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16. Summary/Notes

*The mesospheric ozone density at a height of 88 km has been deduced from simultaneous ground based observations of neutral sodium density and sodium nightglow intensity, using a photochemical equilibrium model. The data have been obtained at São José dos Campos (23°S, 46°W). Sodium densities are measured as a function of height between 76 and 106 km by laser radar, and the nightglow intensities by a tilting filter photometer. The ozone density shows a strong seasonal variation with well defined maxima at the equinoxes, and a mean annual value of 8 x 10$^7$ cm$^{-3}$. The average nocturnal variation shows a factor of 2 increase between sunset and sunrise.*

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# SEASONAL VARIATION OF OZONE IN THE MESOSPHERE

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## ABSTRACT

The mesospheric ozone density at a height of 88 km has been deduced from simultaneous ground based observations of neutral sodium density and sodium nightglow intensity, using a photochemical equilibrium model. The data have been obtained at São José dos Campos (23$^{o}$S, 46$^{o}$W). Sodium densities are measured as a function of height between 76 and 106 km by laser radar, and the nightglow intensities by a tilting filter photometer. The ozone density shows a strong seasonal variation with well defined maxima at the equinoxes, and a mean annual value of 8 x $10^7$ $cm^{-3}$. The average nocturnal variation shows a factor of 2 increase between sunset and sunrise.

## Introduction

Although the density of atmospheric sodium (Na) is many orders of magnitude smaller than the densities of the major atmospheric constituents, it is possible to measure the Na concentration making use of its large resonance backscattering cross-section.

The laser radar technique is able to measure the density of atmospheric Na as a function of height. The basic procedure is the emission of short duration and small bandwidth laser light pulses, which excite only the atmospheric neutral atomic sodium population. The resonant backscattered photons are collected by a mirror receiver, which feeds the returns to a photomultiplier, counting and storing electronics. Short term laser changes are monitored during operation and taken into account in the calibration. The accuracy of the measurement depends mainly on the uncertainty in the determination of the laser bandwidth (± 10%) and on the integration time of the data sample. The errors are probably not larger than ± 15%.

Using this resonance scattering technique, the atmospheric Na layer, situated between about 76 and 106 km, has been monitored [ Sandford and Gibson, 1970; Kirchhoff and Clemesha, 1973 ] revealing a number of features of its morphology [ Megie and Blamont, 1977; Simonich et al., 1979 ]. Sodium densities have been measured at São José dos Campos ($23^oS$, $46^oW$) since 1972, using the above technique. In mid 1976 a tilting filter photometer was installed at the same location for the measurement of the Na nightglow, primarily for the simultaneous measurements of the neutral and excited sodium atom populations [ Clemesha et al., 1978 ].

The interference filter, with 3 Å bandwidth, is spectrally narrow enough to isolate the sodium D lines, permitting the monitoring of the $D_2$ line. The filter is controlled by a motor driven cam such that tilting with respect to the zenith direction results in an almost linear sweep in wavelength. Contamination by the Q branch of the OH (8,2) band is properly taken into account [Kirchhoff et al., 1979], and the filter is maintained at constant temperature to avoid wavelength drifts. The transmission curves are determined in the laboratory and checked from time to time. The absolute intensities are believed to be accurate to ± 15%. More detailed descriptions of equipment and calibration can be found in Simonich et al. [1979], and Kirchhoff et al. [1979].

Usually the data are taken at intervals of about 10 min. For the present analysis data from mid 1976 to 1979 have been used. Among these, 53 nights had simultaneous density and intensity data over periods of more than five hours.

It should be noted that although a number of ozone density measurements have been reported at mesospheric heights, mainly using the stellar occultation technique [Hays and Roble, 1973; Riegler et al., 1976, 1977], there is considerable uncertainty concerning absolute ozone density values and little, if anything, is known on nocturnal and seasonal variations of ozone at these altitudes.

Based on the generally accepted mechanism for the sodium nightglow excitation, the ozone density is deduced as shown in the next section. The objective of this paper is to exploit the relationship between the sodium parameters and the mesospheric ozone, deducing the seasonal and nocturnal variations of the latter.

## Determination of ozone density

The basic chemical reactions for the excitation of sodium in the upper atmosphere are believed to be [Hunten, 1967]

$$Na + O_3 \rightarrow NaO + O_2, \; k_1 = 3.3 \times 10^{-10} \; cm^3 \; s^{-1}$$

and

$$NaO + O \rightarrow Na^* + O_2, \; k_2 = 1.6 \times 10^{-10} \; cm^3 \; s^{-1}$$

where the reaction rates $k_1$ and $k_2$ are from Kolb and Elgin [1976], and where Na* designates excited sodium. It may be shown, based on recent Na layer modeling, [i.e. Liu and Reid, 1978] that the above reactions are much faster than any other competing production or loss process. Therefore, in photochemical equilibrium, using brackets to indicate densities, one has

$$[Na]\cdot[O_3]\cdot k_1 = [NaO]\cdot[O]\cdot k_2 = P(Na^*) \qquad (1)$$

where P(Na*) indicates the production of excited sodium atoms per unit volume and time. The Na nightglow is obtained by integrating (1) with height, z,

$$\int [Na]\cdot[O_3]\cdot k_1 \, dz = \int P(Na^*) dz = I \qquad (2)$$

This is now transformed into a summation in steps of 2 km, corresponding to the height resolution of the laser radar data,

$$\Delta z \sum [Na]\cdot[O_3]\cdot k_1 = I \qquad (3)$$

It is not possible, of course, to invert equation (3) to obtain a time varying ozone profile, but if we specify a given height distribution, which varies only with respect to its magnitude, it is possible to determine the ozone density at a given height. To this end we write

$$[O_3] = A \cdot f(z) \qquad (4)$$

For the calculations f(z) was taken from the Hays and Roble [1973] $O_3$ profile for $25^{o}$N, normalized such that A represents the ozone density at 88 km, the height of maximum sodium emission [Clemesha et al., 1978]. The summation is performed from 80 to 98 km, and after including appropriate constants for unit transformations, equations (3) and (4) give (for $O_3$ given in $cm^{-3}$, at 88 km)

$$O_3\ (88) = 2.3 \times 10^{10}\ R/\sum\ [Na] \cdot f(z) \qquad (5)$$

where R is the nightglow intensity in Rayleighs and [Na] is in $cm^{-3}$. This expression has been used to deduce the seasonal and nocturnal variations of $O_3$.

The method described above, for determining ozone densities in the mesosphere, suffers from two major imperfections: firstly, the absolute densities calculated depend on the value assumed for $k_1$, which has not been measured in the laboratory, and secondly, the densities depend on the assumed vertical distribution function. The first of these defects affects only the absolute densities, and does not invalidate the derived nocturnal and seasonal variations, but the second is more serious. We have tried to estimate the effects of changing the distribution function by displacing it vertically. We find that for a typical sodium distribution, a ± 4 km displacement of f(z) produces an approximately ± 50% change in the $O_3$ density calculated for 88 km. Although this variation is by no means negligible, it is felt that the almost complete lack of measurements of the nocturnal and seasonal variation in mesospheric ozone justifies the use of the method described.

## Results and discussion

The seasonal variation of the ozone density is shown in Figure 1 for the four years analysed. The strongest feature appears to be the density increase at the equinoxes, a characteristic that repeats itself from year to year, with minimum densities in June-July-August. It appears that there is considerable variation from year to year in the duration of the equinoctial increase. The magnitude of the density varies between a minimum of about $3 \times 10^7$ in July and a maximum of $3.4 \times 10^8$ molecules $cm^{-3}$ in April. Average monthly means are shown in Figure 2 (continuous line). From autumn to winter, the density decreases by a factor of 3.

The nocturnal variation is shown in Figure 3. In a, only the nocturnal variation of the sodium nightglow is shown, and in b, the nocturnal variation of $\sum [\text{Na}] \cdot f(z)$. Figure 3c shows the deduced nocturnal variation of the ozone density.

Nighttime $O_3$ loss in the height range of interest is almost entirely via the reaction with H, and production is by the three body reaction $O + O_2 + M$, giving an equilibrium $O_3$ density

$$[O_3] = [O] \cdot [O_2] \cdot [M] \cdot k_3 / [H] \cdot k_4 \qquad (6)$$

We have derived atomic oxygen densities from OI 5577 Å nightglow measurements, making suitable allowance for the F-region component, assuming the Chapman mechanism for the excitation process. The OI 5577 Å observations were made at Cachoeira Paulista (23°S, 45°W), during the same period as the sodium measurement. The seasonal variation of peak atomic oxygen densities derived in this way is plotted (dashed line) in Figure 2. As may be seen from this figure, the atomic oxygen densities also show equinoctial increases, but of smaller magnitude. From fall to winter, the atomic oxygen density at the peak decreases by a factor of 1.4, from almost $4 \times 10^{11}$ to $2.8 \times 10^{11}$ $cm^{-3}$. This factor would increase to 1.6 had we assumed the Barth-Hildebrandt mechanism instead of the Chapman one, for the production of the OI 5577 Å emission. Detailed differences between the variations in atomic oxygen and ozone could be due to variations in $[H]$, and to the fact that the o densities refer to the height of emission of the OI 5577 Å line, which is probably some 6 km above the height of peak Na D emission.

It is interesting to note that the seasonal variation of the OH emission intensities, observed at our latitude, is much weaker than that observed for $O_3$ and O. Takahashi et al. (1977) see only a small increase in OH (8,3) at the autumnal equinox, corresponding to the stronger of the equinoctial maxima which we observe in our derived $O_3$ density. Neglecting quenching, the OH emission intensity should be proportional to [H] · [$O_3$], and thus to the atomic oxygen density (equation 6). It would appear then, that the seasonal variation in atomic oxygen at the height of the OI 5577 Å emission, about 94 km, is almost entirely absent at the height of the OH emission, about 84 km. If this is indeed the case, it suggests that the seasonal variation in O, at 88 km, should be smaller than that derived from the OI 5577 Å measurements, implying a strong seasonal variation in [H] with equinoctial minima, necessary to explain the large equinoctial maxima in our derived $O_3$ density.

The increase during the night of the derived $O_3$ density is unexpected. Model calculations (Shimazaki and Laird, 1972) show an almost constant $O_3$ concentration above 85 km after the rapid post-sunset rise caused by the cessation of photolysis. A post-midnight increase in the OI 5577 Å intensity has been explained by Takahashi et al. (1977) as a result of the solar semi-diurnal tide. A similar explanation for the ozone variation is not very satisfactory because the $O_3$ density continues to rise after 0400 LT when tidal effects should cause decreasing densities. It should be remembered here that the derived ozone variation depends on the assumed height distribution of ozone. The sodium variation shown in Figure 3 b is almost entirely due to changes which occur below 88 km, and a displacement of the ozone profile to greater heights would greatly decrease the influence of these changes. If our derived variation in $O_3$ density is real, however, taken together with the nocturnal variation in the OH (8,3) emission intensity observed by Takahashi et al. (1977), it implies a rapid decrease in hydrogen concentration during the pre-midnight period, and that the hydrogen decrease must be larger than the corresponding atomic oxygen decrease. Although such a decrease is not predicted by model calculations for heights above 80 km, it may be significant that, on the basis of the Liu and Reid (1978) model, it would explain the rapid post-sunset loss of sodium at 80-84 km, observed by Simonich et al. (1979).

## Conclusions

Based on the sodium photochemistry, mesospheric ozone densities have been derived from measured sodium density distributions and simultaneous Na nightglow intensities.

The seasonal variation of the derived ozone density shows pronounced equinoctial maxima, the peak at the autumnal equinox being larger than that at the vernal equinox. The decrease in density from fall to winter is by a factor of 3. A comparison of this seasonal variation with variations of OI 5577 Å and OH (8,3), observed at our latitude, suggests that the hydrogen concentration at 88 km must show a seasonal variation opposite to that of the ozone. The derived nocturnal variation indicates an increase in $O_3$ density by about a factor of 2 between sunset and sunrise. Comparison of this variation with the measured nocturnal variation in OH emission intensity suggests a large decrease in hydrogen concentration at 84 km during the night.

The annual mean ozone density at a height of 88 km is found to be $8 \times 10^7$ $cm^{-3}$.

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## Figure Captions

Fig. 1. Seasonal variation of ozone density at 88 km for 1976, 1977, 1978, and 1979.

Fig. 2. Seasonal variation of ozone density at 88 km, monthly means of previous figure (continous line), and seasonal variation of [O] (dashed line).

Fig. 3. Nocturnal variation of: a, sodium nightglow intensity; b, $\sum$ [Na]. f(z); and c, derived ozone density.

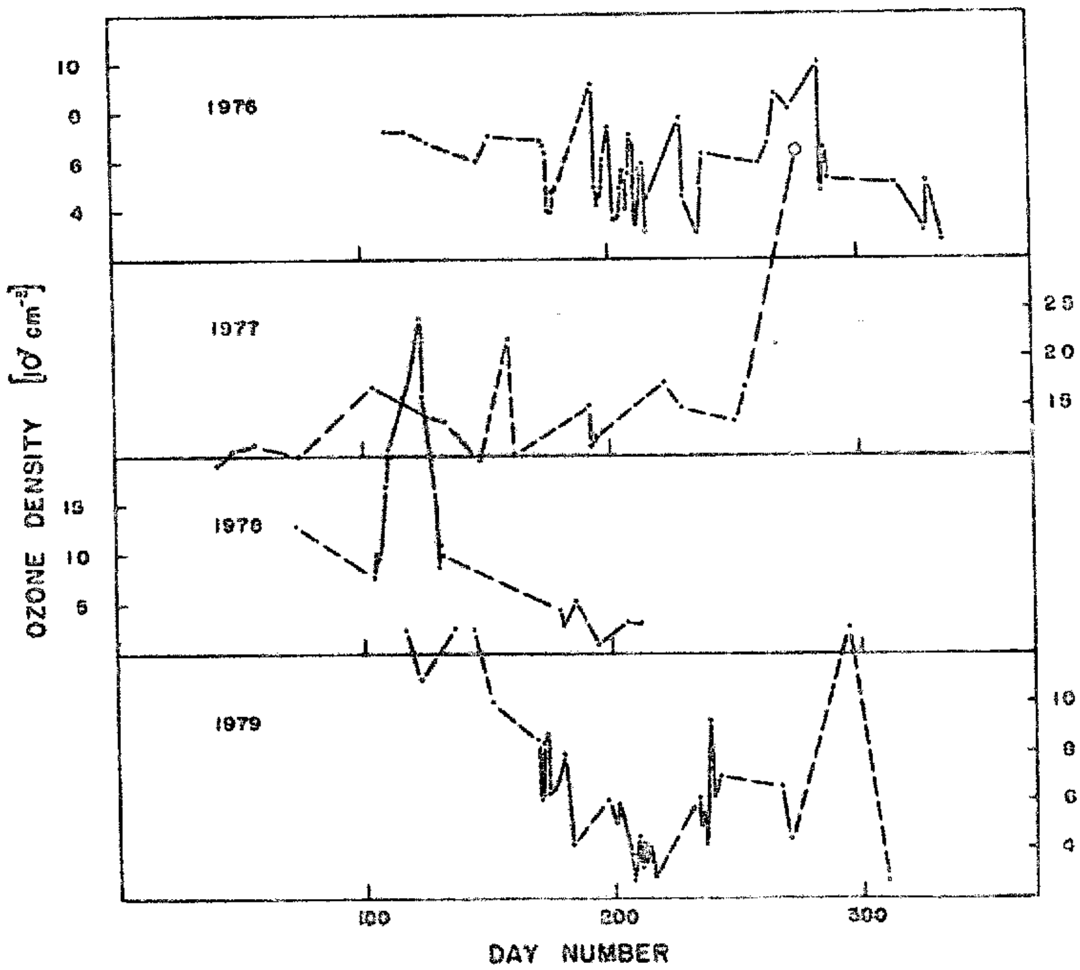


Fig. 1 - Seasonal variation of ozone density at 88 km for 1976, 1977, 1978, and 1979.

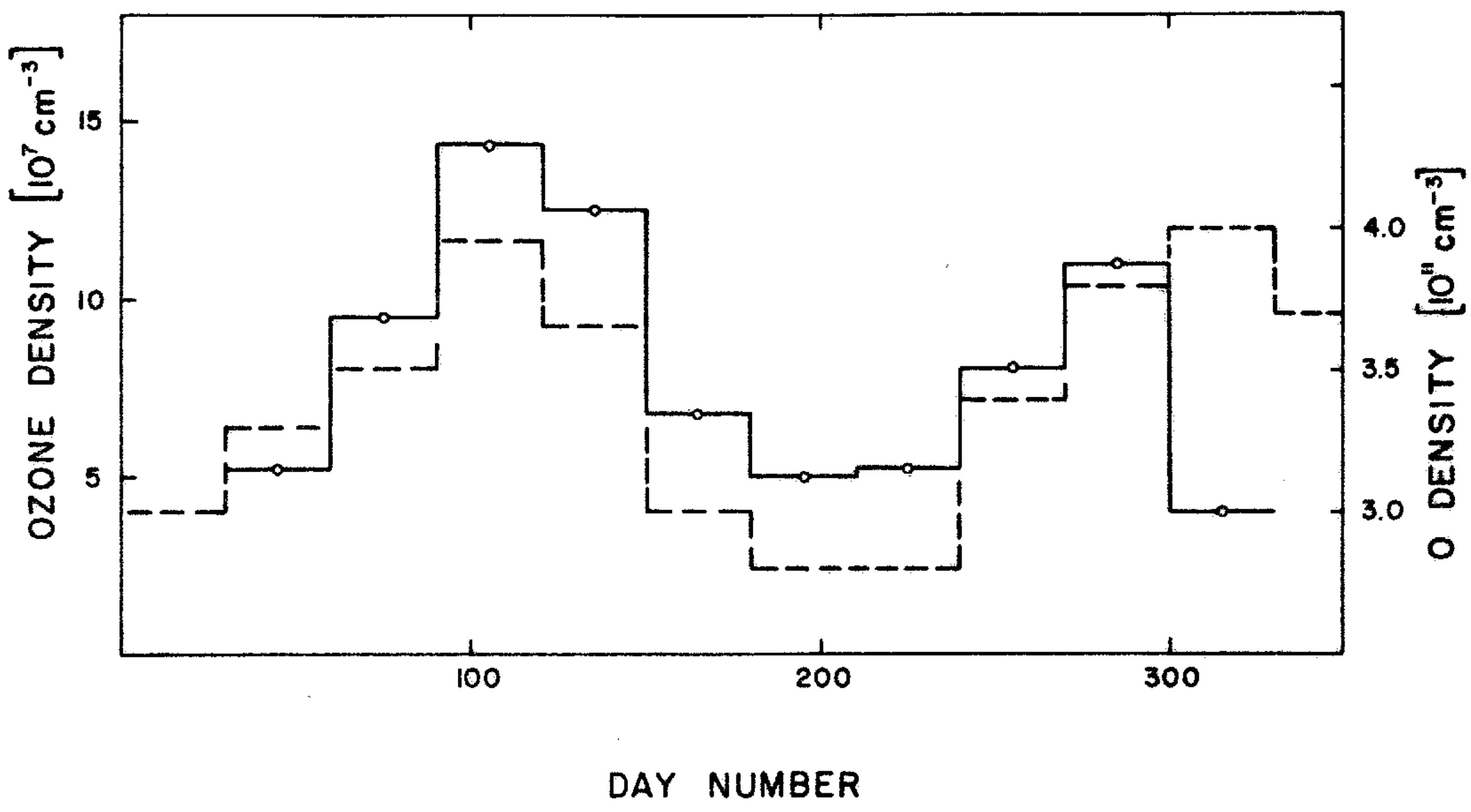


Fig. 2 - Seasonal variation of ozone density at 88 km, monthly means of previous figure (continuous line), and seasonal variation of [O] (dashed line).

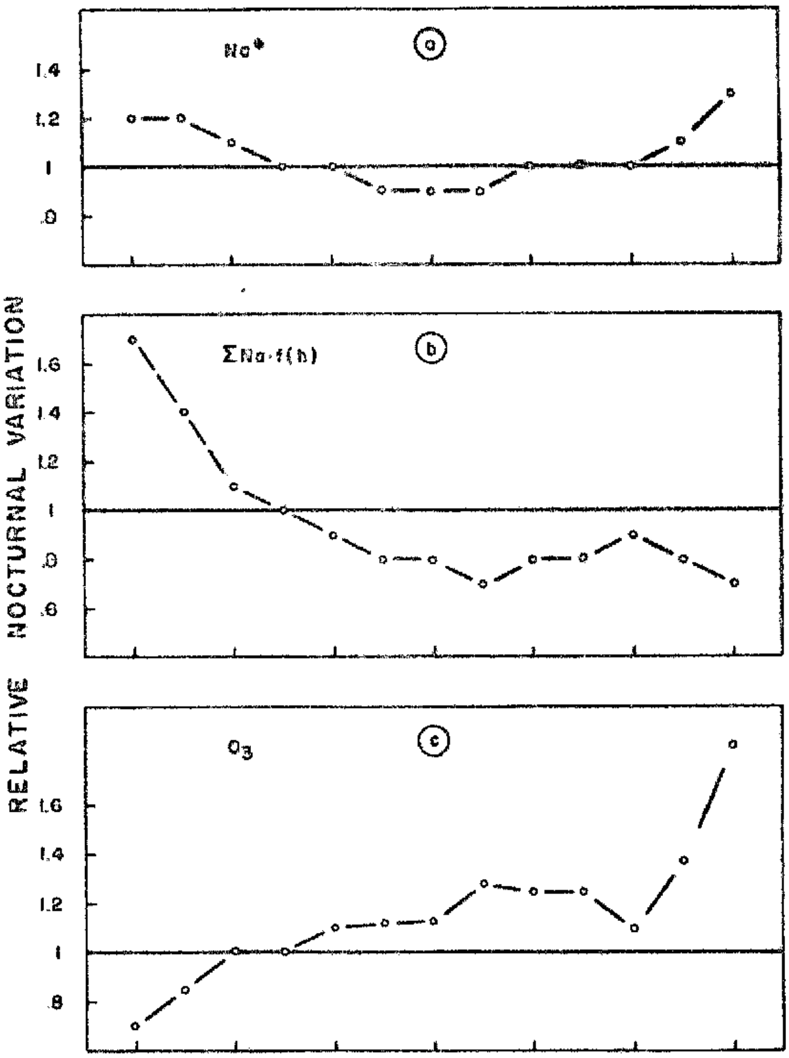


Fig. 3 - Nocturnal variation of: a, sodium nightglow intensity; b, $\sum [Na] \cdot f(\bar{z})$; and c, derived ozone density.

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