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UARS measurements of ClO and NO_2 at 40 and 46 km and implications for the model "ozone deficit"

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Abstract. We present the first diurnally-resolved measurements of ClO and NO_2 at 3.1 and 1.4 hPa, approximately 40 and 46 km. Comparisons between the measurements of ClO and a zero-dimensional box model utilizing standard photochemistry and constrained by Upper Atmosphere Research Satellite (UARS) tracer measurements show that photochemical models overpredict ClO by a factor of two or more at 3.1 hPa and by a factor of 1.5-2.0 at 1.4 hPa. NO_2 is well simulated by the model at 3.1 hPa, but systematically overestimated at 1.4 hPa. The model overestimate of ClO results in an overestimate of ozone loss in the upper stratosphere of 10-40%.

Introduction

Because of the short lifetime of ozone (O_3) in the upper stratosphere, transport can be neglected and the assumption can be made that production and loss balance when averaged over 24-hours [e.g., *Eluszkiewicz and Allen*, 1993, Fig. 1]. Despite the relative simplicity afforded by the neglect of transport, early attempts to model O_3 in this region predicted 40% to 60% lower ozone than was measured [e.g., *Froidevaux et al.*, 1985, *Jackman et al.*, 1986], a fact which became known as the "ozone deficit" or the "40-km problem".

Most analyses of the discrepancy between modeled and measured upper stratospheric O_3 used atmospheric observations to constrain the radicals and/or radical precursors in a model and either compare the resulting O_3 prediction with observations or compare production and loss of O_3. Analyses constrained by LIMS measurements generally underpredict O_3. The most recent studies find that model O_3 is ~10 to 25% less than measurements [*Eluszkiewicz and Allen*, 1993, *Natarajan and Callis*, 1989, *Siskind et al.*, 1995] in the 40 and 45 km region. Analyses constrained by ATMOS measurements [*Minschwaner et al.*, 1993, *Natarajan and Callis*, 1989] predict model O_3 in agreement with observations at 40 km, with a 10-20% deficit at 46 km. Analyses incorporating UARS HALOE measurements [*Crutzen et al.*, 1995] predict model O_3 within a few percent of observations at 40 and 46 km.

In this paper, we investigate issues related to the ozone deficit at ~40 and 46 km using measurements of ClO and NO_2 made throughout the day. This represents an advance because ClO and NO_2 are two of the three radicals that *directly* determine the rates of the ozone-destroying catalytic cycles.

UARS NO_2 and ClO Measurements

Measurements of ClO were made by the Microwave Limb Sounder (MLS), and minor adjustments have been applied to the version 3 data according to *Waters et al.* [1996]. Over the altitude range considered here, the accuracy of the ClO data is estimated to be the root-sum-of-squares of an 8% scaling uncertainty and a 75-pptv bias uncertainty (all uncertainties discussed in this paper are ~68% confidence limits, i.e., "1σ"). This translates into accuracy estimates of ±20-25% for these data.

Measurements of the NO_2 were made by the Cryogenic Limb Array Etalon Spectrometer (CLAES). Estimation of the accuracy of the CLAES NO_2 measurement is more problematic because the version 7 CLAES NO_2 data are not validated. However, the HALOE instrument, also aboard UARS, measures sunrise and sunset NO and NO_2, the sum of which is NO_x. These measurements can be used to calibrate the CLAES NO_2 measurements throughout the day [see the detailed discussion of this procedure in Dessler, A. E. et al., "A test of the partitioning between ClO and $ClONO_2$ using simultaneous UARS measurements of ClO, NO_2, and $ClONO_2$", *J. Geophys. Res., submitted,* 1996]. Briefly, we increase CLAES NO_2 measurements throughout the day by a factor (1.16 to 1.67, depending on latitude and altitude) such that CLAES NO_2 measurements made just after sunset agree with HALOE

Table 1. Inputs to Zero-Dimensional Model

		0°N		35°N		55°N	
	Source*	3.1 hPa	1.4 hPa	3.1 hPa	1.4 hPa	3.1 hPa	1.4 hPa
O3 (ppmv)	MLS	7.6	3.9	7.1	4.4	6.5	4.7
	HALOE	6.5	3.1	6.5	3.9	6.4	4.2
NOy (ppbv)	HALOE NOx (see text)	15.4	12.9	12.1	10.9	12.0	10.7
Cly (ppbv)	HALOE HCl and MLS ClO (see text)	3.1	3.4	3.2	3.2	3.1	3.0
H2O (ppmv)	Avg. of MLS and HALOE	5.0	5.8	5.8	5.9	5.8	6.1
CH4 (ppmv)	HALOE	0.96	0.47	0.64	0.50	0.55	0.40
Temp (K)	Avg. of MLS and CLAES	248	266	248	260	241	252

*These data were obtained between Feb. 12 and March 16, 1993 and averaged over the latitude bands 0°±5°, 35°N±5°, and 55°N±5°, except for 0° HALOE data which are averaged over 0°±10°. The data have been interpolated onto the 3.1 and 1.4 hPa pressure surfaces.

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NO_x measurements at sunset. In this way, the calibration from HALOE is combined with the diurnal cycle information of CLAES to produce an adjusted NO_2 data set. Combining the uncertainty in the HALOE NO and NO_2 data (±15% each [*Gordley et al.*, 1996]) with the uncertainty in the magnitude of the CLAES NO_2 diurnal cycle (±25% [Dessler et al., *submitted*]) as a root-sum-of-squares yields a total accuracy estimate for the adjusted NO_2 data of ±34%.

Model diurnal profiles of ClO and NO_2 are obtained from a zero-dimensional model incorporating the chemical integrator and photolysis code from the Goddard three-dimensional Chemical Transport Model (3D CTM) [*Kawa et al.*, 1995]. This model includes the photochemistry listed in the JPL-94 report [*DeMore et al.*, 1994]. The model is initialized with the UARS measurements listed in Table 1. The initial estimates of total odd nitrogen ($NO_y = NO_x + HNO_3 + 2xN_2O_5$ + minor species) and total inorganic chlorine (Cl_y = HCl + ClO + HOCl + minor species) are determined from a combination of model calculations and UARS data. Model simulations and previous measurements [*Russell et al.*, 1988] of NO_y constituent species at these altitudes indicate that at sunset, NO_x makes up greater than 94% of NO_y. Based on this, we assume that NO_y is 1.00 to 1.06 times sunset NO_x measured by HALOE, depending on latitude and altitude. The model Cl_y is determined by summing sunset HCl (measured by HALOE) and sunset ClO and making a small adjustment (<10%) to account for HOCl. Cl_y estimated in this way is in good agreement with the Cl_y estimate from the Goddard 2D model and with 1994 ATMOS measurements [*Michelsen et al.*, 1996]. Initial values for constituents not listed in Table 1 are taken from the 3D CTM run discussed in *Kawa et al.* [1995] at noon local time on March 1, 1992, at 180° longitude and the appropriate latitude and pressure. Model-derived diurnal cycles are obtained after running the model for four days, which at these altitudes closely approximates running the model to steady state.

Figures 1 and 2 compare the diurnal cycles of UARS ClO and NO_2 with model-derived ClO and NO_2. The UARS measurements were obtained between Feb. 12 and March 16, 1993, and at pressures of 3.1 and 1.4 hPa, corresponding approximately to altitudes of 40 and 46 km, respectively. Data from the latitude bands 0°±5°, 35°N±5°, and 55°N±5° are sorted by local solar time into one-hour and three-hour bins for the 3.1- and 1.4-hPa data, respectively. These bins are then averaged to obtain the diurnal cycle. Note that while the CLAES and HALOE NO_2 data are retrieved on the 3.1 and 1.4 hPa pressure surfaces, the MLS ClO data are actually retrieved on the 4.6, 2.2, and 1.0 hPa pressure surfaces and interpolated onto the 3.1 and 1.4 hPa surfaces. Because of the shape of the ClO profile, this could potentially introduce a low bias in the interpolated MLS ClO data not likely to exceed ~20%.

The disagreement shown in Fig. 1 between model-predicted and UARS-measured ClO abundance is significant, with modeled ClO a factor of two higher than measured ClO at 3.1 hPa and a factor of 1.5-2.0 higher at 1.4 hPa. These differences greatly exceed the uncertainty of the measurements. Because Cl_y in this model is constrained by UARS measurements, we conclude that differences between modeled and measured ClO reflect problems with our understanding of how Cl_y is partitioned at these altitudes between its major reservoirs, ClO and HCl. Such problems with model predictions of ClO in the mid and upper stratosphere have been seen elsewhere [e.g., *Michelsen et al.*, 1996, *Stachnik et al.*, 1992].

Figure 2 shows general agreement between measured NO_2 and the model. At 3.1 hPa, our UARS adjusted daytime NO_2 data agree within ~20% with our model estimate of NO_2, within uncertainty of the data. There is a slight tendency for model NO_2 to be higher than the UARS ad-

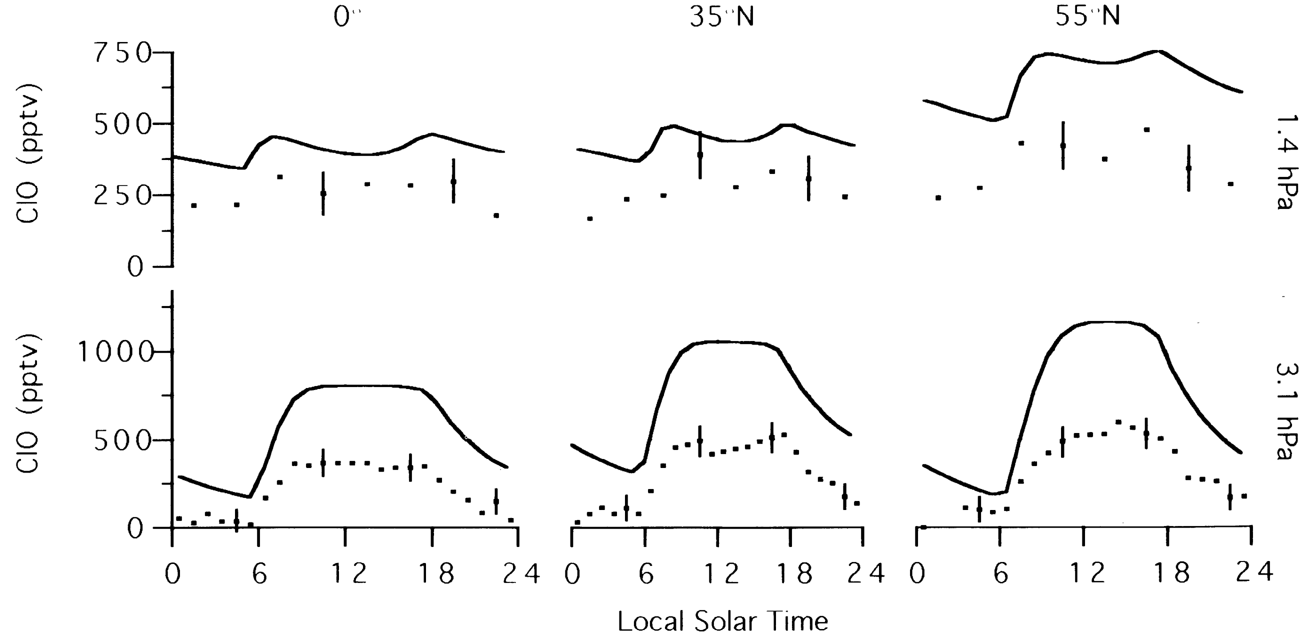

Figure 1. ClO (mixing ratio) vs. local solar time (hr) at 3.1 and 1.4 hPa, and 0°, 35°N, and 55°N latitude. The solid line is ClO from the profile model, the dots are ClO measurements from MLS. Error bars are the root-sum-of-squares of a 8% scaling uncertainty and a 75-pptv bias uncertainty (~±20-25%).

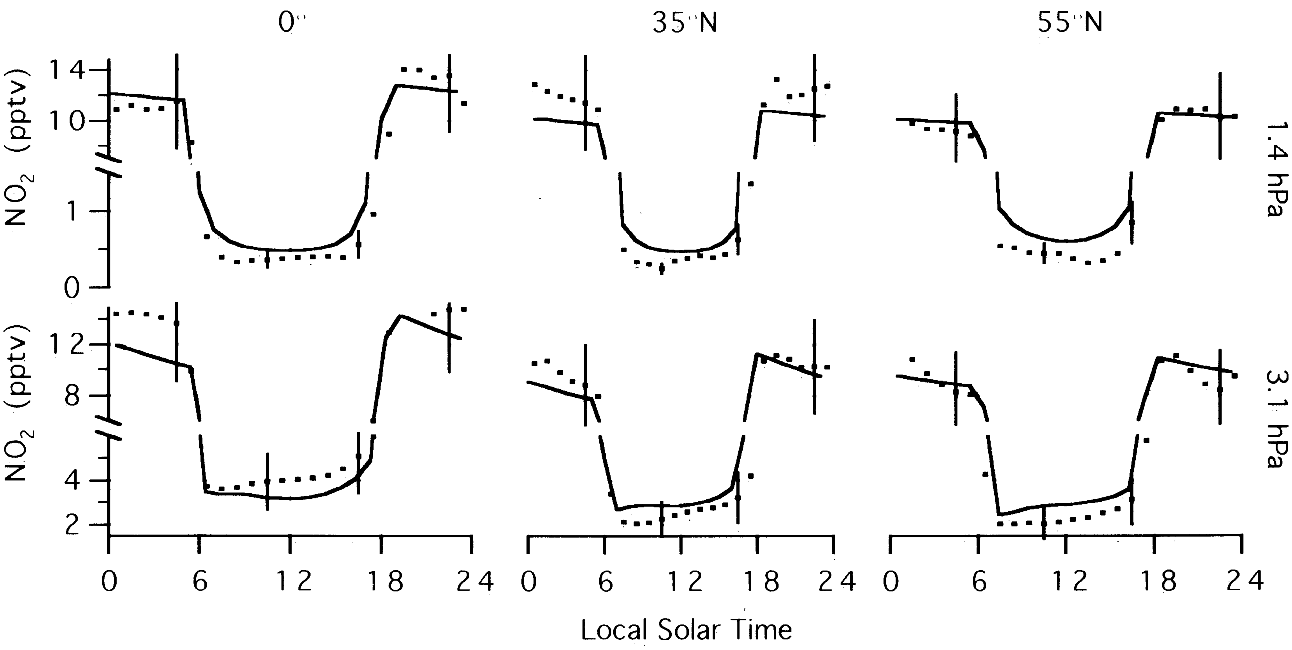

Figure 2. NO_2 (mixing ratio) vs. local solar time (hr) at 3.1 and 1.4 hPa, and 0°, 35°N, and 55°N latitude. The solid line is NO_2 from the profile model, the dots are the NO_2 measurements (see text). Error bars are ±34%.

justed NO_2 data. This is consistent with the previously discussed model overestimate of ClO, which causes NO_2 abundance to be increased through the enhancement of the reaction between ClO and NO. Taking this into account, the agreement at 3.1 hPa is excellent. At 1.4 hPa, the nighttime UARS adjusted NO_2 data agree within ~20% with our model's nighttime estimate. During the day, however, the UARS adjusted NO_2 data is on average ~50% lower than the model NO_2, a difference in excess of our estimate of the uncertainty of the UARS adjusted NO_2 data. This disagreement is not likely due to an overestimate in the model's NO_y because NO_y in the model is constrained by UARS measurements. About one fifth of the daytime discrepancy can be attributed to errors in the model's ClO abundance. The remainder of the difference is just beyond the limit of our uncertainty in the NO_2 measurement, suggesting an error in the model partitioning of NO_y. However, because the uncertainty in the measurement (±34%) is only slightly smaller than the unattributed disagreement between model and measurement (~±40%), there is no evidence that a model partitioning error for NO_2 exceeds a few percent.

The Upper Stratospheric Model Ozone Deficit

In this section, we perform a simple calculation of O_3 production and loss at 40 and 46 km using the UARS measurements of ClO and NO_2. The instantaneous production rate of O_3 can be calculated using the expression,

$$P = 2J_{O2}[O_2] \qquad (1)$$

where J_{O2} is the photolysis rate constant for O_2 (s^{-1}) and $[O_2]$ is the number density of O_2 (molecules cm^{-3}). The instantaneous loss rate of O_3 is the sum of the rates of the limiting steps of the catalytic cycles and the rate of O_3+O,

$$\begin{aligned} L = {} & 2k_{ClO+O}[ClO][O] + 2k_{NO2+O}[NO_2][O] \\ & + 2k_{HO2+O}[HO_2][O] + 2k_{O3+O}[O_3][O] \end{aligned} \qquad (2)$$

where k_{X+Y} is the rate constant for the reaction between species x and y (cm^3/molecule/sec). The concentration of O atoms is determined from a steady-state relation,

$$[O] = \frac{J_{O3}[O_3]}{k_{O2+O}[O_2][M]} \qquad (3)$$

Photolysis rates for O_2 and O_3 (J_{O2} and J_{O3}) are calculated based on pressure, temperature, overhead O_3, and solar zenith angle. The photolysis rate routine is taken from the Goddard 3D CTM [*Kawa et al.*, 1995]. Overhead O_3 is determined from zonally averaged MLS O_3 measurements (205 GHz, version 3) obtained between Feb. 26 and March 5, 1993. Note that the results are essentially unchanged if HALOE O_3 measurements are used for the overhead column. The radiation calculations are for clear-sky conditions, and a surface albedo of 0.3. All photolysis cross sections and rate constants used in this analysis are taken from JPL-94 [*DeMore et al.*, 1994].

To determine the balance between O_3 production and loss, we first calculate instantaneous production and loss rates every 15 minutes for an entire day using March 1 solar conditions. At each time step, ClO and NO_2 either from UARS measurements or the zero-dimensional model, HO_2 from the zero-dimensional model (constrained by UARS measurements of H_2O, O_3, and NO_y), O atom concentration determined from Eq. (3), average O_3 (from either MLS or HALOE) and temperature from UARS (see Table 1) are combined in Eqs. (1) and (2) to determine the instantaneous production and loss rates. 24-hour averages are determined by averaging the instantaneous rates.

Table 2 lists the ratios of 24-hour average production to 24-hour average loss of O_3 (hereafter referred to as P/L). Because of the short lifetime of O_3 at these altitudes, average production should equal average loss; in other words, P/L should equal one. P/L values less than (greater than) one imply that the model can balance production and loss given less (more) O_3 than specified, leading to a model

Table 2. Ratio of 24-hour Average Production to 24-hour Average Loss

	0°N	35°N	55°N	0°N	35°N	55°N
	UARS ClO and NO_2, MLS O_3			Model ClO and NO_2, MLS O_3		
3.1 hPa	0.88	1.10	1.19	0.78	0.78	0.80
1.4 hPa	0.85	0.92	1.01	0.74	0.75	0.77
	UARS ClO and NO_2, HALOE O_3			Model ClO and NO_2, HALOE O_3		
3.1 hPa	1.06	1.22	1.22	0.95	0.86	0.81
1.4 hPa	1.13	1.08	1.16	0.98	0.87	0.87

ozone deficit (surplus). Table 2 shows an ozone deficit for all cases using model-derived ClO and NO_2 radical abundances, consistent with results from our 2D model and many previous model analyses. When using UARS-measured ClO and NO_2 radical abundances, P/Ls are considerably higher and are generally greater than one. P/L calculated using HALOE O_3 data is 0.01-0.28 higher than P/L calculated using MLS O_3. Table 2 also shows that virtually any answer between a deficit of 25% and a surplus of 20% can be obtained depending on the choice of latitude, O_3 data set and various other parameters.

Deviations of P/L from one represent either errors in the parameters that are used to calculate P/L (e.g., errors in O_3 or k_{O3+O} measurements, J_{O2} calculations, etc.) or problems in our understanding of O_3 photochemistry in this region of the atmosphere. Standard error propagation of the uncertainties of the individual parameters suggests that the uncertainty in our calculation of P/L is ~±0.3 (1σ). Deviations of P/L from one that are less than 0.3 can therefore be wholly explained by the stated uncertainties in the parameters used in the calculation. Deviations of P/L from one that are greater than 0.3 suggest problems in our understanding of the photochemistry of the upper stratosphere.

All of the cases shown in Table 2 and virtually all of the analyses in the current literature concern deviations of P/L from one that are less than 0.3 (deficits or surpluses less than 30%). Differences between the various literature estimates of P/L can often be explained by the choice of the parameters going into the calculations. For example, the calculation of *Crutzen et al.* [1995] showing production equaling loss (P/L ~ one) is likely attributable to their use of the lower HALOE O_3 values as well as their choice of a relatively low latitude (23°). Had they used the higher MLS O_3 values, our analysis suggests that their slight surplus would have likely become a 15 to 20% deficit (P/L~0.80-0.85), consistent with other recent analyses [*Eluszkiewicz and Allen*, 1993, *Siskind et al.*, 1995]. This underscores the large uncertainties associated with calculations of P/L.

Conclusions

In this paper, we have investigated the photochemistry of O_3 at 3.1 and 1.4 hPa, approximately 40 and 46 km. For the first time, we have incorporated diurnally-resolved daytime measurements of both ClO and NO_2. From our analysis, we draw the following conclusions:

(1) Comparisons between measurements of ClO and a zero-dimensional model using standard JPL-94 photochemistry show that models overpredict ClO by about a factor of two at 3.1 and a factor of 1.5-2.0 at 1.4 hPa. This discrepancy exceeds the uncertainty in the measurements and is likely due to problems with our understanding of Cl_y partitioning. Comparisons between measurements of NO_2 and the model show that NO_2 is well simulated at 3.1 hPa, but is systematically overestimated by the model at 1.4 hPa.

(2) Because of model overestimates of ClO, models incorporating standard JPL-94 photochemistry will produce a loss of O_3 whose magnitude is 10 to 40% larger than calculations utilizing measured ClO. Note that the systematic disagreement between measured and modeled NO_2 at 1.4 hPa does not have a significant effect on O_3 loss because NO_2+O is not an important loss pathway for O_3 at 1.4 hPa.

(3) Because of the large uncertainty in the P/L calculation (~±0.3, 1σ), only extremely large deviations of P/L from one can be used as evidence of problems in our understanding of upper stratospheric photochemistry. Virtually all of the recent analyses of upper stratospheric O_3 produce surpluses or deficits that are within this uncertainty. This suggests that O_3 P/L calculations are no longer sensitive tests of our understanding of O_3 photochemistry. Instead, we believe that a better approach to testing the photochemistry of this region is to compare measurements and model calculations of the radicals involved in the rate limiting steps of the catalytic cycles that control ozone abundance.

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