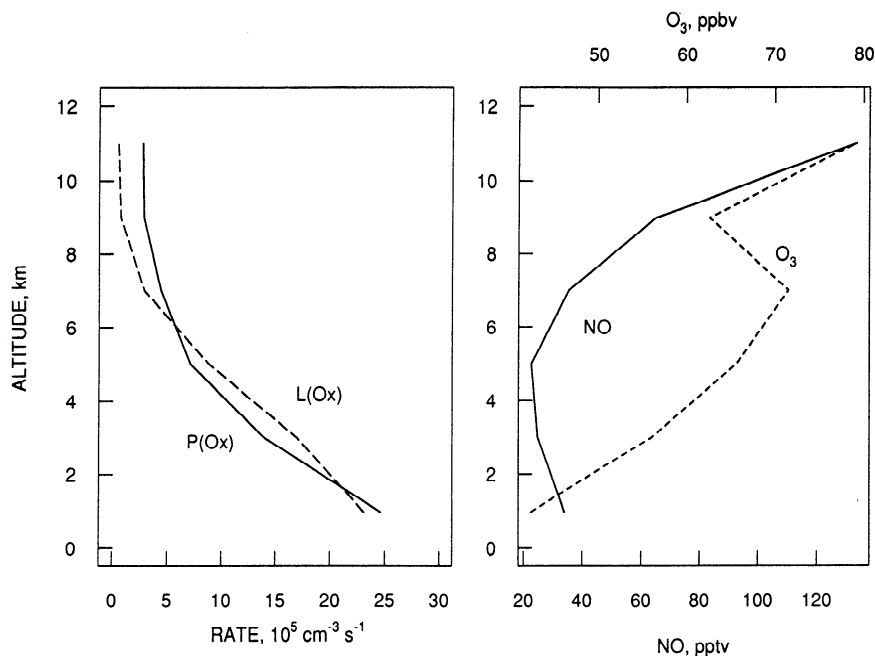


Figure 4. (Left) Median 24-hour average production and loss rates of  $O_x$  in the southern hemisphere TRACE A data as a function of altitude. (Right) Median concentrations of  $O_3$  and NO.

105 days at 8–12 km (Table 4). As the altitude increases, the loss of  $O_3$  becomes increasingly controlled by subsidence. Subsidence from the upper to the lower troposphere over the South Atlantic takes place on a timescale of the order of 10 days [Krishnamurti *et al.*, this issue]; we thus expect a characteristic time of about 2 weeks for  $O_3$  to adjust to chemical steady state in the 0 to 12-km column. Such a characteristic time is sufficiently long that horizontal mass exchange with other regions could represent an important term in the budget of tropospheric  $O_3$  over the South Atlantic basin. However, it appears from our close regional balance between chemical production and loss that this term does not provide either a major net source or a major net sink of  $O_3$  in the South Atlantic basin troposphere, i.e., that the horizontal flux divergence is small. A general representation of the  $O_3$  budget in the tropical troposphere consistent with this view is presented in section 7.

Tropospheric  $O_3$  columns observed over the South Atlantic basin during the wet season are about 40% lower than observed in

TRACE A [Kirchhoff *et al.*, 1991; Olson *et al.*, this issue; Thompson *et al.*, this issue]. We examined whether these wet season columns could be sustained by in situ photochemical production in the same way as in TRACE A. For this purpose we decreased the NO and CO levels in the one-dimensional model to represent an atmosphere unaffected by biomass burning. Singh *et al.* [1990] reported a median NO concentration of 8 pptv at 0 to 6-km altitude over the Amazon basin in April–May (wet season), with little vertical gradient. Drummond *et al.* [1988] reported a median NO concentration of 60 pptv at 11.5-km altitude between Rio de Janeiro and Dakar in June, at the beginning of the dry season when biomass burning influence is small and tropospheric  $O_3$  columns still assume wet season values [Kirchhoff *et al.*, 1991]. We took these observations, which are about 3 times lower than in TRACE A, as constraints in the model. We further adopted a background CO concentration of 50 ppbv. Hydrocarbon concentrations were not modified from their values in Table 1a because they have little effect on  $O_3$  production. As shown in Figure 5,

**Table 4.** Budget of Tropospheric Ozone Over the South Atlantic Basin

	Altitude, km		
	0–4	4–8	8–12
Number of Model Points			
	292	246	574
Production and loss, ppbv d <sup>-1</sup>			
$P_{Ox}$	8.0	3.8	2.9
$L_{Ox}$	9.0	3.6	0.7
$(P-L)_{Ox}$	-0.7	0.3	2.1
Column rates, 10 <sup>10</sup> cm <sup>2</sup> s <sup>-1</sup>			
$P_{Ox}$	77	23	11
$L_{Ox}$	80	24	3
$(P-L)_{Ox}$	-6	2	8
$O_3$ lifetime ( $[O_3]/L_{Ox}$ ), days	6	25	105
$O_3$ replacement time ( $[O_3]/P_{Ox}$ ), days	7	20	24

Median 24-hour average rates and characteristic times computed in the model for the southern hemisphere TRACE A data.  $O_x$  is odd oxygen ( $O_x = O_3 + O + NO_2 + HNO_4 + (2x)NO_3 + (3x)N_2O_5$  + peroxyacylnitrates). Column rates refer to the 4-km altitude bands. Because values are medians instead of means,  $(P-L)_{Ox}$  and  $P_{Ox} - L_{Ox}$  are not identical.

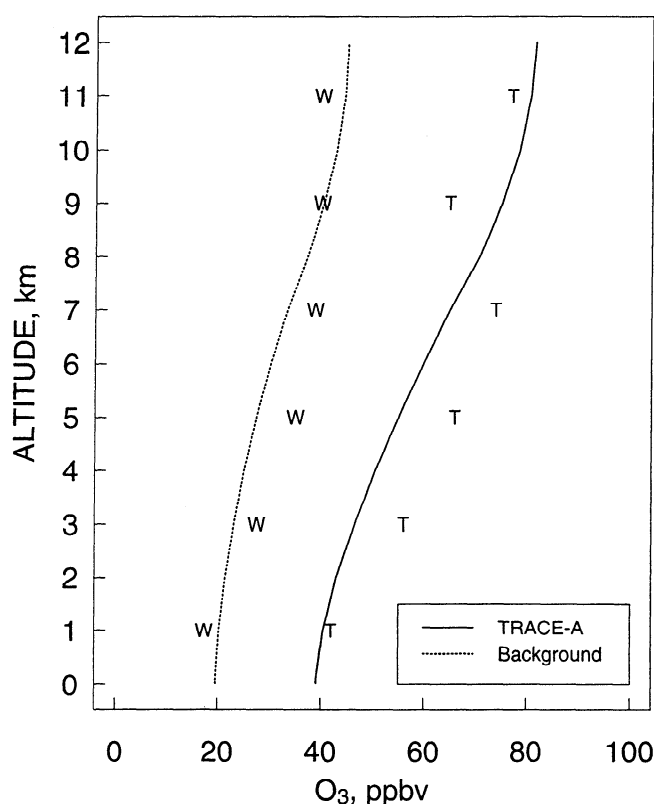


Figure 5. Steady state  $O_3$  concentrations computed in a one-dimensional photochemical model constrained with the median TRACE A observations for  $O_3$  precursors (solid line) and with NO and CO concentrations reduced to reflect a background atmosphere free of biomass burning influence (dotted line). The model uses a zero-flux boundary condition at 12-km altitude. The "T" symbols are the median  $O_3$  concentrations in the southern hemisphere TRACE A data. The "W" symbols are the mean wet season (March-May)  $O_3$  concentrations observed at Natal, Brazil [Kirchhoff et al., 1991].

the vertical  $O_3$  profile computed in the one-dimensional model is consistent with the mean wet season ozonesonde observations by Kirchhoff et al. [1991] at Natal, Brazil. It thus appears that the tropospheric  $O_3$  column over the South Atlantic basin during the wet season can be sustained fully by in situ production, similarly to the dry season. Although  $NO_x$  levels are lower than in the dry season, the  $O_3$  levels to be sustained are also lower.

The above analysis implies a strong sensitivity of tropospheric  $O_3$  over the South Atlantic basin to the supply of  $NO_x$ . We show in Figure 6 the dependence of the net  $O_3$  production rate on  $NO_x$  concentrations in the model for points representing the median conditions observed in TRACE A at 0 to 4 km, 4 to 8 km, and 8 to 12-km altitude (Table 1a). Even at the relatively high  $NO_x$  concentrations observed in TRACE A,  $O_3$  production is still  $NO_x$  limited throughout the 0 to 12 km column. A number of authors have noted that  $NO_x$  levels in the remote troposphere are near the turnover point for net  $O_3$  production versus net loss [Chameides et al., 1987, 1990; Jacob et al., 1992; Liu et al., 1992; Mauzerall et al., 1996; Carroll and Thompson, 1995], and this is also found in the TRACE A data below 8 km (Figure 6). Based on the discussion above, we explain this general result as reflecting the tendency of  $O_3$  to approach a chemical steady state determined by the  $NO_x$  concentration.

## 6. Nitrogen Oxides

Several authors have examined the primary sources of  $NO_x$  over the South Atlantic basin in TRACE A by correlating the observed NO concentrations with chemical variables and with back-trajectories [Smyth et al., this issue; Singh et al., this issue; Talbot et al., this issue; Pickering et al., this issue]. They conclude that biomass burning was a major source of  $NO_x$  throughout the tropospheric column, and that lightning was also a major and perhaps dominant source in the upper troposphere. Soil emissions would provide an additional source of  $NO_x$  in the continental boundary layer [Jacob and Wofsy, 1988, 1990] but the TRACE A data are not well suited for assessing the importance of this source. Transport from the stratosphere was a negligible contributor to the  $NO_x$  budget even in the upper troposphere [Smyth et al., this issue].

Chemical cycling between  $NO_x$  and its oxidation products played probably a major role in maintaining high  $NO_x$  concentrations over the South Atlantic during TRACE-A. The mean lifetime of  $NO_x$  against reactions (8)-(10) computed in the model for the TRACE A conditions is only 4 hours at 0-4 km and 2.4 days at 8-12 km. Plate 2 shows the distribution of  $NO_x$  concentrations over the South Atlantic basin as a function of longitude and altitude (NO is measured and  $NO_2$  is from the photochemical model). Concentrations are high in the continental boundary layer and the upper troposphere, consistent with primary sources

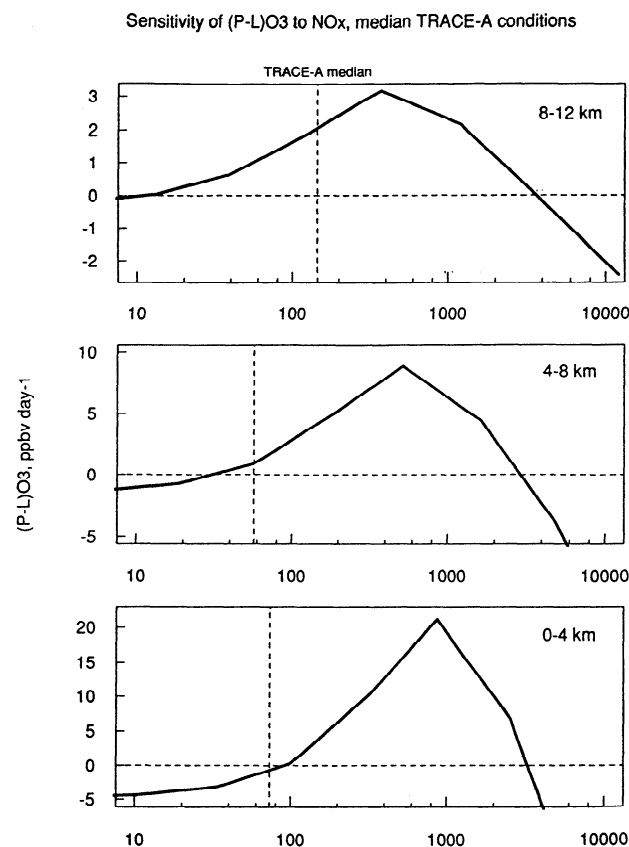


Figure 6. Dependence of the computed 24-hour average net  $O_3$  production rate on  $NO_x$  concentrations for the TRACE A conditions. All variables other than  $NO_x$  are specified at their median TRACE A values given in Table 1a for 0-4, 4-8, and 8-12 km altitude. The dashed vertical lines show the median  $NO_x$  concentrations in the southern hemisphere TRACE A data for the different altitude bands.



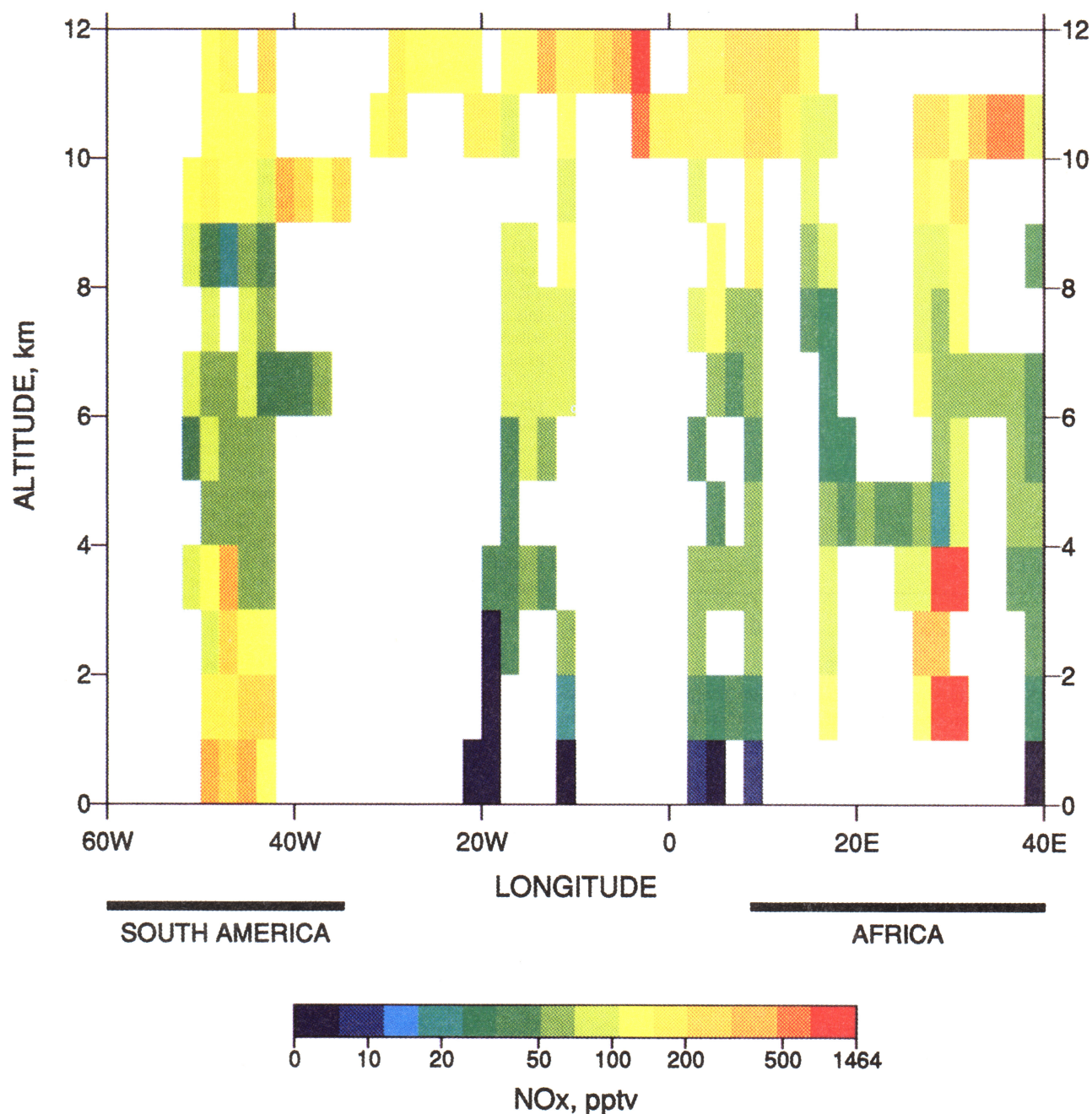


Plate 2. Mean concentration of  $\text{NO}_x$  in TRACE A at  $0^\circ$ – $30^\circ\text{S}$  latitude, as a function of longitude and altitude.

from combustion, soils, and lightning; during deep convective events over the continents,  $\text{NO}_x$  from combustion and soils is injected to the upper troposphere, and additional  $\text{NO}_x$  is produced by lightning. However, above 4 km we find no significant decrease of  $\text{NO}_x$  from continents to oceans, even though the primary sources of  $\text{NO}_x$  are continental (there is little lightning over the oceans) and the lifetime of  $\text{NO}_x$  is short. It appears that the high concentrations over the oceans must be maintained by chemical recycling.

We used our photochemical model to diagnose the degree to which  $\text{NO}_x$  levels in TRACE A could be maintained by chemical recycling based on current understanding of tropospheric chemistry. For this purpose we computed the chemical production and loss rates of  $\text{NO}_x$  at individual points in the merged time series matched to the  $\text{HNO}_3$  sampling times, using the model con-

strained with measurements of  $\text{NO}$ ,  $\text{HNO}_3$ , and PAN (details of the approach are given in section 2). Figure 7 shows the ratio of chemical loss to chemical production of  $\text{NO}_x$  for individual points as a function of altitude, and Table 5 summarizes the contributions of individual reactions to the  $\text{NO}_x$  budget at different altitudes. Below 4 km there is considerable scatter for individual points, reflecting primarily the relative abundances of  $\text{NO}_x$  and PAN; on average, we find a balance between the source of  $\text{NO}_x$  from decomposition of PAN and the sinks of  $\text{NO}_x$  from oxidation to  $\text{HNO}_3$  and PAN. The data below 4 km are not inconsistent with a scenario where PAN produced in biomass burning plumes decomposes to sustain  $\text{NO}_x$  levels in the lower troposphere on the regional scale, but the paucity of points precludes any reliable analysis.

Above 8 km we find a systematic imbalance in the chemical

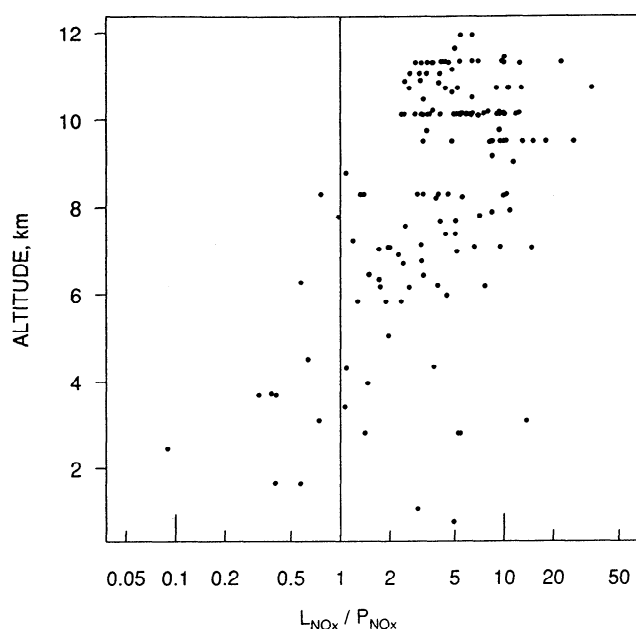


Figure 7. Ratio of 24-hour average chemical loss to chemical production rates of  $\text{NO}_x$  as a function of altitude for individual measurement time intervals in the southern hemisphere TRACE A data.

budget for  $\text{NO}_x$  (Figure 7), with production of  $\text{NO}_x$  balancing on average only 16% of the loss. This deficit is due to insufficient recycling of  $\text{HNO}_3$  to  $\text{NO}_x$ ; recycling of PAN is not an issue because rates for  $\text{NO}_x$ -PAN cycling are slow and PAN is near chemical steady state (Table 5). The median rate of conversion of  $\text{NO}_x$  to  $\text{HNO}_3$  at 8–12 km in the model is  $57 \text{ pptv day}^{-1}$ , while the median observed  $\text{HNO}_3$  concentration at that altitude is 59 pptv. A  $\text{HNO}_3$  lifetime of 1 day would be necessary to balance the  $\text{HNO}_3$  budget, but the median lifetime of  $\text{HNO}_3$  against pho-

tolysis and reaction with OH is 12 days. It thus appears that a major mechanism for high-altitude conversion of  $\text{HNO}_3$  to  $\text{NO}_x$  may be missing from the model. The problem would remain even if  $\text{N}_2\text{O}_5$  conversion to  $\text{HNO}_3$  in aerosols did not proceed, as this reaction accounts, on average, for only 30% of the conversion of  $\text{NO}_x$  to  $\text{HNO}_3$  (Table 5).

The above analysis suggests that  $\text{HNO}_3$  in the upper troposphere must be consumed on a timescale of 1 day to eventually regenerate  $\text{NO}_x$ . Chatfield (1994) proposed that rapid reaction of  $\text{HNO}_3$  with  $\text{CH}_2\text{O}$  in acid aerosols might take place and yield  $\text{NO}_x$  and formic acid as immediate products. We find, however, no correlation between  $\text{HNO}_3$  and  $\text{NO}_x$  concentrations in the TRACE A data above 8 km (Figure 8), which argues against direct conversion of  $\text{HNO}_3$  to  $\text{NO}_x$  on a short time scale. Fan *et al.* [1994] proposed that the reaction of  $\text{HNO}_3$  with  $\text{CH}_2\text{O}$  in acid aerosols may not produce  $\text{NO}_x$  but hydroxymethylnitrate  $\text{H}_2\text{C}(\text{OH})\text{ONO}_2$ ; this species could then photolyze to yield  $\text{NO}_x$  on a timescale of one week, based on laboratory data for other organic nitrates [Barnes *et al.*, 1993]. The Fan *et al.* [1994] mechanism would be more consistent with the lack of correlation between  $\text{NO}$  and  $\text{HNO}_3$  in the TRACE A data.

## 7. Schematic for Ozone in the Tropical Troposphere

Our analysis of the TRACE A data suggests a simple schematic for the regional budget of tropospheric  $\text{O}_3$  over the South Atlantic basin. Continental  $\text{NO}_x$  emissions from South America and southern Africa are pumped to the middle and upper troposphere by convection, leading to ubiquitous net production of  $\text{O}_3$  in the upper troposphere. Eventually, the air subsides over the Atlantic Ocean and net loss of  $\text{O}_3$  takes place. Low-level advection to the continents closes the  $\text{O}_3$  cycle. We propose that this schematic can be extended to other tropical regions and provides a general explanation for the origin of  $\text{O}_3$  in the tropical troposphere, as illustrated in Figure 9. In this figure, the large-scale circulation of the tropical atmosphere is represented by the

Table 5. Chemical Cycling of  $\text{NO}_x$  over the South Atlantic Basin

	Altitude Band, km		
	0–4	4–8	8–12
Number of Model Points			
	15	37	149
$\text{NO}_x$ loss, $\text{pptv d}^{-1}$			
$\text{NO}_2 + \text{OH}$	230	50	41
$\text{N}_2\text{O}_5 + \text{aerosol}$	141	37	16
$\text{CH}_3\text{CO}_3 + \text{NO}_2$	132	19	7
$\text{RO}_2 + \text{NO}_x^a$	74	4	1
Total Loss	787	112	67
$\text{NO}_x$ production, $\text{pptv d}^{-1}$			
$\text{HNO}_3$ photolysis	14	3	2
$\text{HNO}_3 + \text{OH}$	24	3	2
PAN thermolysis	728	6	<1
PAN photolysis	6	8	7
Total Production	900	31	12
$\text{NO}_x$ lifetime, days	0.18	0.66	2.4

Median 24-hour average rates and lifetimes computed in the model for the southern hemisphere TRACE A data. Because the values shown are medians, the sum of the individual rates does not add up to the total production or loss of  $\text{NO}_x$ , and the median lifetime does not match exactly the corresponding concentration and loss rate; this effect is particularly noticeable at 0–4 km where the scatter of rates for individual points is large and the number of points is small. The rates of production and loss of PAN have been corrected for internal cycling within the  $(\text{CH}_3\text{CO}_3 + \text{PAN})$  family as described in Appendix B.

<sup>a</sup> Formation of all organic nitrates other than PAN. These organic nitrates are assumed inert in the model.



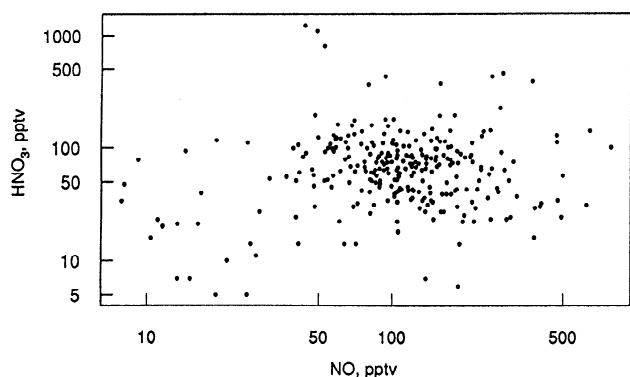


Figure 8. Relationship of  $\text{HNO}_3$  and  $\text{NO}$  concentrations in the TRACE A daytime data (0800–1600 local time) at 8 to 12-km altitude.

Walker cells [after Newell, 1979]. Transfer of air from the lower to the upper troposphere takes place mainly by deep wet convection over South America, Africa, and Oceania (rising branches of the Walker cells). These convective motions inject to the upper troposphere  $\text{NO}_x$  emitted over the continents by combustion and soils, and additional  $\text{NO}_x$  produced by lightning in the convective column. The injection of  $\text{NO}_x$  then drives  $\text{O}_3$  production in the upper troposphere. It must be pointed out that although production of  $\text{O}_3$  in the upper troposphere is necessary to explain the observed increase of  $\text{O}_3$  concentrations with altitude and to balance the net  $\text{O}_3$  loss in the lower troposphere, most of the  $\text{O}_3$  production in the tropospheric column actually takes place in the lower and middle troposphere (Figure 4).

Some support for the schematic in Figure 9 is offered by data from the equatorial Pacific. Piotrowicz *et al.* [1991] found that the distribution of  $\text{O}_3$  concentrations in surface air over the equatorial Pacific is highly sensitive to seasonal and interannual movements of the Pacific Walker cell. Fishman *et al.* [1990] reported a west-to-east gradient of increasing tropospheric  $\text{O}_3$  columns across the Pacific which may be explained by net  $\text{O}_3$  production in the upper troposphere westerlies and net loss in the lower troposphere easterlies. It is well established that the lower troposphere of the equatorial Pacific is a net sink for  $\text{O}_3$  [Liu *et al.*, 1983; Johnson *et al.*, 1990]. Limited aircraft data for the western tropical Pacific indicate net  $\text{O}_3$  loss taking place below 6-km altitude and net production taking place above, with  $\text{O}_3$  production balancing 60% of  $\text{O}_3$  loss in the 0 to 12-km column [Davis *et al.*, 1996].

Our representation of the budget of  $\text{O}_3$  in the tropical troposphere goes back to the earliest papers arguing that the tropospheric  $\text{O}_3$  budget is dominated by in situ production and that transport from the stratosphere is small in comparison [Chameides and Walker, 1973; Crutzen, 1973; Fishman *et al.*, 1979; Liu *et al.*, 1980]. Much uncertainty was attached to these early studies because of the lack of reliable  $\text{NO}$  data. Liu *et al.* [1980] first proposed the idea of a photochemical steady state of  $\text{O}_3$  in the tropospheric column with net production in the upper troposphere compensating for net loss in the lower troposphere. They argued that the  $\text{NO}_x$  in the upper troposphere driving the in situ production would originate from the stratosphere, but the TRACE A data as well as previous work [Kasibhatla *et al.*, 1991; Penner *et al.*, 1991; Murphy *et al.*, 1993] show that stratospheric influx is negligible compared to combustion and lightning as a source of  $\text{NO}_x$  in the tropical upper troposphere.

## 8. Conclusions

Photochemical modeling of TRACE A aircraft observations over the South Atlantic basin up to 12-km altitude indicates a close balance between chemical production and loss of  $\text{O}_3$  in the 0 to 12-km column, with net production in the upper troposphere balancing weak net loss in the lower troposphere. Influx from the stratosphere is unimportant as a source of tropospheric  $\text{O}_3$  in the region. We conclude that the tropospheric  $\text{O}_3$  column can be maintained solely by in situ photochemistry. The photochemical production of  $\text{O}_3$  is limited by the supply of  $\text{NO}_x$ , even in the upper troposphere. Past observations of the remote troposphere indicate that  $\text{NO}_x$  concentrations are generally near the turnover point for net  $\text{O}_3$  production versus net  $\text{O}_3$  loss; we interpret this observation as reflecting the tendency of  $\text{O}_3$  concentrations to adjust to a chemical steady state defined by the available  $\text{NO}_x$ .

Biomass burning and lightning were the two primary sources of  $\text{NO}_x$  over the South Atlantic basin in TRACE A. Considering the short lifetime of  $\text{NO}_x$  against oxidation (only 2–3 days at 8–12 km altitude), it appears that the high  $\text{NO}_x$  levels observed throughout the South Atlantic basin were maintained by chemical recycling of  $\text{NO}_x$  from its oxidation products. The low  $\text{HNO}_3/\text{NO}$  concentration ratios observed above 8 km imply rapid conversion of  $\text{HNO}_3$  to  $\text{NO}_x$  by a mechanism not considered in current models.

We presented a simple schematic for the origin of  $\text{O}_3$  in the South Atlantic basin troposphere linking the large-scale Walker circulation to in situ photochemistry. Convection over South America and southern Africa injects  $\text{NO}_x$  from combustion, soils, and lightning to the middle and upper troposphere, leading to net

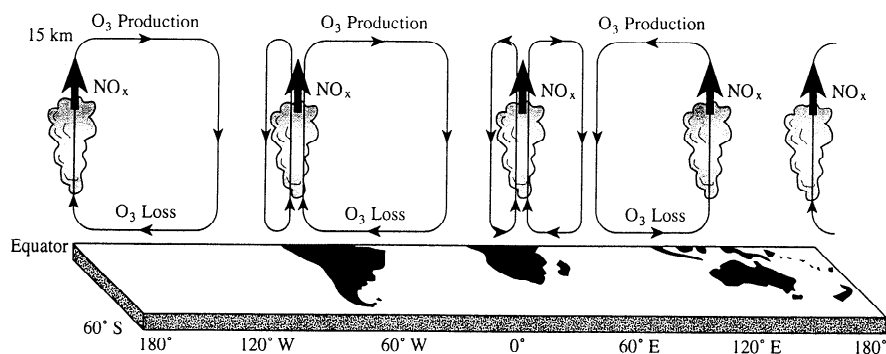


Figure 9. Schematic depiction of the  $\text{O}_3$  budget in the tropical troposphere. Net  $\text{O}_3$  production in the upper troposphere balances net  $\text{O}_3$  loss in the lower troposphere. Mass exchange between the lower and the upper troposphere is represented by the Walker circulation [after Newell, 1979]. Deep convective motions over South America, southern Africa, and Oceania (rising branches of the Walker circulation) inject  $\text{NO}_x$  from combustion, soils, and lightning to the upper troposphere, driving  $\text{O}_3$  production. Eventually, the air subsides over the oceans and net  $\text{O}_3$  loss takes place in the lower troposphere due to low  $\text{NO}_x$  concentrations and high humidities, closing the  $\text{O}_3$  cycle.

O<sub>3</sub> production; eventually, the air subsides over the Atlantic Ocean and net loss of O<sub>3</sub> takes place in the lower troposphere due to reduced NO<sub>x</sub> levels and high humidities. Low-level advection of marine air to the continents closes the O<sub>3</sub> cycle. We proposed that the same schematic applies to other tropical regions and offers a general representation of the O<sub>3</sub> budget in the tropical troposphere. This mechanism would imply a great sensitivity of the global oxidizing power of the atmosphere to NO<sub>x</sub> emissions from tropical continents.

Peroxide concentrations measured aboard the aircraft in TRACE A offered a sensitive test of the O<sub>3</sub> production and loss rates computed in our photochemical model. We found that the model captures 78% and 74% of the observed variances of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH concentrations, respectively. Below 8-km altitude there is no mean bias for H<sub>2</sub>O<sub>2</sub> and a 30% negative bias for CH<sub>3</sub>OOH. Above 8-km the model underestimates H<sub>2</sub>O<sub>2</sub> by a factor of 1.8 and CH<sub>3</sub>OOH by a factor of 3.6. Even allowing for these discrepancies, the agreement between modeled and observed peroxide concentrations is sufficiently good to lend confidence in our conclusions regarding the O<sub>3</sub> budget in the tropospheric column.

Formaldehyde concentrations measured aboard the aircraft provided another test of photochemistry in the model. The model captures 62% of the variance of measured CH<sub>2</sub>O concentrations but tends to overestimate concentrations in the lower troposphere (0–4 km) and underestimate concentrations in the middle troposphere (4–8 km). The largest discrepancy between model and observations is in the marine boundary layer, where the model is too high by a factor of 3. A review of previous data in the tropical marine boundary layer indicates considerable variability in measured CH<sub>2</sub>O concentrations that cannot be explained with current models. The issue requires further investigation.

## Appendix A: Photochemical Model

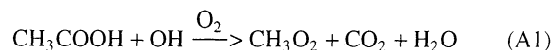
Our photochemical mechanism includes inorganic and methane chemistry from *DeMore et al.* [1994], and non-methane hydrocarbon chemistry from *Atkinson et al.* [1993] and *Atkinson* [1994]. The rate constant and branching ratio for the CH<sub>3</sub>OOH+OH reaction are from *Vaghjiani and Ravishankara* [1989]. The yield of O(<sup>1</sup>D) from photolysis of O<sub>3</sub> is from *Michelsen et al.* [1994]. Recent data are used for the photolysis of HNO<sub>3</sub> [*Burkholder et al.*, 1993], PAN [*Talukdar et al.*, 1995], and ketones [*Raber and Moortgat*, 1995].

Hydrolysis of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> in aerosols is included with a rate constant determined by the collision frequency of N<sub>2</sub>O<sub>5</sub> molecules on aerosol particles [*Fuchs and Sutugin*, 1971] and a reaction probability of 0.1 based on data for aqueous surfaces [*DeMore et al.*, 1994]. The collision frequency is computed using the aerosol size distribution (range 0.12 to 2 μm radius) measured aboard the aircraft with 10-s resolution. The reaction probability of N<sub>2</sub>O<sub>5</sub> on the aerosol surface would be low if the aerosol were solid [*Mozurkewich and Calvert*, 1988]. At the temperatures and humidities found above 8-km altitude in TRACE A, the stable phase of the binary H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system is usually solid H<sub>2</sub>SO<sub>4</sub>•4H<sub>2</sub>O (sulfuric acid tetrahydrate, or SAT). The reaction probability of N<sub>2</sub>O<sub>5</sub> on SAT is only 0.001–0.01 [*Hanson and Ravishankara*, 1993]. However, the aerosol could be in a metastable liquid state. Considering that our model uses NO as an input variable, the inclusion of N<sub>2</sub>O<sub>5</sub> hydrolysis has no significant effect on the model photochemistry, but it provides a significant term in the computed mass balance for NO<sub>x</sub>. On the one hand, the rate of hydrolysis could be underestimated if there is significant aerosol surface area outside of the 0.12 to 2-μm particle size range; on the other hand, it could be overestimated if the aerosol includes a significant population of dry particles.

Photolysis frequencies are computed at each point using the clear-sky radiation model of *Logan et al.* [1981] with a surface

albedo of 0.1. They are then scaled for cloud and albedo effects using a factor  $CF = J_{\text{NO}_2, \text{Epplly}} / J_{\text{NO}_2, \text{clear}}$ , where  $J_{\text{NO}_2, \text{clear}}$  is the clear-sky NO<sub>2</sub> photolysis frequency computed with the radiation model at the local time of observation, and  $J_{\text{NO}_2, \text{Epplly}}$  is the value derived from the Epplly UV radiometer measurements using the parameterization of *Madronich* [1987], as described by *Davis et al.* [1993]. This parameterization is applicable only to solar zenith angles less than 70° and we therefore restrict our calculations to this range (97% of observations). Mean CF values in TRACE A were 0.99 at 0–2 km and 1.35 at 8–12 km; values of CF higher than 2 (maximum 2.51) were found when the aircraft flew through clouds or above stratus decks under high-Sun conditions. There was no significant dependence of CF on Sun angle. To check for consistency between the  $J_{\text{NO}_2}$  values computed from our clear-sky radiation model and those inferred from the Epplly data, we searched for cloud-free conditions in the aerosol lidar data and in videos taken from forward and nadir cameras aboard the aircraft. The only unambiguous clear-sky period was on flight 12 over Namibia (1200–1240 GMT), with the aircraft cruising at 10-km altitude. The mean CF for this period was 1.06.

Model results for CH<sub>3</sub>OOH and CH<sub>2</sub>O are sensitive to the oxidation mechanism assumed for acetic acid. Acetic acid concentrations measured in TRACE A averaged 2–3 ppbv throughout the 0 to 12-km column (Table 1a). No laboratory data are available to our knowledge for the products of acetic acid oxidation by OH. The mechanism proposed by *Atkinson* [1994],



would result in acetic acid providing a major source of CH<sub>3</sub>OOH and CH<sub>2</sub>O in the upper troposphere; at 230 K, 3 ppbv of acetic acid would produce as much CH<sub>2</sub>O as 1700 ppbv of CH<sub>4</sub>. However, the TRACE A data show no correlation between measured acetic acid and CH<sub>2</sub>O in the upper troposphere, even when measured acetic acid is as high as 8 ppbv (Figure A1). We conclude that either there is an error in the measurements, or the oxidation of acetic acid does not produce CH<sub>2</sub>O. To side step this problem, we assume for the purposes of the model that the oxidation of acetic acid follows the scheme of *Madronich and Calvert* [1989], which bypasses CH<sub>3</sub>OOH and CH<sub>2</sub>O formation:

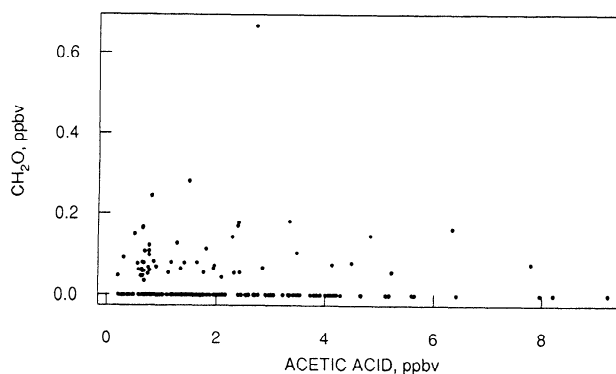
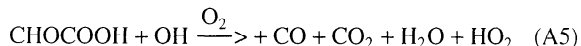
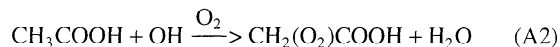


Figure A1. Relationship of CH<sub>2</sub>O and acetic acid concentrations in the TRACE A data at 8 to 12-km altitude.

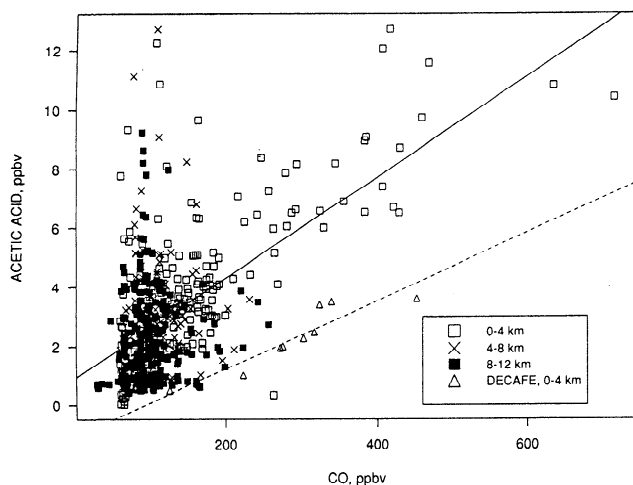


Figure A2. Relationship of acetic acid and CO concentrations in the southern hemisphere TRACE A data (squares, crosses) and in the DECAFE aircraft data over the Congo rainforest [Helas *et al.*, 1992]. The solid and dashed lines are linear best fits to the TRACE A and DECAFE data, respectively. The DECAFE data set consists of only 10 points.

When NO concentrations are low, formation of the organic peroxide  $\text{CH}_2(\text{OOH})\text{COOH}$  provides a temporary reservoir but does not change the ultimate fate of the carbon. With this mechanism, acetic acid has little effect on the model photochemistry even at the high concentrations measured in TRACE A.

The origin of the high acetic acid concentrations observed in TRACE A remains a puzzle. There are to our knowledge no previous observations in the upper troposphere that can be used for comparison. Figure A2 shows the relationship between acetic acid and CO in TRACE A, and compares to the relationship found in 10 dry season measurements taken at 0–4 km over the Congo rainforest during the Dynamique et Chimie en Forêt Equatoriale (DECAFE) expedition [Helas *et al.*, 1992]. Both the TRACE A and the DECAFE data show correlations between acetic acid and CO at 0–4 km, with similar slopes, indicating acetic acid emission from biomass burning; however, the TRACE A data include, also, a major component not correlated with CO, resulting in acetic acid concentrations about 3 ppbv higher than in DECAFE for the same amount of CO. The acetic acid concentrations measured in the upper troposphere in TRACE A were not correlated with CO or any of the other variables measured aboard the aircraft except formic acid. They do, however, show a pattern of higher values over Brazil and Africa than over the South Atlantic.

## Appendix B: Treatment of $\text{NO}_x$ -PAN Interconversion in $\text{NO}_x$ Budget Calculations

When assessing the importance of  $\text{NO}_x$ -PAN interconversion in a regional  $\text{NO}_x$  budget calculation constrained with observations for  $\text{NO}_x$  (or NO) and PAN, and with  $\text{CH}_3\text{CO}_3$  taken to be at steady state, one must correct the rates of reactions (10), (13), and (14) to account for cycling within the chemical family  $\text{PAN}_x = \text{CH}_3\text{CO}_3 + \text{PAN}$ . To illustrate the need for this correction, consider a situation where reactions (10), (13), and (14) dominate the production and loss of  $\text{CH}_3\text{CO}_3$ . Under this situation, given any specified input pair of  $\text{NO}_x$  and PAN concentrations, the steady state  $\text{CH}_3\text{CO}_3$  concentration computed in the model yields an apparent steady state between  $\text{NO}_x$  and PAN; this steady state plays, however, no role in regulating  $\text{NO}_x$  since loss of  $\text{NO}_x$  and  $\text{CH}_3\text{CO}_3$  by reaction (10) forces production of  $\text{NO}_x$  by reactions

(13) and (14) to maintain the  $\text{CH}_3\text{CO}_3$  steady state. Use of uncorrected rates  $R_{10}$ ,  $R_{13}$ , and  $R_{14}$  to construct a  $\text{NO}_x$  budget can lead to the illusion of a close balance between production and loss of  $\text{NO}_x$  and to an underestimate of the chemical lifetime of  $\text{NO}_x$ .

We account for this effect in our  $\text{NO}_x$  budget analyses by using corrected rates  $R'$ :

$$R'_{10} = R_{10} \frac{P_{\text{PAN}_x}}{P_{\text{PAN}_x} + R_{13} + R_{14}} \quad (\text{B1})$$

$$R'_{13} = R_{13} \frac{L_{\text{PAN}_x}}{P_{\text{PAN}_x} + R_{13} + R_{14}} \quad (\text{B2})$$

$$R'_{14} = R_{14} \frac{L_{\text{PAN}_x}}{P_{\text{PAN}_x} + R_{13} + R_{14}} \quad (\text{B3})$$

where  $P_{\text{PAN}_x}$  and  $L_{\text{PAN}_x}$  are the chemical production and loss rates of the  $\text{PAN}_x$  family. In the TRACE A data set, the correction factor  $P_{\text{PAN}_x}/(P_{\text{PAN}_x} + R_{13} + R_{14})$  ranges from 0.03 to 0.72 at 0–4 km and from 0.80 to 0.99 at 8–12 km. The correction factor  $L_{\text{PAN}_x}/(P_{\text{PAN}_x} + R_{13} + R_{14})$  ranges from 0.23 to 0.71 at 0–4 km and from 0.76 to 0.97 at 8–12 km. The largest corrections are in the lower troposphere, where thermal decomposition of PAN often dominates the  $\text{CH}_3\text{CO}_3$  source.

**Acknowledgements.** This work was supported by the NASA Global Tropospheric Chemistry Program and by the National Science Foundation (ATM-93-20778). We thank G.M. Gardner for compiling the merged time series, A.M. Thompson for providing us with the TOMS  $\text{O}_3$  data, V.W.J.H. Kirchhoff and two reviewers for insightful comments, and J.H. Yin for producing the color Figures.

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(Received February 24, 1995; revised December 22, 1995; accepted January 4, 1996.)