UC Irvine
Faculty Publications

Title

Photochemical evolution of ozone in the lower tropical stratosphere

Permalink

Journal

ISSN

Authors

Avallone, L. M
Prather, M. J

Publication Date

1996

DOI

Copyright Information

Peer reviewed

Photochemical evolution of ozone in the lower tropical stratosphere

L. M. Avallone and M. J. Prather

Earth System Science, University of California, Irvine

Abstract. Rarely does the atmosphere allow direct observation of the photochemical evolution of ozone. In most of the troposphere and lower stratosphere this slow chemistry cannot be understood without including much larger changes caused by the circulation. Yet in the tropical stratosphere, where ozone-poor air of tropospheric origin enters and rises slowly in near isolation, it can be demonstrated that O_3 is created by dissociation of O_2 at a rate consistent with current theory. The parallel photolytic destruction of the unreactive source gases (for example, N_2O and $CFCl_3$) and the consequent evolution of chemically active odd-nitrogen (NO_y) and chlorine (Cl_y) species, however, indicate a small amount of mixing of much older, photochemically aged air from the midlatitude stratosphere into this tropical plume.

Introduction

The average motion of air in the stratosphere described as the Brewer-Dobson circulation [*Brewer*, 1949] begins at the tropopause with net upward movement in the tropics, spreading, and eventual subsidence at middle and high latitudes where photochemically aged air reenters the troposphere. Calculations of the radiative balance in the stratosphere [*Rosenfield et al.*, 1987] (see examples of *Prather and Remsberg* [1993]) show an intense narrow plume in the tropics (15°S-15°N) with heating rates corresponding to ascent of about 1/40 km/day. These velocities are also consistent with independent estimates of the flushing time of the stratosphere [*Rosenlof and Holton*, 1993] if the upward plume is confined to the tropics (for example, the "tropical pipe" model of *Plumb* [1996]). Measurements of CO_2 and other source gases in the midlatitude lower stratosphere [*Boering et al.*, 1994] demonstrate a rapid connection with the tropical rather than midlatitude troposphere [*Hall and Prather*, 1993] and hence point to significant lateral outflow from the tropical fountain [*Newell and Gould-Stewart*, 1981].

We adopt here a simple chemical model that follows the upward motion of the tropical core as was done by *Kinne et al.* [1992], assuming that it evolves in isolation. The model is tested against two historical data sets that have shown distinct differences between tropical and extratropical air: balloon measurements of N_2O and $CFCl_3$ from the 1970s [*Schmeltekopf et al.*, 1977; *Goldan et al.*, 1980; *Vedder et al.*, 1981] and ER-2 observations of O_3, NO_y, and CO from the 1987 component of the Stratospheric Tropospheric Exchange Program (STEP)[*Pfister and Russell*, 1993; *Murphy et al.*, 1993; *Hipskind and Gaines*, 1988]. To the extent that this model matches the observed chemical tracers in the lower tropical stratosphere, we can assert (1) that the basic component of Chapman chemistry, production of O_3, is demonstrated in the stratosphere and (2) that aged air from the extratropical stratosphere does not readily flow into the plume to be relofted into the middle stratosphere.

Calculations

The tropical fountain begins at the tropopause with small concentrations of the reactive compounds O_3 and NO_y and with large concentrations of source gases such as N_2O and $CFCl_3$. Mean tropospheric values are used to initialize source gases in the model, and the abundances of O_3, H_2O, NO_y, and CO are based on the tracer-tracer correlations of ER-2 measurements from the STEP mission in the tropics [*Pfister and Russell*, 1993; *Murphy et al.*, 1993; *Hipskind and Gaines*, 1988]. These observations show that O_3 and NO_y are, for he most part, smoothly and linearly related in the lower tropical stratosphere, with apparent initial values of 50 ppb and 0.5 ppb, respectively, and with no evidence of substantial pulses of NO_y entering the stratosphere or being produced in situ. Lightning is an important source of NO_y observed in the upper tropical troposphere [*Murphy et al.*, 1993], and it controls the amount of NO_y entering the tropical stratosphere, an effect included here by selecting observations as boundary conditions. If lightning in the stratosphere (as opposed to that in the troposphere) were a significant source of stratospheric NO_y, then the correlations with O_3 or N_2O would show "spikes" of enhanced NO_y well above the observed patterns.

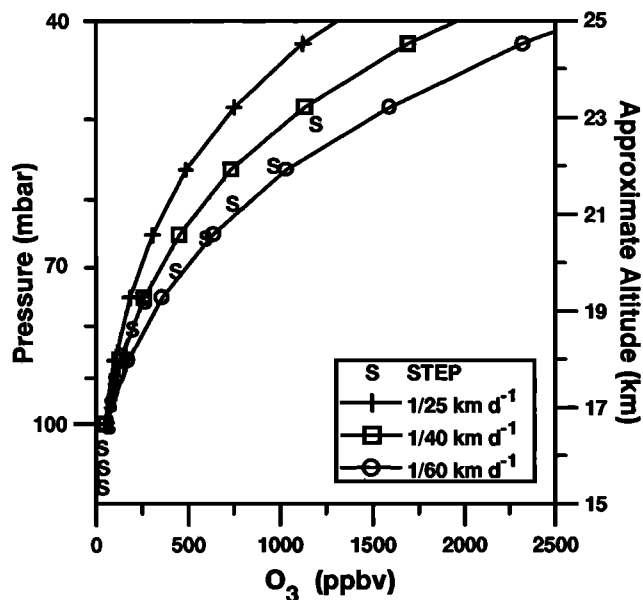Ozone evolves from the photodissociation of molecular oxygen,

Figure 1. Volume mixing ratio of ozone (in parts per billion) as a function of pressure (and altitude) in the tropics as measured during STEP [*Hipskind and Gaines*, 1988] and as calculated in a box chemical model with ascent rates of 1/25 (crosses), 1/40 (squares), and 1/60 km/day (circles). The STEP data (S) have been averaged over 5-mbar bins. The assumed constant ascent rates are consistent with radiative calculations that show roughly constant vertical velocities in the lower tropical stratosphere [*Rosenfield et al.*, 1987; *Prather and Remsberg*, 1993].
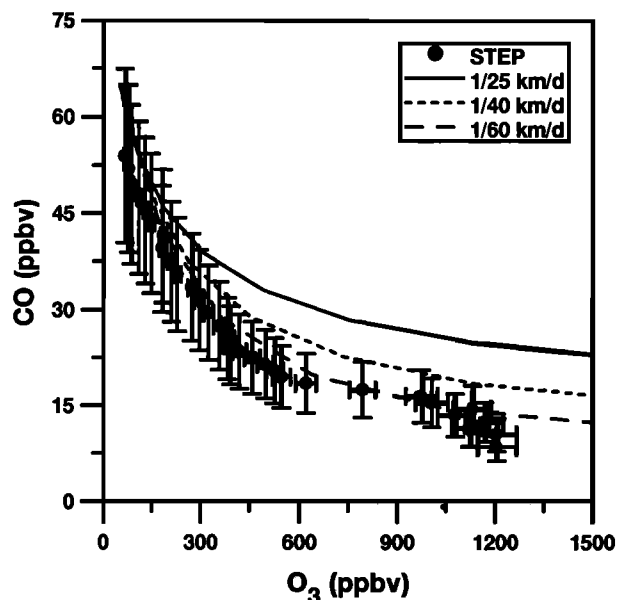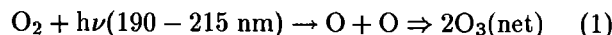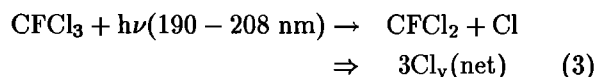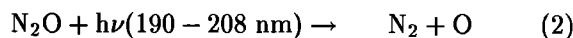

Figure 2. Volume mixing ratio of carbon monoxide (CO) in parts per billion as a function of O_3 in tropical STEP observations and as calculated in a box chemical model (see Figure 1). The STEP data have been averaged over 1-ppb bins in CO. Error bars represent accuracy as specified by the experimenters.

$$O_2 + h\nu(190 - 215 \text{ nm}) \rightarrow O + O \Rightarrow 2O_3(\text{net}) \quad (1)$$

and because loss processes in the lower tropical stratosphere are slow, its growth represents the accumulation of oxygen photolysis. Most source gases are destroyed at similar wavelengths,

$$N_2O + h\nu(190 - 208 \text{ nm}) \rightarrow \quad N_2 + O \quad (2)$$

$$CFCl_3 + h\nu(190 - 208 \text{ nm}) \rightarrow \quad CFCl_2 + Cl$$

$$\Rightarrow \quad 3Cl_y(\text{net}) \quad (3)$$

and reactive chlorine species (Cl_y) evolve from the destruction of halocarbons. A small fraction of total N_2O loss, approximately 5%, occurs through a reaction with $O(^1D)$, an excited oxygen atom produced from photolysis of O_3.

$$N_2O + O(^1D) \rightarrow NO + NO \Rightarrow 2NO_y(\text{net}) \quad (4)$$
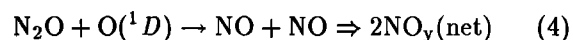
This channel is the primary source of reactive nitrogen species (NO_y). The photochemical box model [*Prather and Jaffe*, 1990] has been updated to include new rate coefficients and cross sections [*DeMore et al.*, 1992; *Minschwaner et al.*, 1992].

Discussion

Figure 1 shows the evolution of O_3 in the model for ascent rates ranging from 1/25 to 1/60 km/day. These predictions bound the observed mean profile from STEP as a function of altitude over the range 16 to 22 km, corresponding to 0.05 to 2.5 ppm volume mixing ratio of O_3. Thus we conclude like *Kinne et al.* [1992], that primary production of O_3, through reaction (1) alone, can explain the observed vertical distribution over this scale height. This result is relatively robust, considering the range in ascent rates and the simple chemistry of this region, and consistent with the traditional Chapman chemistry of odd oxygen [*Chapman*, 1930]. The decay of carbon monoxide (CO) through reaction with hydroxyl radicals (OH) is observed to parallel the increase in O_3 (see Figure 2) and provides a further verification of the combination of chemistry and ascent rates used here. We find that the OH concentrations are extremely sensitive to temperature and certain rate coefficients, and thus simulation of the $CO-O_3$ relationship must be done with caution.

The photolytic destruction of N_2O and $CFCl_3$ occurs at the same wavelengths as O_2 dissociation and should be well produced in this simple model. Thus we would expect to match the tropical observations shown in Figure 3 [*Schmeltekopf et al.*, 1977; *Goldan et al.*, 1980; *Vedder et al.*, 1981]. The relatively rapid falloff of $CFCl_3$ compared to N_2O is well reproduced. Although the model lies at the upper bound of measurements, the majority of data indicate more rapid loss than predicted. Because of the good match with O_3 profiles we believe that the photochemical losses are accurate. In

this first indication of problems with our isolated ascent model we are tempted to argue for mixing with midlatitude air, but the limited and variable balloon data are not convincing.

The numerous measurements of NO_y versus O_3 by aircraft in the lower stratosphere show distinct differences between tropical and extratropical air, as summarized in Figure 4 [*Murphy et al.*, 1993; *Hipskind and Gaines*, 1988]. They also clearly define the tropical plume with sharp gradients at the boundaries, about 15°S and 15°N. In the model the evolution of NO_y occurs much too slowly, by about a factor of 4, to account for the tropical observations, whose precision and accuracy leave no doubt as to the large discrepancy. Once again we believe that uncertainties in the photochemical model for production of NO_y are small.

It does not seem possible to generate these observed O_3-N_2O and O_3-NO_y relationships with known photochemistry. If the photolytic rates were increased by a factor of 3, then the N_2O falloff would better match observations, but the production of O_3 would also increase threefold and would disagree radically with measurements. More rapid production of NO_y would require fourfold greater concentrations of $O(^1D)$, which are well beyond model uncertainties and would greatly enhance OH. Model calculations (not shown) in which the $O(^1D)$ concentrations were arbitrarily increased by a factor of 4 have higher OH concentrations, resulting in much more rapid destruction of the initial CO, and are inconsistent with the CO-O_3 correlation shown in Figure 2. The much higher ratio of NO_y to O_3 in midlatitude air (Figure 4) is a common feature of global stratospheric models [*Prather and Remsberg*, 1993] and evolves in the middle stratosphere, where O_3 is in photochemical balance and does not continue to increase as N_2O is lost and NO_y generated.

The most compelling explanation of the tropical data is the inclusion of NO_y-rich (and N_2O-poor) air from midlatitudes. Would such mixing destroy the O_3 model that we have built here? If we consider mixing along constant potential temperature surfaces, then a 2:1 mix of isolated tropical with midlatitude air would change NO_y by +300% but O_3 by only +15%. We believe the NO_y-O_3 relationship provides one of the most sensitive measures of exchange between the tropical plume and the rest of the stratosphere.

Conclusions

It is impossible with the limited data used here to build a quantitative model for mixing of midlatitude air into the tropical fountain. It is important to realize the timescales over which this net mixing can occur. The production of about 1.5 ppm of O_3 takes 4 to 10 months, depending on ascent rate. Thus intrusion of extratropical air may be continuous at a small rate or may occur sporadically, depending on season and dynamical condi-
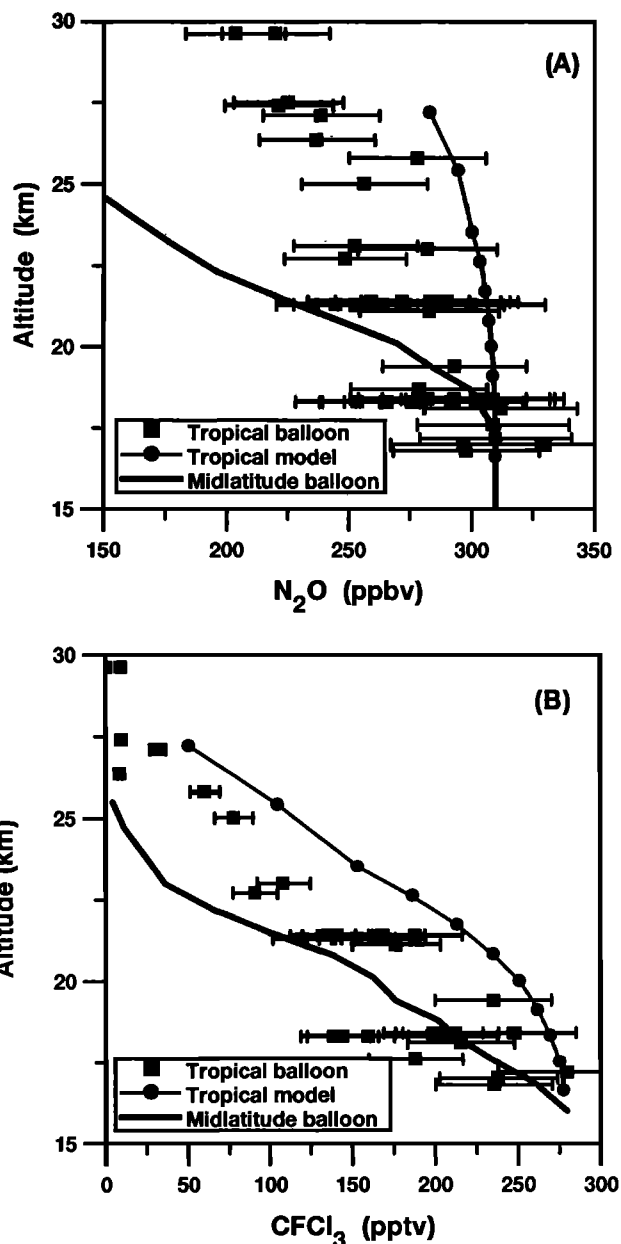

Figure 3. Volume mixing ratios of (a) N_2O and (b) $CFCl_3$ as a function of altitude. The tropical, balloon-borne observations (solid squares, see text) have been rescaled to current tropospheric concentrations of 310 ppb (N_2O) and 280 ppt ($CFCl_3$). Error bars represent accuracy as reported in the original publications. The model calculations for an ascent rate of 1/40 km/day are shown (solid circles). An estimate is made of the equivalent profiles of midlatitude air by shifting these profiles to match the potential temperatures of the tropical profiles.

tions [*Trepte and Hitchman*, 1992]. Close examination of Figure 4 shows regions (300–700 ppb and 800–1600 ppb of O_3) in which the NO_y-O_3 relationship can only be ascribed to photochemical coevolution of these two species.

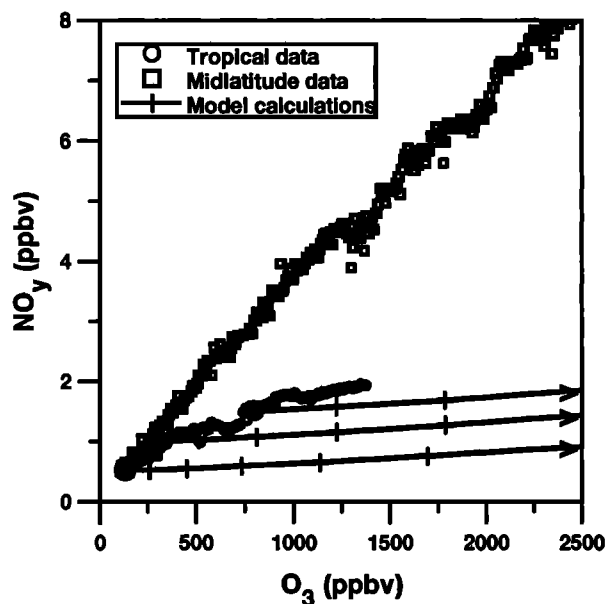Inclusions of midlatitude air in the tropical plume result in recycling and relofting of photochemically aged

Figure 4. The coevolution of O_3 and NO_y in the lower tropical stratosphere from the model (solid lines) is compared with observations from the tropics (circles) and the midlatitudes (squares). The tropical data are from STEP [*Hipskind and Gaines*, 1988], and the midlatitude data from AASE II [*Gaines et al.*, 1993]. The measurements have been averaged over 10-ppb bins in O_3. Solid circles represent the starting conditions for each of the model curves, with tick marks every 40 days of parcel evolution.

air. Most global models effectively include similar mixing. If, on the other hand, this study had shown complete isolation of the plume core, then air in the lower stratosphere at midlatitudes could only follow the mean Brewer-Dobson circulation and reenter the troposphere. For example, this study demonstrates the potential for a fraction of aircraft exhaust emitted in the midlatitude stratosphere to enter the tropical upwelling, disperse globally, and impact ozone chemistry in the middle stratosphere. Only further observations of the tropical-extratropical differences in long-lived chemical tracers, including altitudes above the STEP and recent ASHOE/MAESA ER-2 missions, can provide an accurate measure of this mixing, which is a fundamental component of the global stratospheric circulation. Recognizing that the discrepancies between the model and observations can be resolved by only small amounts of mixing, we believe this is a primary demonstration of the most basic O_3 photochemistry, with atmospheric observations providing verification of the photolysis of O_2 leading to production of O_3.

References

Boering, K. A., B. C. Daube Jr., S. C. Wofsy, M. Loewenstein, J. R. Podolske, and E. R. Keim, Tracer-tracer relationships and lower stratospheric dynamics: CO_2 and N_2O correlations during SPADE, *Geophys. Res. Lett.*, *21*, 2567-2570, 1994.

Brewer, A. W., Evidence for a world circulation provided by measurements of helium and water vapour distribution in the stratosphere, *Q. J. R. Meteorol. Soc.*, *75*, 351-363, 1949.

Chapman, S., A theory of upper atmospheric ozone, *Mem. R. Meteorol. Soc.*, *3*, 103-125, 1930.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, Publ. 92-20, Jet Propul. Lab., Pasadena, Calif., 1992.

Gaines, S., P. Hathaway, and S. Hipskind (Eds.), Airborne Arctic Stratospheric Expedition II, CD-ROM, *NASA/ UARP-004*, NASA Ames Res. Cent., Moffett Field, Calif., July 1993.

Goldan, P. D., W. C. Kuster, D. L. Albritton, and A. L. Schmeltekopf, Stratospheric $CFCl_3$, CF_2CCl_2, and N_2O height profile measurements at several latitudes, *J. Geophys. Res.*, *85*, 413-423, 1980.

Hall, T. M., and M. J. Prather, Simulations of the trend and annual cycle in stratospheric CO_2, *J. Geophys. Res.*, *98*, 10,573-10,581, 1993.

Hipskind, R. S., and S. E. Gaines (Eds.), Stratosphere-Troposphere Exchange Project, CD-ROM, *NASA/UARP-001*, NASA Ames Res. Cent., Moffett Field, Calif., Nov. 1988.

Kinne S., O. B. Toon, and M. J. Prather, Buffering of stratospheric circulation by changing amounts of tropical ozone: A Pinatubo case study, *Geophys. Res. Lett.*, *19*, 1927-1930, 1992.

Minschwaner, K., G. P. Anderson, L. A. Hall, and K. Yoshino, Polynomial coefficients for calculating O_2 Schumann-Runge cross sections at 0.5 cm^{-1} resolution, *J. Geophys. Res.*, *97*, 10,103-10,108, 1992.

Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 8751-8773, 1993.

Newell, R. E., and S. Gould-Stewart, A stratospheric fountain?, *J. Atmos. Sci.*, *38*, 2789-2796, 1981.

Pfister, L., and P. B. Russell, Preface to the Tropical Experiment of the Stratosphere-Troposphere Exchange Project, *J. Geophys. Res.*, *98*, 8562, 1993.

Plumb, R. A., A "tropical pipe" model of stratospheric transport, *J. Geophys. Res.*, in press, 1996.

Prather, M., and A. Jaffe, Global impact of the Antarctic ozone hole: Chemical propagation, *J. Geophys. Res.*, *95*, 3473-3492, 1990.

Prather, M. J., and E. E. Remsberg (Eds.), The atmospheric effects of stratospheric aircraft: Report of the 1992 models and measurements workshop, *NASA Ref. Publ. 1292*, 1993.

Rosenfield, J. E., M. R. Schoeberl, and M. A. Geller, A computation of the stratospheric diabatic circulation using an accurate radiative transfer model, *J. Atmos. Sci.*, *44*, 859-876, 1987.

Rosenlof, K. H., and J. R. Holton, Estimates of the stratospheric residual circulation using the downward control principle, *J. Geophys. Res.*, *98*, 10,465-10,479, 1993.

Schmeltekopf, A.L., et al., Stratospheric nitrous oxide altitude profiles at various latitudes, *J. Atmos. Sci.*, *34*, 729-736, 1977.

Trepte, C. R., and M. H. Hitchman, Tropical stratospheric circulation deduced from satellite aerosol data, *Nature*, *355*, 626-628, 1992.

Vedder, J. F., E. C. Y. Inn, B. J. Tyson, C. A. Boitnott, and D. O'Hara, Measurements of CF_2CCl_2, $CFCl_3$, and N_2O in the lower stratosphere between 2°S and 73°N latitude, *J. Geophys. Res.*, *86*, 7363-7368, 1981.

L. M. Avallone and M. J. Prather, Earth System Science, University of California, Irvine, CA 92717-3100. (e-mail: lmavallo@uci.edu; mprather@uci.edu)