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Solar occultation measurement of mesospheric ozone by SAGE III/ISS: Impact of variations along the line of sight caused by photochemistry

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Abstract. Twilight gradients in the concentration of atmospheric species with short photochemical lifetimes influence the transmission data obtained in a solar occultation instrument like the Stratospheric Aerosol and Gas Experiment III aboard the International Space Station (SAGE III/ISS). These photochemically induced changes result in nonlinear asymmetries in the species distribution near the tangent altitude along the line of sight (LOS). The bias introduced by neglecting the effects of twilight variations in the retrieval of mesospheric ozone is the focus of this study. O_3 in the mesosphere exhibits large variations near the terminator during sunrise and sunset based on current understanding of the photochemistry of this altitude region. The algorithm used in the SAGE III/ISS standard retrieval procedure for mesospheric ozone does not include the effects of these gradients. This study illustrates a method for implementing a correction scheme to account for the twilight variations in mesospheric O_3 and gives an estimate of the error in the standard retrieval. We use the results from a diurnal photochemical model

conducted at different altitudes to develop a database of ratios of mesospheric O_3 at different zenith angles around 90° to O_3 at a zenith angle of 90° for both sunrise and sunset conditions. These ratios are used to scale the O_3 at levels above the tangent altitude for appropriate zenith angles in the calculation of the optical depth along the LOS. In general, the impact of the twilight variations is to increase the optical depth thereby reducing the retrieved O_3 concentration at the tangent altitude. We find that at sunrise the mesospheric O_3 including the diurnal corrections is lower by more than 20% compared to the archived O_3. We show the results obtained for different latitudes and seasons. In addition, for nearly co-located sunrise and sunset scans, we note that these corrections lead to better qualitative agreement in the sunrise to sunset O_3 ratio with the photochemical model prediction.

1 Introduction

The solar occultation measurement technique has been the workhorse among various methods used for monitoring the composition of the earth's atmosphere for over 4 decades. This is evidenced by many successful experiments such as SAGE, SAGE II, HALOE, ATMOS, ACE-FTS, POAM, SAGE III/M3M and SAGE III/ISS. Major advantages of this technique include high signal to noise ratio, high vertical resolution, longer path length, and long-term accuracy provided by the 'self-calibrating' nature of the instrument operation. Limited global coverage ranks high among the disadvantages of this method. In the occultation experiments, the absorption of solar radiance measured by the instrument as a function of tangent height altitude or pressure is related to the optical depth and hence the abundance of the species along the line of sight (LOS). The bulk of the absorption, in general, occurs around the tangent point because of

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the exponential decrease in atmospheric density with altitude and due to the slant path determined by the spherical geometry. Standard algorithms used in the retrievals assume that the species distribution in atmospheric layers is homogeneous and, therefore, the distribution along the LOS is symmetrical around the tangent point location. This assumption is quite valid for species such as CH_4, H_2O, and stratospheric O_3 because of their long photochemical lifetimes. In the case of species with short lifetimes, the sudden changes in the photolysis rates near day/night terminator trigger rapid variations in the concentration as a function of zenith angle. These variations result in nonlinear asymmetry along the LOS.

The influence of twilight variations in NO and ClO on the interpretation of solar occultation measurements was described by Boughner et al. (1980). Correction factors based on photochemical models, as discussed in the above study, have been routinely applied in the retrievals of stratospheric NO and NO_2 profiles in HALOE (Gordley et al., 1996; Russell et al., 1988) and in ATMOS (Newchurch et al., 1996). Brohede et al. (2007) described the role of diurnal variations in the retrieval of NO_2 from OSIRIS measurements. The algorithm used in the retrieval of NO_2 in SAGE, SAGE II, SAGE III/M3M, and SAGE III/ISS neglects the twilight variations. Recent study of the NO_2 retrieval from SAGE III/ISS by Dube et al. (2021) describes the importance of considering the diurnal variations along the LOS.

Mesospheric O_3 is also characterized by short photochemical lifetimes and steep twilight gradients and, therefore, it is a potential candidate species requiring appropriate corrections in a retrieval from solar occultation instruments. Natarajan et al. (2005) noted that the diurnal correction factors used in the retrieval of mesospheric ozone from HALOE (Version 19) needed

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to be updated. The new factors were derived from a diurnal photochemical model of mesospheric ozone. They illustrated the impact of the corrections using a small subset of retrieved HALOE mesospheric O_3 profiles. In the present study, we describe the application of similar corrections to the SAGE III/ISS retrieval of mesospheric O_3. Table 1 of the Data Product User's Guide for SAGE III/ISS (2021) lists the release status of mesospheric O_3 data as a Beta version that is yet to be validated, because it is still potentially impacted by spectral stray light within the instrument. Our goal is to quantify the impact of the corrections on the archived data and to see whether the changes can support other known criteria. A description of the mesospheric O_3 variations under twilight conditions as calculated with a diurnal photochemical model is given in section 2. The occultation geometry and the diurnal correction factors for mesospheric O_3 are described in section 3. Results from the application of the factors to correct the archived data are discussed in section 4. We also include the results from an approximate retrieval using the archived transmission data with and without diurnal corrections. This is followed by a discussion of sunrise to sunset mesospheric O_3 ratios using appropriate co-located scans and a comparison to theoretical values. The final summary section reiterates the importance of corrections for photochemically induced twilight mesospheric O_3 variations in solar occultation retrievals.

2 Mesospheric O_3 variations at sunrise/sunset

Diurnal variations in reactive species can be obtained using a time-dependent diurnal photochemical model. A detailed description of the model used in this study is given in Natarajan et al. (2005). For the present study, we have updated the chemical rate constant data using the JPL Publication 19-5 (2020). Calculated diurnal O_3 variation in June at the latitude of

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11.25°S and at different altitudes of interest to this work is illustrated in Figure 1. O_3 concentration is shown as a function of time starting at midnight. Nighttime O_3 has a constant value representing the total odd oxygen in the lower mesosphere. A sharp decrease at sunrise is mainly caused by photolysis of O_3 forming atomic oxygen. The recombination of atomic oxygen and O_2 quickly balances the loss of O_3 from photolysis. This reaction is pressure dependent and becomes slower at higher altitudes. The photolysis of O_2 generates additional odd oxygen (O_X = O + O_3) and in the morning hours this leads to an increase in both O_X and O_3. The formation of odd hydrogen species from the reaction of O(1D) with H_2O during the day triggers the catalytic destruction of odd oxygen through reactions involving OH. It is noted that in this altitude range odd oxygen itself has a daytime variation caused by the competing production and destruction reactions. In the early morning there is a net gain of O_X and in the evening there is net loss of O_X, which continues even after sunset until atomic oxygen is depleted. The large increase in O_3 seen after sunset is mainly due to the recombination of atomic oxygen and O_2. At higher altitudes, not shown here, model predictions indicate a dramatic shift in the diurnal behavior of O_3. The diurnal model extends to 100 km; however, since the quoted uncertainty above 70 km in the archived SAGE III/ISS O_3 is large, we will focus on the region below 70 km.

The results of the full diurnal cycle are of general interest about the model simulation. But, with reference to solar occultation measurements, the sharp gradients seen in the O_3 concentration near a zenith angle of 90° are more critical. The significance of the twilight variations to the retrieval of mesospheric O_3 under sunrise/sunset conditions can be understood with the help of the schematic shown in Figure 2. This illustrates the occultation geometry in the plane containing the LOS. The red line denotes the LOS at a tangent altitude of Z_T. Points F and N represent the

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intersection of the LOS with an atmospheric layer at an altitude of Z shown in green. For a species with little or no twilight variations, the concentrations at the locations F and N are nearly equal to that at the location U, the tangent point at an altitude of Z. In this case, the concentrations at tangent height Z_T can be derived in a straightforward manner from the measured transmission using a retrieval algorithm. However, if the photochemistry causes significant gradients near 90°, as in the case of mesospheric O_3, the distribution around the tangent point becomes nonlinearly asymmetric because the concentrations at F and N depend on the respective local zenith angles. This variation must be incorporated in the evaluation of O_3 specific optical depth along the LOS.

To illustrate the impact of diurnal variations on slant-path column of O_3, we selected a typical event from the SAGE III/ISS data and applied the calculated O_3 variations in the slant-path column evaluation. The required parameters include month, date, event type (sunrise or sunset), tangent altitude, latitude, longitude, spacecraft latitude and longitude. These data are taken from the current Version 5.2 SAGE III/ISS data available from the Atmospheric Sciences Data Center (ASDC) at NASA LaRC. We used the model results for June at 11.25°S latitude to get the O_3 at sunrise variation along the LOS corresponding to different tangent altitudes from 56 to 76 km. The latitude of the chosen SAGE III/ISS measurement is 11.35°S. The results for tangent altitude of 64 km are shown in the left panel of Figure 3. The X-axis shows the distance along the LOS relative to the tangent point with positive direction towards instrument and negative direction towards the Sun. Corresponding zenith angles are shown at the top. The dotted line corresponds to the O_3 concentration along the LOS when the diurnal variations are neglected and only the values corresponding to 90° zenith angle from the layers above the tangent altitude are used. The

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solid line represents the O_3 including the diurnal variations at the respective altitudes. The increased O_3 concentrations on the instrument side of the LOS is readily seen. The ratio of the O_3 column along the LOS with diurnal variations to the column without the diurnal variations is shown as a function of tangent altitude in the panel on the right side. The peak difference of the order of 30% occurs in the altitude range from 61 to 72 km. Underestimation of the O_3 slant-path column in the standard retrieval translates to overestimation of the retrieved O_3. The error committed by the neglect of twilight variations can be evaluated with the help of the diurnal model results.

The technique is to express the O_3 variation as a function of zenith angle in terms of concentration normalized to O_3 at a zenith angle of 90°. Figure 4 shows the distribution of the ratio $O_3/O_3(\theta=90°)$ near sunrise as a function of zenith angle and altitude obtained from the model results for 11.25°S latitude in June. For a given tangent height, the total slant-path O_3 column comprises of partial slant-path columns corresponding to the layers at and above the tangent height. Spherical geometry dictates that the partial pathlength along the LOS is maximum for the layer immediately above the tangent height (i.e., the lowest layer) and decreases dramatically for higher layers. This, combined with decreasing O_3 concentration with height in the lower mesosphere, results in a total slant-path column dominated by contributions from a few layers right above the tangent point. Therefore, only a small range of zenith angles, say between 86° and 94°, centered at 90° are important. At 62 km the O_3 ratio is less than 1.0 for zenith angle less than 90° and it increases gradually for zenith angles greater than 90°. At higher altitudes, the ratio shows a much steeper increase for zenith angles greater than 92°. The ratio, in

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some cases, is even slightly larger than 1.0 at zenith angles less than 90°. From the occultation geometry shown in Figure 2, it is seen that as one moves away from a zenith angle of 90° along the LOS at any tangent altitude, the corresponding altitude layer of interest moves upwards. Figure 5 illustrates the O_3 twilight ratio as a function of zenith angle and altitude for sunset conditions for the same latitude and month. The changes in the ratio for sunset condition are smaller and more gradual especially for zenith angles greater than 90° compared to the sunrise case. It should be recalled that the daytime variation in the odd oxygen concentration in the lower mesosphere impacts the O_3 concentration differently at sunrise and sunset. The differences between the O_3 variations for sunrise and sunset conditions suggest that the effects on the retrievals are different for sunrise and sunset occultations. The twilight O_3 ratios for altitude layers above the tangent altitude can be used to get the O_3 concentration and hence the optical depth along the LOS more accurately. An earlier study with HALOE mesospheric O_3 data (Natarajan et al. 2005), showed that the twilight ratio is quite robust and small changes in the atmospheric parameters such as temperature and H_2O do not impact this ratio much.

3 SAGE III/ISS Mesospheric ozone

The Sage III/ISS instrument payload was launched in February 2017 and successfully attached to the ISS. The ISS occupies a low earth orbit at an inclination of 51.64° that provides occultation coverage of low- and mid-latitude regions. Description of the experiment and early validation of the O_3 measurements are given in McCormick et al. (2020) and Wang et al. (2020). More detailed information on the various wavelength channels and data used for retrieving a suite of atmospheric species including mesospheric O_3 are given in SAGE III Algorithm Theoretical

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Basis Document (ATBD, 2002) and in the SAGE III/ISS Data Products User's Guide Version 3.0 (2021) (DPUG). Among the three different O_3 profile measurements made by the instrument, the one based on short wavelengths in the Hartley-Huggins bands refers exclusively to mesospheric O_3. Three Charge-Coupled Device (CCD) pixel groups (PGs 0-2) are assigned to the short wavelengths in the 280 – 293 nm range, though only one (PG 1 centered at 286 nm) is currently used for the retrieval. According to the DPUG, mesospheric O_3 data have not been fully validated. We also note that the uncertainty in the archived O_3 concentration becomes larger than 10% above 70 km and there are some spurious negative data pointing to uncertainties in the transmission. The present study focusses only on SAGE III/ISS O_3 in the lower mesosphere up to an altitude of 70 km even though the retrieval itself starts at 90 km. The diurnal model described in the previous section extends up to 100km. We use the Version 5.2 transmission and species data obtained from ASDC at NASA LaRC. For each year and month, we have categorized the scans according to event type, sunrise, or sunset. The input data for our analysis include the tangent point latitude and longitude, spacecraft latitude and longitude, vertical profiles of neutral density, mesospheric O_3, and transmission. We use only the transmission data from the science pixel group 1 (PG1), which has a center wavelength of 286.124 nm, since the predominant species active in this wavelength region is O_3.

A database of O_3 twilight ratios for sunrise and sunset conditions has been generated from the diurnal model results. These ratios cover for each month the latitude range from 56.25°N to 56.25°S at an interval of 11.25°, zenith angles from 84° to 96° at 0.5° intervals, and altitudes from 56 to 90 km at 0.5 km intervals. Using the input data from each of the SAGE III/ISS occultations and spherical geometry relations, for every tangent altitude, we compute the zenith

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angles as well as partial pathlengths corresponding to overlying layers. This generates a pathlength matrix like the one used in the standard retrieval. Appropriate O_3 twilight ratios are then obtained by interpolation using the zenith angle and layer altitude. Multiplication of the standard pathlength matrix by the O_3 ratios yields the modified pathlength matrix including the effects of diurnal variations.

The twilight ratios can either be used to modify the O_3 profiles from the standard retrieval or be incorporated in a new retrieval from measured transmission profile. The first method is like the procedure described by Dube et al. (2021) for making diurnal corrections to stratospheric NO_2 data from SAGE III/ISS. The archived SAGE III/ISS O_3 profile and the standard pathlength matrix are used to recreate the O_3 specific slant optical depth, as shown by the equation

$$\tau = \sigma \, S \, n, \qquad (1)$$

where τ is the O_3 slant optical depth profile, σ is the O_3 cross section corresponding to the center wavelength of PG1, and n is the O_3 profile from the standard retrieval. S represents the pathlength matrix with each row corresponding to a tangent point altitude. This can be written as a triangular matrix because of the geometric symmetry on opposite sides of the tangent point as can be seen from Figure 2. The slant optical depth can then be converted to a O_3 vertical profile corrected for diurnal variations using the modified pathlength matrix described earlier, as shown by the equation

$$n_{wd} = (S_{wd})^{-1} \, \tau/\sigma = (S_{wd})^{-1} \, S \, n \qquad (2)$$

where S_{wd} is the modified pathlength matrix with diurnal correction and n_{wd} is the corrected O_3 profile. Here it is assumed that the O_3 absorption coefficient remains constant along the LOS. This procedure gives a quantitative estimate of the over-prediction by the standard retrieval. The

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results for a sunrise event on June 14, 2021 (Event ID =2021061438SR) are shown in Figure 6. The left panel displays the O_3 concentration profiles – the solid red line is the archived data from standard retrieval and the solid black line represents the profile after applying the diurnal correction ratios to the pathlength matrix. The percent difference between the standard and the modified profiles is shown by the solid line on the right panel. For this occultation, the difference exceeds 40% above 64 km. This is consistent with the change in O_3 slant column due to the diurnal correction shown in Figure 3. The right panel in Figure 3 shows around 30% increase in the slant-path column between 61 and 72 km. We also note that the retrieval becomes noisy in the upper altitudes as O_3 concentrations reach near detection limits. In the second method, instead of evaluating the slant optical depth using equation 1, the archived slant-path transmission data, which corresponds to PG1, is used along with the standard and modified pathlength matrices to retrieve the vertical O_3 profiles. The change in the slant-path transmission corresponding to the science CCD channel PG 1 for each tangent altitude below an upper boundary of 90 km is related to the total slant optical depth made up mainly of O_3 absorption and Rayleigh scattering contributions. After removing the Rayleigh scattering part corresponding to the center wavelength of 286.124 nm, the slant-path O_3 column can be estimated using the O_3 absorption coefficient at this wavelength taken from Bogumil et al. (2003), which is the same database used in the SAGE retrieval algorithm. The standard and modified pathlength matrices are then used to get the vertical O_3 profiles both without and with corrections for diurnal variations. The retrieved O_3 profiles for the sunrise event mentioned earlier are given by the dashed lines on the left panel of Figure 6, the red color denoting the standard retrieval without diurnal corrections and the black color the modified retrieval with diurnal corrections. We have used a very simple algorithm and assumed that the transmission data corresponds to a single

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wavelength to simplify the calculation. The actual retrieval procedure used for the archived products may have included more refinements. The agreement between results of the two different methods is very good, both for the vertical O_3 profiles and for the percent differences. Results for a sunset event, closer to the above sunrise event in location and within a day (Sunset event ID = 2021061515SS) are shown in Figure 7. The impact of the diurnal correction is much smaller for sunset conditions. The maximum difference between the standard and modified profiles is less than 10%. The two different procedures for incorporating diurnal effects yield very nearly same results.

We have applied the diurnal corrections following the procedure described above to all the SAGE III/ISS measurements from June 2021, categorized by the event type of sunrise or sunset. Individual O_3 profiles were grouped together in 11 latitude bands, 11.25° wide between 56.25°N and 56.25°S. The percent difference between the standard retrieval profile and the corresponding modified profile, defined as $(O_3/O_{3,\,WD} - 1) * 100$, was calculated and the mean for each latitude band was evaluated. Figure 8 shows the resulting distribution of the mean, which represents the over-estimation by the standard retrieval, as a function of latitude and altitude. There is a latitudinal dependence with peak values occurring near 64 km and the summer hemisphere showing smaller difference. Values higher than 100% (dark violet region) are seen in the upper altitudes of the winter hemisphere. The O_3 profile has a sharp gradient reaching a very low minimum in winter between and 70 and 80 km. The retrieved data in this region are very noisy and thus sometimes include negative concentrations. The percent difference between the two retrievals also displays a very noisy distribution with large values of both signs. Near the upper boundary of 90 km, the data is smooth, and the bias caused by the diurnal variations is very

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small. At these high altitudes, the day-night terminator occurs at higher solar zenith angles and the variation around 90° is small. The distribution of percent differences for sunset measurements is shown in Figure 9. The values are much smaller as discussed earlier, since the diurnal corrections are not significant for sunset. To look at the seasonal dependence of the impact of diurnal corrections on the retrieved O_3, we have repeated the procedure with SAGE III/ISS data from January 2021. Figure 10 displays the results for sunrise conditions. The differences between the standard and modified retrievals are larger again in the winter hemisphere with peak values occurring near 64 km. This agrees qualitatively with Figure 11 of Natarajan et al. (2005), which showed the percent difference in retrieved HALOE sunrise O_3 for January 1995 with updated diurnal correction factors compared to the retrieval with HALOE version 19 correction factors. The archived HALOE version 19 retrieval used correction factors from a diurnal calculation at 61 km for all mesospheric tangent altitudes above. Since a partially corrected (version 19) retrieval was used as the basis, the contour levels are negative and smaller in magnitude.

4 Sunrise to Sunset Ratio

Brühl et al. (1996), in their paper on HALOE O_3 channel validation, discussed the sunrise to sunset differences in O_3 around 0.1 hPa (about 64 km). Mesospheric layers are under sunlit conditions even at zenith angles slightly greater than 90° at dawn and dusk. As explained earlier, the viewing geometry in solar occultation observations leads to an increase in the O_3 optical depth because O_3 concentrations corresponding to varying zenith angles greater than 90° are seen along the LOS. We have noted that the impact is larger during sunrise than sunset measurement.

The sunrise to sunset O_3 concentration ratio becomes larger if the diurnal variations along the LOS are not considered in the retrieval. Solar occultation experiments occasionally offer the opportunity to approximately check this ratio as a test of consistency of measurement and agreement with theory. This is possible when sunrise and sunset orbits cross over each other within a reasonably short interval of time and physical proximity. Such near coincidences are quite rare. We selected sunrise/sunset pairs of measurements by SAGE III/ISS having tangent locations within 1.5° latitude, and 15° longitude of each other and separated by a maximum of 36 hours. The effect of advection by the prevailing westerly wind requires that the time and longitude differences are in the correct direction. There are just 10 pairs of sunrise /sunset measurements in June 2021 that satisfy the above criteria, all of them in low latitudes with a mean latitude of 10.46°S at sunrise and 10.27°S at sunset. The mean of the sunrise to sunset ratio of O_3 concentration for these 10 scans is shown in Figure 11. The solid line corresponding to the standard retrieval shows ratios greater than 1.1 in the altitude range considered. The modified retrieval yields a ratio shown by the dashed line decreasing from 1.01 at 60 km to lower values above. The diamond symbols represent the ratio from the diurnal model and the decreasing model value with altitude is in qualitative agreement with the modified retrieval. This comparison serves as an independent criterion to highlight the importance of including the LOS variations in the retrieval of mesospheric O_3 in solar occultation measurements. We noticed that very few such pairs of measurements occurred during other months in SAGE III/ISS data, which satisfied the criteria we have chosen. We have also looked at the latitudinally averaged sunrise and sunset data for June 2021 obtained for generating figures 8 and 9. For the latitude band centered at 11.25° S, the sunrise to sunset ratio as a function altitude (not shown) is similar to

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Figure 11, which used only collocated data. Other independent measurements are needed to verify the altitude variation of the ratio of sunrise to sunset O_3 concentrations.

5 Summary

Photochemically induced changes in species concentration at twilight can cause asymmetries in the distribution along the LOS of a solar occultation observation, variations that must be considered in the retrieval algorithm. Prominent among the species that need corrections for twilight variations are NO and NO_2 in the stratosphere and O_3 in the mesosphere. The SAGE III/ISS instrument uses the measurements in the short-wave Hartley-Huggins band to get mesospheric O_3 profiles. The standard retrieval procedure does not consider the LOS variations in O_3 caused by photochemistry. This study describes a procedure to use results from diurnal photochemical model simulations to develop correction factors for different altitudes, latitudes, and months. These factors were used along with the archived SAGE III/ISS mesospheric O_3 data for selected time periods to obtain modified O_3 profiles. For the month of June 2021, it is shown that neglecting the diurnal variations can result in over 30% overestimation of O_3 at 64 km and low latitudes. An approximate retrieval using the transmission data from SAGE III/ISS also indicates similar behavior in the profiles obtained with and without diurnal corrections. The retrievals were repeated for January 2021 to study the seasonal impact. Larger differences are seen generally between 70 and 80 km in high latitude winter hemisphere, and this is most likely due to very low O_3 concentrations and large uncertainties in the data. The results from this study are in good agreement with those obtained for the retrieval of HALOE mesospheric O_3 data.

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SAGE III/ISS data include a few nearly collocated sunrise and sunset measurements, mostly in the low latitudes and about a day apart. There are 10 pairs of such sunrise and sunset measurements in June 2021. An analysis of the sunrise to sunset ratio profile from these data indicates that the retrievals that include the diurnal variations show qualitatively better agreement with theoretical prediction. We note that dynamical causes such as diurnal tides may also introduce variations in the sunrise to sunset O_3 ratio especially in the low latitudes. The diurnal corrections described for occultation retrievals depend mainly on the short period variations around 90° solar zenith angle and dynamical impacts will not be significant compared to the photochemical effects.

Data Availability

SAGE III/ISS version 5.2 data is available from https://asdc.larc.nasa.gov/project/SAGE%20III-ISS/g3bssp_52. The O_3 twilight ratios used in this study are available from the author. They can also be obtained from any diurnal photochemical model of the mesosphere.

Author Contribution

MN conducted the photochemical model calculations, SAGE III/ISS O_3 retrievals, and the analyses described in the study, and he wrote the manuscript. RD and DF provided information and guidance on the use of SAGE III/ISS mesospheric O_3 data as well as comments on the manuscript.

Competing Interests

The authors declare that there is no competing interest for this study.

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References

Bogumil, K., Orphal, J., Homann, S., Voigt, P., Spietz, O., Fleischmann, A., Vogel, M., Hartmann, H., Bovensmann, J., Frerick, J., and Burrows, J.: Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote sensing in the 230-2380 nm region, J. Photochemistry and Photobiology A: Chemistry, Vol 157, No. 2-3, 167-184, 2003.

Boughner R. E., Larsen, J. E., and Natarajan., M.: The influence of NO and ClO variations at twilight on the interpretation of solar occultation measurements, Geophys. Res. Lett., 7, 231 – 234, 1980.

Brohede, S. M., Haley, C. S., McLinden, C. A., Sioris, C. E., Murtagh, D. P., Petelina, S. V., Llewellyn, E. J., Bazureau, A., Goutail, F., Randall, C. E., Lumpe, J. D., Taha, G., Thomasson, L. W., and Gordley, L. L.: Validation of Odin/OSIRIS stratospheric NO_2 profiles, J. Geophys. Res.-Atmos., 112, D07310, https://doi.org/10.1029/2006JD007586, 2007.

Brühl, C., Drayson, S. R., Russell III, J. M., Crutzen, P. J., McInerney, J. M., Purcell, P. N., Claude, H., Gernandt, H., McGee, T. J., McDermid, I. S., and Gunson, M. R.: Halogen Occultation Experiment ozone channel validation, J. Geophys. Res., Vol. 101, NO. D6, 10,217 - 10,240, 1996.

https://doi.org/10.5194/amt-2022-266
Preprint. Discussion started: 28 September 2022

Dube, K., Bourassa, A., Zawada, D., Degenstein, D., Damadeo, R., Flittner, D., and Randel, W.: Accounting for the photochemical variation in stratospheric NO_2 in the SAGE III/ISS solar occultation retrieval, Atmos. Meas. Tech., 14, 557 – 566, https://doi.org/10.5194/amt-14-557-2021, 2021.

Gordley, L. L., Russell III, J. M., Mickley, L. J., Frederick, J. E., Park, J. H., Stone, K. A., Beaver, G. M., McInerney, J. M., Deaver, L. E., Toon, G. C., Murcray, F. J.,Blatherwick, R. D., Gunson, M. R., Abbatt, J. P. D., Mauldin III, R. L., Mount, G. H., Sen, B., and Blavier, J. F.: Validation of nitric oxide and nitrogen dioxide measurements made by the Halogen Occultation Experiment for UARS platform, J. Geophys. Res.-Atmos., 101,10241–10266, 1996.

JPL Publication 19-5, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 19, 2020. https://jpldataeval.jpl.nasa.gov/pdf/NASA-JPL%20Evaluation%2019-5.pdf

McCormick, M. P., Lei, L., Hill, M. T., Anderson, J., Querel, R., and Steinbrecht, W.: Early results and validation of SAGE III-ISS ozone profile measurements from onboard the International Space Station, Atmos. Meas. Tech., 13, 1287-1297, https://doi.org/10.5194/amt-13-1287-2020, 2020.

Natarajan, M., Deaver, L. E., Thompson, E., and Magill, B.: Impact of twilight gradients on the retrieval of mesospheric ozone from HALOE, J. Geophys. Res., Vol. 110, doi:10.1029/2004JD005719, 2005.

Newchurch, M. J., Allen, M., Gunson, M. R., Salawitch, R. J., Collins, G. B., Huston, K. H., Abbas, M. M., Abrams, M. C., Chang, A. Y., Fahey, D. W., Gao, R. S., Irion, F. W., Loewenstein, M., Manney, G. L., Michelson, H. A., Podolske, J. R., Rinsland, C. P., and Zander,

https://doi.org/10.5194/amt-2022-266
Preprint. Discussion started: 28 September 2022

Atmospheric Measurement Techniques Discussions

R.: Stratospheric NO and NO_2 abundances from ATMOS Solar-Occultation Measurements, Geophys. Res. Lett., 23, 2373-2376., https://doi.org/10.1029/96GL01196,1996.

Russell III, J. M., Farmer, C. B., Rinsland, C. P., Zander, R., Froidevaux, L., Toon, G. C., Gai, B., Shaw, J., and Gunson, M.: Measurements of Odd Nitrogen Compounds in the Stratosphere by the ATMOS Experiment on Spacelab 3, J. Geophys. Res., Vol 3, D2, 1718-1736, 1988.

SAGE III Algorithm Theoretical Basis Document (ATBD) Solar and Lunar Algorithm, LaRC 475-00-109, Version 2.1, 2002. https://eospso.gsfc.nasa.gov/sites/default/files/atbd/atbd-sage-solar-lunar.pdf

SAGE III/ISS Data Products User's Guide, Version 3.0, 2021. https://asdc.larc.nasa.gov/documents/sageiii-iss/guide/DPUG-G3B-2-0.pdf

Wang, H. J. R., Damadeo, R., Flittner, D., Kramarova, N., Taha, G., Davis, S., et al.: Validation of SAGE III/ISS solar occultation ozone products with correlative satellite and ground-based measurements, J. Geophys. Res., 125, e2020JD032430. https://doi.org/10.1029/2020JD032430

https://doi.org/10.5194/amt-2022-266
Preprint. Discussion started: 28 September 2022

Atmospheric Measurement Techniques Discussions

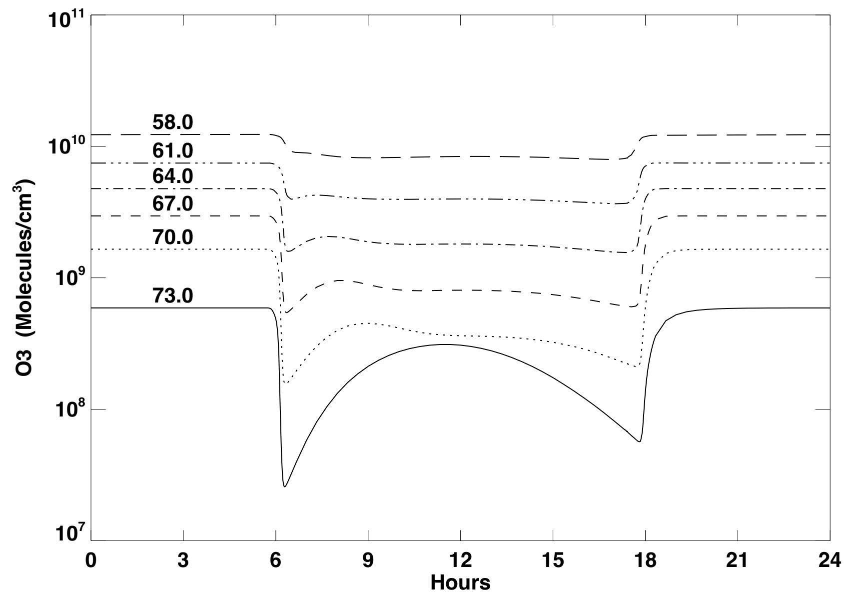

Figure 1. Diurnal variation in O_3 at 11.25°S in June at altitudes from 58 to 73 km. 0 hours denote midnight.

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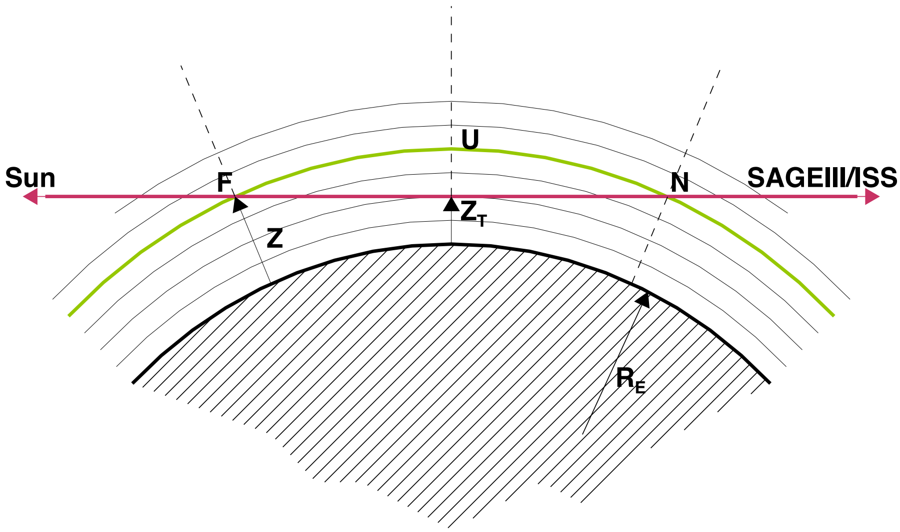

Figure 2. Schematic representation of the solar occultation measurement. Z_T is the tangent altitude, red line is the LOS, Z is the altitude of a layer above the tangent altitude, F (towards sun) and N (towards SAGE III/ISS) are the points of intersection of layer at Z with the LOS, and R_E is the earth radius.

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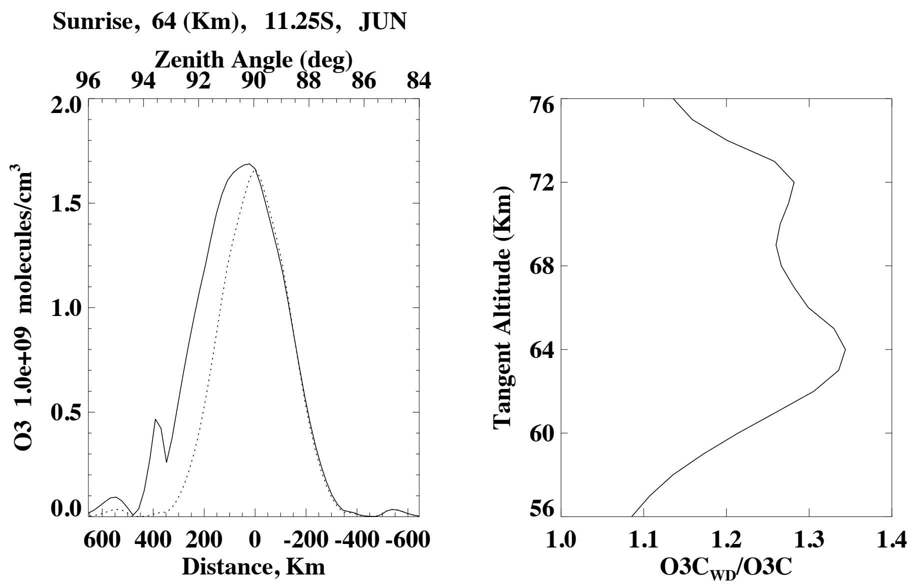

Figure 3. (Left) O_3 concentration along the LOS for a tangent altitude of 64 km at 11.25°S latitude in June. Solid line shows O_3 with diurnal variations and the dotted line represents O_3 without diurnal variations. (Right) Ratio of the O_3 column along the LOS with appropriate diurnal variations to the O_3 column without diurnal variations, plotted as a function of altitude at 11.25°S in June.

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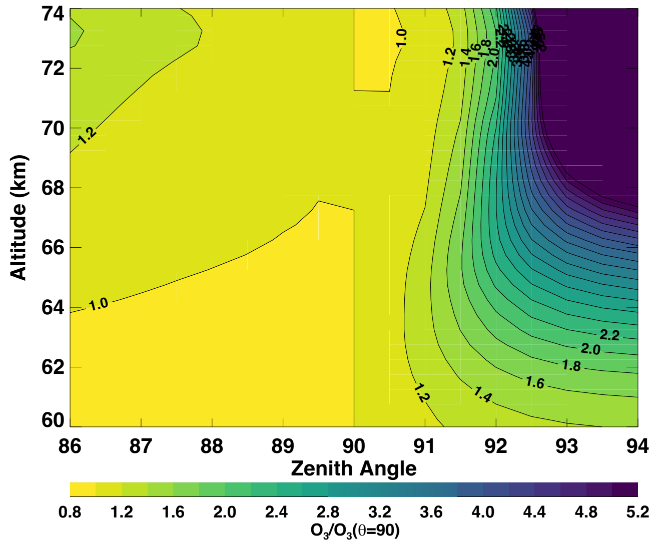

Figure 4. Ozone twilight ratio, defined as O_3 at zenith angle θ/O_3 at θ=90°, as a function of zenith angle and altitude for sunrise in June and 11.25°S latitude.

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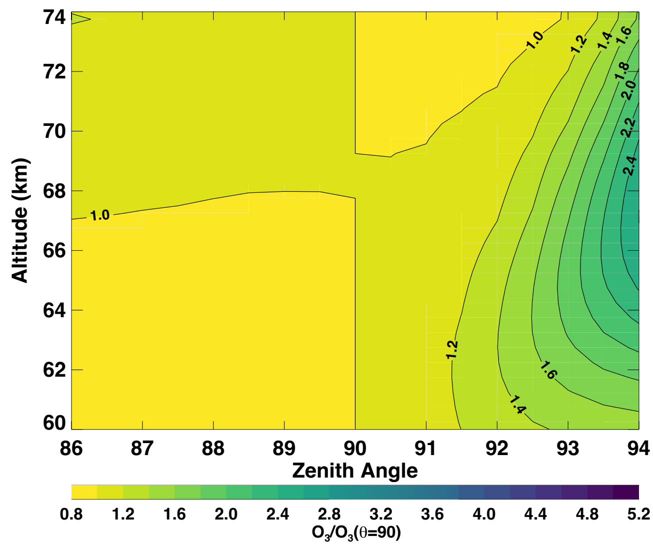

Figure 5. Same as Figure 4 for sunset conditions

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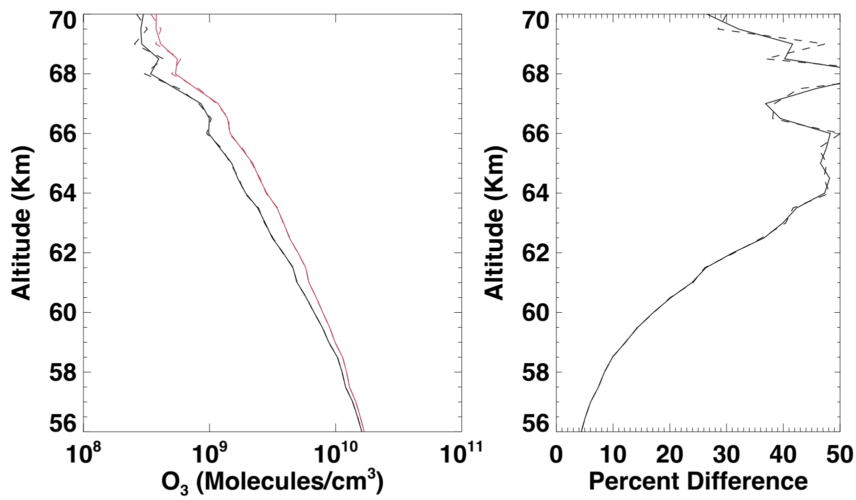

Figure 6. SAGE III/ISS sunrise O_3 for a sunrise event on June 14, 2021 (Event ID 2021061438SR). (Left panel) Red solid line shows the standard SAGE III retrieval, and the black solid line represents the retrieval including the diurnal variations along LOS. The dashed lines represent the retrievals using the transmission data, the red color for the standard retrieval and the black denoting the retrieval with diurnal corrections. (Right panel) Percent difference between the standard retrieval and the one with diurnal corrections; solid line using the archived standard retrieval of O_3 concentration, and the dashed line based on the approximate retrieval using the transmission data.

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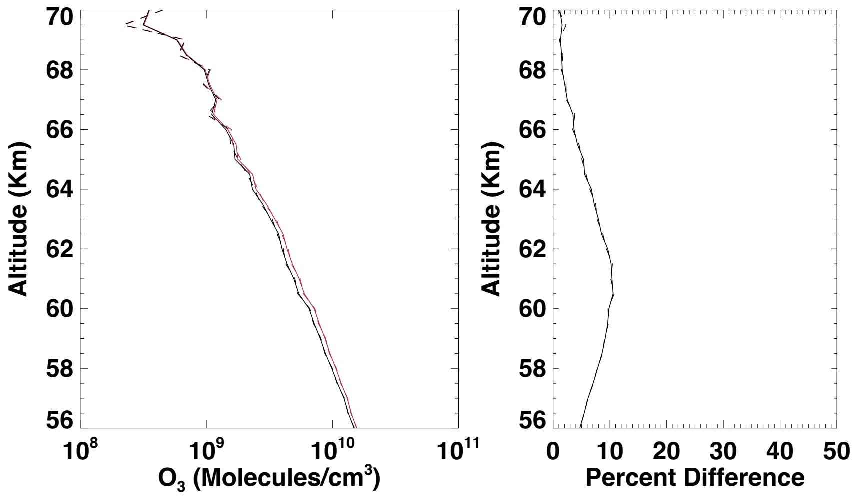

Figure 7. Same as Figure 6 but for a sunset event (Event ID 2021061515SS) closer to the sunrise event shown in Figure 6.

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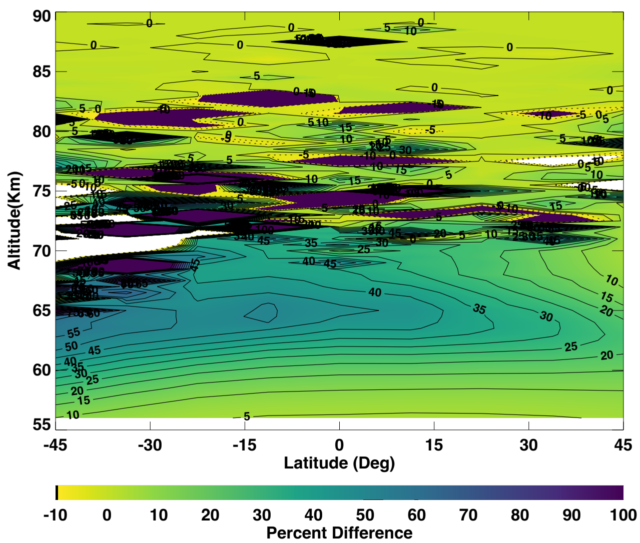

Figure 8. Latitudinal average of the percent difference in sunrise O_3 between the standard (archived) retrieval and a retrieval including diurnal variations along the LOS, as a function of latitude and altitude for June 2021

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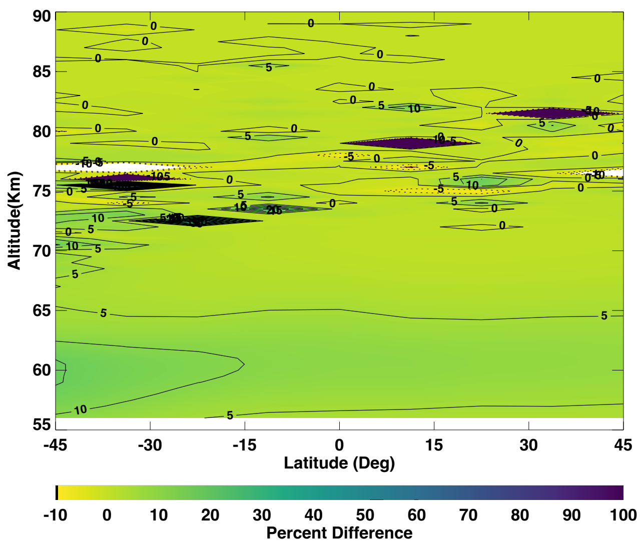

Figure 9. Same as Figure 8 but for sunset conditions.

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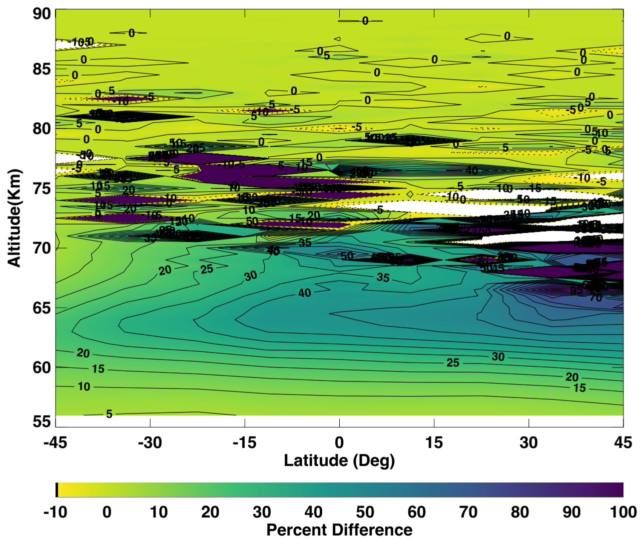

Figure 10. Same as Figure 8 but for January 2021.

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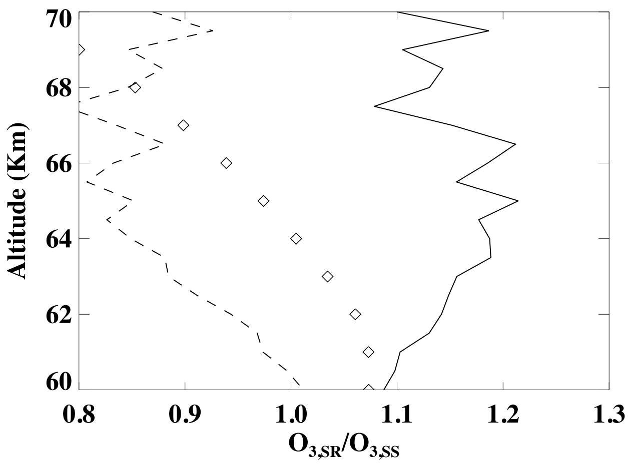

Figure 11. Vertical profile of O_3 sunrise to sunset ratio in June 2021. Nearly collocated 10 pairs of sunrises (mean latitude 10.46°S) and sunsets (mean latitude 10.27°S) data are used for this plot. Solid line represents the standard (archived) retrieval, and the dashed line shows the retrieval including diurnal variations along the LOS. The diamond symbols are from diurnal photochemical calculations at 11.25°S for June.