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Chemical Modeling of Stratospheric Chlorine Partitioning and Diurnal Variation of NO_2 and O_3 for MAS and POAM

Grant Number N00014-94-1-G034

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Summary

Using the JPL/CalTech 0-D, time-dependent photochemical model, we compared the ATLAS-3 MAS measurements to theoretical expectations. The latitudinal and altitudinal gradients are similar for latitudes south of 50 degrees North. Poleward of 50 degrees, unresolved differences remain. After using the model to identify potential problems, the altitude of the peak ClO volume mixing ratio is now in concert with theory. Additional study into the high-latitude disagreement and into the absolute magnitude of the Cl_y partitioning is warranted.

Statement of Work

During this three-year study we proposed to apply a 1-D photochemical model in conjunction with measurements of ClO, HCl, and $ClONO_2$ from the ATLAS sensors MAS and ATMOS to study the stratospheric chlorine partitioning. We also proposed to use MAS ozone measurements to verify the model upper-stratospheric and lower-mesospheric ozone diurnal-variation calculations that are used in the ATMOS limb-scan inversion of ozone measurements. Lastly, we proposed to use the photochemical model to provide information about the diurnal variation of NO_2 at the terminators for use in the POAM limb-scan inversion of its NO_2 measurements.

Scope

Following the 1985 Spacelab-3 flight of ATMOS, a number of modelers (Allen and Delitsky, 1991, Weisenstein et al., 1992, Newchurch et al., 1993) have attempted to reconcile the partitioning of Cly in to its primary stratospheric components: HCl, $ClONO_2$, and ClO. Because ATMOS SL-3 did not measure ClO, researchers have appealed to a second measurement platform (Stachnik et al, 1992) to obtain a proxy for the ClO. This method introduced comparison disparities due to the differences in space and time between measurement platforms. The collocation of ATMOS and MAS on ATLAS 1, 2, and 3 allows the first rigorous test of chlorine partitioning. We report here the results of using the ATMOS and MAS measurement in conjunction with the JPL 1-D photochemical model to test the current understanding of stratospheric chlorine

photochemistry. The Mesospheric ozone diurnal-variation work, planned for year two, and the NO_2 diurnal-variation work planned for years two and three are suspended due to the unavailability of second-year funding; however, as a result of work we did designing and applying diurnal corrections to ATMOS NO and NO_2 retrievals [*Newchurch et al.,* 1995], we are well positioned to commence this work immediately.

Results

Using the JPL/CalTech 0-D, time-dependent photochemical model [*Eluszkiewicz and Allen*, 1993] initialized by ATMOS ATLAS-3 zonal-mean constituent measurements, we calculated the ClO volume mixing ratio (VMR) as a function of latitude and altitude to compare to the MAS ClO measurements. The noon calculations, shown in Figure 1a, extend from 10 degrees North to 47 degrees North and from 20 to 50 km in altitude. The color-coded ClO VMRs peak at approximately 1 ppbv ($1x10^{-9}$) at 40 km between 30 and 50 degrees North. The peak ClO values diminish poleward of 30 degrees to approximately 0.6 ppbv at 10 degrees North latitude. The analogous cross sections for sunset, sunrise, and midnight appear in Figures 1b, 1c, and 1d respectively. The sunset values are only slightly lower than the noon values; while the midnight and sunrise values are significantly lower as one would expect from the photochemistry controlling the ClO abundances. Altitude profiles of the five zonal mean calculations (10 to 47 degrees) for the four time periods (noon, sunset, sunrise, and midnight) appear in Figures 1e, 1f, 1g, and 1h respectively. Both the latitudinal and altitudinal variations of the ClO abundances are apparent in these profiles.

The MAS observations appear in Figure 1i. Comparing this figure to 1a indicates that the model calculations produce similar gradients, but larger magnitudes than the MAS observations. Because of known deficiencies in the model photochemical formulation of Cl_y partitioning, we expect this model overprediction of ClO. The compatible altitude/latitude gradients between model and measurements give confidence that the measurements are consistent over this domain.

The other species of the Cl_y budget, HCl, HOCl, and $ClONO_2$ appear in figures 2a-2d for noon, sunset, sunrise, and midnight respectively at 30 degrees North. To confirm that the model ClO was in equilibrium, we calculated the day-to-day change in ClO as a function of altitude for days 1-15 shown in Figure 3a and 3b. After 6 days, the daily change in ClO is less than 1%. Therefore, the initial Cl_y conditions (Figure 3c) have come to equilibrium after 6 days (Figure 3d) and do not change up to day 15 (Figure 3e). Additional study into the comparison of measurements and theory concerning the Cl_y partitioning is warranted.

At latitudes above 50 degrees, both MAS (Figure 1i) and MLS (Figure 4e) maintain their 40-km ClO peak value near 0.7 ppbv to 70 degrees North; the model, however, calculates diminishing ClO VMRs reaching half their 50-degree peak value at 70 degrees north (Figure 4a-4d). These results used the 47-degree ATMOS values at all latitudes north of 47 degrees, the most northerly ATMOS observation. Suspecting that the ATMOS CH4 profiles from 47 degrees may not be applicable to the 60 and 70-degree latitudes because of the latitudinal gradient in CH4, we used HALOE CH4 profiles (Figure 5) along with the MAS H2O measurements in the model atmosphere. The lower HALOE CH4 amounts resulted in only 0.1 ppbv increases in ClO, relieving for less than 25% of the model ClO gradient. This disagreement is unresolved at this time. The solution may be related to seasonal variations in ClO or to the lack of Cl_y and NO_y measurements at the high latitudes.

In order to assess the comparison of model and measurement altitude gradients and peaks in ClO, we normalized both profiles to their respective peaks. The results, shown for

latitudes 30 to 70 degrees North appear in Figures 6a-6e. For latitudes 30 to 60 degrees North, the altitude of the model peak agrees well with the altitude of the MAS-measured peak. The altitude peak at 70 degrees, however, caused some concern. A further analysis of the MAS retrieval indicated that an adjustment to move the MAS peak up 2 km should be made. This reevaluation was subsequently made to the dataset.

Related Work

As a result of the validation of the MAS ClO measurements supported by this work, we are now using these MAS measurements in conjunction with other ATLAS-3 observations to assess the model ozone deficit in the stratosphere [*Newchurch et al., 1996*]. The model ozone deficit problem has become a continuous issue following the publication of an analysis of HALOE data discounting the model ozone deficit [*Crutzen et al, 1995*]. The ATLAS-3 experiment, because of the combination of MAS and ATMOS, provides an excellent dataset to address this issue.

Appendix

Table I lists the file locations of the various files used in the model calculations. Figures 7a-7e plot the MAS ClO, neutral density, O_3, temperature, and H_2O used in the model calculations. Figure 8 plots the HALOE CH_4 profiles used in the model calculations.

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