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Authors
Avallone, L. M
Prather, M. J

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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$_2$O and CFC$_{13}$) 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 Holloa, 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 [Boerlug 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$_2$O and CFC$_{13}$ 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$_2$O and CFC$_{13}$. Mean tropospheric values are used to initialize source gases in the model, and the abundances of O$_3$, H$_2$O, 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 the 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$_2$O would show “spikes” of enhanced NO$_y$ well above the observed patterns.

Ozone evolves from the photodissociation of molecular oxygen,
$O_2 + h\nu(190 - 215 \text{ nm}) \rightarrow O + O \Rightarrow 2O_3(\text{net})$ (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,

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

$\text{CFC}_13 + h\nu(190 - 208 \text{ nm}) \rightarrow \text{CFC}_12 + \text{Cl}$

$\Rightarrow 3\text{Cl}_y(\text{net})$ (3)

and reactive chlorine species ($\text{Cl}_y$) 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 $O_3$.

$N_2O + O(^1D) \rightarrow NO + NO \Rightarrow 2\text{NO}_y(\text{net})$ (4)

This channel is the primary source of reactive nitrogen species ($\text{NO}_y$). 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 $1/60 \text{ km/day}$. 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 $\text{CFC}_13$ 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 $\text{CFC}_13$ 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 NOy versus O3 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 NOy 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 NOy are small.

It does not seem possible to generate these observed O3-N2O and O3-NOy relationships with known photochemistry. If the photolytic rates were increased by a factor of 3, then the N2O falloff would better match observations, but the production of O3 would also increase threefold and would disagree radically with measurements. More rapid production of NOy 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-O3 correlation shown in Figure 2. The much higher ratio of NOy to O3 in midlatitude air (Figure 4) is a common feature of global stratospheric models [Prather and Remsberg, 1993] and evolves in the middle stratosphere, where O3 is in photochemical balance and does not continue to increase as N2O is lost and NOy generated.

The most compelling explanation of the tropical data is the inclusion of NOy-rich (and N2O-poor) air from midlatitudes. Would such mixing destroy the O3 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 NOy by +300% but O3 by only +15%. We believe the NOy-O3 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 O3 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 conditions [Trepte and Hitchman, 1992]. Close examination of Figure 4 shows regions (300-700 ppb and 800-1600 ppb of O3) in which the NOy-O3 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...
The coevolution of $O_3$ and $NO_y$ in the lower tropical stratosphere from the model (solid lines) 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.

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 $O_3$.

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References


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)

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