Origin of ozone and NO\textsubscript{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 O\textsubscript{3}, with net production at high altitudes compensating for weak net loss at low altitudes. This balance implies that O\textsubscript{3} concentrations in the 0-12 km column can be explained solely by in situ photochemistry; influx from the stratosphere is negligible. Simulation of H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, and CH\textsubscript{2}O concentrations measured aboard the aircraft lends confidence in the computations of O\textsubscript{3} production and loss rates, although there appears to be a major gap in current understanding of CH\textsubscript{2}O chemistry in the marine boundary layer. The primary sources of NO\textsubscript{x} over the South Atlantic Basin appear to be continental (biomass burning, lightning, soils). There is evidence that NO\textsubscript{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 HNO\textsubscript{3} to NO\textsubscript{x} in the upper troposphere by a mechanism not included in current models. A general representation of the O\textsubscript{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 NO\textsubscript{x} from combustion, soils, and lightning to the upper troposphere, leading to O\textsubscript{3} production; eventually, the air subsides and net O\textsubscript{3} loss takes place in the lower troposphere, closing the O\textsubscript{3} cycle. This scheme implies a great sensitivity of the oxidizing power of the atmosphere to NO\textsubscript{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 O\textsubscript{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 (NO\textsubscript{y} = NO + NO\textsubscript{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 O\textsubscript{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; Brownell et al., this issue; Loring et al., this issue]. There is also considerable uncertainty regarding the origin of NO\textsubscript{x}, the limiting precursor for O\textsubscript{3} production in the troposphere [Levy and Montzka, 1989; Penner et al., 1991; Kasibhatla et al., 1991, 1992].

We examine here the origin of O\textsubscript{3} and NO\textsubscript{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 O\textsubscript{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 O\textsubscript{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 NO\textsubscript{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 O\textsubscript{3} column observed in TRACE A, not just the biomass burning enhancement, and to draw general inferences regarding the budget of O\textsubscript{3} in the tropical troposphere. As pointed out by
Thompson et al. [this issue], the tropospheric O3 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 O3 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 H2O2, CH3OOH, and CH2O concentrations measured aboard the aircraft. Regional budgets for O3 and NOx over the South Atlantic basin are derived in sections 5 and 6, respectively. A general representation of the O3 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 O3, CO, NO, peroxyacetylinitrate (PAN), peroxypropionylnitrate (PPN), HNO3, speciated hydrocarbons, acetone, CH2O, CH3OOH, CH3O, and organic acids. Meteorological variables, UV fluxes, and aerosol number 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 |
|---------------------------------|-----------------|-----------------|-----------------|
|                                | 0-4 km          | 4-8 km          | 8-12 km         |
| Temperature, K                 | 284             | 258             | 230             |
| Dew point, K                   | 275             | 244             | 218             |
| UV flux, mW cm⁻²               |                 |                 |                 |
| zenith                         | 4.7             | 5.3             | 5.8             |
| nadir                          | 0.75            | 1.5             | 2.0             |
| O3, ppbv                       | 50              | 69              | 74              |
| CO, ppbv                       | 112             | 103             | 93              |
| CH32, ppbv                     | 1695            | 1707            | 1715            |
| NO, pptv                       | 25              | 29              | 120             |
| PAN, pptv                      | 175             | 294             | 223             |
| PPN, pptv                      | 4               | 3               | 2               |
| HNO3, pptv                     | 390             | 130             | 59              |
| Ethane, pptv                   | 590             | 630             | 670             |
| Propane, pptv                  | 48              | 46              | 58              |
| C4,5 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             |
| CH3COOH, pptv                  | 3030            | 2550            | 1900            |
| H2O2, pptv                     | 2800            | 760             | 150             |
| CH3OOH, pptv                   | 1200            | 320             | 60              |
| CH3O, pptv                     | 200             | <40             | <40             |
| Aerosol number, cm⁻³           |                 |                 |                 |
| 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 >C5 alkanes, >C3 alkenes, xylenes, isoprene, and terpenes were below the detection limit of 2 pptv. Concentrations of NO2 were measured in TRACE A, but the measurement is considered unreliable [Crawford et al., 1996] and is not used in the paper.

a Measured with an Eppley radiometer (Eppley, Inc., Newport, Rhode Island).
important). Loss of O\(_3\) is principally by reactions (3)-(5):

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} + \text{D}\quad \text{(3a)}
\]

\[
\text{O}(\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(3b)}
\]

where RO\(_2\) is any organic peroxy radical (CH\(_3\)O\(_2\) is the most important). Loss of O\(_3\) is principally by reactions (3)-(5):

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(1)}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad \text{(2)}
\]

where RO\(_2\) is any organic peroxy radical (CH\(_3\)O\(_2\) is the most important). Loss of O\(_3\) is principally by reactions (3)-(5):

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_3 \quad \text{(4)}
\]

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(5)}
\]

Calculation of O\(_3\) production and loss rates requires knowledge of the concentrations of HO\(_2\) radicals (OH, HO\(_2\), RO\(_2\)) 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.

A major objective of this paper is to derive a chemical budget for O\(_3\) in the tropospheric column over the South Atlantic basin (section 5). Our approach is to calculate 24-hour average O\(_3\) 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\(_3\) and other members of the odd-oxygen family (O\(_3\) = O\(_3\) + O + NO\(_2\) + HNO\(_2\) + (2x)NO\(_3\) + (3x)N\(_2\)O\(_5\) + peroxynitrates), hence the budget analysis must be based on O\(_3\) rather than on O\(_7\). Considering that Ox accounts typically for over 99% of O\(_3\), the budgets of O\(_3\) and O\(_7\) can be viewed as equivalent. Production of O\(_3\) is mainly by reactions (1) and (2):

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(1)}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad \text{(2)}
\]

where RO\(_2\) is any organic peroxy radical (CH\(_3\)O\(_2\) is the most important). Loss of O\(_3\) is principally by reactions (3)-(5):

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} + \text{D}\quad \text{(3a)}
\]

\[
\text{O}(\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(3b)}
\]

Table 2. Merged Time Series of TRACE A Data

<table>
<thead>
<tr>
<th>Matched Species</th>
<th>Time Resolution, min</th>
<th>Number of Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxides</td>
<td>4-5</td>
<td>1254</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>1</td>
<td>1496</td>
</tr>
<tr>
<td>NO</td>
<td>3</td>
<td>1781</td>
</tr>
<tr>
<td>HNO(_2)</td>
<td>2-15</td>
<td>722</td>
</tr>
</tbody>
</table>

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).

Comparison of simulated and observed peroxy concentrations (section 3).

Comparison of simulated and observed CH\(_3\)O concentrations (sections 4).

O\(_3\) production and loss rates and NO\(_2\) concentrations (sections 5 and 6).

Chemical budget of NO\(_x\) (section 6).
Table 3. Input Variables for the Photochemical Model Calculation

<table>
<thead>
<tr>
<th>Variable Type</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meteorological</td>
<td>pressure, temperature, humidity</td>
</tr>
<tr>
<td>Radiation</td>
<td>solar declination, latitude, O₃ column, cloud correction factor CF²</td>
</tr>
<tr>
<td>Chemical</td>
<td>O₂, CO, NO, PAN, HNO₃, CH₂O, C₆H₅ alkanes, C₃-7 alkanes, ethene, propene, C₆-11 alkenes, acetylene, benzene, toluene, xylene, isoprene, acetone, ethanol, formic acid, acetic acid, aerosol number concentrations in three size classes</td>
</tr>
</tbody>
</table>

² The total O₃ column is distributed vertically using the mean O₃ profiles measured by ozonesondes at Ascension Island and southern Africa during TRACE A [Thompson et al., 1995].
³ The cloud correction factor (CF) is calculated from the UV flux observations as described in Appendix A.
⁴ The model calculation assumes a constant concentration of NO (NO = NO + NO₂ + NO₃ + (2x)N₂O₅ + HNO₃ + HNO₂) over the diel cycle and adjusts the concentration of NO₃ to match the observed NO concentration at the time of day of observation.
⁵ Data for HNO₃ and PAN are required only for the NOx budget calculation of section 6. For other applications, if HNO₃ 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.
⁶ If data are not available for these variables, default values are used of 1.7 ppmv for CH₄ and zero for formic acid, acetic acid, and aerosol number concentrations.
⁷ See Table 1a for size class information.

Concentrations of H₂O₂, CH₂OOH, and CH₂O 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 HO₂ chemistry [Heikes, 1992; Liu et al., 1992]. Hydrogen peroxide is particularly valuable as a test of O₃ production in the model because its source,

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_3 \quad (7) \]

varies quadratically with the concentration of HO₂, the principal peroxy radical responsible for O₃ production. At low altitudes where H₂O₂ is the principal sink of HO₂, the concentration of H₂O₂ reflects the rate of the O(1D)+H₂O reaction which is the principal source of HO₂ and the principal sink of O₂.

We will also apply the model to study the chemical cycling of NOₓ over the South Atlantic basin in light of the concurrent measurements of NO, HNO₃, and PAN made aboard the aircraft (section 6). Oxidation of NOₓ to HNO₃ and PAN takes place on a timescale of the order of 1 day:

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (8) \]
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (9a) \]
\[ \text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (9b) \]
\[ \text{N}_2\text{O}_5 \rightarrow \text{2HNO}_3 \quad (9c) \]
\[ \text{NO}_3 + \text{CH}_2\text{CO}_3 + \text{M} \rightarrow \text{PAN} + \text{M} \quad (10) \]

Organic nitrates other than PAN are also formed but represent only minor sinks for NOₓ in the model. The species HNO₃ and PAN can act as reservoirs for NOₓ, decomposing to release NOₓ far from its point of origin:

\[ \text{HNO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{OH} \quad (11) \]
\[ \text{HNO}_3 + \text{OH} \rightarrow \text{NO}_3 + \text{H}_2\text{O} \quad (12a) \]

We compute the 24-hour average rates of reactions (8)-(14) in the model at individual points using the observed concentrations of NO, HNO₃, and PAN as constraints, as discussed above. The resulting mass balance between sources and sinks of NOₓ allows us to estimate the degree to which NOₓ concentrations are maintained by chemical recycling from HNO₃ and PAN through the above set of reactions. In such a NOₓ budget calculation it is necessary to correct the rates of conversion between NOₓ and PAN to account for cycling within the (CH₂CO₃+PAN) family: the correction is described in Appendix B.

Table 1b gives the median concentrations of OH, HO₂, CH₂O, NO₂, NOₓ, and HNO₃ computed in the model for the southern hemisphere TRACE A data set. Diel steady state for these species and for CH₂O is typically approached to within 10% after 2 days of integration in the model. The peroxydes, 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 NOₓ 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) C₃H₆ 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 HNO3 and PAN are critical only for the NO3 mass balance analysis presented in section 6. For all other applications, when data for HNO3 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 HO2 levels and other relevant model results.

3. Peroxides

Figure 2 compares simulated and observed concentrations of H2O2 and CH3OOH 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 H2O2 concentrations. This variance is determined strongly by water vapor (\( r^2 = 0.51 \) between observed H2O2 and H2O 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 H2O2 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 H2O2 against photochemical loss is relatively short (1.5 days below 2 km). The underestimate of H2O2 in the upper troposphere could reflect a missing HO2 source in the model but is also within the low-temperature uncertainties of the rate constants in the mechanism.

For CH3OOH 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, 0.70 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 CH3OOH+HO2, which is the only CH3OOH 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 CH3OOH could suggest the presence of major hydrocarbon precursors missing from the model, we find no parallel underestimate of CH2O that would support this hypothesis (see section 4).

The successful simulation of the peroxides below 8-km altitude lends confidence in the O3 production and loss rates computed by the model. At 8 to 12-km altitude the ~40% underestimate of H2O2 could imply an ~20% underestimate of HO2. Considering that HO2 accounts for ~90% of total peroxy radicals in that altitude range (Table 1b), we may expect the O3 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 HO2 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 H2O2, CH3OOH, HO2, and 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 HO2 makes the model underestimate of peroxy concentrations in the upper troposphere significantly worse.

4. Formaldehyde

Figure 3 compares simulated and observed CH2O concentrations for individual points in the merged time series matched to the CH2O 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 CH$_2$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 CH$_2$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 concentrations 26 parts per billion by volume (ppbv) O$_3$, 66 ppbv CO, 3 pptv NO, 0.015 vol/vol H$_2$O), where the mean observed concentration of CH$_2$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 H$_2$O$_2$ and CH$_3$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 H$_2$O$_2$ could be due to deposition [Heikes et al., 1990], but these discrepancies are small compared to CH$_2$O. We repeated the model calculation for the marine boundary layer points using observed concentrations of H$_2$O$_2$ and CH$_3$OOH as constraints, and assuming a deposition rate constant of 4x10$^{-2}$ s$^{-1}$ for CH$_2$O as a representative of a deposition velocity of 0.4 cm s$^{-1}$ over the ocean [Thompson and Zafiriou, 1983]. The mean CH$_2$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 CH$_2$O chemistry.

Our model results for CH$_2$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 CH$_2$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 CH$_2$O photolysis frequencies.

We compared the marine boundary layer measurements of CH$_2$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°N-30°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 CH$_2$O concentrations in the northern tropics during the Polarstern cruise and found a mean concentration of 0.37 ppbv at 10°N (they made no measurements further south). During the same cruise, Carlier et al. [1991] reported mean CH$_2$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°N; 30 ppbv O$_3$, 90 ppbv CO, 1.3 ppbv H$_2$O$_2$, 15 ppbv NO$_x$, 0.017 mol/mol H$_2$O, temperature of 293 K, and actinometer values of $J_{N_2}$ and $J_{Po}$ [Platt et al., 1992; Jacob and Klockow, 1992; Brouwers and Hofzumahaus, 1992; Hofzumahaus et al., 1992]. We obtained a model CH$_2$O concentration of 0.42 ppbv, in good agreement with the observations.

Other published measurements of CH$_2$O concentrations in clean tropical marine boundary layers include 0.4-1.1 ppbv over the Pacific [Zafiriou 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 CH$_2$O with organics in the marine aerosol. To our knowledge, the only concurrent gas phase and aerosol measurements of CH$_2$O in marine air are those of Kipling and Warneck [1980]. These authors found evidence that CH$_2$O in the aerosol is predominantly present as CH$_3$O$_2$ complexes, but they also found that the aerosol contributes only a small fraction of total atmospheric CH$_2$O.

In summary, our results point to a major gap in current understanding of CH$_2$O concentrations in the marine boundary layer. Either some of the CH$_2$O measurements are flawed or a large CH$_2$O sink is missing from the models under some conditions. Liu et al. [1992] previously noted that CH$_2$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 CH$_3$OOH and that CH$_2$O concentrations calculated in a model constrained with observed CH$_3$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 CH$_3$OOH and CH$_2$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 CH$_2$O in TRACE A is far greater than for CH$_3$OOH; also, as discussed above, there is no evidence in TRACE A for a model overestimate of CH$_2$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 CH$_3$OOH 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, $P_{O_3}$, and the net production rate, $P-L_{O_3}$, 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 $P_{O_3}$ and $L_{O_3}$ caused by the fixed-hydrocarbon approximation are small; for those points where the full model (including hydrocarbons) can be applied, the median ratio of $P_{O_3}$ to $L_{O_3}$ obtained in the full versus fixed-hydrocarbon versions of the model is 1.02±0.09 (1σ) when $P_{O_3}$ is less than 20 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 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 O$_3$ decreases on average with altitude while the net production increases with altitude. Median vertical profiles of $P_{O_3}$ and $L_{O_3}$, for the southern hemisphere TRACE A data are plotted in Figure 4, and a summary 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 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 O$_3$ taking place below 2-km altitude, but this portion of the budget is highly uncertain because of the large variability of O$_3$ production rates for individual points; there is a sharp contrast between the
of $10 \times 10^{16}$ cm$^{-2}$ 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 $17 \times 10^{16}$ cm$^{-2}$ 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 $5 \times 10^{16}$ molecules cm$^{-2}$ 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 cm s$^{-1}$, a uniform vertical eddy diffusion coefficient $K_v = 3 \times 10^5$ cm$^2$ 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$_3$ against chemical loss over the South Atlantic basin is 6 days at 0-4 km, 25 days at 4-8 km, and 8-12 km.

Plate la. Twenty-four-hour average gross production rates of odd oxygen (O$_x$ = O$_3$ + O + NO$_2$ + HNO$_3$ + (2x)NO$_3$ + (3x)N$_2$O$_5$ + peroxyacetylitrates) computed at 0 to 4-km, 4 to 8-km, and 8 to 12-km altitude in TRACE A.

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 $P_{O_3}$ and $L_{O_3}$ for the 0 to 12-km column are both $1.1 \times 10^{12}$ cm$^{-2}$ 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 $1 \times 10^{10}$ cm$^{-2}$ 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 $P_{O_3}$ at 8 to 12-km altitude is $1 \times 10^{11}$ cm$^{-2}$ 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 $1.7 \times 10^{16}$ cm$^{-2}$ s$^{-1}$ during TRACE A. Fan et al. [1990] measured a 24-hour average O$_3$ deposition flux of $8 \times 10^{15}$ cm$^{-2}$ 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 $17 \times 10^{16}$ cm$^{-2}$ 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 $5 \times 10^{16}$ molecules cm$^{-2}$ s$^{-1}$ [Olson et al., this issue].

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The median lifetime of O$_3$ against chemical loss over the South Atlantic basin is 6 days at 0-4 km, 25 days at 4-8 km, and 8-12 km.

Plate lb. Twenty-four-hour average net O$_3$ production rates computed at 0 to 4-km, 4 to 8-km, and 8 to 12-km altitude in TRACE A.
105 days at 8-12 km (Table 4). As the altitude increases, the loss of O₃ 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 O₃ 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 O₃ 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 O₃ in the South Atlantic basin troposphere, i.e., that the horizontal flux divergence is small. A general representation of the O₃ budget in the tropical troposphere consistent with this view is presented in section 7.

Tropospheric O₃ 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 O₃ 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 3 because they have little effect on O₃ production. As shown in Figure 5,

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

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>0-4</th>
<th>4-8</th>
<th>8-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Model Points</td>
<td>292</td>
<td>246</td>
<td>574</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Production and loss, ppbv d⁻¹</th>
<th>P_{O₃N}</th>
<th>L_{O₃N}</th>
<th>(P-L)_{O₃N}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>9.0</td>
<td>-0.7</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Column rates, 10¹⁰ cm⁻² s⁻¹</th>
<th>P_{O₃N}</th>
<th>L_{O₃N}</th>
<th>(P-L)_{O₃N}</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>80</td>
<td>-6</td>
<td></td>
</tr>
</tbody>
</table>

| O₃ lifetime ([O₃]/L_{O₃N}), days | 6 | 24 | 105 |
| O₃ replacement time ([O₃]/P_{O₃N}), days | 7 | 20 | 24 |

Median 24-hour average rates and characteristic times computed in the model for the southern hemisphere TRACE A data. O₃ is odd oxygen (O₃ = O₃ + O + NO₂ + HNO₃ + (2x)NO₃ + (3x)N₂O₅ + peroxyacylnitrates). Column rates refer to the 4-km altitude bands. Because values are medians instead of means, (P-L)_{O₃N} and P_{O₃N} - L_{O₃N} 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 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. We show in Figure 6 the dependence of the net $O_3$ production rate on NO 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 concentrations observed in TRACE A, $O_3$ production is still NO limited throughout the 0 to 12 km column. A number of authors have noted that NO 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; Mauler 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 concentration.

6. Nitrogen Oxides

Several authors have examined the primary sources of NO 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 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 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 budget even in the upper troposphere [Smyth et al., this issue].

Chemical cycling between NO and its oxidation products played probably a major role in maintaining high NO concentrations over the South Atlantic during TRACE-A. The mean lifetime of NO 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 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 concentrations for the TRACE A conditions. All variables other than NO 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 concentration in the southern hemisphere TRACE A data for the different altitude bands.
from combustion, soils, and lightning; during deep convective events over the continents, NO\textsubscript{x} from combustion and soils is injected to the upper troposphere, and additional NO\textsubscript{x} is produced by lightning. However, above 4 km we find no significant decrease of NO\textsubscript{x} from continents to oceans, even though the primary sources of NO\textsubscript{x} are continental (there is little lightning over the oceans) and the lifetime of NO\textsubscript{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 NO\textsubscript{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 NO\textsubscript{x} at individual points in the merged time series matched to the HNO\textsubscript{3} sampling times, using the model constrained with measurements of NO\textsubscript{y}, HNO\textsubscript{3}, and PAN (details of the approach are given in section 2). Figure 7 shows the ratio of chemical loss to chemical production of NO\textsubscript{x} for individual points as a function of altitude, and Table 5 summarizes the contributions of individual reactions to the NO\textsubscript{x} budget at different altitudes. Below 4 km there is considerable scatter for individual points, reflecting primarily the relative abundances of NO\textsubscript{x} and PAN; on average, we find a balance between the source of NO\textsubscript{x} from decomposition of PAN and the sinks of NO\textsubscript{x} from oxidation to HNO\textsubscript{3} and PAN. The data below 4 km are not inconsistent with a scenario where PAN produced in biomass burning plumes decomposes to sustain NO\textsubscript{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
The above analysis suggests that HNO₃ in the upper troposphere must be consumed on a timescale of 1 day to eventually regenerate NOₓ. Chatfield (1994) proposed that rapid reaction of HNO₃ with CH₃O in acid aerosols might take place and yield NOₓ and formic acid as immediate products. We find, however, no correlation between HNO₃ and NO concentrations in the TRACE A data above 8 km (Figure 8), which argues against direct conversion of HNO₃ to NOₓ on a short timescale. Fan et al. (1994) proposed that the reaction of HNO₃ with CH₃O in acid aerosols may not produce NOₓ but hydroxymethylnitrate H₂C(OH)ONO₂; this species could then photolyze to yield NOₓ 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 NO and HNO₃ 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 O₃ over the South Atlantic basin. Continental NOₓ emissions from South America and southern Africa are pumped to the middle and upper troposphere by convection, leading to ubiquitous net production of O₃ in the upper troposphere. Eventually, the air subsides over the Atlantic Ocean and net loss of O₃ takes place. Low-level advection to the continents closes the O₃ cycle. We propose that this schematic can be extended to other tropical regions and provides a general explanation for the origin of O₃ 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 NOₓ over the South Atlantic Basin |
|-----------------|-----------------|--------------|
|                | Altitude Band, km |               |
|                 | 0-4              | 4-8          | 8-12         |
| **NOₓ loss, pptv d⁻¹** |               |               |              |
| NO₂ + OH        | 230             | 50           | 41           |
| NO₃ + aerosol   | 141             | 37           | 16           |
| CH₃CO + NO₃    | 132             | 19           | 7            |
| RO₂ + NO₃      | 74              | 4            | 1            |
| Total Loss      | 787             | 112          | 67           |
| **NOₓ production, pptv d⁻¹** |              |               |              |
| HNO₃ photolysis | 14              | 3            | 2            |
| HNO₃ + OH       | 24              | 3            | 2            |
| PAN thermolysis | 728             | 6            | <1           |
| PAN photolysis  | 6               | 8            | 7            |
| Total Production| 900             | 31           | 12           |
| **NOₓ 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 NOₓ, 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 (CH₃CO + PAN) family as described in Appendix B.

* Formation of all organic nitrates other than PAN. These organic nitrates are assumed inert in the model.
Our representation of the budget of $O_3$ in the tropical troposphere goes back to the earliest papers arguing that the tropospheric $O_3$ 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 NO data. Liu et al. [1980] first proposed the idea of a photochemical steady state of $O_3$ in the tropospheric column with net production in the upper troposphere compensating for net loss in the lower troposphere. They argued that the 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 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 $O_3$ 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 $O_3$ in the region. We conclude that the tropospheric $O_3$ column can be maintained solely by in situ photochemistry. The photochemical production of $O_3$ is limited by the supply of NO$_x$, even in the upper troposphere. Past observations of the remote troposphere indicate that NO$_x$ concentrations are generally near the turnover point for net $O_3$ production versus net $O_3$ loss; we interpret this observation as reflecting the tendency of $O_3$ concentrations to adjust to a chemical steady state defined by the available NO$_x$.

Biomass burning and lightning were the two primary sources of NO$_x$ over the South Atlantic basin in TRACE A. Considering the short lifetime of NO$_x$, against oxidation (only 2-3 days at 8-12 km altitude), it appears that the high NO$_x$ levels observed throughout the South Atlantic basin were maintained by chemical recycling of NO$_x$ from its oxidation products. The low HNO$_3$/NO$_x$ concentration ratios observed above 8 km imply rapid conversion of HNO$_3$ to NO$_x$ by a mechanism not considered in current models. We presented a simple schematic for the origin of $O_3$ in the South Atlantic basin troposphere linking the large-scale Walker circulation to in situ photochemistry. Convection over South America and southern Africa injects NO$_x$ from combustion, soils, and lightning to the middle and upper troposphere, leading to net...
O₃ production; eventually, the air subsides over the Atlantic Ocean and net loss of O₃ takes place in the lower troposphere due to reduced NOx levels and high humidities. Low-level advection of marine air to the continents closes the O₃ cycle. We proposed that the same scheme applies to other tropical regions and offers a general representation of the O₃ budget in the tropical troposphere. This mechanism would imply a great sensitivity of the global oxidizing power of the atmosphere to NOx emissions from tropical continents.

Peroxide concentrations measured aboard the aircraft in TRACE A provided another test of the O₃ production and loss rates computed in our photochemical model. We found that the model captures 78% and 74% of the observed variances of H₂O₂ and CH₂O concentrations, respectively. Below 8-km altitude there is no mean bias for H₂O₂ and a 30% negative bias for CH₂O. Above 8-km the model underestimated H₂O₂ by a factor of 1.8 and CH₂O 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 O₃ 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 CH₂O 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 CH₂O 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 CH₂O+OH reaction are from Vaghjiani and Ravishankara [1989]. The yield of O(1D) from photolysis of O₃ is from Michelsen et al. [1994]. Recent data are used for the photolysis of HNO₃ [Burkholder et al., 1993], PAN [Talukdar et al., 1995], and ketones [Rober and Moortgat, 1995].

Hydrolysis of N₂O₅ to HNO₃ in aerosols is included with a rate constant determined by the collision frequency of N₂O₅, molecules on aerosol particles [Fuchs and Sungin, 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 N₂O₅ on aerosol surfaces 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 H₂SO₄-H₂O system is usually solid H₂SO₄·nH₂O (sulfuric acid tetrahydrate, or SAT). The reaction probability of N₂O₅ 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 N₂O₅ hydrolysis has no significant effect on the model photochemistry, but it provides a significant term in the computed mass balance for NO₃. 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.

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Hydrolysis of N₂O₅ to HNO₃ in aerosols is included with a rate constant determined by the collision frequency of N₂O₅, molecules on aerosol particles [Fuchs and Sungin, 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 N₂O₅ on aerosol surfaces 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 H₂SO₄-H₂O system is usually solid H₂SO₄·nH₂O (sulfuric acid tetrahydrate, or SAT). The reaction probability of N₂O₅ 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 N₂O₅ hydrolysis has no significant effect on the model photochemistry, but it provides a significant term in the computed mass balance for NO₃. 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.

Peroxide concentrations measured aboard the aircraft in TRACE A provided another test of photochemistry in the model. The model captures 78% and 74% of the observed variances of H₂O₂ and CH₂O concentrations, respectively. Below 8-km altitude there is no mean bias for H₂O₂ and a 30% negative bias for CH₂O. Above 8-km the model underestimated H₂O₂ by a factor of 1.8 and CH₂O 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 O₃ 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 CH₂O 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 CH₂O concentrations that cannot be explained with current models. The issue requires further investigation.
When NO concentrations are low, formation of the organic peroxy CH2(OOH)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 high concentrations measured in TRACE A.

The origin of the high acetic acid concentrations observed in TRACE A remains a puzzle. There are 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 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 NOx-PAN Interconversion in NOx Budget Calculations

When assessing the importance of NOx-PAN interconversion in a regional NOx budget constrained with observations for NOx (or NO) and PAN, and with CH2CO1 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 PAN = CH2CO1 + PAN. To illustrate the need for this correction, consider a situation where reactions (10), (13), and (14) dominate the production and loss of CH2CO1. Under this situation, given any specified input pair of NOx and PAN concentrations, the steady state CH2CO1 concentration computed in the model yields an apparent steady state between NOx and PAN; this steady state plays, however, no role in regulating NOx since loss of NOx and CH2CO1 by reaction (10) forces production of NOx by reactions (13) and (14) to maintain the CH2CO1 steady state. Use of uncorrected rates R10, R13, and R14 to construct a NOx budget can lead to the illusion of a close balance between production and loss of NOx, and to an underestimate of the chemical lifetime of NOx.

We account for this effect in our NOx budget analyses by using corrected rates R':

\[
R'_{10} = \frac{P_{PAN}}{L_{PAN} + R_{13} + R_{14}}
\]

\[
R'_{13} = \frac{L_{PAN}}{P_{PAN} + R_{13} + R_{14}}
\]

\[
R'_{14} = \frac{L_{PAN}}{P_{PAN} + R_{13} + R_{14}}
\]

where \(P_{PAN}\) and \(L_{PAN}\) are the chemical production and loss rates of the PAN family. In the TRACE A data set, the correction factor \(P_{PAN}/L_{PAN} = R_{13} + R_{14}\) 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 \(L_{PAN}/R_{13} + R_{14}\) 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 CH2CO1 source.

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