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Catalysis by NO_x as the Main Cause of the Spring to Fall Stratospheric Ozone Decline in the Northern Hemisphere[†]

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We address the cause of the largely natural total ozone decline in the stratosphere from its spring maximum to fall minimum in the northern hemisphere and show that this is mainly due to NO_x-catalyzed ozone destruction. While in an earlier paper, using HALOE satellite observations, an analysis was made only for the year 1993, here we also analyze later years, yielding very similar results. We emphasize the role of the subtropical meridional transport barrier in isolating the chemistry at middle to high latitudes from that over the tropics. We find that for all years net ozone production takes place between the "subtropical barrier", at about 30° N, and 50° N. Nevertheless, also in this latitude region the ozone content declines due to transport to higher latitudes where very strong chemical ozone loss takes place due to summer time NO_x activation. An interesting result of the analysis is that, rather irrespective of the starting values of total ozone in early spring, chemical ozone loss yields about the same minimum total ozone amounts in early fall. The result of our study strongly depends on improved determinations of rate coefficients of several reactions in the stratospheric ozone budget.

1. Introduction

A recent analysis based on data obtained with the Halogen Occultation Experiment (HALOE) on the UARS (Upper Atmosphere Research Satellite) for the year 1993 and a photochemical model[3] indicated that NO_x-catalyzed ozone destruction[1,2] via the pair of reactions

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ O + NO_2 &\rightarrow NO + O_2 \end{aligned} \qquad (1)$$

is largely responsible for the ozone decline in middle to high latitudes from spring to fall. NO_x catalysis is enhanced by NO_y ($NO_x + NO_3 + 2N_2O_5 + HNO_3 + HNO_4 + ClONO_2$) to NO_x ($NO + NO_2$) activation, which is strongly favored by long daylight hours during summer, which hinder NO_3, N_2O_5, and thereby HNO_3 formation by the heterogeneous reaction $N_2O_5 + H_2O \rightarrow 2HNO_3$ on stratospheric sulfate aerosol.[4] Model estimates of NO_y (mainly HNO_3) to NO_x conversion have been substantially enhanced by recent updates of the rate constants for the reactions $OH + NO_2 + (M) \rightarrow HNO_3 + (M)$ and $OH + HNO_3 \rightarrow H_2O + NO_3$.[5−7] Estimated ozone loss is also enhanced by the larger measured rate coefficient for the reaction $O + NO_2 \rightarrow NO + O_2$.[8] In the present study we extend the analysis of the seasonal total ozone decline to several years after 1993.

2. Seasonal Cycle of Total Ozone in the Northern Hemisphere

To assess the impact of the changes in odd nitrogen chemistry on the hemispheric ozone budget and the spring to fall total ozone decline at high and middle latitudes, the Mainz two-dimensional (2-D) model[9] was applied, fed with HALOE data. As in Brühl et al.,[3] latitude sweeps of zonal average HALOE data (O_3, H_2O, CH_4, $NO + NO_2$, HCl, and total inorganic and reactive chlorine deduced from HF) were entered daily for 5 days about every month to reduce errors due to deficiencies in the dynamics of the model. Between these times, and in regions where HALOE data were not available, all species are calculated from model dynamics and chemistry. Rate coefficients of relevant reactions not discussed above have been taken from De More et al.[10] Figure 1 shows, as an example, calculated net ozone destruction for June 1994 with the contributions of the NO_x, ClO_x, and HO_x catalytic cycles (eq 1 and Table 1). It demonstrates the large role played by NO_x in ozone destruction during summer. The budget analysis is restricted to the region below the 10 hPa level. We have found that higher up there is a growing net ozone destruction with height, possibly indicating still existing problems with the rate constants adopted for reactions, such as $O + OH \rightarrow H + O_2$, $O + HO_2 \rightarrow OH + O_2$, and $OH + HO_2 \rightarrow H_2O + O_2$, and maybe in O_2-photolysis, reminiscent of the "ozone deficit" problem, which have been discussed for more than a decade.[13] Because this discrepancy increases with altitude and the mentioned reactions are significant only above the 10 hPa height level, we assume that this problem is not significantly affecting our analysis below the 10 hPa level. Because of short chemical relaxation times of less than 3 days, transport cannot be fast enough to transfer any

TABLE 1: Most Important Odd Oxygen ($O + O_3$) Destruction Catalytic Cycles in the Stratosphere Besides the NO_x Cycle of Eq 1

ClO_x[11]:	$Cl + O_3 \rightarrow ClO + O_2$ $ClO + O \rightarrow Cl + O_2$	(2)
HO_x[12]: below about 30 km:	$OH + O_3 \rightarrow HO_2 + O_2$ $HO_2 + O_3 \rightarrow 2\ OH + O_2$	(3)
and higher up:	$OH + O_3 \rightarrow HO_2 + O_2$ $HO_2 + O \rightarrow OH + O_2$	(4)

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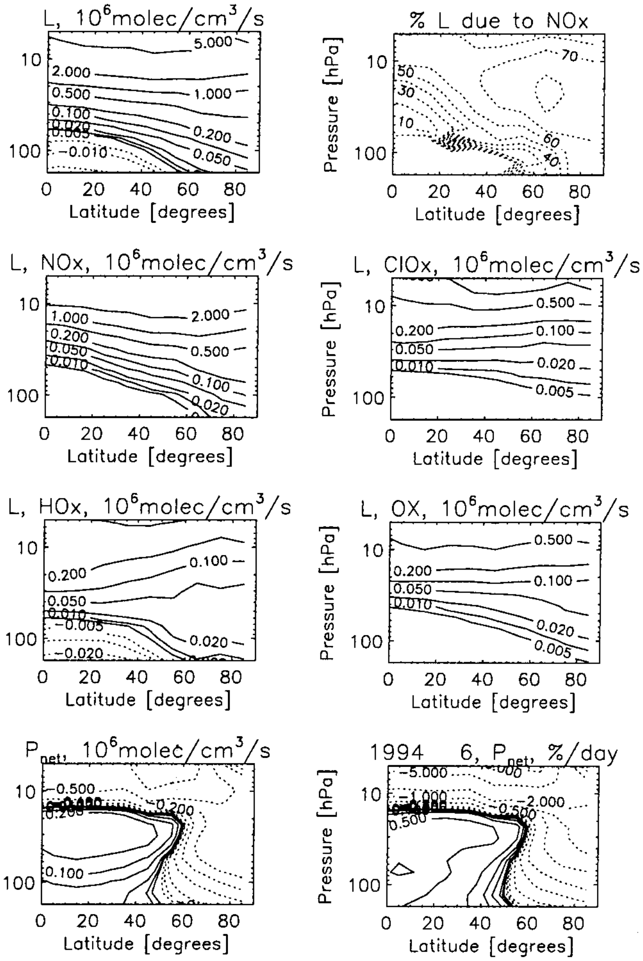

Figure 1. Diurnal average net ozone chemical production and destruction rates as calculated by a 2-D model reinitialized daily with HALOE data (in 10^6 (molecules/cm^3)/s and percentage changes), also showing absolute and relative contributions of the different catalytic cycles for June 1994. The panel Ox is the contribution of the Chapman reaction and reactions involving O(^{1}D). Contours are 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 (both signs).

chemical ozone disequilibrium from above to below 10 hPa. Furthermore, above 10 hPa less than 20% of all stratospheric ozone is located with little seasonal change in the observed ozone column (see Figure 2).

Figure 3 shows the calculated chemical ozone changes between 10 and 100 hPa during the four summer months (May to August) during the years 1993 to 1999 as functions of latitude, except for 1997 when the HALOE data set had too large gaps in middle latitudes. All budget terms are expressed in Dobson units (DU), area weighted by the cosine of the latitude. The 100 hPa level was chosen because at lower altitudes, chemical ozone loss is too slow to contribute significantly to the seasonal ozone decrease (see Figure 1). Instead, the decrease of ozone between the 100 hPa level and the tropopause is largely due to downward transport into the troposphere.

Calculated chemical column ozone destruction north of ≈50° N, which is strongly determined by NO_x catalysis, more than compensates for the net chemical ozone production occurring between the subtropical meridional transport barrier at 25−30° N and about 50° N. Figure 3 also contains the changes in column ozone in the lower stratosphere that are directly derived from the HALOE profiles for which Figure 2 shows examples for two extreme years. Note the large difference in the change of ozone profiles in the high-latitude lowermost stratosphere between a cold stratospheric winter and spring season (1993) with significant ClO_x-induced ozone depletion and a warm winter and spring season without significant chemical ozone loss (1994).

Figure 4 shows the different terms of modeled and observed May−August ozone budget in the lower stratosphere for the years 1993−1999, now in Teragram (Tg) added up for two latitude regions. 1997 was excluded because of too large uncertainties due to data gaps. Gaps in HALOE data also lead to larger uncertainties during 1996, 1998, and 1999 than in the years 1993−1995. The difference between the calculated chemical net ozone production term and the measured total column change between 10 and 100 hPa is balanced by (meridional) transport. Thus, although net ozone production of 59−85 Tg (Figure 4a, + symbols) is calculated for the 30° to 50° N region, the observed ozone column actually decreased (9−35 Tg, Figure 4a, × symbols). This is due to an export of 89−113 Tg to the region north of 50° N (◇ symbols), where large chemical ozone loss takes place (114−190 Tg, * symbols) due to strongest NO_x activation caused by long daylight hours, which reduce NO_y formation from NO_x, as discussed in the Introduction. Within uncertainty limits the observed decline of 54−100 Tg in high latitudes (△ symbols) is consistent with the model estimates for transport and chemistry (25−96 Tg, □ symbols, Figure 4a).

Because chemical loss is slow (Figure 1), observed ozone decreases in the lowermost stratosphere below about 100 hPa, including those due to the seasonal upward shift of the tropopause, contribute to tropospheric ozone. Making the somewhat daring assumption that the difference between average area-weighted calculated chemical ozone loss and observed total ozone loss of 40−74 Tg (Figure 4b, ◇, shown as negative numbers) is due to transport into the troposphere, a stratosphere to troposphere ozone flux of $(4-7) \times 10^{10}$ (molecules/cm^2)/s during four months north of 30° N is calculated, or $(2-3.5) \times 10^{10}$ (molecules/cm^2)/s averaged over the entire northern hemisphere. Considering that the maximum downward flux of ozone near the tropopause occurs in spring, our estimate is consistent with earlier estimated annual average O_3 fluxes of $\approx 3 \times 10^{10}$ [14] and 4×10^{10} (molecules/cm^2)/s.[15] It is interesting to note that the largest flux into the troposphere is calculated for the year 1994 which had almost no ClO_x-induced ozone depletion in the polar vortex region during winter and spring (Figure 4b). Whether stratospheric ozone depletion by ClO_x can have a feedback on tropospheric chemistry is an interesting issue, which, however, is of greater significance in the southern hemisphere.

The ozone budget presented here is consistent with the main role being played by NO_x catalysis in the spring to fall total ozone decline north of 30° N. It is remarkable that for those years in which insignificant ClO_x-induced ozone loss had taken place in winter/spring, calculated chemical ozone loss during late spring and summer was so much larger so that in the fall about the same total ozone amounts (≈580 Tg between 100 and 10 hPa and north of 30° N) were calculated and measured as in the ClO_x perturbed years (Figures 2 and 4). This gives credence to the presented ozone budget and the approach taken in this study. The consistent ozone budget, which is presented here, very much depended on major improvements in the rate coefficients defining NO_x/NO_y ratios, as mentioned in the Introduction.

3. Vertical Winds in the Tropics

From Figure 2 it can also be seen that the tropics seem to be

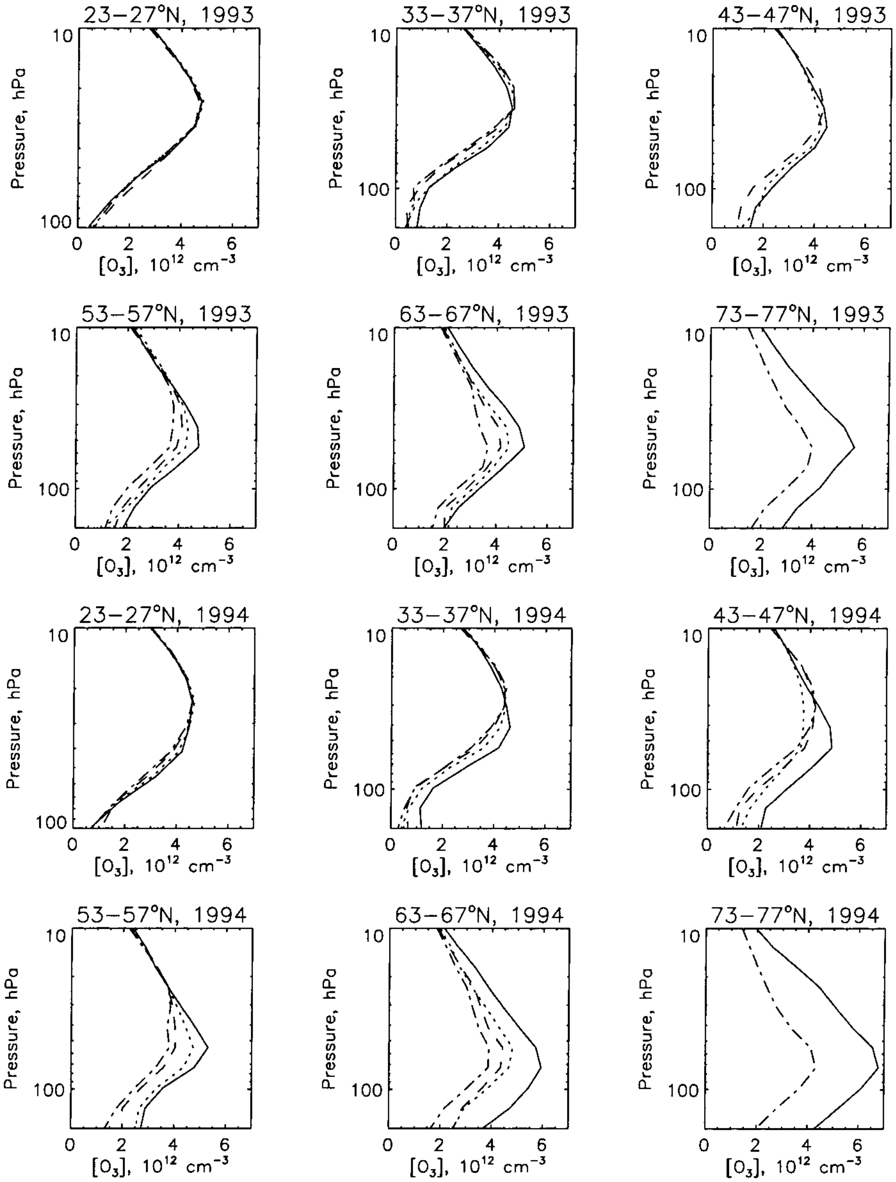

Figure 2. Zonal average profiles of ozone concentrations in the lower stratosphere as observed by HALOE for latitudes between 25° N and 75° N (step 10°) in 1993 and 1994. The labels above each plot give the selected latitude bands. Key: (solid lines) late April; (dotted lines) late May; (dashed lines) July; (dash−dotted lines) August. HALOE can retrieve only down to ≈175 hPa. The uncertainty of the zonal average ozone data below 100 hPa in high latitudes and middle latitudes is on the order of 10−20%;[17] above 50 hPa, 5% is typical.[18]

decoupled from the rest of the hemisphere since the profiles show almost no change with season, despite, for example, near 25° N, a calculated weighted column ozone production of 86 DU in the 10−100 hPa range. This tropical chemical ozone production appears to be compensated by ozone loss through upward motion (see Figure 2). Net chemical production rates of up to $\approx 5 \times 10^5$ (molecules/cm^3)/s (Figure 1) are consistent with an upward velocity of the order of 0.5 mm/s, according to the formula

$$w(z) \approx \frac{1}{[O_3]}\int_{18\,\mathrm{km}}^{z} P_n(O_3)\,\mathrm{d}z'$$

where $P_n(O_3)$ denotes net ozone production, $[O_3]$ the ozone concentration, and w the upward velocity, both at altitude z. Figure 5 shows resulting vertical velocities for data of the years 1993 and 1994 for altitudes between 22 and 28 km together with values derived from HALOE water vapor distributions using the “tropical tape-recorder” method.[16] These velocities also agree with the mean upward velocities derived from net radiative heating rates.

4. Conclusions

Ozone destruction by NO_x catalysis in the altitude range between 10 and 100 hPa at high to middle latitudes is largely responsible for the total ozone decline from May to August in the extratropical northern hemisphere. This effect becomes particularly clear after recent revisions of critical rate constants that enhance NO_y to NO_x conversion (NO_x activation) and catalytic ozone destruction.[4−8] The ozone budget and seasonal ozone decline are characterized by net ozone production in the 30° to 50° N latitude region, strong net O_3 destruction poleward of 50° N, with the largest value in the year 1994 when almost no chlorine-induced ozone depletion took place in winter and spring, and export of ozone from the 30° to 50° N to higher latitudes causing in both regions the observed seasonal decrease in ozone. We also tentatively estimate an ozone flux of ≈40−75 Tg from the stratosphere to the troposphere between May

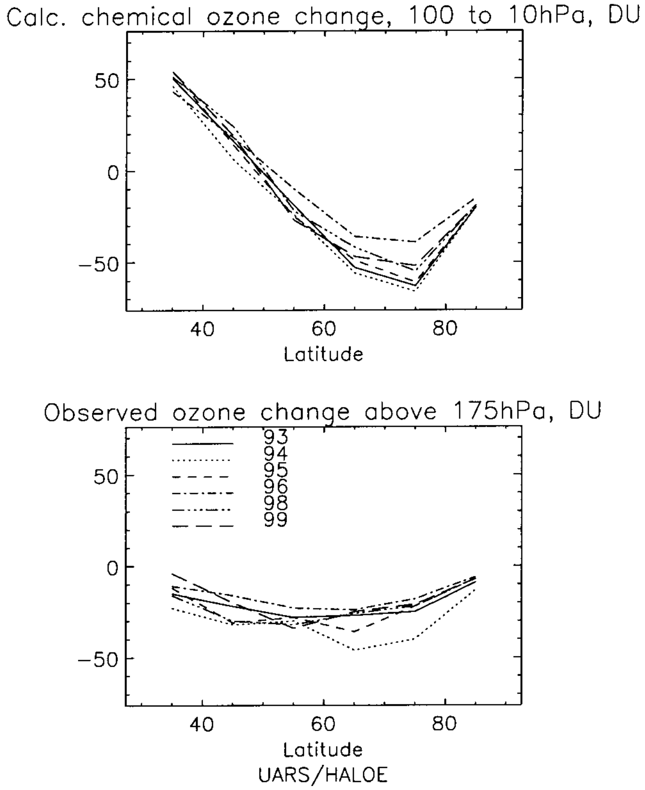

Figure 3. Calculated chemical column ozone loss between 100 and 10 hPa during May to August as a function of latitude (panel a) and observed column ozone loss above 175 hPa (HALOE satellite data, panel b) for the years 1993−1999 in DU weighted by the cosine of latitude. 1997 is not shown because of too large gaps in the HALOE data.

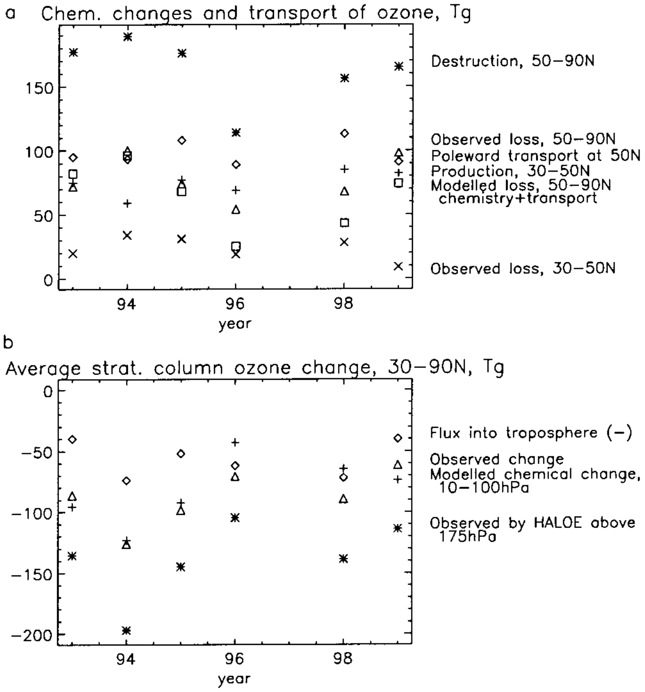

Figure 4. Calculated and observed ozone budget terms for the summer lower stratosphere of the years 1993−1999 (May to August). Panel a: separate terms for regions south and north of 50° N, 100 to 10 hPa. Panel b: terms for the whole area north of the subtropical barrier.

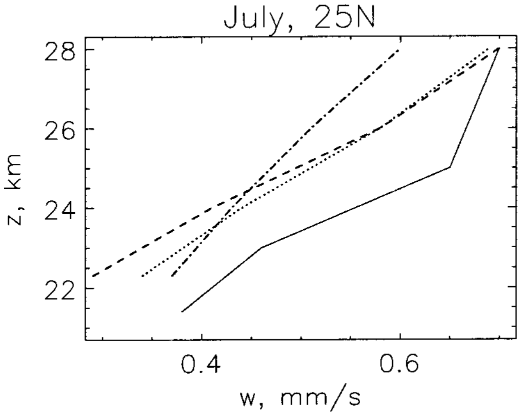

Figure 5. Vertical velocities in the tropics derived from the ozone budget in the years 1993 (dotted line) and 1994 (dashed line), from the HALOE water vapor "tape recorder" (solid line), and from radiative heating (dash−dotted line).

and August with largest values in the years 1994 and 1998 when little ClO_x-induced winter to early springtime ozone depletion took place. The tropical region appears to be largely self-contained and to play only a minor role in the seasonal O_3 decline. In this region, net ozone production below ≈30 km is compensated by upward transport with velocities of the order of 0.5 mm/s, in accordance with the estimate by Mote et al.[16] based on upward propagation of the seasonal signal of HALOE water vapor mixing ratios in the tropical stratosphere.

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