Final Report for the Period
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for

Investigations of SAGE II
Ozone and NO₂ Measurements

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Publications


Current work

Graphics show current activities in the following areas are enclosed.

(1) Comparisons of SAGE II column ozone measurements against TOMS.
   (a) The long term trends are slightly different.
   (b) Similar results are evident for the QBO sampled at SAGE coincidences.

(2) Comparisons against SBUV version 6:

Differences are being examined, with the following conclusions

   (a) Large differences can arise because measurements of temperature were unavailable to SAGE at certain times.
   (b) There exist other sources of large differences occasionally affecting SAGE.
   (c) Following fully sunlit periods, SAGE data possesses questionable values.
   (d) SAGE sunrise data appears to be biased at high altitudes in the tropics.
Validation of SAGE II Ozone Measurements


The error budget of the Stratospheric Aerosol and Gas Experiment (SAGE) II ozone profile measurements is discussed in depth. Five ozone profiles are compared against coincident ROCOZ-A and electrochemical concentration cell (ECC) ozonesonde measurements at Natal, Brazil (6°S) and Wallops Island, Virginia (36°N). The mean difference between all the measurements is approximately 1% and the agreement is within 7% at all altitudes between 20 and 53 km. Using ozonesonde and National Weather Service satellite observations of temperature, the agreement is almost equally as good for ozone mixing ratios on pressure surfaces. A comparison of the intrinsic SAGE II measurement errors with measured tropical variances suggests that the precision of the ozone profiles is approximately 5% between 24 and 36 km, degrading to 7% at an altitude of 48 km. It is inferred that the measurement errors possess a vertical correlation distance of 3 km and that therefore the profile precision improves by a factor of approximately 1.3 if the profiles were to be smoothed over 5 km vertically. The repeatability of SAGE II ozone profiles depends also upon the uncertainty in the profiles' reference altitudes. These errors are correlated over 7-day periods and increase to 200 m over that period of time. The accuracy of SAGE II ozone profiles is expected to be 6% above 25 km altitude. The SAGE II profiles provide useful ozone information up to approximately 60 km altitude and are more precise than the SAGE I profiles. SAGE II profiles, combined with revised SAGE I profiles, form an excellent data base for estimating the long-term trend in stratospheric ozone since 1979.

1. INTRODUCTION

The Stratospheric Aerosol and Gas Experiment (SAGE) II experiment is a part of the Earth Radiation Budget Satellite (ERBS), which was launched from the space shuttle October 5, 1984. It was maneuvered into a 610-km circular orbit at an inclination of 56°. The instrument is a seven-channel Sun photometer, similar to the SAGE I instrument [McCormick et al., 1979], that makes measurements at the wavelengths of 0.02, 0.94, 0.60, 0.525, 0.453, 0.448, and 0.385 μm. SAGE II vertically scans the solar surface as the atmosphere on the Earth's limb passes between the Sun and the spacecraft. The ray path from the Sun to the spacecraft traverses the atmosphere at minimum (or tangent) heights between cloud top and maximum heights of 200 km [Mauldin et al., 1985]. The instrument field of view in the direction normal to the ray is 0.5 km vertically by 5 km horizontally.

Ozone concentration profiles are retrieved from the irradiance measurements in the 0.6-μm channel, which is located at the center of the Chappuis absorption band. The inversion of the radiometric data involves the removal of contributions from molecular scatterers, NO2, and aerosol [Chu et al., this issue]. SAGE II performs 15 sunset and 15 sunrise measurements each day. Because of the orbital characteristics of the ERBS spacecraft, the spatial coverage of the SAGE II measurements extends over a seasonally dependent latitude range of approximately 70°S to 70°N over the period of about 1 month. The annual latitudinal coverage of the SAGE II measurements is shown in Figure 1 (for SAGE II, the sample locations and times repeat from year to year). SAGE II ozone data, together with the aerosol, NO2, and H2O data, are processed at NASA Langley Research Center, Hampton, Virginia, and are archived at the National Space Science Data Center (NSSDC) at NASA Goddard Space Flight Center, Greenbelt, Maryland.

The objective of this paper is to test the validity of the ozone measurements from the SAGE II instrument. The approach is similar to that used for the validation of the SAGE I ozone data [McCormick et al., 1984; Reiter and McCormick, 1982] and is based primarily on comparisons with correlative measurements by both rocket ozonesondes and electrochemical concentration cell (ECC) ozonesondes. A detailed analysis of the SAGE II ozone profile errors is also included to assess the precision of each of the measurements.

2. THE OZONE RETRIEVAL ALGORITHM

The procedure for retrieving ozone from SAGE II irradiances [Chu et al., this issue] is similar in approach to that for SAGE I, described by Chu and McCormick [1979]. However, in the SAGE II algorithm the tangent altitude corresponding to each measurement is determined solely from the satellite ephemeris and the inferred scanning rate of the scan mirror. This contrasts with SAGE I, in which tangent altitudes in the most recent, 1987-produced, data set are determined primarily by matching measured molecular densities at approximately 30 km altitude against meteorological data from the National Weather Service (NWS) (with only minimal constraints being applied, based on the satellite ephemeris information).

The algorithm first establishes the position of each SAGE II measurement, both in the atmosphere (expressed as the tangent altitude relative to Earth's sea level) and on the Sun. A Sun scan for a tangent altitude of approximately 120 km is used as a reference relative to which atmospheric transmissions are inferred. The scan mirror moves back and forth across the Sun 20-30 times during an event. Slant path atmospheric transmissions determined at each instant are grouped into 70 consecutive 1-km altitude bins, beginning at the lowest measurement altitude. For each event the arithmetic means of the measured optical depths at each altitude are computed. The estimated uncertainty in the optical depth

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Validation of SAGE II NO$_2$ Measurements

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Stratospheric aerosol and gas experiment (SAGE) II satellite-borne measurements of the stratospheric profiles of NO$_2$ at sunset have been made since October 1984. The measurements are made by solar occultation and are derived from the difference between the absorptions in narrow bandwidth channels centered at 0.448 and 0.453 $\mu$m. The precision of the profiles is approximately 5% between an upper altitude of 36 km and a latitude-dependent lower altitude at which the mixing ratio is 4 ppbv (for example, approximately 25 km at mid-latitudes and 29 km in the tropics). At lower altitudes the precision is approximately 0.2 ppbv. The profiles are nominally smoothed over 1 km except at altitudes where the extinction is less than $2 \times 10^{-5}$/km (approximately 38 km altitude), where 5 km smoothing is employed. The profile measurement noise has an autocorrelation distance of 3-5 km for 1 km smoothing and more than 10 km for 5 km smoothing. The absolute accuracy of the measurements is estimated to be 15% based on uncertainties in the absorption cross-sections and their temperature dependence. Comparisons against two sets of balloon profiles and atmospheric trace molecules spectroscopy experiment (ATMOS) measurements show agreement within approximately 10% over the altitude range of 23 to 37 km at mid-latitudes. SAGE II NO$_2$ measurements are calculated to be approximately 20% smaller at the mixing ratio peak than average limb infrared monitor of the stratosphere (LIMS) measurements in the tropics. They show acceptable agreement with SAGE I sunset NO$_2$ measurements in the tropics in 1979-1981 when the limited resolution and precision of the SAGE I measurements and the differences between the two measurement techniques are considered.

1. INTRODUCTION

The stratospheric aerosol and gas experiment (SAGE) II instrument was launched from the space shuttle on October 5, 1984. It was maneuvered into a 610-km circular orbit with an inclination of 56°. The instrument is a seven channel Sun photometer which makes measurements at the wavelengths of 1.02, 0.94, 0.60, 0.525, 0.453, 0.448, and 0.385 $\mu$m. The instrument scans back and forth across the solar disk as the Sun is occulted by the Earth's atmosphere. One product of these measurements is NO$_2$ profiles at a 90° solar zenith angle (sunrises and sunsets) at the points where the line of sight from the instrument to the Sun are tangential to the Earth's atmosphere. The instrument field of view in the direction normal to the line of sight is 0.5 km vertically by 2.5 km horizontally.

NO$_2$ profiles are retrieved on the basis of the difference between the measured irradiances at 0.448 and 0.453 $\mu$m (i.e., a differential technique). Using two wavelengths produces good separation of the NO$_2$ absorption signature from that of other gases and scatterers and makes the technique conceptually similar to the NO$_2$ measurement technique (which however utilizes many more wavelengths) which has been used to produce many years of ground-based NO$_2$ measurements [e.g., Noxon, 1979, 1980; Johnston and McKenzie, 1988] and more recently to make balloon-borne NO$_2$ measurements [e.g., Pommereau et al., 1987]. Contributions from ozone, aerosols, and neutral density must be removed before the NO$_2$ profiles can be obtained. The latitude of the NO$_2$ profiles (and the other atmospheric constituents, aerosols, ozone, and water vapor) observed by SAGE II change from one day to the next such that sampling of the global atmosphere between approximately 70°N and 70°S is produced over a 1-year period (see Figure 1). The orbit of SAGE II is such that the coverage of the global atmosphere is exactly repeated each 364.44 days. The SAGE II data are processed at NASA Langley Research Center, Hampton, Virginia, and are being archived at the National Space Science Data Center (NSSDC) at NASA Goddard Space Flight Center, Greenbelt, Maryland.

The objective of this report is to test the validity of the SAGE II NO$_2$ measurements within the measurement accuracy of approximately 15%. This is also the estimated (approximate) accuracy of the measurement systems against which the SAGE II NO$_2$ measurements will be compared. There are, unfortunately, only a few (almost) coincident balloon-borne measurement of NO$_2$, and thus validation must also depend upon comparisons against climatological distributions of NO$_2$ and on the self-consistency of the observations.

2. NO$_2$ RETRIEVALS

The general procedure for retrieving constituent profiles from the SAGE II irradiance measurements is described by Chu [1989] and Chu et al. [1989]. The algorithm is based on the set of equations:

$$\tau(\lambda_i) = \tau_r(\lambda_i) + a \tau_{O_3}(\lambda_i) + b \tau_{NO_2}(\lambda_i) + \tau_s(\lambda_i) \quad (1)$$
PRELIMINARY ASSESSMENT OF POSSIBLE AEROSOL CONTAMINATION EFFECTS ON SAGE OZONE TRENDS IN THE LOWER STRATOSPHERE

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ABSTRACT
An investigation of the validity of long term ozone trends in the lower stratosphere derived from SAGE I and II measurements is described. At altitudes below approximately 20 km, it is important to separate the ozone and aerosol contributions to SAGE extinction at 600 nm. The correlation between SAGE II measurements of ozone and aerosols indicates that most of the variability in these parameters is associated with physically induced variations resulting from quasi-horizontal motions of air parcels. The SAGE ozone measurements are however found to be as much as 20\% larger than coincident ozonesonde measurements between 15 and 20 km altitude. A sudden change in the difference at approximately 14.5 km altitude for which there is a change in the SAGE aerosol retrieval procedure suggests that SAGE ozone trends below 20 km altitude may be more sensitive to aerosol variations. Between 20 and 25 km altitude, however, both SAGE and the ozonesondes indicate a reduction in ozone of approximately 0.5\%/year over the period 1979 to 1989 at mid-latitudes of the Northern Hemisphere.

INTRODUCTION
SAGE I and II satellite observations have provided important information on long term changes in stratospheric ozone (e.g. /1/). The changes reported up until this time have emphasized the region above 25 km altitude both because of the possibility of contamination of the ozone signal by aerosols below this altitude (see for example, /2/) and because it is more difficult to validate the ozone observations below 25 km altitude because of the expected short time and space scales of ozone variability in the lower stratosphere. Nevertheless, it is important to assess long term ozone change in the lowest part of the stratosphere, especially because the ozonesonde observations suggest that a substantial decrease has occurred in this region over the past decade. This report is part of an ongoing study of ozone change in the lower stratosphere implied by SAGE I and II observations.

Several approaches have been taken in this assessment. Correlations between the coincident ozone and aerosol observations have been examined for spurious correlations which might be produced by retrieval uncertainties. Variations on both orbit to orbit and month to month time scales are being studied. It is not, however, easy to identify a spurious correlation in the month to month variations because of the large seasonal cycle in ozone at mid-latitudes and the quasi-biennial oscillation in the tropics which unfortunately has a phase which is correlated with volcanic aerosol injections into the stratosphere in the mid 1980's. On the other hand, we observe large orbit to orbit aerosol variations and it is the correlation with ozone variations on this time scale which will be described in this report. A comparison of SAGE I and II ozone profiles with "coincident" ozonesondes is also described.

SAGE II SHORT TERM OZONE/AEROSOL CORRELATIONS
SAGE II retrievals provide profiles of ozone concentrations and mixing ratios at local sunrises and sunsets at 1 km altitude intervals based on atmospheric absorption at 600 nm and neutral densities derived from temperature observations from the operational satellites of the National Weather Service (NWS). Aerosol extinctions are derived from the SAGE II data at several wavelengths. Here we use the extinctions at 1020 nm which are the least affected by Rayleigh scattering and absorption by the other gases being measured. Figure (1) shows the correlations between ozone concentrations and aerosol extinctions/km (typically proportional to aerosol concentrations) during each month from November 1984 to April 1990. The data analyzed includes only those profiles obtained between 45\°N and 55\°S and thus each monthly value is based on fewer than 100 profiles and a few days of observations per month. The correlations are predominantly positive below the aerosol maximum (not shown) but are negative above this maximum between 18 and 22 km. The correlations again become positive above 22 km altitude. It is important to also note that the correlations are large and seasonally variable with the largest correlations occurring in winter.
The wintertime correlation coefficient maximum and the approximate coincidence of the positive to negative correlation coefficient transition with the aerosol concentration/mixing ratio maximum strongly suggests that the correlations are the result of atmospheric motions. For example, upward moving air parcels located below the aerosol peak would contain relatively small mixing ratios of both ozone and aerosols. However if this physical picture is correct, it is not obvious why the correlation reverses from negative to positive near the ozone concentration peak and several kilometers below the ozone mixing ratio peak. To explain this, it is necessary to consider both vertical and horizontal motions of air parcels and it is useful to employ a more transport conservative analysis procedure using mixing ratios on pressure surfaces.

Figure 2 shows the correlation coefficient and $R_{x_1x_2}$ (where $x_1$ and $x_2$ are the standard deviations of ozone and aerosols) for SAGE II data for November 1984 determined after moving the data to pressure surfaces and dividing by air molecule concentrations. The pressure surfaces are numbered such that level 1 corresponds to a pressure of 1000 x 2$^{1/2}$ mb. Thus the transition from negative to positive correlations occurs in this case at level 26.5 (approximately 30 mb and 24.5 km). Figure 3 shows the mean mixing ratio profile of ozone and the profile of the proxy for aerosol mixing ratio for the days of observation. Also shown are the local mean horizontal and vertical gradients plotted as vectors on a relative scale of 1000 vertically to 1 horizontally. Assuming that air parcels primarily undergo elliptical plane orbits in the meridional in the stratosphere (/3/), the correlated aerosol/ozone variations produced by advection can be expressed in terms of products of the zonal mean horizontal and vertical gradients of the constituents together with terms describing the amplitude of the ellipses and their tilt relative to the horizontal. From Figure 3 the transition at level 17.5 is associated with a reversal of the horizontal gradient in the aerosol mixing ratio; this is also very close to the location of the aerosol mixing ratio peak. The transition at level 26.5 is associated with a reversal of the horizontal gradient of the ozone mixing ratio. Thus provided that the ellipse tilt is less than 1 in 1000, a situation associated with quasi-horizontal mixing in the stratosphere, the correlation coefficient profile may be understood. An examination of the meridional distribution of stratospheric ozone indicates that the horizontal ozone gradient typically reverses between 20 and 40 mb (levels 29 and 34) at 50° latitude.

As further evidence of the importance of horizontal, meridional gradients, Figure 4 shows the levels of zero correlation between ozone and aerosol mixing ratios during the first year of SAGE II measurements (November 1984–November 1985). Also shown is the upper level at which $H_2H_3=0$. The mean level at which $H_2H_3=0$ and the mean zero correlation level are coincident but seasonal differences between the two levels suggest that the slope of meridional mixing surfaces undergo a seasonal cycle. Several more years of observation are however required to understand this cycle because not only does the ozone gradient vary from month to month, but there are also important variations in the aerosol gradient.

Most of the aerosol and ozone variations on a time scale of less than one month are thus produced by (primarily horizontal) advections of these constituents. The required magnitude of the stratospheric trajectories is of order 1 km vertically by 2000 km horizontally at 50° latitude. There is considerable information on atmospheric variability in the SAGE II ozone and aerosol records. However, the possibility of an underlying anomalous correlation large enough to affect SAGE II ozone trends in the lower stratosphere cannot yet be ruled out.
relation between concentrations of aerosol at the altitude 30 km altitude and the blackened effect that the ozone mixing ratio is reduced. The ozone concentration could contain errors due to the blackened effect. The ozone mixing ratio at 30 km altitude is reduced.

An extensive comparison of SAGE I and II ozone profiles against both ECC and Brewer-Mast ozonesonde observations has been conducted by R.E.V. This comparison has been made by interpolation of ozonesonde observations using WMO temperature profiles provided for each SAGE profile. The sondes data were uniformly reduced by 3% to conform to the currently accepted ozone cross-sections for Dobson column ozone measurements. Coincident colocation criteria were 0.5 days and 1000 km. Using the SAGE aerosol profiles, care was taken to identify and filter out low altitude ozone profiles which might be affected by clouds. Several representations of the data were tried in order to obtain a statistically normal distribution of the measurements but the results were not significantly different. Only those ozonesonde profiles with a total ozone correction factor of less than 15% were included in this comparison.

Figure 5 shows the comparisons grouped by latitude - with the southern hemisphere station at Hohenpeissnberg included in the "mid-latitude" data. Clearly there is better agreement between SAGE II and the ozonesonde data than between SAGE I and the sondes below 20 km altitude. The latitude dependence of the SAGE-sonde differences are probably associated with the substantial increase of ozone mixing ratios with latitude which occurs in the lower stratosphere. The sudden change in the differences which occurs at approximately 15 km altitude is almost certainly associated with a change in the procedure used to infer the aerosol contribution to the 600 nm extinction. Above 14.5 km altitude the 385 nm channel is used in defining the aerosol extinction; below this altitude it is not used because of the large opacity at this wavelength. A contribution to the SAGE-sonde differences may also arise from the time-lag of the sondes measurement system during ascent through the large vertical ozone gradient characteristic of the lower stratosphere.

Above 20 km altitude the SAGE-sonde differences are small and insignificant. It is thus useful to compare the SAGE-derived long term ozone trends above 20 km altitude against those inferred from the ozonesonde observations at Hohenpeissnberg and the combined data from Edmonton and Goose Bay. Figure 6 shows these results based on using all the profiles at these sites (not just the coincident profiles) during the period 1979-1989. The SAGE data used here consists of daily zonal means within a 10° wide latitude band centered at 48 and 53°N respectively. The trends expressed as differences over the 11 year period are shown in Figure 6. There is excellent agreement between the trends inferred from the SAGE and Canadian sondes observations and the SAGE and Hohenpeissnberg trends only differ at the 95% confidence level at 20.5 km altitude, these observations indicate that there has been a decrease in ozone between 20 and 25 km altitude of approximately 0.5%/year between 1979 and 1989, with the decrease being larger at the lower altitudes in this height range.

A decrease in ozone is also indicated below 20 km altitude; however because of the possible effect of aerosol on the SAGE ozone profile retrievals in this region, this result requires further validation. It is worth emphasizing that the relative aerosol contribution to the
SAGE ozone signal is more than two orders of magnitude smaller above 30 km altitude than at 15 km altitude and aerosols are therefore very unlikely to be contaminating SAGE ozone trends in the upper stratosphere. On the other hand, the different altitude registration procedures for SAGE I and SAGE II can result in systematic reference altitude differences within the stated uncertainties of approximately 0.2 km for each experiment.

Fig. 4. The pressure levels at which there is zero correlation between SAGE II ozone and aerosol mixing ratios over the period November 1984 to August 1985. The seasonal cycle is derived from monthly analysis of profiles between 44 and 56°N and 44 and 56°S (plotted with a 6 month phase shift). Also shown is the seasonal cycle in the level where the product of the Northward gradients \((\text{CH}_1 \times \text{H}_2)\) equals zero (line with dots; at the lower level this curve is indistinguishable from the zero correlation level curve).

Fig. 5. (a) Ozonesonde - SAGE I mean differences relative to SAGE I, and (b) ozonesonde - SAGE II mean differences relative to SAGE II. The dashed lines represent 95% confidence intervals on the mean percentage difference.

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REFERENCES


MESOPHERIC OZONE MEASUREMENTS BY SAGE II

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Abstract

SAGE II observations of ozone at sunrise and sunset (solar zenith angle = 90°) at approximately the same tropical latitude and on the same day exhibit larger concentrations at sunrise than at sunset between 55 and 65 km. Because of the rapid conversion between atomic oxygen and ozone, the onion-peeling scheme used in SAGE II retrievals, which is based on an assumption of constant ozone, is invalid. A one-dimensional photochemical model is used to simulate the diurnal variation of ozone particularly within the solar zenith angle of 80° - 100°. This model indicates that the retrieved SAGE II sunrise and sunset ozone values are both overestimated. The Chapman reactions produce an adequate simulation of the ozone sunrise/sunset ratio only below 60 km, while above 60 km this ratio is highly affected by the odd oxygen loss due to odd hydrogen reactions, particularly OH. The SAGE II ozone measurements are in excellent agreement with model results to which an onion peeling procedure is applied. The SAGE II ozone observations provide information on the mesospheric chemistry not only through the ozone profile averages but also from the sunrise/sunset ratio.

Introduction

The diurnal variation of ozone in the mesosphere has been discussed recently in several models such as Rusch and Liu (1981), Prather (1981) and Allen et al (1984). They all display a similar pattern for the ozone diurnal variations, however none of them have compared model results and measurements in the transition period such as at sunrise and sunset because of the lack of observations. SAGE II ozone measurements are however made at 90° solar zenith angle and thus provide an excellent opportunity to examine the behavior of ozone at sunrise and sunset, or more particularly the variation between sunrise and sunset (i.e. the ozone sunrise/sunset ratio), and thus to test mesospheric ozone photochemistry.

The SAGE II data we examined are for the five-year period, 1985-1990. The vertical resolution of the ozone observations is approximately 1 km. The SAGE II ozone channel is centered at 0.6 μm in the Chappuis band. The orbital period is approximately 1.5 hours which results in 30 events per day (15 sunrises and 15 sunsets). The separation of each sunrise or sunset event is approximately 24 degrees in longitude and less than one half a degree in latitude. Each retrieved ozone profile is approximately representative of the atmosphere at local sunrise or sunset but it is derived on the basis of the assumption that temporal ozone variation is not included.

A one-dimensional photochemical model is utilized to investigate the ozone variation during twilight hours. Although transport effects might be important on time scales of an hour or more the resulting ozone changes are equally as likely to be positive or negative in the tropics and should thus be averaged out over many observations. Two types of chemical schemes were used to study the ozone diurnal variation: pure oxygen photochemistry and the photochemistry involving both odd oxygen and odd hydrogen.

The model simulations clearly show unequal sunrise and sunset ozone profiles (i.e. sunrise > sunset) at altitudes between 55 and 65 km. The SAGE II ozone profiles had also shown the differences between sunrise and sunset at that altitude range. Above 65 km the SAGE II retrieved ozone concentrations are controlled by retrieval constraints because of measurement noise (Cunnold et al, 1989; Chu et al 1989). The differences between sunrise and sunset of SAGE II ozone are found to be much larger than those modeled at 90° solar zenith angle. This paper emphasizes the ozone sunrise/sunset ratio rather than the individual sunrise or sunset profiles in order to test our understanding of mesospheric ozone chemistry during twilight and nighttime hours.

One-dimensional, time-dependent model

As already indicated above the modeling effort is focused on the behavior of ozone between sunset and sunrise. The overnight loss of odd oxygen caused by reactions between atomic oxygen and odd hydrogen radicals is included. Odd hydrogen concentrations in the mesosphere are poorly known. The twilight behavior of odd hydrogen species is therefore modeled. We have not however attempted to simulate the full diurnal cycle of ozone because this would introduce additional modeling uncertainties and SAGE II provides no information on daylight ozone concentrations in the mesosphere.

The geometry of the model is displayed in Figure 1. The chemical species abundance is a function of solar zenith angle and altitude. The coverage of the model is from 50 to 80 km and from 80° to 120° solar zenith angle. Photochemical reactions used in the model are tabulated in Table 1. Photochemical equilibrium of ozone is assumed at 80° solar zenith angle and the ozone first guess values are from the U.S. Standard Atmosphere (1976). The model time step is set equal to 2 seconds to accommodate the fast chemical time scale of atomic oxygen variations at 50 km altitude (i.e. 10 seconds). The height increment is 0.5 km which is one-half of the SAGE II vertical resolution.

In order to obtain the initial slant path ozone abundances, which are needed to compute the photodissociation rate of ozone, a Chapman function (Smith and Smith, 1972) is employed at the upper boundary (= 80 km) and at the initial state as well (i.e. = 80° solar zenith angle). Elsewhere linear interpolation is applied to the ozone concentrations at the nearest intersection of the altitude and solar zenith angle grid. The absorption cross section of ozone and solar irradiances are from Atmospheric Ozone (1985), and the cross sections of molecular oxygen in Schumann-Runge bands are from Frederick and Hudson (1980).
calculated time-dependent profiles. Of odd oxygen through the following reactions

\[
egin{align*}
O + OH & \rightarrow H + O_2 \\
H + O_2 + M & \rightarrow HO_2 + M \\
O + HO_2 & \rightarrow OH + O_2 \\
\end{align*}
\]

The model geometry used to calculate columnar ozone amounts and photodissociation rates. \(O_0\) indicates the local solar zenith angle of incremental contributions.

The integration procedure at sunset is straightforward and requires no iteration. Due to the model geometry (see Figure 1) the ozone column along the sunset ray contains contributions from different solar zenith angles (i.e. earlier times for which calculations have been completed). For the sunrise ray, on the other hand, the grid points correspond to later times for which the calculations have not yet been made. To obtain the ozone profile at sunrise, the model was thus integrated starting from the nighttime ozone values until the convergence is attained. In each iteration the updated slant path columns produce updated ozone profiles. The model seeks convergence at each altitude and solar zenith angle grid point. Six iterations are typically required using a factor of 0.0001 times the ozone concentration as the convergence criterion at each grid point.

It is assumed in these calculations that ozone absorption is much larger than the effect of Rayleigh scattering. Anderson (1983) pointed out that the multiple scattering of solar radiation can be ignored at altitudes above 50 km at wavelengths less than 0.31 \(\mu\)m. Although it can become important at larger solar zenith angles (> 93-94) (Noxon et al., 1979), the substantial absorption by ozone at these angles results in negligible photodissociations below 70 km altitude. At lower altitudes where the reflection of solar radiation may be strong it can also be ignored compared to the absorption by ozone. The effect due to multiple scattering and ground albedo is thus neglected, however, the singly scattered solar radiation from an infinitesimally thin layer (Solomon et al. (1987)) is included.

Because of the sensitivity of the calculations to the initial ozone profile, it is important that the calculated sunrise/sunset ratio is constrained by the observed ozone profile. The initial ozone profile is therefore iterated until the calculations yield the observed ozone profile (1% difference is assumed) at sunset. It should be noted that the agreement between the calculated profile and the observed SAGE II mean profile is obtained only after the onion peel inversion procedure has been applied to the calculated time-dependent profiles.

**HOX-OX Photochemistry**

Odd hydrogen compounds contribute to an overnight loss of odd oxygen through the following reactions

\[
egin{align*}
O + OH & \rightarrow H + O_2 \\
H + O_2 + M & \rightarrow HO_2 + M \\
O + HO_2 & \rightarrow OH + O_2 \\
\end{align*}
\]

![Fig. 1 Model geometry used to calculate columnar ozone amounts and photodissociation rates. \(O_0\) indicates the local solar zenith angle of incremental contributions.][1]

![Diagram of sunlight and ozone profile with numbers 120, 80, 60 km, and 0.5 km][2]

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**Table 1 Photochemical reactions used in the model**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) (O_3 + hv \rightarrow O + O_2)</td>
<td>(\lambda &lt; 0.31 \mu)m</td>
</tr>
<tr>
<td>(R2) (O + O_2 + M \rightarrow O_3 + M)</td>
<td>6.0 x 10^{-34} (300/k) (2.3)</td>
</tr>
<tr>
<td>(R3) (O + OH \rightarrow H + O_2)</td>
<td>2.3 x 10^{-14} (exp^{-90/k})</td>
</tr>
<tr>
<td>(R4) (O + HO_2 \rightarrow OH + O_2)</td>
<td>2.8 x 10^{-11} (exp^{-172/k})</td>
</tr>
<tr>
<td>(R5) (H + O_2 + M \rightarrow HO_2 + M)</td>
<td>1.76 x 10^{-8} (T^{-1.4})</td>
</tr>
<tr>
<td>(R6) (OH + HO_2 \rightarrow H_2O + O_2)</td>
<td>8.4 x 10^{-11}</td>
</tr>
<tr>
<td>(R7) (OH + OH \rightarrow H_2O + O_2)</td>
<td>4.5 x 10^{-12} (exp^{-275/k})</td>
</tr>
<tr>
<td>(R8) (HO_2 + HO_2 \rightarrow H_2O_2 + O_2)</td>
<td>2.4 x 10^{-14} (exp^{-1250/k})</td>
</tr>
<tr>
<td>(R9) (O + O_3 \rightarrow 2O_2)</td>
<td>1.5 x 10^{-11} (exp^{-2218/k})</td>
</tr>
<tr>
<td>(R10) (O_2 + hv \rightarrow O + O)</td>
<td>0.17 &lt; (A &lt; 0.25 \mu)m</td>
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<tr>
<td>(R11) (H + O_3 \rightarrow OH + O_2)</td>
<td>1.4 x 10^{-10} (exp^{-270/k})</td>
</tr>
<tr>
<td>(R12) (OH + O_3 \rightarrow HO_2 + O_2)</td>
<td>1.6 x 10^{-12} (exp^{-940/k})</td>
</tr>
</tbody>
</table>

The reaction constants are all from Allen et al., 1984 except (R2) (which is from J. Phys. Chem., Vol. 11, 1982), photodissociation rates of ozone and molecular oxygen are calculated in the model itself.

which encompass a major catalytic destruction of odd oxygen above the stratopause. The OH abundances taken from Allen et al. (1984) around 1800 hr are used as initial values. The HOX is derived in the photochemical balance as follows

\[
[HO_2] = \frac{K_{12}[OH] + K_{11}[H][O]_3}{K_4[O]}
\]

These catalytic reactions are able to destroy atomic oxygen very efficiently and when the abundance of atomic oxygen is greater than \(10^5 \text{cm}^{-3}\) (-1/400 of its daytime value) a significant loss of \(O_2\) is thus expected. The equation controlling the loss of odd oxygen in this model can be written as

\[
\frac{d[O_3]}{dt} = 2 J_{O_3} [O_2] - 2 K_3 [O][OH] - 2 K_9 [O][O_3]
\]

Figure 2 depicts the variability of odd oxygen from 80° to 110° solar zenith angle between 50 and 70 km. At 70 km, approximately 35% of the initial odd oxygen is destroyed within a two hour period around sunset. A 15% loss of odd oxygen occurs before sunset and a 20% loss takes place after dark. During the period before sunset the \(O_3/O_2\) ratio remains constant, with \(O\) of an order of magnitude larger than \(O_2\). In the early part of night during which the \(O_3/O_2\) ratio decreases by a factor of two, no significant increase of ozone occurs. This is because oxygen atoms are removed by \(O+OH\) catalytic reactions instead of being converted to \(O_3\). At solar zenith angles greater than 93° (at which time \(O\) has decreased to just a factor of two larger than \(O_2\) oxygen begins to increase substantially. At 65 km altitude, the odd oxygen loss is primarily concentrated in a hour period before sunset, and the loss of odd oxygen is approximately 30%. The \(O_3/O_2\) ratio however, in the same period, tends to remain a constant. At 60 km the loss of odd oxygen is 15% and only occurs before sunrise. Below 60 km the loss of odd oxygen is small - only 5% at 55 km and 2% at 50 km.
Fig. 2: The calculated variation of odd oxygen of HOx-Ox chemistry at sunset between 80° and 110° solar zenith angle from 50 to 70 km altitude.

Table 2: Selected days of SAGE II ozone observations

<table>
<thead>
<tr>
<th></th>
<th>sunrise</th>
<th>sunset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov 6</td>
<td>21.3° N</td>
<td>21.3° N</td>
</tr>
<tr>
<td>Jan 16 &amp; 17</td>
<td>17.5° N</td>
<td>17.1° N</td>
</tr>
<tr>
<td>May 6 &amp; 7</td>
<td>20.7° S</td>
<td>21.5° S</td>
</tr>
<tr>
<td>July 18</td>
<td>17.0° S</td>
<td>17.8° S</td>
</tr>
</tbody>
</table>

Figures 3(a) and 3(b) show the variation of ozone between 80° and 110° solar zenith angles during sunset and sunrise, respectively. The modeled ozone variations for both sunset and sunrise show good agreement with Allen et al. (1984).

OH oscillates up and down within the two-hour period around sunset at 70 km. Figure 4 illustrates the OH variations with solar zenith angle. The variations of HOx (not shown) are photochemically coupled with OH. The variations of OH are less important during the period before sunrise (not shown) than in the period after sunset not only because OH concentrations are approximately an order magnitude smaller but also because the abundances of atomic oxygen are small. Therefore, the destruction of O3 due to HOx is not effective just before sunrise, and only the conversion of ozone to atomic oxygen needs to be considered in this period.

The photodissociation of water vapor is not included in the model because (1) the photodissociation of H2O is quite small at twilight in the mesosphere and (2) there is no direct impact on O3 due to H2O. In addition, SAGE II does not measure H2O above the stratosphere. Furthermore, we would like to keep the photochemical reaction set as simple as possible in order to better understand the photochemistry in the mesosphere. The results indicates that at 70 km a 5% OH change will induce a 1% change in O3. The one hour average of JH2O before sunset contributes approximately 5% increase in OH. Therefore, 1% ozone change is expected. But this can be neglected compared to SAGE II measurement uncertainty.

The comparisons of model results and SAGE II ozone measurements

Because of seasonal and latitudinal variations in the ozone diurnal changes, the selection of SAGE II measurements used in the comparison becomes significant. In one year of SAGE II data, only five days (four days in tropical region and one at mid-latitude) have been found where sunrise and sunset events are within one degree of latitude difference in a 24 hour period. Table 2 exhibits selected profiles when the average zonal mean latitudes of sunrise and sunset events are within 1 degree of each other. In this comparison, only SAGE II zonal mean values are used. The longitudinal variation of the ozone measurements is affected by random noise (Cunnold et al, 1984 and 1989) particularly in the tropical region - where most of the sunrise and sunset coincidences occur.
Fig. 5 (a) The comparisons of ozone profiles on the selected days between 50 and 65 km at sunset; star with error bar: SAGE II ozone profile; solid line: retrieved ozone profile of model results; dotted line: ozone profile at 90° solar zenith angle of model results. (b) same as (a) except at sunrise.

Within the four tropical zonal means, it is found that the model results display nearly identical ozone variations both at sunrise and sunset. Therefore the ensemble mean of the zonal average of the four coincident events (per year) can be used to compare with the model predictions. Figures 5(a) and 5(b) show the means (stars) and standard deviations (shown as error bars) of the twenty events at both sunrise and sunset of the selected days over the five-year SAGE II data set. In the calculations reported here SAGE II sunset profiles have been used as a constraint on the ozone near 90° solar zenith angle.

An onion-peeling algorithm applied to slant column inferred from the model results begins at 78 km (ozone at 78 km is assumed initially.) The ozone concentration is estimated by subtracting the sum of the ozone concentrations weighted by the path length in all higher altitude layers from the slant column content. In the onion peeling inversion, homogeneous spherical shells with constant ozone concentrations are assumed. This procedure produces a hypothetical ozone profile inferred from the model calculations which may be directly compared against retrieved SAGE II ozone profiles.

For pure oxygen chemistry the modeled and observed sunrise/sunset ratio agrees well only at the altitudes between 50 and 60 km. Overestimates of the ratio are found above 60 km with a maximum of 30% at 63 km. The overestimation is totally attributable to the excess of oxygen atoms above 60 km in the model at sunset, which then produce excessive nighttime ozone concentration. Consequently an excessively large and asymmetric ozone variation is produced at sunrise. Because the asymmetry will propagate downward via the onion peel procedure, the more asymmetric the variation about 90° the deeper the effect will penetrate.

When the chemistry of odd oxygen and odd hydrogen is included, fewer oxygen atoms are available to be converted into ozone and therefore there is a tendency for an increase in the ozone photodissociation rate. At 70 km, the transition from O to O3 is thus deferred at sunset, and an earlier transition occurs oppositely at sunrise. The time difference corresponds to approximately one degree solar zenith angle. At lower altitudes because of the smaller ozone diurnal variation the effect is less pronounced.

Figures 5(a) and 5(b) have also displayed the simulated ozone (i.e. the solid lines) after the onion-peeling retrieval method has been applied. The agreement between SAGE II ozone means and modeled ozone is within 1% at sunset and better than 5% at sunrise. We consider these differences to be small compared to the measurement uncertainties of SAGE II. Furthermore, the photochemical reactions used in the model, disregarding the photodissociation of water vapor, are sufficient to describe sunset and sunrise ozone variations in the altitudes from 50 to 65 km.

Also, in Figures 5(a) and 5(b) the ozone values at 90° solar zenith angle are shown as dotted line. According to the ozone profiles at 90° solar zenith angle and the simulated ozone profile (at which the onion-peeling method has been applied), we can infer the correction factors for the SAGE II ozone measurements. Table 3 shows the correction factors between 55 and 65 km. Below 55 km only 1% corrections are needed.

Acknowledgements

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References


Atmospheric Ozone, 1985


Table 3 Correction factors of SAGE II ozone profiles at sunrise and sunset in the tropics

<table>
<thead>
<tr>
<th>km</th>
<th>65</th>
<th>64</th>
<th>63</th>
<th>62</th>
<th>61</th>
<th>60</th>
<th>59</th>
<th>58</th>
<th>57</th>
<th>56</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>sr</td>
<td>1.29</td>
<td>1.30</td>
<td>1.29</td>
<td>1.26</td>
<td>1.21</td>
<td>1.16</td>
<td>1.12</td>
<td>1.09</td>
<td>1.06</td>
<td>1.03</td>
<td>1.03</td>
</tr>
<tr>
<td>ss</td>
<td>1.03</td>
<td>1.04</td>
<td>1.05</td>
<td>1.06</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
<td>1.06</td>
<td>1.06</td>
<td>1.04</td>
<td>1.03</td>
</tr>
</tbody>
</table>

sr: sunrise; ss: sunset
5. Comparison of SAGE II ozone against UARS data

SAGE II ozone profiles were compared against MLS, CLAES (blocker 8 and blocker 9) and ISAMS measurements over the periods: January 9-11 (45 UARS nighttime profiles between 5S and 10N, and 45 UARS daytime profiles at 21-34N), April 15-17 (42 UARS nighttime profiles at 22-36N), and for January 9 separately using the new "TEST" ISAMS data. Comparisons were also made for August 25-28 (56 UARS daytime profiles at 44-53S) with CLAES data being unavailable for August 27 and ISAMS not operating throughout the period, for April 18-20 (45 UARS nighttime profiles at 5-22N, and 44 UARS nighttime profiles at 3-29N). The time differences between the SAGE II and the UARS measurements varied between 0 and 7 hours (averaging 3 hours) and the spatial colocation differences varied within each comparison period over the range 0 to 14 degrees longitude (averaging ~7 degrees) and 0 to 2 degrees in latitude (average ~1 degree). Data was only utilized if the error bars for the two instruments being compared were less than 50% of the measured ozone mixing ratios. The SAGE II profiles were all smoothed over the altitude range of ~2.5 km between UARS pressure levels.

Figure 5.2.1.5-1 shows the mean differences of the UARS ozone measurements from the SAGE II measurements over the period January 9-11 between 21 and 34N. The standard errors in the differences are seen to be small (typically < 0.2 ppmv). MLS and ISAMS show differences of less than ~0.5 ppm except below 5 mb where the ISAMS (V0006) measurements are known to be contaminated by aerosols and at 46 mb for MLS where the SAGE II measurements are lacking precision also because of aerosol effects. The CLAES (B9 differences) possess a strongly varying structure with altitude with minima at 0.68, 3.2 and 14.7 mb. Figure 5.2.1.5-2 shows a similar comparison for January 9 but using the "TEST" ISAMS algorithm; it suggests that this revised algorithm has been successful in removing much of the aerosol contamination.

Figures 5.2.1.5-3 and -4 compares standard deviations of the UARS-SAGE II differences over the January 9-11 period to the means of the error bars provided with each profile. Of the intercomparison periods analyzed, only this period (at these latitudes) and the August 25-28 period showed covariances (i.e. stratospheric variability?) exceeding 1% of the product of the ozone measurements, and even then only near 1 and 10 mb. The vertical structure of the MLS/SAGE II correlation reflects this with a minimum being exhibited near 3 mb; this is consistent with our understanding of vertical differences in the variability of atmospheric ozone. If the error bars are realistic, the standard deviations of the UARS-SAGE II differences should be equal, in a statistical sense, to the square root of the sum of the square of the errors. It should be noted, however, that the SAGE II error bars need to be reduced by a factor of ~1.2 for the smoothing of the SAGE II profiles to the UARS levels. A good consistency is then shown in this MLS/SAGE II comparison between 10 and 0.46 mb. Note that there exists little correlation of SAGE II and MLS at 0.46 mb almost certainly because the errors substantially exceed atmospheric
variability in this period at this level. While the SAGE II error bars appear to be somewhat too large below 10 mb, the MLS/SAGE II correlation becomes small in this region almost certainly because of SAGE II errors introduced by aerosol effects.

Figure 5.2.1.5-3 also shows that for ISAMS there is significant correlation with the SAGE II measurements between 2.2 and 0.32 mb and that the ISAMS error bars may be slightly too large above 1 mb. The strong correlation at 10 mb suggests that the aerosol effects on the ISAMS profiles, at least in this case, may be fairly systematic. The CLAES (B9) results show that the altitudes where B9 ozone values are small, correspond to large error bars and maximum variability in CLAES (B9)/SAGE II differences. The CLAES (B9) error bars appear to be a factor of ~2 too large (perhaps corresponding to the inclusion of some systematic errors). For CLAES (B8), the standard deviations of the CLAES (B8)/SAGE II differences are no worse than for B9, indicating that the differences between CLAES (B8) and SAGE II are dominated by systematic errors. The error bars given for CLAES (B8) are larger than for B9, probably because of the inclusion of some of these larger systematic errors in blocker 8.

The results shown in Figures 5.2.1.5-1 and 5.2.1.5-2 are typical of the intercomparisons. Figures 5.2.1.5-5 and -6 shows the means and standard deviations of the intercomparison period differences (each period receiving equal weight). The standard deviations shown are similar to the instrumental error bars, indicating that the measurement differences are a function of latitude and/or season (perhaps in part because of variations in temperature structure and aerosol loading). Although most of the UARS observations used in these comparisons were nighttime measurements, because of variations in the measured differences, obvious differences between the nighttime and the daytime intercomparisons were not apparent. Of the intercomparison periods considered, the January 9-11 period near the equator (SAGE II sunrises) exhibits the largest differences between the SAGE II and the UARS instruments, almost certainly because of the exceptionally large aerosol loading at this time (and the effects of aerosols on the SAGE II and the infrared sensors almost certainly extends considerably above 10 mb in this case).

The mean differences between SAGE II and the other instruments (over the latitude range 0-55 degrees) show MLS approximately 3% larger than SAGE II between 1.5 and 10 mb and smaller than SAGE II outside this range. ISAMS ozone profiles possess a steeper vertical gradient than SAGE II with the current ISAMS algorithm being known to be influenced by aerosols near 10 mb and with ISAMS concentrations ~15% smaller near 1 mb. The CLAES (B9) mean differences exhibit the strongly banded structure seen in the January intercomparison although somewhat smoothed in altitude. Ozone is being significantly underestimated by CLAES (B9) near 1 and 10 mb.
Combining the standard deviations shown in Figures 5.2.1.5-5 and -6 with the "typical" random errors inferred from the standard deviations of the differences given in Figures 5.2.1.5-3 and -4, a self-consistent set of profile repeatability values for each instrument are shown in Table 1. This table also shows biases with respect to SAGE II obtained by taking means and standard deviations of the altitudinal differences shown in Figures 5.2.1.5-5 and -6. We conclude that the accuracy and precisions are approximately 5% for MLS, 10% for ISAMS (where aerosol contamination effects are small) and 15% for CLAES (B9). Note that if the biases can be removed from the CLAES (B8) values, they have the potential to provide ozone values to 10% precision. The accuracies and precisions listed may extend to altitudes below 32 mb, for MLS in particular, but it is not possible to conclude this from these intercomparisons because of potentially significant aerosol-related errors in the SAGE II profiles at low altitudes during this intercomparison period.

Table 1. Instrumental repeatability of UARS ozone measurements inferred from differences with SAGE II measurements between 0 and 55 latitude over data intercomparison periods between January and August 1992. Also shown are mean and standard deviations of the mean altitudinal differences.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Repeatability</th>
<th>Pressure Range</th>
<th>Bias with respect to SAGE II</th>
<th>Pressure Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLS</td>
<td>&gt; 5%</td>
<td>1.5 - 15 mb</td>
<td>0 +/- 5%</td>
<td>0.46 - 32 mb</td>
</tr>
<tr>
<td>ISAMS</td>
<td>&gt; 10%</td>
<td>0.46 - 5 mb</td>
<td>-5 +/- 7%</td>
<td>0.32 - 7 mb</td>
</tr>
<tr>
<td>CLAES (B9)</td>
<td>&gt; 15%</td>
<td>0.46 - 32 mb</td>
<td>-7 +/- 8%</td>
<td>0.46 - 32 mb</td>
</tr>
<tr>
<td>CLAES (B8)</td>
<td>&gt; 10%</td>
<td>1 - 21 mb</td>
<td>23 +/- 5%</td>
<td>2 - 21 mb</td>
</tr>
<tr>
<td>SAGE II</td>
<td>&gt; 5%</td>
<td>0.46 - 10 mb</td>
<td>accuracy approx.</td>
<td>0.32 - 10 mb</td>
</tr>
</tbody>
</table>

One comparison has been made between HALOE and SAGE II consisting of 15 profiles on May 6 at 50S (Figure 5.2.1.5-7). HALOE mixing ratios are 5-10% larger than SAGE II between 1.5 and 32 mb. There is agreement within approximately 5% between 1 and 0.46 mb. At latitudes above 0.46 mb, HALOE values are ~30% larger than SAGE II. Rms differences are approximately 10% at all altitudes when the mean differences are removed. These differences are illustrated in Figure 5.2.1.5-8, where they are shown as a function of longitude.

6. Balloon Comparisons
MLS–SAGE (o) ISAMS (*) CLAES8 (+) CLAES9 (Δ) For Jan 9–11 SS Near 27.5 Deg LAT

Ozone Difference (ppmv) vs. Pressure (mb)

-4 -3 -2 -1 0 1 2 3 4

100.0 10.0 1.0 0.1
MLS-SAGE (o) ISAMS (*) CLAES8 (+) CLAES9 (Δ) For 1/9/92 SS Near 23.5 Deg LAT
MLSSACE 03 DIFFERENCE & ERROR

Difference (%)

Pressure (mb)

ISAMS/SAGE 03 DIFFERENCE & ERROR

Difference (%)

Pressure (mb)
FIGURES ILLUSTRATING
RECENT ACTIVITIES
Ozone Trend (percent/year) from Oct., 1984 to May, 1991

TOMS

SAGE
TOMS 03 deviation from seasonal mean (percent) 6 term regression
O3 deviation from seasonal mean (percent) SAGE - TOMS
O3 deviation from seasonal mean (percent) SAGE
03 deviation from seasonal mean (percent) TOMS
SAGE/SBUV total ozone at Umkehr layer 9

---

Ozone (DU)

Time (Day)

1986 SS
SAGE/SBUV total ozone at Umkehr layer 9

![Graph showing SAGE and SBUV total ozone over time](image-url)
The difference between SAGE and SBUV (percent) from 10/84 to 1/87 (SBUV - SAGE)
SAGE/SBUV total ozone at Umkehr layer 9

Ozone (DU)

Time (Day)

--- SAGE

--- SBUV

1985 SR
SAGE II Observed Locations

Latitude vs. Time (Day)

- SUNRISE
- SUNSET
The differences of SAGE II ozone from SBUV

The graph shows the differences in percent between SAGE II ozone and SBUV ozone, with pressure (mb) on the y-axis and percent (%) on the x-axis. The graph includes multiple profiles, with profiles 1-7 shown by solid lines and profiles 8-14 shown by dashed lines. The differences are plotted for various pressures, with the x-axis representing the percent difference and the y-axis representing the pressure in millibars (mb).
The differences of profiles 8–14 from 1–7

lat. = -48.76
day 145, 1985 (SS)
Ozone Trend (percent/year) from Oct., 1984 to May, 1991